ORGANIC REACTIONS

CHAPTER 1

RADICAL ALLYLATION, VINYLATION, ALLENYLATION, ALKYNYLATION, AND PROPARGYLATION REACTIONS USING TIN REAGENTS

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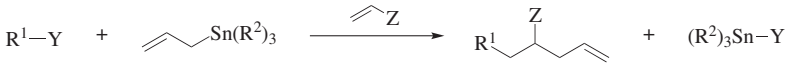
INTRODUCTION

Over the past thirty years, radical allylation using allyltin reagents has been developed to provide a useful synthetic method. Kosugi and Grignon reported the first examples of these reactions in 1973[1,2] and, beginning about a decade later, Keck began to systematically explore the application of the reaction to target-directed synthesis.[3,4] In its simplest form, the reaction involves the generation of a carbon-based radical from an appropriate precursor, followed by the addition of this radical to an allyltrialkyltin reagent to form the allylated product (Scheme 1).

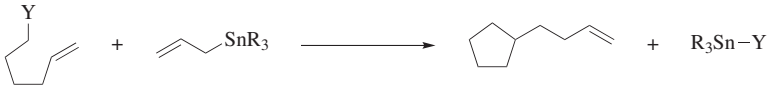
Scheme 1

Direct allylations are possible with a variety of carbon-centered radicals. Most examples involve alkyl radicals (primary, secondary, or tertiary), and the reaction is compatible with substituents located at the radical center. Reactions of vinyl, aryl, and acyl radicals are well-studied, and allylations of heteroatom-substituted radicals are also known. Some substituents on the tin reagent are tolerated, further expanding the scope of the simple transformation shown above. In addition, the radical precursor and the allyltrialkyltin moiety can be incorporated into the same molecule, leading to intramolecular trapping of the radical.

The great versatility of this allylation reaction lies in the fact that it can be coupled with other radical transformations to enable formation of two or more carbon–carbon bonds in a single reaction sequence. The initial radical that is generated from a radical precursor can undergo either inter- or intramolecular addition to an alkene (Schemes 2 and 3, respectively), followed by trapping with an allyltrialkyltin; longer sequences that combine multiple intermolecular addition or cyclization events can build significant complexity in a one-pot process.



Scheme 2



Scheme 3

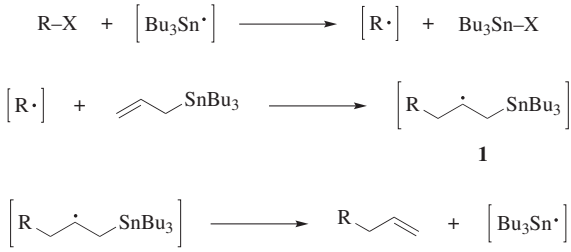
Further variations on the basic allylation reaction use vinyl-, propargyl-, alkynyl-, and allenyltrialkyltin reagents to effect vinylation, allenylation, alkynylation, and propargylation reactions, respectively, and these transformations are also discussed in the chapter.

The literature on the deployment of tin reagents for radical allylation and vinylation reactions has not previously been reviewed in depth, although some aspects of this chemistry have been described.[5–8] This chapter and the accompanying Tabular Survey provide a comprehensive review of the literature up to the beginning of 2021. Note that all available diastereomeric and enantiomeric ratios are provided if they were available in the primary literature.

MECHANISM AND STEREOCHEMISTRY

Mechanism

Scheme 4 illustrates the major mechanistic steps in the simple allylation reaction of a generic alkyl halide substrate with allyltributylstannane. This chain process involves initial generation of an alkyl radical by abstraction of a halogen by the tributyltin radical (typically formed by reaction of a radical initiator with the allylstannane). This alkyl radical then adds to the terminal end of the allylstannane to produce an intermediate radical **1**, which undergoes rapid β-fragmentation to afford the allylated product and regenerate the chain-carrying tributyltin radical.

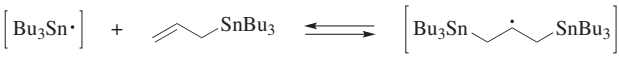


Scheme 4

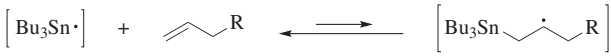
Early work on the allylation reaction established that the mechanism is a radical-chain process. For instance, the reaction is promoted by radical initiators, it is inhibited by radical scavengers, it results in the racemization of enantioenriched halides, and it is subject to well-known radical rearrangements.[1,2] In a later study, the initial alkyl intermediate radical formed in an allylation reaction of diethyl 2-iodoadipate was observed directly by mass spectrometry as a complex with scandium triflate.[9] One question that has not been carefully investigated is whether adduct radical **1** is a distinct intermediate or if the addition of the alkyl radical and loss of tributyltin radical is a concerted process, although a recent report concludes that the analogous reaction of allyl chloride is consistent with a concerted process.[10] If radical **1** is a distinct intermediate, it must be short-lived since other processes are not known to compete with β-elimination of the trialkylstannyl radical.

The rapid rate of the unimolecular β-elimination is a critical aspect of the effectiveness of this reaction. As with any radical process, competition between different pathways available to each intermediate radical in the mechanism can lead to multiple products. For the initial tin radical, the alternatives to abstracting a halogen atom from

the alkyl halide substrate are either addition to allyltributylstannane or addition to the alkene of the allylation product. Addition to the allylstannane is degenerate, reforming the allylstannane and tin radical by β-elimination (Scheme 5), and addition to the allylation product is reversible, favoring the starting materials (Scheme 6).[11] The lack of productive alternatives for the tin radical means that relatively unreactive radical precursors such as chlorides and sulfides can be used. Once formed, radical **1** could also add to either allyltributylstannane or a product alkene; however these bimolecular addition processes are too slow to compete with the rapid unimolecular β-elimination. As a result, the relatively slow rate constants for addition of alkyl radicals to allylstannanes can be offset by carrying out the reactions at high concentrations. The alkyl radical can also add to either the allylstannane, as desired, or to a product alkene. Kinetic experiments demonstrate that the rate of addition of a primary radical to allyltributylstannane is approximately 3×10^4 $M^{-1}s^{-1}$ at 50°, and the rate of addition of a secondary radical to allyltributylstannane is approximately 1×10^5 $M^{-1}s^{-1}$ at 80°.[12] These rates are about an order of magnitude faster than the rates of the analogous additions of alkyl radicals to propene, so there is a small but decided preference for the addition to the allylstannane over addition to the product alkene.



Scheme 5



Scheme 6

The origin of the rate acceleration for the addition of simple alkyl radicals to the allylstannane, relative to propene, is not definitively established. It is well known that the rates of addition of alkyl radicals to alkenes are affected primarily by a combination of electronic and steric effects.[13,14] For electron-rich, nucleophilic radicals like alkyl radicals, the rate of addition is accelerated by the presence of electron-withdrawing groups on the alkene, especially at the β-carbon, but the stannylmethyl group does not provide this sort of electron-withdrawing activation. However, EPR studies indicate that the most stable conformation of the 2-stannylethyl radical places the carbon–tin bond in a position eclipsing the singly occupied p-orbital (Figure 1).[15,16] The resulting hyperconjugative interaction is estimated to stabilize the radical by approximately 2 kcal•mol^{-1}, and thus, the developing hyperconjugation in the transition state of the radical addition is likely responsible for the rate acceleration.

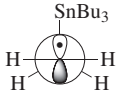
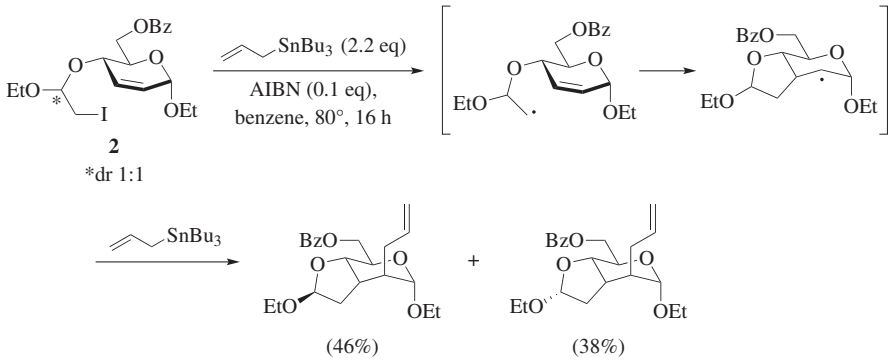
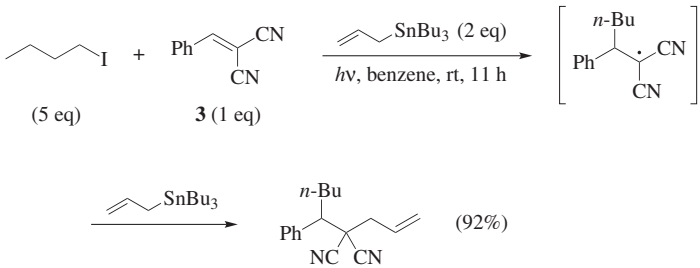


Figure 1. Most stable conformation of the 2-stannylethyl radical.

Because the addition of an alkyl radical to an allylstannane is generally (albeit only marginally) faster than addition to an unactivated alkene, allylstannane-trapping reactions can be incorporated into multistep cascade processes. For example, carbohydrate iodide **2** reacts with tributyltin radical to form a primary radical, which undergoes a rapid 5-*exo*-trig cyclization before trapping with allyltributylstannane (Scheme 7).[17,18] Similarly, in the reaction of iodobutane with 1,1-dicyano-2-phenylethene (**3**) in the presence of allyltributylstannane, the initially formed butyl radical intermolecularly adds more rapidly to the electron-poor, activated alkene **3** than to the allylstannane. The resulting adduct radical is now electron poor, so it reacts faster with allyltributylstannane than with the activated alkene **3**, and the three-component product is generated in high yield (Scheme 8).[19]



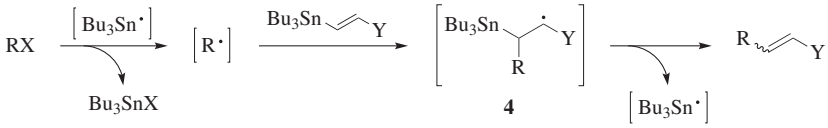
Scheme 7



Scheme 8

While most reactions involving β-fragmentation of stannyl radicals are allylation reactions, numerous examples of vinylation, allenylation, alkynylation, and propargylation reactions (occurring by closely related mechanisms) have also been reported. Of these processes, vinylations are the most common. In these reactions, radical addition must occur at the carbon bearing the stannyl group to form a β-stannyl radical adduct that can then fragment and generate the final product. An efficient reaction is only possible when the vinylstannane substrate bears an activating substituent, (Y), at the 2-position to increase the rate of radical addition to C-1. Suitable

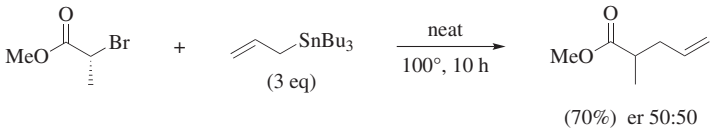
substituents include phenyl groups and strongly electron-withdrawing substituents such as carbonyl or sulfonyl groups. After the initial addition, β-fragmentation occurs rapidly to form the vinylated product (Scheme 9). For vinylation reactions, it is clearly established from the stereochemical outcome of reactions (vide infra) that the addition–elimination is a two-step process wherein intermediate radical **4** has a short but distinct lifetime.[20]



Scheme 9

Stereochemistry

Allylation Reactions. There are three important aspects of the stereochemical outcome of allylation reactions. The first, and simplest, is the fate of the stereochemical configuration when the group used to generate the initial radical is bonded to the substrate at a stereogenic center. As expected for a radical reaction, allylation occurs with racemization at the stereogenic center. For example, the reaction of enantioenriched methyl (2*R*)-2-bromopropionate provides the desired allylation product as a racemate in good yield (Scheme 10).[21] Because the reaction is conducted under neutral conditions and epimerization of the product via the enolate is therefore unlikely, the observed racemization is consistent with the conclusion that the allylation reaction occurs by a radical mechanism.

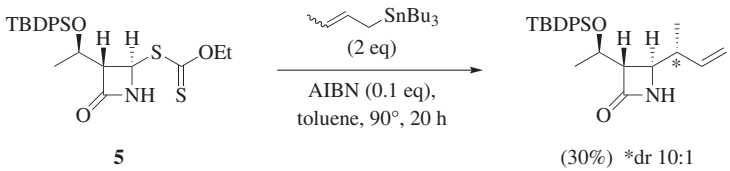


Scheme 10

In cases where the allylation reaction occurs at a prochiral radical center, neighboring stereocenters in the substrate radical can influence the stereochemical outcome. Over the past three decades, significant effort has been dedicated to probing the factors involved in controlling the stereochemistry of free-radical reactions.[22–24] Since allylation reactions are generally efficient and simple to perform, they have often been used as test reactions to develop stereoselective radical processes. The influence of neighboring stereogenic centers on cyclic and acyclic radical substrates has been investigated in depth, as has the use of chiral auxiliaries for controlling the stereochemistry of reactions of acyclic radicals. More recently, numerous examples of enantioselective allylation reactions have been reported. Each of these approaches

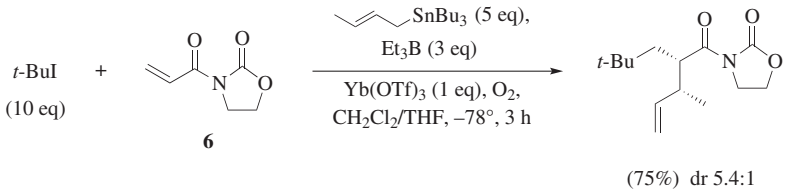
to stereoselective allylation reactions is discussed in detail in the "Scope and Limitations" section.

The final stereochemical consideration in allylation reactions centers on the allylstannane itself: if the allylstannane possesses a substituent at the 3-position, this carbon will be a stereogenic center in the product. Although substitution at the 3-position causes complications and limits the utility of these reagents (vide infra), 3-substituted allylstannanes have been employed in several instances with moderate control of stereochemistry. For example, a cyclic radical derived from azetidinone **5** adds to crotyltributylstannane in poor yield to afford a 10:1 ratio of products, differing in configuration at the new, acyclic, methyl-bearing stereocenter, favoring the *threo* diastereomer (Scheme 11).[25] The reaction delivers the (*R*)-configuration at the initial site of the radical, and this selectivity is driven by the inherent conformational bias of the substituents on the ring.



Scheme 11

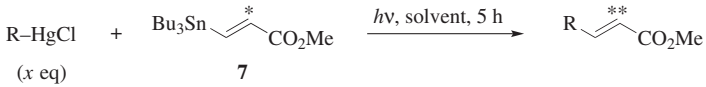
In the presence of ytterbium(III) triflate at low temperature, the addition of *tert*-butyl radical to acrylimide **6** is followed by trapping with crotyltributylstannane to furnish the product as a 5.4:1 mixture of diastereomers, favoring the *syn* product (Scheme 12).[26] The stereoselectivity decreases when the alkyl radical group is smaller than *tert*-butyl, and the reaction is unsuccessful in the absence of a Lewis acid. Steric factors in the competing transition states that lead to the *syn* and *anti* products are believed to be responsible for controlling the stereochemical outcome of the reaction.



Scheme 12

Vinylation Reactions. In vinylation reactions, the primary stereochemical consideration is the configuration of the alkene in the product. Regardless of the stereochemistry of the starting vinylstannane, the (*E*) isomer of the product is favored in these reactions, albeit the selectivity is usually higher if the vinylstannane precursor is (*E*)-configured. In one study, the addition of cyclohexyl radical to

(*E*)- and (*Z*)-stannylacrylates **7** affords 23:1 and 2.1:1 selectivity for the (*E*) product, respectively (Scheme 13).[20] The (*E*)/(*Z*) selectivity is also impacted by the size of the radical that adds to the vinylstannane. The larger *tert*-butyl radical adds to acrylate **7** with >50:1 selectivity for the (*E*) isomer, regardless of the stereochemistry of the starting stannylacrylate. Conversion of (*Z*) vinylstannanes to the corresponding (*E*) products provides evidence that the vinylation reactions occur in two steps through the intermediacy of β-stannyl radicals.



R	*x*	*Config	Solvent	Yield (%)	**(*E*)/(*Z*)
c-C_6H_{11}	1.5	(*E*)	benzene/DMSO	66	23:1
c-C_6H_{11}	1.5	(*Z*)	benzene/DMSO	70	2.1:1
t-Bu	1.6	(*E*)	benzene	36	>50:1
t-Bu	1.6	(*Z*)	benzene	49	>50:1

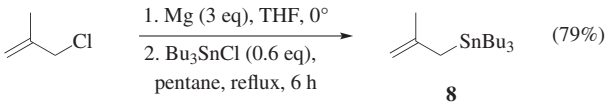
Scheme 13

SCOPE AND LIMITATIONS

Preparation of Allyl and Vinyl Stannanes

The most frequently used allylation reagents—allyltributylstannane, allyltriphenylstannane, and methallyltributylstannane—are commercially available. Because other allyl- or vinylstannanes are not readily available from commercial sources, numerous methods have been developed for the synthesis of stannane reagents,[27] and five of the most commonly used strategies are discussed below.

The addition of a Grignard reagent to a trialkyltin halide can be used to synthesize a variety of allyl- and vinylstannanes. This method is used, for example, to prepare methallyltributylstannane (**8**) (Scheme 14).[28]



Scheme 14

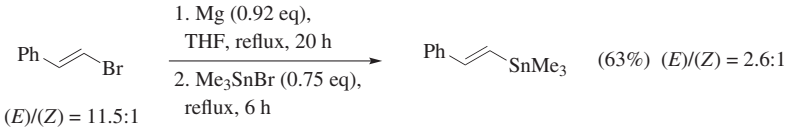
Slight variations on the Grignard reaction have been devised to prepare numerous other radical allylation reagents. For example, allyltributylstannane is produced by the reaction of allylmagnesium bromide with bis(tributyltin) oxide[29] or by the ultrasound-promoted Grignard reaction of allyl chloride and tributyltin chloride in the presence of magnesium.[30,31] The latter method can also be used to

make tributyl-2,4-pentadienylstannane (**9**) (Figure 2).[30,31] 2-Phenyl-substituted allylstannane **10** is prepared by a Grignard reaction that is catalyzed by a small amount of lead dibromide.[32,33]

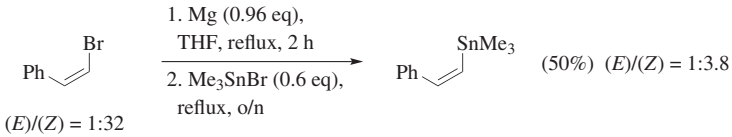
9 **10**

Figure 2. Examples of substituted allylstannanes synthesized via Grignard reagents.

β-Styryltrimethyltin is prepared by a Grignard reaction, and the stereochemistry of the product depends on the stereochemistry of the starting β-bromostyrene, although the stereoselectivity is modest in both cases (Schemes 15 and 16).[34] For instance, the (*E*) isomer of β-bromostyrene provides the product in a 2.6:1 ratio of (*E*)/(*Z*) isomers, whereas a 1:3.8 mixture of (*E*)/(*Z*) isomers is obtained using (*Z*)-β-bromostyrene. The tributylstannyl version of this compound can be prepared by several different methods, each providing the product with a slightly different (*E*)/(*Z*) ratio.[35]

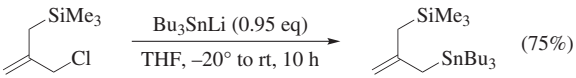


Scheme 15



Scheme 16

A second method for the preparation of allylstannanes involves the reaction of a trialkyl or triarylstannyl lithium compound with an allylic halide. For example, 2-(trimethylsilyl)methylallylstannane (**11**) is generated by the addition of tributylstannyl lithium to 2-(chloromethyl)allyltrimethylsilane (Scheme 17).[36] This approach can also be used for the synthesis of crotylstannane (**12**),[37] bis(triphenylstannylmethyl)stannane (**13**),[38] and 2-trimethylsilylstannane (**14**)[39] (Figure 3).



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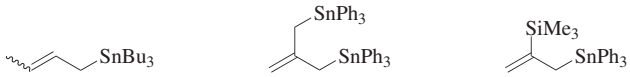
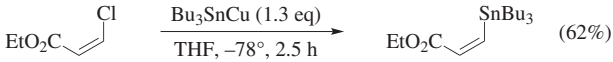
Scheme 17



12 **13** **14**

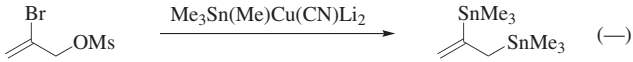
Figure 3. Examples of substituted allylstannanes synthesized by the addition of tributyl- or triphenylstannyl lithium to an allylic halide.

Allyl- and vinylstannanes substituted with nucleophile-sensitive groups must be prepared by other methods. One such approach employs a softer nucleophile, such as a cuprate, to improve chemoselectivity. Carboethoxy-substituted vinylstannane **15** can be accessed by addition of tributyltincopper to the corresponding vinyl chloride, presumably by an addition–elimination mechanism (Scheme 18).[40] The reaction is stereospecific, and the (*E*) vinyl chloride provides the (*E*) vinylstannane. Similarly, the cuprate reagent $Me_3Sn(Me)Cu(CN)Li_2$ can be used to prepare 2-(trimethylstannyl)allylstannane **16** (Scheme 19),[41] which can also be accessed by the $Pd(PPh_3)_4$-catalyzed addition of hexamethylditin to propa-1,2-diene.[42] Allyl acetates can be converted to allylstannanes using Bu_3SnOMe and a nickel catalyst under mild conditions.[43] These nickel-catalyzed reactions are compatible with relatively acidic alcohol or α-keto protons.



15

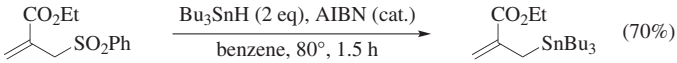
Scheme 18



16

Scheme 19

A second strategy for the synthesis of compounds bearing nucleophile-sensitive groups is to use radical-induced substitution of a sulfone or sulfide with a trialkylstannyl group. This approach has been employed to prepare 2-carboethoxy-substituted allylstannane **17** (Scheme 20),[44] as well as 2-chloro, 2-cyano, and 2-(trimethylstannyl)methyl derivatives **18**,[45] **19**,[45] and **20**,[27] respectively (Figure 4).



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Scheme 20

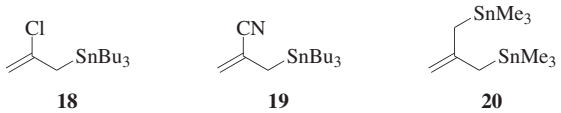
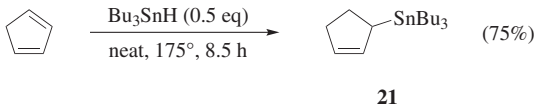


Figure 4. Examples of substituted allylstannanes prepared by addition of a trialkylstannyl radical to an allyl sulfone.

In a related process, radical hydrostannylation of conjugated 1,3-dienes can be used to prepare allylstannanes such as tributyl-2-cyclopenten-1-ylstannane (**21**) (Scheme 21).[46]



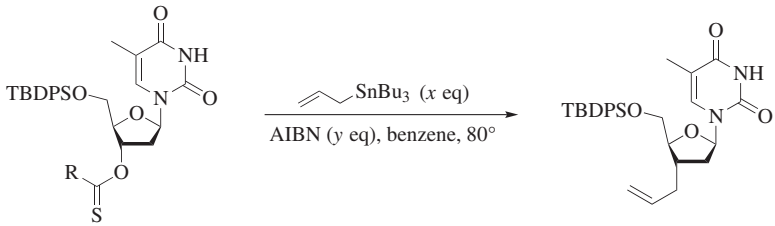
Scheme 21

Methods for Radical Generation

Numerous methods have been used to generate the radical species needed for allylation and vinylation reactions. The most common radical precursors are halides (chloride, bromide, and iodide) or phenyl selenides, and the reactions proceed either at elevated temperatures in the presence of a radical initiator (usually 2,2′-azobisisobutyronitrile (AIBN)), or at ambient temperature by photolysis in the presence or absence of added initiator. Reactions using chloride and bromide radical precursors can also be carried out using a photoredox catalyst.[47] Initiation at ambient temperature or lower using a radical initiator is frequently accomplished using triethylborane and oxygen[48,49] or using zinc chloride diethyl etherate.[50,51] Direct comparisons of radical precursors are difficult, as few examples have been reported with different precursors under otherwise identical reaction conditions, but the typical order of reactivity with stannyl radicals follows the order I > Br > PhSe > Cl.[52] Reactions with chlorides generally result in lower yields, whereas the yields using bromides, iodides, and selenides are often similar. Therefore, the choice of radical precursor should be based on stability and the convenience of preparation.

When the radical is formed at a carbon initially bearing a hydroxyl group, especially with carbohydrate- or nucleoside-based substrates, a thioacyl derivative is typically employed as the radical precursor; xanthates (ROC(S)SR′), *O*-aryloxythiocarbonyl derivatives (ROC(S)OAr), and *O*-thiocarbonylimidazole derivatives (ROC(S)Im) are the most common. Although some reactions using thioacyl radical-generating groups have been accomplished photochemically at ambient temperature, these reactions are typically conducted at reflux in either benzene or toluene in the presence of AIBN. Again, carefully controlled studies of reactions with different radical-generating groups under identical conditions have not been reported, but the *O*-aryloxythiocarbonyl derivatives are the most frequently

used and appear to deliver the highest yields. In one example where reasonably close comparisons exist, allylation of thymidine derivative **22** proceeds in yields ranging from 22–90%, depending on the exact nature of the radical precursor (Scheme 22).

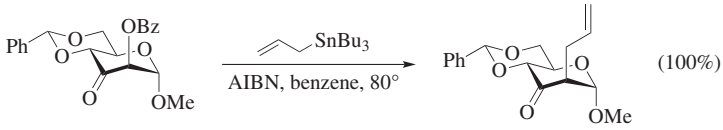


22

R	*x*	*y*	Time (h)	Yield (%)	Ref
MeS	5	0.55	96	22	53
PhO	—	—	12	85	54
4-TolO	5	0.68	15	84	55
C_6F_5O	5	0.55	2	90	53
Im	5	0.55	7	77	53

Scheme 22

In substrates where a radical is generated adjacent to a carbonyl group, an acetoxy, benzoyloxy, or even methoxy group can be used as the precursor. For example, the D-arabinose-derived benzoyl ester **23** reacts with allyltributylstannane in refluxing benzene to give the allylation product in quantitative yield (Scheme 23).[56]

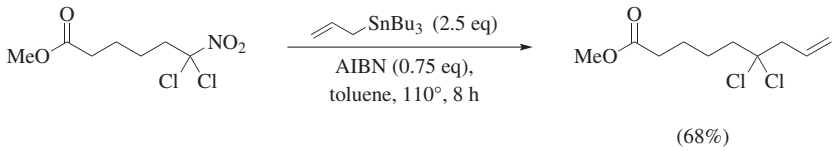


23

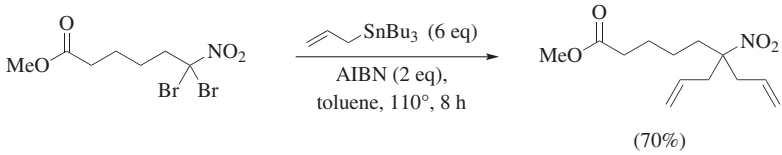
Scheme 23

Cleavage of a carbon–sulfur bond occurs with many radical-generating groups, the most common of which is the thiophenyl group, although substituted thiophenyl (4-TolS–R) and thioalkyl groups can also been used. The reactivity of the thiophenyl group towards stannyl radicals is slightly less than the corresponding chloride.[57] *S*-Thioacyl derivatives analogous to the *O*-thioacyl derivatives discussed above have also been used successfully.[25] For both the sulfide and *S*-thioacyl precursors, the radical must be stabilized by an adjacent group such as a carbonyl or a heteroatom as, for example, at the anomeric position of a carbohydrate substrate. Allylation does not typically occur using sulfoxides and sulfones as radical precursors,[58,59] and numerous examples exist where sulfoxides and sulfones have survived untouched in allylation reactions of substrates bearing more reactive radical precursors.[60,61]

Other groups that have been used as radical precursors for allylation and vinylation reactions include mercuric halide salts, nitro groups, and diazo groups. Alkyl mercuric halides form alkyl radicals upon irradiation at room temperature; this method of generating radicals has been used most often in studies of vinylation reactions.[62] The nitro group is more reactive than a chloride but less reactive than a bromide, as demonstrated in Schemes 24 and 25.[63] Only one study reports the use of the diazo group as a radical precursor, and in each example, the diazo group is alpha to a carbonyl.[64] It should also be noted that Barton esters, which are commonly used as substrates for a number of other radical processes, are not good substrates for allylation reactions because the radicals, once generated, add to a second equivalent of Barton ester faster than they add to allyltributylstannane.[12,65]

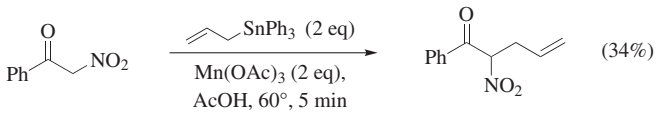


Scheme 24

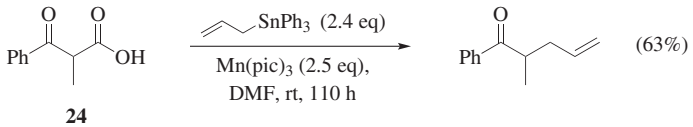


Scheme 25

Manganese(III) salts can be used to mediate allylation reactions, although this methodology has not been widely deployed. In one example, nitroacetophenone reacts with allytriphenylstannane in the presence of manganese(III) acetate in acetic acid to form the allylation product in 34% yield (Scheme 26).[66] In this case, the radical is formed at the carbon between the carbonyl and the nitro group by an electron-transfer process involving the manganese enolate. In a related process, keto acid **24** reacts with allytriphenylstannane and manganese(III) tris(2-pyridinecarboxylate) ($Mn(pic)_3$) in DMF at room temperature to form an allylated product after decarboxylation (Scheme 27).[67] In this case, it is believed that the radical is generated by oxidation of the carboxylate followed by loss of carbon dioxide.

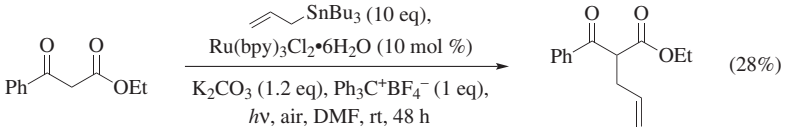


Scheme 26



Scheme 27

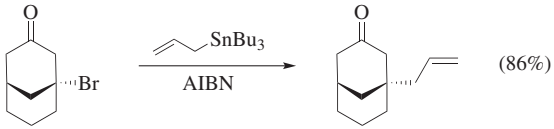
In a similar process, β-keto esters can be allylated using photocatalytic oxidation. Visible light irradiation of ethyl benzoylacetate with allyltributylstannane under basic conditions in the presence of $Ru(bpy)_3Cl_2$ and triphenylcarbenium tetrafluoroborate affords a 28% yield of the allylated product (Scheme 28).[68] In this reaction, the enolate of the β-keto ester is oxidized to the corresponding radical by electron transfer from an excited-state $Ru(bpy)_3Cl_2$, and this radical undergoes allylation. The triphenylcarbenium tetrafluoroborate oxidizes the resulting reduced $Ru(bpy)_3Cl_2$ species to regenerate the active catalyst. Yields of allylated products increase when substituted allylstannanes are used.



Scheme 28

Direct Allylation Reactions Using Allyltributylstannane

Alkyl Radicals. A broad range of alkyl radicals successfully react with allyltributylstannane. Simple acyclic and cyclic primary, secondary, tertiary, and benzylic radicals all undergo allylation, although these reactions are often slow and require a large excess of stannane. For example, the reaction of a slight excess of benzyl bromide with allyltributylstannane in refluxing benzene affords the allylated product in only 3% yield, whereas a 10-fold excess of stannane increases the yield to 86%.[37] Similarly, bromocyclohexane undergoes radical allylation using 10 equivalents of allyltributylstannane in refluxing benzene to furnish the product in 86% yield.[37] More complex cyclic substrates such as 1-bromoadamantane[69] and bromododecahedrane[70] can be successfully allylated as well, although the dodecahedryl radical requires 200 equivalents of allylstannane, and the product is obtained in only 30% yield. Allylation is also efficient with bridgehead radicals, as depicted in Scheme 29.[71]



Scheme 29

A variety of functional groups not directly attached to the radical center are compatible with the reaction conditions, including alcohols, ethers, silyl ethers, acetals, amines, ketones, esters, amides, and carbamates. Figure 5 shows a sampling of substrates that have been successfully allylated with allyltributylstannane as well as the yields of the allylation products.

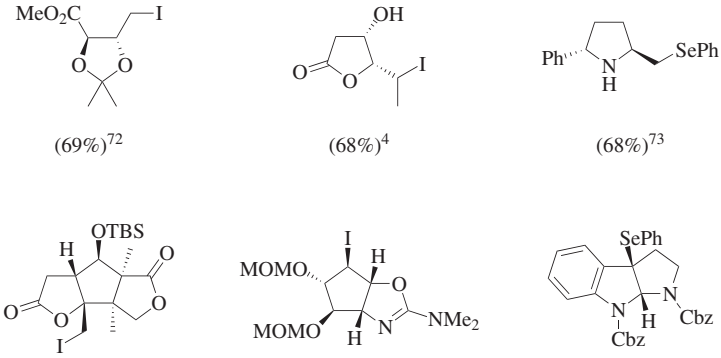
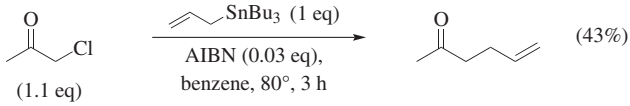


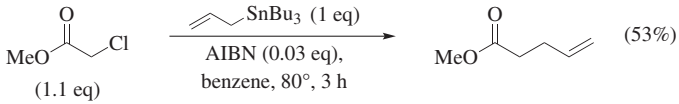
Figure 5. Example substrates showing the diversity of functional groups tolerated in allylation reactions with allyltributylstannane.

Owing to the electron-rich nature of allyltributylstannane, reactions are generally more efficient when the radical center is substituted with an electron-withdrawing group. Allylation of radicals adjacent to a carbonyl group have been the most broadly studied, and aldehyde, ketone, ester, amide, and imide substrates have all been used successfully. In one study that allows direct comparison of the reactivity of α-keto and α-carboalkoxy radicals with that of simple alkyl radicals, the carbonyl-substituted radicals react more efficiently.[37] Allylation of a slight excess of either chloroacetone (Scheme 30) or methyl chloroacetate (Scheme 31) with allyltributylstannane in benzene at reflux in the presence of AIBN affords the products in 43% and 53% yields, respectively. Under identical conditions, the allylation of benzyl chloride provides only a trace of product; in the same study, bromocyclohexane was allylated in 86% yield but 10 equivalents of the allylstannane were necessary.



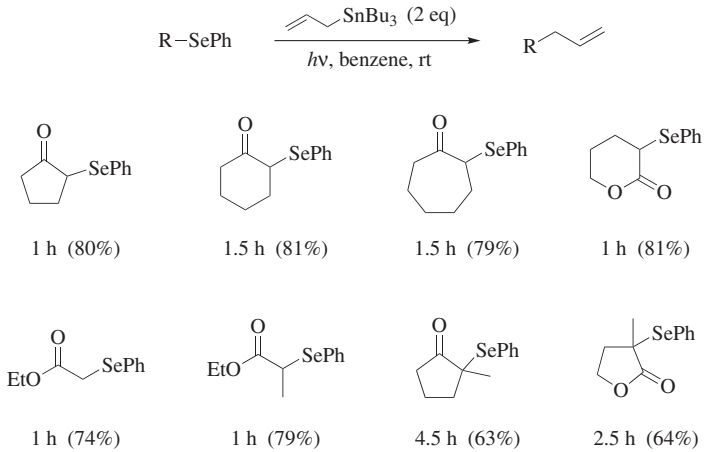
Scheme 30

In a systematic study of allylation reactions of α-phenylseleno carbonyl compounds, ketones and esters were found to afford similar yields of products, as were cyclic and acyclic substrates; with cyclic substrates, yields are independent of ring



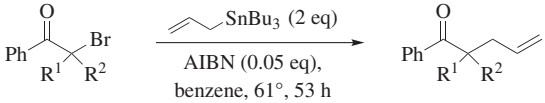
Scheme 31

size (Scheme 32).[77] Although primary and secondary substrates generate products in comparable yields, the two tertiary substrates examined react more slowly and are lower yielding.



Scheme 32

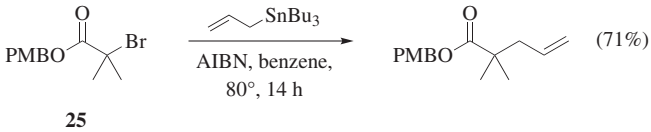
The lower efficiency of allylation reactions with tertiary α-keto radicals is further illustrated by a study of allylation reactions of acetophenone derivatives (Scheme 33).[59] The primary and secondary radicals form the product in high yields, whereas the tertiary substrate only affords a trace amount of product. This poor yield is thought to be a result of the relatively slow rate of addition of the more sterically hindered tertiary radical to allyltributylstannane, which prevents the radical chain from propagating effectively. Interestingly, the tertiary α-bromo ester **25** reacts with



R^1	R^2	Yield (%)
H	H	95
Me	H	99
Me	Me	trace

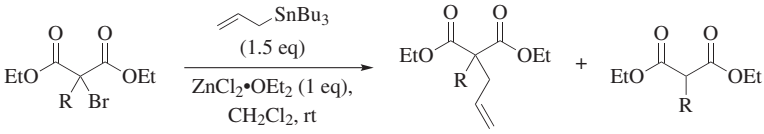
Scheme 33

allyltributylstannane to give the allylation product in 71% yield (Scheme 34),[78] suggesting that the poor reaction of tertiary radicals may be specific to tertiary α-keto radicals.



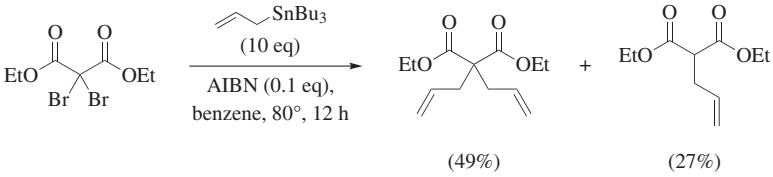
Scheme 34

Numerous examples have been reported that involve the reaction of dicarbonyl-substituted radicals with allyltributylstannane. In a study of malonyl radicals, the tertiary substrate exclusively forms the allylation product in 59% yield, whereas the reaction of the secondary substrate gives a 30% yield of the allylation product, which is accompanied by 25% of the reduction product (Scheme 35).[50,51] The related dibromomalonate derivative reacts with 10 equivalents of allyltributylstannane to afford a 49% yield of the diallylated product and 27% of the debrominated monoallyl product (Scheme 36).[79]



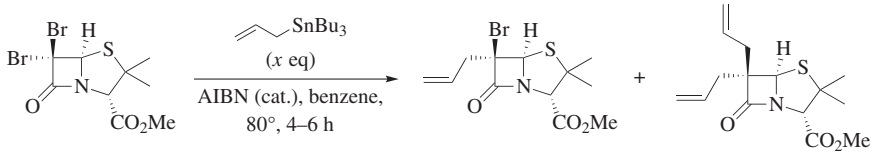
R	Yield (%)	
Me	59	0
H	30	25

Scheme 35



Scheme 36

With other α,α-dibromocarbonyl substrates, it is sometimes possible to control the amount of mono- versus diallylation product. Penicillin derivative **26** reacts with 1.7 equivalents of allyltributylstannane to furnish primarily the monoallylation product **27**, whereas the analogous reaction with three equivalents of stannane provides the diallylation product **28** in excellent yield (Scheme 37).[80,81] It is noteworthy that that the monoallylation product **27** is formed with complete control of facial selectivity.

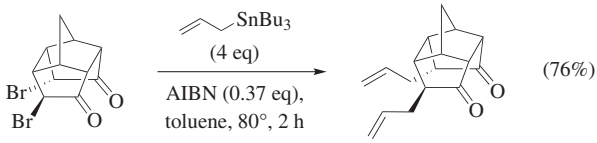


26 **27** **28**

	Yield (%)	
x	**27**	**28**
1.7	54	13
3	0	84

Scheme 37

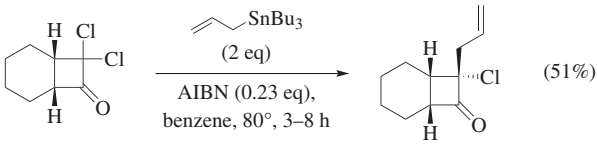
Non-geminal dibromides of caged diketones such as **29** undergo efficient diallylation when heated in toluene with four equivalents of allyltributylstannane in the presence of AIBN (Scheme 38).[82] Attempted enolate-based diallylation of the corresponding non-brominated diketone is unsuccessful, thereby illustrating the synthetic utility of this approach.



29

Scheme 38

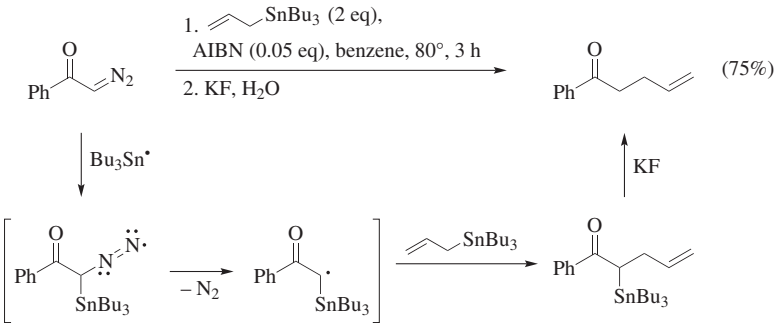
α,α-Dichloro carbonyl substrates behave differently from the analogous α,α-dibromocarbonyl substrates, undergoing selective monoallylation even with excess allylstannane. Bicyclic substrate **30** and numerous analogues react with two equivalents of allyltributylstannane at reflux in benzene in the presence of AIBN to form monoallylated products in moderate-to-good yields (Scheme 39).[83–85] Allylation occurs exclusively on the more accessible convex face of the bicyclic system. The initial allylation is facilitated by the stability of the α-chloro-α-keto radical. Further allylation is likely prohibited by the steric inaccessibility of the chlorine atom on the *endo* face in the mono-allylation product.



30

Scheme 39

An unusual approach to the allylation of α-carbonyl radicals uses α-diazo ketones and esters as the precursors. For example, the reaction of α-diazoacetophenone with allyltributylstannane in benzene at reflux in the presence of AIBN for three hours affords the allylation product in 75% yield (Scheme 40).[64] The reaction is believed to proceed by initial addition of tributylstannyl radical to the α-carbon, followed by loss of nitrogen. The resulting radical reacts with allyltributylstannane to give the initial product, which has a tributylstannyl group at the α-position. The tin is removed upon treatment with potassium fluoride. Several other α-diazo ketones and ethyl diazoacetate are allylated in comparable yields by this method.



Scheme 40

Allylation substrates can employ other electron-withdrawing groups to stabilize the intermediate radical, including nitro groups, sulfides, sulfoxides, and sulfones, fluorine and chlorine atoms, and trifluoromethyl groups. In the case of nitro-substituted radicals, simple secondary and tertiary α-nitro bromide substrates provide the desired allylation products in good yields. Bromonitromethane, which forms a primary radical, also undergoes allylation, albeit in a low yield (35%) (Figure 6).[86]

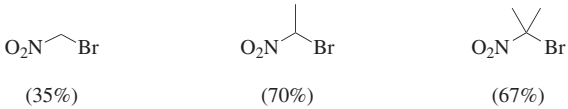
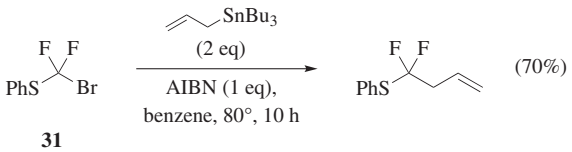


Figure 6. Yields for allylation of simple primary, secondary, and tertiary α-nitro bromides.

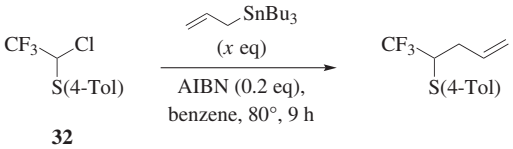
Although the nitro group can serve to stabilize a radical, it can also be used as a radical precursor (vide supra). When a substrate contains a single bromine or chlorine atom attached to the same carbon as the nitro group, the halogen is abstracted and replaced by an allyl group upon reaction with allyltributylstannane.[86] Alternatively, if two bromines are attached to the same carbon as the nitro group, the bromines are abstracted and replaced by a pair of allyl groups (see Scheme 25). However, if the substrate possesses two chlorines, it is the nitro group that is replaced by an allyl group (see Scheme 24).[63] In the only example of an α-nitro iodide reacting with

allyltributylstannane, allyl iodide is the only product reported, and the fate of the nitroalkyl group is not addressed.[86]

Like nitro groups, aryl sulfides can act as radical-generating groups, but their reactivity in this role is attenuated, and therefore aryl sulfide substituted radicals can be formed from substrates bearing a more reactive radical-generating group, such as a bromine. In practice, this transformation has only been accomplished with substrates bearing an additional electron-withdrawing functional group at the radical center. For instance, the thiophenyl-bearing, geminal difluoride **31** reacts with allyltributylstannane to form the allylation product in 70% yield (Scheme 41).[87] Similarly, the trifluoromethyl-substituted bromide **32** is allylated in 21% yield when two equivalents of allyltributylstannane are used and in 45% yield using four equivalents (Scheme 42).[88] In contrast, the aryl sulfone derivative is much more reactive, furnishing an 89% yield of the allylated product with two equivalents of allylstannane. Allylation reactions of sulfone substrates that do not bear an additional electron-withdrawing group are also efficient and are compatible with amines, ethers, ketones, esters, and nitro groups present within the substrate.[89] Interestingly, the sulfoxide-substituted analogue of **32** fails to undergo allylation, albeit many successful examples of allylation of sulfoxide-substituted radicals have been reported.[88] These reactions generally proceed with moderate-to-good diastereocontrol, directed by the sulfoxide stereocenter, and are discussed in greater detail below.



Scheme 41

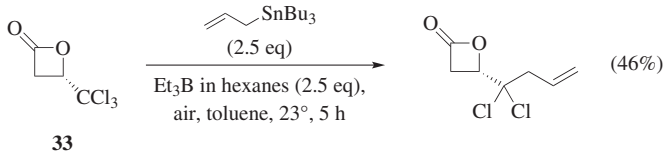


x	Yield (%)
2	21
4	45

Scheme 42

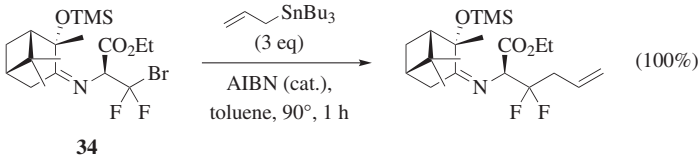
Chloroform and carbon tetrachloride are both allylated with allyltributylstannane under radical conditions, although the reaction using carbon tetrachloride affords the product in significantly higher yield (73% versus 40% for chloroform).[37] Reaction of the more complex trichloromethyl substrate **33** with allyltributylstannane is incomplete with one equivalent of stannane and affords a 46% yield with 2.5 equivalents (Scheme 43).[90]

α,α-Difluorobenzyl chloride is allylated in 54% yield, but five equivalents of the stannane are necessary.[91,92] The analogous reaction of non-fluorinated benzyl chloride requires ten equivalents of allyltributylstannane to afford the product in 68%



Scheme 43

yield since one equivalent only generates a trace amount of the desired product.[37] In contrast, the difluoro substrate **34** delivers the monoallylation product quantitatively using only three equivalents of allyltributylstannane in toluene at 90° (Scheme 44).[93]



Scheme 44

Chlorodifluoromethylated heterocyclic substrates react in good-to-excellent yields with 2.5 equivalents of allyltributylstannane in refluxing benzene. This reaction is successful with several pyridine, pyrimidine, and pyrazole substrates (Figure 7).[94]

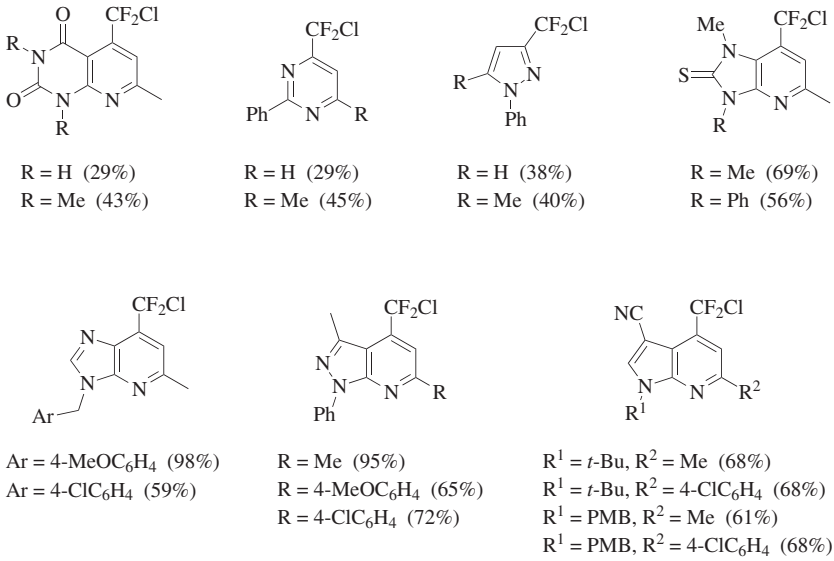


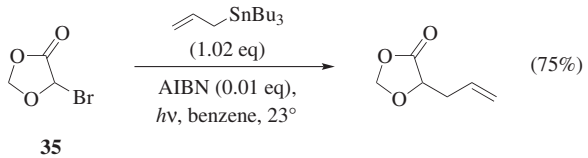
Figure 7. Successfully allylated chlorodifluoromethyl pyridine, pyrimidine, and pyrazole substrates with percent yields for the allylation reactions.

Perfluorinated alkyl halides also provide good substrates for the allylation with allyltributylstannane, in which both primary and secondary radicals are successful, as are simple and branched substrates (Figure 8). In these reactions, the separation of the products from the tin byproducts can be conveniently accomplished by liquid–liquid extraction with a fluorous solvent,[95] by either eluting through fluorous reverse-phase silica gel[96] or eluting through standard silica gel using a fluorous solvent.[97]

$CF_3(CF_2)_5I$	$(CF_3)_2CFI$	$CF_3(CF_2)_7I$	$(CF_3)_2CF(CF_2)_8I$
(39%)[98]	(37%)[98]	(81–83%)[95–97]	(91%)[96]

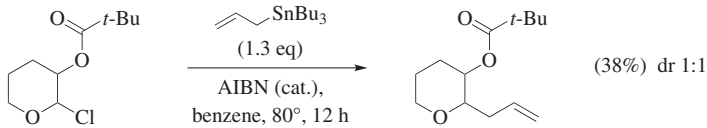
Figure 8. Yields for allylation of perfluoroalkyl iodide substrates.

Captodative radicals, such as the radical formed from the reaction of 1,3-dioxolane-4-one **35** under photolytic conditions at 23°, react with allyltributylstannane in good yield (Scheme 45).[99]

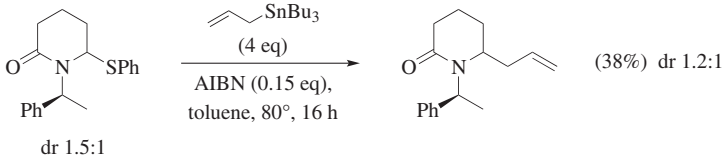


Scheme 45

Although most allylation reactions with allyltributylstannane involve an electron-poor radical, even electron-rich α-alkoxycarbonyl and α-alkoxy radicals are reactive (Scheme 46).[100] However, most examples involve carbohydrate-derived radicals, and the reactions of simple radicals adjacent to oxygen atoms are usually lower yielding than reactions of their electron-poor counterparts. Allylations of radicals adjacent to nitrogen atoms have been reported but are generally inefficient (Scheme 47).[101]



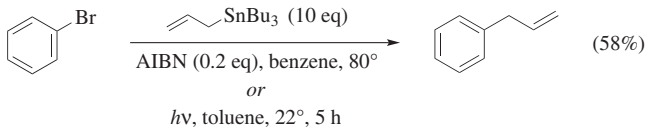
Scheme 46



Scheme 47

Aryl and Vinyl Radicals. In general, radical addition reactions using sp^2-hybridized aryl and vinyl radicals are much less common than reactions of sp^3-hybridized radicals, and this is also the case for allylation reactions. The formation of sp^2-hybridized radicals is generally not a limiting factor: the rate of iodine/bromine atom abstraction by tributyltin radical from aryl or vinyl iodides/bromides is actually quite high (on the order of 10^6–10^8 $M^{-1}s^{-1}$).[52] Furthermore, aryl radicals are known to add to alkenes with rate constants greater than 10^7 $M^{-1}s^{-1}$, demonstrating that the addition step is also not a problem.[102] However, these radicals are so reactive that other processes occur at competitive rates, and the most common side reaction is an intramolecular 1,5-hydrogen-atom abstraction. As will be discussed later in this section, this efficient intramolecular process can be used to generate substrate radicals without the need to install a direct radical precursor (cf. Schemes 102, 170).

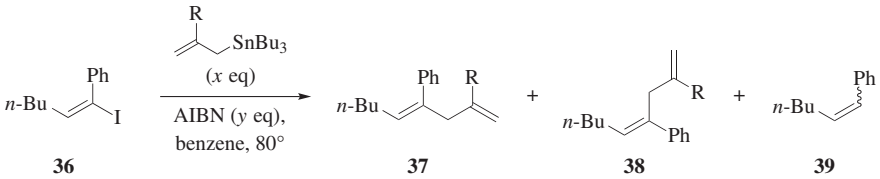
An early study of the general synthetic utility of allylations with allylstannanes employed bromobenzene as a substrate.[37] The reaction of bromobenzene with allyltributylstannane requires 10 equivalents of the allylstannane for optimal yields, and allylbenzene was obtained in 58% yield irrespective of whether the reaction was performed with AIBN as an initiator in benzene at reflux or photochemically in toluene at room temperature (Scheme 48). Only two other allylations of aryl radicals have been reported, each involving addition of a substituted aryl radical to a modified allylstannane reagent.[36,103]



Scheme 48

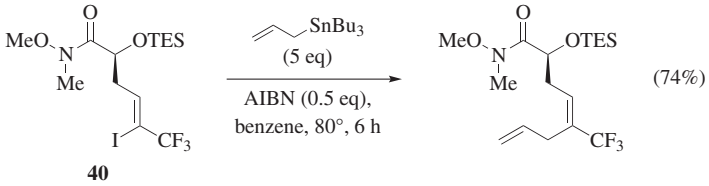
The allylation reactions of vinylic radicals have received slightly more attention. Vinyl radicals are nucleophilic, so the reactions are most efficient with allylstannanes that are substituted with electron-withdrawing groups. For example, (*E*)-1-iodo-1-phenyl-1-hexene (**36**) reacts with allyltributylstannane to form the diastereomeric allylation products **37** and **38** in only 5% yield after 24 hours at 80° (Scheme 49).[104] The competing reduction product **39** is formed in 4% yield, and 61% of the starting iodide **36** is recovered. In contrast, the carbomethoxy- and cyano-substituted allylstannanes react to afford the allylation products in 86% and 70% yield, respectively, after only a few hours in refluxing benzene. The (*Z*)-isomer **37** is formed preferentially because attack of the allylstannane with the linear sp-radical occurs from the less-hindered face opposite the *n*-butyl group.

The reaction of vinyl radicals with unsubstituted allyltributylstannane is more effective when the alkenes are electron-deficient. For instance, the trifluoromethyl-substituted vinyl iodide **40** reacts with allyltributylstannane in refluxing benzene to form the allylated product in 74% yield (Scheme 50).[105] In another example, the uracil-derived vinyl iodide **41** is allylated in 80% yield when



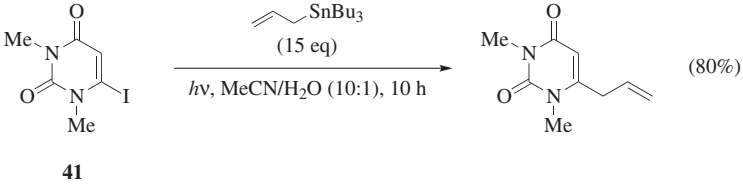
R	x	y	Time (h)	Yield (%) 37 + 38	39	37/38
H	2	0.15	24	5	4	6.1:1
MeO_2C	3	0.05	4	86	—	6.7:1
NC–	3	0.05	1	70	—	8.1:1

Scheme 49



Scheme 50

photolyzed with allyltributylstannane in an acetonitrile–water mixture at ambient temperature (Scheme 51).[106] There are also numerous examples of reactions of allylstannanes with vinyl radicals in the course of allylstannylation reactions that are discussed later (cf. Scheme 182).

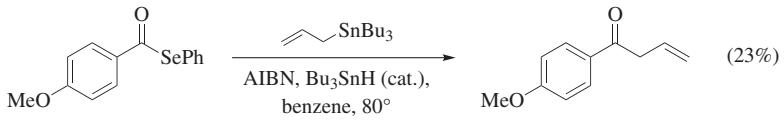


Scheme 51

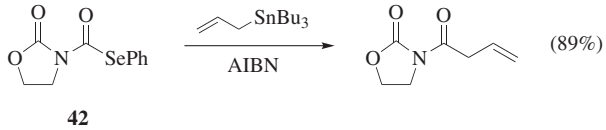
Acyl Radicals. The chemistry of acyl radicals has been thoroughly reviewed.[107] Acyl radicals can be generated by a number of methods, but the most common method involves the reaction of a trialkylstannyl radical with a phenyl selenoester. Once formed, decarbonylation of acyl radicals can be competitive with other processes. If the radical formed by decarbonylation is relatively unstable (primary, vinyl, aryl), loss of carbon monoxide is usually slow, although the rate increases at higher temperature.[108] However, if the radical is secondary or tertiary, a significant

amount of decarbonylation often occurs, even at lower temperatures. Acyl radicals can also be formed by the addition of an alkyl, aryl, or vinyl radical to carbon monoxide. This latter approach has been combined with additions to allylstannanes in multicomponent reaction processes that are discussed below (see Schemes 89–96).

In intermolecular atom abstractions (from tributyltin hydride or bromotrichloromethane), cyclization reactions, and addition reactions, acyl radicals exhibit rate constants similar to those of simple alkyl radicals.[109,110] In the context of allylation reactions, acyl radicals are typically nucleophilic, and therefore, additions to the parent allyltributylstannane are not high yielding. 4-Methoxybenzoyl radical adds to allyltributylstannane in a yield of only 23% (Scheme 52), while the addition of this radical to more electron-deficient alkenes (non-allylstannanes) is much higher yielding.[111] Interestingly, the radical derived from the oxazolidinone-substituted acyl selenide **42** is much less nucleophilic in character and adds more effectively to electron-rich alkenes, such as allyltributylstannane, to afford the allylation adduct in 89% yield (Scheme 53).[112] Acyl radicals derived from α-amino acids undergo rapid decarbonylation to form alkyl radicals that then react with allylstannanes (Scheme 54).[113]

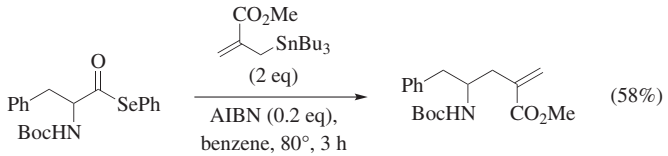


Scheme 52



42

Scheme 53

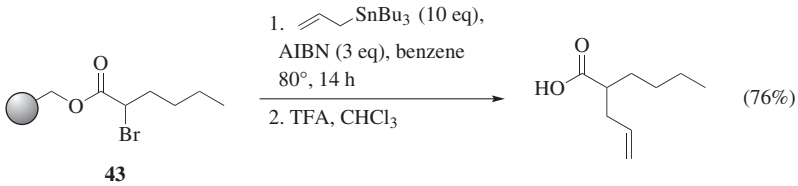


Scheme 54

Polymer-Bound Substrates and Reagents. One drawback to allylstannane reagents is that the organostannane byproducts are toxic and can be difficult to remove. One approach to overcoming this limitation is to tether one of the reactants

to a polymeric support, which allows the polymer-supported product or byproduct to be separated from the reaction mixture by filtration. The use of polymer supports for radical chemistry has been reviewed.[114]

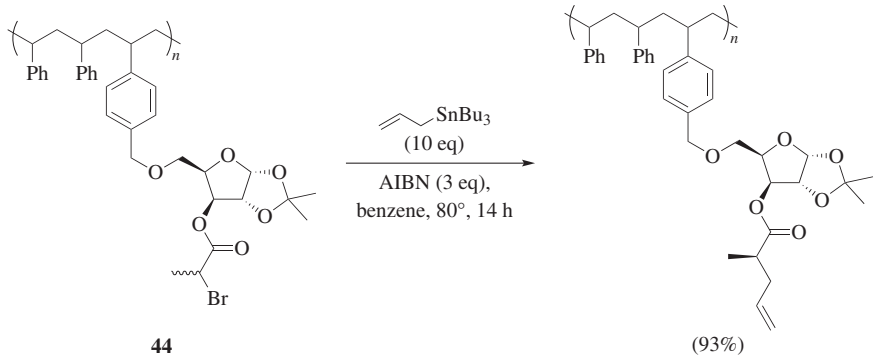
Either the substrate or the allylstannane can be attached to the polymer, but the former approach is more common. Cross-linked or non-cross-linked polymers can be used, resulting in hetero- and homogeneous reaction mixtures, respectively. In a typical case, an α-bromo acid bromide is attached via the pendant hydroxymethyl groups on Wang resin. The resulting insoluble polymer-bound substrates such as **43** react with allyltributylstannane in yields that are just slightly lower than those obtained with the analogous non-polymer-bound benzyl esters (Scheme 55).[78] However, 10 equivalents of allyltributylstannane and three-to-four equivalents of AIBN are necessary for efficient reactions with the polymer-bound substrates.

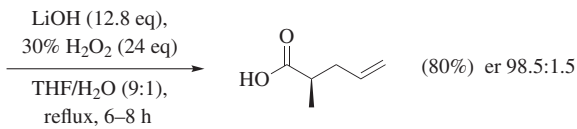


Scheme 55

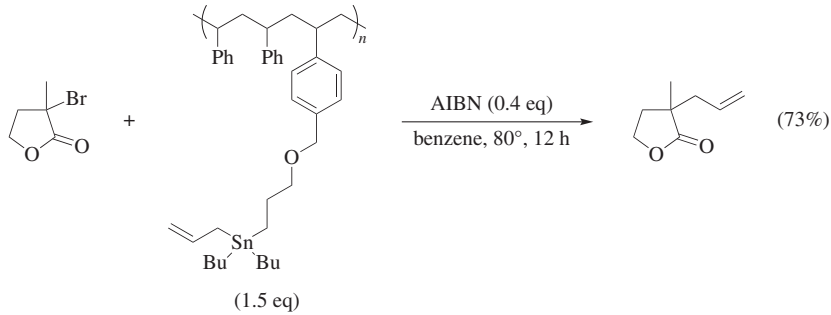
Non-cross-linked polymers derived from a 2:1 mixture of styrene and chloromethylstyrene can be coupled to α-bromo acids, and the resulting soluble substrates react to generate the products in high yields using three equivalents of allyltributylstannane and a catalytic amount of AIBN. At the conclusion of the reaction, the product-bound polymer can be precipitated from methanol, permitting easy separation from the tin byproducts; the product is then released from the polymer by alkaline hydrolysis. A chiral carbohydrate linker between the polymer and the α-bromo ester group can be used to control the stereochemistry in reactions of prochiral substrates, as in the reaction depicted in Scheme 56.[115] In this case, the radical reaction of **44** delivers a 93% yield of the allylated polymer. Basic saponification to cleave the product from the polymer proceeds in 80% yield, and (*R*)-2-methyl-4-pentenoic acid is isolated as a 98.5:1.5 mixture of enantiomers.

There is only one report of the use of a polymer-bound allylstannane reagent. The allylstannane is attached to a soluble, non-cross-linked polymer and reacts with secondary and tertiary α-bromo esters and ketones in good yields (Scheme 57).[116] After allylation, the polymer containing the tin byproduct is precipitated from methanol, and the purified allylation products have very low levels of residual tin. Relative to non-polymer-bound allylstannane reagents, this reagent exhibits increased reactivity towards electron-poor radicals: the tin atom is thought to complex with the oxygen atom in the tether, making the allyl group more electron-rich than that of allyltributylstannane.





Scheme 56



Scheme 57

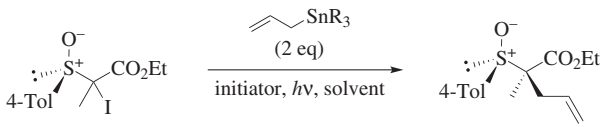
Direct Additions to Substituted Allylstannanes

Effect of Changing the Non-Allylic Substituents on Tin. While the majority of allylation reactions use allyltributylstannane, groups other than *n*-butyl can be used as the non-allylic substituent on the tin. Importantly, the alkyl/aryl groups can impart different reactivities to the allylstannane reagents, and the use of polar, fluorinated alkyl, polyaromatic, or inorganic substituents facilitates the separation of tin-containing byproducts.

Alternative Alkyl/Aryl Groups. Allylstannanes with methyl and phenyl groups attached to tin have been used in place of allyltributylstannane, and of the two, allyltriphenylstannane is more common. In the few examples where there is a relatively direct comparison, the yields are usually slightly better with allyltributylstannane

than with allyltrimethylstannane. For example, the allylation of methyl chloroacetate occurs in 53% yield using allyltributylstannane in benzene at 80° in the presence of AIBN,[37] whereas neat allyltrimethylstannane at the same temperature with benzoyl peroxide as the initiator delivers the same product in 24% yield.[1] Allyltrimethylstannane is less readily available from commercial sources, and its byproducts are relatively volatile, which may provide an advantage in some situations, but can also increase exposure to hazardous tin substances. Given these factors, allyltrimethylstannane is not often the reagent of choice.

A few studies have compared the allylation reactions using allyltributyl- and allyltriphenylstannane. In some cases, the yields of the two reactions are nearly identical, as in the allylation of the chiral sulfoxide **45**. The yields and diastereomeric ratios are the same regardless of whether the reaction employs allyltributylstannane in dichloromethane[117] or allyltriphenylstannane in benzene (Scheme 58).[60]

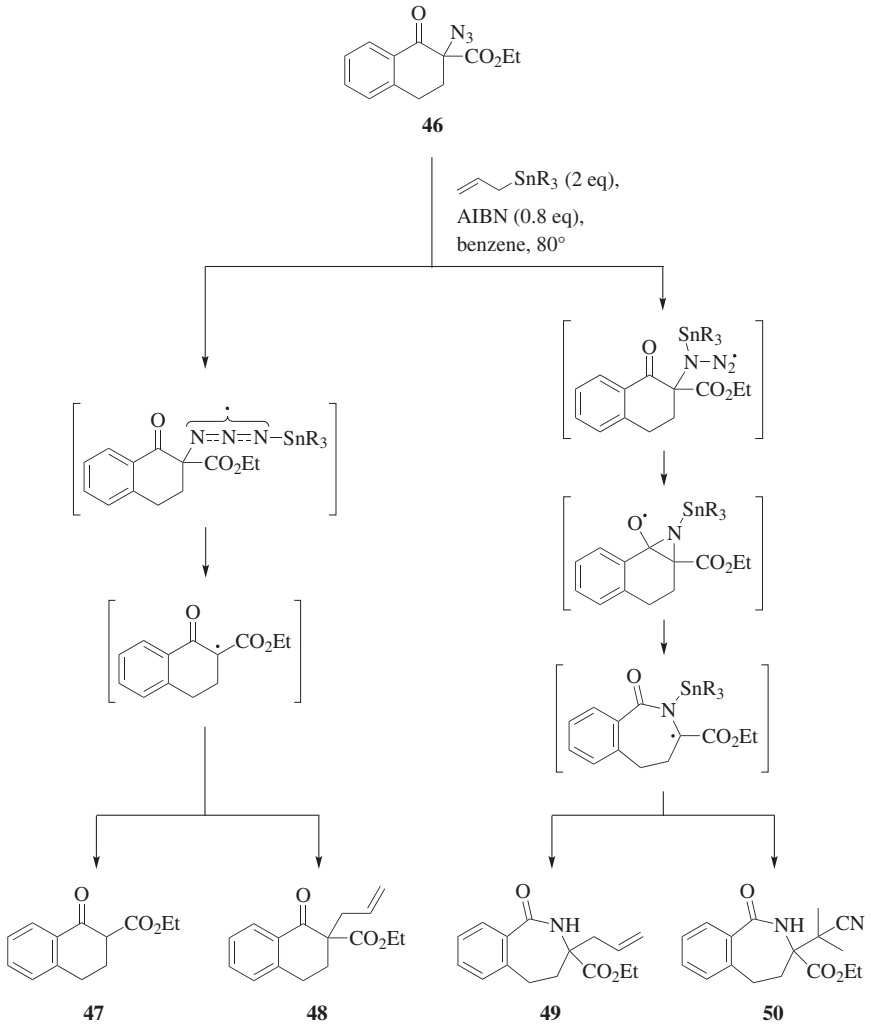


45

R	Initiator	Solvent	Temp (°)	Time (h)	Yield (%)	dr
Bu	AIBN	CH_2Cl_2	15	—	86	49:1
Ph	none	benzene	25	0.5	87	>49:1

Scheme 58

In other cases, however, the allylstannane can dramatically affect the outcome of a reaction. Scheme 59 depicts the attempted synthesis of allylated ε-lactam **49**.[118] The initial reaction of a stannyl radical with **46** can result in addition either at the terminal nitrogen of the azide, leading to products **47** and **48**, or at the internal nitrogen, generating products **49** and **50**. Using allyltributylstannane, addition to the internal nitrogen atom is favored (~2:1 internal/terminal nitrogen addition), but the penultimate radical is trapped by 2-cyanopropyl radical from AIBN (which is used in a nearly stoichiometric amount). With allyltriphenylstannane, the ratio of products from terminal addition to internal addition is 4.5:1 and, again, none of the desired product **49** is formed. The greater propensity for triphenylstannyl radical to add primarily to the terminal nitrogen is believed to be due to its greater steric size. For the products resulting from initial addition to the terminal nitrogen (**47** and **48**), the deazidated radical is completely allylated by allyltriphenylstannane, whereas reaction with allyltributylstannane results in a 4:1 mixture of reduction product to allylation product, although the source of the hydrogen atom necessary to form **47** is not known. This data indicates that the radical intermediate adds more quickly to allyltriphenylstannane than to allyltributylstannane. Several additional reactions have been reported wherein allyltriphenylstannane is necessary to achieve reasonable yields of an allylation product.[119,120]

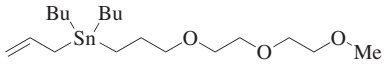


		Yield (%)			
R	Time (h)	**47**	**48**	**49**	**50**
Bu	4.5	22	5	0	48
Ph	4	0	63	0	14

Scheme 59

Reagents that Form Easily Separable Byproducts. Organotin byproducts are notoriously difficult to remove from product mixtures, and this problem is exacerbated by their toxicity. Modifications of the non-allyl substituents on tin can facilitate easier removal of the organotin byproducts from reaction mixtures. For example, reagent **51** has a long, polar substituent in place of one of the butyl groups

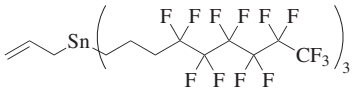
(Figure 9).[121] The organotin byproducts formed in reactions with allyltributylstannane usually streak through a chromatography column, but those formed from **51** are polar enough to elute cleanly from silica gel with pure ether, allowing less polar products to be isolated first. In the few cases where identical substrates have been examined, unoptimized yields of the allylation product formed with reagent **51** are slightly lower than yields with allyltributylstannane.[37,121] However, kinetic studies show that the rate constant for addition of a primary radical to reagent **51** is very similar to the rate constant for addition to allyltributylstannane.[122]



51

Figure 9. Allylstannane **51** contains a polar substituent that facilitates byproduct separation.

When fluorinated alkyl groups are used in place of butyl groups, the fluorous tin halide byproducts can be separated from non-fluorous products either by partitioning with a fluorous solvent or by reverse fluorous solid-phase extraction.[123] A hydrocarbon spacer is needed between the tin and the fluorinated portion of the alkyl group to avoid polar effects that can negatively influence the reactivity of the allylstannane. Compound **52**, which bears a three-carbon spacer and a six-carbon fluorinated chain, generally affords the best results with yields that are slightly higher than those for reactions of identical substrates under similar conditions with allyltributylstannane (Figure 10).[123–125]

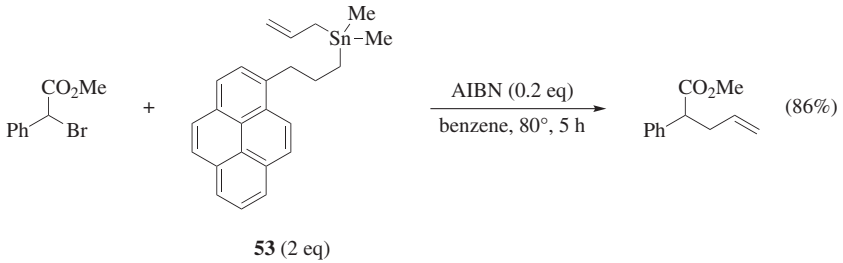


52

Figure 10. Allylstannane **52** contains fluorinated substituents that facilitate byproduct separation.

In an alternative approach, the reaction of allylstannane **53**, which possesses a polyaromatic tin substituent, delivers allylation products in good yields (Scheme 60).[126] Upon completion of the reaction, the crude product mixture is dissolved in a 3:2 mixture of methanol and dichloromethane and stirred with activated charcoal, which adsorbs the tin halide byproducts. Filtration provides the allylation product with >99% purity.

One final variation on this theme is reagent **54** (Figure 11), which can be easily prepared in situ by the reaction of the corresponding allyl bromide with commercially available stannylene $Sn[N(TMS)_2]_2$. The 2-unsubstituted analogue has also been prepared but has not been used for radical allylations.[127] The reaction of compound



Scheme 60

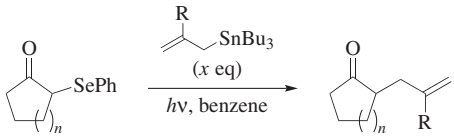
54 with benzyl bromide and a catalytic amount of AIBN in benzene at reflux gives a 73% yield of the allylation product, which is nearly identical to the yield obtained using 2-carboethoxyallyltributylstannane.[128] When the reaction mixture is loaded onto a silica gel chromatography column, the inorganic groups are hydrolyzed to non-toxic inorganic species that are easily separated from the allylated product. ICP–MS analysis reveals that the levels of residual tin in the isolated product are 50 times lower using **54** than with 2-carboethoxyallyltributylstannane.

54

Figure 11. Allylstannane **54** produces an inorganic tin byproduct, which facilitates purification.

Substitution at C-2. Numerous allylstannanes bearing a substituent other than hydrogen at C-2 have been used in radical allylation reactions, and in some cases, the substituent affects the reactivity of the allylstannane. The most common 2-substituted allylstannanes are methallyltributylstannane and either the 2-carboethoxy- or 2-carbomethoxy-substituted derivatives, which are used interchangeably. Methyl substitution makes the allylstannane more electron-rich, thereby enhancing the reactivity towards electron-poor radicals. In contrast, the acrylate derivatives are more electron-deficient and thus are more reactive with electron-rich radicals. Despite these innate differences in reactivity, 2-substitution typically has little effect on product yields. For example, the irradiation of α-phenylselenocycloalkanones and either allyl- or methallyltributylstannane in benzene affords the allylated products in similar yields, regardless of the stannane used (Scheme 61).[77,129]

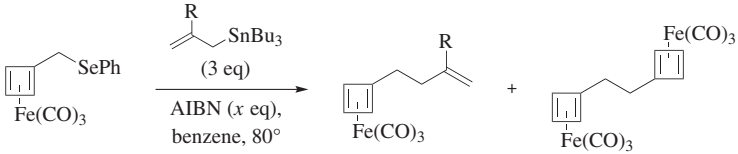
However, in some cases, the yield or selectivity of a reaction can be significantly affected by the nature of the allylstannane. The cyclobutadieneiron tricarbonyl substituted radical derived from phenylselenide **55** is highly stabilized and is a very nucleophilic radical.[130] Hence, the attempted reaction of the radical derived from **55** with allyltributylstannane leads to dimerization to generate **57** in moderate yield with only a trace of the allylation product **56** (R = H). In contrast, the allylation with the



n	R	x	Time (h)	Yield (%)
0	H	2	1	80
0	Me	1.5	1	80
1	H	2	1.5	81
1	Me	1.3	2.5	93
2	H	2	1.5	79
2	Me	2	1	85

Scheme 61

more electron-deficient 2-carboethoxyallyltributylstannane affords **56** (R = CO_2Et) as the sole product in moderate yield (Scheme 62).



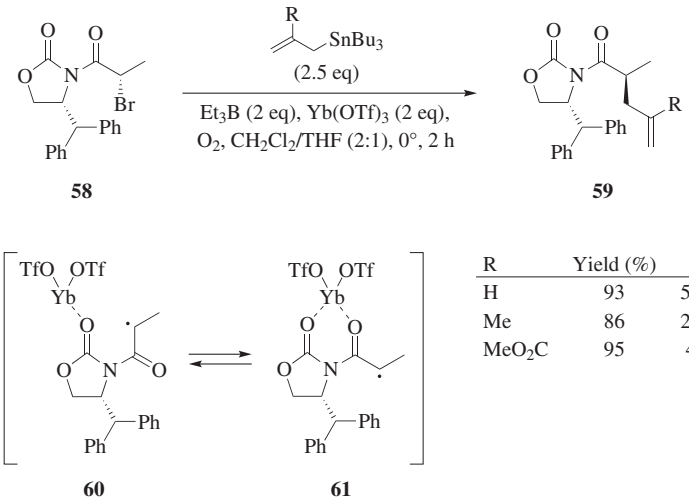
55 **56** **57**

R	x	Time (h)	Yield (%) **56**	Yield (%) **57**
H	1	22	trace	50
EtO_2C	0.2	18	55	0

Scheme 62

In another example, the allylstannane structure has a dramatic effect on the diastereoselectivity in the allylation of the radical derived from the secondary bromide **58** (Scheme 63).[131] This ytterbium(III) triflate mediated reaction is highly diastereoselective only when the radical reacts predominantly from the bidentate conformer **61**, in which the ytterbium is chelated by the two carbonyl oxygens. However, a steric interaction between the bromide and the oxazolidinone substituent prevents effective chelation in the radical precursor **58**, and thus, the initial radical is primarily conformer **60**. Therefore, in order to obtain high diastereoselectivity, the radical must be allowed to rotate from its initial conformation, **60**, to the chelated conformation **61**. Competition experiments have established that, in the reaction with the radical derived from bromide **58,** the relative reactivity of allyltributylstannane to methallyltributylstannane to 2-carbomethoxyallyltributylstannane is 1:5:25. Because allyltributylstannane is the least reactive, the radical formed from **58** is able to rotate to the chelated conformation **61**, and product **59** (R = H) is formed with the highest degree of diastereoselectivity. The reaction with the most reactive allylstannane

(i.e., the 2-carbomethoxy-substituted compound) occurs too rapidly to allow for significant bond rotation from **60** to **61**, and therefore, diastereoselectivity is low.



R	Yield (%)	dr
H	93	50:1
Me	86	22:1
MeO_2C	95	4:1

Scheme 63

A variety of other C-2 substituents have been used either to enhance reactivity or as a handle to install desired functionality or structural units. Allylstannanes bearing the hydrocarbon groups *n*-butyl[132] and phenyl[97] have been used, as have the substituted alkyl groups hydroxymethyl,[133] benzyloxymethyl,[134] $(CH_2)_4CO_2Me$,[77] and triphenylstannylmethyl.[38] The last reagent forms a substituted allylstannane upon addition of the first equivalent of the radical and subsequently reacts with a second equivalent. Electron-withdrawing groups other than the carbomethoxy and -ethoxy groups include the carbobenzyloxy group,[132] the *tert*-butyl amide group,[44] chloro,[45] cyano,[45] and phenylsulfone.[135] One strongly electron-donating group, the acetoxy group, has also been used as a 2-substituent, and while this allylstannane does not react with simple alkyl radicals like *n*-decyl, benzyl, or 1-adamantyl,[44] it does react efficiently with a resin-bound tertiary α-keto radical.[78]

The allylstannanes **62**, **63**, and **11** were designed specifically to allow for subsequent transformations of the allylated products (Figure 12). For example, the trimethylstannyl group in the products derived from the reaction of compound **62** can, in principle, be converted to a halide or used directly in a Stille coupling reaction,[41] although no reports of such applications have been reported.

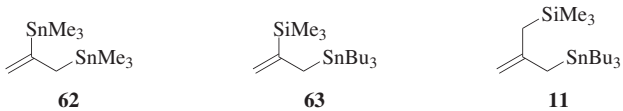
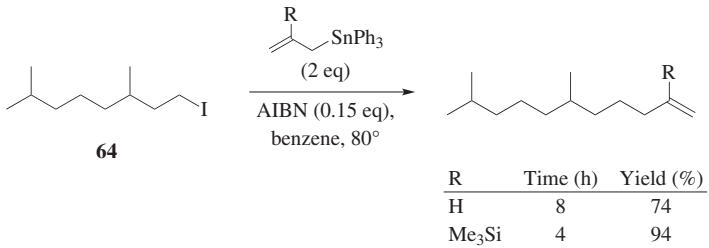


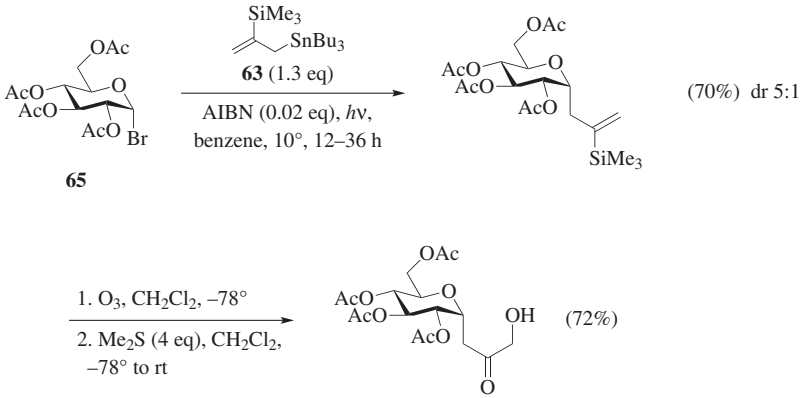
Figure 12. 2-Substituted allylstannanes incorporating stannyl or silyl groups that can be used for further functionalization.

The 2-trimethylsilyl-substituted allylstannane **63** provides synthetic flexibility and also has enhanced reactivity relative to allyltributylstannane: in competition studies, 2-(trimethylsilyl)allyltributylstannane reacts faster with both electron-rich and electron-poor radicals, albeit the rate enhancement is greatest with electron-rich radicals.[61] Few direct comparisons are available, but in one example, the reaction of primary iodide **64** occurs in higher yield in a shorter reaction time when treated with the triphenylstannyl derivative of **63** than with allyltriphenylstannane (Scheme 64).[39]



Scheme 64

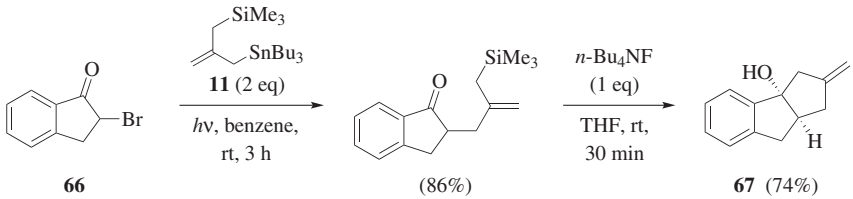
The vinylsilane group of the products derived from the reaction of 2-(trimethylsilyl)allyltributylstannane (**63**) can be converted to a variety of different functionalities, including vinyl halides, methyl ketones, hydroxymethylketones and simple alkenes.[61] Scheme 65 illustrates one example of the potential of this reagent: protected glucopyranosyl bromide **65** reacts with allylstannane **63** to form the allylation product in 70% yield with 5:1 α/β diastereoselectivity. Subsequent ozonolysis of the allylation product converts the vinylsilane to an α-hydroxymethylketone group in good yield.



Scheme 65

2-(Trimethylsilyl)methylallyltributylstannane (**11**) was also designed to take advantage of the synthetic utility of the allylsilane products.[36] This stannane reacts

with both electron-rich and electron-poor radicals but the reactions are generally more efficient with the latter, likely because the β-silyl group raises the energy of the frontier orbitals of the alkene, making the SOMO–HOMO energy gap for reaction with an electron-poor radical smaller than the SOMO–LUMO gap for reaction with an electron-rich radical. Photolysis of α-bromo ketone **66** with 2-(trimethylsilyl)methylallyltributylstannane (**11**) in benzene at room temperature provides the allylation product in 86% yield (Scheme 66). This product is then treated with n-Bu_4NF, which induces a Sakurai-type addition of the allylsilane to the ketone to form the tricyclic alcohol **67** in 74% yield along with 6% of the uncyclized protiodesilylation product.



Scheme 66

Substitution at C-1 or C-3. Allylstannanes with substitution at C-1 or C-3, such as (1-methyl-2-propenyl)tributylstannane (**68**) and crotyltributylstannane (**69**), have been used in radical allylation, but this type of substitution introduces new challenges. For C-3-substituted allylstannanes like crotyltributylstannane, the added steric hindrance slows the rate of radical attack at the substituted carbon. A methyl substituent at C-3 provides a sterically accessible position from which the radical can abstract a hydrogen atom, which, in the case of reagent **69**, generates a resonance-stabilized radical that loses tributylstannyl radical to form 1,3-butadiene. Furthermore, allylstannanes are subject to a tributylstannyl-radical-mediated rearrangement that interconverts the C-1- and C-3-substituted allylstannanes, as shown in Figure 13 for **68** and **69**. The equilibrium in this process usually favors the C-3-substituted compound **69**.

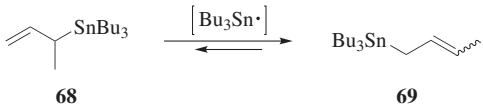
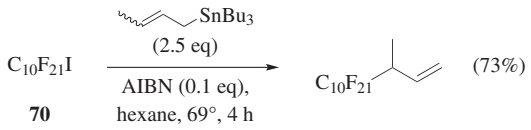


Figure 13. Tributylstannyl-radical-mediated isomerization of (1-methyl-2-propenyl)tributylstannane (**68**) and crotyltributylstannane (**69**).

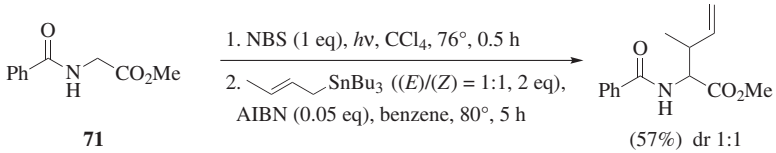
Simple alkyl radicals do not undergo efficient allyl transfer with crotyltributylstannane.[4] Under typical conditions for radical allylation (AIBN at 80° or photochemical initiation at ambient temperature), no reaction occurs. Reactions proceed at elevated temperatures but afford only products resulting from reduction of the radical.

With nucleophilic radicals, the rate of addition to the electron-rich crotylstannane is too slow to compete with hydrogen-atom transfer from the crotylstannane.

Allyl transfer reactions can be performed, however, with more electron-deficient radicals, which are activated for addition to electron-rich alkenes. For example, perfluoroalkyl iodide **70** reacts with crotyltributylstannane in refluxing hexanes containing a catalytic amount of AIBN to form the product in 73% yield along with a trace of the reduction product (Scheme 67).[96] Alternatively, the bromination of **71** with *N*-bromosuccinimide permits the radical allylation reaction, wherein the resulting glycinyl radical reacts with a 1:1 mixture of (*E*) and (*Z*) crotylstannanes to form the allyl-transfer product as an equal mixture of diastereomers in 57% yield for the two steps (Scheme 68).[136] Interestingly, when 8-phenylmenthol is deployed as a chiral auxiliary on the ester, the analogous reaction at 20° generates the product in 83% overall yield with a preference for the (2*S*,3*R*) diastereomer ((2*S*,3*R*)/(2*S*,3*S*) = 1.5:1, and (2*S*)/(2*R*) = 93:7).[137,138]

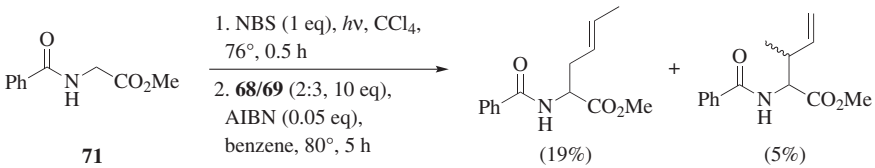


Scheme 67



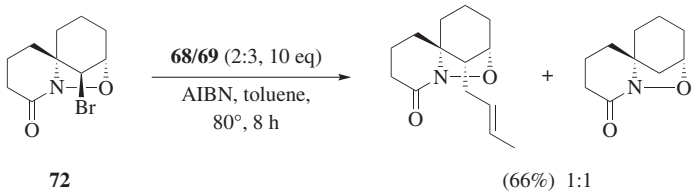
Scheme 68

Highly selective addition reactions with C-1-substituted allylstannanes have not been reported. As mentioned above, C-1-substituted stannanes like **68** are in equilibrium with their C-3-substituted isomers, so it is usually not possible to isolate C-1-substituted stannanes in pure form. Refluxing a mixture of **68/69** (2:3) in benzene with the bromide formed from glycinyl derivative **71** gives 19% and 5% yields of the products resulting from addition to **68** and **69**, respectively (Scheme 69).[136] In a similar reaction, tricyclic bromide **72** reacts with **68/69** (2:3) to furnish an equimolar mixture of the product of addition to stannane **68** and the reduction product in 66%



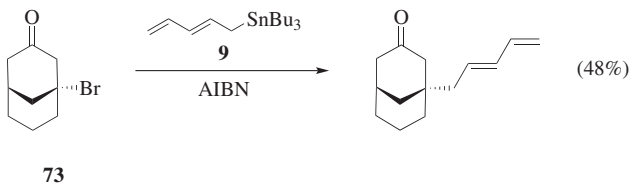
Scheme 69

overall yield (Scheme 70).[139] In this case, the product of addition to stannane **69** is not observed, which is presumably a consequence of the substrate's steric environment.

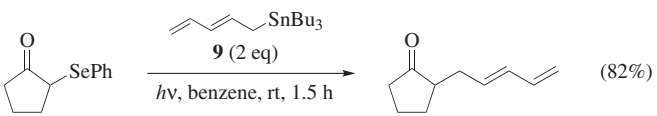


Scheme 70

One unusual C-3-substituted allylstannane, pentadienyltributylstannane (**9**), exhibits broad reactivity. This compound reacts well with both nucleophilic alkyl radicals and electron-poor radicals, with addition occurring exclusively at the terminal end of the diene system to form pentadienylated products. For example, reaction with the tertiary alkyl bridgehead radical generated from bromide **73** affords the pentadienylated product in 48% yield (Scheme 71).[71] Similarly, reaction with α-phenylselenocyclopentanone gives the pentadienyl transfer product in 82% yield (Scheme 72).[129]



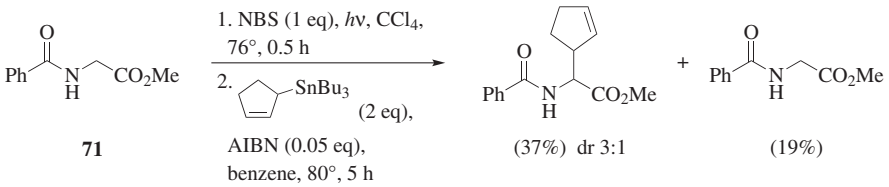
Scheme 71



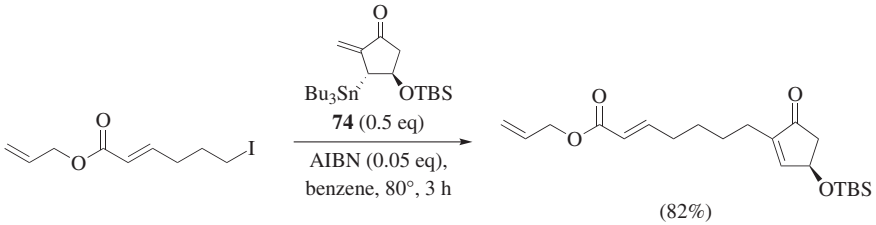
Scheme 72

Cyclic Allylstannanes. Radical allylation typically employs acyclic allylstannanes, but two studies have reported reactions with cyclic allylstannanes. (2-Cyclopentenyl)tributylstannane contains an endocyclic alkene and has been used on just one occasion in a reaction with the bromide formed from glycinyl derivative **71**. The cyclopentenylglycine-derived product is generated as a 3:1 mixture of diastereomers in 37% yield over two steps; the reduction product, the result of hydrogen-atom abstraction from the allylstannane, is also formed in 19% yield

(Scheme 73).[136] The second cyclic allylstannane, **74**, was developed for use in the synthesis of prostaglandin derivatives. This reagent possesses an exocyclic alkene and is electron-deficient owing to its ketone substituent. This allylstannane reacts in high yield with alkyl radicals (Scheme 74), and can also be employed in allylation reactions with aryl and acyl radicals, although yields are low.[103]

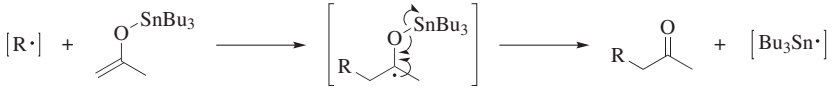


Scheme 73



Scheme 74

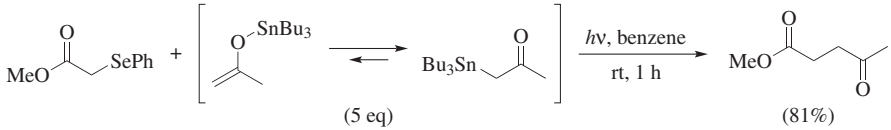
Radical Additions to Tin Enolates. While not technically allylstannanes, tributylstannyl enolates react with radicals via a mechanism similar to that observed with allylstannanes. Addition of a radical (R•) to the enolate α-carbon generates a new radical that undergoes a rapid β-scission to form a carbonyl group and a tributylstannyl radical, which can then propagate the radical-chain process (Scheme 75).



Scheme 75

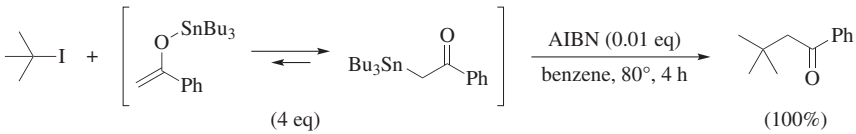
O-Metalated tin enolates exist in equilibrium with their tautomeric *C*-metalated forms. In the earliest investigation of these compounds in radical addition reactions, two tin enolates were specifically chosen because the equilibrium strongly favors the *O*-metalated form; successful reactions were reported only with trichloro- and tribromomethyl radicals.[140] Subsequent reports have expanded the scope of both the tin enolates and the substrates. For example, the tin enolate derived from acetone reacts efficiently with a number of α-phenylselenocarbonyl compounds, despite the fact that the equilibrium for this tin enolate lies heavily towards its *C*-metalated form

(Scheme 76).[141] Control experiments in this study provide evidence for the radical nature of this reaction.



Scheme 76

The alkenyl moiety in a typical *O*-tin enolate is electron-rich, so it is not surprising that the tin enolate derived from acetone is unreactive towards nucleophilic, simple alkyl radicals. However, the *O*-tin enolate derived from acetophenone reacts efficiently with both electron-poor and simple alkyl radicals, although a larger excess of the tin enolate is required to obtain high yields with more electron-rich radicals. For example, *tert*-butyl iodide reacts with the tributylstannyl enolate of acetophenone (two equivalents) in benzene at 80° in the presence of AIBN to afford a 65% yield of the product. However, the use of four equivalents of the tin enolate generates the product in quantitative yield (Scheme 77).[142] The equilibrium for this enolate also favors the *C*-metalated form.



Scheme 77

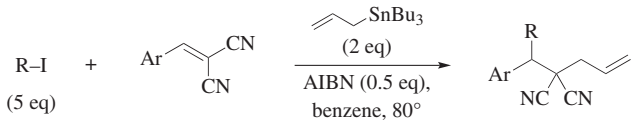
Multicomponent Reactions

Reactions of a Radical Precursor, Alkene, and Allylstannane. Because alkyl (and other nucleophilic) radicals add to allyltributylstannane at a relatively slow rate, the allylation reaction serves as the chain-transfer step in multicomponent radical-cascade processes. In a typical process, an electron-rich radical is generated in the presence of allyltributylstannane and an alkene bearing an electron-withdrawing group. The initial radical adds more rapidly to the electron-deficient alkene to form a new radical, which is electron-poor and thus undergoes selective addition to the more electron-rich double bond of the allylstannane rather than reacting with a second equivalent of the electron-poor alkene.

When the alkene is vicinally disubstituted or trisubstituted, this sequence proceeds smoothly to deliver the desired product of the three-component reaction. Reactions of monosubstituted alkenes are often complicated by competing telomerization reactions, and several strategies have been devised to either minimize or take advantage of this competing process. This type of three-component coupling process has been

used extensively in the development of stereoselective radical reactions; the stereochemical aspects of this process are addressed in the "Scope and Limitations" section.

A study with 1,1-dicyano-2-arylethenes demonstrates that the three-component allylation reaction tolerates a broad range of alkyl radicals and is most effective when the alkene is electron-poor (Scheme 78).[19] Using iodomethane as the radical source, yields are highest and reaction times are shortest for the chloro- and cyano-substituted β-aryl substituents, and least efficient using methyl- and methoxy-substituted aryl groups. The general order of reactivity for unsubstituted alkyl radicals is primary > secondary > tertiary, and this trend is reflected in the yields: iodomethane reacts with the phenyl-substituted electron-deficient alkene to afford the product in 85% yield, while *tert*-butyl iodide delivers the product in only 25% yield. Employing iodobenzene as a precursor to the phenyl radical results in the formation of some product, but the reaction time is long and the yield is poor. Iodide radical precursors deliver the optimal results in these reactions. For instance, using allyl iodide in the three-component reactions affords the product in 73% yield, whereas allyl bromide gives a 15% yield, and only a trace of the product is observed with allyl chloride. Moreover, no product is formed using alkyl bromides and chlorides. Hence, the reaction is tolerant of chloride, bromide, alcohol, ketone, and ester groups in the iodide radical precursor. While Scheme 78 provides yields for reactions performed at reflux with AIBN, the reactions can also be accomplished by photochemical initiation at room temperature. The former conditions are higher yielding when iodomethane is used, but in many other cases, photolytic conditions produce superior results.

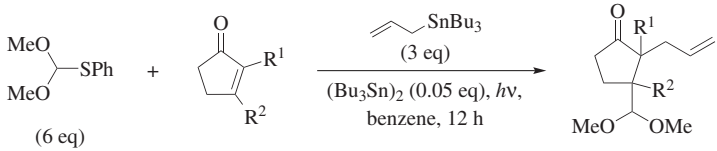


R	Ar	Time (h)	Yield (%)
Me	Ph	6	85
Me	4-NCC_6H_4	6	88
Me	4-ClC_6H_4	6	90
Me	4-Tol	12	66
Me	4-$MeOC_6H_4$	24	29
i-Pr	Ph	12	65
CH_2=$CHCH_2$	Ph	10	73
n-Bu	Ph	11	67
t-Bu	Ph	24	25
c-C_6H_{11}	Ph	12	47
Ph	Ph	48	13

Scheme 78

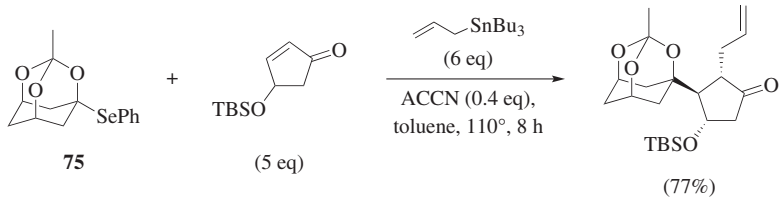
The three-component reaction is also successful when the initial radical is made more electron-rich by substitution with one or more alkoxy groups. Dimethoxy (phenylthio)methane reacts in the presence of allyltributylstannane with methyl acrylate, methyl crotonate, and several cycloalkenones to furnish the three-component

coupling products in moderate yields.[143] For methylcyclopentenone derivatives, methyl substitution at C-3 affords the product in lower yield than substitution at C-2, presumably due to increased steric congestion at C-3, which is the site of initial radical attack (Scheme 79). Stereoselectivity is low in these reactions, ranging from 2:1 to 8:1. Bulky orthoester-substituted selenide **75** can be used as the initial radical precursor in a three-component coupling with methyl acrylate, cyclohexenone, or a cyclopentenone (Scheme 80) as the participating alkene; reactions are conducted at 100°, employing 1,1-azobis(1-cyanocyclohexane) (ACCN) as the initiator.[144] In these reactions, products are obtained with the alkyl and allyl groups oriented *trans* to one another; in the reaction depicted in Scheme 80, the *trans*/*trans* product is obtained exclusively.



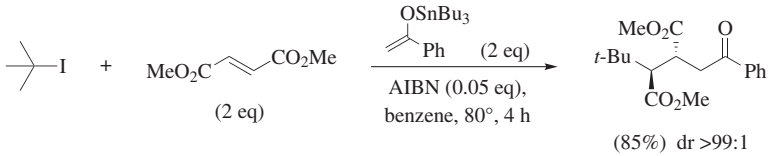
R^1	R^2	Yield (%)	dr
H	Me	28	3:1
Me	H	51	3:1

Scheme 79



Scheme 80

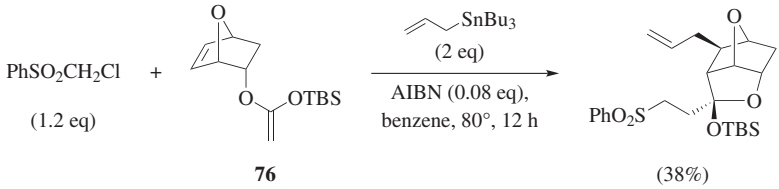
Three-component reactions are especially successful when an electron-rich stannyl enolate is used as the final trapping reagent. The reaction of *tert*-butyl iodide with dimethyl fumarate and the stannyl enolate of acetophenone in refluxing benzene affords an 85% yield of the product with excellent diastereoselectivity (dr >99:1) (Scheme 81).[142] Reactions using methyl acrylate and acrylonitrile as the



Scheme 81

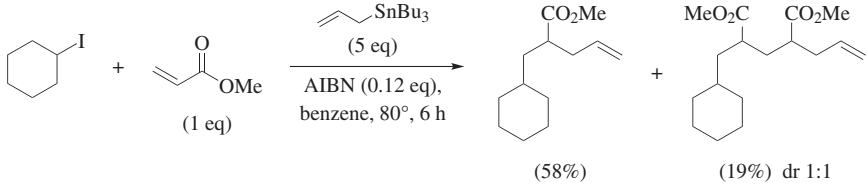
alkenes afford similarly high yields, and the initial radical can also be derived from iodoethane or isopropyl iodide, although stereoselectivities are reduced in reactions of these less bulky radicals with dimethyl fumarate.

If the alkene substrate of a three-component reaction contains a second alkene unit, a cyclization can precede final trapping by the allylstannane, thereby forming an additional carbon–carbon bond in the reaction sequence (Scheme 82).[145] For example, the primary radical generated from chloromethyl phenyl sulfone adds to the terminal alkene in silyl ketene acetal **76**. The resulting radical undergoes a 5-*exo* cyclization onto the pendent alkene in the bicyclic ring, followed by trapping of the cyclized radical by allyltributylstannane. Interestingly, when (phenylthio)acetonitrile is used rather than the sulfone, a 1,5-hydrogen-atom shift occurs from the cyclized radical with the nitrile-substituted carbon atom prior to allylation.



Scheme 82

Three-component allylation reactions with acrylates can generate telomeric products when the initial adduct radical adds to one or more additional equivalents of the acrylate before the allylation with the allylstannane. For example, iodocyclohexane reacts with methyl acrylate (one equivalent) and allyltributylstannane (five equivalents) in refluxing benzene to form the three-component product in 58% yield (Scheme 83).[146] Nevertheless, the competing addition of the adduct radical to another acrylate unit, followed by allylstannane trapping, affords the telomeric ($n = 2$) product in 19% yield ($n =$ the number of alkene units incorporated). The yield of the telomeric product increases if the relative concentration of the acrylate is increased, albeit telomers with $n > 2$ are also formed, but these products have not been well characterized.

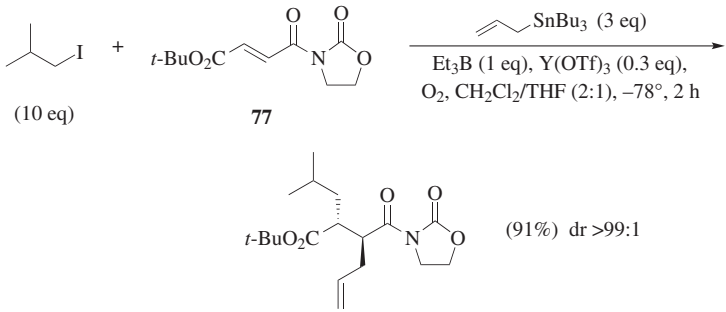


Scheme 83

In the example above, the three-component product is necessarily formed as a racemic mixture and the telomeric ($n = 2$) product is formed as a racemic mixture of

diastereomers (dr 1:1). Diastereoselective examples of this reaction (presented in the "Scope and Limitations" section) have most often been performed using oxazolidinone acrylimides in the presence of a Lewis acid (see Schemes 134, 139, and 144), which makes the alkene more electron-deficient, thereby accelerating the rate of addition of the initial alkyl radical and making the resulting radical more electrophilic. As a result, the addition of the adduct radical to allyltributylstannane is also accelerated. This strategy appears to eliminate the competing telomerization process: no study using Lewis acids has reported the formation of telomeric products. Furthermore, three-component reactions mediated by Lewis acids can be performed below room temperature, which usually improves stereoselectivity.

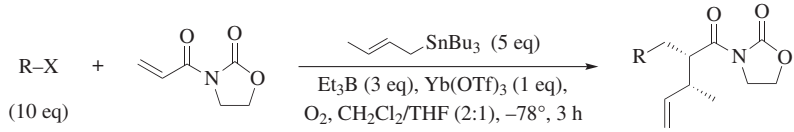
Lewis acid complexation can sometimes enable differentiation between the two alkene carbons of a fumarate derivative. For example, the Lewis acid complexes with the oxazolidinone imide of the fumarate **77** to direct the addition of an isobutyl radical to the ester-substituted alkene carbon (Scheme 84).[147] The three-component product is formed in these reactions with >99:1 diastereoselectivity, and the initial alkyl radical can be primary, secondary, or tertiary, although yields decrease with increased steric bulk.



Scheme 84

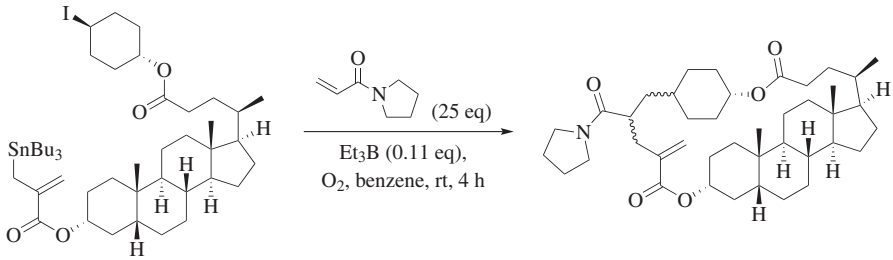
Lewis acid complexation also allows crotyltributylstannane to be employed as the radical trap (Scheme 85).[26] The reaction is compatible with a variety of alkyl halides, and the diastereoselectivity increases modestly as the size of the initial radical increases. The relative configuration of the major isomer was determined to be *syn* for the reaction employing 1-iodobutane, and the products of the related reactions were assigned by analogy.

In the absence of a Lewis acid, telomer dispersity in reactions using acrylate derivatives as the alkene components can be controlled using templating scaffolds that contain both the initial radical precursor and the allylstannane trap. In these templated reactions, the telomerization is terminated by a macrocyclization onto the allylstannane unit. For example, the lithocholic acid based template **78** favors formation of the product that incorporates a single acrylate unit (Scheme 86).[148] This product is isolated as an unselective mixture of all four possible stereoisomers in 51% yield using 25 equivalents of achiral pyrrolidine acrylamide. Trace amounts of



R–X	Yield (%)	dr
$MeOCH_2Br$	48	2.0:1
i-PrI	63	3.0:1
n-BuI	58	3.4:1
t-BuI	75	5.4:1
c-$C_6H_{11}I$	75	3.5:1

Scheme 85



78 (51%)

Scheme 86

the macrocyclic products incorporating two and three acrylamide units are detectable by mass spectrometry; polymeric product is also formed but is easily separable from the macrocyclic product. The same reaction using template **78** can be performed using chiral-auxiliary-substituted acrylamides. Although these reactions occur with lower yields, only two stereoisomeric products are detected. These products are presumed to be diastereomeric at the reacting carbon of the cyclohexyl ring, meaning that the macrocyclic allylation step is highly stereoselective.

Other steroid-based templates are less selective at controlling telomer dispersity. Reactions between pyrrolidine acrylamide and lithocholic acid based templates **79** and **80** (Figure 14), wherein the initial radical center is farther from the allylstannane trap, afford mixtures of macrocycles that incorporate one to four monomer units with little selectivity. For the androstanolone-based template **81**, the 17β isomer only generates polymeric product using pyrrolidine acrylamide. In contrast, the 17α isomer reacts with methyl methacrylate to form trace amounts of macrocycles that incorporate three or four monomer units, albeit the reaction affords mostly polymerized product. The greater flexibility of the lithocholic acid based templates (which have a *cis* A/B ring junction) is thought to allow formation of macrocyclic products, while in contrast, the rigidity of the androstanolones (which have a *trans* A/B ring junction) prevents macrocyclization.

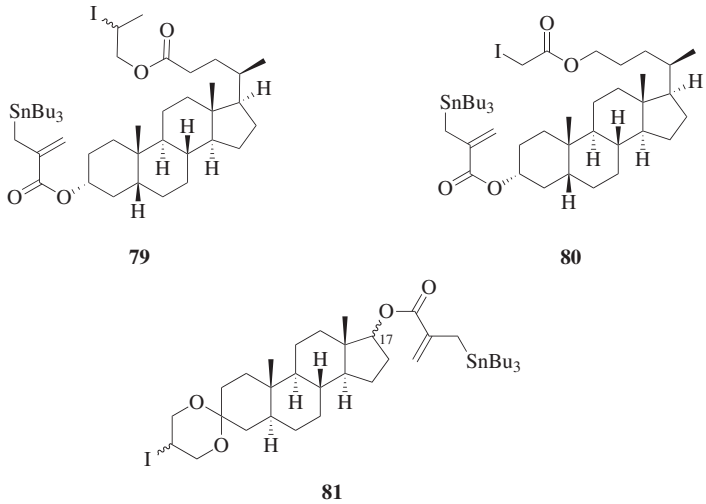
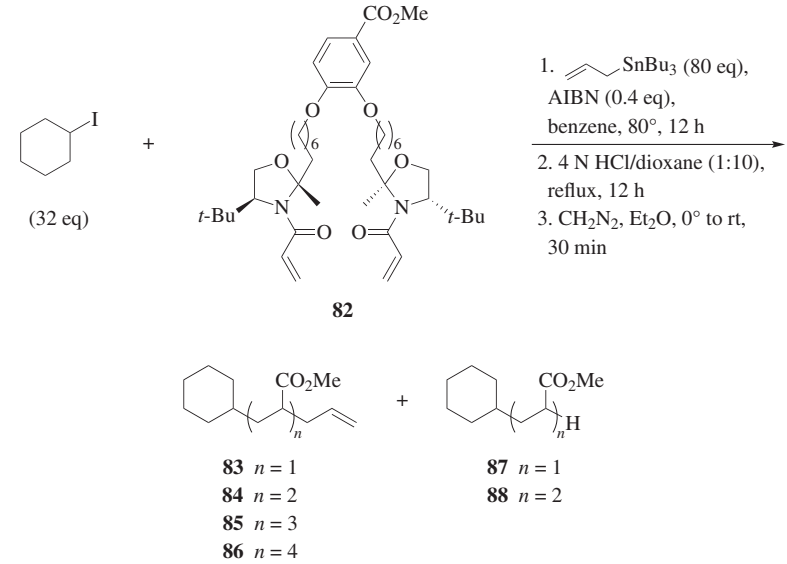


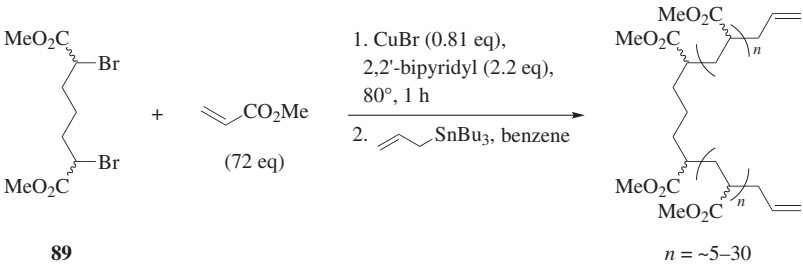
Figure 14. Steroid-based templates for controlling telomer length.

Control of dispersity to form the $n = 2$ product is more successful using templates in which acrylamide units are linked to a rigid base unit through flexible tethers, and the most effective template is catechol-based derivative **82**. The reaction of **82** (2.5 mM) with iodocyclohexane (80 mM) and allyltributylstannane (200 mM) in refluxing benzene with AIBN, followed by hydrolysis and esterification, provides allylstannane-trapping products that contain one to four acrylate units (compounds **83**–**86**, respectively) and a trace of the reduced adducts (**87** and **88**) in which hydrogen-atom abstraction has occurred instead of allylstannane trapping (Scheme 87).[149] The $n = 2$ allylation product **84** makes up 78% of the crude product mixture, and **84** is isolated in 30% yield as a 22:1 mixture of diastereomers. Several related templates (with an isopropyl group in place of the *tert*-butyl group on the oxazolidine ring, a different configuration at the oxazolidine quaternary stereocenter, or various tether lengths) are less selective for the $n = 2$ products and presumably suffer from competitive hydrogen-atom abstraction and reduced stereoselectivity.

Allyltributylstannane can be used to terminate atom-transfer radical polymerization reactions. For example, dibromide **89** in the presence of copper(I) bromide and 2,2′-bipyridyl reacts first with methyl acrylate to initiate a bidirectional polymerization process (Scheme 88).[150] After one hour, allyltributylstannane is added to cap the growing polymer chains with allyl groups. The product polymer, with approximately 5–30 acrylate monomer units incorporated into each side, can subsequently be treated with Grubbs catalyst to induce an end-to-end cyclization of the two termini, creating a cyclic polymer. A similar process can be conducted with a tetrabromide scaffold to form a dendritic type polymer that can be converted to a polymer with figure-eight topography via ring-closing metathesis.[151]



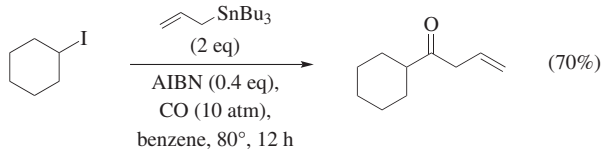
Scheme 87



Scheme 88

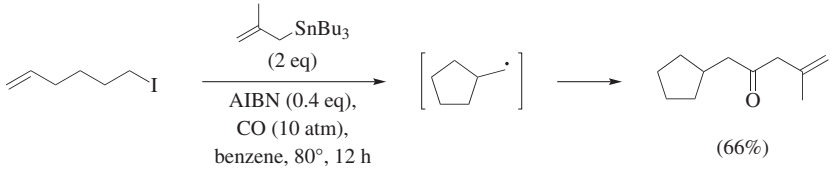
Reactions Involving Carbon Monoxide. Three-component reactions can be executed using carbon monoxide in place of an alkene. For example, when an alkyl iodide, carbon monoxide, and allyltributylstannane are allowed to react, a β,γ-enone is isolated in good yield (Scheme 89).[152] The initial alkyl radical adds selectively to carbon monoxide to form a nucleophilic acyl radical that then adds to the allylstannane. Methallyltributylstannane can be used in place of allyltributylstannane, and primary, secondary, and tertiary radicals participate in the reaction, although moderate pressures of carbon monoxide (typically 10–30 atm) are required for reactions of secondary and tertiary radicals. Reactions that involve primary radicals can be performed at pressures as low as 2 atm with only a slight decrease in yield,

presumably because the rate of decarbonylation (the reverse of the initial addition) is much slower for primary radicals.[107]

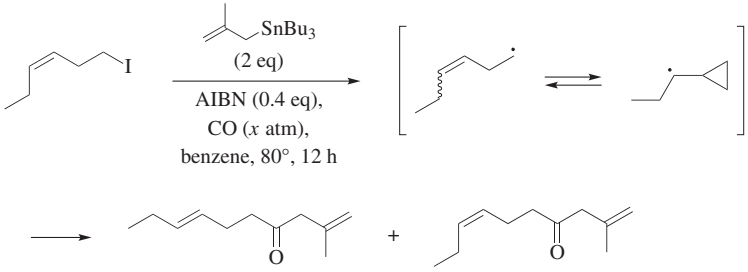


Scheme 89

Both addition steps in this three-component process are slow enough to permit the intervention of a relatively rapid intramolecular process. For example, when 1-iodohex-5-ene is used as the alkyl iodide, a 5-*exo* cyclization precedes addition to carbon monoxide (Scheme 90).[152] Similarly, in the reaction of 1-iodohex-(3*Z*)-ene, significant isomerization to the (*E*) alkene occurs via an intermediate cyclopropylcarbinyl radical (Scheme 91);[152] the degree of isomerization can be decreased by conducting the reaction at higher carbon monoxide pressure.[153]



Scheme 90

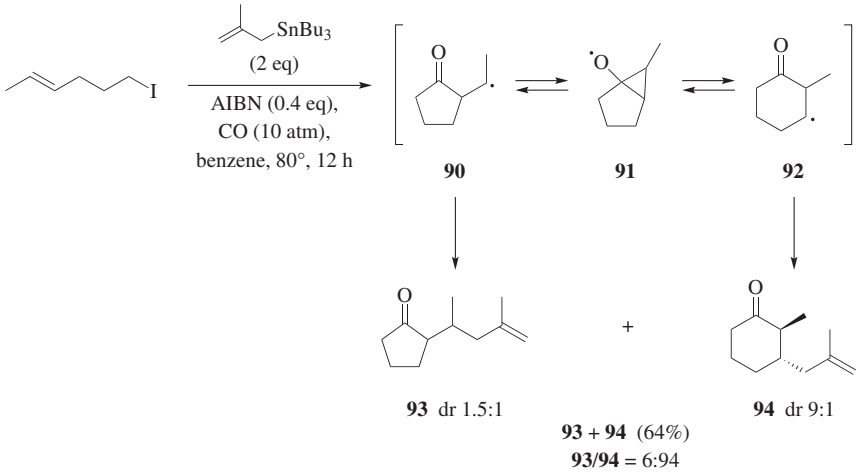


	Yield (%)	
x	$(E) + (Z)$	$(E)/(Z)$
10	68	3:1
30	69	1.1:1

Scheme 91

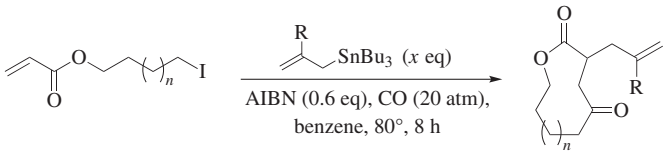
In the reaction of 1-iodohex-(4*E*)-ene, 4-*exo* or 5-*endo* cyclization of the initial alkyl radical is slow, so addition to carbon monoxide occurs first (Scheme 92).[152] The resulting acyl radical then undergoes a 5-*exo* cyclization to form the cyclopentanone

radical **90**, which can add methallyltributylstannane to generate product **93**. Alternatively, the cyclized radical **90** can rearrange via cyclopropyloxy radical **91** to afford cyclohexanone radical **92**, which reacts with the allylstannane to deliver the cyclohexanone **94** as a 9:1 mixture of *trans*/*cis* diastereomers. The equilibrium between **90** and **92** favors the more stable six-membered ring, and under these conditions (0.1 M concentration of the starting iodide), the radical is sufficiently long lived that product **94** predominates.



Scheme 92

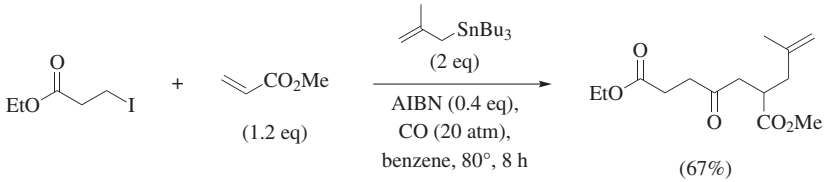
Even relatively slow macrocyclizations can be achieved prior to radical addition to the allylstannane (Scheme 93).[154] Reactions of ω-iodoalkyl acrylates (0.005 M) with allylstannane (6–10 equivalents) and carbon dioxide (20 atm) in refluxing benzene form the macrocyclic products in yields ranging from 47 to 70%, with the yields increasing incrementally with the ring size. Notably, the initial intermolecular radical addition to carbon monoxide precedes the intramolecular macrocyclization reaction, though both the alkyl and acyl radicals are nucleophilic.



n	R	*x*	Yield (%)
3	Me	5	47
5	H	6	56
7	H	10	61
9	H	6	70

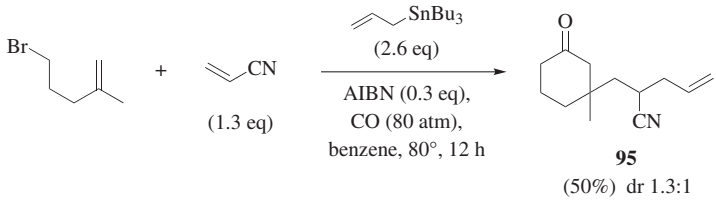
Scheme 93

Because the rate of addition of an acyl radical to an allylstannane is relatively slow, an intermolecular addition to an electron-deficient alkene can be inserted into the sequence, enabling a four-component coupling process (Scheme 94).[155] Primary, secondary, and tertiary alkyl iodides are all suitable substrates, as are vinyl and aryl iodides. The initially formed alkyl, vinyl, or aryl radical adds selectively to carbon monoxide to generate a nucleophilic acyl radical that reacts faster with the electron-poor alkene (SOMO–LUMO) than with the allylstannane. The resulting electron-deficient radical then adds efficiently to the allylstannane (SOMO–HOMO). Acrylates, acrylonitrile, acrolein, and methyl vinyl ketone are suitable alkene components; even an electron-deficient alkyne has been utilized in this process.[153]



Scheme 94

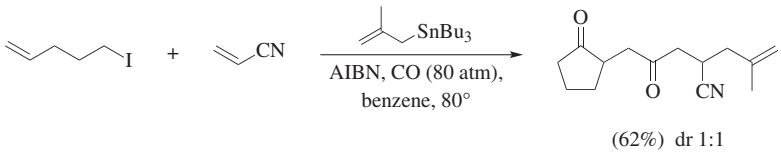
As with the three-component process, a cyclization can be incorporated into the four-component sequence. For example, 1-bromo-4-methylpent-5-ene (0.03 M) reacts with carbon monoxide (80 atm), acrylonitrile, and allyltributylstannane in benzene at 80° in the presence of AIBN to form cyclohexanone **95** in 50% yield as a 1.3:1 mixture of diastereomers (Scheme 95).[156] After addition of the initial alkyl radical to carbon monoxide, the acyl radical undergoes a 6-*endo* cyclization followed by sequential additions to acrylonitrile and the allylstannane. At a higher concentration of the alkyl halide (0.10 M), addition of the acyl radical to acrylonitrile without cyclization competes, thereby generating the corresponding product in 7% yield; however, at a lower concentration (0.03 M) this product is minimized (3% yield).



Scheme 95

In a further extension of this idea, a five-component coupling sequence is possible, although only a single example has been reported (Scheme 96).[153] The primary radical generated from 1-iodopent-5-ene adds to carbon monoxide, and the resulting acyl radical undergoes a 5-*exo* cyclization, followed by a second

carbonylation reaction. This second acyl radical adds to acrylonitrile, and the resulting electron-deficient radical is then trapped by methallyltributylstannane. The final product is formed as a mixture of diastereomers with no stereoselectivity, but in a remarkable 62% yield for a single reaction sequence in which five carbon–carbon bonds are formed.



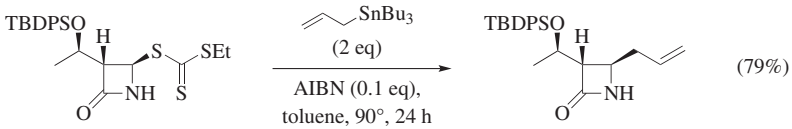
Scheme 96

Stereoselective Allylation Reactions

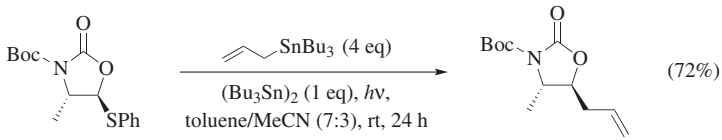
The stereoselectivity of radical reactions has been an area of intense study over the past 30 years. Numerous investigations have demonstrated that the stereochemical outcome of many radical reactions can be controlled with diastereo- and enantioselectivities that often rival or surpass those of the analogous ionic reaction processes. The seminal work on stereoselective radical reactions has been reviewed in a comprehensive book.[23] Subsequent reviews provide updated information on the stereochemistry of intermolecular reactions of cyclic radicals,[157] acyclic radicals,[158] Lewis acid mediated reactions,[159] chiral-auxiliary-mediated reactions,[160] and enantioselective reactions.[24,161] Addition reactions to allylstannanes are often used as a convenient means of assessing strategies for controlling stereochemistry, and the following section highlights important examples of stereoselective allylstannane-mediated radical allylations.

Diastereoselective Reactions of Cyclic Substrates. Whereas steric effects play the largest role in determining the stereochemistry of addition reactions of chiral cyclic radicals to allylstannanes, stereoelectronic effects can also be significant, especially for six-membered-ring substrates. The nature of the transition state for the addition—whether early or late on the reaction coordinate—can play a secondary role in determining selectivity, as can the conformation of the reactive radical, the influence of additives such as Lewis acids, and the solvent.

For four- and five-membered-ring substrates, the minimization of steric interactions between substituents at existing stereocenters and the incoming allylstannane is the major factor in determining on which face of the radical allylstannane addition occurs. For example, the radical derived from azetidinone **96** adds to allyltributylstannane in toluene at 90° to generate a single stereoisomer, which results from addition of the allyl group to the face opposite the C-3 substituent of the β-lactam ring (Scheme 97).[25] Similarly, reactions of radicals at C-5 of an oxazolidinone with a stereocenter at C-4 produce a single diastereomer, even when the C-4 substituent is as small as a methyl group (Scheme 98).[162]

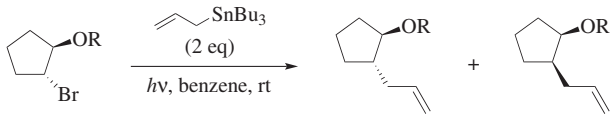


Scheme 97



Scheme 98

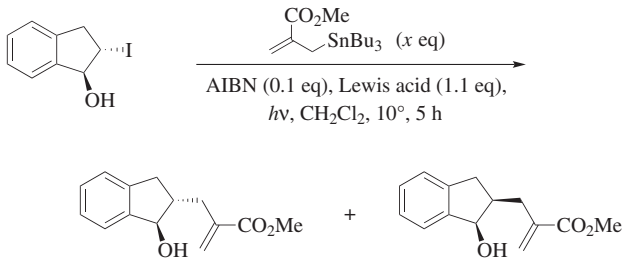
However, having a stereocenter adjacent to the radical does not always impart high selectivity in five-membered-ring substrates. Oxygen-substituted cyclopentyl radicals undergo allylation at room temperature to form mixtures of diastereomers in ratios that range from 7:1 to 11:1, depending on the exact nature of the oxygen substituent (Scheme 99).[4] Notably, the level of stereocontrol does not equate to the relative size of the substituent on oxygen, and the major diastereomer once again results from allylation *trans* to the substituent. In a closely related system, selectivity is increased dramatically when allylation of an α-hydroxy indanyl radical occurs in the presence of methylaluminum bis[2,6-di(*tert*-butyl)-4-methylphenoxide] (MAD) (Scheme 100).[163] In this case, MAD reacts with the alcohol prior to radical formation, generating an aluminum alkoxide with much greater steric bulk than the simple alcohol. Stereoselectivity is also possible in three-component reactions where the relevant prochiral radical is formed from addition of an initial radical to a cyclic alkene (see Schemes 79 and 80).



R	Yield (%)	dr
H	67	10:1
TBS	—	7:1
TBDPS	—	11:1
Bz	—	7:1

Scheme 99

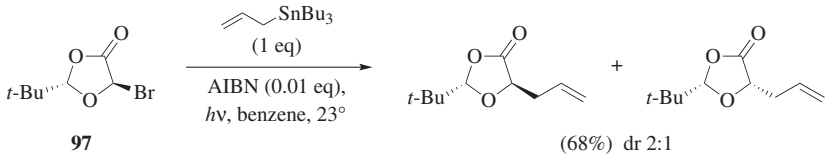
Even substituents positioned two atoms away from the radical center can influence the stereochemical outcome of radical addition reactions. The dioxolanyl



x	Lewis acid	Yield (%)	dr
2	none	67	1.2:1
4	MAD	69	100:1

Scheme 100

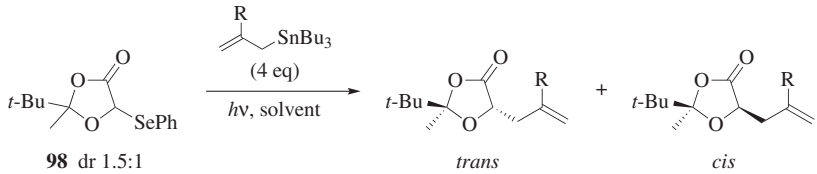
radical derived from bromide substrate **97** reacts with allyltributylstannane at room temperature to form a 2:1 mixture of diastereomers, favoring the *trans* product (Scheme 101).[99] Once again, steric factors are believed to be the primary factor favoring the *trans* product, a conclusion that is supported by calculations.[164] Interestingly, this same radical will abstract a bromine atom from molecular bromine (generated from *N*-bromosuccinimide) with complete selectivity for the *trans* product at 80°, and will abstract a deuterium atom from tributyltin deuteride with 6:1 *trans* selectivity at 10°. The dependence of the selectivity on the nature of the reaction is related to the exothermicity of the reaction, with greater selectivity occurring in reactions that are more exothermic. Because the bromination is highly exothermic, the transition state is highly reactant-like, and therefore steric interactions in the transition state between the *tert*-butyl substituent on the radical and the incoming reagent direct the facial attack. The allylation is the least exothermic of these three reactions, so the transition state is the most product-like, and as such, the energy difference between the two diastereomeric transition states is minimized. Furthermore, calculations show that the *cis* isomer is the more stable product.[99,164]



Scheme 101

The reaction of closely related substrate **98** with a carbomethoxy-substituted allylstannane is more selective than with the parent allyltributylstannane (Scheme 102).[165] Stabilization of the adduct radical by the ester carbonyl group makes addition to the substituted allylstannane more exothermic and therefore more reactant-like and

more selective. Unexpectedly, the reaction of **98** with allyltributylstannane is more selective at higher temperatures. While enthalpic factors favor the *cis* product, entropy favors the *trans* product, so at higher temperatures the stronger influence of entropy decreases the thermodynamic preference for the *cis* product, and the steric preference for the *trans* product becomes the predominant influence.



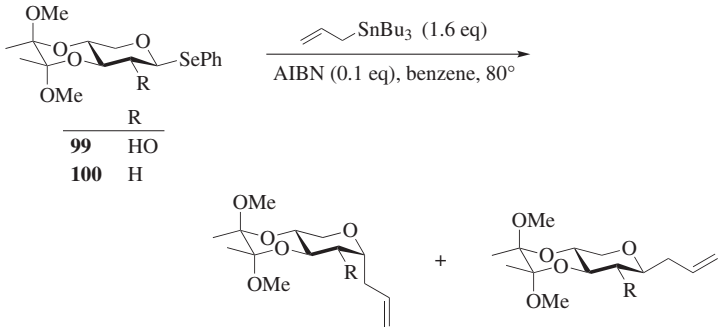
R	Solvent	Temp (°)	Yield (%)	*trans*/*cis*
H	toluene	110	80	4.5:1
H	toluene	80	65	3.3:1
H	toluene	30	55	1.6:1
H	toluene	–10	50	1.4:1
H	benzene	40	30	1.8:1
MeO_2C	benzene	40	43	16:1

Scheme 102

For cyclohexyl radicals, the factors that influence which face undergoes attack are similar to those that control the direction of nucleophile addition to cyclohexanones.[166] Torsional strain destabilizes the transition state for equatorial approach of the reagent, whereas 1,3-diaxial interactions destabilize the axial transition state. For the 4-*tert*-butylcyclohexyl radical, these factors are equally influential, and addition to allyltributylstannane occurs with no selectivity at 80°.[100] Allylation reactions of 2-alkyl-substitued 4-*tert*-butylcyclohexyl radicals have not been reported, but additions to other alkenes demonstrate that an equatorial substituent adjacent to the radical center increases the amount of equatorial attack (from the face *anti* to the substituent), whereas an adjacent axial substituent leads to more axial attack (also from the *anti* face).[166]

For more complicated six-membered-ring radicals, especially carbohydrate-based radicals at the anomeric carbon, stereoelectronic effects also influence the stereochemical outcomes of allylation reactions. The anomeric effect stabilizes the radical adjacent to the ring oxygen and also preferentially stabilizes the transition state for axial attack of the incoming reagent.[167] Additionally, anomeric radicals adjacent to an oxygen substituent at C-2 gain further stabilization when the substituent is axial, allowing overlap of the σ* of the neighboring carbon–oxygen bond with the singly occupied orbital of the radical, referred to as a quasi-homo-anomeric effect.[168] These stereoelectronic effects can influence both the reactive conformations of the radical and the relative kinetics of the addition to one face of the radical over the other. A complex interplay between these stereoelectronic effects gives rise to the unique stereochemical outcome for each reaction.

A series of reactions with conformationally restricted xylose-derived radicals illustrates the explanations described above and demonstrates that the stereochemical outcome of allylation reactions of cyclic radicals can, in some cases, be controlled by a careful choice of substituents.[169] Xylose-derived substrates **99** and **100** are restricted primarily to a $^4C_1$ chair conformation (Scheme 103). Axial attack of an incoming reagent on the α-face of the radical derived from **99** should be more sterically hindered than equatorial attack due to 1,3-diaxial interactions and 1,2-interactions with the neighboring C-2 hydroxyl substituent. However, these substrates react with allyltributylstannane at 80° with high selectivity for approach from the axial α-face. Anomeric stabilization of the axial transition state by the ring oxygen must therefore be the predominant factor in directing the addition. Not surprisingly, the radical derived from **100** reacts with even greater axial selectivity because the hydroxyl group is not present to block attack on the α-face.

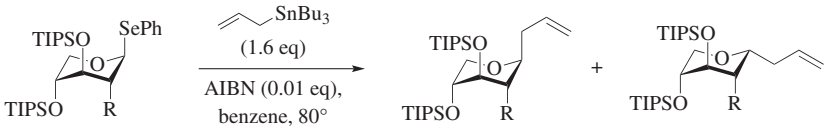


	R
99	HO
100	H

	Yield (%)	dr
99	69	10.1:1
100	74	49:1

Scheme 103

The radical derived from xylose substrate **101** preferentially adopts the alternative $^1C_4$ chair conformation with the silyloxy groups in axial positions to minimize the steric interactions between them. This radical adds to allyltributylstannane at 80° with 99:1 selectivity for formation of the axial, β-isomer that is favored by the stereoelectronic effects of both the ring oxygen and the neighboring axial silyloxy substituent (Scheme 104).[169] In contrast, the analogous 2-deoxy radical derived from **102** adds to the allylstannane under identical conditions to afford nearly equal amounts of the axial and equatorial isomers. The absence of the C-2 silyloxy substituent means that there is no quasi-homo-anomeric stabilization of the axial transition state. Furthermore, an equatorial approach is no longer hindered by a C-2 substituent. Together, these factors lead to a reduced preference for axial attack in the $^1C_4$ conformation. In addition, calculations indicate that the two chair conformations of the radical from **102** are nearly equal in energy. Preferred addition to the α-face of the $^4C_1$ conformation offsets the modest selectivity for addition to the β-face of the $^1C_4$ conformation.

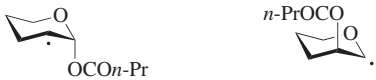


	R
101	TIPSO
102	H

	Yield (%)	dr
101	26	99:1
102	34	1.2:1

Scheme 104

With more conformationally flexible radicals (Figure 15), the influence of stereoelectronic effects on the stereochemistry of allylation reactions is less predictable. For example, radical **103** reacts with allyltributylstannane at 80° preferentially from the axial direction, giving a 3.7:1 mixture of *trans*/*cis* diastereomers.[100] Since this radical is not located at an anomeric position, it is not subject to the quasi-homo-anomeric effect, but a classical anomeric effect leads to a preference for the chair form in which the ester group at C-1 occupies an axial position, which is supported by EPR studies.[168] Because the ester hinders attack on the bottom face, axial attack is preferred. In contrast, radical **104** reacts with allyltributylstannane under the same conditions with no selectivity.[100] In this case, quasi-homo-anomeric stabilization is possible, and EPR data indicates that this radical favors the chair form that places the C-2 oxygen substituent in an axial position, and thus selectivity for the *trans* isomer would be expected.[168] In fact, reaction of radical **104** with tributyltin deuteride does occur with good *trans* selectivity. The difference in selectivity between the deuteration and allylation reactions is attributed to the late transition state for the allylation. The anomeric stabilization of radical **104** also makes the transition state for allylation later than that using radical **103**, which accounts for the different selectivities observed with these two radicals.[100]

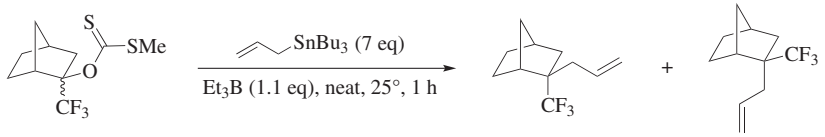


103 **104**

Figure 15. The preferred conformations of conformationally mobile carbohydrate-derived radicals **103** and **104**.

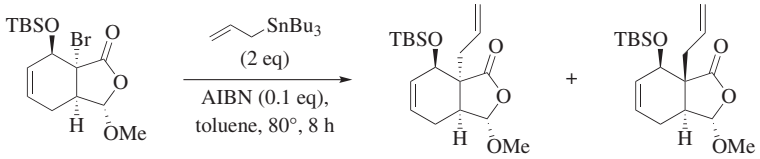
Norbornyl radicals are generally attacked selectively from the *exo* face by a range of reagents, and the few known reactions of norbornyl radicals with allylstannanes follow this trend. For example, xanthate **105** reacts with allyltributylstannane at 25° to form a 24:1 mixture of *exo*/*endo* allylation products in good yield (Scheme 105).[170]

In fused bicyclic substrates, the allylation of a radical at the ring junction position usually generates the *cis* ring fusion. Substrate **106** undergoes allylation at 80° to form a 2.1:1 mixture of products with *cis*/*trans* ring junctions (Scheme 106).[171] Radicals at other positions on fused bicyclic substrates react with allylstannanes from the



105 (84%) dr 24:1

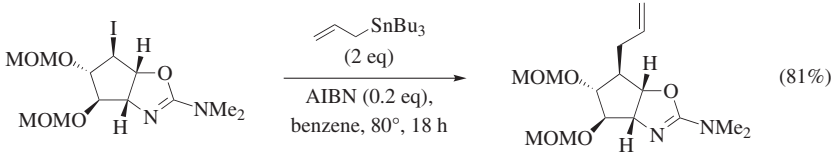
Scheme 105



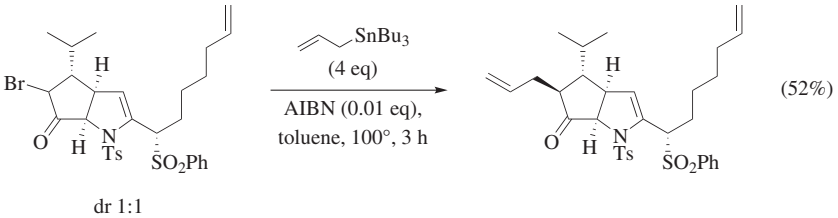
106 (93%) dr 2.1:1

Scheme 106

more sterically accessible convex face (Scheme 107),[75] although a bulky substituent adjacent to the radical can reverse this preference, especially if the radical is one or more carbons removed from the ring junction (Scheme 108).[172]



Scheme 107

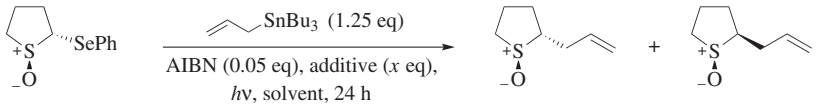


dr 1:1

Scheme 108

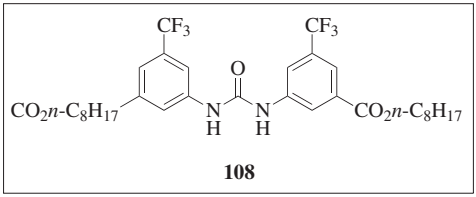
In allylation reactions of radicals adjacent to cyclic sulfoxides, the stereochemistry of the product is influenced by factors similar to those discussed above. For sulfoxides that are part of a five-membered ring, steric effects are the primary controlling factor, and the major products are the result of allylation on the face opposite the sulfoxide oxygen.[132,173] Owing to the dipolar nature of the sulfoxide

functional group, however, solvent effects and Lewis acid complexation significantly influence the degree of selectivity. α-Phenylseleno sulfoxide substrate **107** reacts with allyltributylstannane upon sunlamp irradiation in the presence of AIBN in dichloromethane at 10° to generate a 4.6:1 mixture of *trans*/*cis* products (Scheme 109).[173] The selectivity decreases in benzene or THF because of interaction between the solvent and the positively charged sulfur atom, which makes the face opposite the sulfoxide oxygen more hindered than in a non-complexing solvent. Changing to a hydrogen-bonding solvent like 1,1,1-trifluoroethanol increases the *trans* selectivity: these solvents interact with the sulfoxide oxygen, effectively increasing its steric size. Lewis acids, especially very bulky ones like MAD, have a similar effect: 0.1 equivalents of MAD increases selectivity for allylation in dichloromethane from 4.6:1 to 5.7:1, and a stoichiometric quantity of MAD dramatically enhances selectivity to 70.4:1 and also increases the yield of the reaction. The urea **108** can also be used as an additive to increase selectivity for the *trans* isomer: a substoichiometric amount of **108** increases diastereoselectivity slightly to 3.7:1 *trans*/*cis*, and a full equivalent increases the selectivity to 7.0:1.[174]



107
trans/*cis* = 11.5:1

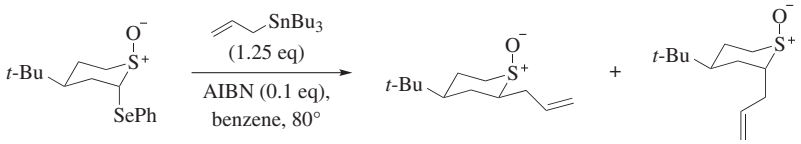
Additive	x	Solvent	Temp (°)	Yield (%)	dr
none	—	CH_2Cl_2	10	63	4.6:1
none	—	benzene	10	78	2.3:1
none	—	THF	10	44	2.2:1
none	—	CF_3CH_2OH	10	83	8.1:1
$Eu(dpm)_3$	1.1	CH_2Cl_2	10	55	8.1:1
MAD	0.1	CH_2Cl_2	10	63	5.7:1
MAD	1.0	CH_2Cl_2	10	80	70.4:1
108	0.2	benzene	15	57	3.7:1
108	1.0	benzene	15	81	7.0:1



108

Scheme 109

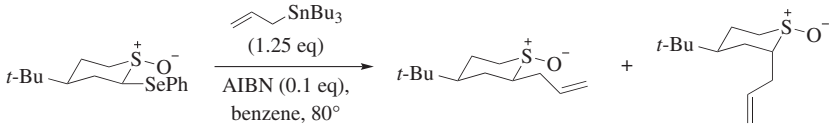
For reactions of six-membered-ring α-sulfoxide radicals, stereoelectronic effects play a role in directing facial selectivity. The radical derived from selenide substrate **109** reacts with allyltributylstannane in benzene at reflux to form the product with a small preference for the equatorial allyl group (Scheme 110).[175] 1,2-Interactions between the incoming allylstannane and the axial sulfoxide oxygen deters the *syn*



109 (58%) dr 2.3:1

Scheme 110

equatorial approach, whereas 1,3-diaxial interactions with the rest of the ring disfavor the *anti* axial approach; in this case, the 1,3-diaxial interactions are slightly stronger, leading to the observed preference for the *syn* approach. For allylation of the radical formed from the diastereomeric selenide **110**, the steric influence of the equatorial sulfoxide oxygen would be expected to increase the selectivity for the equatorial (*anti*) isomer (Scheme 111).[175] In practice, the allylation does favor the equatorial product, but the equatorial/axial ratio is lower than that obtained with **109**. In this case, the transition state for the formation of the axial product is stabilized by overlap of the sulfoxide lone pair with the parallel antibonding orbital of the bond being formed, and as a result, the proportion of axial product is larger than might otherwise be expected.



110 (92%) dr 1.5:1

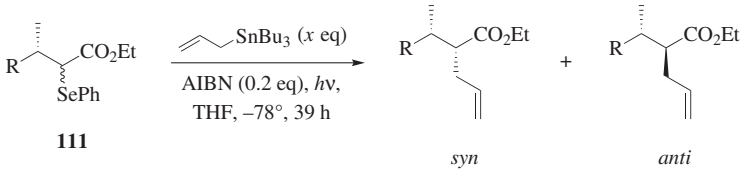
Scheme 111

Diastereoselective Reactions of Acyclic Substrates.

1,2- and 1,3-Induction. The stereochemical outcome of allylation reactions can be influenced by stereocenters present in an acyclic radical, particularly when the existing stereocenter is adjacent to the radical center (1,2-induction), though more remote stereocenters can exert stereocontrol as well. As is the case for reactions of cyclic radicals, both steric and stereoelectronic effects are important, and the presence of Lewis acids can either enhance or reverse the trends. Ground-state models are usually sufficient to make predictions and explain observed stereochemical outcomes, albeit in some cases ground-state models fail to accurately explain experimental results.[176]

Most examples of 1,2-induction involve radicals adjacent to a carbonyl group. Conjugation of the radical with the carbonyl moiety limits the number of potential conformations to those in which the SOMO and the carbonyl π-bond are coplanar. If the stereocenter adjacent to the radical has one hydrogen and two alkyl groups attached to it, allylic-strain considerations can be used to predict the preferred ground-state conformation. Radicals derived from selenide precursor **111** undergo allylation in THF at −78° with moderate control of facial selectivity (Scheme 112).[177] The degree and the direction of the selectivity depend on the nature of the large

group R at the stereocenter. When the R group is *tert*-butyl, ab initio calculations show that the lowest-energy ground-state conformation places the *tert*-butyl group approximately 50° from the plane of the radical, while orienting the hydrogen towards the ester group (Figure 16); ESR experiments support the computational findings.[178] Steric hindrance by the bulky *tert*-butyl group leaves the top face of the radical more accessible to the incoming allylstannane. The phenyldimethylsilyl-substituted substrate presumably reacts from a similar conformation with selectivity enhanced by the size of the silyl substituent. The selectivity of the reaction is reversed when the R group is phenyl, and in this case, calculations reveal that the lowest-energy conformation of the radical has the phenyl group at a dihedral angle of 75° from the singly occupied orbital (Figure 16). Although the methyl group is smaller than the phenyl group, it is in a better position to block the approach of the allylstannane, so the stannane preferentially approaches the bottom face of the radical.



R	*x*	Yield (%)	*syn*/*anti*
t-Bu	6.7	69	1.6:1
Me_2PhSi	10	56	4.6:1
Ph	7.1	86	1:2.8

Scheme 112

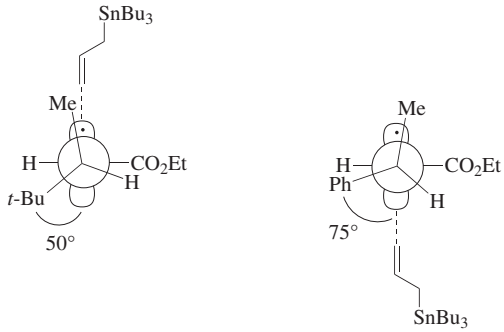
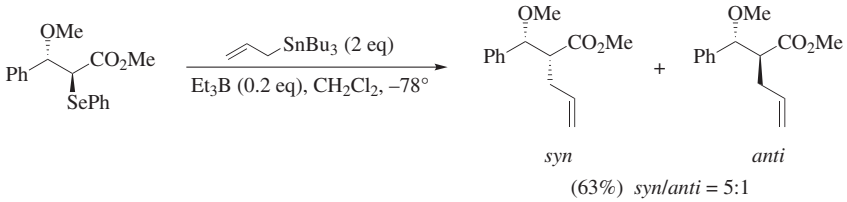


Figure 16. The lowest-energy conformations of radicals derived from selenides **111** when R = *t*-Bu (left) and R = Ph (right).

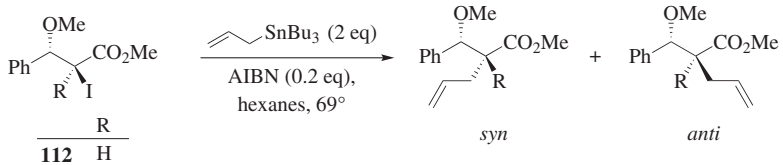
Most examples of 1,2-induction in allylation reactions involve radicals bearing a polar group as one of the substituents at the stereocenter adjacent to an α-carbonyl radical. In these cases, the preferred ground-state conformation minimizes dipole–dipole interactions between the polar group and the carbonyl moiety.

The resulting reduction in the dihedral angle between the large substituent at the stereocenter and the singly occupied orbital places the large substituent in a better position to block one face of the radical. As a result, radicals of this type generally react with better *syn* selectivity than the radicals discussed above that lack a polar group (Scheme 113).[179]



Scheme 113

Selectivity is further enhanced when the radical is tertiary instead of secondary (Scheme 114).[179–181] Increased steric interactions between the large group at the stereocenter and an alkyl group at the radical center push the large group into an optimal position for blocking the approach of the allylstannane. Ab initio calculations on the radical derived from iodide **113** (R = Me) are supported by ESR evidence and indicate that the dihedral angle between the phenyl group and the singly occupied orbital is only 4° (Figure 17).[182]



	R
112	H
113	Me

	Yield (%)	*syn*/*anti*
112	82	5:1
113	75	16:1

Scheme 114

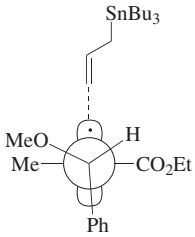
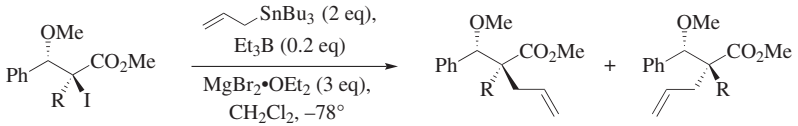


Figure 17. Preferred ground-state conformation of the radical derived from iodide **113**. The dihedral angle between the phenyl group and the singly occupied orbital is 4°.

The selectivity of allylation reactions of radicals **112** and **113** can be reversed in the presence of a Lewis acid such as magnesium bromide ethyl etherate (Scheme 115).[179–181] Under these conditions, the conformation of the radical is determined by chelation of the magnesium between the oxygen atoms of the carbonyl group and the ether (Figure 18). This conformation places the bulky phenyl group on the top face of the radical, leading to preferential approach of allyltributylstannane from the bottom face, which affords the *anti* isomer as the major product. Once again, selectivities are higher for tertiary radicals, relative to the analogous secondary radicals. These reactions require triethylborane as an initiator, and yields are negligible in the presence of radical inhibitors, providing strong evidence that the reactions are free radical in nature.



	R
112	H
113	Me

anti *syn*

	Yield (%)	*anti*/*syn*
112	80	38:1
113	76	>100:1

Scheme 115

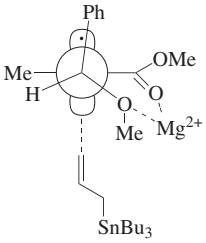
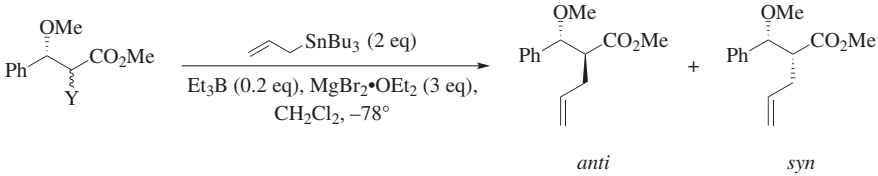


Figure 18. The preferred conformation of the radical derived from iodide **113** in the presence of $MgBr{\bullet}OEt_2$.

Evidence from ^{13}C NMR spectra of radical precursors supports the conclusion that reactions occur through a bidentate, chelated radical.[179,181] Furthermore, the reaction of the TBS ether analogue of **112** favors the opposite stereoisomer, favoring the *syn* isomer in a ratio of 8:1 *syn*/*anti*. Owing to the size and π-accepting ability of the TBS group, a chelated conformation is not possible, so even in the presence of $MgBr{\bullet}OEt_2$, the reaction likely occurs through a monodentate, non-chelated conformation, an idea that is also supported by ^{13}C NMR data.

In Lewis acid mediated reactions of **112**, **113**, and analogous substrates, the stereoselectivity is dependent on the nature of the radical-generating group, with phenyl selenides affording the highest selectivities and bromides the lowest

(Scheme 116).[179,181] Furthermore, if the radical-generating group is an iodide or phenylselenide, lower selectivities are obtained when the radical-generating group is *syn* rather than *anti* to the ether moiety; interestingly, no difference in selectivity between the two orientations is observed when the radical-generating group is bromine. Substrates in which the ether is part of a tetrahydrofuranyl ring (e.g., **114**) react with reduced selectivity compared to the tetrahydropyranyl analogue (e.g., **115**) (Figure 19), which furnishes selectivities similar to those of acyclic ether substrates. These effects are likely due to differences in the ability of the substrates to form a bidentate complex with the magnesium.



Y	Time (h)	Yield (%)	*anti*/*syn*
Br (*anti*)	2	78	19:1
Br (*syn*)	—	80	20:1
I (*anti*)	2	80	38:1
I (*syn*)	2	69	5:1
PhSe (*anti*)	2	90	65:1
PhSe (*syn*)	—	76	38:1

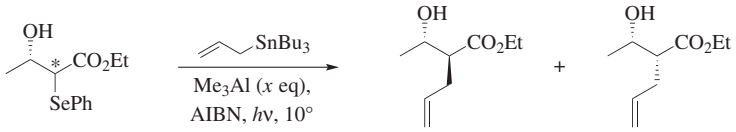
Scheme 116

114 **115**

Figure 19. Substrates that generate radicals α to a cyclic ether.

Lewis acids can also be employed to control stereochemistry in allylation reactions of β-hydroxy ester radicals. When selenide **116** is irradiated in the presence of AIBN and allyltributylstannane, the *anti* product is favored under all conditions reported (Scheme 117).[183] Selectivity for the *anti* product is enhanced by the presence of trimethylaluminum, which presumably reacts with the alcohol to form an aluminum alcoholate. Further chelation of the aluminum to the carbonyl oxygen helps to enforce a preference for the reactive conformation that leads to the *anti* product. As is the case for reactions of the corresponding ethers, the *syn*/*anti* orientation of the radical-generating group influences the selectivity of the reaction in the presence of the Lewis acid.

For the radical derived from selenide **116**, hydrogen bonding likely plays a role in slightly favoring the *anti* product in the absence of a Lewis acid, and this effect has

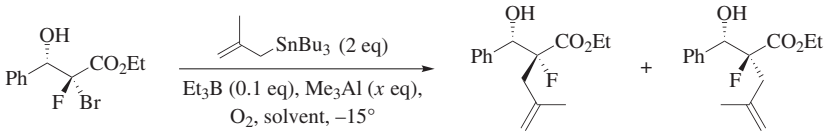


116 *anti* *syn*

*Config	*x*	Yield (%)	*anti*/*syn*
syn	—	86	1.6:1
syn	1.1	80	5.8:1
anti	—	98	1.7:1
anti	1.1	97	20:1
anti	3.0	>70	32:1

Scheme 117

been clearly demonstrated in a study using α-bromo-α-fluoro-β-hydroxy ester **117** (Scheme 118).[184] As the ability of the solvent to act as a hydrogen-bond acceptor increases, the amount of intramolecular hydrogen bonding decreases. In the absence of intramolecular hydrogen bonding in a solvent such as THF, the lowest-energy conformation of the radical will minimize dipole–dipole interactions between the hydroxyl group and the ester, leading to the preferential formation of the *syn* product. In a solvent like toluene, which is a poor hydrogen-bond acceptor, intramolecular hydrogen bonding promotes addition to the opposite face, leading to a slight preference for the *anti* product. The addition of a Lewis acid such as trimethylaluminum enforces this coordinated conformation and dramatically increases selectivity for the *anti* product.



117
dr 1.6:1

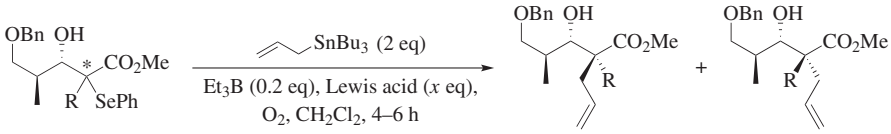
anti *syn*

x	Solvent	Time (h)	Yield (%)	*anti*/*syn*
—	toluene	8	83	1.04:1
—	CH_2Cl_2	8	82	1.04:1
—	MeCN	8	77	1:2.1
—	Et_2O	8	80	1:3.2
—	DME	8	88	1:5.3
—	THF	8	85	1:13.3
1.1	CH_2Cl_2	6	83	19:1

Scheme 118

Lewis acid mediated allylation of β-hydroxy ester radicals can be combined with a Mukaiyama aldol reaction to form products with three contiguous

stereocenters.[185,186] The radical allylation proceeds with high stereoselectivity, regardless of the stereochemical outcome of the preceding aldol reaction, when chelation between the hydroxyl oxygen and the ester carbonyl provides a conformational bias. For substrates **118**, which are the 3,4-*anti* aldol products of the preceding reaction, selectivity is low with boron trifluoride diethyl etherate (a monodentate Lewis acid) (Scheme 119).[185,186] In contrast, using magnesium bromide ethyl etherate (a bidentate Lewis acid), the selectivity is high but the reaction is slow and yields are only moderate. With stronger aluminum-based Lewis acids, the radical is more electron-deficient, which enhances the rate of addition to allyltributylstannane and increases yields. Selectivities are much higher when the selenide group in substrate **118** is *anti* to the hydroxyl group, and good results are obtained with both secondary and tertiary radicals. For substrates **119**, which are the 3,4-*syn* products of the preceding aldol reaction, selectivity in the allylation reaction is insensitive to the substrate stereochemistry (Scheme 120).[186] Tandem reactions combining both the Mukaiyama aldol step and the radical allylation in a single pot can be performed with high diastereoselectivities and in moderate-to-good yields via both *syn*- and *anti*-selective aldol products **118** and **119**.[186]

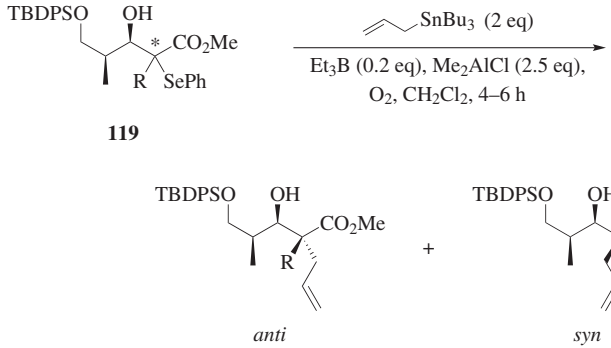


118 *anti* *syn*

R	*Config	Lewis Acid	*x*	Temp	Yield (%)	*anti*/*syn*
H	(*R*)	none	—	–78° to rt	0	—
H	(*R*)	BF_3•OEt_2	1.1	–78 to 0°	69	3:1
H	(*R*)	$MgBr_2$•OEt_2	5	–40 to 0°	62	>20:1
H	(*R*)	Me_2AlCl	2.5	–78°	90	>20:1
H	(*R*)	$AlMe_3$	2.5	–78°	80	>20:1
H	(*S*)	Me_2AlCl	2.5	–78°	53	2:1
H	(*S*)	$AlMe_3$	2.5	–40°	60	6:1
Me	(*R*)	Me_2AlCl	2.5	0°	55	8:1
Me	(*R*)	$AlMe_3$	2.5	0°	58	>20:1

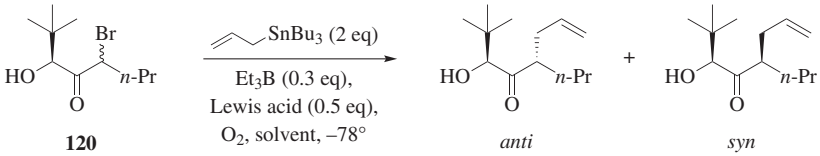
Scheme 119

Hydrogen bonding and/or Lewis acid chelation play a critical role in the few reported examples of 1,3-induction (and even 1,4- and 1,5-induction) in radical allylation reactions. In one example, coordination between the oxygen atoms of an α-hydroxy ketone adjacent to a radical center provides conformational rigidity that leads to high levels of diastereoselectivity: bromide **120** reacts with allyltributylstannane at low temperature to form the *anti* isomer as the major product (Scheme 121).[187] In the presence of a Lewis acid, the predominant reactive conformation is presumed to be **122** (Figure 20), which avoids the $A^{1,3}$ interaction between the *n*-propyl and *tert*-butyl groups present in conformation **121**. Reaction



R	*Config	Temp (°)	Yield (%)	*anti*/*syn*
H	(*R*)	–40	76	>20:1
H	(*S*)	–40	85	>20:1
Me	(*R*)	0	50	>20:1
Me	(*S*)	0	70	>20:1

Scheme 120



Lewis Acid	Solvent	Yield (%)	*anti*/*syn*
none	CH_2Cl_2	33	5:1
$ZnCl_2$	CH_2Cl_2/THF	76	100:1
$MgBr_2$•OEt_2	CH_2Cl_2/Et_2O	81	100:1
$Yb(OTf)_3$	CH_2Cl_2	48	9:1

Scheme 121

via conformation **122** with the allylstannane occurs preferentially on the bottom face, opposite the *tert*-butyl group. Allylation is not as selective for the *anti* product in the absence of a Lewis acid, but likely occurs from an analogous conformation with an intramolecular hydrogen bond restricting rotation around the bond between the ketone and the existing stereocenter.

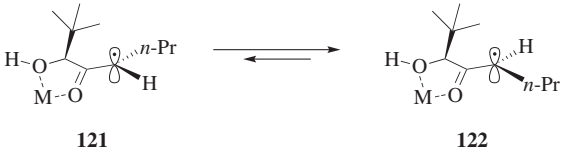
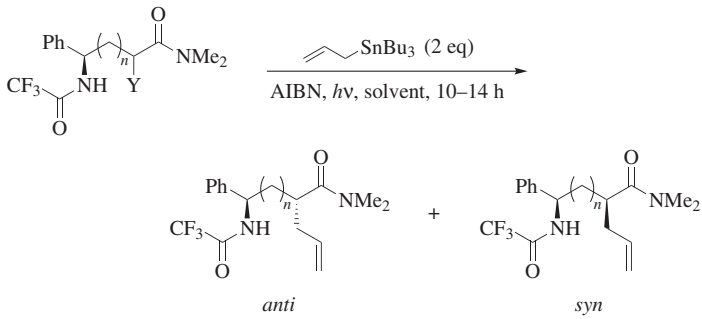


Figure 20. Conformations of the radical derived from bromide **120**.

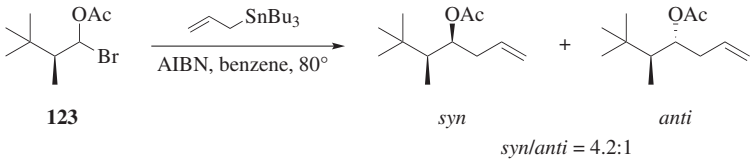
In a second example of stereocontrol by remote centers, hydrogen bonding between an amide NH and a carbonyl oxygen has been used to direct allylation stereochemistry (Scheme 122),[188] and 1,2-, 1,3-, 1,4- and even 1,5-induction has been demonstrated. Reactions in toluene, where intramolecular hydrogen bonding is favorable, afford high diastereoselectivities; in contrast, reactions in DMSO are unselective, providing evidence—at least in cases where 1,2- and 1,3-induction is occurring—that an intramolecular hydrogen bond is critical for selectivity.



n	Y	Solvent	Temp (°)	Yield (%)	*anti*/*syn*
0	PhSe	toluene	–40	76	>49:1
0	PhSe	DMSO	—	—	1.2:1
1	PhSe	toluene	–40	97	1.6:1
1	PhSe	DMSO	—	—	1:1
2	I	toluene	–40	79	6.1:1
3	I	toluene	–40	72	1:2.8

Scheme 122

Examples of 1,2-induction in allylation reactions of radicals adjacent to groups other than a carbonyl are rare but have been reported. For α-oxy radicals, the ground-state conformation seems to be less important than stereoelectronic effects in the transition state. The radical derived from bromide **123** undergoes allylation with moderate selectivity favoring the *syn* product (Scheme 123).[189] The reaction is believed to occur through a Felkin–Anh-like transition state wherein the allylstannane approaches opposite the bulkiest group at the stereocenter (Figure 21). Hydrogen-atom abstraction reactions of similar radicals afford selectivities that closely match those obtained in hydride reductions of analogous carbonyl compounds. Ab initio calculations reveal that the transition-state geometries of the



Scheme 123

radical and ionic processes are similar, with significant tetrahedral character at the radical center at the transition state.[190,191]

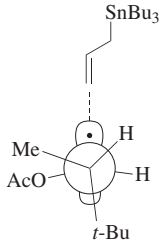
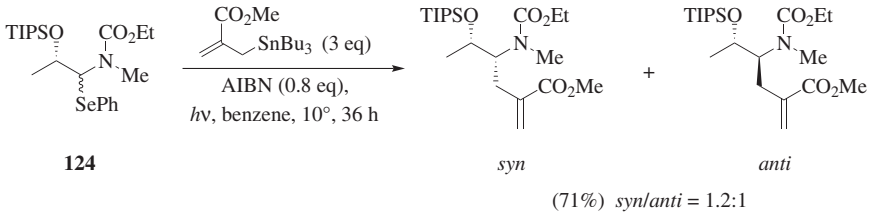


Figure 21. The preferred Felkin–Anh transition state for allylation of an α-oxy radical.

For radicals derived from selenide **124**, which are adjacent to a carbamate nitrogen and a silyloxy-substituted stereocenter, selectivity is influenced by an interplay of steric and stereoelectronic effects. It reacts with minimal selectivity with 2-carbomethoxy-substituted allylstannane (Scheme 124).[192] The preferred ground-state conformation of this radical minimizes $A^{1,3}$ interactions (Figure 22), and the stannane would preferentially approach the bottom face, opposite the bulky triisopropylsilyl ether, to generate the *anti* product. However, owing to significant stereoelectronic interactions between the electrophilic reagent and the electron-donating alkyl group, the reaction occurs instead via a Felkin–Anh transition state, which



Scheme 124

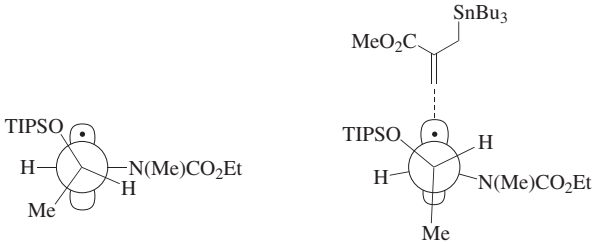
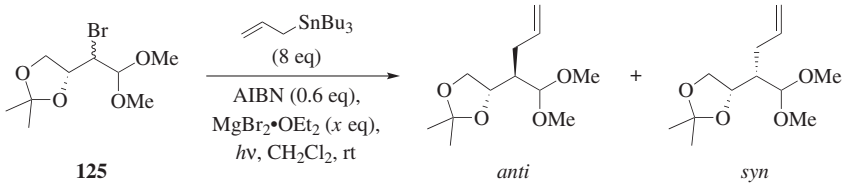


Figure 22. The preferred ground-state conformation (left) and Felkin–Anh transition state (right) for allylation of the radical derived from selenide **124**.

minimizes this stereoelectronic interaction. Interestingly, the *anti* product is favored in a reaction with tributyltin deuteride; in this case, stereoelectronic effects are thought to favor approach of the nucleophilic reagent opposite the silyl ether group, allowing the reaction to occur primarily through a conformation that is close to the preferred ground-state conformation. The use of more electron-rich allylstannanes would probe whether the electronic nature of the stannane influences the balance of steric and stereoelectronic effects, but such a study has not yet been reported.

Conformation restriction—and thus, high selectivity—can also be obtained by metal chelation between an oxygen atom at a stereocenter adjacent to a radical and an ether or acetal oxygen on the other side of the radical. For example, the reaction of bromide **125** with allyltributylstannane provides the allylated product with no diastereoselectivity in the absence of a Lewis acid, but forms the *anti* product with excellent selectivity when 2.5 equivalents of magnesium bromide ethyl etherate are included (Scheme 125).[193] In the presence of a chelating Lewis acid, the radical formed from bromide **125** most likely adopts the conformation illustrated in Figure 23; for steric reasons, the allylstannane would react with this radical from the top face. Similar selectivity is obtained when the dimethyl acetal is replaced with a methyl ether, but the product is obtained in very poor yield (7%).



x	Yield (%)	*anti*/*syn*
—	52	1:1.1
2.5	70	52:1

Scheme 125

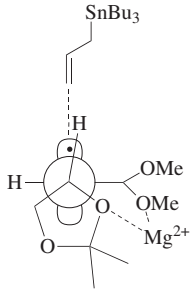
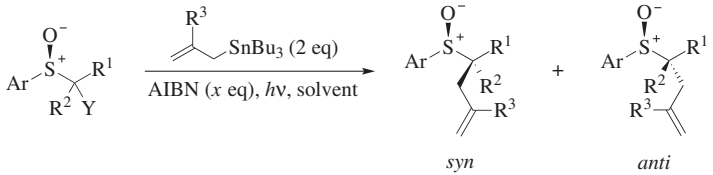


Figure 23. The preferred conformation of the radical formed from bromide **125** in the presence of a chelating Lewis acid.

Acyclic α-Sulfoxide Radicals. The chirality of the sulfoxide group in acyclic α-arylsulfinyl radicals can be used to influence diastereoselective allylation reactions. The factors controlling the preferred conformation of the radical, and thus the stereochemical outcome of the reaction, depend on the nature of the other groups located on the radical center.

When an α-arylsulfinyl radical is substituted with a polar carbonyl or cyano group, dipole–dipole interactions are primarily responsible for controlling the conformation of the radical, and the allylations of these radicals preferentially afford the *syn* isomers (Scheme 126).[60,117,194] Calculations indicate that the two lowest-energy conformations have the sulfur lone pair eclipsed with the singly occupied orbital of the radical. The lowest-energy conformation is an *s-trans* conformation that minimizes dipole–dipole interactions between the sulfur–oxygen bond and the carbonyl or nitrile group (Figure 24).[117] The allylstannane then approaches from the bottom face, opposite the bulky group on the sulfoxide stereocenter. The reaction with the ester-substituted radical is more selective than that with the nitrile-substituted radical because interactions between the ester group and the sulfoxide oxygen cause the ester to rotate out of the plane of the radical in the disfavored *s-cis* conformation. This results in a loss of resonance stabilization of the *s-cis* radical adjacent to the ester, leading to a larger energy difference between the *s-cis* and the *s-trans* conformations.



R^1	R^2	R^3	Ar	Y	*x*	Solvent	Temp	Time (h)	Yield (%)	*syn/anti*
$Me_2N(O)C$	H	H	Ph	Br	0.4	toluene	rt	—	>90	10.1:1
MeO_2C	H	H	Ph	Br	0.4	toluene	rt	—	>90	8.1:1
EtO_2C	Me	H	4-Tol	I	0.06	CH_2Cl_2	15°	0.5	86	49:1
NC–	Me	Me_3Si	Ph	PhSe	0.06	toluene	–20°	2	81	9:1

Scheme 126

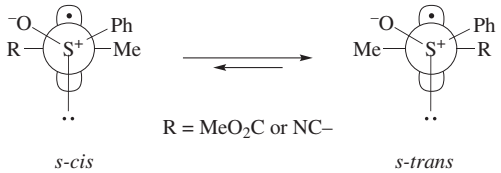
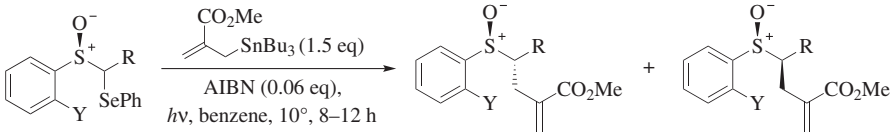


Figure 24. The preferred (*s-trans*) and disfavored (*s-cis*) conformations of α-arylsulfinyl radicals substituted with a polar group.

For α-arylsulfinyl radicals that have an alkyl substituent instead of a polar group, the stereochemistry of the major product is dependent on the exact nature of the

substrate (Scheme 127).[195] Selectivity for the *syn* product improves as the size of the alkyl group increases, and the use of an aryl group bearing a 2-chloro substituent increases the preference for the *anti* product. For these substrates, the primary driving force in determining the ground-state conformations is the minimization of steric interactions between the aryl group on the sulfoxide and the alkyl group attached to the radical center. For the radical bearing a methyl group and an unsubstituted aryl ring, steric interactions are minimal in either conformation and no diastereoselectivity is observed. For all other radicals in this series, steric interactions are more significant in the *s-trans* conformation, and thus the *s-cis* conformation is predominant in the ground state (Figure 25). Formation of the *anti* product occurs by attack of allyltributylstannane from the face opposite the aryl group on the chiral sulfoxide center. This transition state, **126**, is favorable when the alkyl group is small (methyl or ethyl) and the aryl group is bulkier due to 2-chloro substitution. However, with secondary or tertiary alkyl groups, a developing eclipsing interaction between the bulky alkyl group and the sulfoxide oxygen disfavors transition state **126**, and the major product becomes the *syn* isomer, which is formed via transition state **127**.



R	Y	Yield (%)	*anti*/*syn*
Me	H	67	1:1
Et	H	63	1:1.6
i-Pr	H	86	1:3.5
t-Bu	H	61	1:19
Me	Cl	66	4:1
Et	Cl	73	2.6:1
i-Pr	Cl	82	1:1.5

Scheme 127

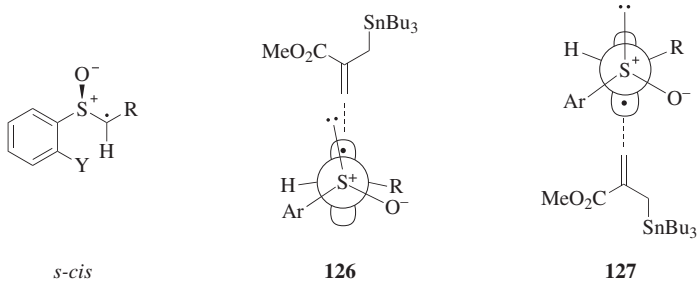
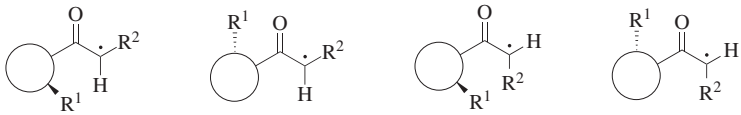


Figure 25. The preferred *s-cis* conformation of alkyl substituted α-arylsulfinyl radicals (left), and the preferred transition states for allylation when R is small (center) and when R is large (right).

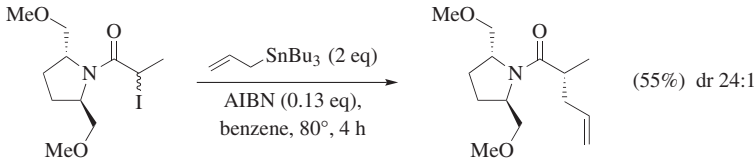
Chiral Auxiliary Control. Secondary radicals substituted with amides, imides, or esters derived from chiral amines, amides, or alcohols, respectively, undergo allylation reactions with excellent control of diastereoselectivity. For reactions of this type to be selective, the radical must react preferentially from a single conformation that places a bulky substituent on a stereogenic center in a position to selectively block the approach from one face of the radical. Connecting the chiral auxiliary to the radical through an amide, imide, or ester group minimizes the number of possible conformations because the singly occupied orbital of the radical will be aligned parallel to the π-system of the carbonyl, as will the lone pair of the connecting nitrogen or oxygen of the auxiliary group. As a result, the radical is restricted to the four possible conformations **128**–**131** (Figure 26). Rotation around the bond between the radical and the carbonyl group is controlled by steric factors, with a preference for conformations **128** and **129**, which place the bulky auxiliary group adjacent to the small hydrogen atom, while the smaller carbonyl oxygen atom is adjacent to the larger R^2 group. A number of strategies have been employed to control rotation around the bond between the chiral auxiliary and the carbonyl carbon (i.e., selectivity for **128** over **129**) including steric interactions, dipole–dipole interactions, and Lewis acid complexation.



128 **129** **130** **131**

Figure 26. Potential conformations of chiral-auxiliary-substituted radicals.

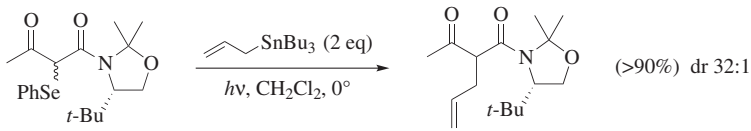
The simplest strategy for controlling the conformation with respect to rotation around the auxiliary–carbonyl bond is to use a C_2-symmetric auxiliary, for which the two possible conformations are degenerate. Although employed in numerous radical addition processes,[160] a C_2-symmetric auxiliary has been reported only once in a radical allylation reaction (Scheme 128).[196] The radical derived from iodide **132** reacts with allyltributylstannane at 80° to form a 24:1 mixture of diastereomers in 55% yield.



132

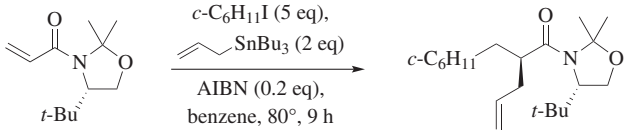
Scheme 128

One major disadvantage of C_2-symmetric amine auxiliaries is that they are typically challenging to prepare. Oxazolidine auxiliaries, however, can be synthesized in one step from readily available 1,2-amino alcohols, and these auxiliaries afford moderate-to-excellent control of stereoselectivity in numerous allylation reactions. Oxazolidines bearing isopropyl, phenyl, benzyl, or *tert*-butyl groups at the stereocenter have all been employed, but only reactions using the *tert*-butyl-substituted oxazolidine are highly selective. Because the quaternary *gem*-dimethyl group is bulkier than the *tert*-butyl-bearing stereocenter, the preferred conformation places the *gem*-dimethyl group adjacent to the smaller carbonyl oxygen, with the *tert*-butyl group oriented towards the substituted radical center, as in **128** (in this case, R^1 = *t*-Bu). In a simple addition reaction, phenylselenide **133** reacts with allyltributylstannane at 0° to provide the product in greater than 90% yield with a diastereoselectivity of 32:1 (Scheme 129);[197] however, the configuration of the major isomer was not definitively assigned. Scheme 130 depicts a three-component reaction in which cyclohexyl radical adds to *tert*-butyl-oxazolidine-substituted acrylamide **134**, and the resulting adduct radical is trapped with allyltributylstannane.[198,199] This reaction occurs in 33% yield with 25:1 selectivity at 80°.



133

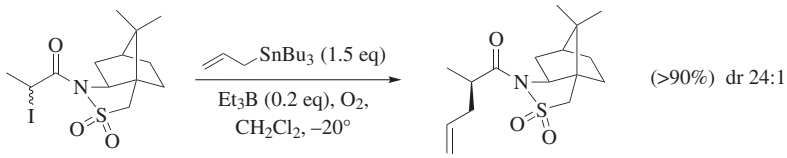
Scheme 129



134 (33%) dr 25:1

Scheme 130

The minimization of dipole–dipole interactions can be used to limit rotation around the bond between the auxiliary and the carbonyl carbon, thereby controlling the reactive conformation. Iodide **135**, which employs Oppolzer's camphor sultam as a chiral auxiliary, reacts with allyltributylstannane at –20° in dichloromethane to form the allylation products in greater than 90% yield with a diastereoselectivity of 24:1 (Scheme 131).[146,200] The preferred conformation of the radical is presumed to orient the carbonyl away from the sulfonyl group (Figure 27). The allylstannane then adds to the top face of this radical, thereby minimizing interactions with the axial sulfone oxygen atom, which blocks the bottom face.



135

Scheme 131

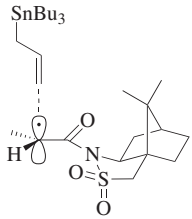
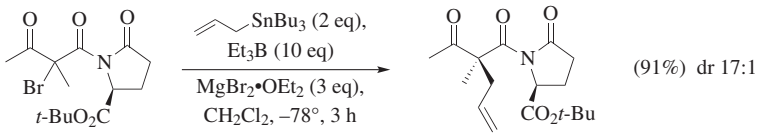


Figure 27. The preferred conformation of the radical derived from iodide **135**.

Using chiral auxiliaries to control the stereochemistry of allylation reactions of tertiary radicals has been a particular challenge. With secondary radicals, rotation around the bond between the radical and the carbonyl group can be controlled by the need to minimize steric interactions, but when a second alkyl group replaces a hydrogen atom on the radical, steric differentiation is lost (assuming there is not a dramatic size difference between the two groups). The most successful example of a chiral-auxiliary-mediated allylation reaction of a tertiary radical uses (1) metal chelation to control rotation around the radical–carbonyl bond and (2) dipole–dipole interactions to control the radical conformation with respect to the auxiliary (Scheme 132).[201] The allylation of **136** likely occurs via the conformation shown in Figure 28, in which the addition of the allyl group occurs at the top face, opposite the ester substituent on the auxiliary, to provide the product in excellent yield and with good stereocontrol (dr 17:1).



136

Scheme 132

Lewis acid chelation can also be used to prevent rotation around the bond between the carbonyl and the auxiliary. This strategy has been used most often with oxazolidinone chiral auxiliaries, which provide the highest levels of selectivity observed for chiral-auxiliary-mediated reactions. Understanding the factors that influence these

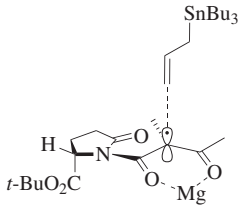
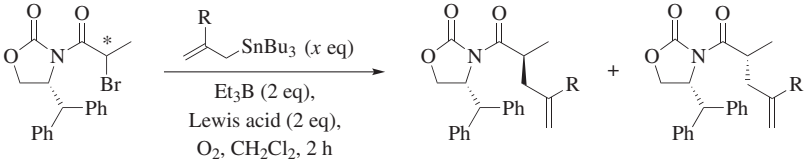


Figure 28. The preferred conformation of the metal-complexed radical derived from bromide **136**.

diastereoselective reactions has been critical for the subsequent development of enantioselective radical allylation reactions.

Oxazolidinones with various substituent groups at the stereocenter have been investigated, but the diphenylmethyl-substituted auxiliary affords the highest reported selectivities. In direct allylation reactions of bromide substrates such as **58**, diastereoselectivities as high as >100:1 are possible in the presence of a chelating Lewis acid (Scheme 133).[131,202] Reactions in the absence of a Lewis acid (or with a monodentate Lewis acid) deliver very modest selectivities for the other diastereomer.



58 **59** **137**

*Config	R	*x*	Lewis Acid	Temp (°)	Yield (%)	**59/137**
rac	H	2	none	–78	93	1:1.8
rac	H	2	BF_3•OEt_2	–78	85	1:1.4
rac	H	2	$MgBr_2$	–78	94	>100:1
(*R*)	H	2.5	$MgBr_2$	–78	70	39:1
(*S*)	H	2.5	$MgBr_2$	–78	91	39:1
(*R*)	H	2.5	$MgBr_2$	0	90	>50:1
(*S*)	H	2.5	$MgBr_2$	0	92	>50:1
(*R*)	Me	2.5	$MgBr_2$	–78	78	24:1
(*S*)	Me	2.5	$MgBr_2$	–78	92	12:1
(*R*)	Me	2.5	$MgBr_2$	0	78	>50:1
(*S*)	Me	2.5	$MgBr_2$	0	95	20:1
(*R*)	MeO_2C	2.5	$MgBr_2$	–78	25	3:1
(*S*)	MeO_2C	2.5	$MgBr_2$	–78	90	1:1
(*R*)	MeO_2C	2.5	$MgBr_2$	0	72	43:1
(*S*)	MeO_2C	2.5	$MgBr_2$	0	70	23:1

Scheme 133

Three aspects of these reactions are worth noting. First, diastereoselectivity is dependent on the structure of the allylstannane: reactions of the least reactive, parent

allyltributylstannane are the most selective, and reactions of the most reactive, ester-substituted allylstannane are least selective. Second, these reactions are less selective at –78° than at room temperature. Third, as with transformations that involve Lewis acid mediated 1,2-induction (vide supra), the stereoselectivity of these reactions is dependent on the configuration at the bromine-bearing stereocenter in the substrate.

A computational study provides insight into the origin of these effects.[203] Three different states of both the precursors and the radicals are important, and these vary in terms of the nature of Lewis acid complexation and the conformation. The initial complexation of a Lewis acid to the substrate primarily forms the *s-trans* conformation **138**, wherein the exocyclic carbonyl is oriented towards the diphenylmethyl substituent (Figure 29). From **138**, rotation affords chelated complex **139**, or complexation of a second equivalent of Lewis acid at the exocyclic carbonyl can generate **140**. Although a radical can be formed from any of these conformations (**141**–**143**), the chelated versions of both the bromide and the radical are the most stable, and only chelated radical **142** reacts with high selectivity. With a highly reactive allylstannane, the radical addition is more likely to occur from the conformation in which the radical is initially formed, leading to more product derived from non-chelated forms **141** and **143**, which affords lower selectivity. With less reactive radical traps, addition is slower and more time is available for rotation into chelated conformation **142**. Higher temperature increases the rate of bond rotation, and therefore also increases the likelihood of reaction from chelated radical **142**, which is consistent with the observation that the room-temperature reactions are more selective than those run at lower temperatures. Finally, different selectivities are observed with epimeric bromide substituents because of differences in the rate of bromine-atom abstraction to form the substrate radical: the rate of bromine-atom abstraction

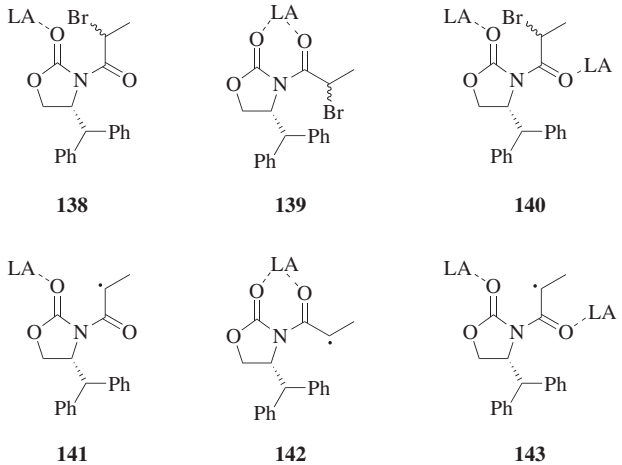
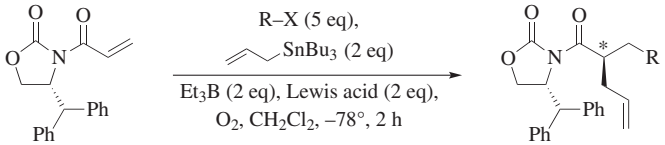


Figure 29. Conformations of oxazolidinone-substituted substrates and radicals in the presence of a Lewis acid.

from the (*R*)-configured bromide is faster for chelated conformation **139** than non-chelated conformation **138**. Thus, the majority of radicals are formed in chelated conformation **142**, which reacts with high selectivity. For the (*S*)-configured bromide, bromine-atom abstraction from chelated conformation **139** is hindered by a steric interaction with the diphenylmethyl group; as a result, radical formation is faster from non-chelated conformation **138**, leading to lower selectivity.

Oxazolidinone chiral auxiliaries can also be used with Lewis acids to control stereoselectivity in three-component reactions. Addition of an alkyl radical to acrylimide **144**, followed by trapping with allyltributylstannane at –78°, affords the products with high selectivities in most cases (Scheme 134).[204] Lower selectivities are obtained with alkyl radicals that bear Lewis basic substituents, and a methyl ether substituent furnishes especially poor selectivity when the Lewis acid is magnesium bromide; high selectivity is restored by switching to ytterbium(III) triflate. As is the case for the direct addition reactions, no selectivity is obtained in the absence of a Lewis acid or in the presence of a monodentate Lewis acid.

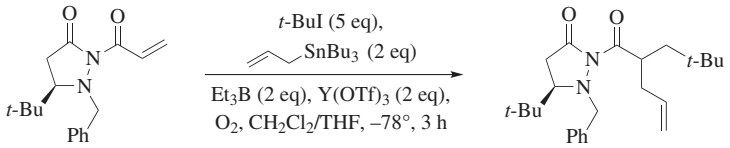


144

R	X	Lewis Acid	Yield (%)	*dr
Et	I	none	90	1:1
Et	I	$MgBr_2$•OEt_2	82	>100:1
$MeOCH_2$	Br	$MgBr_2$	50	1.8:1
$MeOCH_2$	Br	$Yb(OTf)_3$	70	58:1
MeCO	Br	$MgBr_2$	55	50:1
i-Pr	I	$MgBr_2$	85	>100:1
t-Bu	I	$MgBr_2$	94	>100:1

Scheme 134

Pyrazolidinone auxiliaries have been used to control the stereochemistry of a three-component allylation reaction. Chirality is transferred from a permanent stereocenter to a fluxional stereocenter within the auxiliary, and the latter influences the stereochemistry of the allylation. Addition of *tert*-butyl radical to racemic acryloyl pyrazolidinone **145** and subsequent trapping with allyltributylstannane at –78° affords a 15.7:1 ratio of diastereomers in 84% yield (Scheme 135).[205] The Lewis acid yttrium triflate is used to control the conformation with respect to rotation around the carbonyl–auxiliary bond (Figure 30). The fluxional benzyl group attached to the non-imide nitrogen preferentially adopts the configuration opposite the *tert*-butyl group at the permanent stereocenter. The preferred direction of approach of the allylstannane to the radical is likely opposite the fluxional benzyl group, although the configuration of the major diastereomer of these reactions has not been determined.



Scheme 135

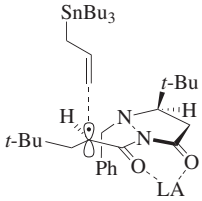
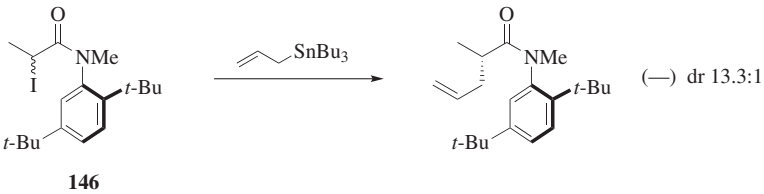


Figure 30. The preferred reactive conformation of the radical formed from addition of *tert*-butyl radical to **145**.

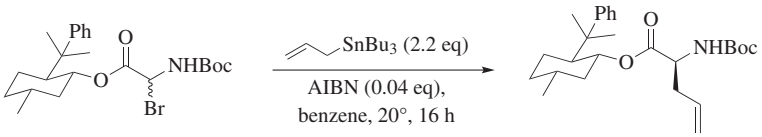
One final strategy of note using amide auxiliaries involves the application of a prochiral auxiliary to control the relative configuration of the product in an addition reaction. α-Iodo amide **146** reacts with allyltributylstannane to form a pair of diastereomers in a ratio of 13.3:1 (the yield was not reported) (Scheme 136).[206] In this case, the aniline component that is used as the auxiliary is achiral but acylation renders it chiral because of hindered rotation around the *N*-aryl bond. Allylation occurs preferentially on the face of the radical opposite the *ortho tert*-butyl group. For this strategy to be practical for asymmetric synthesis, the substrate must either be prepared in optically enriched form using a chiral catalyst or the enantiomers must be resolved. Optically enriched substrates of this type have been employed in radical cyclization reactions, but not in radical allylation reactions.[207]



Scheme 136

Radical conformation is more difficult to control using ester-based chiral auxiliaries, which have the advantage of being removable under milder conditions than amides. As a result, only a few allylation reactions provide good selectivities with ester auxiliaries. For example, using 8-phenylmenthol as an auxiliary, the bromoglycine derivative **147** undergoes allylation at room temperature to afford a 24:1

mixture of diastereomers in 85% yield (Scheme 137).[137,138] The reaction is believed to occur preferentially through the conformation shown in Figure 31, with addition occurring on the front face of the radical. 8-Phenylmenthol can also be used as an auxiliary for allylation of non-amino-acid-derived radicals.[208]



147 (85%) dr 24:1

Scheme 137

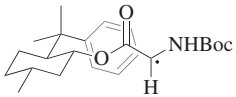
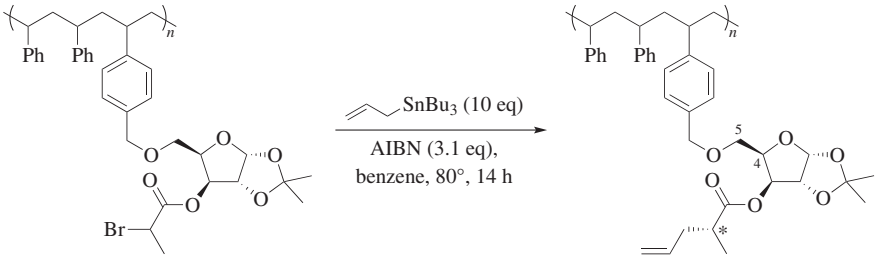


Figure 31. Preferred reactive conformation of the radical formed from bromoglycine substrate **147**.

A unique approach to stereoselective allylation involves a xylose-derived ester that is linked to a soluble polystyrene polymer. With this chiral auxiliary, allylation of an α-bromopropionate unit in benzene at 80° affords the product in 93% yield as a 66:1 ratio of diastereomers (Scheme 138).[115] Precipitation of the allylated polymeric product facilitates separation from the tin-containing byproducts, and subsequent basic hydrolysis delivers 2-methyl-4-pentenoic acid in 80% yield and 98.5:1.5 er. In related studies using a benzyl-protected, non-polymer-bound auxiliary, a Lewis acid is required for high selectivity. The Lewis acid presumably influences the radical conformation by chelating the carbonyl oxygen with the oxygen atoms at C-4 and C-5. In the case of the polymer-bound substrate, the Bu_3SnBr byproduct is thought to function as the Lewis acid, and the addition of another Lewis acid results in cleavage of the sugar from the polymer.

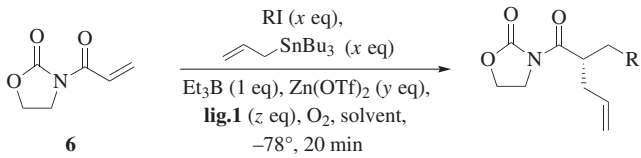


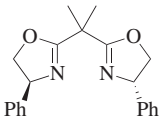
(93%) *dr 66:1

Scheme 138

Enantioselective Reactions. The ability to enhance diastereoselectivity in both substrate- and chiral-auxiliary-mediated reactions using Lewis acids set the stage for the development of enantioselective radical allylation reactions. As with diastereoselective reactions, controlling the conformation of the reactive radical is crucial. This is also accomplished in enantioselective reactions with Lewis acid complexation, and the presence of chiral ligands imparts facial bias for the approach of the allylstannane reagent. Complexation of a Lewis acid adjacent to a radical intermediate makes the radical more electrophilic, enhancing its reactivity towards an electron-rich alkene like an allylstannane. As a result, the reaction of the resulting complex between the radical and the chiral Lewis acid should be faster than the unselective background reaction of the non-complexed, achiral radical, which is a necessary condition for high enantioselectivity.

The most thoroughly explored set of substrates for enantioselective allylation reactions uses achiral oxazolidinones as templates for chelation to chiral Lewis acids. The highest selectivities are obtained from three-component reactions wherein an alkyl radical (derived from an alkyl iodide) adds to acryloyl oxazolidinone **6** in the presence of a chiral Lewis acid, and the resultant adduct radical is trapped by allyltributylstannane (Scheme 139).[209] The most successful reactions use zinc triflate as the Lewis acid and bis(oxazoline) **lig.1** as the chiral ligand at −78°. Two other bis(oxazolines) were examined, but lower selectivities were observed. Only catalytic amounts of the Lewis acid and ligand are necessary to confer enantioselectivity, but enantiomeric ratios are much higher with an equivalent (or more).[210] The enantioselectivity is dependent on the size of the radical that adds initially to substrate **6**: there is a linear correlation with the Taft steric parameter, with larger substituents affording better selectivities. For example, the reaction employing *tert*-butyl iodide delivers the product with an enantiomeric ratio of 94:6, whereas the enantiomeric ratio is only 75:25 for the reaction using cyclohexyl iodide under similar conditions. The reaction is postulated to occur via the conformation depicted in Figure 32. The zinc is tetrahedral, and both the bis(oxazoline) and the acryloyl oxazolidinone are chelated to the metal. The orientation of the oxazolidinone (as shown, or flipped vertically by 180°) is inconsequential because of the C_2 symmetry of the





lig.1

R	x	y	z	Solvent	Yield (%)	er
c-C_6H_{11}	10	1	1	CH_2Cl_2	62	75:25
c-C_6H_{11}	10	1	1	Et_2O	90	82:18
c-C_6H_{11}	10	2	2	Et_2O	61	90:10
t-Bu	5	1	1.2	CH_2Cl_2/pentane (3:2)	78	94:6

Scheme 139

bis(oxazoline). Furthermore, the conformation with respect to rotation around the bond between the carbonyl and the radical center is *s-cis* and is controlled by steric factors. The phenyl group on the front side of the complex blocks the approach of the incoming allylstannane, but the phenyl group on the back face has the opposite orientation and therefore permits the attack.

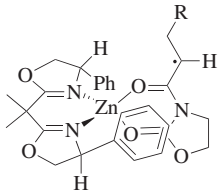
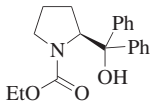


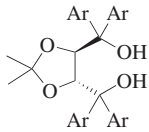
Figure 32. The preferred reactive conformation of the radical formed by addition of an alkyl radical to substrate **6** in the presence of $Zn(OTf)_2$ and chiral ligand **lig.1**.

The radicals generated by addition of an alkyl radical to acrylimide **6** can also be formed directly from the corresponding bromides. However, when these bromides are subjected to allylation conditions identical to those used in the three-component reactions, the allylated products are generated with reduced enantiomer ratios.[210] For example, the enantiomeric ratio drops from 90:10 to 82:18 with two equivalents of Lewis acid when the radical adding to the acrylimide/alkyl substituent on the bromide is cyclohexyl. The reason for this lower enantioselectivity is that the non-selective background reaction of uncomplexed, achiral radicals is more prevalent in reactions of the bromides. Lewis acid complexation has a greater effect on the rate of radical formation by addition to the acrylimide than it does on radical generation from the bromides, and in addition, the alkene substrate is a better Lewis base than the bromide radical precursor, so complex formation is more complete. It is also known that the tributylstannyl halide byproduct of allylation reactions using allyltin reagents can act as a Lewis acid to generate an activated, achiral complex that will react without enantioselectivity. When bromides undergo direct allylation with allylsilane reagents (conditions under which tributylstannyl bromide is not formed), enantioselectivities are noticeably higher (see Scheme 244).[211]

Other catalyst systems can be used for the enantioselective allylation reactions of achiral, oxazolidinone-substituted substrates, albeit with lower enantiomer ratios. Lanthanide Lewis acids, in conjunction with proline-derived chiral ligand **lig.2** (Figure 33), deliver enantiomer ratios as high as 90:10 in three-component reactions of acrylimide **6** at –78°.[212] Yttrium triflate is the most effective Lewis acid in these reactions, and enantioselectivity is enhanced somewhat by the addition of *N*-benzoyl oxazolidinone as an achiral additive. Aluminum-based Lewis acids, which bind to *N*-acyl oxazolidinones through just a single interaction with the acyl oxygen, may also be used. Direct allylation reactions using iodide precursors at –78° are most selective using a 4,4-dimethyl-substituted oxazolidinone template and diol **lig.3** as the chiral ligand, although enantioselectivity is low; the product is obtained in 90% yield, but with an enantiomeric ratio of only 66:34.[213]



lig.2



Ar = 1-naphthyl

lig.3

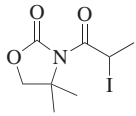
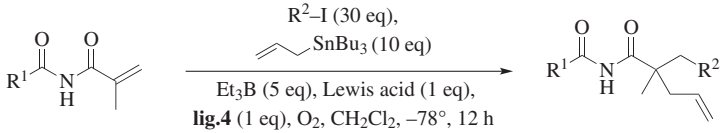
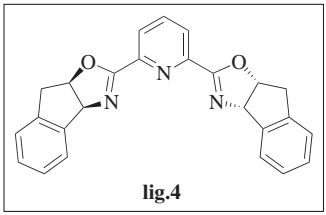


Figure 33. The structures of ligands **lig.2** and **lig.3**, which can be used for enantioselective radical addition reactions, and an example of a 4,4-dimethyl-substituted oxazolidinone substrate.

Substrates other than oxazolidinones can be used to bind a chiral Lewis acid in enantioselective allylation reactions. The three-component reaction of methacrolyl imide **148** with an alkyl iodide and allyltributylstannane generates quaternary stereocenters with moderate enantioselectivities using pybox ligand **lig.4** (Scheme 140).[214] The highest enantioselectivities are obtained with a *tert*-butyl group on the imide (R^1), and selectivity increases as the size of the alkyl radical increases (R^2). Numerous Lewis acids were screened in the reaction, including lanthanide triflates, nickel and magnesium iodides and perchlorates. Yttrium and ytterbium triflate afford the best combination of enantioselectivity and yield. Several other pybox and related ligands were also examined, none of which provides selectivity as high as **lig.4**. The stereochemical configuration of the major enantiomer is not reported, and no model to explain the selectivity has been presented.



148



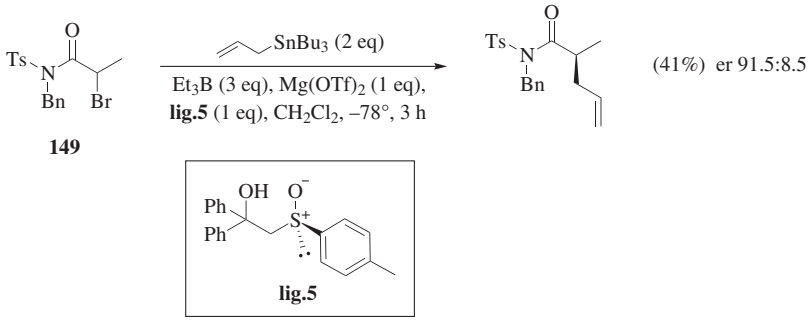
lig.4

R^1	R^2	Lewis Acid	Yield (%)	er
i-Pr	*i*-Pr	$Yb(OTf)_3$	46	55:45
t-Bu	Et	$Y(OTf)_3$	64	61:39
t-Bu	*i*-Pr	$Yb(OTf)_3$	64	85:15
t-Bu	*t*-Bu	$Y(OTf)_3$	64	86.5:13.5
t-Bu	*c*-C_6H_{11}	$Y(OTf)_3$	63	82:18
Ph	*i*-Pr	$Yb(OTf)_3$	42	54.5:45.5

Scheme 140

Acyl sulfonamides can be used as substrates in direct allylation reactions. For instance, the bromosulfonimide **149** reacts with allyltributylstannane at –78° in the presence of chiral Lewis acids to furnish products with enantiomer ratios as high as 91.5:8.5 (Scheme 141).[215] The chiral Lewis acids explored include diamine complexes with triethylaluminium, diol complexes with titanium(IV) isopropoxide, and sulfoxide complexes with magnesium triflate. In all cases, enantiomeric ratios are greater than 75:25, and chemical yields range from 41 to 88%. Chiral sulfoxide **lig.5** provides the highest selectivities, albeit one of the lowest yields. The two sulfonamide

oxygens in the substrate are initially enantiotopic but become diastereotopic when complexed to a Lewis acid in the presence of a chiral ligand. Three of the conformations of this complexed radical are depicted in Figure 34. Conformations that place the 4-tolyl group of the sulfonamide close to the axial phenyl group of the chiral sulfoxide **lig.5** (as in the left-most conformation) are thought to be the least favorable. The middle and right-hand conformations minimize this interaction, but the latter also minimizes steric interactions between the 4-tolyl group of the sulfonamide and the equatorial phenyl substituent of the sulfoxide. The 4-tolyl group of the sulfonamide then blocks approach of the allylstannane from the front face.



Scheme 141

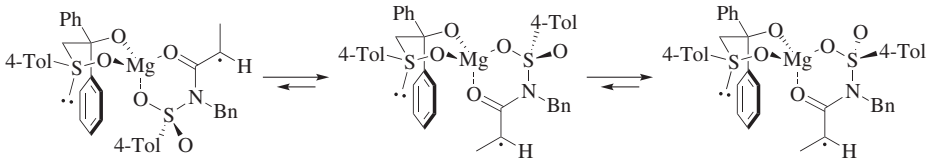
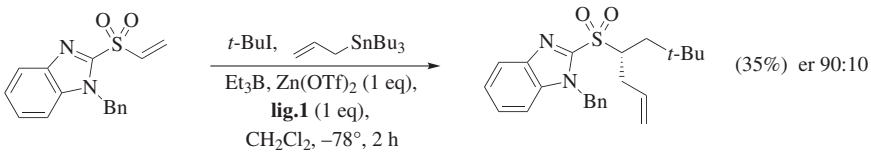


Figure 34. The conformations of the radical derived from bromide **149** when complexed with Mg^{2+} in the presence of chiral ligand **lig.5**.

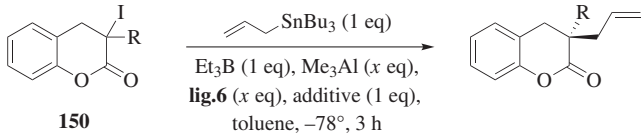
In the examples cited above, the radical undergoing allylation is located adjacent to a carbonyl group. In an alternative approach, the use of α-sulfonyl radicals in enantioselective allylation reactions has been demonstrated in the context of a three-component reaction (Scheme 142).[216] The substrates are vinyl sulfones bearing a heteroaromatic group that is used to chelate a chiral Lewis acid; once again, bis(oxazoline) **lig.1** affords the highest enantioselectivities using zinc triflate as the metal source. Several different allylstannanes were evaluated, including allyltributylstannane, allyltriphenylstannane, tetraallylstannane, and diallyldibutylstannane. Allyltributylstannane provides the product with an enantiomeric ratio of 90:10, but the yield is low (35%) because of the formation of an unidentified side product. The best combination of chemical yield (80%) and enantiomeric ratio (er 92:8) is with diallyldibutylstannane, albeit 10 equivalents of the stannane are required. As with

the acyl sulfonamides discussed above, one of the enantiotopic sulfone oxygens is believed to bind selectively with the zinc complex to minimize steric interactions within the reactive complex and thereby promote selective addition. Interestingly, the radical is believed to exist primarily in an *s-trans* conformation with respect to rotation around the bond between the sulfone and the radical center, the opposite of what is typically observed for carbonyl-based chiral auxiliaries or templates. Basic calculations support this conclusion.



Scheme 142

The enantioselective allylation of cyclic radicals has been less well examined. However, one pair of related papers[217,218] describes the allylation of α-iodo lactones **150** to form quaternary stereocenters (Scheme 143).[217] For these reactions, aluminum-based Lewis acids have been used in combination with either the binaphthol **lig.6**[217] or C_2-symmetric sulfonamides[218] as the chiral ligands; the optimal chiral Lewis acid is derived from trimethylaluminum and binaphthol ligand **lig.6**. Although the best enantioselectivities are obtained with at least 0.5 equivalent of the Lewis acid, only a slight decrease in the enantiomeric ratio is observed when the reaction is carried out with 0.2 equivalent. The preferred reactive complex is postulated to be five-coordinate at the aluminum center (Figure 35), which is consistent with the observation that higher yields and enantiomeric ratios are obtained when one equivalent of diethyl ether (relative to the Lewis acid) is included as an additive. In this complex, the triphenylsilyl group on the back naphthyl ring blocks the back face of the radical to promote the formation of the (*R*) enantiomer as the major product in all of the reactions shown in Scheme 143.



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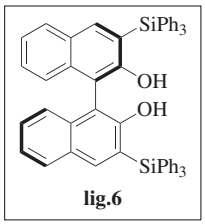


lig.6

R	*x*	Additive	Yield (%)	er
Me	0.1	Et_2O	83	86:14
Me	0.2	Et_2O	81	90:10
Me	0.5	Et_2O	82	90.5:9.5
Me	1	Et_2O	84	90.5:9.5
Me	1	none	72	63.5:36.5
$MeOCH_2$	1	Et_2O	85	91:9
$BnOCH_2$	1	Et_2O	76	95.5:4.5

Scheme 143

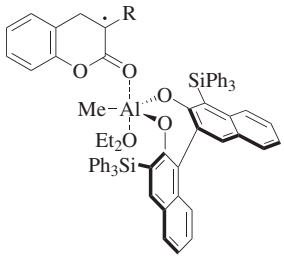
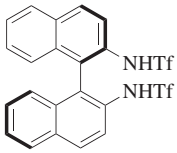


Figure 35. The preferred reactive conformation of the radical derived from α-iodo lactones **150** in the presence of Me_3Al, diethyl ether, and chiral ligand **lig.6**. The triphenylsilyl group on the back naphthyl ring blocks the back face, forcing the allylstannane to approach from the front.

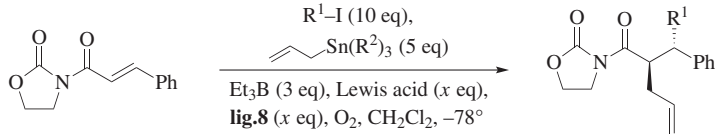
α-Iodo lactones **150** can also undergo enantioselective allylation using an organocatalyst.[219] The binaphthols and C_2-symmetric sulfonamides discussed above can also function as organocatalysts, although the best selectivities are obtained with binaphthyl sulfonamide **lig.7** (Figure 36). Although this study presents an interesting proof of concept, the reaction yields are lower than those obtained using the metallic Lewis acids and chiral ligands, and the highest enantiomeric ratio observed is only 65.0:35.0.

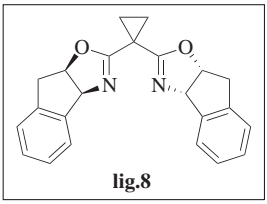


lig.7

Figure 36. The structure of C_2-symmetric sulfonamide ligand **lig.7**.

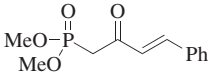
Three-component reactions involving alkyl-radical addition to a cinnamate, followed by trapping with an allylstannane, can be accomplished with control of the configuration at both newly formed stereocenters using Lewis acids and chiral ligand **lig.8** (Scheme 144).[119] Enantiomeric and diastereomeric ratios both increase as the size of the alkyl radical increases, and better selectivities are obtained using substoichiometric quantities of the chiral Lewis acid. Another interesting aspect of this process is that magnesium- and copper-based Lewis acids furnish the products with nearly equal yields and selectivities, but generate opposite enantiomers. Reactions can be performed with crotonate substrates, although the enantio- and diastereoselectivities are lower. The diastereoselectivity in the allylation step is largely due to 1,2-induction by the initial stereocenter that is formed in the enantioselective conjugate addition step, with the allyl group adding *anti* to the largest group. Similar levels of enantio- and diastereoselectivity are possible in conjugate-addition–allyl-trapping reactions of the phosphoric-ester-substituted substrate **151** (Figure 37).[220]





R^1	R^2	Lewis Acid	x	Yield (%)	er	dr
Et	*n*-Bu	MgI_2	0.3	79	88.5:11.5	32:1
i-Pr	*n*-Bu	MgI_2	0.3	93	96.5:3.5	37:1
i-Pr	*n*-Bu	MgI_2	1	82	93:7	19:1
i-Pr	Ph	$Cu(OTf)_2$	0.3	93	10.5:89.5	30:1
t-Bu	*n*-Bu	MgI_2	0.3	84	98.5:1.5	99:1
t-Bu	Ph	$Cu(OTf)_2$	0.3	90	2:98	99:1

Scheme 144



151

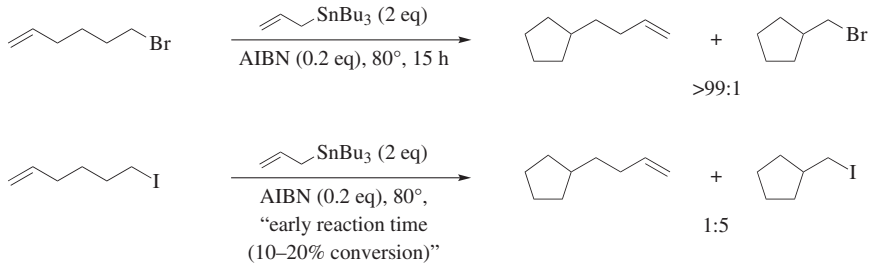
Figure 37. Phosphoric-ester-substituted cinnamate **151**.

Reactions Involving Intramolecular Processes

Reactions Involving a Radical–Alkene Cyclization Followed by Trapping with an Allylstannane. Because most radicals add to allylstannanes at a relatively slow rate, intermolecular allylation reactions are often used as the final step in multistep radical processes. As discussed above, these processes can be part of three- or four-component intermolecular reaction sequences. Alternatively, a multistep process can involve two components—a radical precursor and an allylstannane—with a cyclization reaction preceding the allylation step. 5-*Exo* cyclization processes are most common, but 6-*exo* examples have also been reported (vide infra). The radicals initially undergoing cyclization can be simple alkyl, substituted alkyl, aryl, or acyl derivatives.

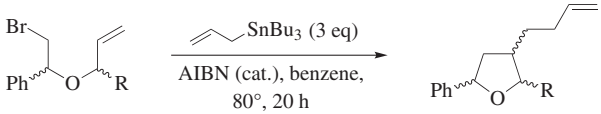
The most well-studied radical cyclization is the 5-*exo* cyclization of the 5-hexenyl radical. Although this cyclization has not been coupled to allylation for synthetic applications, it has been used as a means of estimating the rate of addition of an alkyl radical to allyltributylstannane (see the "Mechanism and Stereochemistry" section).[12] When 5-hexenyl bromide is subjected to radical cyclization conditions in the presence of allyltributylstannane at 80°, butenylcyclopentane is the only product detectable by gas chromatographic analysis (Scheme 145).[12] Nevertheless, with 5-hexenyl iodide, iodine-atom transfer competes with allylation after the cyclization during the early part of the reaction. When 10–20% of the iodide has been consumed,

the ratio of the atom-transfer product to allylation products is 5:1; however, there are no details about final product composition. As anticipated, neither the uncyclized allylation product nor the 6-*endo* product is detected in either case.



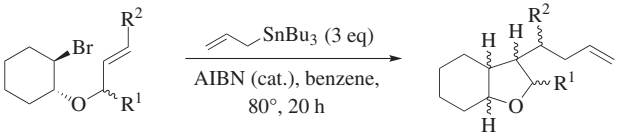
Scheme 145

The most comprehensive study on the use of a cyclization preceding allylation involves the formation of tetrahydrofuran derivatives by 5-*exo* cyclization (Schemes 146 and 147).[221] Both primary and secondary radicals with a variety of substitution patterns are successful in this reaction, which delivers the products in moderate yields. An aryl bromide substrate has also been employed, but no yield was reported. The reaction of one substrate (Scheme 147, $R^1 = Me$, $R^2 = H$) was reported to furnish an equal mixture of two stereoisomeric products, but the configuration of the respective isomers was not determined as was also the case for the reactions using other substrates.



R	Yield (%)
H	35
Me	25

Scheme 146

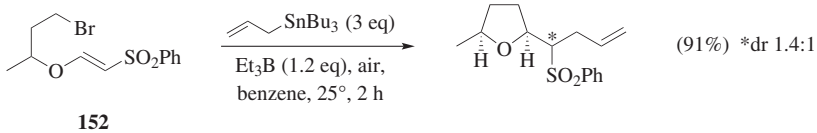


R^1	R^2	Yield (%)
H	H	49
Me	H	48
H	Me	43

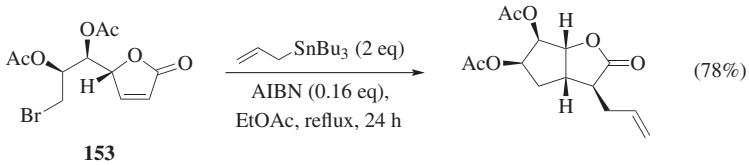
Scheme 147

Improved yields are obtained when the alkene acting as the initial radical acceptor in the cyclization is substituted with an electron-withdrawing group. This substitution accelerates the cyclization and increases the rate of addition of the cyclized radical to allyltributylstannane. The vinylogous sulfone **152** reacts at 25° to generate the 2,5-*cis*-tetrahydrofuran exclusively with a diastereomeric ratio of 1.4:1 at the sulfone-bearing center (Scheme 148).[222,223] Similarly, carbohydrate-derived

bromo lactone **153** undergoes 5-*exo* cyclization, followed by allylation, to afford a single stereoisomeric product in 78% yield (Scheme 149).[224]

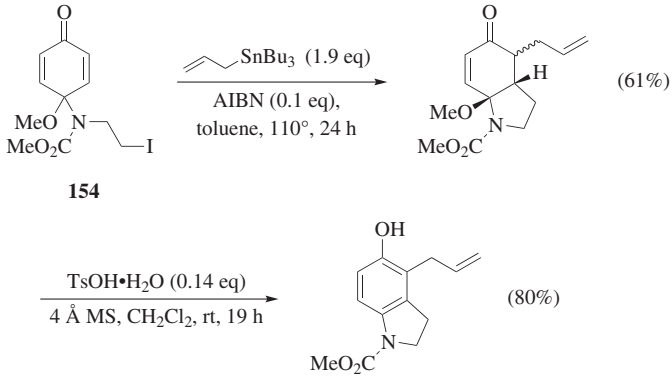


Scheme 148



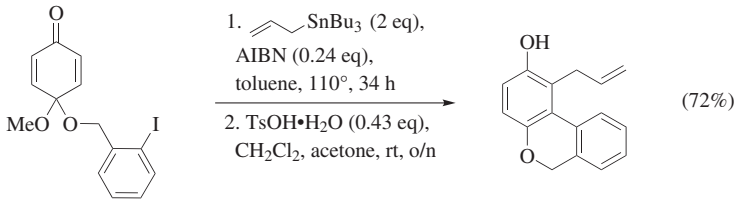
Scheme 149

Cross-conjugated cyclohexadienones also undergo cyclization–allylation cascades. Using substrate **154** in refluxing toluene, the initial 5-*exo* cyclization is followed by allylation to deliver a 61% yield of the product, which can be converted to a 2,3-dihydroindole with mild acid (Scheme 150).[225] A similar substrate, compound **155**, undergoes 6-*exo* cyclization of the aryl radical with the cross-conjugated dienone (Scheme 151).[226,227] Treatment of the intermediate with acid affords a dibenzopyran product in 72% yield over two steps.



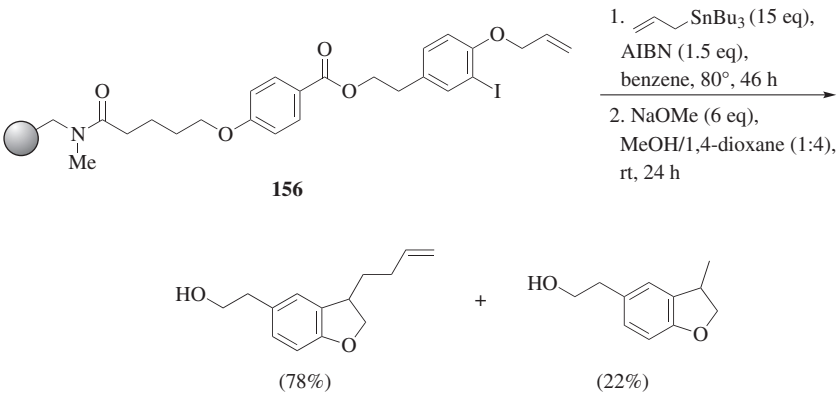
Scheme 150

The sequential radical cyclization/allylation of the polymer-bound aryl iodide **156**, followed by basic cleavage of the product from the polymer resin, results in formation of a dihydrobenzofuran product in 78% yield (Scheme 152).[228] The product of 5-*exo* cyclization and hydrogen abstraction is also formed in 22% yield. The optimal conditions employ 15 equivalents of allyltributylstannane and an



155

Scheme 151



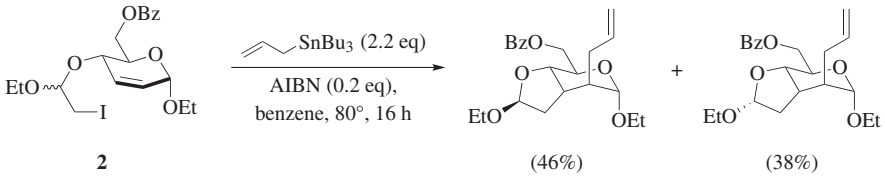
156

Scheme 152

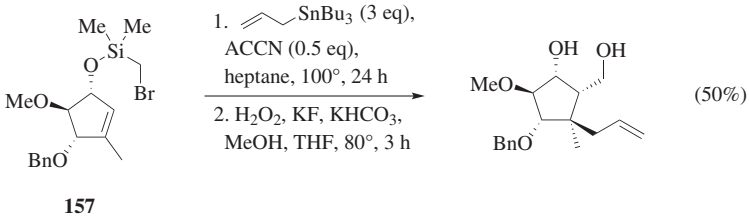
effective substrate concentration of 0.05 M in refluxing benzene. Substrates with a methyl or a phenyl group at the allylic position form analogous products, but in lower yields and with greater proportions of the hydrogen abstraction products. Although the polymer-bound substrate facilitates separation of the product from tin-containing byproducts, greater quantities of the tin reagent are required.

Numerous examples of the Ueno–Stork cyclization strategy coupled to an allylation step have been reported, using both halo acetals and halomethylsilyl ethers as substrates. These reactions are highly selective for the product that possesses *cis* stereochemistry at the new ring junction with the allyl group *trans* to the newly formed ring. For example, treatment of iodoacetal **2** with allyltributylstannane in refluxing benzene results in a 5-*exo* cyclization and allylation of the cyclized radical to generate the product in 84% yield as a pair of stereoisomers that vary at the acetal center (Scheme 153[17,18]; also cf. Scheme 7).

Likewise, the highly functionalized bromomethylsilyl ether substrate **157** undergoes cyclization–allylation at 100° in heptane to form the product as a single stereoisomer (Scheme 154).[229,230] The initial product is treated with hydrogen peroxide and potassium fluoride to furnish the diol in 50% yield over two steps. Interestingly, this transformation was unsuccessful when the substrate was photolyzed at room temperature in the presence of bis(tributyltin).

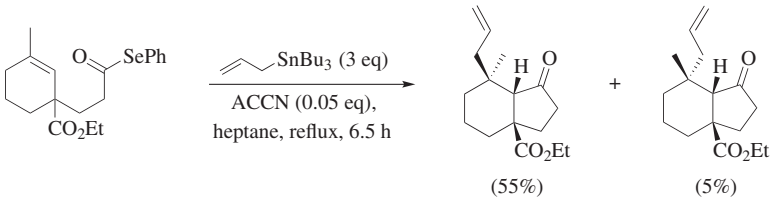


Scheme 153

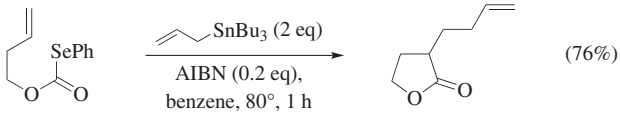


Scheme 154

Acyl radicals undergo 5-*exo* cyclization with rates comparable to those for alkyl radicals. Cyclization of an acyl radical (generated from an acyl selenide) and subsequent allylation can be used to make cyclopentanones (Scheme 155)[231] and γ-lactone derivatives (Scheme 156).[232]

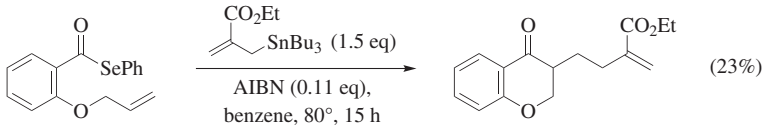


Scheme 155

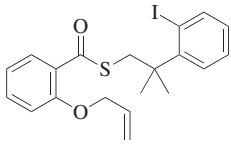


Scheme 156

A suitably substituted acylselenide undergoes 6-*exo* cyclization, followed by allylation, to form a tetrahydropyranone derivative in 23% yield (Scheme 157).[233,234] In a similar reaction, thioester **158** is allylated with allyltributylstannane to afford the analogous product in 56% yield (Figure 38).[235] In this latter case, the initially formed aryl radical undergoes S_H2 substitution at the sulfur atom to form the acyl radical.



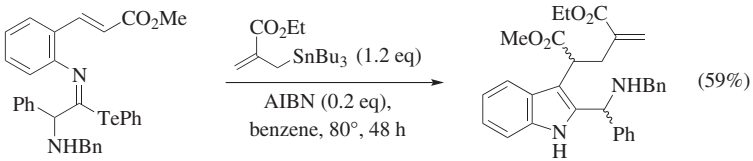
Scheme 157



158

Figure 38. Substrate **158** generates an acyl radical by S_H2 substitution. The radical then undergoes cyclization, followed by allylation.

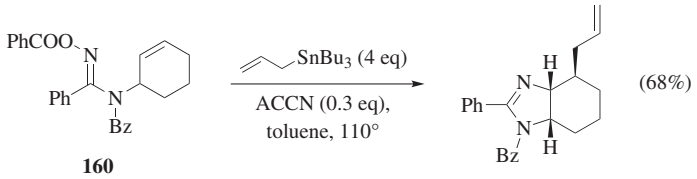
Two strategies have been used to generate nitrogen heterocycles via cyclization–allylation cascades. In one, imidoyltelluride **159** is treated with 2-carboethoxyallyltributylstannane in the presence of AIBN in refluxing benzene to afford an imidoyl radical that undergoes 5-*exo* cyclization onto the alkene (Scheme 158).[236] The intermediary radical then reacts with the allylstannane, and the initially formed product tautomerizes to the indole. The imidoyltelluride precursor **159** is prepared by the reaction of the corresponding arylisocyanide with the *N*-benzyl imine of benzaldehyde and triethoxysilylphenyltelluride.



159

Scheme 158

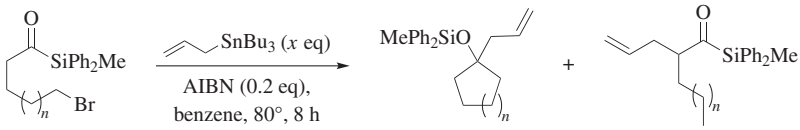
In a second strategy, a nitrogen-centered amidinyl radical (formed by treating substrate **160** with tributyltin radical) undergoes an efficient 5-*exo* cyclization, followed by trapping with allyltributylstannane (Scheme 159).[237] The cyclization affords the *cis* ring junction exclusively, and the allylation occurs from the *exo* face of the cyclized radical to furnish a single diastereomer in 68% yield. The only other reported cyclization/allylation sequence with a nitrogen-centered radical involves a 5-*exo* cyclization of an iminium cation radical.[238] Although the cyclized radical can be trapped with phenyl vinyl sulfone, none of the desired product is isolated with allyltributylstannane.



Scheme 159

Reactions Involving Allylation Following Other Intramolecular Processes. Numerous other intramolecular processes can be coupled with allylation reactions in multistep cascade processes, including acyloxy migrations, ring-opening reactions, fragmentations, and hydrogen-atom-abstraction reactions. Also included in this discussion are sequences involving a cyclization followed by a second intramolecular step prior to allylation.

The 5-*exo* cyclization of an alkyl radical onto a carbonyl group occurs with a rate that is almost as fast as the rate of 5-*exo* cyclization onto a simple alkene,[239] but the former process is usually impractical because the rate of scission of the resulting alkoxy radical is at least two orders of magnitude faster than the rate of cyclization. However, in the case of bromoacylsilane **161** ($n = 1$), cyclization is followed by a rapid 1,2-silyl migration (Scheme 160).[240] The resulting α-silyloxy radical reacts with allyltributylstannane to form the allylated cyclopentane product in 61% yield using three equivalents of allylstannane. Notably, the yields are significantly lower with only one or two equivalents of the allylstannane (23% and 39% after desilylation to the alcohol). In the reaction of a homologous bromoacylsilane (**161**, $n = 2$), 1,5-hydrogen abstraction competes with 6-*exo* cyclization, but the desired cyclization–allylation product is still formed in 60% yield.

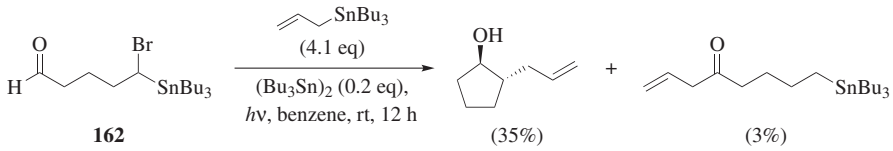


			Yield (%)	
n	x	Time (h)	cyclic	acyclic
1	3	8	61	0
2	4	18	60	21

Scheme 160

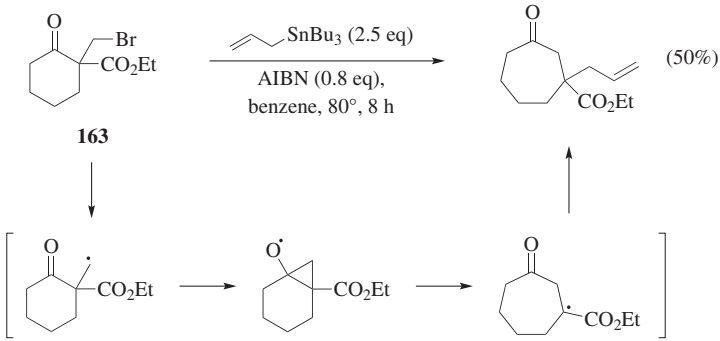
In a related reaction, an α-stannyl radical is generated from bromide **162** under photolytic conditions (Scheme 161).[241,242] This radical cyclizes onto the aldehyde, and the resulting alkoxy radical undergoes a 1,3-migration of the tributylstannyl group, followed by trapping with the allylstannane. A trace of the allylketone is formed by 1,5-hydrogen abstraction of the aldehyde hydrogen by the initial α-stannyl radical, followed by allylation of the resulting acyl radical. Once again, the reaction of a homologous substrate (one additional carbon in the chain) is less successful:

1,5-hydrogen abstraction from the carbon alpha to the carbonyl outcompetes the 6-*exo* cyclization, and the major product is an α-allyl aldehyde.



Scheme 161

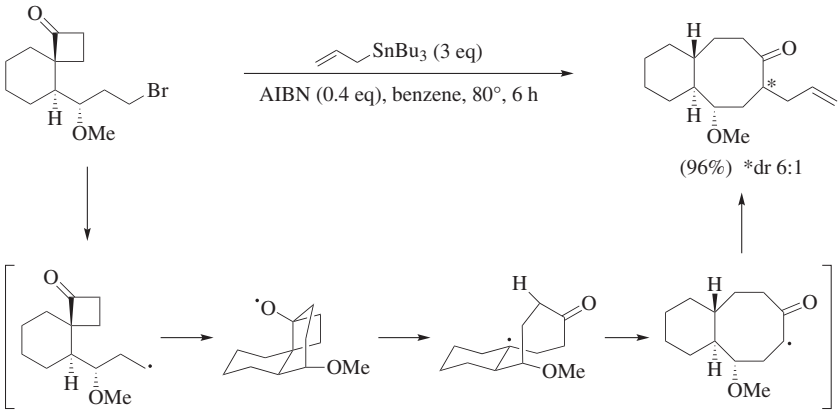
The Dowd–Beckwith reaction also involves a cyclization of an alkyl radical onto a carbonyl group as part of a multistep radical cascade sequence. In this case, the alkoxy radical that forms from the cyclization undergoes fragmentation to form a rearranged radical, usually directed by the presence of a group that stabilizes the new radical. In the original version of the Dowd–Beckwith reaction, this rearranged radical abstracts a hydrogen atom from tributyltin hydride; however, trapping with an allylstannane is also possible and incorporates an additional carbon–carbon bond-forming step into the sequence. Scheme 162 depicts a simple example of this process, wherein bromide **163** is treated with allyltributylstannane in refluxing benzene in the presence of AIBN to promote a 3-*exo* cyclization onto the carbonyl group.[243] The resulting alkoxy radical then fragments to generate a ring-expanded product with a radical adjacent to the ester group, which is trapped with the allylstannane to form the final product in 50% yield. Analogous one-carbon ring-expansion reactions to form six-, eight-, and nine-membered rings occur in comparable yields, thereby making this a more general process.



Scheme 162

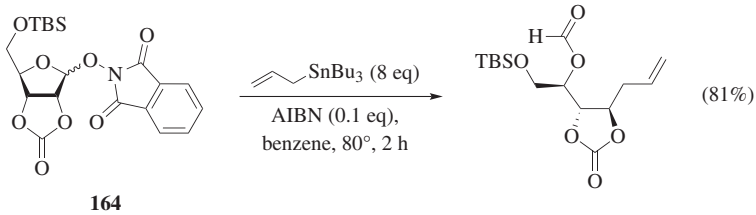
Larger ring expansions are also possible in Dowd–Beckwith reactions. For example, a spirocyclic four-membered ring can be expanded to a fused eight-membered ring (Scheme 163).[244,245] In this case, fragmentation after cyclization places the radical at the ring junction. This radical undergoes 1,5-hydrogen-atom abstraction, translocating the radical to the carbon adjacent to the carbonyl, and

allylation with allyltributylstannane delivers the final product in excellent yield (96%) as a 6:1 mixture of diastereomers. When the configuration of the methoxy group is inverted, the reaction occurs in similar yield and with identical selectivity.



Scheme 163

Alkoxy radicals generated directly from a radical precursor also undergo fragmentation processes, and the resulting radicals can be trapped with an allylstannane. When the *N*-hydroxyphthalimide derivative **164** is treated with allyltributylstannane and AIBN in refluxing benzene, the product of fragmentation and subsequent allylation is isolated in 81% yield (Scheme 164).[246] Replacing the carbonate protecting group with an acetal results in a lower yield, presumably because the less electrophilic intermediate radical adds to the allylstannane more slowly.

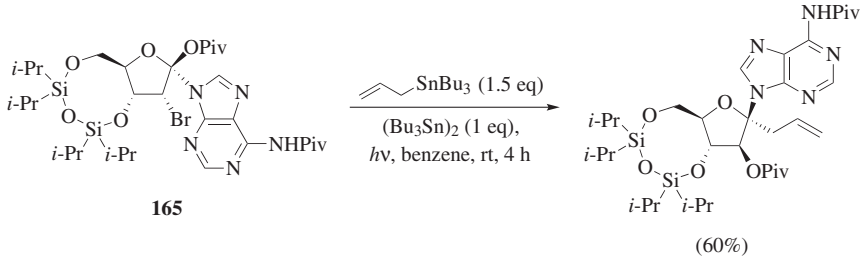


164

Scheme 164

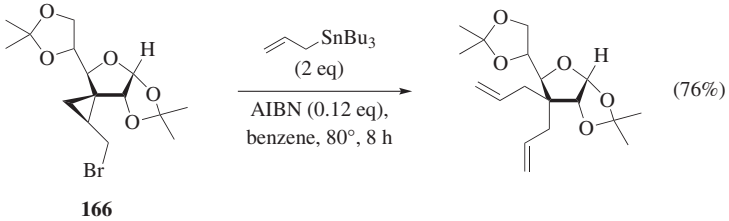
1,2-Acyloxy migrations are well known, especially in carbohydrate and nucleoside substrates.[247] The viability of allylation following an acyloxy migration has not been systematically explored, but a few examples of this process have been reported. When adenine derivative **165** is photolyzed in benzene at room temperature in the presence of bis(tributyltin) and 1.5 equivalents of allyltributylstannane, the acyloxy group migrates to the β face of C-2, leaving a radical at the anomeric position (Scheme 165).[248] Allylation of this radical occurs exclusively from the α face to afford the rearranged product in 60% yield. The product of direct C-2

allylation is also formed in 5% yield as a mixture of stereoisomers, and the quantity increases with higher concentrations of allylstannane. Acyloxy migration followed by allylation also occurs efficiently for the corresponding uracil derivative.



Scheme 165

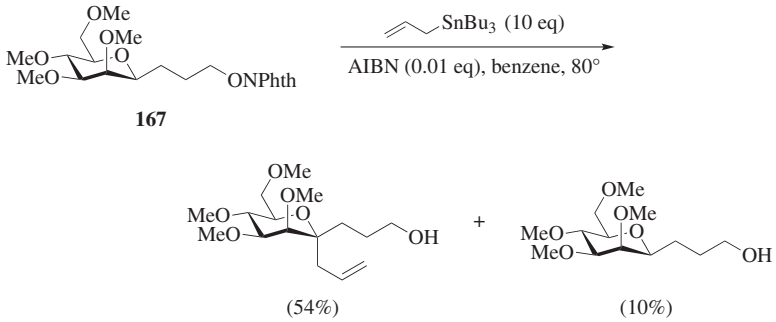
Some of the fastest intramolecular radical processes are ring-opening reactions, so it is not surprising that such a transformation can be coupled with allylation. Thus far, only examples of cyclopropylcarbinyl radical ring-opening, followed by allylation, have been reported. The cyclopropane moiety can be appended onto a simple acyclic or cyclic substrate, or even onto functionalized substrates such as carbohydrates or amino acid derivatives. For example, treatment of carbohydrate-derived substrate **166** with AIBN in refluxing benzene generates a cyclopropylcarbinyl radical that undergoes ring-opening and subsequent allylation, furnishing the diallyl product in 76% yield (Scheme 166).[249,250] A similar reaction is also possible with methallyltributylstannane, albeit in slightly reduced yield. Both the allylated and methallylated products undergo ring-closing metathesis to form spirocyclic products.



Scheme 166

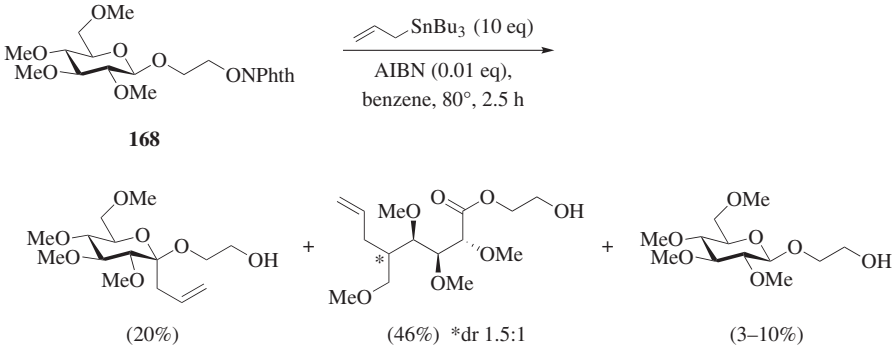
Selective hydrogen-atom abstraction can be used to generate a radical at a position where installing a direct radical precursor is challenging, and several allylation reactions have taken advantage of this strategy. This approach can be used to allylate *C*-glycosides at the anomeric position to create quaternary centers, generally with good stereochemical control. For example, heating alkoxyphthalimide **167** in benzene in the presence of allyltributylstannane and AIBN leads initially to the formation of an alkoxy radical by cleavage of the nitrogen–oxygen bond of the phthalimide group (Scheme 167).[251] This alkoxy radical then undergoes a 1,5-hydrogen-atom

abstraction to form an anomeric radical that reacts with allyltributylstannane to furnish the product in 54% yield along with a small amount of the reduction product. The reaction of the α-anomer generates the same stereoisomer of the product, although in a slightly lower yield (42%). The reaction is also successful with a pentofuranose substrate and when the tether connecting the phthalimide group to the ring is one carbon longer (in this case, a 1,6-hydrogen-atom abstraction occurs).



Scheme 167

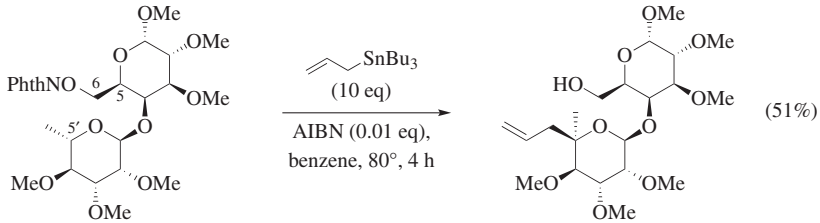
O-Glycosides also participate in the hydrogen-atom-transfer–allylation sequences, although the yields are generally lower. For example, the reaction of the glucose derivative **168** affords the desired product in only 20% yield (Scheme 168).[252] In this case, the major product results from β-fragmentation of the anomeric radical that is formed by 1,5-hydrogen-atom abstraction, followed by allylation at C-5. A small amount of the product of direct reduction of the initial alkoxy radical is also isolated. The increased stability of the anomeric radical formed from the *O*-glycoside likely slows the rate of addition to the allylstannane, thereby allowing the fragmentation process to compete.



Scheme 168

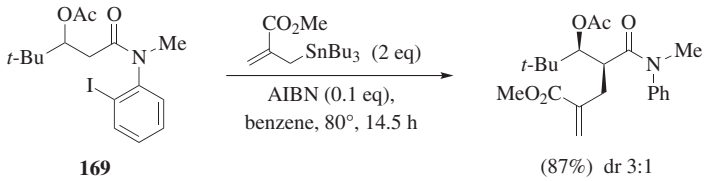
This methodology can be extended to reactions of 1,4′-disaccharides. For example, the alkoxy radical generated from an alkoxyphthalimide group at C-6

of one monosaccharide can be used to create a radical at C-5′ of the second monosaccharide via a 1,8-hydrogen-atom abstraction (Scheme 169).[252] The ring bearing the translocated radical after the hydrogen-atom abstraction exists primarily in a $^1C_4$ chair conformation, leading to allylation on the axial face due to the quasi-homoanomeric effect. Other disaccharide substrates, including several in which the ring bearing the translocated radical is a furanose, deliver moderate-to-good yields of the desired product. However, when both rings are glucose units, fragmentation of the initial alkoxy radical followed by allylation at C-5 is faster than the hydrogen-atom transfer.



Scheme 169

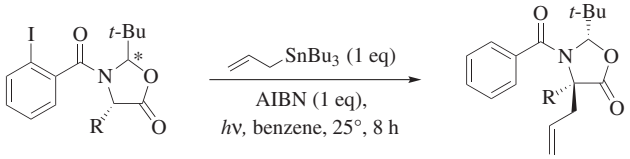
This hydrogen-atom-abstraction–allylation sequence has enabled the development of protecting/radical-translocating groups. In this strategy, a radical precursor is incorporated into a modified version of a standard protecting group, typically as an aryl halide. Radical generation is followed by a 1,5-hydrogen-atom transfer to translocate the radical to the position at which allylation is desired, often at a carbon adjacent to a carbonyl group; the hydrogen-atom transfer is driven by the increased stability of the translocated radical. Protecting/radical-translocating groups have been used to generate radicals to study 1,2-induction in the allylation of chiral, acyclic radicals.[123,125] For example, substrate **169** reacts with 2-carbomethoxyallyltributylstannane in the presence of AIBN in benzene at 80° to afford a 3:1 mixture of diastereomers in 87% yield (Scheme 170).[125] Formation of the *syn* diastereomer is favored and can be rationalized using the ideas discussed earlier (cf. Scheme 113).



Scheme 170

The protecting/radical-translocating group strategy can be used to prepare unnatural tertiary and quaternary amino acids. Common amino acids are protected as oxazolidin-5-ones bearing an *N*-(2-iodobenzoyl) substituent that serves as the

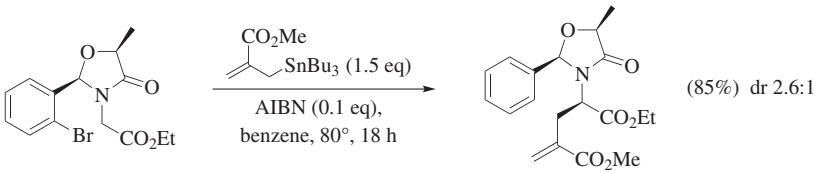
radical-translocating group (Scheme 171).[253] Photolysis in the presence of AIBN and an allylstannane at 25° generates an aryl radical, and subsequent 1,5-hydrogen-atom transfer translocates the radical to the α carbon of the protected amino acid. Reaction with the allylstannane generates the final allylated product, in which the *tert*-butyl group at C-2 of the oxazolidinone directs the diastereoselectivity of the allylation. The reaction of the racemic L-glycine-derived substrate (R = H) affords a single diastereomer. The L-alanine-derived substrate (R = Me) is formed and used as a 1.2:1 mixture of *cis*/*trans* isomers, and the allylation reaction gives a 4:1 diastereomer ratio, favoring the products wherein the newly introduced allyl group is *trans* to the *tert*-butyl group. However, because the substrate contains both (*R*)- and (*S*)-configured *tert*-butyl-substituted stereocenters, an enantiomeric mixture of the allylated diastereomers is formed. The L-valine derived substrate (R = *i*-Pr) is generated as a single diastereomer and reacts, albeit in low yield, to form exclusively the product in which the allyl group is *trans* to the *tert*-butyl substituent. The low yield for the valine derivative is likely due to steric inhibition in the allylation step.



R	*cis/trans	Yield (%)	dr
H	—	42	>95:5
Me	1.2:1	64	4:1
i-Pr	>95:5	5	>95:5

Scheme 171

Expanding the role of a protecting/radical-translocating group one step further, an appropriately substituted group can also function as a chiral auxiliary. When substrate **170** is treated with 2-carbomethoxyallyltributylstannane and AIBN in refluxing benzene, the product is obtained as a mixture of diastereomers (2.6:1) in 85% yield (Scheme 172).[254] Once again, initial formation of an aryl radical is followed by a 1,5-hydrogen-atom abstraction to place the radical adjacent to a carbonyl group, and this radical then reacts with the allylstannane. The aryl ring,

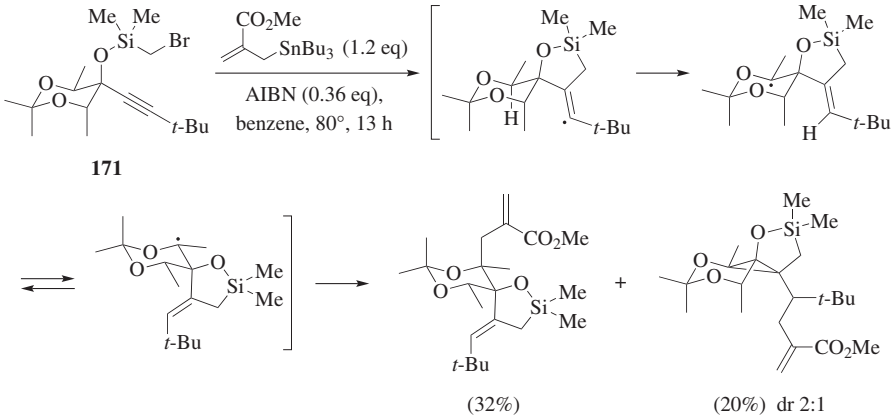


170

Scheme 172

which was the original source of the radical, is the primary source of stereocontrol in the allylation. Furthermore, the methyl group on the oxazolidinone ring is derived from optically pure lactic acid, which enables access to the substrate in optically pure form. This reaction provides another means for the synthesis of amino acid derivatives.

A hydrogen-atom transfer can be incorporated as the penultimate step in a radical cascade process that concludes with an allylation reaction. When treated with AIBN and 2-carbomethoxyallyltributylstannane in refluxing benzene, bromomethylsilyl ether **171** undergoes initial radical formation and 5-*exo* cyclization onto the alkyne (Scheme 173).[255] The resulting vinyl radical undergoes a rapid 1,4-hydrogen abstraction to afford a new radical that, after a chair-to-chair ring flip, adds to the allylstannane exclusively from the axial face. A cyclopropane product is also formed in 20% yield by a 3-*exo* cyclization of the cyclic radical onto the alkene, followed by allylation.

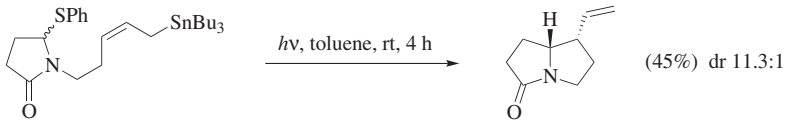


Scheme 173

Cyclization Reactions Involving Intramolecular Trapping by an Allylstannane. When both the radical precursor and allylstannane are incorporated into the substrate, an intramolecular allylation will generate a cyclic product. Although this approach has not been used extensively, several variations on the idea have proven successful.

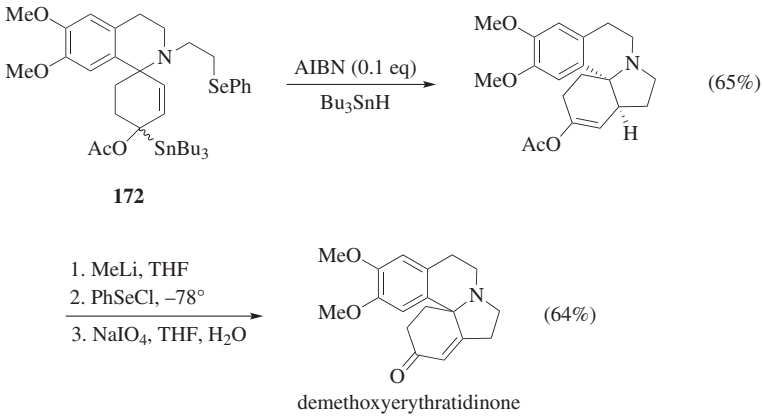
The earliest and simplest example of this process involves a 5-*exo* cyclization of a radical adjacent to the nitrogen atom of a lactam onto the alkene unit of a pendant allylstannane (Scheme 174).[256,257] This reaction occurs with good stereochemical control, and the placement of the vinyl substituent occurs primarily on the *endo* face of the newly formed bicyclic ring system, but the yield is modest.

Functionalization of an allylstannane at the tin-bearing carbon permits direct access to an enol ether in a cyclization reaction. For instance, the primary radical generated from the reaction of selenide **172** with tributyltin hydride undergoes a 5-*exo* cyclization to form the product as a single stereoisomer in 65% yield



Scheme 174

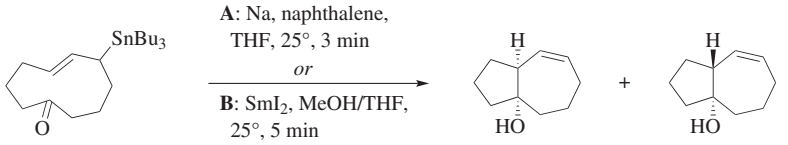
(Scheme 175).[258] Presumably the intramolecular nature of the radical addition and the steric congestion of the alkene minimize the competing rearrangement of the allylstannane, which would be problematic in an intermolecular addition to a C-1-substituted allylstannane (vide supra). This cyclization product is converted in a simple sequence to the natural product demethoxyerythratidinone (racemic), as shown.



Scheme 175

Transannular cyclization onto an allylstannane is also possible. A ketyl radical anion can be formed from ketone **173** by treatment with either sodium naphthalide or samarium(II) iodide at room temperature (Scheme 176).[259] Cyclization of this radical anion is followed by loss of tributylstannyl radical and then protonation of the metal alkoxide to form the alcohol. Both sets of conditions furnish good yields of the product, with either exclusive or predominant formation of the *cis* ring junction. While a careful mechanistic study of the cyclization of substrate **173** has not been reported, computational studies on the cyclization of the analogous substrate lacking the stannyl substituent provide some insight into the *cis* selectivity of the reaction.[260] Calculations show that the radical cyclization step is exothermic by approximately 50 kcal/mol, which is enough to preclude significant reversibility of the cyclization. Furthermore, the two lowest-energy conformations are both oriented to form the *cis*-fused product, and calculations correctly predict that the cyclization to the *cis* isomer has a lower energy barrier than cyclization to the *trans* isomer. Interestingly, reactions performed at 80° with tributyltin hydride afford primarily the *trans* isomer, which is ascribed to a competing, non-radical thermal cyclization that is specific for

the *trans* product. Experiments performed with varying concentrations of tributyltin hydride demonstrate that the stannane-mediated cyclization primarily forms the *cis* product.

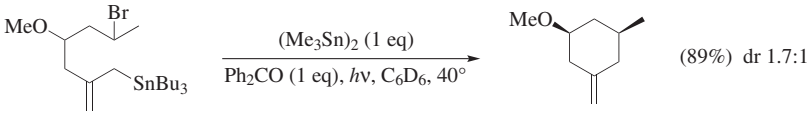


173

Conditions	Yield (%)	*cis*/*trans*
A	56	>99:1
B	64	3.9:1

Scheme 176

Although the most-common radical cyclizations are 5- and 6-*exo* processes, cyclizations in the *endo* mode are possible under appropriate circumstances. For the 5-hexenyl system, the rate of the *exo* cyclization decreases when there is a substituent at the C-5 position, and mixtures of *exo* and *endo* products are typically obtained. Adding a trialkylstannylmethyl group at C-5 slightly accelerates the 6-*endo* cyclization and, in at least one case, this substitution biases the reaction to occur exclusively through the 6-*endo* mode (Scheme 177).[261] At 40°, bromide **174** reacts to form only the 6-*endo* product in 89% yield (determined by ^{1}H NMR spectroscopic analysis), with the *cis* isomer predominating (*cis*/*trans* = 1.7:1). Notably, the reaction at 80° with triphenylstannane and AIBN still favors the 6-*endo* product, albeit some of the 5-*exo* product is also formed (6-*endo*/5-*exo* product > 10:1).

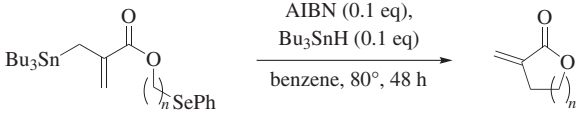


174

Scheme 177

Macrocyclizations are also possible in the endocyclic mode. A systematic study of macrocyclization of ω-phenylselenoalkyl 2-(tributylstannylmethyl)propenoates **175** demonstrates that endocyclic macrocyclization is successful when the ring being formed contains 10 or more atoms (Scheme 178).[262,263] Attempts to prepare smaller rings (i.e., six- to nine-membered rings) resulted only in products of competing intermolecular processes, even at very high dilution (5 mM concentration of the substrate).

The reaction of an alkene with compounds containing both a radical precursor and an allylstannane enable annulation reactions that conclude with an intramolecular allylation step. For example, treatment of substrate **176** with triethylborane and acrylimide **6** in the presence of a Lewis acid, generates a primary radical, which adds to the acrylamide to give an adduct radical that undergoes a 6-*endo* cyclization

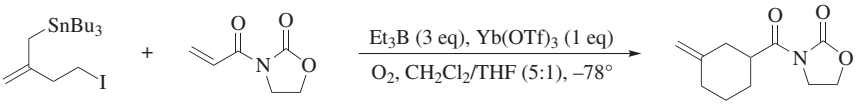


175

n	Yield (%)
6	54
7	46
8	61
9	50
10	80
11	72

Scheme 178

(Scheme 179).[264] This process can also be used to form seven-membered rings, and additional substitution is tolerated both on the initial radical (i.e., secondary radicals can be used) and on the alkene carbon to which the initial radical adds (crotonate and fumarate derivatives). Reactions of these substituted substrates occur with good control of relative stereochemistry, and a chiral oxazolidinone can be used to provide control of the absolute stereochemistry.



176 (4 eq) **6** (77%)

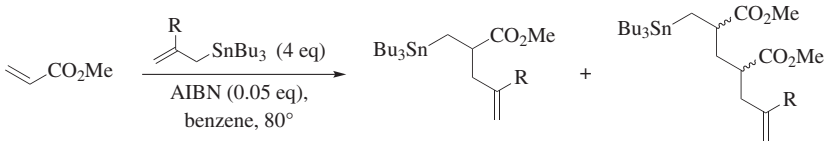
Scheme 179

Allylstannylation Reactions

Allylstannylation is a two-component allylation reaction wherein a stannyl radical (rather than an alkyl radical) adds initially to an alkene or an alkyne, and the resulting adduct radical adds to an allylstannane. This reaction is successful with a range of alkene and alkyne substrates, and it can be combined with rearrangements or cyclizations into multistep cascade sequences.

The optimal allylstannylation reactions with alkenes employ an allylstannane that is substituted with an electron-withdrawing substituent, as demonstrated in Scheme 180.[265,266] The reaction of methyl acrylate with four equivalents of allyltributylstannane and AIBN in benzene at 80° provides the simple allylstannylation product in only 13% yield; the major product of this reaction results from addition of the initial adduct radical to a second equivalent of methyl acrylate prior to trapping by the allylstannane. However, when 2-carbomethoxyallyltributylstannane is used, the desired allylstannylation product is formed exclusively in 88% yield. Reducing the quantity of the allylstannane to two equivalents results in a slightly lower yield (77%). As is observed for the addition reactions of ambiphilic carbonyl-substituted radicals to methyl acrylate,[267] the ester substituent on the allylstannane increases the rate of addition, making allylation of the initial adduct radical more favorable than addition to a second equivalent of methyl acrylate.

Allylstannylation reactions of alkenes are also more efficient when the alkene is substituted with an electron-withdrawing group. Allylstannylation of 1-decene with four equivalents of 2-carbomethoxyallyltributylstannane affords none of the desired

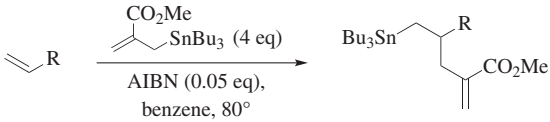


177 **178**

R	Time (h)	Yield (%) **177**	Yield (%) **178**
H	4	13	40
MeO_2C	1	88	0

Scheme 180

product (Scheme 181).[265,266] However, styrene under the same conditions affords the desired product in 40% yield, and the reactions of acrylonitrile and methyl acrylate furnish the adducts in 83% and 88% yields, respectively. The yields are slightly reduced with 1,1-disubstituted alkenes, whereas 1,2-disubstituted alkenes are unsuccessful with methyl crotonate, but proceed in moderate-to-good yields with dimethyl maleate, dimethyl fumarate, and fumaronitrile. In these cases, the product is partially destannylated under the reaction conditions, and therefore, the initial product mixture is treated with acid to complete the destannylation process before product isolation. Reactions can also be performed with chiral-auxiliary-substituted acrylate and acrylamide derivatives.[266] However, because the reaction is incompatible with Lewis acids, reactions employing oxazolidinone auxiliaries proceed with minimal stereoselectivity. The most successful chiral-auxiliary-mediated reactions use 8-phenylmenthol as the auxiliary, and products are isolated in good yields with up to 9:1 stereoselectivity.

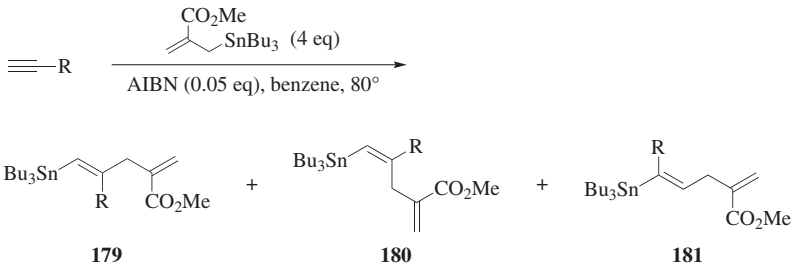


R	Time (h)	Yield (%)
n-C_8H_{17}	24	0
Ph	2	40
NC–	4	83
MeO_2C	1	88

Scheme 181

Allylstannylation reactions of alkynes are similar to those of alkenes, in that they proceed more efficiently with allylstannanes bearing an electron-withdrawing substituent. For terminal alkynes, however, a greater range of substituents is tolerated (Scheme 182).[266,268] Reactions are highly selective for formation of the (*Z*)-isomeric products, and attack of the stannyl radical occurs primarily or exclusively at the terminal carbon of the alkyne. Reactions of internal alkynes are high yielding if at

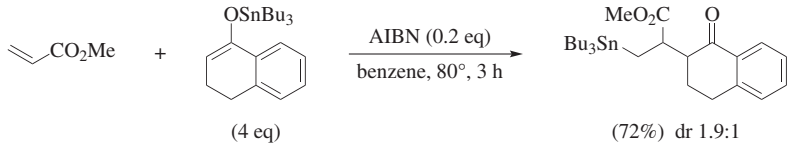
least one substituent is an electron-withdrawing group, such as an ester[266,268] or trifluoromethyl group.[269] The regioisomeric product resulting from addition to the carbon bearing the electron-withdrawing group is formed preferentially.



		Yield (%)		
R	Time (h)	**179**	**180 + 181**	**180/181**
n-$C_{10}H_{21}$	6	44	0	—
$HOCH_2CH_2$	2	69	0	—
Ph	1	94	0	—
MeO_2C	1	70	<15	2.7:1

Scheme 182

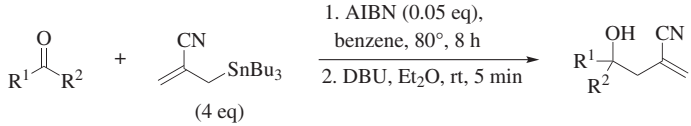
Allylstannylation-type reactions of alkenes and alkynes can be effected using stannyl enolates (Scheme 183).[270] Once again, the reaction is only efficient with electron-poor alkenes, but the scope of useful alkyne substrates is broader. Stannyl enolates derived from aliphatic ketones do not react, and those derived from acetophenone and propiophenone give only moderate yields of product, up to 40%. However, the stannyl enolates of the cyclic ketones indanone and tetralone provide the desired product with improved yields as high as 76%.



Scheme 183

Treating an aldehyde or a ketone with 2-cyanoallyltributylstannane in the presence of AIBN results in allylstannylation of the carbonyl group (Scheme 184),[266] but no reaction occurs in the absence of AIBN. The addition of a tributylstannyl radical to the carbonyl oxygen generates a new carbon radical at the carbonyl carbon, which then adds to the activated allylstannane. Destannylation from the oxygen by treatment with DBU affords the final product. The scope of this process has not been explored extensively, but the reaction is successful with several aromatic aldehydes and with

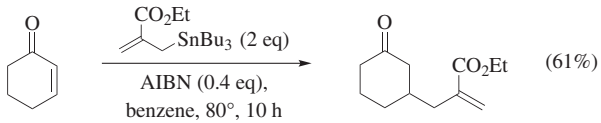
acetophenone. However, no product was obtained with the one aliphatic aldehyde examined.



R^1	R^2	Yield (%)
Ph	H	59
$PhCH_2CH_2$	H	0
Ph	Me	29

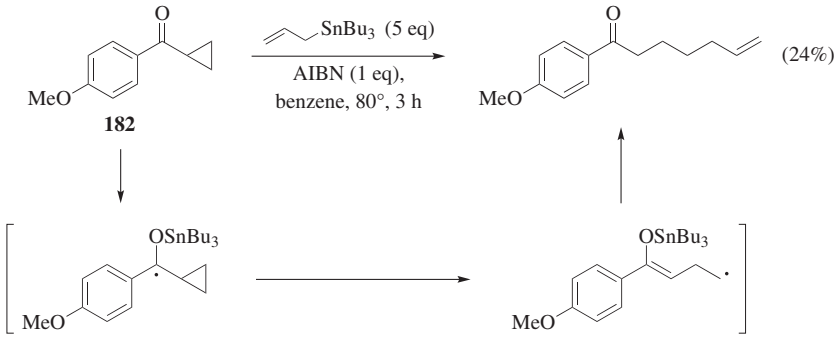
Scheme 184

When α,β-unsaturated ketones are used as substrates, the allylation reaction occurs at the β-position (Scheme 185).[271] Both cyclic and acyclic ketones are competent substrates, and additional substitution is tolerated at the α-carbon. Overall, this process is the equivalent of a Michael addition via a radical process.



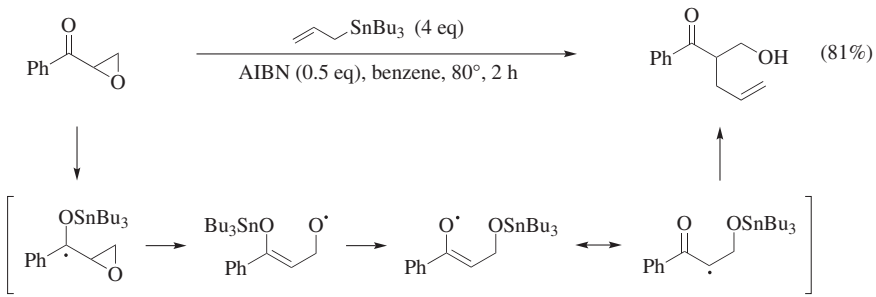
Scheme 185

Allylstannylation of cyclopropyl ketones occurs with ring opening to afford the γ-allylation product (Scheme 186).[272,273] The reaction of cyclopropyl ketone **182** begins with addition of tributylstannyl radical to the ketone oxygen. Rapid opening of the cyclopropyl ring is followed by addition of the resulting radical to allyltributylstannane. Hydrolysis of the stannyl enol ether furnishes the homologated ketone.



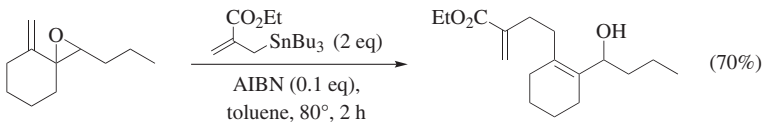
Scheme 186

α,β-Epoxy ketones also undergo ring-opening when subjected to allylstannylation conditions (Scheme 187).[274] In this case, however, the ring-opened alkoxy radical undergoes 1,5-stannyl migration to form an enol radical that is then allylated at the α-position.



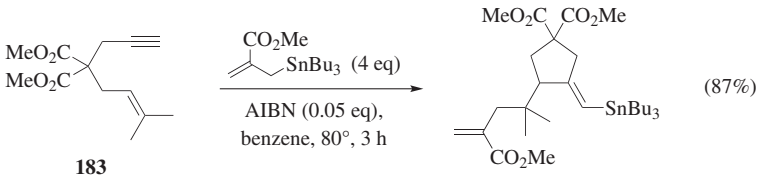
Scheme 187

A similar rearrangement occurs in the allylstannylation reactions of vinyl epoxides (Scheme 188):[275] a 1,5-stannyl migration generates an allylic carbon-centered radical that then undergoes allylation with the allylstannane. This reaction, however, requires an electron-withdrawing substituent on the allylstannane, since no product is obtained when allyltributylstannane and methallyltributylstannane are employed.



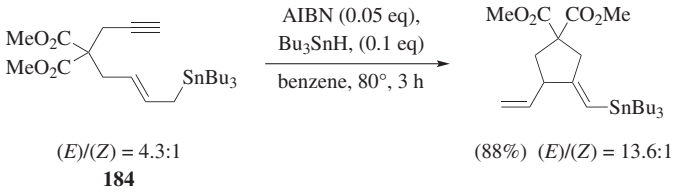
Scheme 188

With appropriate substrates, a cyclization reaction can be included in an allylstannylation reaction. For example, 1,6-enyne **183** reacts with 2-carbomethoxyallyltributylstannane in the presence of AIBN in benzene at 80° to form an allylstannylated five-membered-ring product in 87% yield (Scheme 189).[32] The use of allyl- or methallyltributylstannane affords the analogous products, albeit in low yields. With 2-carbomethoxyallyltributylstannane as the allylstannane source, a 1,7-enyne generates a six-membered-ring product, and ether- and amine-containing 1,6-enyne substrates provide tetrahydrofuran and pyrrolidine products, respectively.

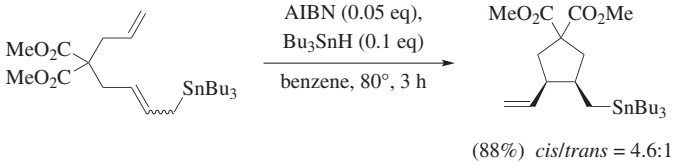


Scheme 189

Allylstannylation can be terminated by cyclization onto a pendant allylstannane. Heating substrate **184** ((*E*)/(*Z*) = 4.3:1) in benzene with catalytic amounts of both AIBN and tributyltin hydride gives the cyclopentane product in 88% yield as a 13.6:1 ratio of (*E*) and (*Z*) isomers (Scheme 190).[276] Tributyltin hydride is critical for this process since its omission leads to low yields. Under the same conditions, the homologous 1,7-enyne furnishes a six-membered-ring product, but in slightly lower yield (68%). The reaction is also successful with internal alkynes. When the alkyne has a methyl substituent, two regioisomeric products are formed in a 3.2:1 ratio because of the unselective addition of tributylstannyl radical to the alkyne in the first step. However, with a phenyl substituent, the initial addition of the tributylstannyl radical occurs exclusively at the alkyne carbon beta to the phenyl group to form a single product in 87% yield. Reactions of 1,6-dienes occur in excellent yields provided the alkene carbon to which the tributylstannyl radical initially adds is unsubstituted (Scheme 191).[276] In contrast, the reaction does not occur when C-1 is substituted or with a 1,7-diene substrate.



Scheme 190



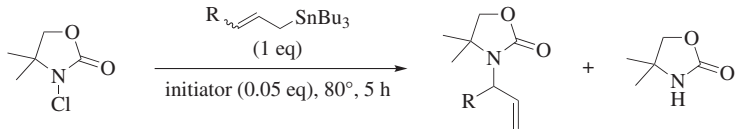
Scheme 191

Allylation Reactions of Heteroatom-Centered Radicals

Nitrogen, sulfur, selenium, phosphorus, and boron-centered radicals undergo efficient allylation with allylstannane reagents. The few examples of allylation reactions of nitrogen-centered radicals all involve nitrogen atoms that are substituted with electron-withdrawing groups. This result is not surprising because neutral aminyl radicals are known to be relatively unreactive toward addition to alkenes. The rates of intermolecular addition reactions are not known, but the rate of 5-*exo* cyclization of amidyl radicals is four-to-five orders of magnitude faster than the rate of 5-*exo* cyclization of aminyl radicals.[277]

Because hydrogen-atom abstraction reactions are competitive, significant amounts of reduction products are often obtained in reactions of amidyl radicals

with allylstannanes. For example, the treatment of *N*-chlorooxazolidinone **185** with allyltributylstannane at 80° in the presence of AIBN affords the allylation product **186** in only 25% yield along with 33% of the reduced amide **187** (Scheme 192).[278] The reaction of the same substrate with crotyltributylstannane favors the reduction product even more dramatically (9% allylation and 52% reduction).

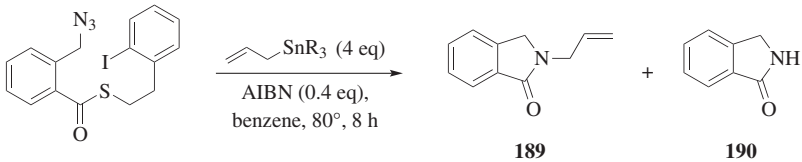


185 **186** **187**

		Yield (%)	
R	Initiator	**186**	**187**
H	AIBN	25	33
Me	$(PhCO_2)_2$	9	52

Scheme 192

Another means of generating amidyl radicals is by the addition of an acyl radical to an azide. For example, heating thioester **188** with an allylstannane and AIBN in benzene initially forms an aryl radical, which undergoes substitution at the sulfur atom (Scheme 193).[279] The resulting acyl radical undergoes a 5-*exo* cyclization onto the internal nitrogen atom of the azide, and an amidyl radical is formed by loss of dinitrogen. Allylation of the amidyl radical affords **189**; however, reduction competes with the allylation reaction, and isoindolinone (**190**) is isolated in significant quantities. Notably, the efficiency of the allylation is much higher with allyltriphenylstannane than with allyltributylstannane.



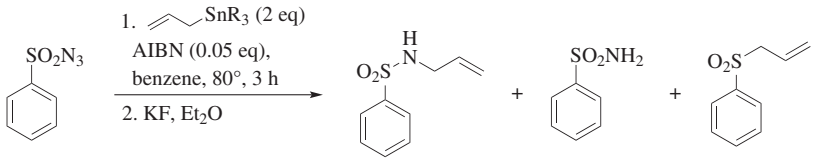
188 **189** **190**

	Yield (%)	
R	**189**	**190**
Bu	40	45
Ph	60	25

Scheme 193

The azide group can also be used as a precursor to sulfonamidyl radicals, which can then be allylated. For example, benzenesulfonyl azide reacts with an allylstannane in refluxing benzene in the presence of AIBN to furnish three different products: *N*-allylbenzenesulfonamide, benzenesulfonamide, and allyl phenyl sulfone

(Scheme 194).[280] In this reaction, the initial trialkylstannyl radical can add to either the internal or the terminal nitrogen atom of the azide. Addition to the internal nitrogen atom leads to loss of dinitrogen and formation of an *N*-stannylsulfonamidyl radical that can either add to the allylstannane or undergo a hydrogen-atom abstraction, yielding the two sulfonamide products after destannylative workup. The sulfone product results from addition of the initial stannyl radical to the terminal nitrogen, followed by loss of trialkylstannyl azide; the resulting sulfonyl radical is then *S*-allylated by the allylstannane. The distribution of the three products is dependent on the nature of the alkyl/aryl groups of the allylstannane. Triphenylstannyl is highly selective for addition to the internal nitrogen atom of the azide, trimethylstannyl is somewhat less selective, and tributylstannyl is the least discriminating and affords a significant amount of **193** (the result of addition to the terminal nitrogen atom). From the sulfonamidyl radical, allylation is favored with allyltriphenyl- and allyltrimethylstannane, while and hydrogen abstraction is the dominant pathway with allyltributylstannane. These results reflect differences in the rates of addition to the stannanes, but may also be a result of the fact that an intramolecular 1,5-hydrogen-atom abstraction is possible with a butyl substituent but not with methyl or phenyl. Benzenesulfonyl azides substituted at the 4-position with methyl, methoxy, and fluorine groups are tolerated, but a 4-nitro group greatly reduces the rate of reaction. Octanesulfonyl azide is less efficient in formation of the *N*-allylated product, and in the reaction with allyltriphenylstannane, delivers a 1.3:1 mixture of allylated sulfonamide to allylated sulfone.

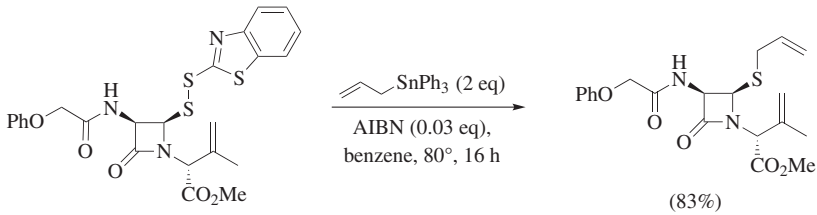


R	191/192/193
Me	81:7:12
Bu	6:64:30
Ph	91:4:5

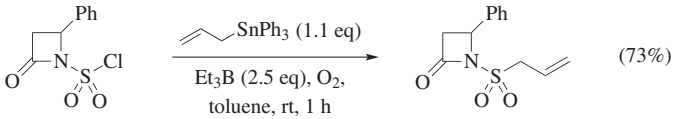
Scheme 194

Sulfur-centered radicals generated by more traditional means also undergo allylation. Irradiation of PhSSPh, $PhCH_2SSCH_2Ph$, $PhSO_2Cl$, and PhC(O)SSePh in the presence of allyltributylstannane afford the *S*-allylation products in good yields (76–86%).[140,281] The allylation of thiyl radicals from more complex substrates is similarly efficient (Scheme 195),[282,283] as is the allylation of *N*-substituted sulfonyl radicals (Scheme 196).[284] The latter substrates afford higher yields using electron-rich methallyltributylstannane than with the electron-poor 2-carbomethoxy-allyltributylstannane, suggesting that such radicals are electrophilic in nature. Diphenyl diselenide is allylated by allyltributylstannane under photolytic conditions

with efficiency similar to that of diphenyl disulfide (56% versus 63% after four hours), but diphenyl ditelluride reacts extremely slowly (<2% after 12 hours).[285]

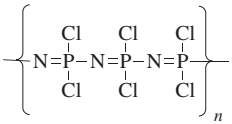


Scheme 195



Scheme 196

Phosphorus-centered radicals of several different types can be allylated with allyltributyl- or allyltrimethylstannane. Photolysis of PCl_3, $P(O)Cl_3$, $P(O)Ph_2Cl$, $Cl_2PN(i\text{-}Pr)_2$, and Cl_2PCHCl_2 in the presence of an equimolar amount of an allylstannane affords the *P*-allylation products in 75–95% yields.[286] In the case of Cl_2PCHCl_2, allylation occurs only on the phosphorus atom. The same study reports that $PhBCl_2$ is allylated under identical conditions in 90% yield, and this is the only report of an allylation of a boron-centered radical. Photolysis of poly(dichlorophosphazene) **194** (Figure 39) with allyltrimethylstannane (0.75 equivalents per chlorine atom) provides a product in which 8% of the phosphorus atoms are diallylated, 26% are monoallylated, and the remaining 66% are unallylated.[287] Using higher concentrations of the allylstannane leads to cross-linking of the polymer.



194

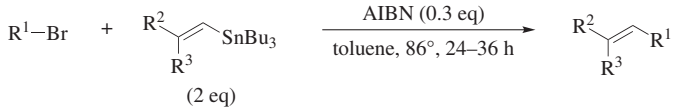
Figure 39. The structure of poly(dichlorophosphazene) **194**.

Vinylation Reactions

Radical vinylation with stannane reagents has not been as widely explored as allylation, but the reaction is successful with a variety of substrates. An

electron-withdrawing group is necessary at the β-carbon of the vinylstannane both to increase the rate of addition to the double bond and to direct addition to the tin-substituted α-carbon.[62,288] Most examples of this vinylation reaction use simple alkyl radicals, but α-ester,[288] α-keto,[71] α-amino,[289,290] α-alkoxy,[134] and captodative[291] radicals have also been employed.

The most common vinyl stannanes used in radical vinylations are β-(tributylstannyl)styrene and ethyl (or methyl) β-(tributylstannyl)acrylate. These compounds react with primary, secondary, and tertiary alkyl bromides to form vinylated products in moderate yields, albeit with generally excellent (*E*)/(*Z*) selectivities (Scheme 197).[288]



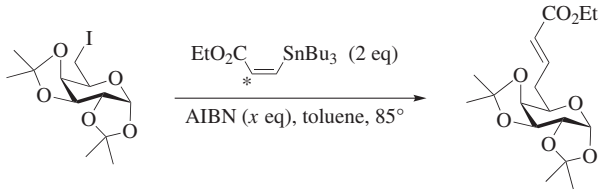
	R^2	R^3
195	Ph	H
196	H	EtO_2C

R^1	Stannane	Yield (%)	(*E*)/(*Z*)
$HOCH_2CH_2$	**195**	32	>99:1
$AcOCH_2CH_2$	**195**	41	>99:1
$AcOCH_2CH_2$	**196**	43	>99:1
$(EtO)_2CHCH_2$	**195**	52	>99:1
$(EtO)_2CHCH_2$	**196**	52	>99:1
c-C_6H_{11}	**195**	51	>99:1
c-C_6H_{11}	**196**	57	3.4:1
1-adamantyl	**195**	42	>99:1
1-adamantyl	**196**	56	>99:1

Scheme 197

Reactions favor the formation of the (*E*) isomer, even when the starting material is a (*Z*)-configured vinyl stannane, although the degree of selectivity can depend on the reaction conditions and on the nature of both the substrate and the vinyl stannane. As illustrated in Scheme 197, (*E*)-β-(tributylstannyl)styrene (**195**) and (*Z*)-β-(tributylstannyl)acrylate **196** both react with a variety of alkyl bromides (primary, secondary, and tertiary) to deliver the alkene product with excellent (*E*)-selectivity. Among the examples in Scheme 197, only the reaction of cyclohexyl bromide with (*Z*)-β-(tributylstannyl)acrylate **196** gives a measurable amount of the (*Z*)-configured product. While the reactions of the (*E*) stannyl styrene (**195**) shown in Scheme 197 afford the (*E*)-configured products exclusively, the (*Z*) isomer may also be formed as a minor product under different reaction conditions. For example, the photolysis of methyl bromoacetate with **195** in benzene at 35° furnishes a 5:1 mixture of the (*E*)/(*Z*) isomers.[292] In cases where a direct comparison can be made, selectivity for the (*E*) isomer of the product is highest when starting with an (*E*) vinyl stannane, but the reaction is faster and yields are slightly higher with the (*Z*)-configured substrate (Scheme 198).[293]

Other simple vinyl stannanes have also been used in radical vinylations, including those substituted with phenylsulfone (**197**)[62,294] and diphenylphosphine oxide (**198**)[294] groups, as well as β-diphenyl-substituted vinyl stannane **199**



*Config	x	Time (d)	Yield (%)	(E)/(Z)
(Z)	0.48	1.5	94	4.2:1
(E)	0.96	3	79	>99:1

Scheme 198

(Figure 40).[62,292] Cyclic vinyl stannanes also undergo radical vinylation reactions, and cyclobutenedione **200** reacts with alkyl halides, albeit the yields are only moderate with primary iodides (39–56%) and are poor with a secondary iodide (21%) and a primary bromide (7%).[295] Lactone **201**, with an exocyclic vinylstannane moiety, reacts with aryl iodides in moderate yields (44–58%).[296]

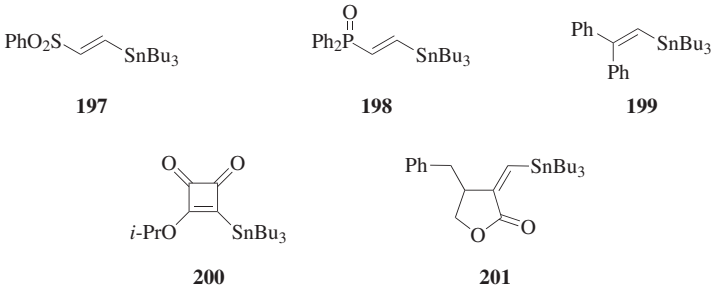
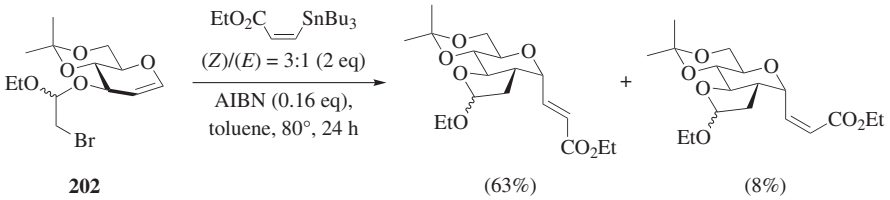


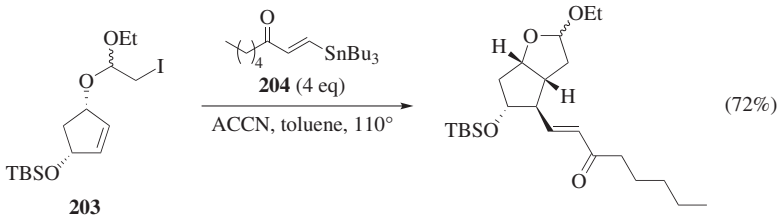
Figure 40. The structures of vinylstannanes that have been used in radical vinylation reactions.

The rate of radical addition to substituted vinyl stannanes has not been measured quantitatively, but the rate of addition of cyclohexyl radical to (E)-β-(tributylstannyl)styrene is known to be more than ten times faster than the rate of addition to allyltributylstannane.[62] Vinylation rates are slow enough that the 5-hexenyl radical, which is generated in the presence of (E)-β-(tributylstannyl)styrene by the photolysis of 5-hexenyl mercuric chloride in benzene at 35° (concentration = 0.1 M), affords only products of vinylation after 5-*exo* cyclization.[62] This cyclization/vinylation sequence has been used for synthetic purposes, and in one example, substrate **202** undergoes a Ueno–Stork cyclization followed by trapping with β-(tributylstannyl)acrylate to exclusively form the β-*C*-glycoside product, albeit as a mixture of (E) and (Z) products that are isolated in 63% and 8% yield, respectively (Scheme 199).[297]



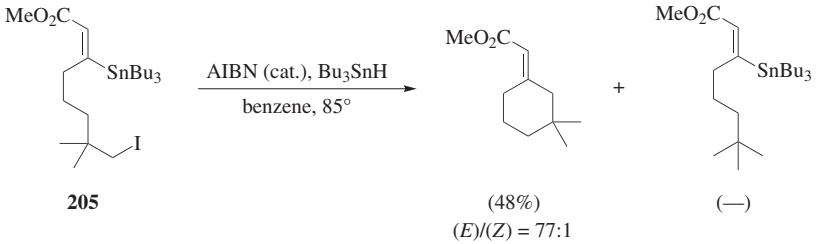
Scheme 199

Similarly, β-stannyl enone **204** can be used to trap a radical generated by the Ueno–Stork cyclization of iodoalkene **203** to form an advanced precursor to prostaglandin $F_{2\alpha}$ (Scheme 200).[298] Although the allylation of substrate **203** at 80° using AIBN as the initiator affords the desired product in only 43% yield, switching the initiator to ACCN and performing the reaction at 110° provides the desired (*E*)-configured product in 72% yield.



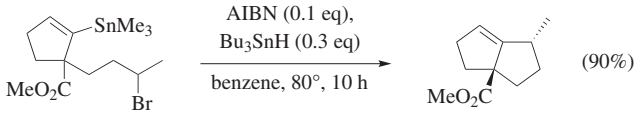
Scheme 200

Direct cyclization onto a vinylstannane is also possible: treatment of the neopentyl iodide **205** with tributyltin hydride and AIBN in refluxing benzene initiates a 6-*exo* cyclization onto the (*E*)-vinylstannane moiety to generate a β-stannyl radical. Fragmentation with loss of tributylstannyl radical affords the cyclized product in 48% yield along with an unspecified amount of the direct reduction of the iodide **205** (Scheme 201).[299] From the (*E*)-configured starting material, the product is obtained as a 77:1 mixture of (*E*) and (*Z*) isomers. The cyclization is stereospecific, given that the reaction of the corresponding (*Z*) vinylstannane affords a 14:1 mixture of the product, favoring the (*Z*) isomer, in 35% yield.



Scheme 201

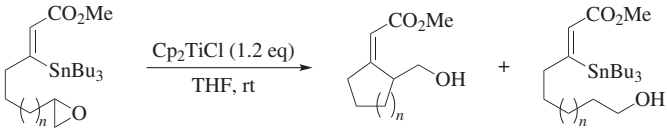
For intramolecular processes, the presence of an electron-withdrawing group on the vinylstannane is not necessary for an efficient reaction. Bromide **206**, which contains a vinylstannane, reacts with a catalytic amount of tributyltin hydride and AIBN in benzene at 80° to afford the cyclized product as a single diastereomer in excellent yield (Scheme 202).[300]



206 dr 1:1

Scheme 202

The size of the ring being formed can affect radical cyclizations onto vinylstannanes. For example, epoxy vinylstannane **207** undergoes homolytic cleavage of the secondary carbon–oxygen bond of the epoxide with a titanium(III) reagent (Scheme 203).[301] 5-*Exo* cyclization of the resulting radical onto the vinylstannane provides the product **209** in 83% yield with retention of the alkene stereochemistry. Under identical conditions, the homologous epoxy vinylstannane **208** generates only product **210**, which results from a homolytic epoxide ring opening followed by reduction; no products resulting from 6-*exo* cyclization are observed. Performing the reaction at reflux in benzene leads to deoxygenation of the epoxide to form a terminal alkene.



207 $n = 1$
208 $n = 2$

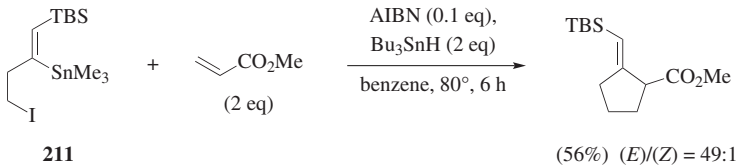
209 **210**

		209		
	n	Yield (%)	(Z)/(E)	**210** Yield (%)
207	1	83	>98:2	0
208	2	0	—	—

Scheme 203

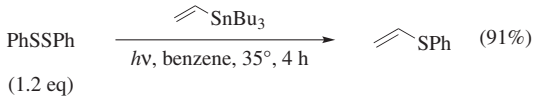
Analogous to the two-component annulation reactions of allylstannanes (cf. Scheme 179), vinylstannanes that contain a radical precursor can react with an alkene in an annulation process that concludes with cyclization onto the vinylstannane. Iodovinylstannane **211** reacts with methyl acrylate in the presence of AIBN and an excess of tributyltin hydride to form the vinylcyclopentane product in 56% yield (Scheme 204).[302] The reaction of the alkyl iodide **211** with methyl vinyl ketone, phenyl vinyl sulfone, acrylonitrile, and *N*-phenylmaleimide all occur with similar yields and selectivities for the (*E*)-alkene product. In principle, only

a catalytic amount of tributyltin hydride is required, but reactions conducted with less than an equivalent afford low yields. Unlike the transformations involving cyclizations onto vinylstannanes discussed above, these reactions proceed with inversion of the configuration of the alkene: the steric interaction of the bulky silyl group with the ester substituent is thought to inhibit rotation of the cyclized radical into the conformation that leads to the (*Z*) isomer of the vinyl silane. An analogue of **211**, which lacks the silyl group, only undergoes a successful annulation reaction with *N*-phenylmaleimide; none of the desired annulated product is obtained using methyl acrylate or phenyl vinyl sulfone. In these latter two unsuccessful reactions it is suspected that the radical adduct that is formed by addition to the alkene preferentially undergoes a 6-*endo* cyclization.



Scheme 204

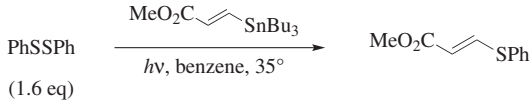
Vinylations of sulfur-, selenium-, and phosphorus-centered radicals are known,[303] in which the most well-studied are sulfur-centered radicals; reactions of phenylthiyl, benzylthiyl, phenylsulfonyl,[303] and phenylcarbonothiyl (PhC(O)S•)[281] have all been reported. The presence of an electron-withdrawing group at the β-carbon of the vinylstannane is not required for heteroatom addition, as is the case for the vinylation of alkyl radicals. For example, photolysis of diphenyl disulfide with vinyltributylstannane in benzene affords phenyl vinyl sulfide in 91% yield (Scheme 205).[303]



Scheme 205

Heteroatom vinylations are selective for formation of the (*E*) isomers, although in this case the degree of selectivity is dependent on the reaction time since the products can isomerize by addition–elimination of a second phenylthiyl radical. For example, the irradiation of diphenyl disulfide in benzene with the (*E*) isomer of methyl β-(tributylstannyl)acrylate for five minutes provides an 8.9:1 mixture of the (*E*)/(*Z*) products. However, if the photolysis is allowed to proceed for eight hours, the product is isolated as a 3.8:1 mixture of (*E*)/(*Z*) isomers (Scheme 206).[20]

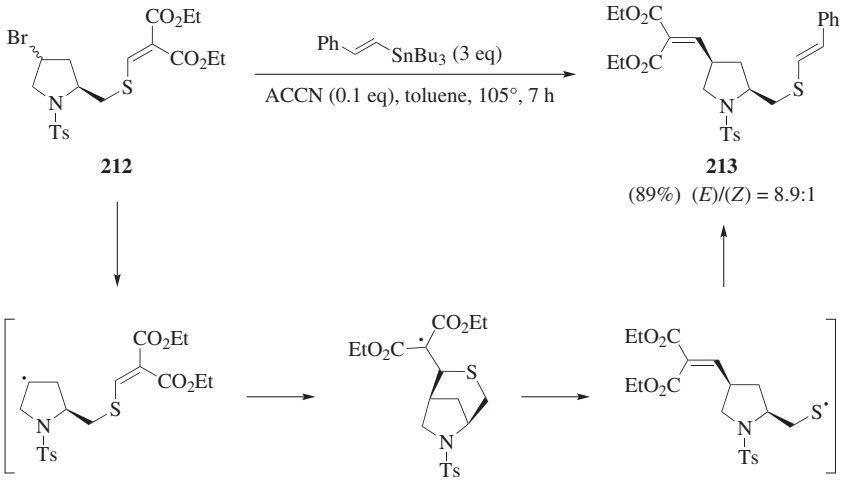
The vinylation of a thiyl radical can be used as the terminating step in a radical-cascade process. For example, the bromide **212** reacts with β-(tributylstannyl)styrene in toluene at 105° in the presence of ACCN to form vinyl sulfide **213** in 89% yield as an 8.9:1 mixture of alkene (*E*)/(*Z*) isomers



Time	Yield (%)	(*E*)/(*Z*)
5 min	—	8.9:1
8 h	79	3.8:1

Scheme 206

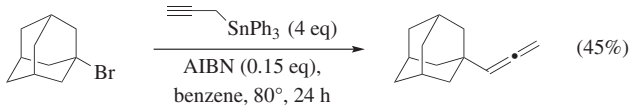
(Scheme 207).[304] In this transformation, abstraction of the bromine atom produces a radical that undergoes a 6-*exo* addition onto the diester-substituted alkene, which occurs to give the *cis* ring fusion exclusively. The resulting radical undergoes β-scission to form the thiyl radical that then reacts with the stannylstyrene to deliver product **213**.



Scheme 207

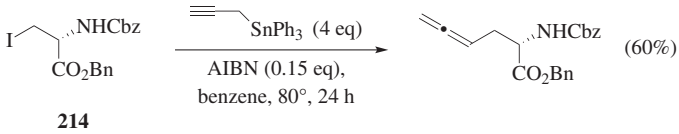
Allenylation Reactions

The reaction of a radical with propargyltriphenylstannane permits the installation of an allene group via the addition of the radical to the terminus of the alkyne followed by β-scission of the triphenylstannyl group. The only simple alkyl radical that has been allenylated is the 1-adamantyl radical, which reacts with four equivalents of propargyltriphenylstannane in refluxing benzene for 24 hours to form the product in 45% yield (Scheme 208).[305] Allenylation reactions occur at slower rates than the corresponding allylation reactions and, where direct comparisons can be made, they afford significantly lower yields. For example, the allylation reaction analogous to the allenylation shown in Scheme 208 provides an 88% yield of product after 12 hours at reflux with two equivalents of the allylstannane.[44]



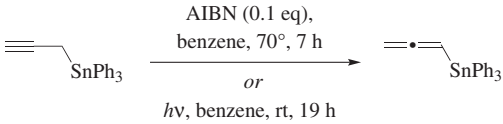
Scheme 208

Few additional examples of allenylation reactions are known, but based on the reactions that have been reported, the substrate scope is reasonably broad. Allenylations have been performed using chloroform and carbon tetrachloride,[140] as well as using primary, secondary, and tertiary radicals bearing functional groups that include esters, amides, ketones, alcohols, and silyl ethers. For example, protected amino acid derivative **214** is allenylated in 60% yield upon reaction with propargyltriphenylstannane in the presence of AIBN in refluxing benzene (Scheme 209).[305]



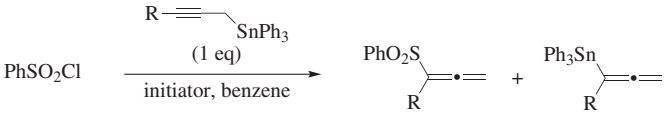
Scheme 209

Propargyltriphenylstannane undergoes rearrangement to the more stable 1,2-propadienyltriphenylstannane under typical photochemical or thermal allenylation reaction conditions (Scheme 210).[140] This side reaction necessitates the use of excess propargylstannane, but the propadienylstannane is much less reactive towards radicals, so competing addition to form propargylated byproducts is usually not problematic.



Scheme 210

2-Butynyltriphenylstannane does not undergo the analogous alkyne-to-allene rearrangement, and the reaction with phenylsulfonyl radical delivers the *S*-allenylated product in 42% yield (Scheme 211).[140] In contrast, the same reaction with



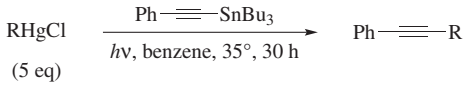
R	Initiator	Temp (°)	Time (h)	Yield (%)	
Me	*hν*	35	35	42	0
H	AIBN (0.1 eq)	70	8	36	36

Scheme 211

propargyltriphenylstannane generates a mixture of the *S*-allenylated product (36%) and 1,2-propadienyltriphenylstannane (36%). To date, reactions of carbon-centered radicals with 2-butynyltriphenylstannane have not been reported.

Alkynylation and Propargylation Reactions

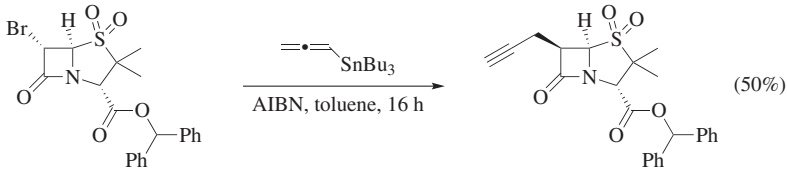
Alkylmercuric chlorides react with 2-phenylethynyltriphenylstannane to form alkynylated products in a process analogous to a vinylation reaction (Scheme 212).[62,306] The rate of addition of cyclohexyl radical to 2-phenylethynyltriphenylstannane is 3.5-fold slower than the rate of addition to the corresponding vinyl compound. The only other radical that has been alkynylated, besides those shown in Scheme 212, is the phenylthiyl radical, which reacts to form the product in 60% yield when generated by photolysis of diphenyl disulfide in benzene.[303]



R	Yield (%)
n-Bu	13
t-Bu	61
c-C_6H_{11}	43

Scheme 212

As mentioned above, propargyltriphenylstannane reacts much faster with alkyl radicals than the 1,2-propadienyltriphenylstannane that forms upon rearrangement of the propargylstannane. However, if only 1,2-propadienyltriphenylstannane is present, it can react with an alkyl radical to afford a propargylated product (Scheme 213).[307]



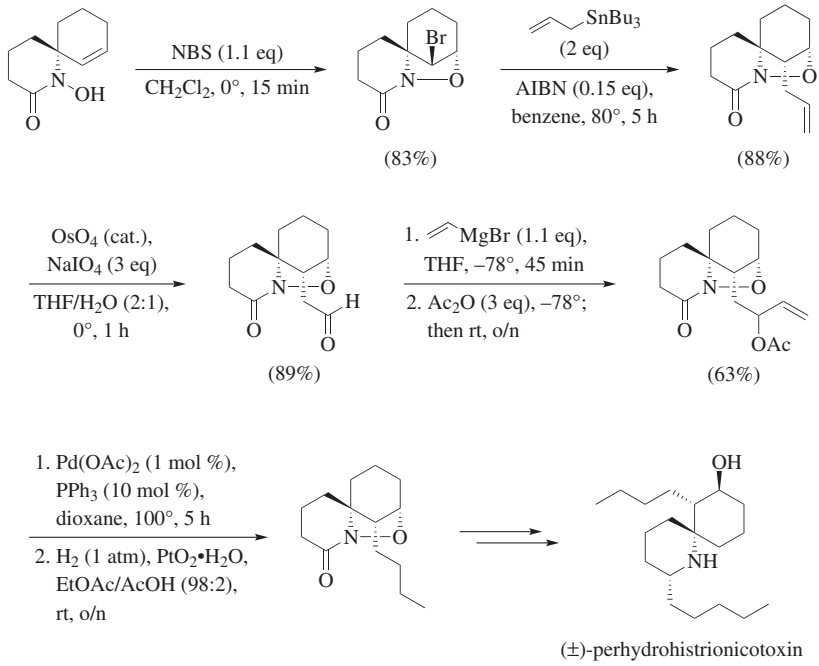
Scheme 213

APPLICATIONS TO SYNTHESIS

As detailed above, many strategies have been developed that utilize allyl- and vinylstannanes in radical processes. The following synthetic examples have been chosen to illustrate the range of strategies that can be applied for synthesis. In many cases, the installation of the radical precursor is a critical part of the synthetic route and has therefore been highlighted in the discussion. Furthermore, these examples demonstrate the variety of ways that the allyl group has been manipulated after the radical-based installation.

(±)-Perhydrohistrionicotoxin

Direct allylation is used as a key step in a synthesis of (±)-perhydrohistrionicotoxin (Scheme 214).[308] The requisite radical precursor is created in an intramolecular bromo ether-forming reaction that also sets the stereochemistry for a key hydroxyl group. Reaction of the bromo ether with allyltributylstannane affords a single stereoisomer of the allylated product in 88% yield. The allyl group is then converted to the necessary *n*-butyl group by oxidative cleavage to the aldehyde, followed by addition of vinylmagnesium bromide and quenching with acetic anhydride. The palladium-catalyzed elimination of acetic acid generates a diene, and subsequent hydrogenation delivers the *n*-butyl group. Although the allylation occurs with complete stereocontrol, the allyl group is placed on the wrong face, necessitating a three-step epimerization of the *n*-butyl group, after reduction of the nitrogen–oxygen bond, to complete a formal synthesis of (±)-perhydrohistrionicotoxin.

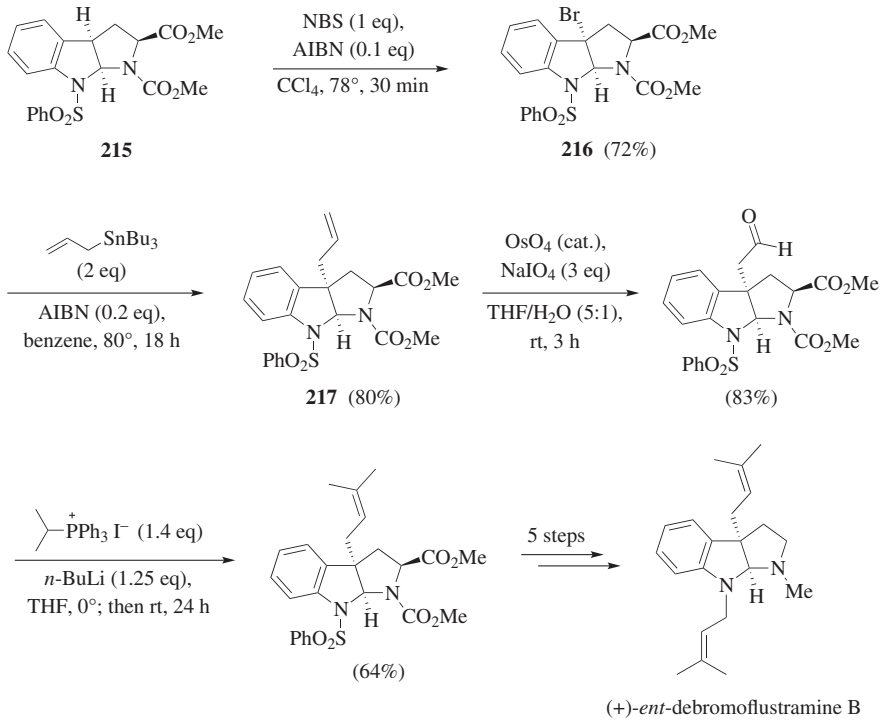


Scheme 214

(+)-*ent*-Debromoflustramine B

Allylation is used to introduce a prenyl group at a quaternary center in a synthesis of (+)-*ent*-debromoflustramine B (Scheme 215).[309] The requisite bromide radical precursor **216** is formed by radical halogenation of intermediate **215** with *N*-bromosuccinimide, and the subsequent radical allylation occurs with complete stereochemical control to give product **217** in 80% yield. The allyl group is converted

to a prenyl group by oxidative cleavage and Wittig olefination of the resulting aldehyde. Attempts at introducing the prenyl group directly from bromide **216** using organometallic reagents were unsuccessful. Alternatively, the addition of the radical derived from bromide **216** to either methyl vinyl ketone or methyl acrylate (mediated by tributyltin hydride) affords the expected products but in lower yields than that obtained for the allylation reaction. Allylation is also used to introduce a prenyl group in a synthesis of garsubellin A.[310] In this case, the allyl group is converted to a prenyl group in a single step by a cross-metathesis reaction.

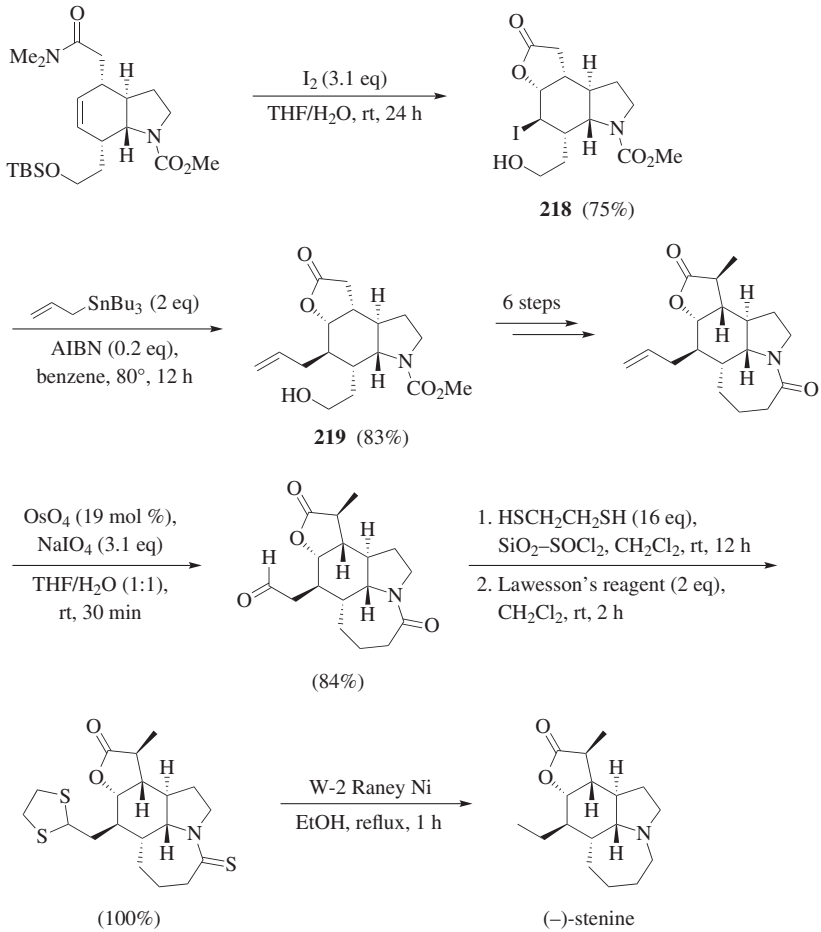


Scheme 215

(−)-Stenine and (−)-Tuberostemonine

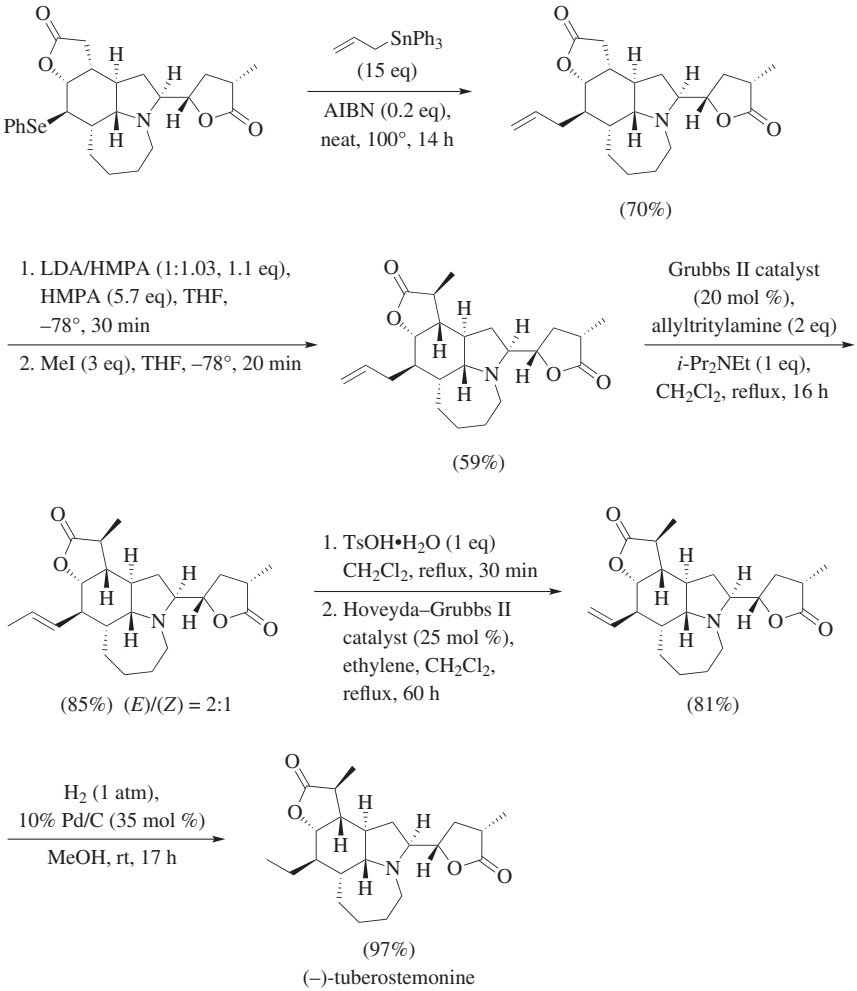
Multiple syntheses of stenine—in both racemic and optically pure form—employ a late-stage radical allylation to introduce a substituent that ultimately becomes an ethyl group in the alkaloid.[311–317] In each case, an iodolactonization generates a lactone ring and introduces an iodide radical precursor (Scheme 216).[311] Refluxing the iodide **218** with allyltributylstannane in the presence of AIBN provides a single diastereomer of the allylated product **219** in 83% yield. After methylation alpha to the lactone carbonyl and a series of reactions to create the seven-membered ring lactam, the allyl group is then converted to an ethyl group. In one approach, the allyl group is cleaved oxidatively, and the resulting aldehyde is converted to a dithioacetal

that is reduced with Raney nickel with concomitant reduction of a thioamide to a tertiary amine.[311] An alternative approach for converting the allyl group to an ethyl group involves oxidative cleavage of the alkene, followed by reduction to the alcohol, Grieco elimination via the corresponding selenide, and then catalytic hydrogenation of the vinyl group.[312]



Scheme 216

A similar sequence is used to introduce an ethyl group in the synthesis of the related but more complex natural product (–)-tuberostemonine (Scheme 217).[120,318] In this case, the allyl group cannot be converted to the ethyl group using either of the conditions described above because of complications with the oxidative cleavage. Instead, isomerization of the allyl double bond is followed by an ethylene cross-metathesis to afford a vinyl group that is then reduced by catalytic hydrogenation.

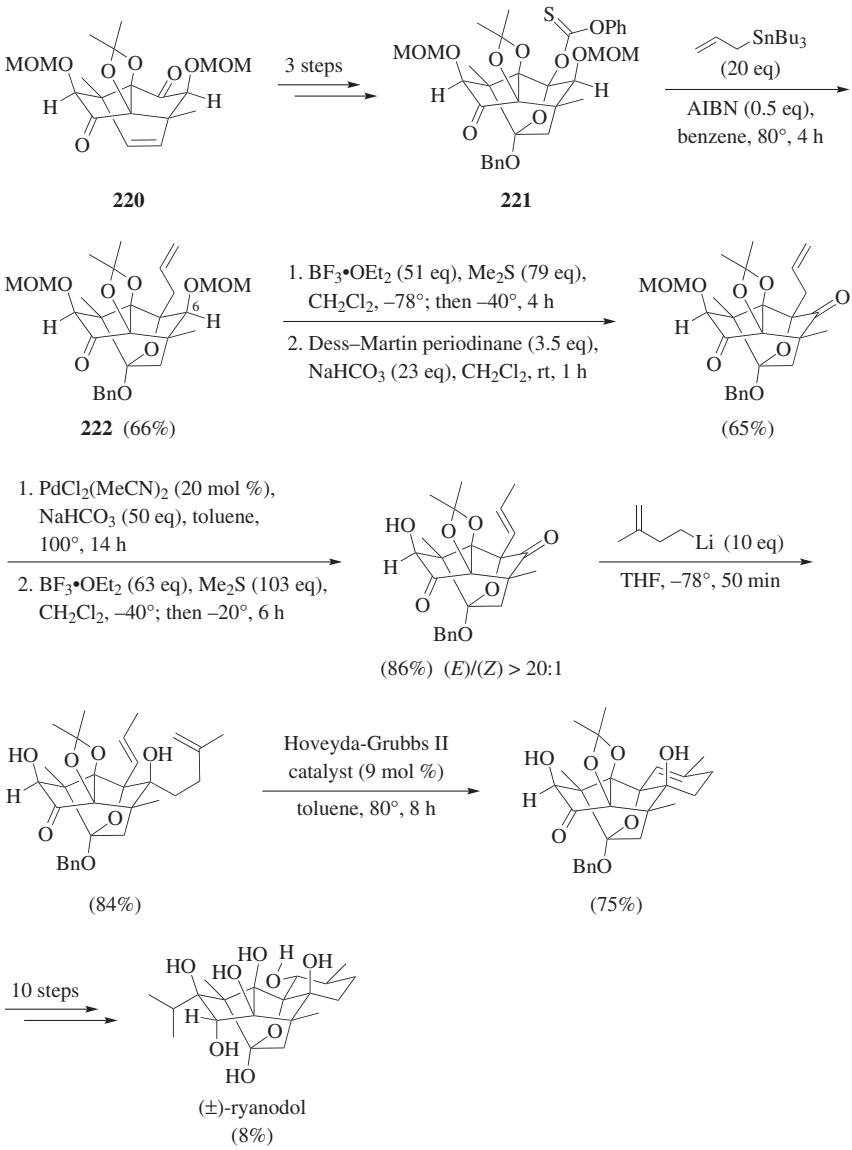


Scheme 217

(±)-Ryanodol

Direct allylation is used to introduce a key bond at a congested, tetrasubstituted center in a synthesis of the highly functionalized natural product ryanodol in racemic form (Scheme 218).[319] The symmetrical diketone **220** is converted to the thiocarbonate radical precursor **221** in three steps, and this intermediate undergoes allylation via an α-alkoxy bridgehead radical to generate the desired stereoisomer **222** exclusively. Introduction of the allyl group by Grignard addition to the symmetrical diketone **220** results in addition to the wrong face of the molecule.[320] From intermediate **222**, the allyl group is used to construct the final ring of ryanodol. The MOM ether protecting group at C-6 is cleaved, and the resulting alcohol is

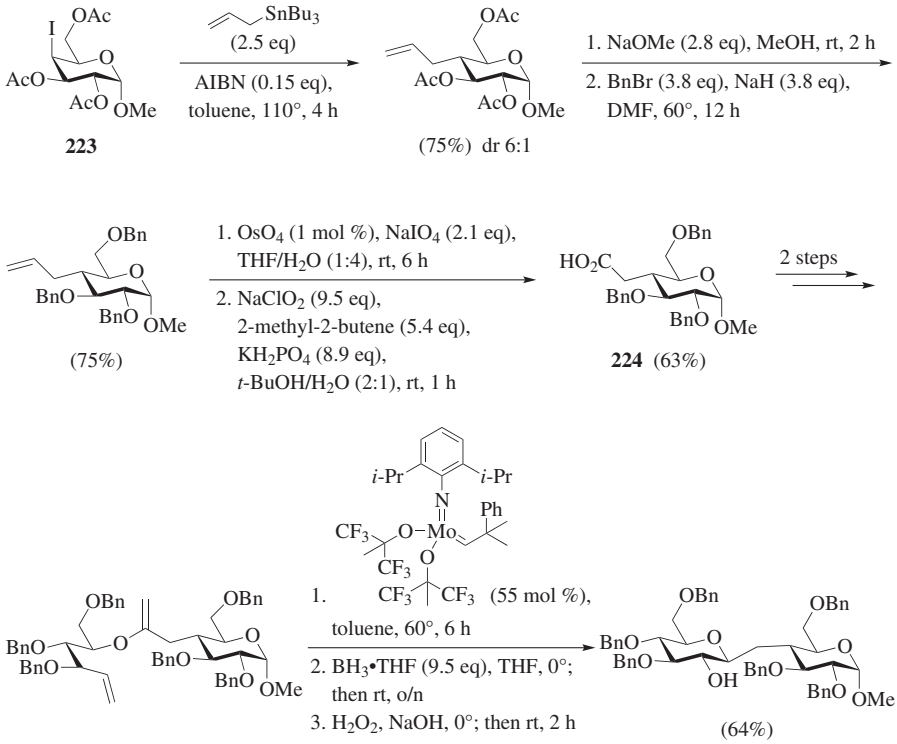
oxidized to the ketone. The terminal double bond of the allyl group then is isomerized using $PdCl_2(MeCN)_2$, providing the corresponding internal alkene. Addition of (3-methylbut-3-en-1-yl)lithium to the C-6 ketone installs an alkene-containing substituent at C-6 that is used for ring-closing metathesis using the second generation Hoveyda–Grubbs catalyst. The synthesis of ryanodol is completed in an additional 10 steps that have a combined yield of 8%.



Scheme 218

Carbon-Linked Disaccharides

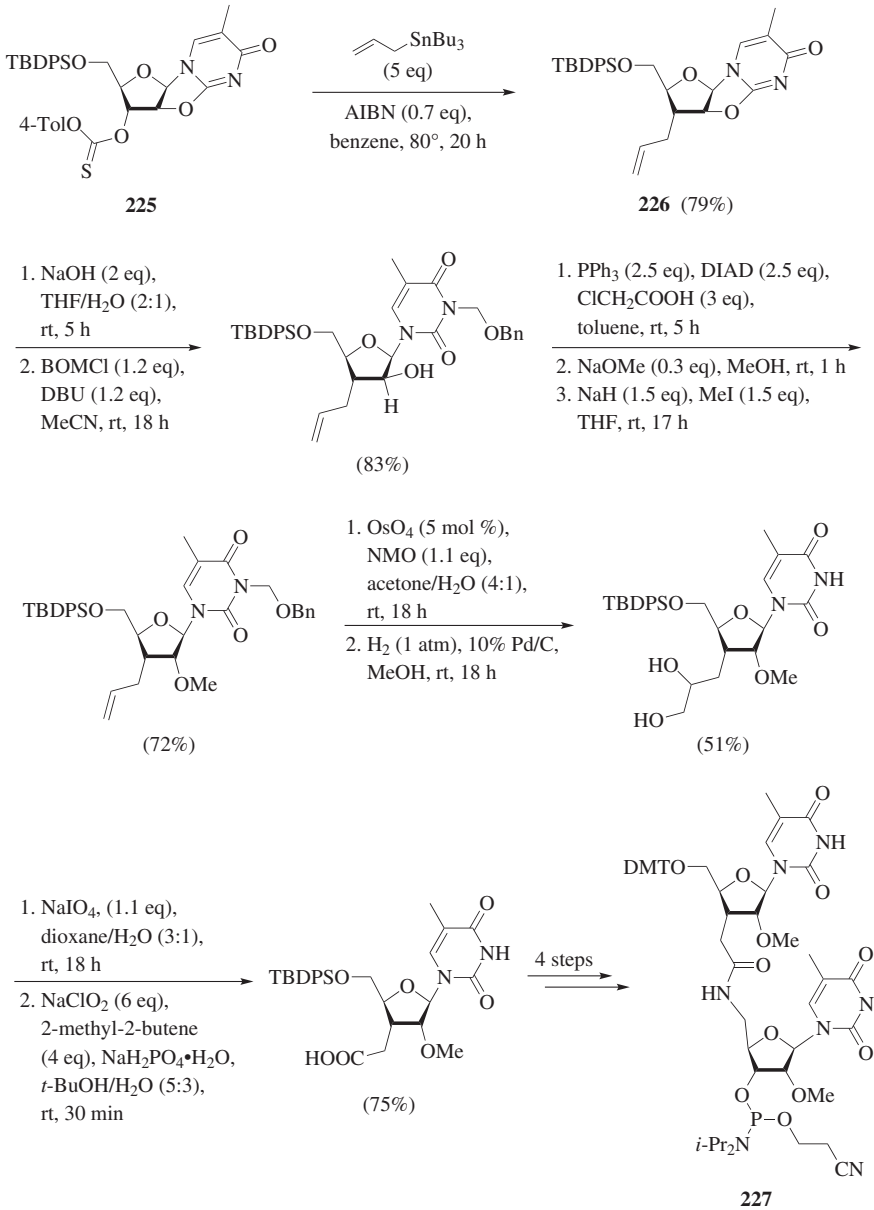
Carbohydrates have frequently been used as substrates for radical allylation reactions with allylstannane reagents. Allylation has generally been successful at every position on pyranose and furanose ring systems, including numerous examples of reactions at the anomeric position. In one interesting application, a radical allylation enables the preparation of carbon-linked disaccharides (Scheme 219).[321,322] Galactose-derived iodide **223** reacts with allyltributylstannane in refluxing toluene to form a 6:1 mixture of isomers of the allylated product in 75% overall yield, favoring the equatorial isomer. After replacing the acetyl protecting groups with benzyl groups, the allyl group is oxidatively cleaved to the corresponding aldehyde. The mixture of isomers is separated, and the aldehyde is further oxidized to form carboxylic acid **224**. Coupling with a substituted 5-hexen-2-ol generates an ester, and the carbonyl group is converted to a methylene group that undergoes ring-closing metathesis to form the second ring. Hydroboration–oxidation of the cycloalkene delivers the final carbon-linked disaccharide. A similar sequence of reactions can be used to prepare disaccharides linked through C-2 and C-3 and can also be used to construct trisaccharides containing two different carbon linkages.[323]



Scheme 219

Amide-Linked Dinucleotides

The sugar backbone of nucleosides can be modified using radical allylation and vinylation reactions. Among the applications of this chemistry is an approach to making amide-linked dinucleotides (Scheme 220).[324] Radical allylation of the *O*-aryloxythiocarbonyl derivative **225** (which is prepared from 2,2′-anhydrothymidine)

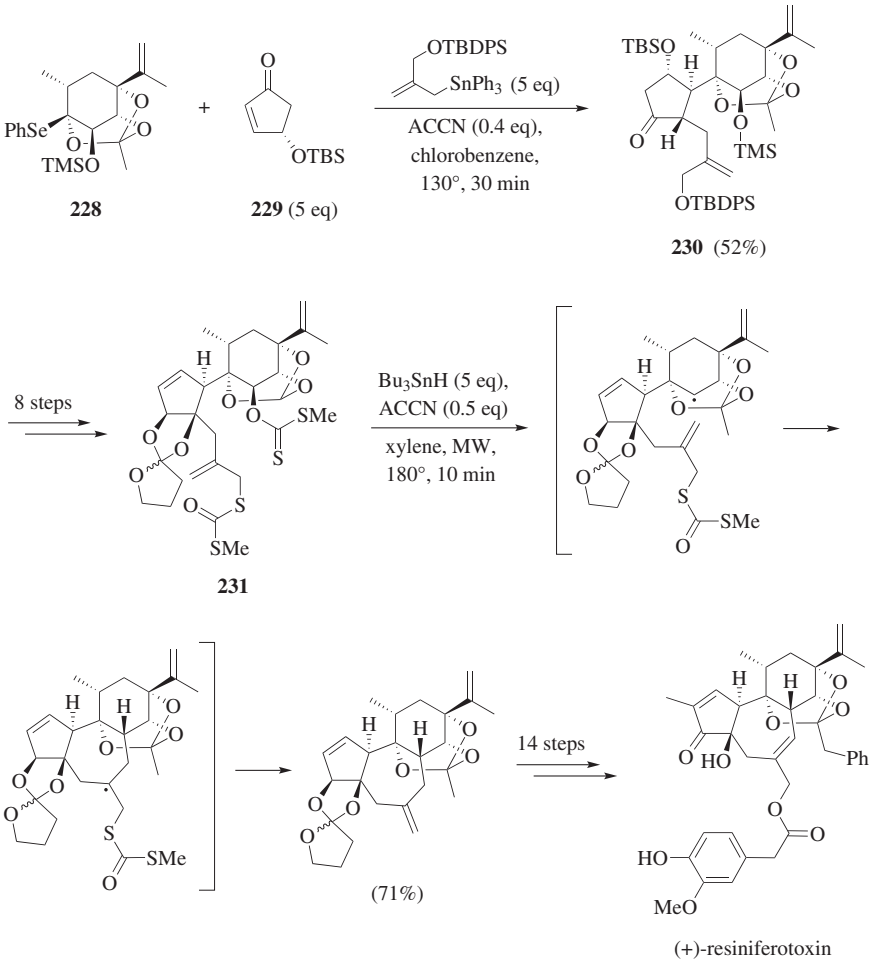


Scheme 220

affords product **226** in good yield, with allylation occurring exclusively on the α-face. After opening the anhydro ring, protecting the thymidine nitrogen, and inverting and protecting the exposed C-2 hydroxyl group, the allyl group is cleaved to the carboxylic acid. This acid is then coupled to a second nucleoside containing an amino group at the C-5 position, followed by functional-group interconversion to create a dimer, **227**, that is suitable for solid-phase oligonucleotide synthesis. Oligonucleotides that incorporate these amide-linked dinucleotides are less prone to cleavage by endo- and exonucleases, and duplexes formed with complementary RNA strands have greater thermodynamic stability than wild-type oligonucleotides.

(+)-Resiniferatoxin

The construction of the core skeleton of (+)-resiniferatoxin illustrates the power of three-component radical-addition–allylation processes in synthesis (Scheme 221).[325]



Scheme 221

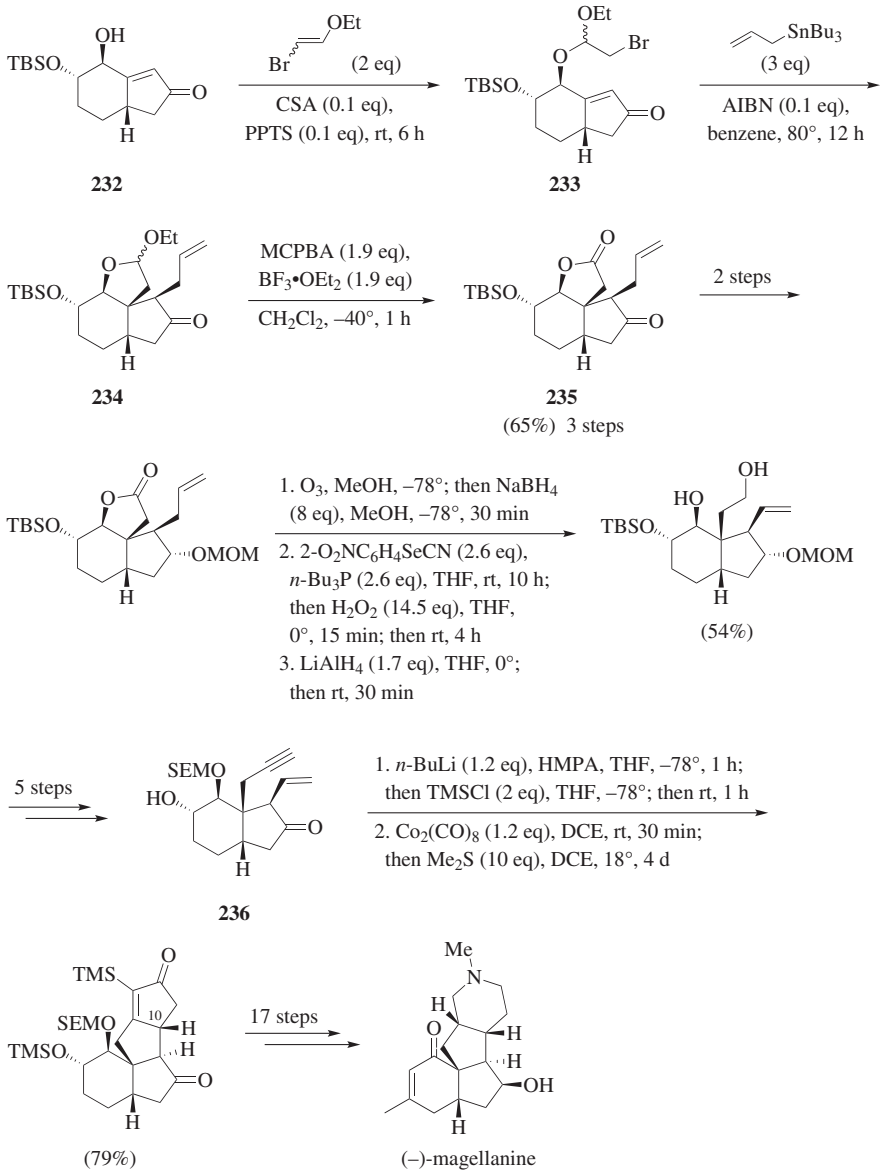
The reaction of selenide **228** with cyclopentenone **229** and a substituted allylstannane provides the addition–allylation product **230** in 52% yield. The tandem radical reaction creates two new carbon–carbon bonds in a highly complex and congested environment with control of the stereochemistry at three newly created stereocenters and sets the stage for a second key radical step. To access the desired tetracyclic framework, an eight-step sequence converts the three-component coupling product to the xanthate radical precursor to **231**. The radical formed by reaction of **231** with tributyltin hydride (in the presence of initiator ACCN) undergoes a 7-*endo* cyclization onto the alkene that was created in the tandem radical addition–allylation. Subsequent β-scission of the dithiocarbonate group from the cyclized radical generates an exocyclic methylene group on the seven-membered ring, affording the product in 71% yield. This compound is elaborated to (+)-resiniferatoxin in 14 additional steps.

(−)-Magellanine

A reaction involving a radical cyclization and subsequent trapping with allyltributylstannane is central to a synthesis of (–)-magellanine (Scheme 222).[326] The first of two Pauson–Khand reactions is followed by a selective silyl ether deprotection to generate the first key intermediate, bicyclic unsaturated ketone **232**. Treatment with 1-bromo-2-ethoxyethylene furnishes α-bromo acetal **233**, which undergoes a Ueno–Stork reaction to afford **234** after the initial cyclized radical is trapped with allyltributylstannane. This process creates two new stereocenters, including a quaternary center at the ring junction; attempts to install this quaternary stereocenter by a Michael addition to intermediate **232** were unsuccessful. The acetal of **234** is oxidized to γ-lactone **235** in an overall yield of 65% for the three steps from ketone **232**. The allyl group is then converted to a vinyl group by a sequence involving ozonolysis, reduction of the resulting aldehyde, and elimination of the alcohol by the Grieco method. After reduction of the lactone, the product of this sequence is isolated in 54% yield, and five additional steps generate compound **236**. Trimethylsilylation of the alkyne is followed by a second Pauson–Khand reaction to form the alkaloid C ring, and further elaboration delivers (–)-magellanine.

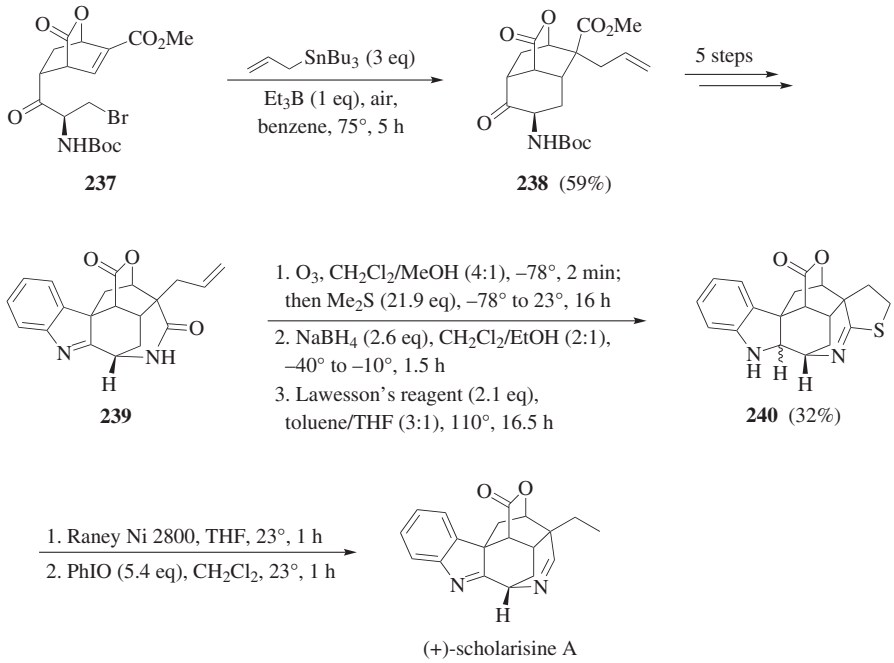
(+)-Scholarisine A

A cyclization/allylation sequence is a key step in a particularly efficient synthesis of (+)-scholarisine A (Scheme 223);[327] this route is ten steps shorter than the only alternative.[328,329] Cyclization of the radical formed from the bromide in precursor **237** onto the alkene of the bridged bicyclic ring, followed by trapping with allyltributylstannane, installs two contiguous stereogenic centers, one of which is quaternary, to generate product **238**. Five additional steps transform **238** into intermediate **239**. From the latter, the completion of the synthesis requires conversion of the allyl group to an ethyl group and reduction of the lactam to an imine. However, the lactam proved resistant to direct reduction,



Scheme 222

which prompted the formation of thioimidate **240** by oxidative alkene cleavage of the allyl group, reduction of the resulting aldehyde, and treatment with Lawesson's reagent. Raney nickel reduction then generates both the desired imine and the necessary ethyl substituent, and a final oxidation reaction delivers (+)-scholarisine A.



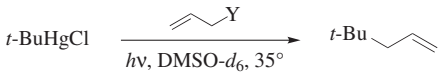
Scheme 223

COMPARISON WITH OTHER METHODS

There are numerous methods, in addition to radical-based procedures, that can be used to incorporate allylic or vinylic groups. Primary examples include metal-catalyzed cross-coupling reactions, metal-catalyzed allylic substitution reactions (Tsuji–Trost and related processes), and the addition of allylstannane, allylsilane, and allylboron reagents to aldehydes. A complete discussion of the breadth of methods for allylation and vinylation is beyond the scope of this chapter. Instead, the following section will focus on comparing radical allylation and vinylation reactions using stannane and non-stannane reagents.

Radical allylation and vinylation reagents that contain non-stannyl moieties capable of undergoing β-elimination are well known. These reagents include allyl and/or vinyl sulfides, sulfoxides, sulfones, silanes, halides, ethers, and alcohols, as well as reagents containing alternative metals and metalloids (cobalt, mercury, zirconium, gallium, indium, boron). The major advantage of using stannane reagents is that the stannyl radicals produced upon β-elimination are excellent chain-propagating species and thus participate in reactions with a broad range of radical precursors and substrate structures. Alternative reagents are not typically as effective, although the recent development of visible-light-mediated reactions, especially those using photoredox catalysis,[330] has broadened the scope of radical-generating groups for reactions with non-tin allylation and vinylation reagents. Furthermore, the rate of addition of a radical to the allylstannane is slightly accelerated by the presence of the stannyl group, which helps to favor the desired reaction over competing processes.[12]

The rate advantage of allylstannanes, relative to several alternative allylating reagents, has been quantified. *tert*-Butyl radical (formed by the photolysis of *tert*-butylmercuric chloride at 35°) adds fastest to allyltriphenylstannane followed by, in descending order, allyl bromide, allyl chloride, allyl phenyl sulfone, and allyl phenyl sulfide. These relative reactivities were determined by direct competition reactions between each of the allyl reagents and 2,2-diphenylethenyl iodide (Scheme 224).[331] Owing to this rate advantage and the many options for radical precursors, allylstannanes are the most commonly used reagents for radical allylation reactions, particularly for the installation of simple, unsubstituted allyl groups.



Y	k_{rel}
Ph_3Sn	2.9
Br	2.2
Cl	1
PhO_2S	0.73
PhS	0.45

Scheme 224

Employing allyl- and vinylstannanes for radical reactions has some major limitations. For example, some types of structures are not accessible by stannane-mediated allylation reactions: as discussed in the "Scope and Limitations" section, allylstannane reagents substituted at C-1 and C-3 are generally poor reaction partners for radical allylations. Steric effects decrease the rate of addition of radicals to C-3-substituted allylstannanes, whereas C-1-substituted reagents are subject to a tributylstannyl-radical-mediated rearrangement that converts them primarily to their C-3-substituted isomers (cf. Figure 13), a process that is usually faster than the desired radical addition. These limitations can be overcome, in many cases, using non-stannane reagents. More importantly, stannane reagents create several significant ecological concerns because of their inherent toxicity. Moreover, the reactions proceed with poor atom economy: allyltributylstannane has a molecular weight of 331 amu, but the allyl group that is added to the substrate comprises only 41 amu of the total mass of the reagent, and the reactions frequently require multiple equivalents of allylstannane to achieve optimal yields (vide supra). Furthermore, the tin-containing byproducts are very toxic to a wide range of organisms; in mammals they act as endocrine disruptors and obesogens, and they display immunogenic effects.[332] As a further complication, the tin-containing byproducts are often difficult to separate completely from the desired organic products. Numerous experimental approaches can be used to remove tin-containing byproducts (discussed below in the "Experimental Conditions" section), but the difficulties associated with their complete removal has limited the use of allyl- and vinylstannane-based methodologies in the pharmaceutical industry.

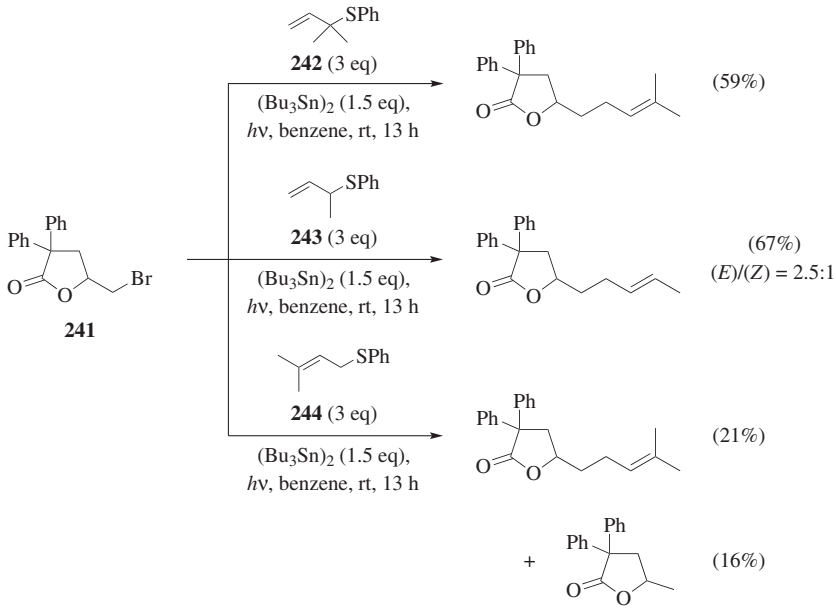
This section will highlight uses of non-tin reagents that offer specific benefits over their stannyl analogues. The chemistry of many of these reagents has been addressed in reviews. The chemistry of allyl and vinyl sulfides is discussed in detail in a comprehensive review of the chemistry of thiyl radicals.[333] Several targeted reviews discuss various aspects of allyl and vinyl sulfone chemistry.[334–336] Although outside the scope of this chapter, it is also worth noting that allyl sulfides and allyl sulfones are

commonly used as addition–fragmentation chain-transfer agents in radical polymerization processes.[337]

Sulfides

Reactions of allyl sulfides with standard radical precursors (halides, selenides, etc.) must be performed in the presence of a tin reagent, usually $(Bu_3Sn)_2$, in a stoichiometric quantity: the thiyl radicals formed upon β-elimination do not react efficiently with the radical precursor group and thus do not propagate the chain well. Allyl sulfides can be used for tin-free allylation reactions of alkyl radicals that are generated from Barton ester precursors but, in direct comparisons, the use of allyltriphenylstannane produces higher yields.[65] Allyl sulfides are also known to react with acyl radicals under tin-free conditions.[338,339]

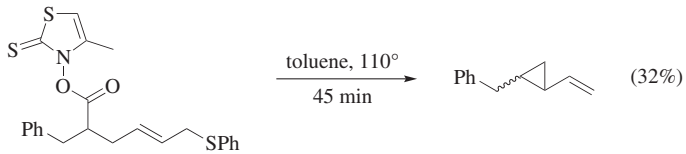
Although reactions of halide radical precursors with allyl sulfides require tin reagents for successful reaction, one distinct advantage in using allyl sulfides is that the allylating reagent can be substituted at C-1. These reagents equilibrate with their C-3-substituted isomers under radical conditions,[340] but the rate of isomerism appears to be slower than for the corresponding stannanes. For example, it is possible to use allyl sulfides **242** and **243** in allylation reactions, whereas the analogous allylstannane reagents undergo significant isomerization to their C-3 substituted isomers, leading to mixtures of products (Scheme 225).[341] The reaction of the primary bromide **241** with allyl sulfide **242** provides the prenylated product in 59% yield, whereas reaction with **243** affords a mixture of alkene diastereomers, favoring the (*E*) isomer, in 67% yield. Several other primary and secondary alkyl



Scheme 225

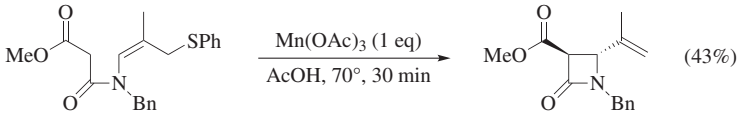
radical precursors react with allyl sulfides **242** and **243**, but reactions of aryl bromides and iodides furnish only the reduction products. However, the reaction of the 3,3-disubstituted allyl sulfide **244** affords only the product of addition to the rearranged allyl sulfide **242** (or its tributylstannyl analogue, formed in the context of the reaction) along with the reduction product in nearly equal amounts.

Radical cyclizations onto allylstannanes can be used to form five- and six-membered rings, and macrocyclization reactions to prepare 10- to 15-membered rings have been reported (see the "Scope and Limitations" section). However, allylic sulfides are more commonly used in radical cyclization reactions and can be employed to generate three- to six-membered rings. For example, thiohydroxamic acid **245** cyclizes in refluxing toluene under tin-free conditions to form the vinylcyclopropane product in 32% yield (Scheme 226).[342] The manganese-mediated cyclization of enamides such as **246** delivers β-lactam derivatives. Specifically, the reaction of enamide **246** with one equivalent of manganese(III) acetate in acetic acid at 70° affords a 43% yield of exclusively the *trans* diastereomeric product (Scheme 227).[343] The reaction of the analogous sulfoxide substrate occurs with a similar outcome.



245

Scheme 226

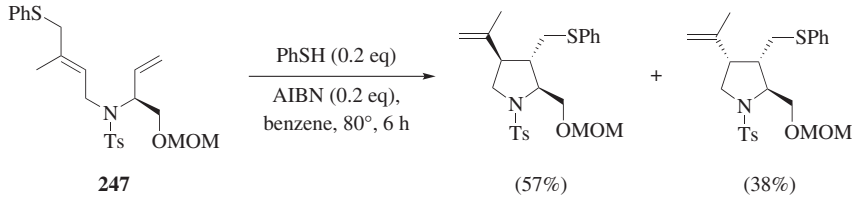


246

Scheme 227

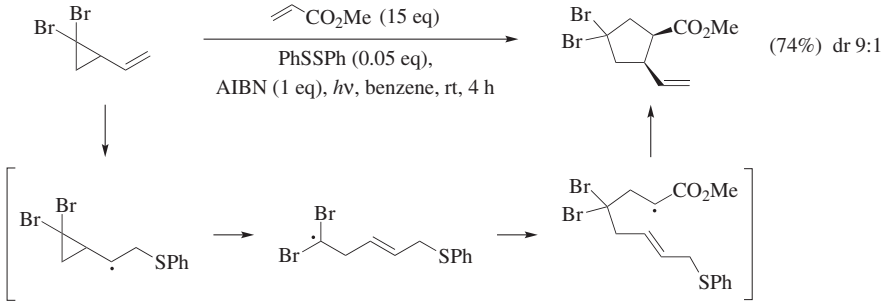
In another example of a tin-free cyclization reaction, the addition of a phenylthiyl radical to an alkene initiates a cascade process that terminates with cyclization onto an allyl sulfide and regeneration of a thiyl radical (Scheme 228).[344] Thus, the reaction of diene **247** with a catalytic amount of benzenethiol and AIBN furnishes a mixture of two diastereomeric pyrrolidines in yields of 57% and 38%. The major *cis* isomer provides the necessary intermediate for conversion to the natural product (–)-kainic acid in seven steps.

A similar strategy can be used in the context of a cascade sequence to construct vinylcyclopentanes from readily accessible vinylcyclopropanes (Scheme 229).[345] Upon addition of a phenylthiyl radical to the terminus of a vinylcyclopropane, the



Scheme 228

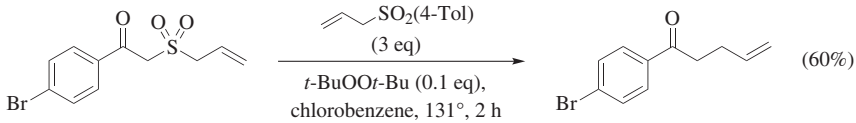
resulting radical undergoes a rapid ring-opening to form an allyl sulfide, and the intermediary radical then adds to methyl acrylate. Cyclization onto the allyl sulfide delivers the final product after loss of a phenylthiyl radical. In this specific example, the product forms in 74% overall yield as a 9:1 mixture of stereoisomers, favoring the *cis* isomer.



Scheme 229

Sulfones

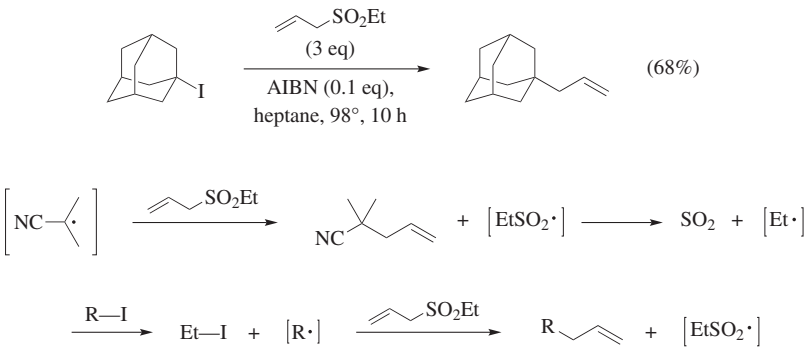
Several methods are available for tin-free allylation reactions using allyl sulfones. The first deploys an allyl alkyl sulfone as the substrate and an allyl aryl sulfone as the allylating agent (Scheme 230).[346] These reactions generally occur in good yields and are compatible with three-component reactions in which the alkyl radical adds to an alkene prior to allylation. However, the need to prepare the requisite alkyl allyl sulfones is a disadvantage for this approach.



Scheme 230

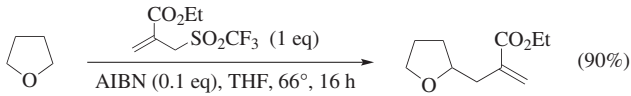
A second method employs allyl ethyl sulfone as the allylating agent (Scheme 231).[347] Addition of an isobutyronitrile radical (from the initiator,

AIBN) to allyl ethyl sulfone generates an ethanesulfonyl radical, which loses sulfur dioxide to form an ethyl radical. This ethyl radical can then react with an iodide (as illustrated) or xanthate radical precursor to form the radical of interest; addition to allyl ethyl sulfone affords the allylation product and regenerates an ethanesulfonyl radical to propagate the chain. This method relies on a favorable atom transfer from the radical precursor to the ethyl radical and therefore is limited to iodides and xanthates. Radical vinylations using analogous vinyl ethyl sulfones (substituted at C-2 of the alkene to direct the regiochemistry of addition) are also known.[348]



Scheme 231

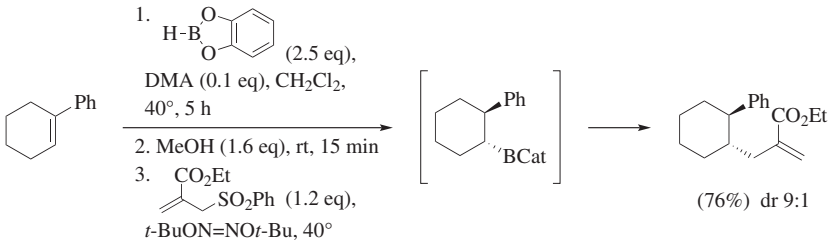
The allylation of substrates not bearing a specific radical-generating group is possible using allyl trifluoromethyl sulfones (triflones) (Scheme 232).[349] In this case, the trifluoromethanesulfonyl radical (which is eliminated after radical addition to the allyl triflone) rapidly loses sulfur dioxide to form a relatively stable trifluoromethyl radical. Because it is highly electrophilic, this radical will selectively abstract hydrogen atoms from positions adjacent to ethers or thioethers and will also abstract hydrogen atoms from simple alkanes at a rate fast enough to propagate the chain efficiently. Vinylation and alkynylation reactions can also be performed with triflate reagents.[350,351] Yields are generally good to excellent, but the substrate must be used as the solvent, and the scope of suitable substrates is limited. Radical vinylation of activated carbon–hydrogen bonds (adjacent to an oxygen or nitrogen atom) is possible using photoexcited benzophenone to generate the desired radical by selective hydrogen-atom abstraction. The radical then reacts with 1,2-bis(phenylsulfonyl)ethylene to afford the vinyl sulfone product.[352]



Scheme 232

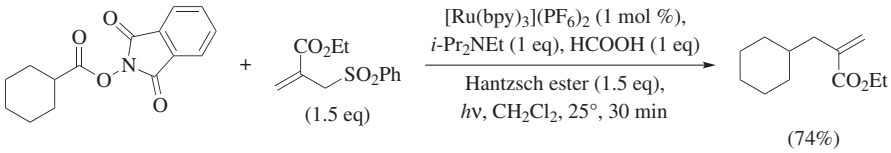
Alkylcatecholboranes can be employed as radical precursors for tin-free allylation reactions with allyl phenyl sulfones (Scheme 233).[353] A *tert*-butoxy radical (derived

from the initiator, di-*tert*-butylhyponitrite) reacts with the borane to generate an alkyl radical that adds to the allyl sulfone, forming the allylation product and a phenylsulfonyl radical. The phenylsulfonyl radical then reacts with another alkylcatecholborane to propagate the chain. This method can be used in three-component couplings that insert an additional alkene between the group derived from the alkylcatecholborane and the allyl group,[354] and can be performed with vinyl and alkynyl sulfones.[355] Thiohydroxamate esters can also be used as radical-generating groups for tin-free reactions with allyl phenyl sulfones.[356]



Scheme 233

Reactions mediated by visible light have expanded the range of radical-generating groups that can be used in allylation reactions with allylsulfones. The radical-generating group with the broadest demonstrated substrate scope is the *N*-hydroxyphthalimide ester.[357] A series of alkyl *N*-acyloxyphthalimides and allyl aryl sulfones substituted at the 2-position with an electron-withdrawing group can be irradiated in the presence of the photoredox catalyst $[Ru(bpy)_3](PF_6)_2$, formic acid, and the reductants diisopropylethylamine and Hantzsch ester. The allylation products are obtained in moderate-to-excellent yields, one example of which is depicted in Scheme 234. The reaction is compatible with primary, secondary, and tertiary alkyl radicals, benzylic radicals, and radicals with an α-oxygen or α-nitrogen atom. The electron-withdrawing group at the 2-position of the allylsulfone can be an ester, phenyl group, bromine atom, or chlorine atom. A drawback of this approach is the poor atom economy: the large phthalimide group is a byproduct, and the reaction requires the inclusion of two reductants.

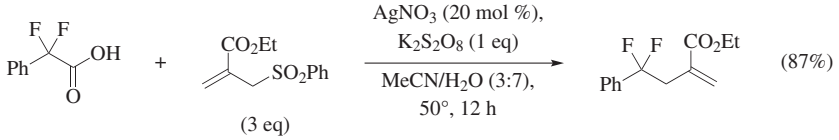


Scheme 234

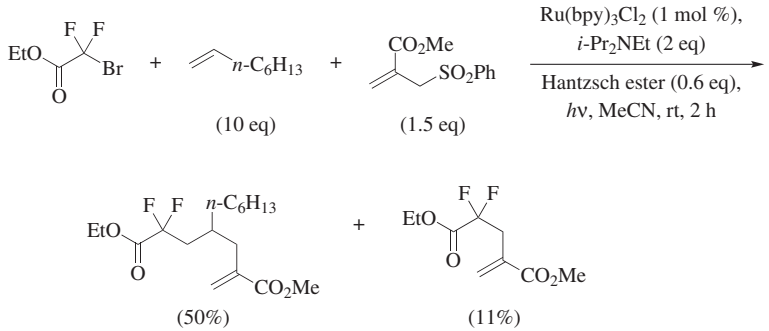
Unmodified carboxylic acids can also be used as radical precursors for reactions with allyl sulfones, although the substrate scope is narrower. In one report, amino acids are used as substrates for reactions catalyzed by an iridium-based photoredox

catalyst.[358] In a second, riboflavin tetraacetate is used as a photoredox catalyst for allylations of radicals with an α-oxygen, α-nitrogen, or α-keto group.[359] In this latter study, the yield is poor with the 1-adamantyl radical, and no product is obtained with either a cyclohexyl or a secondary *n*-butyl radical.

Carboxylic acids can be employed as precursors in the non-light-mediated allylation of α,α-difluorophenylacetic acids; this reaction is accomplished using silver nitrate as the catalyst and potassium persulfate as the stoichiometric oxidant (Scheme 235).[360] The corresponding reaction of alkyldifluorobromides and iodides employs $Ru(bpy)_3Cl_2$ as a photoredox catalyst,[361] The reaction of alkyldifluorohalides can also be performed in the presence of an additional alkene to afford three-component products in modest yields as outlined in Scheme 236.

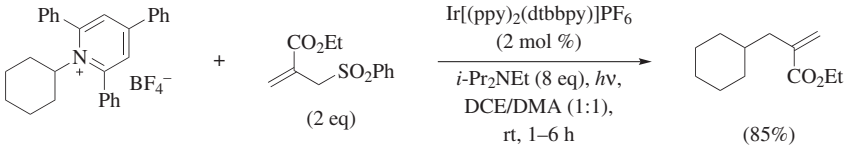


Scheme 235



Scheme 236

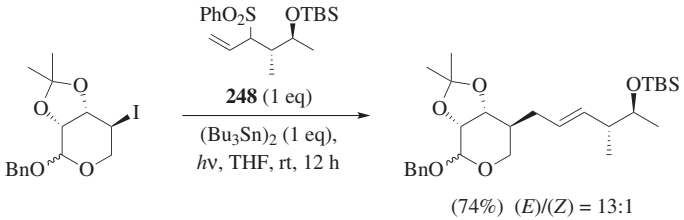
Other radical precursors compatible with photoredox-mediated allylations using allyl sulfones include hypervalent iodine species,[362] alkyltrifluoroborate salts,[363] and Katritzky salts (Scheme 237).[364]



Scheme 237

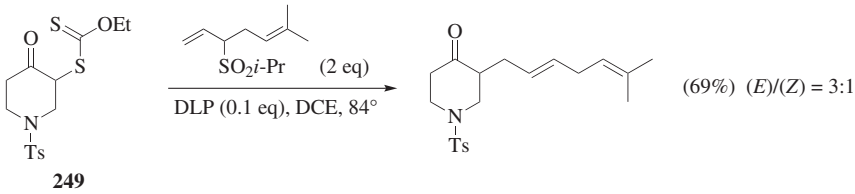
An early report, in the context of a synthesis of the natural product (+)–pseudomonic acid C, demonstrates that selective reactions of C-1-substituted

allyl sulfones are possible (Scheme 238).[365] For instance, the reaction of a carbohydrate-derived secondary iodide with the complex allyl sulfone **248** provides the desired allylation product in 74% yield with complete selectivity for the configuration of the stereogenic center on the ring and 13:1 selectivity for the (*E*) alkene. The reaction is very sensitive to reaction conditions, and the product yield is optimal when a solution of the allyl sulfone and hexabutylditin is added via syringe-pump to an irradiated solution of the iodide.



Scheme 238

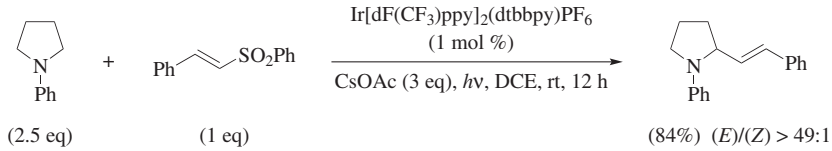
The potential for allylation reactions using allyl sulfones branched at C-1 under tin-free conditions has been explored.[366] Significant rearrangement is observed with allyl ethyl sulfones (via addition of an ethylsulfonyl radical), but this rearrangement is minimized with allyl isopropyl sulfones because isopropylsulfonyl radicals lose sulfur dioxide more rapidly. As an example, xanthate **249** reacts with a branched sulfone in refluxing 1,2-dichloroethane using dilauroyl peroxide (DLP) as a radical initiator to form the non-conjugated diene product in 69% yield (Scheme 239). Disubstitution at C-1 is tolerated to facilitate the preparation of prenylated and other types of branched products. Prenylations of aryl halides, aryl diazonium ions, and α-bromo carbonyl compounds are also possible using isoprenyl phenyl sulfone in the presence of a photoredox catalyst.[367]



Scheme 239

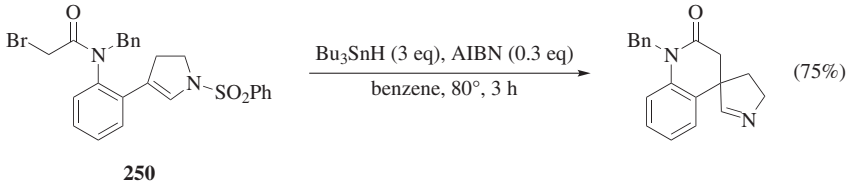
Vinylsulfones are effective reagents for photoredox-catalyzed vinylation reactions. As is the case for vinylstannane reagents, the vinyl sulfone must possess an electron-withdrawing substituent at C-2 to direct radical addition to the alkene carbon bearing the sulfone group. Alkyl halides,[368] carboxylic acids,[369,370] and alkyltrifluoroborates[363] all provide radical-generating groups. Reactions with alkyl halides exhibit the broadest substrate scope, but also require a full equivalent of tris(trimethylsilyl)silane to mediate the reaction.[368] The reaction can also be

performed via selective activation of a carbon–hydrogen bond adjacent to an aryl amine (Scheme 240).[369]



Scheme 240

One additional type of substrate, unique to sulfones, bears mentioning: *N*-alkenylsulfonamides can act as radical acceptors, losing a sulfonyl radical from the nitrogen atom by β-elimination after radical addition to the alkene. For example, abstraction of the bromine atom from substrate **250** affords a radical that cyclizes onto the *N*-alkenylsulfonamide to give the spirocyclic product in 75% yield (Scheme 241).[371] Intermolecular versions of this reaction process are also known.[372]



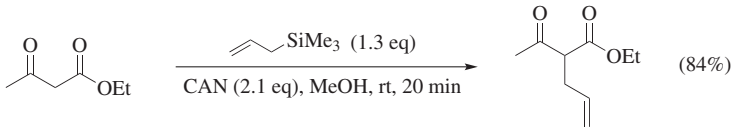
Scheme 241

Silanes

β-Silyl radicals usually do not undergo facile β-elimination,[285] but the β-silyl radical formed by addition to allyl tris(trimethylsilyl)silane is an exception. This reagent and a number of 2-substituted analogues can be used for tin-free allylation reactions with bromide and iodide radical precursors.[373] The reactions of allyl tris(trimethylsilyl)silanes are more sensitive to electronic effects than the reactions of allylstannanes, and the parent allyl tris(trimethylsilyl)silane only reacts with electron-deficient radicals. However, nucleophilic alkyl radicals react in good yields with allyl tris(trimethylsilyl)silanes bearing electron-withdrawing groups at C-2.

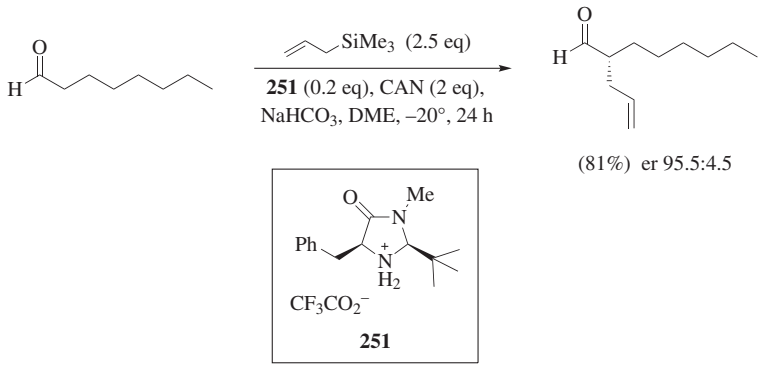
The use of allyltrimethylsilanes is advantageous when the radical is generated in a redox process. For example, when ethyl acetoacetate is treated with allyltrimethylsilane and ceric ammonium nitrate (CAN) in methanol, the allylation product is formed in 84% yield (Scheme 242).[374] In this case, because β-elimination is slow, the initial radical adduct is oxidized to a carbocation that undergoes cationic β-elimination to form the final product. When manganese(III) acetate is used as the oxidant, the intermediate β-silyl carbocations undergo cyclization followed by loss of a proton to form dihydrofurans. The reactions of allylsilanes in the presence of photoredox catalysts can also deliver the final product by oxidation of the initial radical adduct

followed by cationic β-elimination. Photoredox-catalyzed reactions can be performed using α-bromo carbonyl compounds as the radical precursors,[375,376] or by addition of trifluoromethyl radical (derived from either a hypervalent iodine compound or a diaryl(trifluoromethyl)sulfonium salt).[377] This latter study uses allylsilanes with substitution at C-1 and/or C-3.



Scheme 242

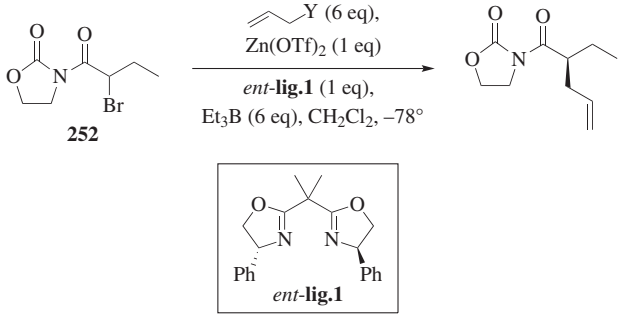
Allylsilanes are useful reagents for asymmetric α-allylations of aldehydes using organo-SOMO catalysis (Scheme 243).[378,379] Octanal reacts with organocatalyst **251** to form an enamine, and oxidation with CAN generates a radical cation that undergoes a one-electron addition to the allylsilane. The adduct radical is oxidized, and the resulting cation undergoes a β-elimination to generate the allyl group. Iminium-ion hydrolysis releases the organocatalyst, providing the product in 81% yield and 95.5:4.5 er. This reaction is also effective with ketones,[380] and cyclizations onto tethered allylsilanes are possible, either directly or as part of a three-component reaction (with addition of an alkene prior to cyclization).[381,382]



Scheme 243

The use of allylsilanes is also advantageous in stereoselective reactions that rely on metal coordination for selectivity. Compared to the analogous reactions using allylstannanes, allylsilanes afford higher stereoselectivities in Lewis acid mediated enantioselective reactions. For example, the allylation of bromide **252** in the presence of zinc triflate and chiral bisoxazoline *ent*-**lig.1** provides an enantiomeric ratio of 80:20 with allyltriethoxysilane versus 71:29 with allyltributylstannane (Scheme 244).[211] The decreased selectivity with the allylstannane is presumably because the tributyltin bromide byproduct formed in the reaction can compete

with the chiral Lewis acid to complex the radical precursor, giving rise to an alternative catalyzed pathway that leads to racemic product. Similarly, the use of allyltrimethylsilane delivers higher levels of diastereoselectivity in reactions where metal chelation is used to control substrate conformation.[383] Note that in these examples of both enantio- and diastereoselective additions, reactions are performed under tin-free conditions. In the absence of tin to help propagate the radical chain, the initial adduct formed by addition to the allylsilane undergoes an atom-transfer process with the radical precursor, and the resulting β-silyl halide or selenide forms the alkene by an ionic elimination.



Y	Yield (%)	er
Bu_3Sn	84	71:29
$(EtO)_3Si$	65	80:20

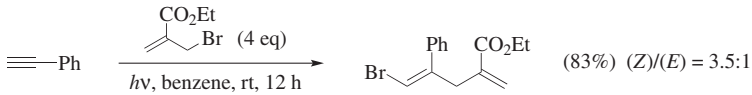
Scheme 244

Halides

Allyl- and vinylstannanes, sulfides, sulfones, etc. are often prepared from the corresponding allyl and vinyl halides, and as such, it would be ideal to employ halides directly for radical allylations and vinylations. β-Elimination of bromine and chlorine atoms is more favorable than β-elimination of sulfones and sulfides, so the use of allyl and vinyl halides is feasible, but there are challenges. With typical radical precursors, the halogen radical formed upon β-elimination does not propagate the chain well, and successful reactions require the inclusion of a tin reagent.[384] However, because bromine atoms will abstract hydrogen atoms, allyl and vinyl bromides can be used under tin-free conditions to allylate and vinylate selectively at activated positions (benzylic carbons or carbons adjacent to oxygen or nitrogen atoms). The optimal reactions utilize allyl or vinyl bromides containing an electron-withdrawing substituent at C-2 and often require a large excess of the substrate.[385,386] Allyl and vinyl halides can also be used for allylation and vinylation of radicals that are generated from aryl diazonium ions in a non-chain reaction process.[387,388]

Allyl bromides can be employed for bromoallylation reactions of alkynes (Scheme 245).[389] For example, the photolysis of phenylacetylene with four equivalents of ethyl 2-(bromomethyl)acrylate in benzene affords the bromoallylation product in 83% yield as a 3.5:1 mixture of alkene stereoisomers, favoring the (*Z*) isomer. After initiation, a bromine radical adds to the terminus of the alkyne, and the resulting vinyl radical then adds to the allyl bromide to form the product and regenerate a bromine radical. The reaction is also successful with allyl bromides

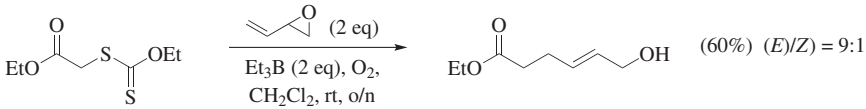
not bearing an electron-withdrawing group, although these reactions require a large excess of the allyl bromide and must be performed at higher temperatures. Bromoallylations of allenes and alkylidenecyclopropanes have also been reported.[390,391]



Scheme 245

Ethers and Alcohols

The barrier for homolysis of a typical carbon–oxygen bond usually makes β-elimination of an alkoxy radical slow, but allylation using allyl ethers is possible when the structure of the ether facilitates fragmentation. Using vinyl epoxides, relief of ring strain upon β-elimination enables the formation of allylic alcohols in good yields; these reactions employ xanthates as radical precursors and triethylborane as the initiator (Scheme 246).[392] Thus, the reaction of xanthate **253** with butadiene monoepoxide affords the allylated product in 60% yield as a 9:1 mixture of alkene diastereomers. The process is also successful with xanthate precursors that afford tertiary radicals and with vinyl epoxides bearing a substituent at C-2 on the epoxide ring. The use of triethylborane as the initiator is crucial because the ring-opened alkoxy radical reacts with the borane to form a borinate (which is later hydrolyzed), and an ethyl radical that propagates the chain.

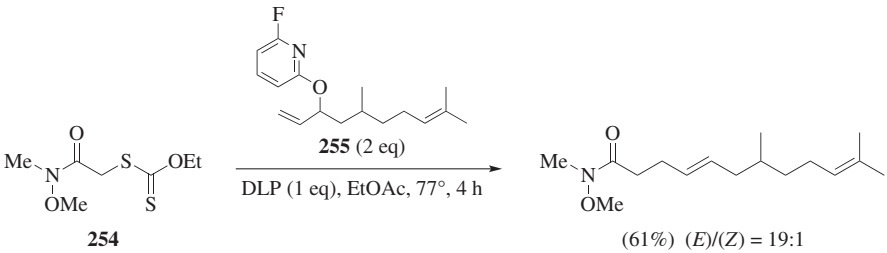


253

Scheme 246

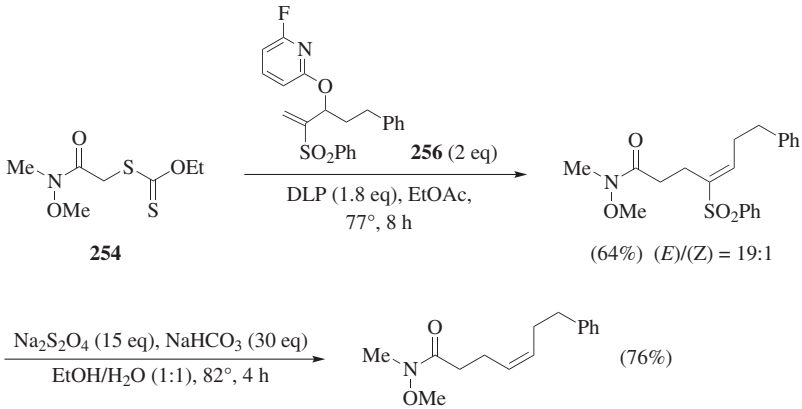
Perhaps the best solution for using C-1-substituted allylating reagents involves allyl ethers that are substituted on the ether oxygen with a 2-fluoropyridyl group. These reagents are readily available by addition of a vinyllithium or vinyl Grignard reagent to an aldehyde or ketone, followed by reaction of the resulting allylic alcohol with sodium hydride and 2,6-difluoropyridine. Upon radical addition to these substrates, β-elimination is accelerated (compared to typical allylic ethers) because of the relative weakness of the benzylic carbon–oxygen bond and resonance stabilization of the developing phenoxyl radical. For example, xanthate **254** reacts with allylic ether **255** under peroxide initiation to form the product in 61% yield with high selectivity for the (*E*) isomer (Scheme 247).[393] Because β-elimination of the 2-fluoro-6-pyridyloxy radical is still a relatively slow process, using xanthates as radical precursors is critical. If the initially formed β-alkoxy radical does not

fragment, it will undergo reversible addition to another xanthate starting material. This addition product can either revert back to the β-alkoxy radical or form a xanthate transfer product, both of which can eventually form the desired product. This reversible addition effectively increases the lifetime of the adduct radical, allowing the slow elimination of the β-alkoxy radical to occur. The nature of the starting xanthates is limited to those that form a radical more stable than a simple secondary radical.



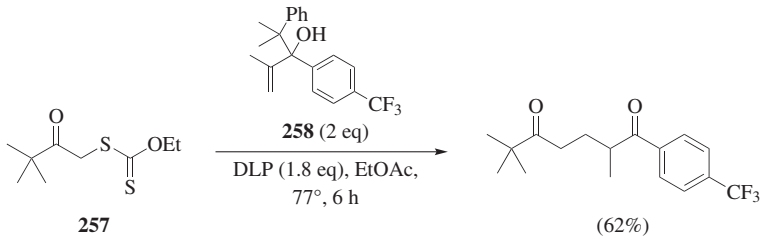
Scheme 247

Reactions of 2-fluoro-6-pyridyloxy allyl ethers work well with allyl ethers derived from aldehydes (as above) and from both cyclic and acyclic ketones, providing access to a wide range of substitution patterns in the allylated products. Substitution is also possible at C-2 of the allyl ether with alkyl groups, ethers, thioethers, trifluoromethyl groups, and fluorine atoms.[394] Whereas reactions typically afford the (*E*)-alkene isomer as the major product, the use of 2-sulfonyl-substitited allyl ethers enables the selective synthesis of (*Z*) alkenes (Scheme 248).[395] For example, the reaction of xanthate **254** with allyl ether **256** affords a 19:1 mixture of alkenes, favoring the (*E*) isomer, in 64% yield. Reaction of this vinyl sulfone product with sodium dithionite removes the sulfonyl group with retention of the alkene stereochemistry to deliver the corresponding (*Z*) alkene.



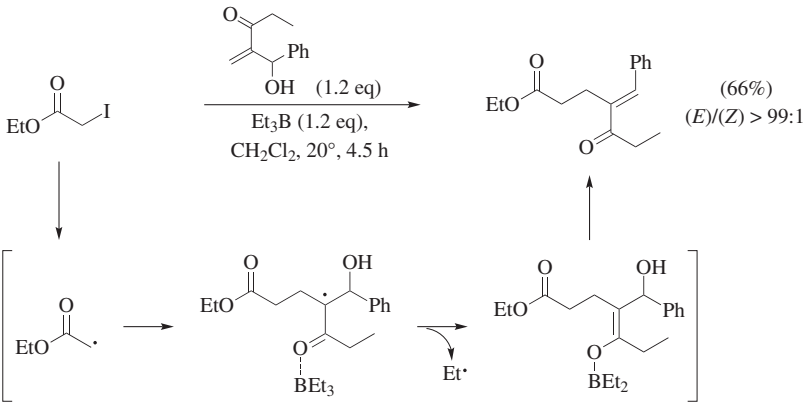
Scheme 248

When the C-1 substituent on a 2-fluoro-6-pyridyloxy allyl ether is a cumyl group, there is a competition between β-elimination of the 2-fluoro-6-pyridyloxy radical and a cumyl radical. As such, 1-cumyl-substituted allyl alcohols can be used in lieu of 2-fluoro-6-pyridyloxy allyl ethers as allylating reagents that, upon elimination of the cumyl radical, furnish enols that then tautomerize to ketones. These species react particularly well with α-keto xanthates, giving 1,5-diketones as the final products. Xanthate **257** reacts with allyl alcohol **258** in refluxing ethyl acetate using dilauroyl peroxide as a radical initiator to afford the 1,5-diketone product in 62% yield (Scheme 249).[396] In all reported cases, the allyl alcohol bears an alkyl group, a sulfide, or a sulfone at the C-2 position.



Scheme 249

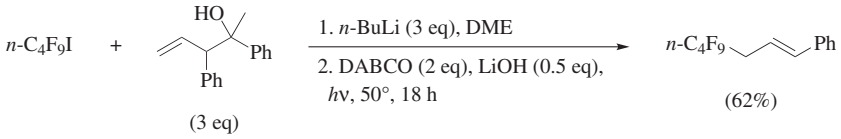
Secondary allylic alcohols bearing a ketone group at C-2 can also act as allylating reagents with alkyl iodide radical precursors when triethylborane is used as the initiator (Scheme 250).[397] In this case, the carbonyl oxygen of the initial adduct radical is thought to complex with triethylborane. Subsequent scission of an ethyl radical creates a boron enolate that then eliminates hydroxide via an E1cB process to form the allylation product.



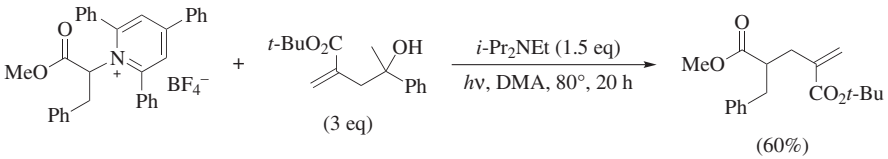
Scheme 250

Homoallylic alcohols can serve as allylating agents in visible-light-mediated reactions of perfluoroalkyliodides or Katritzky salt radical precursors.[398] Both reactions

require base to fragment the initial radical adduct to the product. The best substrates are tertiary alcohols bearing an aryl group at the alcohol-substituted carbon, and substitution is tolerated at the β- and γ-carbons of the homoallylic alcohol. Reactions of the perfluoroalkyliodides use either *n*-butyllithium (Scheme 251)[398] or potassium phosphate as the base. Calculations reveal that deprotonation of the alcohol under these conditions destabilizes the initial radical adduct, lowering the barrier for carbon–carbon bond cleavage to form a ketyl radical anion. Using Katritzky salts, the optimal conditions employ a much weaker base that will hydrogen bond with—but not deprotonate—the alcohol (Scheme 252).[398] This has a smaller effect on the barrier for breaking the carbon–carbon bond, and therefore, higher reaction temperatures are necessary. This reaction is compatible with Katritzky salts that generate primary and secondary alkyl radicals, benzyl radicals, and an ester-substituted radical derived from phenylalanine.



Scheme 251

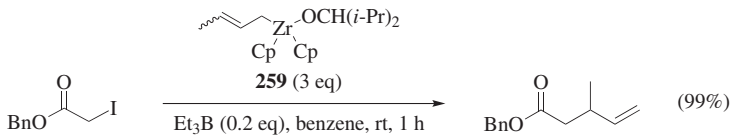


Scheme 252

Non-Tin Metals and Metalloids

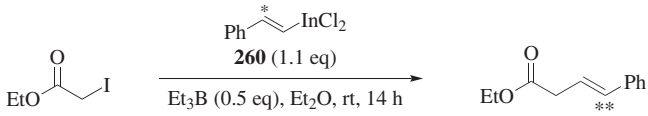
Allylcobaloximes,[399] allylmercury reagents,[331] allylzirconocenes,[400] allylgallium reagents,[401] and allylindium reagents[402] can all be used for radical allylation reactions under tin-free conditions. The latter three organometallics are the most effective and provide yields that are slightly higher than those obtained from reactions of similar substrates with allyltributylstannane. Reports are thus far limited to α-bromo and α-iodo carbonyl compounds as substrates. A decided advantage of the zirconocene, gallium, and indium reagents is the reactivity of the crotyl derivatives towards radical addition. Zirconocene derivative **259** delivers the best reported yield, reacting with benzyl iodoacetate to afford a 99% yield of the crotylation product (Scheme 253).[400] In contrast, the reaction of ethyl bromoacetate with neat crotyltributylstannane provides the product in only 36% yield.[37]

Vinylindium reagents also have a distinct advantage over vinylstannanes in vinylation reactions. β-Styrylindium dichloride (**260**) (predominantly the (*E*) isomer) reacts with ethyl iodoacetate in ether at room temperature to form a 9:1 mixture of the



Scheme 253

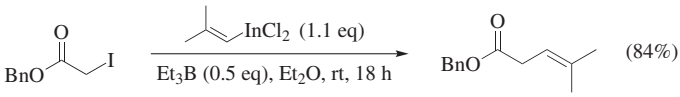
vinylation products, favoring the (*E*) alkene, in 91% yield (Scheme 254).[402] When the (*Z*) isomer of **260** is used, the product is formed in 93% yield as a 1.9:1 mixture favoring the (*Z*) alkene. A similar yield (88%) is obtained in the reaction between ethyl bromoacetate and **260** (predominantly the (*E*) isomer), although this reaction requires two equivalents of the styrylindium reagent; for comparison, the reaction of methyl bromoacetate with β-styryltributylstannane affords only a 38% yield.[292]



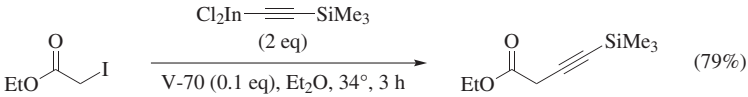
*(*E*)/(*Z*)	Yield (%)	**(*E*)/(*Z*)
82:18	91	9:1
1:99	93	1:1.9

Scheme 254

Vinylindium chlorides that lack a radical-stabilizing group at C-2 react to afford vinylation products in good yields (Scheme 255),[402] whereas the reactions of the analogous stannane reagents are unsuccessful.[62,288] Similarly, alkynylation products are obtained in good yield from the reactions of three different alkynylindium reagents with ethyl iodoacetate.[402] For example, the treatment of ethyl iodoacetate with trimethylsilylethynylindium dichloride in the presence of the initiator 2,2′-azobis(2-cyano-4-methoxybutane) (V-70) furnishes the alkynylated product in 79% yield (Scheme 256).

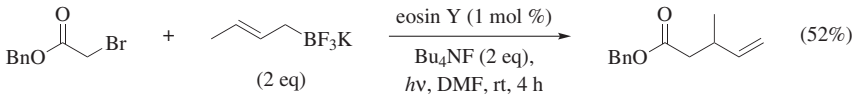


Scheme 255

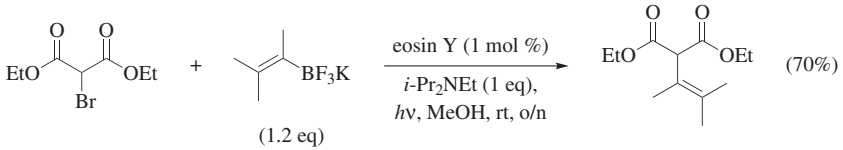


Scheme 256

Allyl- and vinyltrifluoroborates can be used under tin-free, photoredox-mediated conditions. Known examples are limited to the addition of electrophilic radicals derived from α-bromo or α-iodo carbonyl compounds,[403,404] benzyl bromides,[404] and α-bromo *N*-sulfonylimines.[405] Allylations can be performed with either allyltrifluoroborate or crotyltrifluoroborate (Scheme 257).[403] Vinyltrifluoroborates without a radical-stabilizing group at C-2 participate in this reaction, and even tetrasubstituted-alkene substrates react (Scheme 258).[404]



Scheme 257



Scheme 258

EXPERIMENTAL CONDITIONS

Hazards

CAUTION! Tri- and tetraorganotin compounds are known to be toxic to organisms ranging from bacteria to humans.[332,406] *Trimethyltin compounds are more toxic than tributyl- or triphenyltin compounds.*[407] *Reactions using organotin compounds should be carried out in a fume hood, and appropriate personal protective equipment should be worn to prevent skin contact. Efforts must be made to ensure the removal of residual organotin compounds from reaction products before conducting biological testing.*

Reaction Conditions

The most common solvents used for allylation and related reactions are benzene and toluene. Like most radical reactions, however, allylations are relatively insensitive to solvent effects, and other solvents can be used if advantageous for solubility or other factors; reactions in hexanes, ether solvents, ethyl acetate, acetonitrile, dimethyl sulfoxide, and alcohols have been reported. Even mixed solvent systems containing water as a minor component are tolerated. Reactions requiring high temperatures are performed in xylenes or chlorobenzene, and trifluoromethyltoluene is typically employed for reactions involving a fluorinated substrate or a fluorinated allylstannane. Stereoselective reactions using a Lewis acid are typically performed

in dichloromethane or in a mixture of dichloromethane and either tetrahydrofuran or ether. Sluggish reactions are sometimes carried out in neat allyltributylstannane.

Although AIBN is the most common initiator for reactions performed at elevated temperatures, other initiators such as benzoyl peroxide, di-*tert*-butyl peroxide, or dilauryl peroxide may be used, particularly for reactions carried out at temperatures above 110°. Initiation at room temperature or below can be accomplished with triethylborane and oxygen or by photochemical irradiation; some photochemical reactions employ an initiator, usually AIBN or hexabutyldistannane. Reactions are usually carried out under an inert atmosphere.

Isolation of Products

A typical reaction mixture consists of the desired product along with excess allylstannane and the byproduct R_3SnX. Separating the desired product from the tin-containing contaminants is often a challenge.[408] As discussed above in "Scope and Limitations", the use of modified allylstannanes can provide a solution: replacing one of the trialkyl groups with a polar, fluorous, or polyaromatic group facilitates separation, as does the use of inorganic groups in place of the trialkyl groups. Alternatively, a polymer-supported substrate or polymer-supported stannane reagent can be employed. Although these modified reagents can be efficient at mediating allylation reactions, they are not commercially available, and as such, their use is limited by convenience. The large majority of allylation reactions are performed using trialkyl- or triphenylallylstannanes.

The desired product can be separated from trialkylstannane-containing contaminants by partitioning the crude reaction mixture between hexanes and acetonitrile.[409] The stannanes have a high affinity for the hexanes, while most organic products are more soluble in acetonitrile. This approach does not work when the reaction product is non-polar and, at least in one case where the efficiency of this partitioning has been quantified, tin contamination of the acetonitrile fraction is in excess of 25 mol %.[410] Direct chromatographic separation of the compounds on silica gel is usually ineffective because R_3SnX byproducts tend to slowly hydrolyze and streak through the column.

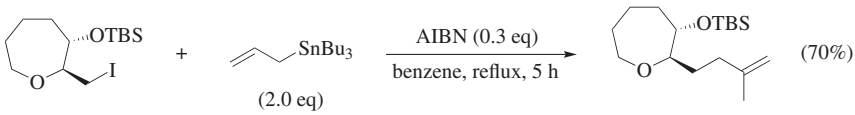
Reaction byproducts such as R_3SnX can instead be removed by conversion either to R_3SnF, which is insoluble in organic and aqueous solutions, or to an equilibrium mixture of R_3SnOH and $R_3SnOSnR_3$, which is retained on a silica gel column. Conversion to R_3SnF is achieved by treating a solution of the crude reaction mixture with an alcoholic or aqueous solution of KF, followed by filtration of the R_3SnF precipitate (and separation of the layers when an aqueous solution is used).[411,412] When R_3SnX is derived from a xanthate or similar radical precursor, rather than a halide, it may be necessary to reflux the crude product in CCl_4 and titrate with molecular iodine to convert R_3SnX to R_3SnI prior to treatment with KF.[413] The use of solid-supported sources of fluoride ion such as 2:1:1 CsF/CsOH/silica,[414] KF on Celite,[415] or KF/CaF_2[416] may be more efficient. Additionally, R_3SnX can be removed by elution of the crude product mixture through a column using a stationary phase consisting of 10% KF and 90% silica gel,[410] although the hygroscopic nature of this mixture can make its storage and use inconvenient.[417]

Conversion to $R_3SnOH/R_3SnOSnR_3$ is accomplished by treating the crude reaction mixture with DBU in wet ether and then titrating with molecular iodine.[418] The resulting mixture is then eluted through a short silica gel column to separate the desired product from the majority of the tin-containing byproducts. A solution of the crude reaction mixture can also be stirred vigorously with a 1 M aqueous solution of sodium hydroxide.[419] This biphasic method is more suitable for base-sensitive compounds. In a direct chromatographic approach, R_3SnX can be sequestered as $R_3SnOH/R_3SnOSnR_3$ using 10% K_2CO_3 and 90% silica gel as a stationary phase.[417] This method can reduce tin contamination to levels below 15 ppm.

The methods described above are generally successful unless the products are reactive towards fluoride ion or base. In such cases, the R_3SnX byproducts can be transformed into non-polar derivatives that can be separated chromatographically from polar reaction products. One approach involves treating the crude product mixture with $NaBH_3CN$, which converts R_3SnX to R_3SnH.[420] Alternatively, trimethylaluminum can be employed to convert R_3SnX to R_3SnMe.[419]

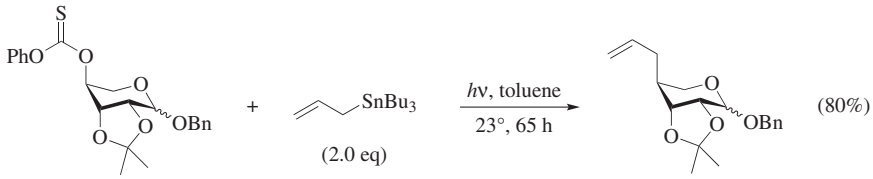
Allyltributylstannane is very non-polar and elutes quickly from a silica gel column using hexanes as the eluent, and therefore, separation of excess allyltributylstannane from polar reaction products is not usually difficult. This method is not applicable to non-polar products, but the problem can be overcome by treating the crude reaction mixture with diethylazodicarboxylate (DEAD), which inserts into the tin–allyl bond to create a highly polar product that is strongly retained on silica gel.[421]

EXPERIMENTAL PROCEDURES



(2′*R,3′*S**)-4-[3′-(*tert*-Butyldimethylsiloxy)-2′-oxepanyl]-1-butene [Direct Allylation with Thermal Initiation].**[422] (2*R**,3*S**)-3-(*tert*-Butyldimethylsiloxy)-2-(iodomethyl)oxepane (6.4 g, 17.3 mmol) was dissolved in dry benzene (34 mL) and charged with allyltributylstannane (10.8 mL, 34.6 mmol) and AIBN (0.85 g, 5.19 mmol). The resulting solution was heated in the dark at reflux under Ar for 5 h and then was allowed to cool to 23°. The crude reaction mixture was concentrated at reduced pressure, diluted with ether (300 mL), and washed with H_2O (2 × 100 mL). The organic layer was dried over $MgSO_4$ and concentrated. Purification of the residue by silica gel column chromatography (hexane/EtOAc, 99:1–98:2) afforded the title compound as an oil (3.44 g, 70%): R_f 0.6 (hexane/EtOAc, 97.5:2.5); IR ($CHCl_3$) 3030, 3020, 2925, 1643, 1380, 1265, 1100, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (m, 1H), 5.02 (d, J = 17.1 Hz, 1H), 4.95 (d, J = 9.8 Hz, 1H), 3.95 (ddd, J = 12.0, 6.3, 5.3 Hz, 1H), 3.53 (m, 2H), 3.19 (ddd, J = 7.2, 7.2, 2.0 Hz, 1H), 2.24 (m, 1H), 2.09 (m, 1H), 1.86 (m, 1H), 1.72 (m, 3H), 1.55 (m, 2H), 1.44 (m, 1H), 1.30 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 114.8, 85.2, 76.7, 71.4, 36.1, 33.8, 31.4, 30.4, 26.4, 20.7, 18.4, –3.4,

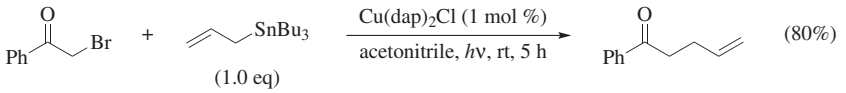
–4.3; LRMS–EI (*m/z*): $[M]^+$ 284 (1), 229 (3), 227 (37), 185 (68), 159 (8), 143 (42), 135 (13), 131 (34), 115 (13), 101 (28), 93 (33), 85 (29), 75 (100), 67 (65); HRMS (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{33}O_2Si$, 285.2250; found, 285.2266.



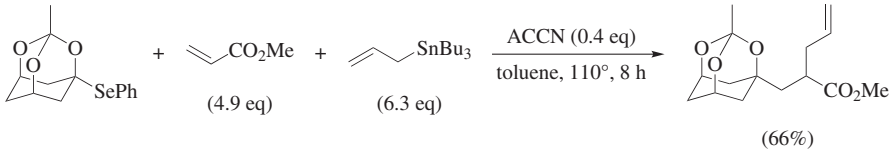
Phenylmethyl 4-Deoxy-2,3-*O*-(1-methylethylidene)-4-(2-propen-1-yl)-L-lyxopyranoside (Mixture of Anomers) [Direct Allylation with Photochemical Initiation].[423] The thionocarbonate (11.16 g, 26.8 mmol) was placed in a Hanovia photolysis apparatus along with allyltributylstannane (17.68 g, 53.6 mmol) and toluene (54 mL). After thoroughly degassing the solution with Ar, the mixture was irradiated at 23° for 65 h with a 450 W Hanovia lamp with a Pyrex filter. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (hexanes/ether, 95:5) to afford the title product as a pair of anomers (ratio unspecified) as a colorless oil (6.25 g, 80%).

Higher R_f anomer: mp 43–44°; R_f 0.36 (hexanes/ether, 80:20); $[\alpha]^{25}{}_D$ – 70.3 (*c* 0.0774, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 5H), 5.74 (m, 1H), 5.00 (m, 2H), 4.86 (d, *J* = 2.1 Hz, 1H), 4.61 (AB q, *J* = 12.0 Hz, 2H), 3.95 (m, 2H), 3.58 (dd, *J* = 12.0, 3.8 Hz, 1H), 3.48 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.33 (m, 1H), 1.95 (m, 2H), 1.44 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 136.0, 128.7, 128.4, 128.1, 117.2, 109.0, 98.2, 76.1, 74.2, 69.3, 61.4, 38.1, 34.1, 28.2, 26.5.

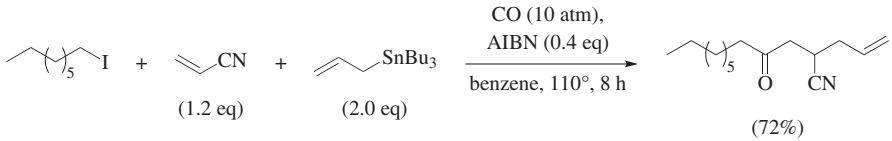
Lower R_f anomer: R_f 0.29 (hexanes/ether, 80:20); IR (neat) 3060, 3020, 2920, 1640, 1375, 1080, 735, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 5H), 5.78 (m, 1H), 5.06 (m, 2H), 4.72 (AB q, *J* = 11.8 Hz, 2H), 4.48 (d, *J* = 5.7 Hz, 1H), 4.31 (dd, *J* = 6.3, 3.2 Hz, 1H), 3.96 (dd, *J* = 11.6, 6.1 Hz, 1H), 3.74 (dd, *J* = 11.6, 6.1 Hz, 1H), 3.45 (m, 1H), 2.18 (m, 1H), 2.02 (m, 2H), 1.36 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 135.7, 128.7, 128.5, 128.3, 117.1, 109.4, 100.1, 75.7, 74.0, 70.1, 64.3, 35.7, 32.3, 27.5, 25.7; LRMS–CI (isobutene) (*m/z*): $[M + H]^+$ 305 (5), 197 (100), 139 (47), 91 (56); HRMS (*m/z*): $[M]^+$ calcd for $C_{18}H_{24}O_4$, 304.1674; found, 304.1656.



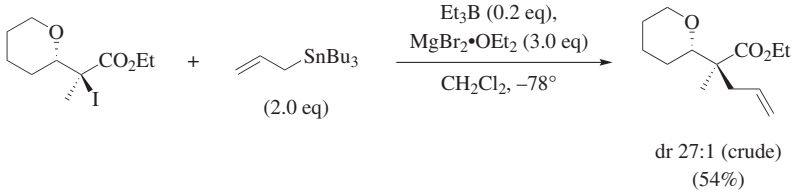
1-Phenylpent-4-en-1-one [Direct Allylation Using a Photoredox Catalyst].[47] An oven-dried 10-mL vial equipped with a plastic septum and magnetic stir bar was charged with $Cu(dap)_2Cl$ (2 mg), 2-bromoacetophenone (0.050 g, 0.25 mmol), and allyltributylstannane (0.083 g, 0.25 mmol). The flask was purged with nitrogen, and acetonitrile (1.0 mL) was added. The resulting mixture was sparged with N_2 for 5 min, placed at a distance of approximately 0.5–1.0 cm from a green 530-nm LED lamp, and irradiated for 5 h, at which point TLC analysis showed that the starting material had been consumed. The mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexanes/EtOAc) to afford the title product as a colorless liquid (0.032 g, 80%): R_f 0.51 (hexane/EtOAc, 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99–7.95 (m, 2H), 7.59–7.53 (m, 1H), 7.49–7.43 (m, 2H), 5.97–5.84 (m, 1H), 5.12–4.99 (m, 2H), 3.08 (t, J = 7.1 Hz, 2H), 2.54–2.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 137.3, 136.9, 133.0, 128.6, 128.0, 115.3, 37.7, 28.1; LRMS–EI (*m/z*): $[M]^+$ 160.1 (4.8), 105.0 (100.0), 77.0 (31.8).



3-Methyl-α-2-propen-1-yl-2,4,10-trioxatricyclo[3.3.1.1^{3,7}]decane-1-propanoic Acid Methyl Ester [Three-Component Reaction of a Radical Precursor, Alkene, and Allyltributylstannane].[144] A solution of the *O*,*Se*-acetal (27 mg, 0.087 mmol), methyl acrylate (39 μL, 0.43 mmol), allyltributyltin (170 μL, 0.55 mmol), and ACCN (8.6 mg, 0.035 mmol) in toluene (0.45 mL) was degassed by three freeze–thaw cycles, and then was stirred under Ar at 110° for 8 h. The resultant mixture was cooled to rt and then concentrated. The residue was purified by chromatography using a column consecutively packed with 10 g of silica gel and 10 g of silica gel containing KF (10% w/w) (hexane/EtOAc, 5:1 to 2:1) to afford the title product as a colorless oil (16 mg, 66%): IR (NaCl) 2952, 1736, 1395, 1167, 1127 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (ddt, J = 17.4, 10.0, 7.0 Hz, 1H), 5.06 (ddt, J = 17.4, 1.8, 1.4 Hz, 1H), 5.04, (ddt, J = 10.0, 1.8, 0.9 Hz, 1H), 4.37 (m, 2H), 3.66 (s, 3H), 2.71 (dddd, J = 10.5, 7.8, 6.4, 2.7 Hz, 1H), 2.49 (dtt, J = 13.3, 2.3, 2.3 Hz, 1H), 2.38–2.19 (m, 3H), 2.14 (m, 1H), 2.00 (dd, J = 14.6, 10.5 Hz, 1H), 1.55 (d, J = 11.0 Hz, 1H), 1.54 (dt, J = 12.8, 1.4 Hz, 1H), 1.52 (dd, J = 14.6, 2.7 Hz, 1H), 1.49 (dd, J = 12.8, 1.8 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 134.8, 117.3, 110.2, 72.0, 68.0, 67.9, 51.5, 43.0, 39.0, 38.1, 36.44, 36.37, 32.3, 26.0; HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{15}H_{22}NaO_5$, 305.1359; found, 305.1354.

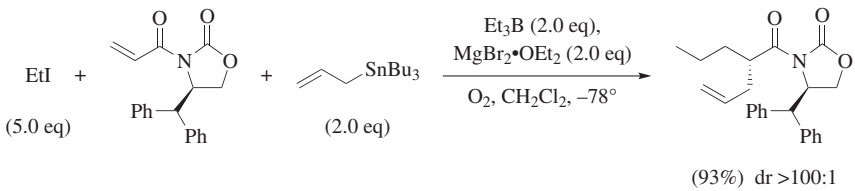


4-Cyano-1-tetradecen-6-one [Four-Component Reaction of a Radical Precursor, Carbon Monoxide, Alkene, and Allyltributylstannane].[155] Benzene (20 mL), 1-iodooctane (120 mg, 0.50 mmol), allyltributylstannane (330 mg, 1.00 mmol), acrylonitrile (31 mg, 0.59 mmol), and AIBN (33 mg, 0.20 mmol) were placed in a 50-mL stainless steel autoclave lined with a round-bottomed glass tube. The mixture was pressurized with CO (10 atm) and then was stirred at 80° for 8 h. After excess CO was discharged at rt, the benzene was evaporated. The residue was purified by silica gel column chromatography (Et_2O/hexane, 0:100, 10:90) to afford the title product (84 mg, 72%): R_f 0.2 (hexane/Et_2O, 9:1); IR (neat) 2241, 1717, 1644 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 5.79 (m, 1H), 5.21 (d, J = 9.3 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 3.16 (m, 1H), 2.81 (dd, J = 18.0, 6.8 Hz, 1H), 2.67 (dd, J = 18.0, 6.6 Hz, 1H), 2.40 (m, 4H), 1.55 (br m, 2H), 1.27 (br s, 10H), 0.88 (app t, J = 6.3 Hz, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.2, 132.5, 121.1, 119.5, 43.3, 42.9, 35.5, 31.7, 29.2, 29.0 (2C), 25.5, 23.6, 22.6, 14.0; LRMS–EI (*m/z*): $[M]^+$ 235 (2), 156 (29), 141 (45), 137 (37), 109 (58), 96 (38), 94 (32), 80 (36), 71 (96), 58 (100), 57 (82), 55 (37), 43 (77), 41 (76); HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{15}H_{25}NO$, 235.1936; found, 235.1965.

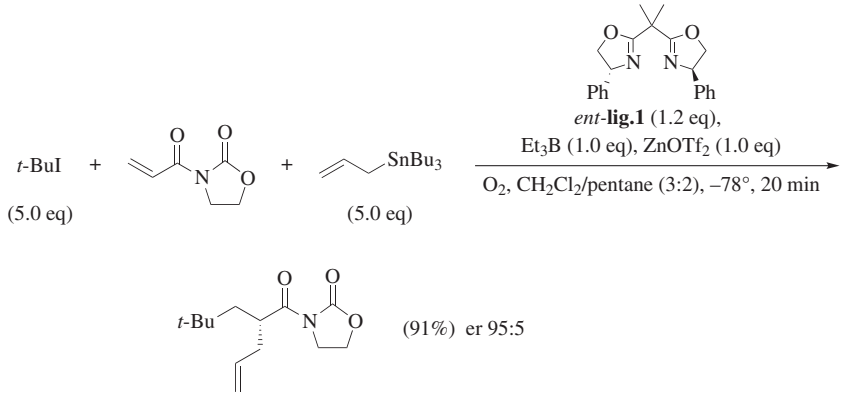


(±)-(2*S)-2-[(2*S**)-Tetrahydropyran-2-yl]-2-[propen-3-yl]-2-methylpropanoic Acid Ethyl Ester [Allylation with 1,2-Asymmetric Induction Mediated by a Lewis Acid].**[179] To a stirred solution of the α-iodoester (148 mg, 0.48 mmol) in dry CH_2Cl_2 (4.8 mL, 0.1 M) at –78° was added $MgBr_2$•OEt_2 (372 mg, 1.44 mmol). The mixture was stirred at –78° for 15 min, and then allyltributyltin (298 μL, 318 mg, 0.96 mmol) and Et_3B (96 μL, 96 μmol, 1.0 M solution in hexanes) were added. The resulting suspension was stirred at –78°, and 0.2 equivalents of Et_3B (96 μL, 96 μmol) was added every 30 min until the reaction was judged to be complete by TLC. 1,3-Dinitrobenzene (16 mg, 0.096 mmol) was then added to the solution, and the mixture was stirred for an additional 15 min at –78°. The reaction mixture

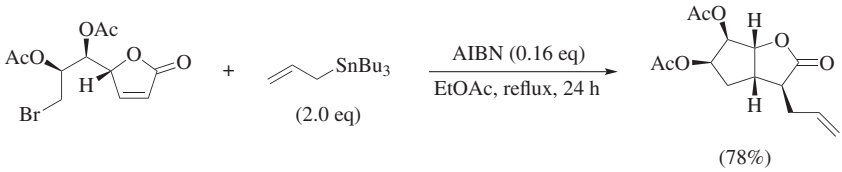
was poured into a saturated $NaHCO_3$ solution and was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Analysis of the crude isolate by GC revealed a 27:1 ratio of *anti*/*syn* products. The major diastereomer was isolated by column chromatography on silica gel (hexanes/EtOAc, 90:10) to afford the title product as a colorless oil (59 mg, 54%): IR (neat) 2930, 2870, 1725, 1640, 1435, 1080, 920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.69–5.63 (m, 1H), 5.07–5.01 (m, 2H), 4.22–4.07 (m, 2H), 3.97–3.93 (m, 1H), 3.52–3.48 (m, 1H), 3.41–3.33 (m, 1H), 2.38 (dd, J = 13.5, 7.2 Hz, 1H), 2.07 (dd, J = 13.5, 7.8 Hz, 1H), 1.89–1.85 (m, 1H), 1.57–1.27 (m, 5H), 1.24 (t, J = 7.1 Hz, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 133.7, 117.8, 82.5, 68.9, 60.1, 50.3, 40.0, 26.0, 25.3, 23.6, 15.9, 14.1; LRMS–FAB (*m/z*): $[M + H]^+$ 227 (100), 199 (13), 185 (33), 151 (38), 135 (28); HRMS (*m/z*): $[M + H]^+$ calcd for $C_{13}H_{23}O_3$, 227.1647; found, 227.1654.



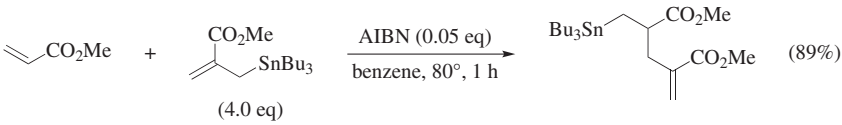
(2*S*,4*R*)-3-(2-Propyl-4-pentenoyl)-4-diphenylmethyl-2-oxazolidinone [Three-Component Diastereoselective Reaction Using a Chiral Auxiliary].[204] To a flask containing the *N*-propenoyloxazolidinone (154 mg, 0.5 mmol), $MgBr_2{\bullet}Et_2O$ (258 mg, 1.0 mmol), and CH_2Cl_2 (5 mL) were added ethyl iodide (425 mg, 2.5 mmol) and allyltributylstannane (333 mg, 1 mmol) at –78° under N_2. Triethylborane (1.0 mL, 1 mmol, 1 M in hexane) was then added. Gaseous O_2 (5 mL) was finally added via syringe over 2 h. The reaction mixture was stirred at –78° until TLC analysis indicated that the *N*-propenoyloxazolidinone had been consumed, and then CH_2Cl_2 (20 mL) was added. The solution was washed with brine (3 × 3 mL), the organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification of the residue by silica gel column chromatography (hexane/EtOAc, 4:1) afforded the title product (175 mg, 93%): mp 103–105°; $[\alpha]^{26}_D$ – 147.270 (*c* 0.605, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.10 (m, 10H), 5.72–5.58 (m, 1H), 5.38–5.30 (m, 1H), 5.09–4.98 (m, 2H), 4.73 (d, J = 5.96 Hz, 1H), 4.42–4.36 (m, 2H), 3.76–3.70 (m, 1H), 2.40 (dt, J = 13.19, 6.60 Hz, 1H), 2.08 (dt, J = 13.92, 6.60 Hz, 1H), 1.65–1.52 (m, 1H), 1.44–1.38 (m, 1H), 1.28–1.19 (m, 2H), 0.88 (t, J = 7.52 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 153.5, 139.9, 138.3, 135.9, 129.6, 129.1, 129.0, 128.7, 128.1, 127.3, 117.2, 65.1, 56.9, 51.3, 42.5, 36.3, 33.6, 20.7, 14.4. Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71. Found: C, 76.41; H, 7.29; N, 3.95.



3-[(2*R*)-2-(2,2-Dimethylpropyl)-1-oxo-4-penten-1-yl]-2-oxazolidinone [Three-Component Enantioselective Reaction].[209] A CH_2Cl_2/pentane solution (7 mL, 3:2) of the chiral bis(oxazoline) ligand *ent*-**lig.1** (56 mg, 0.17 mmol) and $Zn(OTf)_2$ (51 mg, 0.14 mmol) was stirred under Ar at rt for 1 h, and then the *N*-propenoyloxazolidinone (20 mg, 0.14 mmol) was added. The resulting mixture was stirred at rt for 10 min, and then was cooled to –78° for 20 min. *tert*-Butyl iodide (83 μL, 129 mg, 0.70 mmol) and allyltributylstannane (217 μL, 232 mg, 0.70 mmol) were added in one portion via syringe, and the solution was stirred at –78° for 10 min. The resulting solution was purged with dry air for 2 min, and Et_3B (0.14 mL, 0.14 mmol, 1 M in hexane) was added via syringe. The reaction mixture was stirred at –78° under dry air for 20 min, and then Et_3N and H_2O were added. The mixture was extracted with ether (3 × 8 mL), and the crude product was purified by silica gel column chromatography (*n*-pentane/ether, 4:1) to afford the title product as a colorless oil (30 mg, 91%, er 95:5): GC (Chiraldex GTA); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (m, 1H), 5.03 (m, 2H), 4.39 (t, J = 8.13 Hz, 2H), 4.09 (m, 1H), 3.99 (t, J = 8.13 Hz, 2H), 2.38–2.16 (m, 2H), 2.01 (dd, J = 14.11, 10.14 Hz, 1H), 1.29 (dd, J = 14.11, 1.99 Hz, 1H), 0.85 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 153.3, 135.2, 117.2, 61.7, 44.8, 42.9, 39.7, 38.3, 30.7, 29.6; HRMS–FAB (*m/z*): $[M + H]^+$ calcd for $C_{13}H_{22}NO_3$, 240.1600; found, 240.1610.

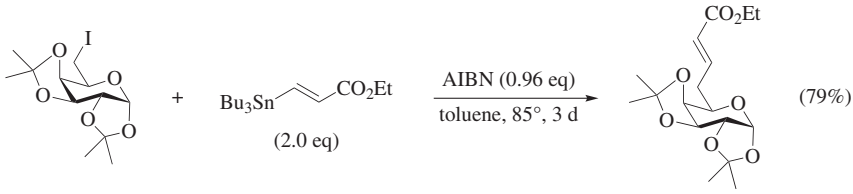


(3*S*,3a*S*,5*R*,6*R*,6a*R*)-5,6-Bis(acetyloxy)hexahydro-3-(2-propen-1-yl)-2*H*-cyclopenta[*b*]furan-2-one [Allylation Following Radical–Alkene Cyclization].[224] 5,6-Di-*O*-acetyl-7-bromo-2,3,7-trideoxy-D-arabino-hept-2-enono-l,4-lactone (1.00 g, 3.1 mmol) was dissolved in dry EtOAc (10 mL) and the resulting solution was heated to reflux. A solution of allyltributylstannane (1.95 mL, 6.3 mmol) and AIBN (0.08g, 0.5 mmol) in dry EtOAc (10.5 mL) was added over 5 h, and the reaction mixture was heated at reflux for an additional 19 h, after which the solution was concentrated to dryness. The residue was dissolved in MeCN (50 mL), and the solution was washed with hexane (4 × 30 mL). The acetonitrile was evaporated, and the crude product was purified by silica gel column chromatography (EtOAc/hexane, 1:2) to afford the title product as a colorless oil (0.68 g, 78%): $[\alpha]^{20}_{D}$ – 86 (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (dddd, *J* = 17.0, 10.5, 7.0, 1.0 Hz, 1H), 5.36 (dt, *J* = 5.5, 4.5 Hz, 1H), 5.21 (t, *J* = 4.5 Hz, 1H), 5.18 (m, 2H), 4.81 (dd, *J* = 8.5, 4.5 Hz, 1H), 2.88 (dddd, *J* = 9.0, 8.5, 5.5, 4.5 Hz, 1H), 2.58 (ddd, *J* = 14.5, 7.0, 4.5 Hz, 1H), 2.50 (dt, *J* = 8.5, 4.5 Hz, 1H), 2.35 (ddd, *J* = 14.5, 8.5, 1.0 Hz, 1H), 2.28 (ddd, *J* = 14.0, 9.0, 4.5 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.89 (dt, *J* = 14.0, 5.5 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.0, 169.5 (2C), 133.2, 118.0, 83.0, 76.6, 72.1, 46.1, 38.3, 35.0, 34.3, 20.1, 19.9. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.33; H, 6.49. Found: C, 59.33; H, 6.49.



2-Methylene-4-[(tributylstannyl)methyl]pentanedioic Acid 1,5-Dimethyl Ester [Allylstannylation Reaction].[265] Under a N_2 atmosphere, a solution of AIBN (4.1 mg, 0.025 mmol), methyl acrylate (43 mg, 0.50 mmol), and 2-carbomethoxyallyltributylstannane (780 mg, 2.0 mmol) in benzene (2.5 mL) was stirred at 80° for 1 h. The resulting reaction mixture was concentrated under reduced pressure. Purification of the crude product by silica gel column chromatography (hexane/ether, 15:1) afforded the title product (210 mg, 89%): bp 150° (0.17 mm Hg); IR (neat) 2955, 2920, 2850, 1733, 1457, 1438, 1220, 1196, 1163, 1147 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.17 (br s, 1H), 5.55 (br s, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 2.84 (dddd, *J* = 8.9, 8.6, 6.6, 5.6 Hz, 1H), 2.63 (ddd, *J* = 13.9, 8.9, 0.7 Hz, 1H), 2.42 (ddd, *J* = 13.9, 5.6, 1.0 Hz, 1H), 1.55–1.23 (m, 12H), 1.11–0.71 (m, 17H);

^{13}C NMR (68.7 MHz, $CDCl_3$) δ 176.9, 167.0, 138.0, 126.9, 51.9, 51.5, 42.5, 38.7, 29.1, 27.4, 13.7, 12.4, 9.3; LRMS–EI (*m/z*): 420 (21), $[M]^+$ 419 (100), 418 (40), 417 (74), 416 (31) 415 (44), 151 (26), 149 (19), 41 (20). Anal. Calcd for $C_{21}H_{40}O_4Sn$: C, 53.07; H, 8.48. Found: C, 53.01; H, 8.50.



(7*E*)-[6,7,8-Trideoxy-1,2,3,4-bis-*O*-(1-methylethylidene)]-α-D-*galacto*-non-7-enopyranuronic Acid Ethyl Ester [Vinylation Reaction].[293] A solution of the iodide (424 mg, 1.14 mmol), ethyl 3-(tributylstannyl)propenoate (887 mg, 2.28 mmol), and AIBN (30 mg, 0.18 mmol) in toluene (1.1 mL) was thoroughly degassed with Ar. The solution was heated at 85° for 3 d; additional AIBN (30 mg, 0.18 mmol) was added every 12 h (0.96 mmol total AIBN). The solvent was removed under reduced pressure, and the resulting material was subjected to silica gel column chromatography (petroleum ether/EtOAc, 95:5) to afford the title product as an oil (309 mg, 79%): $[\alpha]^{21}_D$ – 50.9 (*c* 1.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.96 (d, *J* = 15.7 Hz, 1H), 5.52 (d, *J* = 5.0 Hz, 1H), 4.59 (dd, *J* = 7.7, 2.4 Hz, 1H), 4.30 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.12 (dd, *J* = 7.7, 1.7 Hz, 1H), 3.86 (m, 1H), 2.50 (m, 2H), 1.51 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 149.4, 123.6, 109.3, 108.5, 96.5, 72.2, 70.8, 70.3, 66.4, 60.2, 32.9, 29.1, 26.6, 26.0, 24.9, 24.5; LRMS–CI (NH_3) (*m/z*): $[M + NH_4]^+$ 360, $[M + H]^+$ 343. Anal. Calcd for $C_{17}H_{26}O_7$: C, 59.6; H, 7.7. Found: C, 59.5; H, 7.8.

TABULAR SURVEY

The tables include all reactions reported in the primary literature through the beginning of 2021. Unlike a typical *Organic Reactions* chapter where the tables are organized by substrate class, the tables here are organized by the general type of reaction. Tables 1A–1D contain reactions involving direct intermolecular addition of a radical to an allylstannane. Table 2A has examples of reactions in which an initially formed radical adds to either carbon monoxide or an alkene before reaction with an allylstannane; in Table 2B, addition to both carbon monoxide and an alkene occurs before allylation. Table 3 covers examples wherein an initial radical undergoes a cyclization before intermolecular reaction with an allylstannane. In Table 4, allylation follows other intramolecular processes, including hydrogen-atom abstraction; ring-opening processes; beta-scission; cyclization followed by a 1,3-stannyl shift, 1,2-silyl shift, 1,2-germyl shift, or a hydrogen-atom abstraction; 1,4-acyl rearrangement; or Dowd–Beckwith-type rearrangement. Tables 5A and 5B include reactions that terminate with an intramolecular addition onto an allyl- or vinylstannane, either by a radical formed directly from a stannane-containing substrate (Table 5A) or by a radical that is generated by addition of a radical formed from a stannane-containing substrate to an alkene (Table 5B). Table 6 includes reactions that begin with addition of a stannyl radical to the alkene, alkyne, or carbonyl group of a substrate, followed by either (i) direct addition to an allyl- or vinylstannane in an inter- or intramolecular process, or (ii) a cyclization or other rearrangement before addition to a stannane. Table 7 lists reactions involving direct intermolecular addition of radicals to stannyl enolates. Tables 8, 9, and 10 contain intermolecular vinylation, allenylation, and alkynylation and propargylation reactions, respectively. Tables 11A–C include examples of reactions of heteroatom-centered radicals (boron, nitrogen, phosphorus, sulfur, selenium, tellurium). Table 11A contains allylation reactions, Table 11B includes vinylations, and Table 11C contains allenylation and alkynylation reactions.

For Tables 1A–1D, 3, 4, 5A and 7–11, the entries are listed in order of increasing carbon count for the reagent from which the radical is initially generated. For Tables 2A, 2B, 5B, and 6, the entries are organized first by increasing carbon count of the substrate to which the initial radical adds and then by the carbon count of the species that serves as the initial radical precursor. Carbon counts do not include protecting groups, chiral auxiliaries, simple *N*-substituents in amines, *N*-substituents in amides, *O*-substituents in ethers and esters, *S*-substituents in thioethers, sulfoxides or sulfones, *Se*-substituents in selenides, or carbons included in groups lost upon formation of the initial radical. The ordering of entries within a carbon count is based first on structural similarities within the substrates and then by similarities in the stannane reagent.

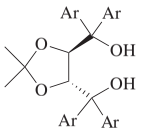
The tables are preceded by a chart showing the structures of chiral ligands and additives used in the tables. The stereodescriptors with the ligand numbers are assigned from left to right for the stereocenters in the drawn structures.

In addition to those listed in "*The Journal of Organic Chemistry* Standard Abbreviations and Acronyms," the following abbreviations are used in the Tabular Survey and text.

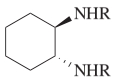
ACCN	1,1-azobis(1-cyanocyclohexane)
Ada	1-adamantanyl
AIBME	dimethyl 2,2′-azobisisobutyrate
All	allyl
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthalene
BOM	benzyloxymethyl
BTF	benzotrifluoride; trifluorotoluene
Cat	catechol
CSA	camphorsulfonic acid
c-C_5H_9	cyclopentyl
c-C_6H_{11}	cyclohexyl
dap	2,9-bis(4-methoxyphenyl)-1,10-phenanthroline
dF(CF_3)ppy	2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine
DLP	dilauroyl peroxide
DMT	4,4′-dimethoxytrityl
dNbpy	4,4′-dinonyl-2,2′bipyridyl
dpm	dipivaloylmethane; 2,2,6,6-tetramethyl-3,5-heptanedionate
dtbbpy	4,4′-di-*tert*-butyl-2,2′-dipyridyl
fod	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate
HMTETA	1,1,4,7,10,10-hexamethyltriethylenetetramine
ICP	inductively coupled plasma
Im	imidazol-1-yl
MABR	methylaluminum bis[2,6-di(*tert*-butyl)-4-bromophenoxide]
MAD	methylaluminum bis[2,6-di(*tert*-butyl)-4-methylphenoxide]
MAP	methylaluminum bis(phenoxide)
MCPBA	3-chloroperoxybenzoic acid
Mes-Acr^+	9-mesityl-10-methylacridinium
MS	molecular sieves
MW	microwave irradiation
NHS	*N*-hydroxysuccinimide
o/n	overnight
PhthN	phthalimido
pic	2-pyridinecarboxylate
PMDETA	*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine

PMP	4-methoxyphenyl
PNB	4-nitrobenzyl
ppy	2-phenylpyridinato
pybox	2,6-pyridine-bis(oxazoline)
SEM	*N*-2-(trimethylsilyl)ethoxymethyl
TBAP	tetrabutylammonium perchlorate
TBDPS	*tert*-butyldiphenylsilyl
Teoc	2-(trimethylsilyl)ethoxycarbonyl
4-Tol	4-methylphenyl
V-70	2,2′-azobis(2-cyano-4-methoxybutane)

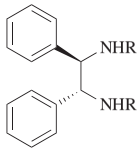
CHART 1. CHIRAL LIGANDS AND ADDITIVES USED IN THE TABLES



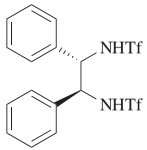
	Ar
(*R*,*R*)-**L1a**	Ph
(*R*,*R*)-**L1b**	1-$C_{10}H_7$
(*R*,*R*)-**L1c**	2-$C_{10}H_7$



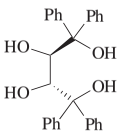
	R
(*R*,*R*)-**L2a**	H
(*R*,*R*)-**L2b**	Ts
(*R*,*R*)-**L2c**	Tf



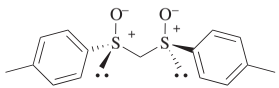
	R
(*R*,*R*)-**L3a**	H
(*R*,*R*)-**L3b**	Ts
(*R*,*R*)-**L3c**	Tf
(*R*,*R*)-**L3d**	$CF_3CH_2SO_2$
(*R*,*R*)-**L3e**	$C_6F_5SO_2$



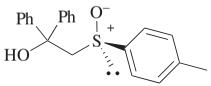
(*S*,*S*)-**L3c**



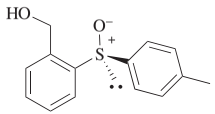
(*R*,*R*)-**L4**



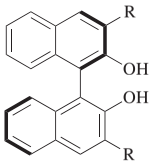
(*S*,*S*)-**L5**



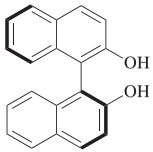
(*R*)-**L6**



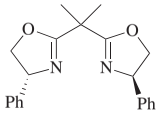
(*S*)-**L7**



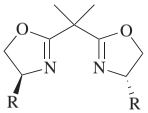
	R
(*R*)-**L8a**	H
(*R*)-**L8b**	Ph_3Si



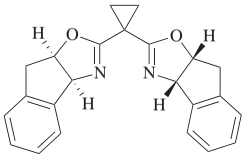
(*S*)-**L8a**



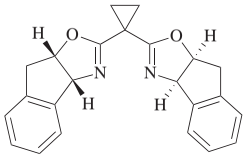
(*R*,*R*)-**L9a**



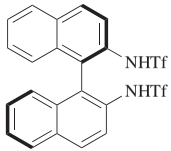
	R
(*S*,*S*)-**L9a**	Ph
(*S*,*S*)-**L9b**	*t*-Bu
(*S*,*S*)-**L9c**	*i*-Pr
(*S*,*S*)-**L9d**	Bn



(*S*,*R*,*R*,*S*)-**L10**

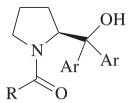


(*R*,*S*,*S*,*R*)-**L10**

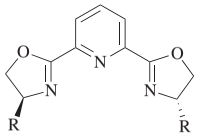


(*R*)-**L11**

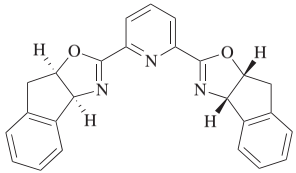
CHART 1. CHIRAL LIGANDS AND ADDITIVES USED IN THE TABLES (*Continued*)



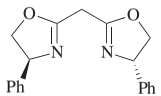
	R	Ar
(*S*)-**L12a**	EtO	Ph
(*S*)-**L12b**	*i*-BuO	Ph
(*S*)-**L12c**	*t*-BuO	Ph
(*S*)-**L12d**	NMe_2	Ph
(*S*)-**L12e**	BnO	Ph
(*S*)-**L12f**	EtO	2-$C_{10}H_7$
(*S*)-**L12g**	EtO	3,5-$Me_2C_6H_3$



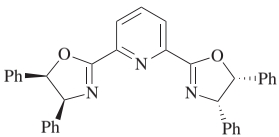
	R
(*S*,*S*)-**L13a**	*i*-Pr
(*S*,*S*)-**L13b**	Ph
(*S*,*S*)-**L13c**	*t*-Bu



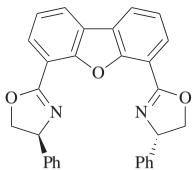
(*S*,*R*,*R*,*S*)-**L14**



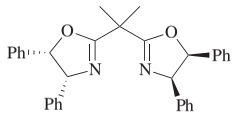
(*S*,*S*)-**L15**



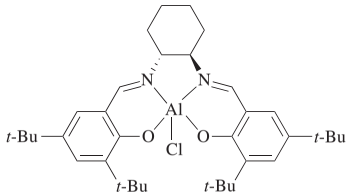
(*R*,*S*,*S*,*R*)-**L16**



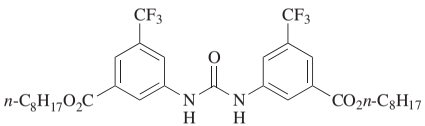
(*S*,*S*)-**L17**



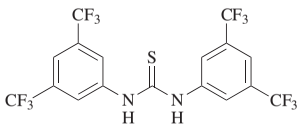
(*S*,*R*,*R*,*S*)-**L18**



(*R*,*R*)-**A1**



A2



A3

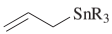
TABLE 1. DIRECT ALLYLATIONS
A. ACYCLIC SUBSTRATES

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

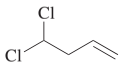
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_1

$CHCl_3$

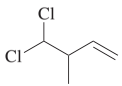


Conditions, initiator, solvent



R	Conditions	Initiator	Solvent	Temp (°)	Time (h)		Refs.
Me	—	$(PhCO_2)_2$	neat	80	15	(37)	1
Bu	$h\nu$	AIBN	neat	—	5	(41)[a]	21
Bu	—	AIBN	benzene	80	3	(40)	37
Bu	$h\nu$	none	benzene	22	1	(28)	37

Conditions, initiator, solvent



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Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	neat	80	3	(22)
$h\nu$	none	benzene	22	5	(15)

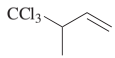
CCl_4

Conditions, initiator, solvent

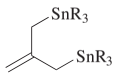
R	Conditions	Initiator	Solvent	Temp (°)	Time (h)		Refs.
Me	—	$(PhCO_2)_2$	neat	80	15	(47)	1
Bu	—	AIBN	neat	80	24	(70)	21
Bu	—	AIBN	benzene	80	3	(73)	37
Bu	$h\nu$	none	benzene	22	1	(62)	37
Bu	—	none	neat	80	3	(70)	37

CCl_4

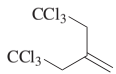
Conditions, initiator, solvent



Conditions	Initiator	Solvent	Temp (°)	Time (h)		
hν	AIBN	neat	—	36	(55)	21
—	AIBN	toluene	80	3	(26)	37
—	AIBN	neat	80	3	(45)	37
hν	none	benzene	22	5	(67)	37

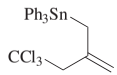


AIBN, neat, 70°, 60 h



I

+

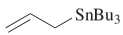


II

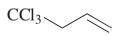
38

R	**I**	**II**
Me	(62)	(0)
Ph	(65)	(18)

CCl_3SO_2Cl



hν, benzene, 6 h



(31)[a]

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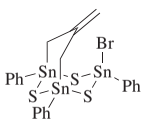
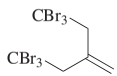
CBr_4



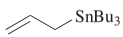
AIBN, benzene, 95°



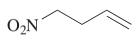
(60)

424

O_2N Br



AIBN, 100°, 15 h



(35)

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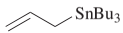
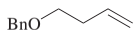
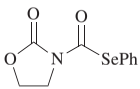
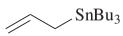
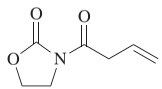
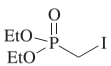
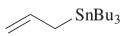
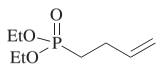
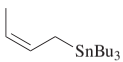
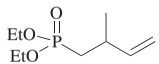
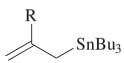
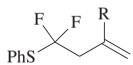
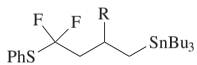
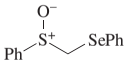
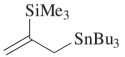
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

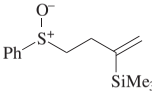
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_1				
		$ZnCl_2 \bullet OEt_2$, CH_2Cl_2, –78°	 (83)	51
		AIBN	 (89)	112
		Conditions, initiator, MeCN, 4 h		425
			Conditions / Initiator / Temp / (%): — / AIBN / 80° / (88); *hν* / none / rt / (84)	
		Conditions, initiator, MeCN, 4 h		425
			Conditions / Initiator / Temp / (%): — / AIBN / 80° / (8); *hν* / none / rt / (8)	
		Initiator, additive, solvent	 **I** +  **II**	87

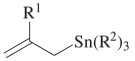
R	Initiator	Additive	Solvent	Temp	Time	I	II
H	SmI_2	none	THF	0°; then rt	20 min; then 2 h	(72)	(—)
H	AIBN	none	benzene	80°	10 h	(70)	(—)
H	Et_3B, O_2	none	CH_2Cl_2	rt	o/n	(61)	(—)
MeO_2C	AIBN	none	benzene	80°	10 h	(40)	(—)
MeO_2C	AIBN	Bu_3SnH	benzene	80°	10 h	(12)	(47)
MeO_2C	Et_3B, O_2	none	CH_2Cl_2	rt	o/n	(32)	(—)
MeO_2C	Et_3B, O_2	Bu_3SnH	CH_2Cl_2	rt	o/n	(12)	(12)

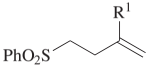
$h\nu$, AIBN, benzene, 10°



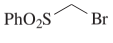
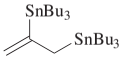
(75) 61



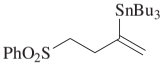
$h\nu$, AIBN, solvent



R^1	R^2	Solvent	Temp (°)	Time (h)		
Me_3Si	Bu	benzene	10	—	(63)	61
Me_3SiCH_2	Bu	DME	15–20	12	(81)	36
Me_3SiCH_2	Ph	DME	15–20	12	(85)	36

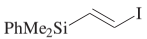
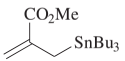
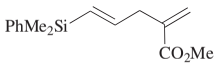
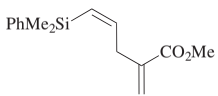



$h\nu$, toluene, 60°, 0.5 h

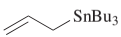
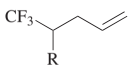


(56)[b] 426

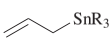
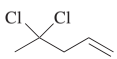
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_2				
		Initiator, benzene	 **I** +  **II**	104

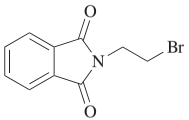
Initiator	Temp (°)	Time (h)	**I + II**	**I/II**
AIBN	80	1	(65)	49:1
Et_3B	25	5	(60)	>99:1

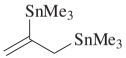
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	 *x* eq	AIBN, benzene, 80°		88

R	*x*	Time (h)	
4-MeC_6H_4S	2	9	(21)
4-MeC_6H_4S	4	9	(45)
4-MeC_6H_4SO	2	9	(0)
4-$MeC_6H_4SO_2$	2	3	(89)
4-$MeC_6H_4SO_2$	4	3	(91)

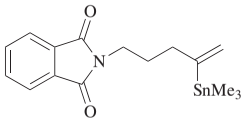
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
$MeCCl_3$		Conditions, initiator, solvent		

R	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
Me	—	$(PhCO_2)_2$	neat	80	15	(14)	1
Bu	—	AIBN	benzene	80	3	(42)	37
Bu	$h\nu$	none	benzene	22	3	(57)	37





AIBN, benzene, 80°, 18 h



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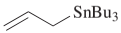
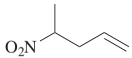


AIBN, 100°, 15 h



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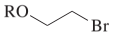
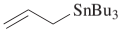
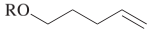


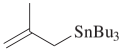


AIBN, toluene, 80°

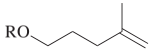


R	
THP	(98)[c]
Ph	(65)[c]

3, 4
4



AIBN, toluene, 80°

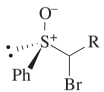
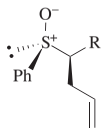
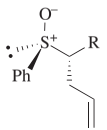


R	
THP	(89)[c]
Ph	(89)[c]

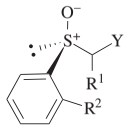
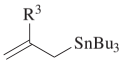
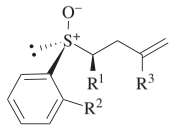
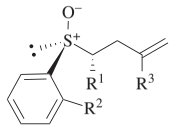
4

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2 		*h*ν, AIBN, solvent	 **I** +  **II**	194

R	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**
Me_2NCO	toluene	25	1	(>90)	10.1:1
Me_2NCO	toluene	–30	4	(>90)	13.9:1
Me_2NCO	MeCN	25	1	(>90)	5.3:1
Me_2NCO	EtOH	25	1	(>90)	4.4:1
Me_2NCO	CF_3CH_2OH	25	1	(>90)	1.8:1
MeO_2C	toluene	25	1	(>90)	8.1:1
MeO_2C	toluene	0	2	(>90)	11.4:1
MeO_2C	toluene	–35	3	(>90)	13:1
MeO_2C	toluene	–78	4	(>90)	20:1

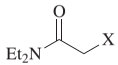
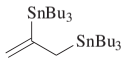
C_{2-5} 		*h*ν, AIBN, solvent	 **I** +  **II**	

R^1	R^2	Y	R^3	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
Me	H	SePh	H	benzene	10	12	(64)	1.6:1	427
Me	H	SePh	TMS	benzene	10	12	(80)	1.8:1	427
Me	H	SePh	MeO_2C	benzene	10	—	(67)	1:1	195
Me	Cl	SePh	H	benzene	10	12	(54)	7.3:1	428
Me	Cl	SePh	MeO_2C	benzene	10	12	(66)	4:1	428
Me	Cl	SePh	TMS	benzene	10	12	(60)	9:1	428
Me	Cl	SePh	TMS	toluene	–70	12	(20)	19:1	428
Me	Br	SePh	TMS	benzene	10	12	(47)	9:1	428
Me	HO	SePh	TMS	benzene	10	12	(50)	1.9:1	428
Me	THPO	SePh	TMS	benzene	10	12	(55)[d]	3.8:1	428
Me	MOMO	SePh	TMS	benzene	10	12	(60)	4.6:1	428
Me	*n*-PrO	SePh	TMS	benzene	10	12	(70)	4.3:1	428
Me	PivO	SePh	TMS	benzene	10	12	(65)	2.4:1	428
Me	TBSO	SePh	TMS	benzene	10	12	(62)	2.1:1	428
Me	TsO	SePh	TMS	benzene	10	12	(74)	4.3:1	428
CF_3	H	Cl	H	benzene	10	12	(61)	1:4.3	427
CF_3	H	Cl	TMS	benzene	10	12	(83)	1:4.6	427
Et	H	SePh	MeO_2C	benzene	10	—	(63)	1:1.6	195
Et	Cl	SePh	MeO_2C	benzene	10	—	(73)	2.6:1	195
i-Pr	H	SePh	MeO_2C	benzene	10	—	(86)	1:3.5	195
i-Pr	Cl	SePh	MeO_2C	benzene	10	—	(82)	1:1.5	195
t-Bu	H	SePh	MeO_2C	benzene	10	—	(61)	1:19	195

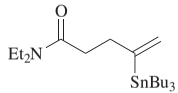
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
PhO_2S, Cl	$SiMe_3$, $SnPh_3$	*h*ν, AIBN, DME, 15–20°, 24 h	PhO_2S, $SiMe_3$ (70)	36
NC, Cl	$SnBu_3$	Conditions, initiator, benzene, 3 h	NC	37
		Conditions: — / *h*ν; Initiator: AIBN / none; Temp (°): 80 / 22; (40) / (51)		
	$SnBu_3$	AIBN, neat, 80°, 3 h	NC (49)	37
NC, Br	$SiMe_3$, $SnBu_3$	Conditions, initiator, benzene	NC, $SiMe_3$	429
		Conditions: — / *h*ν; Initiator: AIBN / none; Temp (°): 80 / 0; Time: 15 h / 10 min; (90) / (85)		
	$SnBu_3$, $SnBu_3$	*h*ν, toluene, 60°, 0.5 h	NC, $SnBu_3$ (89)[b]	426

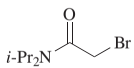
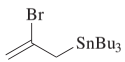



$h\nu$, $(Bu_3Sn)_2$, toluene

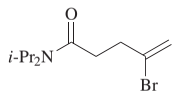


426

X	Temp	Time (min)	
Cl	rt	60	(31)
I	60–80°	5	(71)
I	60°	30	(61)[b]

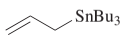



AIBN, toluene, 80°, 2–4 h

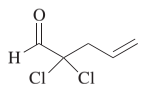


(73)

430



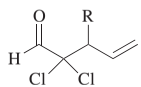
AIBN, 200°, 15 h



(13)

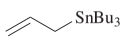
21

AIBN, 200°, 5 h

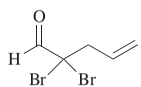


R	
Me	(70)
Ph	(80)[c]

21



AIBN, 100°, 17 h



(10)[a]

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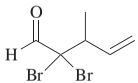
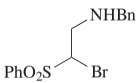
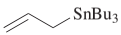
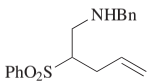
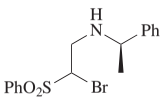
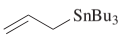
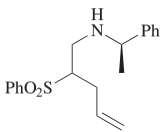
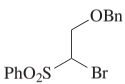
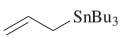
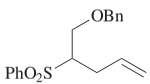
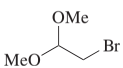
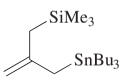
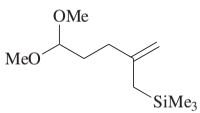
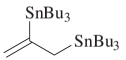
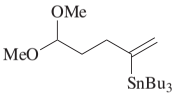
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
		AIBN, 150°, 3 h	 (33)[a]	21
		AIBN, benzene, 80°, 4 h	 (70)	89
		AIBN, benzene, 80°, 4 h	 (72) dr = 1.5:1	89
		AIBN, benzene, 80°, 2 h	 (85)	89
		Conditions, initiator, benzene		429

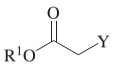
Conditions	Initiator	Temp (°)	Time (h)	
—	AIBN	80	12	(63)
hν	none	0	1	(56)



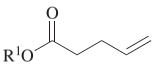
Et_3B, O_2, $(Bu_3Sn)_2$, THF, 0° to rt, 0.5 h



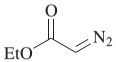
(31) 426



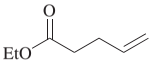
Conditions, initiator, solvent



R^1	Y	R^2	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
Me	Cl	Me	—	$(PhCO_2)_2$	neat	80	15	(24)	1
Me	Cl	Bu	—	AIBN	benzene	80	3	(53)	37
Me	Cl	Bu	*hν*	none	benzene	22	1	(54)	37
Me	Br	Bu	—	AIBN	benzene	80	3	(60)	37
Me	Br	Bu	*hν*	none	benzene	22	1	(70)	37
Et	Cl	Bu	—	AIBN	neat	200	6	(30)[a]	21
Et	SePh	Bu	*hν*	none	benzene	—	1	(74)	77
Et	Br	$CH_3((CH_2)_2O)_2O(CH_2)_3$	—	AIBN	benzene	80	16	(44)	121
Ph	Br	$CF_3(CF_2)_5(CH_2)_3$	*hν*	none	BTF	25	3–30	(72)	123
$PhCH_2$	Br	Bu	*hν*	$Cu(dap)_2Cl$	MeCN	rt	8	(80)	47



1. AIBN, benzene, 80°, 3 h
2. KF, H_2O



(82)[e] 64

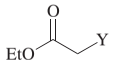
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

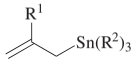
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

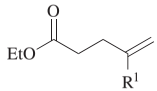
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_2

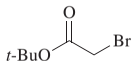


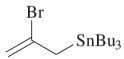


Conditions, initiator, benzene

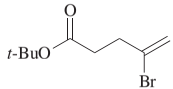


Y	R^1	R^2	Conditions	Initiator	Temp	Time		Refs.
PhSe	Me	Bu	*h*ν	none	—	30 min	(87)	129
Br	Me_3SiCH_2	Bu	—	AIBN	80°	12 h	(83)	429
Br	Me_3SiCH_2	Bu	*h*ν	none	0°	1 h	(80)	429
Br	EtO_2C	$CH_3((CH_2)_2O)_2O(CH_2)_3$	—	AIBN	80°	16 h	(30)	121
Br	EtO_2C	$CH_3((CH_2)_2O)_2O(CH_2)_3$	—	Et_3B/O_2	rt	10 min	(60)	121

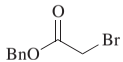


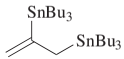


AIBN, toluene, 80°, 2–4 h

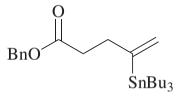


(61) 430



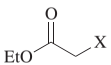


*h*ν, $(Bu_3Sn)_2$, toluene

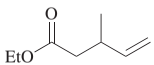


426

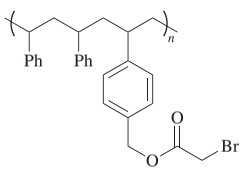
Temp	Time (min)	
rt	30	(81)
60°	60	(73)[b]

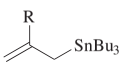


AIBN, solvent

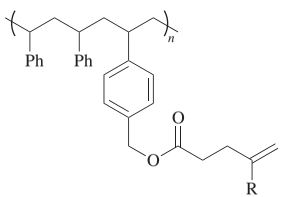


X	Solvent	Temp (°)	Time (h)		
Cl	—	200	15	(0)[a]	21
Br	neat	80	3	(36)	37

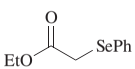


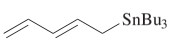


AIBN, benzene, 80°, 12 h

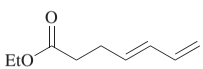


R		
H	(96)	115
Me	(98)	

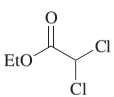


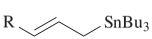


*h*ν, benzene, 1.8 h

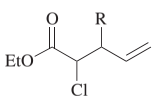


(93) 129

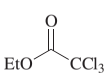


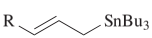


AIBN, 200°, 4 h

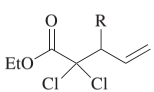


R		
H	(36)[a]	21
Me	(22)[a]	



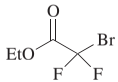
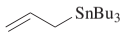
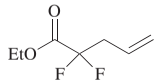
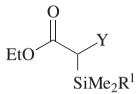
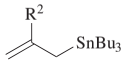
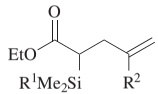


AIBN, 200°, 4 h

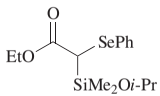
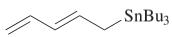
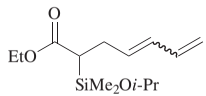
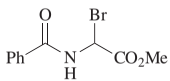
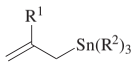
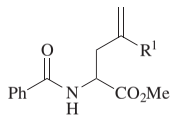


R		
H	(52)	21
Me	(50)	

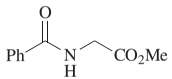
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

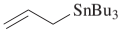
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
		Cu, DMSO, 55°, 24 h	 (9)	431, 432
		Conditions, initiator, benzene		433

R^1	Y	R^2	Conditions	Initiator	Temp (°)	Time (h)	
i-PrO	PhSe	Me	—	AIBN	80	2	(58)
i-PrO	PhSe	MeO_2C	—	AIBN	80	2	(67)
i-PrO	PhSe	Me_3Si	—	AIBN	80	2	(44)
t-BuO	Cl	H	—	AIBN	80	2	(86)
t-BuO	Br	H	—	AIBN	80	2	(97)
t-BuO	PhSe	H	—	AIBN	80	2	(95)
Ph	PhSe	H	—	AIBN	80	2	(65)
Ph	PhSe	H	*hν*	none	20	—	(68)

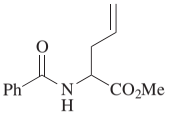
	 (*E*)/(*Z*) = 4.9:1	AIBN, benzene, 80°, 2 h	 (62)	433
		AIBN, toluene, 85°		45

R^1	R^2	Time (h)	
H	Ph	2	(65)
Cl	Bu	2	(50)
EtO_2C	Bu	0.5	(67)
NC–	Bu	1	(74)

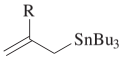




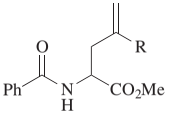
1. $h\nu$, NBS, CH_2Cl_2, 40°
2. Allylstannane, $h\nu$, CH_2Cl_2, 25°



(62)[e] 434

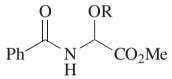


1. $h\nu$, NBS, CCl_4, 77°
2. Allylstannane, AIBN, benzene, 80°, 5 h

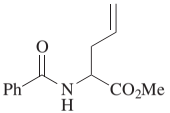


R	
H	(63)[e]
Me	(56)[e]

136



AIBN, benzene, 80°



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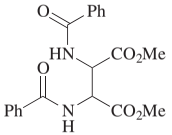

I **II** dr = 1:1

R	**I**	**II**
Me	(34)	(tr)
Bz	(47)	(16)

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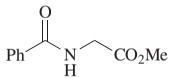
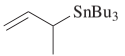
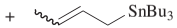
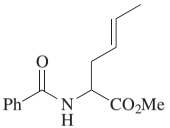
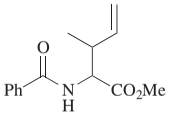
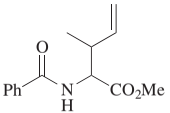
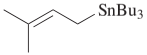
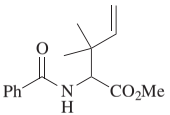
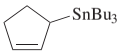
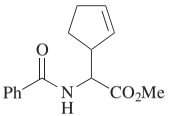
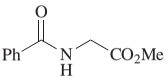
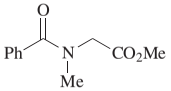
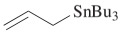
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

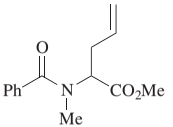
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
	 **I** +  **II** **I/II** = 40:60	1. *h*ν, NBS, CCl_4, 76°, 0.5 h 2. Allylstannanes, AIBN, benzene, 80°, 5 h	 (19)[e] +  (5)[e]	136
	(*E*)/(*Z*) = 1:1	1. *h*ν, NBS, CCl_4, 76°, 0.5 h 2. Allylstannane, AIBN, benzene, 80°, 5 h	 (57)[e] dr = 1:1	136
		1. *h*ν, NBS, CCl_4, 76°, 0.5 h 2. Allylstannane, AIBN, benzene, 80°, 5 h	 (15)[e]	136
		1. *h*ν, NBS, CCl_4, 76°, 0.5 h 2. Allylstannane, AIBN, benzene, 80°, 5 h	 (37)[e] dr = 3:1 +  (19)[e]	136



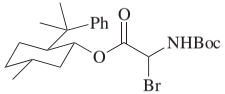


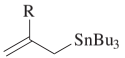
1. $h\nu$, NBS, CH_2Cl_2, 40°
2. Allylstannane, $h\nu$, 25°



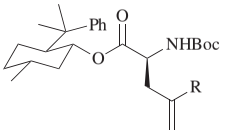
(58)[e]

434



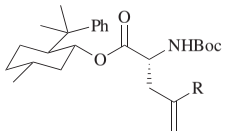


AIBN, benzene



I

+



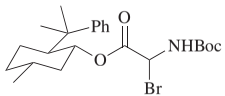
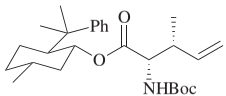
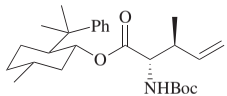
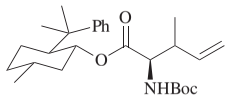
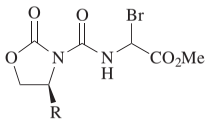
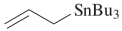
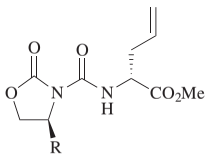
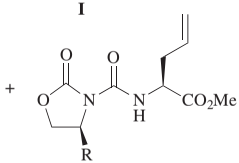
II

137, 138

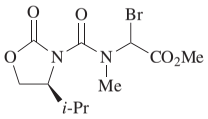
R	Temp (°)	Time (h)	**I + II**	**I/II**
H	80	—	(78)	11.5:1
H	20	16	(85)	24:1
H	5	—	(49)	15.7:1
Me	20	16	(81)	19:1

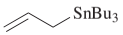
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

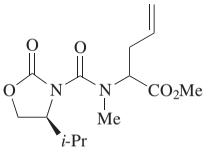
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2 		AIBN, benzene, 20°, 16 h	 **I** +  **II** +  **III** **I + II + III** (83) **I/II/III** = 8.0:5.3:1	137, 138
		Conditions, initiator, Lewis acid (x eq), CH_2Cl_2	 **I** +  **II**	50, 51

R	Conditions	Initiator	Lewis Acid	x	Temp (°)	Time (min)	**I + II**	**I/II**
i-Pr	—	none	none	—	–50	10	(11)	—
i-Pr	$h\nu$	AIBN	none	—	–50	10	(25)	—
i-Pr	—	none	none	—	–78	10	(0)	—
i-Pr	—	none	none	—	–78 to rt	—	(56)	1.1:1
i-Pr	—	AIBN	none	—	80	60	(66)	1.1:1
i-Pr	—	none	$ZnCl_2 \bullet OEt_2$	2	–78	10	(40)	13.3:1
i-Pr	—	none	$ZnCl_2 \bullet OEt_2$	2	–78	60	(85)	6.7:1
i-Pr	—	none	$ZnCl_2 \bullet OEt_2$	0.1	–78	60	(65)	2:1
i-Pr	$h\nu$	AIBN	$ZnCl_2 \bullet OEt_2$	2	–78	10	(60)	—
i-Bu	—	none	$ZnCl_2 \bullet OEt_2$	2	–78 to rt	—	(83)	1.5:1
t-Bu	—	none	$ZnCl_2 \bullet OEt_2$	2	–78 to rt	—	(100)	2.3:1
$PhCH_2$	—	none	$ZnCl_2 \bullet OEt_2$	2	–78 to rt	—	(92)	2.8:1





Initiator, CH_2Cl_2

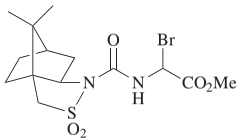
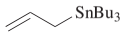
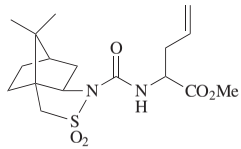


51

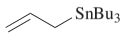
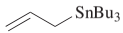
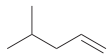
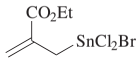
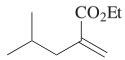
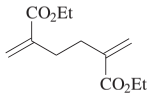
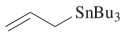
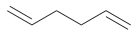
Initiator	
none	(0)
$ZnCl_2 \bullet OEt_2$	(31)

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2 		Initiator, CH_2Cl_2		51

Initiator	Temp (°)		dr
none	rt	(85)	1.3:1
none	–78	(0)	—
$ZnCl_2 \bullet OEt_2$	–78 to rt	(70)	1.1:1
$EtAlCl_2$	–78 to rt	(54)	1:2.8
Me_2AlCl	–78 to rt	(74)	1:1.3

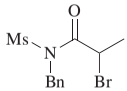
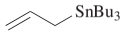
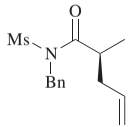
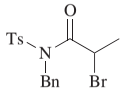
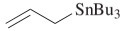
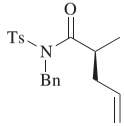
C_3 *n*-PrI		*h*ν, AIBN, 12 h	(32)	21
		*h*ν, benzene, rt	 Time (h): 5 (22)[f]; 29 (32)[f]	285
		AIBN, benzene, 80°, 12 h	 (11) +  (69)	128, 436
		*h*ν, AIBN, 24 h	 (60)[a]	21

$CF_3CF_2CF_2I$	$SnBu_3$	AIBN, neat, 70°, 5 h	$CF_3CF_2CF_2$	(36)	98
F, CF_3, CF_3, I	$SnBu_3$	AIBN, neat, 70°, 5 h	F, CF_3, CF_3	(37)	98
Br, NO_2	$SnBu_3$	AIBN, neat, 100°, 15 h	NO_2	(60)	86
O_2N, X	$SnBu_3$	Conditions, initiator, solvent	O_2N		86

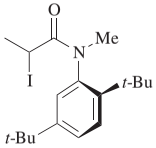
X	Conditions	Initiator	Solvent	Temp (°)	Time (h)	
Cl	—	AIBN	neat	100	24	(65)
Br	—	AIBN	neat	100	24	(67)
Br	$h\nu$	none	benzene	25	10	(65)
I	—	AIBN	neat	100	24	(0)

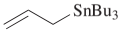
t-Bu, *t*-Bu, Si, O, H, I	$SnBu_3$	AIBN, benzene, 80°	*t*-Bu, *t*-Bu, Si, O, H (50)[c] + *t*-Bu, *t*-Bu, Si, O, I (19)[c] + *t*-Bu, *t*-Bu, Si, O, H (12)[c]			437
t-BuO, Br	$SnBu_3$	AIBN, benzene, 80°, 36 h	*t*-BuO	(50)		438

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

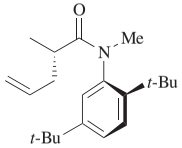
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Et_3B, Ti(O*i*-Pr)$_4$, (*R*,*R*)-**L1a**, CH_2Cl_2, –78°, 3 h	 (83) er = 52.5:47.5	215
		Et_3B, Lewis acid, ligand, CH_2Cl_2, –78°, 3 h		215

Lewis Acid	Ligand		er
Et_3Al	(*R*,*R*)-**L2a**	(72)	76.5:23.5
Et_3Al	(*R*,*R*)-**L2b**	(68)	80.0:20.0
Et_3Al	(*R*,*R*)-**L2c**	(83)	79.0:21.0
Et_3Al	(*R*,*R*)-**L3a**	(88)	76.5:23.5
Et_3Al	(*R*,*R*)-**L3b**	(80)	82.0:18.0
Et_3Al	(*R*,*R*)-**L3c**	(83)	81.5:18.5
Ti(O*i*-Pr)$_4$	(*R*,*R*)-**L1a**	(44)	75.0:25.0
Ti(O*i*-Pr)$_4$	(*R*,*R*)-**L4**	(52)	76.0:24.0
$Mg(OTf)_2$	(*S*,*S*)-**L5**	(65)	76.0:24.0
$Mg(OTf)_2$	(*R*)-**L6**	(41)	91.5:8.5
$Mg(OTf)_2$	(*S*)-**L7**	(64)	75.0:25.0



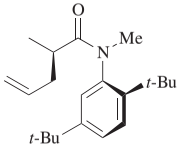


Not reported



I

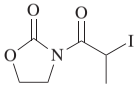
+

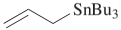


II

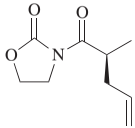
I + **II** (—) **I/II** = 13.3:1

206



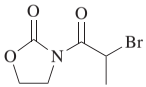


hν, AIBN, Me_3Al, ligand, CH_2Cl_2, 10°, 9 h

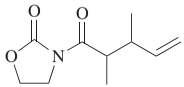


Ligand		er
(*S*)-**L8a**	(90)	50.0:50.0
(*S*,*S*)-**L3c**	(89)	60.0:40.0
(*R*,*R*)-**L1b**	(88)	57.5:42.5

213

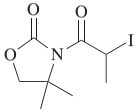


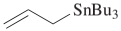
Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2/THF, –78°, 3 h



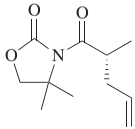
(78) dr = 3:1

26





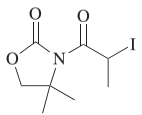
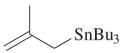
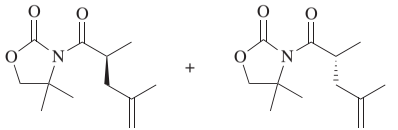
Et_3B, O_2, Me_3Al, (*R*,*R*)-**L1b**, CH_2Cl_2, –78°, 20 min



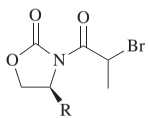
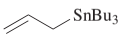
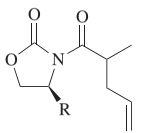
(90) er = 66.0:34.0

213

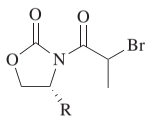
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

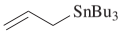
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Conditions, initiator, R_3Al, ligand	 **I** + **II**	213

Conditions	Initiator	R	Ligand	Temp (°)	Time	**I + II**	**I/II**
*h*ν	AIBN	Me	(*S*)-**L8a**	10	9 h	(92)	1:1.1
—	Et_3B, O_2	Me	(*S*)-**L8a**	–78	20 min	(93)	1:1.2
*h*ν	AIBN	Me	(*S*,*S*)-**L3c**	10	9 h	(93)	1.2:1
—	Et_3B, O_2	Me	(*S*,*S*)-**L3c**	–78	20 min	(80)	1.2:1
*h*ν	AIBN	Me	(*R*,*R*)-**L1a**	10	9 h	(80)	1:1
*h*ν	AIBN	Me	(*R*,*R*)-**L1b**	10	9 h	(95)	1:1.6
—	Et_3B, O_2	Me	(*R*,*R*)-**L1b**	–78	20 min	(93)	1:2
—	Et_3B, O_2	Me	(*R*,*R*)-**L1c**	–78	20 min	(93)	1:1
—	Et_3B, O_2	Et	(*R*,*R*)-**L1c**	–78	20 min	(90)	1:1.2

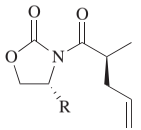
		Et_3B, O_2, Lewis acid, CH_2Cl_2, –78°, 2 h		202

R	Lewis Acid		dr
i-Pr	none	(—)	1:1
i-Pr	$MgBr_2$	(85)	2.8:1
Ph	none	(—)	1.5:1
Ph	$MgBr_2$	(92)	3:1



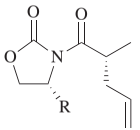


Et_3B, O_2,
Lewis acid (x eq),
solvent, –78°, 2 h



I

+



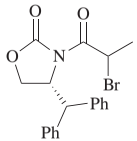
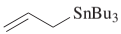
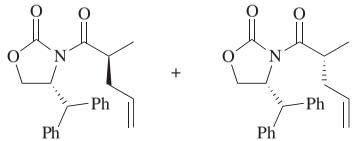
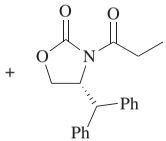
II

202

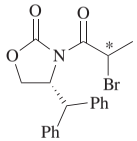
R	Lewis Acid	x	Solvent	**I + II**	**I/II**
Bn	none	—	CH_2Cl_2	(—)	1:1
Bn	$MgBr_2$	2	CH_2Cl_2	(84)	17:1
Bn	$Sc(OTf)_3$	1	Et_2O	(91)	58:1
CH_2CPh_3	none	—	CH_2Cl_2	(—)	1:1
CH_2CPh_3	$MgBr_2$	2	CH_2Cl_2	(94)	>100:1
CH_2CPh_3	$Sc(OTf)_3$	1	Et_2O	(88)	>100:1

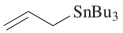
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

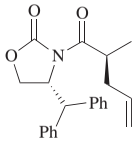
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Et_3B, O_2, Lewis acid (x eq), solvent	 **I** + **II** +  **III**	202

Lewis Acid	x	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	**III**
none	—	CH_2Cl_2	–78	3	(93)	1:1.8	(0)
$BF_3{\bullet}OEt_2$	2	CH_2Cl_2	–78	2.5	(85)	1:1.4	(0)
Et_2AlCl	2	CH_2Cl_2	–78	3	(44)	1.8:1	(0)
$ZnCl_2$	2	CH_2Cl_2	–78	2	(95)	6:1	(0)
$Zn(OTf)_2$	2	CH_2Cl_2/THF (1:1)	–78	2	(86)	7.6:1	(0)
MgI_2	2	CH_2Cl_2	–78	2	(57)	>100:1	(39)
$MgBr_2$	2	CH_2Cl_2	–78	2	(94)	>100:1	(0)
$MgBr_2$	2	CH_2Cl_2	25	2	(94)	30:1	(0)
$Yb(OTf)_3$	1	CH_2Cl_2/THF (1:1)	–78	2	(64)	5:1	(14)
$Yb(OTf)_3$	1	THF	–78	2	(86)	5:1	(5)
$Yb(OTf)_3$	1	Et_2O	–78	2	(91)	16:1	(0)
$Yb(OTf)_3$	1	Et_2O/H_2O (10 eq)	–78	2	(77)	9:1	(3)
$Sm(OTf)_3$	1	Et_2O	–78	2	(90)	7:1	(0)
$Sc(OTf)_3$	1	Et_2O	–78	2	(94)	>100:1	(0)



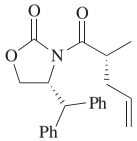


Et_3B, O_2, Lewis acid, solvent, 2 h



I

+

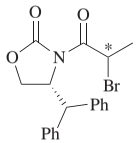
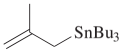
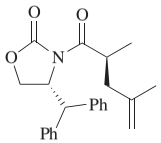
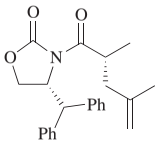


II

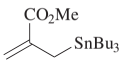
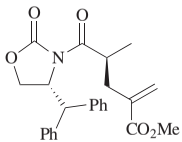
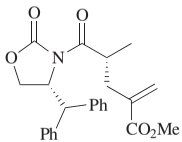
131

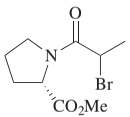
*	Lewis Acid	Solvent	Temp	**I + II**	**I/II**
(*R*)	$MgBr_2$	CH_2Cl_2	–78°	(70)	39:1
(*S*)	$MgBr_2$	CH_2Cl_2	–78°	(91)	39:1
(*R*)	$MgBr_2$	CH_2Cl_2	0°	(90)	>50:1
(*S*)	$MgBr_2$	CH_2Cl_2	0°	(92)	>50:1
(*R*)	$MgBr_2$	CH_2Cl_2	rt	(82)	>50:1
(*S*)	$MgBr_2$	CH_2Cl_2	rt	(88)	>50:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	–78°	(46)	>100:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	–78°	(90)	2:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	0°	(95)	5:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	0°	(93)	50:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	rt	(92)	>50:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	rt	(95)	>50:1

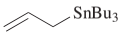
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3 		Et_3B, O_2, Lewis acid, solvent, 2 h	 **I** +  **II**	131

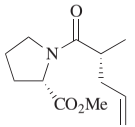
*	Lewis Acid	Solvent	Temp	**I + II**	**I/II**
(*R*)	$MgBr_2$	CH_2Cl_2	–78°	(78)	24:1
(*S*)	$MgBr_2$	CH_2Cl_2	–78°	(92)	12:1
(*R*)	$MgBr_2$	CH_2Cl_2	0°	(78)	>50:1
(*S*)	$MgBr_2$	CH_2Cl_2	0°	(95)	20:1
(*R*)	$MgBr_2$	CH_2Cl_2	rt	(75)	>50:1
(*S*)	$MgBr_2$	CH_2Cl_2	rt	(95)	30:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	–78°	(81)	1:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	–78°	(93)	1:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	0°	(88)	>50:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	0°	(86)	22:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	rt	(71)	>50:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	rt	(95)	20:1

	Et_3B, O_2, Lewis acid, solvent, 2 h	 **I** +  **II**	131





Et_3B, Lewis acid, CH_2Cl_2, –78°, 3 h



I

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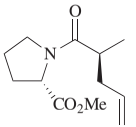


II

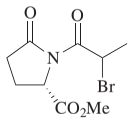
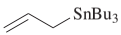
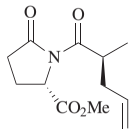
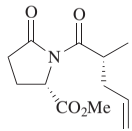
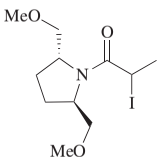
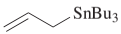
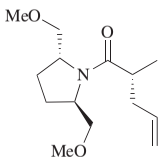
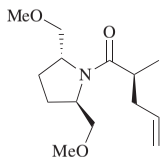
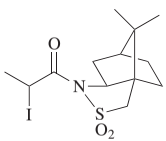
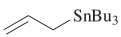
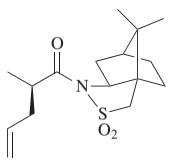
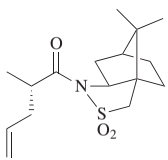
201

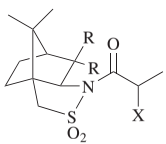
*	Lewis Acid	Solvent	Temp	**I + II**	**I/II**
(*R*)	$MgBr_2$	CH_2Cl_2	–78°	(25)	3:1
(*S*)	$MgBr_2$	CH_2Cl_2	–78°	(90)	1:1
(*R*)	$MgBr_2$	CH_2Cl_2	0°	(72)	43:1
(*S*)	$MgBr_2$	CH_2Cl_2	0°	(70)	23:1
(*R*)	$MgBr_2$	CH_2Cl_2	rt	(80)	40:1
(*S*)	$MgBr_2$	CH_2Cl_2	rt	(68)	20:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	–78°	(41)	1:2
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	–78°	(70)	1:2
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	0°	(81)	4:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	0°	(95)	4:1
(*R*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	rt	(70)	5:1
(*S*)	$Yb(OTf)_3$	CH_2Cl_2/THF (2:1)	rt	(76)	4:1

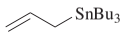
Lewis Acid	**I + II**	**I/II**
none	(0)	—
$MgBr_2 \bullet OEt_2$	(97)	2.3:1
MAD	(0)	—

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

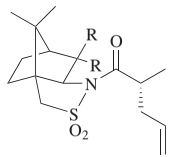
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Et_3B, Lewis acid, CH_2Cl_2, –78°, 3 h	 **I** +  **II**	201
			Lewis Acid / **I + II** / **I/II**: none (0) —; $MgBr_2 \cdot OEt_2$ (91) 4.2:1; $ZnCl_2 \cdot OEt_2$ (91) 2.7:1; MAD (0) —	
		AIBN, benzene, 80°, 4 h	 **I** +  **II**	196
			I + II (55) **I/II** = 24:1	
		Conditions, initiator, solvent	 **I** +  **II**	146, 200





AIBN, benzene, 80°



I

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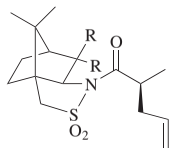


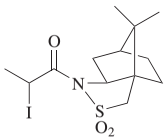
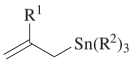
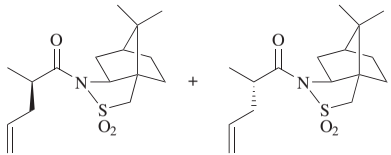
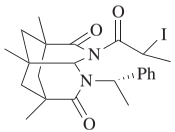
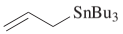
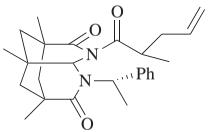
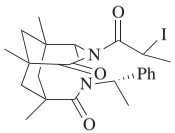
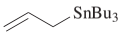
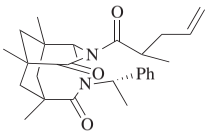
II

146

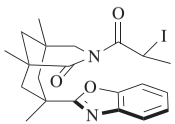
Conditions	Initiator	Solvent	Temp (°)	**I + II**	**I/II**
—	AIBN	benzene	80	(≥90)	11.5:1
sealed tube	AIBN	CH_2Cl_2	80	(≥90)	11.5:1
sealed tube	Et_3B	CH_2Cl_2	80	(≥90)	11.5:1
*h*ν	none	benzene	25	(≥90)	10.1:1
—	Et_3B	benzene	25	(≥90)	13.3:1
—	Et_3B	CH_2Cl_2	25	(≥90)	13.3:1
—	Et_3B	CH_2Cl_2	0	(≥90)	19:1
—	Et_3B	CH_2Cl_2	–20	(≥90)	24:1
*h*ν	none	toluene	–20	(—)	13.3:1
—	Et_3B	CH_2Cl_2	–78	(≤66)	>32:1
*h*ν	none	toluene	–78	(—)	32:1

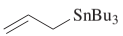
R	X	**I + II**	**I/II**
Cl	Br	(≥90)	32:1
MeO	I	(≥90)	66:1

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

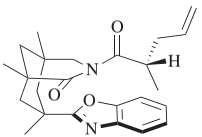
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Conditions, initiator, benzene, 25°	 **I** + **II**	146, 200
		AIBN, benzene, 80°, 4 h	 (69) dr = 1.7:1	439
		AIBN, benzene, 80°, 4 h	 (64) dr = 3.5:1	439

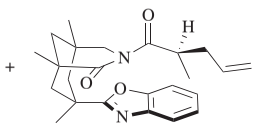
R^1	R^2	Conditions	Initiator	**I + II**	**I/II**
Me	Bu	—	Et_3B	(≥90)	13.3:1
MeO_2C	Ph	*h*ν	none	(≥90)	9:1
MeO_2C	Ph	—	Et_3B	(≥90)	15.7:1





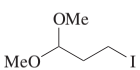
AIBN, benzene, 80°, 4 h

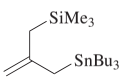




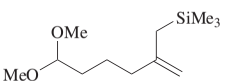
I + **II** (38) **I/II** = 24:1

196



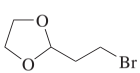


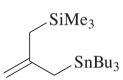
*h*ν, AIBN, benzene, rt, 12 h



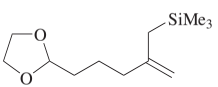
(72)

36





Conditions, initiator, solvent



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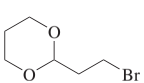
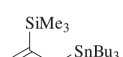
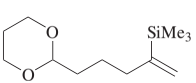
Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	benzene	80	12	(52)
*h*ν	none	benzene	0	2.5	(58)
*h*ν	none	DME	0	2.5	(58)





*h*ν, AIBN, benzene, 10°



(40)

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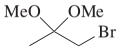
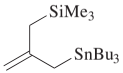
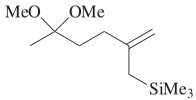
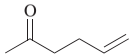
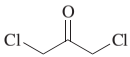
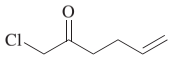
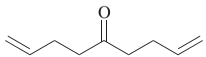
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Conditions, initiator, benzene		429
		Conditions: — / AIBN / 80 / 12 h / (52) *hν* / none / 0 / 10 min / (95)		
		Conditions, initiator, solvent		
		Conditions / Initiator / Solvent / Temp (°) / Time (h)		
		— / AIBN / benzene / 80 / 3 / (43)		37
		sealed tube / AIBN / CH_2Cl_2 / 80 / 5 / (39)		440
		hν / none / benzene / 22 / 1 / (42)		37
	 1 eq R = $(CH_2)_3O((CH_2)_2O)_2Me$	AIBN, benzene, 80°, 16 h	 (41)	121
	 2.2 eq R = $(CH_2)_3O((CH_2)_2O)_2Me$	AIBN, benzene, 80°, 16 h	 (40)	121

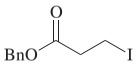
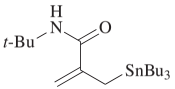
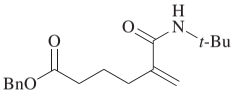
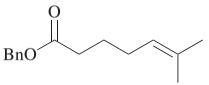
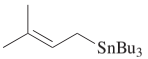
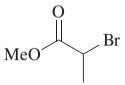
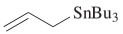
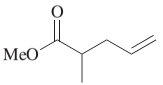
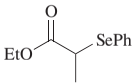
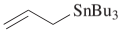
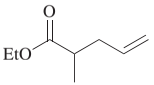
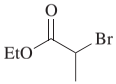
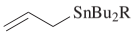
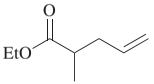
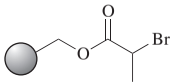
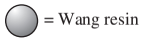
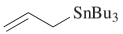
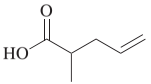
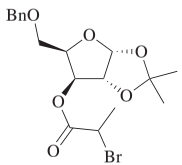
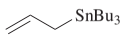
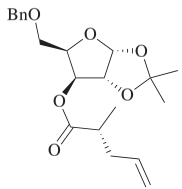
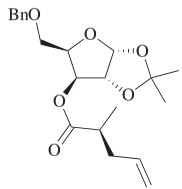
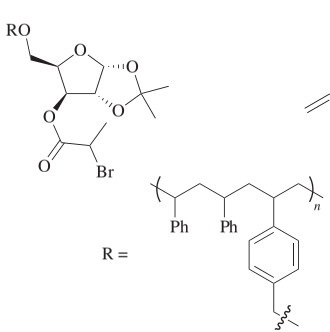
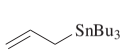
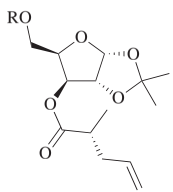
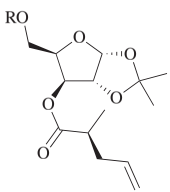
		AIBN, benzene, 80°		(62)	44
		AIBN, toluene, 110°, 48 h	 +  (<5) (48)		44
		AIBN, 100°, 10 h		(70)	21
		*h*ν, benzene, 1 h		(79)	77
	 $R = (CH_2)_3O((CH_2)_2O)_2CH_3$	AIBN, benzene, 80°, 16 h		(51)	121
  = Wang resin		1. AIBN, benzene, 80°, 14 h 2. TFA, $CHCl_3$		(63)[e]	78

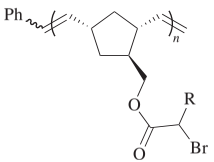
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

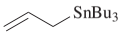
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3 		Initiator, Lewis acid, solvent	 **I** +  **II**	115

Initiator	Lewis Acid	Solvent	Temp (°)	**I + II**	**I/II**
AIBN	none	benzene	80	(72)	7:1
Et_3B, O_2	none	CH_2Cl_2	0	(80)	12:1
Et_3B, O_2	$MgBr_2$	CH_2Cl_2/THF (4:1)	–78	(—)	12:1
Et_3B, O_2	$ZnCl_2$	CH_2Cl_2/THF (4:1)	–78	(83)	28:1
Et_3B, O_2	$Yb(OTf)_3$	CH_2Cl_2/THF (4:1)	–78	(—)	9:1

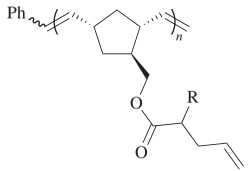
		AIBN, benzene, 80°, 14 h	 **I** **I + II** (93) **I/II** = 66:1 +  **II**	115

C_{3-8}



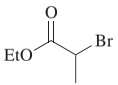


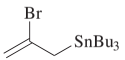
AIBN, benzene, 80°



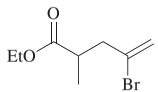
R		
Me	(95)	441
Ph	(85)	

C_3

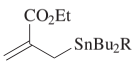




AIBN, toluene, 80°, 2–4 h

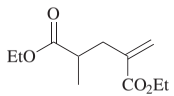


(68) 430



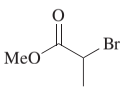
$R = (CH_2)_3O((CH_2)_2O)_2Me$

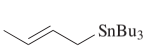
Initiator, benzene



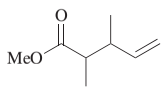
121

Initiator	Temp	Time	
AIBN	80°	16 h	(30)
Et_3B, O_2	rt	10 min	(70)

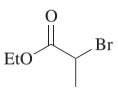


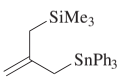


AIBN, 150°, 40 h

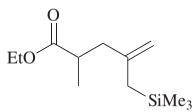


(30)[a] 21



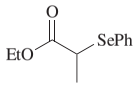
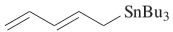
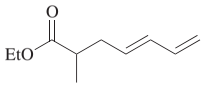
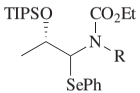
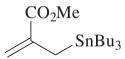
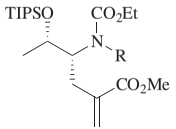
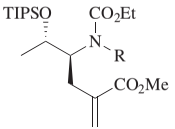
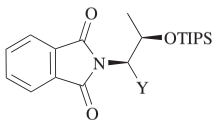
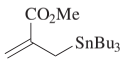
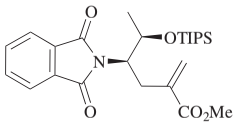
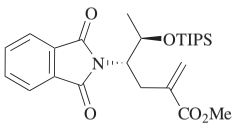


hν, AIBN, DME, 15–20°, 20 h



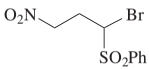
(70) 36

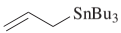
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		*hν*, benzene, 2 h	 (79)	129
		*hν*, AIBN, benzene, 10°	 +  **I** **II**	
			R / Time (h) / **I + II** / **I/II**	
			Me / 36 / (71) / 1.2:1	192
			i-Pr / 26 / (61) / 1:2	192
			Bn / 24 / (65) / 2.1:1	192, 442
		Conditions, AIBN, benzene	 **I** +  **II**	

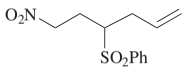
Conditions	Y	Temp (°)	Time (h)	**I + II**	**I/II**	
*h*ν	PhSe	10	9	(84)	1:1.6[g]	443, 444
—	PhSeCO	80	2	(65)	1:1	444

C_3



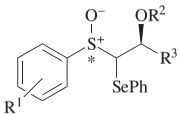


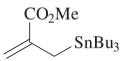
AIBN, benzene, 80°, 3 h



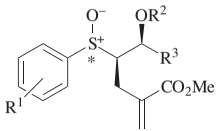
(70) 89

C_{3-8}



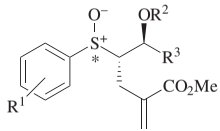


*h*ν, AIBN, benzene, 10°, 24 h



I

+



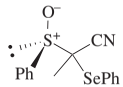
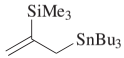
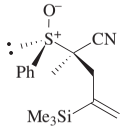
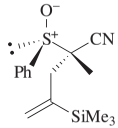
II

445

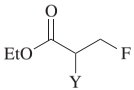
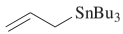
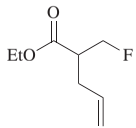
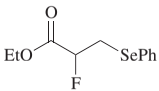
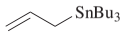
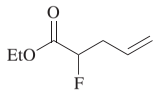
*	R^1	R^2	R^3	**I + II**	**I/II**
(*S*)	2-Cl	H	Me	(96)	4:1
(*S*)	2-Cl	H	Ph	(84)	4:1
(*S*)	2-Cl	TBS	Me	(76)	1:1.8
(*R*)	4-Me	H	Me	(89)	2.2:1

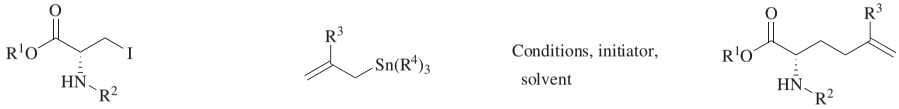
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

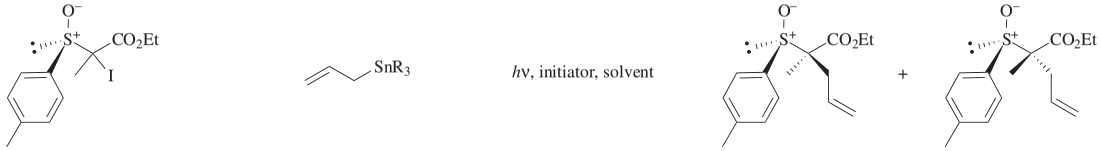
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		*h*ν, AIBN, solvent, –20°	 **I** +  **II**	117

Solvent	**I + II**	**I/II**
CH_2Cl_2	(95)	3:1
toluene	(81)	9:1

		AIBN, benzene, 80°, 2 h		Y I (68) PhSe (75)	446 447
		AIBN, benzene, 80°, 2 h		(0)	447



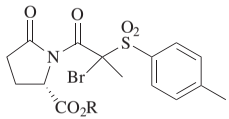
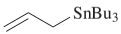
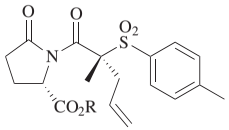
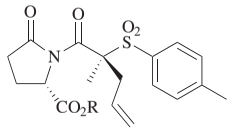
R^1	R^2	R^3	R^4	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
Bn	Boc	EtO_2C	Bu	—	AIBN	benzene	80	—	(70)	44
Bn	Cbz	EtO_2C	Bu	—	AIBN	toluene	70	3	(61)	448, 449
Bn	Cbz	*t*-BuHNCO	Bu	—	AIBN	benzene	80	—	(62)	44
Bn	Cbz	$HOCH_2$	Ph	*h*ν	none	Et_2O	—	—	(70)	133
Me	Cbz	Me_3SiCH_2	Bu	*h*ν	none	benzene	15–20	20	(74)	36



I **II**

R	Initiator	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
Bu	AIBN	CH_2Cl_2	15	—	(86)	49:1	117
Ph	none	benzene	25	0.5	(87)	>49:1	60

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3 		Et_3B, Lewis acid, CH_2Cl_2	 **I** +  **II**	201

R	Lewis Acid	Temp (°)	Time (h)	**I + II**	**I/II**
Me	none	–78	10	(27)	1.1:1
Me	$ZnCl_2$•OEt_2	0	5	(73)	1.5:1
Me	$Zn(OTf)_2$	–78	5	(63)	1.2:1
Me	$MgBr_2$•OEt_2	–78	5	(76)	1.6:1
Me	$Mg(OTf)_2$	–78	5	(86)	1.7:1
Me	$Ti(O\textit{i}\text{-}Pr)_4$	–78	5	(72)	2.7:1
Me	MAD	–78	5	(78)	9.5:1
t-Bu	none	–78	10	(33)	1.1:1
t-Bu	$ZnCl_2$•OEt_2	0	5	(52)	1.7:1
t-Bu	$Zn(OTf)_2$	–78	5	(58)	1.9:1
t-Bu	$MgBr_2$•OEt_2	–78	5	(52)	1.9:1
t-Bu	$Mg(OTf)_2$	–78	5	(47)	4.6:1
t-Bu	MAD	–78	5	(77)	10.8:1

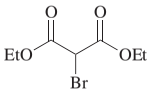
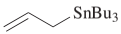
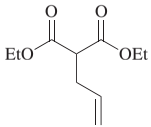
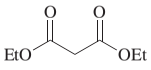
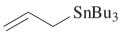
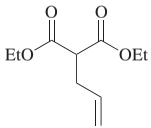
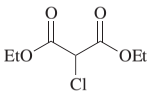
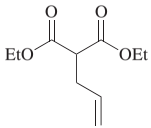
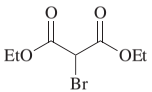
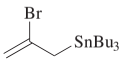
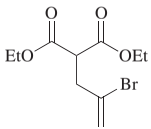
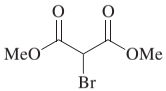
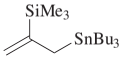
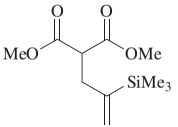
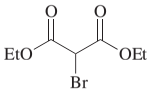
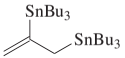
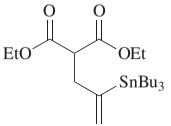
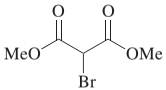
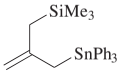
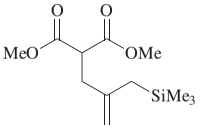
		$ZnCl_2 \bullet OEt_2$, CH_2Cl_2, rt	 (30) +  (25)		50, 51
		*hν*, $Cu(dap)_2Cl$, MeCN, rt, 4.5 h		(70)	47
	$R = (CH_2)_3O((CH_2)_2O)_2Me$	AIBN, benzene, 80°, 16 h		(65)	121
		AIBN, toluene, 80°, 2–4 h		(64)	430

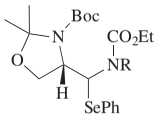
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

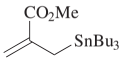
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		*h*ν, AIBN, benzene, 10°	 (80)	61
		Conditions, initiator, $(Bu_3Sn)_2$, solvent		426

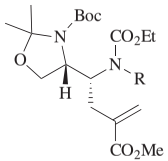
Conditions	Initiator	Solvent	Temp	Time (min)	
—	Et_3B, O_2	THF	0°	5	(76)
*h*ν	none	benzene	rt	15	(83)
—	none	benzene	80°	5	(93)
—	AIBN	benzene	80°	5	(88)
*h*ν	none	toluene	60°	30	(82)[b]

		*h*ν, AIBN, benzene, 15–20°, 8 h	 (90)	36





hν, AIBN, benzene, 10°



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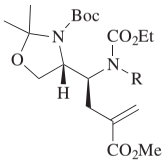
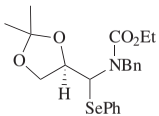
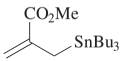


192

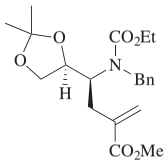
I **II**

R	Time (h)	**I + II**	**I/II**
Me	12	(47)	1.3:1
Bn	27	(58)	2.6:1





hν, AIBN,
benzene, 10°, 24 h



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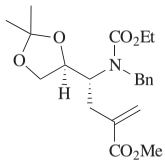


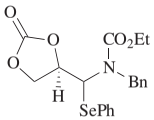
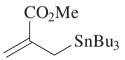
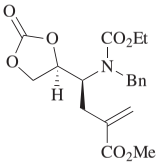
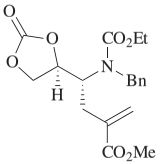
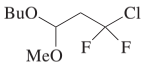
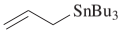
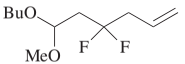
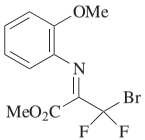
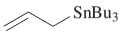
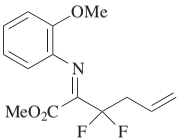
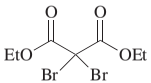
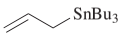
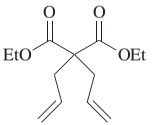
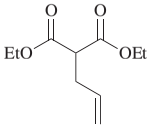
192

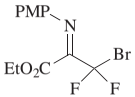
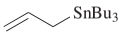
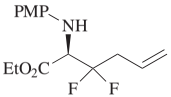
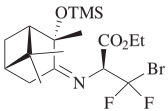
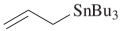
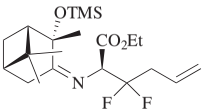
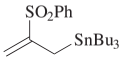
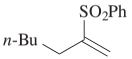
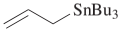
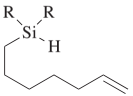
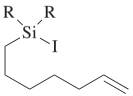
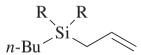
I **II**

I + II (62) **I/II** = 1.1:1

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

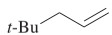
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		*h*ν, AIBN, benzene, 10°, 16 h	 **I** +  **II** **I + II** (73) **I/II** = 1:2	192
		AIBN, benzene	 (69)	450
		AIBN, toluene, 90°, 2 h	 (85)	451
	 10 eq	AIBN, benzene, 80°, 12 h	 (49) +  (27)	79

			1. H_2, $Pd(OCOCF_3)_2$, (*R*)-BINAP, CF_3CH_2OH, 48 h 2. AIBN, toluene, 90°, 2 h		(56)[e] er = 93.5:6.5	452
			AIBN, toluene, 90°, 1 h		(100)	93, 453
C_4						
	n-BuBr		AIBN, benzene, 80°, 24 h		(85)	135
			AIBN, benzene, 80°	 **I** +  **II** +  **III** + **IV** + **V**		437

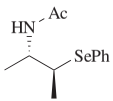
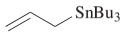
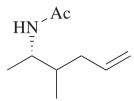
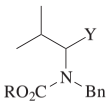
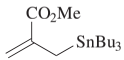
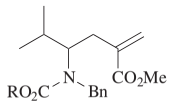
R	**I**[c]	**II**[c]	**III**[c]	**IV**[c]	**V**[c]
t-Bu	(44)	(0)	(0)	(7)	(38)
Ph	(22)	(<5)	(5)	(8)	(49)

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

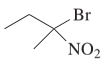
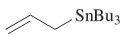
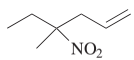
A. ACYCLIC SUBSTRATES (*Continued*)

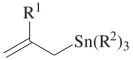
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
t-BuHgCl		*hν*, additive (*x* eq), solvent, 40°		331

R	Additive	*x*	Solvent	Time (h)	
Bu	none	—	benzene/DMSO (1:1)	4	(57)[c]
Bu	NaI	10	DMSO	1	(73)[c]
Ph	none	—	benzene	6	(65)[a]
Ph	NaI	10	benzene/DMSO (1:2)	1.5	(84)[a]

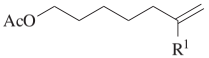
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		AIBN, toluene, 80°, 1 h	 (—)	454
		*hν*, AIBN, solvent		

R	Y	Solvent	Temp (°)		
Me	PhSe	—	—	(65)	442
Et	PhS	benzene	10	(0)	192
Et	PhSe	benzene	10	(65)	192

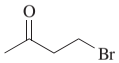
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		AIBN, 100°, 24 h	 (45)	86

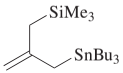


AIBN, benzene, 80°

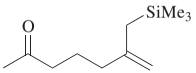


R^1	R^2	Time (h)		
Me_3Si	Ph	4	(96)	39
Me_3Sn	Me	12	(51)	41



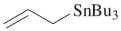


Conditions, initiator, solvent

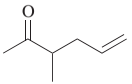


429

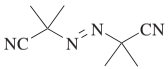
Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	benzene	80	14	(61)
hν	none	DME	25	2.5	(25)
hν	none	benzene	0	6	(0)

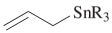


AIBN, CH_2Cl_2, sealed tube, 80°, 5 h



(36) 440

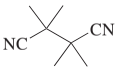




Benzene, 80°

I

+



II

37

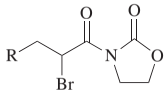
R	**I**	**II**
Me	(50)	(10)
Bu	(50)	(12)

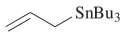
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

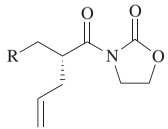
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{4-9}



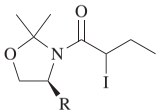


Et_3B/O_2, $Zn(OTf)_2$ (x eq), (R,R)-**L9a**, CH_2Cl_2, pentane, –78°

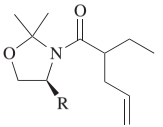


R	x		er	
Me	0.2	(60–90)[h]	58.0:42.0	210
Me	0.6	(60–90)[h]	62.5:37.5	210
Me	1	(60–90)[h]	71.0:29.0	210
Me	1	(84)[i]	29.0:71.0	211
Me	2	(60–90)[h]	73.0:27.0	210
Et	0.2	(60–90)[h]	61.0:39.0	210
Et	0.6	(60–90)[h]	68.0:32.0	210
Et	1	(60–90)[h]	75.0:25.0	210
Et	2	(60–90)[h]	76.5:23.5	210
t-Bu	0.2	(60–90)[h]	76.0:24.0	210
t-Bu	0.6	(60–90)[h]	82.0:18.0	210
t-Bu	1	(60–90)[h]	87.0:13.0	210
t-Bu	1	(63)[i]	87.0:13.0	211
t-Bu	2	(60–90)[h]	88.0:12.0	210
c-C_6H_{11}	0.2	(60–90)[h]	63.0:37.0	210
c-C_6H_{11}	0.6	(60–90)[h]	71.5:28.5	210
c-C_6H_{11}	1	(60–90)[h]	79.0:21.0	210
c-C_6H_{11}	2	(60–90)[h]	82.0:18.0	210

C_4

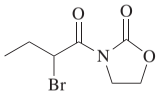


AIBN, benzene, 80°, 4.5 h

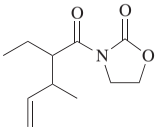


R		dr
i-Pr	(60)	5:1
Ph	(34)	3:1

199

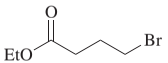


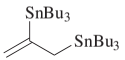
Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2, THF, –78°, 3 h



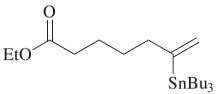
(78) dr = 2.1:1

26



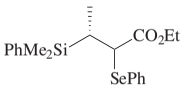


*h*ν, $(Bu_3Sn)_2$, toluene, 60°, 2 h

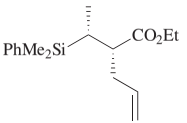


(29)[b]

426



Conditions, AIBN, solvent



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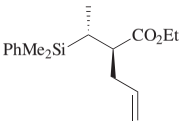


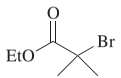
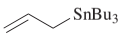
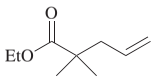
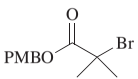
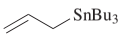
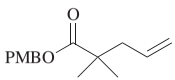
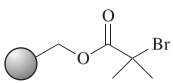
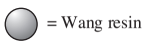
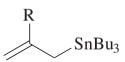
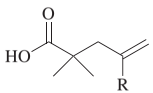
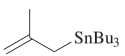
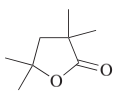
177

I **II**

Conditions	Solvent	Temp (°)	**I + II**	**I/II**
—	benzene	80	(62)	3.5:1
*h*ν	THF	–78	(56)	4.6:1

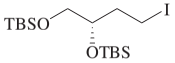
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

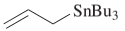
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
	 *x* eq	CuBr, ligand, solvent		455
		AIBN, benzene, 80°, 14 h	 (71)	78
  = Wang resin		1. AIBN, benzene, 80° 2. TFA		78
		1. AIBN, benzene, 80° 2. TFA	 (70)[e]	78

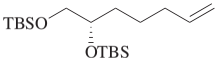
x	Ligand	Solvent	Temp (°)	Time (h)	
1	PMDETA	toluene	65	17	(21)
1	PMDETA	DMF	rt	72	(94)
1.5	HMTETA	THF	60	24	(99)

R	Time (h)	
H	14	(58)[e]
MeO_2C	—	(95)[e]
AcO	—	(95)[e]

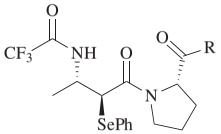


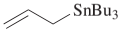


AIBN, benzene, 80°

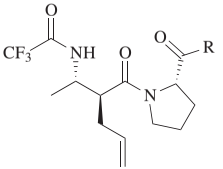


(82) 456

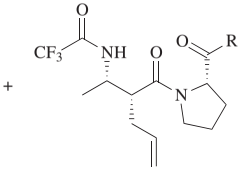




*h*ν, AIBN, toluene, 0°



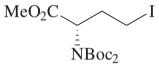
I

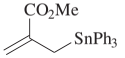


II

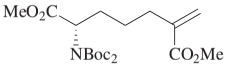
457

R	I + II	I/II
MeO	(78)	>49:1
Me_2N	(70)	>49:1





AIBN, benzene, 80°



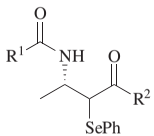
(60) 458

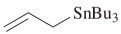
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

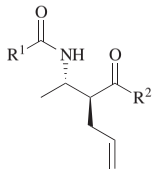
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_4



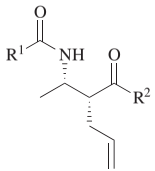


*h*ν, AIBN, solvent, –40°



I

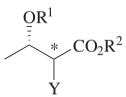
+

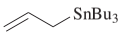


II

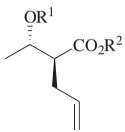
188

R^1	R^2	Solvent	**I + II**	**I/II**
BnO	MeO	toluene	(—)	4.6:1
BnO	MeO	DMSO	(—)	1:4
CF_3	MeO	toluene	(90)[j]	>49:1
CF_3	MeO	DMSO	(—)	1.2:1
CF_3	$Me_3Si(CH_2)_2O$	toluene	(78)	>49:1
CF_3	Me_2N	toluene	(90)[j]	>49:1



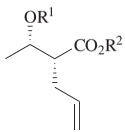


Conditions, initiator, Lewis acid (*x* eq), solvent



I

+



II

R^1	R^2	Y	*	Conditions	Initiator	Lewis Acid	*x*	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
H	Et	Cl	(*R*)	—	AIBN	none	—	benzene	80	—	(55)	1.2:1	459
H	Et	Br	(*R*,*S*)	—	Et_3B	none	—	benzene	25	—	(—)	1.2:1	176
H	Et	PhSe	(*R*)	*h*ν	AIBN	none	—	—	10	—	(86)	1.6:1	183
H	Et	PhSe	(*R*)	*h*ν	AIBN	Me_3Al	1.1	—	10	—	(80)	5.8:1	183

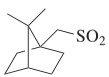
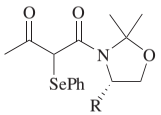
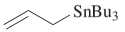
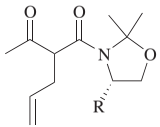
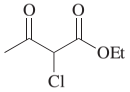
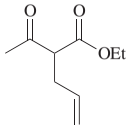
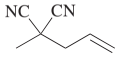
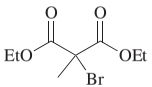
H	Et	PhSe	(*S*)	*h*ν	AIBN	none	—	—	10	—	(98)	1.7:1	183
H	Et	PhSe	(*S*)	*h*ν	AIBN	Me_3Al	1.1	—	10	—	(97)	20:1	183
H	Et	PhSe	(*S*)	*h*ν	AIBN	Me_3Al	3	—	10	—	(>70)	32:1	183
H	Et	PhSe	(*S*)	*h*ν	AIBN	none	—	THF	–78	—	(75)	1:3.3	177
H	Et	PhSe	(*S*)	*h*ν	AIBN	none	—	toluene	–78	—	(75)	1.5:1	177
Me	Et	Br	(*S*)	—	AIBN	none	—	benzene	80	—	(71)	1:2.3	177
Me	Me	I	(*S*)	—	AIBN	none	—	hexane	70	—	(73)	1:3	179, 180
Me	Me	I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(79)	51:1	179–181
Me	Et	Br	(*S*)	*h*ν	AIBN	none	—	THF	–78	39	(75)	1:4.9	177
TBS	Et	Br	(*R*,*S*)	*h*ν	$(Bu_3Sn)_2$	none	—	benzene	80	4	(—)	1.5:1	176
TBS	Et	Br	(*S*)	*h*ν	AIBN	none	—	CH_2Cl_2	32	2	(94)	2.2:1	460
TBS	Et	Br	(*S*)	*h*ν	AIBN	$Eu(fod)_3$	0.1	CH_2Cl_2	32	2	(91)	4.0:1	460
TBS	Et	Br	(*S*)	*h*ν	AIBN	$Eu(fod)_3$	1.1	CH_2Cl_2	32	2	(81)	4.1:1	460
TBS	Et	Br	(*S*)	*h*ν	AIBN	$Pr(fod)_3$	0.1	CH_2Cl_2	32	2	(58)	3.3:1	460
TBS	Et	Br	(*S*)	*h*ν	AIBN	$La(fod)_3$	0.1	CH_2Cl_2	32	2	(67)	3.4:1	460
TBS	Et	Br	(*S*)	*h*ν	AIBN	$La(fod)_3$	0.5	CH_2Cl_2	32	2	(62)	3.4:1	460
TBS	Et	Br	(*R*,*S*)	—	Et_3B	none	—	benzene	0	—	(0)	—	176
TBDPS	Et	Br	(*R*,*S*)	*h*ν	$(Bu_3Sn)_2$	none	—	benzene	80	4	(—)	1:1	176
TBDPS	Et	Br	(*S*)	*h*ν	AIBN	none	—	CH_2Cl_2	40	2	(66)	1.2:1	460
TBDPS	Et	Br	(*S*)	*h*ν	AIBN	$Eu(fod)_3$	0.1	CH_2Cl_2	32	2	(94)	1.7:1	460
TBDPS	Et	Br	(*R*,*S*)	—	Et_3B	none	—	benzene	25	—	(0)	—	176
TBDPS	Et	Br	(*R*,*S*)	—	Et_3B	none	—	benzene	0	—	(0)	—	176
TBDPS	Et	Br	(*R*,*S*)	—	Et_3B	none	—	benzene	–78	—	(0)	—	176
	Et	Br	(*R*,*S*)	*h*ν	$(Bu_3Sn)_2$	none	—	benzene	80	4	(99)	1:1	176

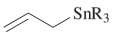
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		Conditions, initiator, solvent		197

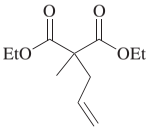
R	Conditions	Initiator	Solvent	Temp (°)		dr
i-Pr	*h*ν	none	CH_2Cl_2	0	(>90)	2.6:1
t-Bu	—	AIBN	benzene	80	(>90)	13:1
t-Bu	*h*ν	none	CH_2Cl_2	–78	(>75)	>100:1
t-Bu	*h*ν	none	CH_2Cl_2	0	(>90)	32:1
t-Bu	*h*ν	none	CH_2Cl_2	25	(>90)	24:1
Bn	*h*ν	none	CH_2Cl_2	–78	(>75)	3.1:1
Bn	*h*ν	none	CH_2Cl_2	0	(>90)	2.5:1

	 $R = (CH_2)_3O(CH_2CH_2O)_2CH_3$	AIBN, benzene, 80°, 16 h	 (73)	121
		$ZnCl_2 \bullet OEt_2$, CH_2Cl_2, –78°	 (36) + (44)	50, 51

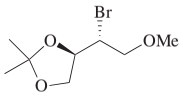


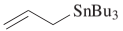


Conditions, initiator, solvent

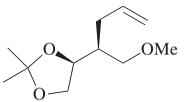


R	Conditions	Initiator	Solvent	Temp	Time (h)		
Bu	—	$ZnCl_2 \bullet OEt_2$	CH_2Cl_2	rt	—	(59)	50, 51
$n\text{-}C_6F_{13}(CH_2)_3$	—	AIBN	BTF	80°	2–5	(76)	123
$n\text{-}C_6F_{13}(CH_2)_3$	$h\nu$	none	BTF	25°	3–30	(38)	123



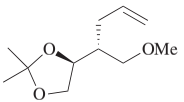


$h\nu$, AIBN, Lewis acid (x eq), CH_2Cl_2, rt



I

+

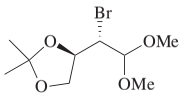
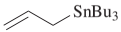
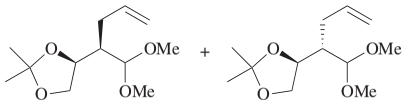
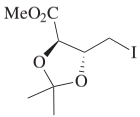
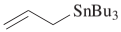
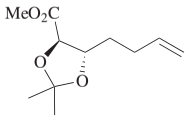
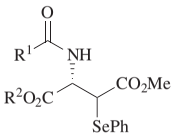
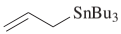
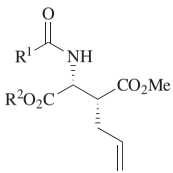
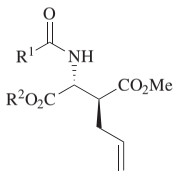


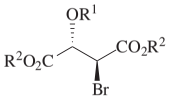
II

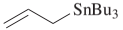
193

Lewis Acid	x	**I + II**	**I/II**
none	—	(59)	1.2:1
$MgBr_2 \bullet OEt_2$	1	(60)	2.3:1
$MgBr_2 \bullet OEt_2$	2.5	(7)	40:1

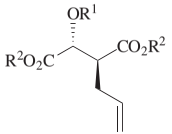
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		*h*ν, AIBN, Lewis acid (*x* eq), CH_2Cl_2, rt	 **I** + **II**	193
			Lewis Acid / *x* / **I + II** / **I/II**: none / — / (52) / 1:1.1; $MgBr_2 \cdot OEt_2$ / 2.5 / (70) / 52:1	
		AIBN, toluene, 80°, 12 h	 (69)	72
		*h*ν, AIBN, toluene, –40°	 **I** +  **II**	188
			R^1 / R^2 / **I + II** / **I/II**: CF_3 / Me / (74)[j] / 24:1; BnO / *t*-Bu / (71)[j] / 19:1	



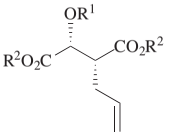


hν, AIBN,
Lewis acid (*x* eq),
solvent



I

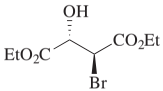
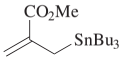
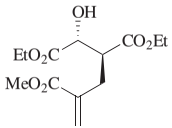
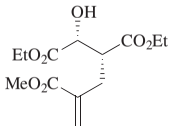
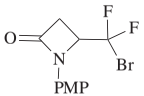
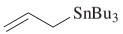
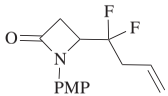
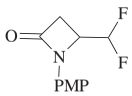
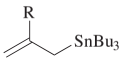
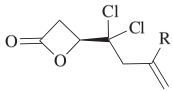
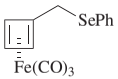
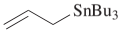
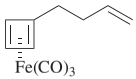
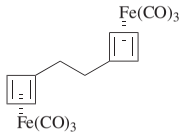
+



II

R^1	R^2	Lewis Acid	*x*	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
H	Et	none	—	CH_2Cl_2	40	2	(85)	1.9:1	460, 461
H	Et	Eu(fod)$_3$	1.1	CH_2Cl_2	40	2	(63)	1:1.7	460, 461
H	Et	none	—	—	10	—	(91)	1.8:1	183
H	Et	Me_3Al	1.3	—	10	—	(44)	1:1.4	183
Ac	Et	none	—	CH_2Cl_2	40	2	(56)	1:1.8	460, 461
Ac	Et	Eu(fod)$_3$	1.1	CH_2Cl_2	40	2	(72)	1:3.4	460, 461
TMS	Et	none	—	CH_2Cl_2	40	2	(63)	1:1.3	460, 461
TMS	Et	Eu(fod)$_3$	0.1	CH_2Cl_2	40	2	(45)	1:3.0	460, 461
TMS	Et	Eu(fod)$_3$	1.1	CH_2Cl_2	40	2	(62)	1:8.6	460, 461
TBS	Et	none	—	CH_2Cl_2	40	2	(57)	1:1.1	460, 461
TBS	Me	Eu(fod)$_3$	0.1	CH_2Cl_2	40	2	(81)	1:2.7	460, 461
TBS	Me	Eu(fod)$_3$	0.1	CH_2Cl_2	32	2	(73)	1:4.9	460, 461
TBS	Et	Eu(fod)$_3$	0.3	CH_2Cl_2	40	2	(61)	1:4.1	460, 461
TBS	Et	Eu(fod)$_3$	1.1	CH_2Cl_2	40	2	(67)	1:5.7	460, 461
TBS	Et	La(fod)$_3$	0.1	CH_2Cl_2	32	2	(63)	1:5.4	460, 461
TBS	Et	La(fod)$_3$	0.1	CH_2Cl_2	3	2	(68)	1:8.6	460, 461
TBS	Et	La(fod)$_3$	0.1	CH_2Cl_2	–10	2	(71)	1:4.3	460, 461
TBS	Et	La(fod)$_3$	1.1	CH_2Cl_2	3	2	(63)	1:10.9	460, 461
TBS	*i*-Pr	Eu(fod)$_3$	1.1	CH_2Cl_2	40	2	(77)	1:1.7	460, 461
TBDPS	Et	Eu(fod)$_3$	1.1	CH_2Cl_2	40	2	(66)	1:1.5	460, 461

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		*h*ν, AIBN, MAD, 10°	 +  **I** **I + II** (40) **I/II** 1:>25 **II**	183
		AIBN, benzene, sealed tube, o/n	 +  (25) (31)	462
		Et_3B, O_2, toluene, 23°		90
			R / Time (h): H 5 (46); Me 6 (45)	
C_5				
		AIBN, benzene, 80°, 22 h	 +  (tr) (50)	130

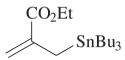
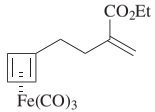
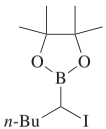
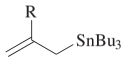
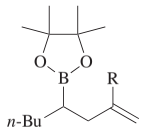
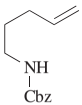
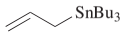
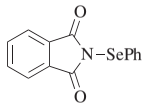
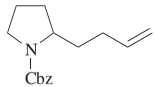
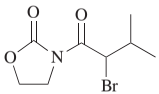
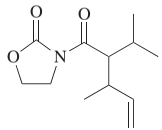
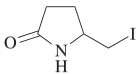
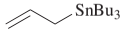
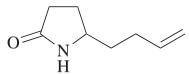
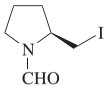
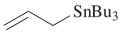
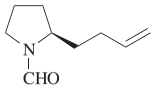
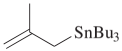
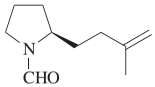
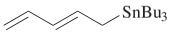
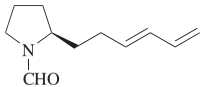
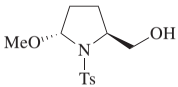
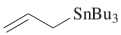
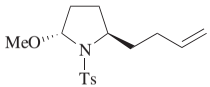
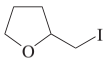
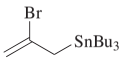
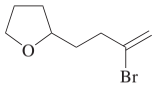
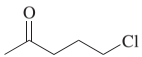
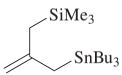
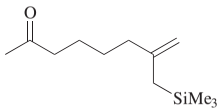
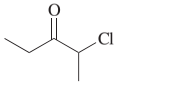
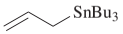
		AIBN, benzene, 80°, 18 h		(55)	130
		AIBME, benzene, 80°		R H (70) MeO_2C (87)	463
		1.  , CH_2Cl_2 2. Allylstannane, AIBN, toluene, 110°		(70)[e]	464
		Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (2:1), 3 h		Temp (°) / dr 20 (74) 1:1 –78 (82) 1.2:1	26
		AIBN, toluene, 80°, 1 h		(—)	454

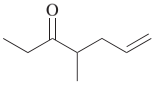
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		AIBN, benzene, 80°, 5.5 h	 (44)	465
		ACCN, benzene, 80°, 5 h	 (40)	465
	 (*E*)/(*Z*) = 6.1:1	ACCN, benzene, 80°, 5 h	 (46) (*E*)/(*Z*) = 4:1	465
		1. PhOC(S)Cl, *n*-BuLi, –78° 2. Allylstannane, *h*ν, toluene	 (76)[e]	466
		AIBN, toluene, 80°, 2–4 h	 (41)	430
		Conditions, initiator, solvent		429

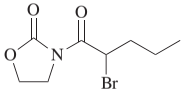
Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	benzene	80	12	(65)
*h*ν	none	DME	25	2.5	(42)
*h*ν	none	benzene	0	6	(0)

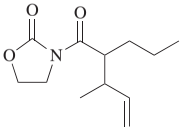
AIBN, benzene, 80°, 5 h



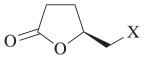
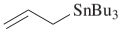
(58) 440



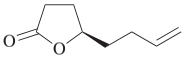
Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (2:1), −78°, 3 h



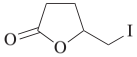
(85) dr = 2.9:1 26

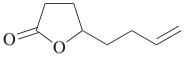
AIBN, toluene



X	Temp (°)	Time (h)		
Br	110	30	(70)	467
I	80	—	(91)	468



AIBN, CCl_4, flow microwave reactor, 100°, 100 min



(78)

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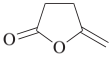

(12)

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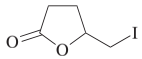
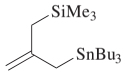
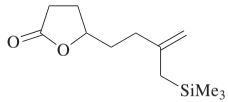
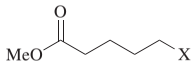
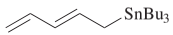
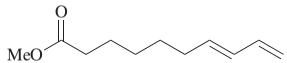
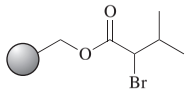
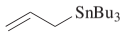
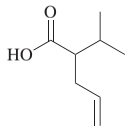
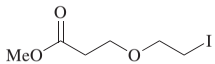
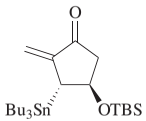
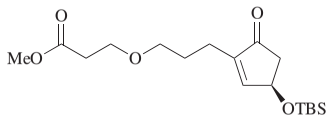
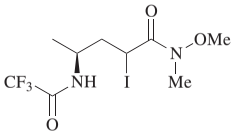
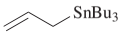
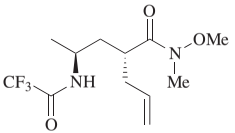
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		*h*ν, benzene, 15–20°, 17 h	 (75)	36
		*h*ν, benzene, 1 h	 X: Br (51); I (89)	129
 = Wang resin		1. AIBN, benzene, 80°, 14 h 2. TFA, $CHCl_3$	 (63)[e]	78
		AIBN, benzene, 80°, 3 h	 (74)	103



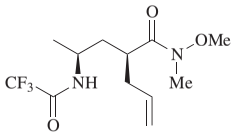


hν, AIBN,
CH_2Cl_2 or toluene,
–40 or –20°



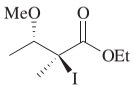
I

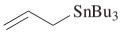
+



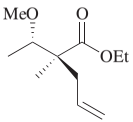
II

I + II (72) **I/II** = 3:1 188





Initiator, Lewis acid,
solvent



I

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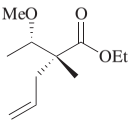


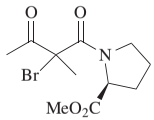
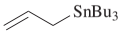
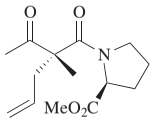
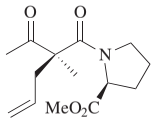
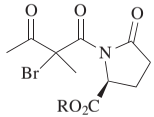
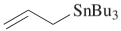
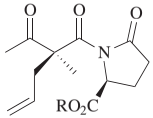
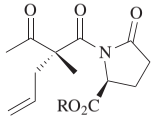
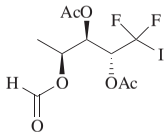
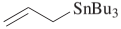
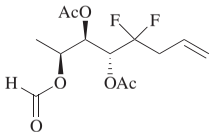
II

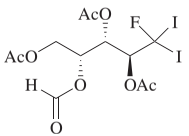
179, 180

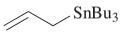
Initator	Lewis Acid	Solvent	Temp	**I + II**	**I/II**
AIBN	none	hexanes	reflux	(44)	1:4.5
Et_3B	$MgBr_2 \cdot OEt_2$	CH_2Cl_2	–78°	(65)	>100:1

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

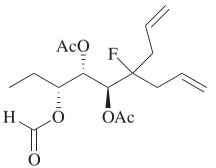
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		Et_3B, Lewis acid, CH_2Cl_2, –78°, 3 h	 +  **I** **II**	201
			Lewis Acid / **I + II** / **I/II**: $ZnCl_2$•OEt_2 (48) 2.3:1; $MgBr_2$•OEt_2 (51) 2.3:1	
		Et_3B, Lewis acid, CH_2Cl_2, 3 h	 +  **I** **II**	201
			R / Lewis Acid / Temp (°) / **I + II** / **I/II**: Me, $ZnCl_2$•OEt_2, –78, (81), 2:1; Me, $MgBr_2$•OEt_2, –78, (82), 3.3:1; *t*-Bu, $MgBr_2$•OEt_2, 0, (87), 10.1:1; *t*-Bu, $MgBr_2$•OEt_2, –78, (91), 17.2:1	
		AIBN, benzene, 80°, 1 h	 (90)	470, 471





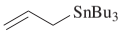
AIBN, benzene, 80°, 40 min



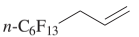
(87) 471

C_6

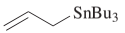
n-$C_6F_{13}I$



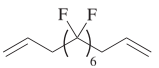
Conditions, initiator, neat



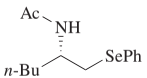
Conditions	Initiator	Temp (°)	Time (h)		
$h\nu$	none	rt	2	(42)	98
—	AIBN	70	5	(39)	472

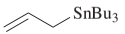


AIBN, neat, 80°, 16 h

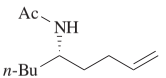


(27) 473

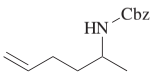


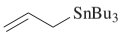


AIBN, toluene, 80°, 1 h

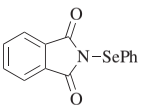


(—) 454





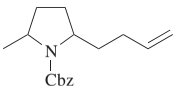
1.



,

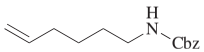
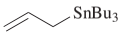
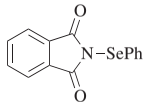
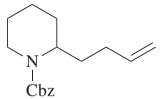
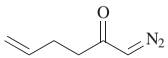
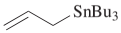
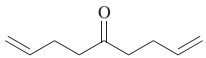
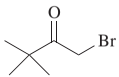
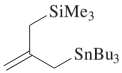
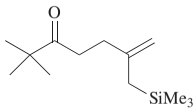
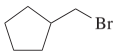
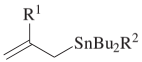
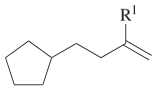
CH_2Cl_2

2. Allylstannane, AIBN, toluene, 110°

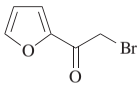
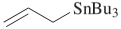
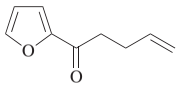


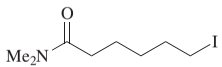
(—) dr = 1:1 464

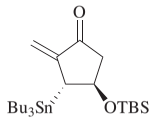
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		1.  , CH_2Cl_2 2. Allylstannane, AIBN, toluene, 110°	 (73)[e]	464
		1. AIBN, benzene, 80°, 3 h 2. KF, H_2O	 (58)[e]	64
		*h*ν, benzene, 15–20°, 15 h	 (59)	36
		Initiator, solvent		

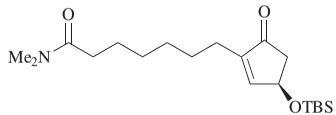
R^1	R^2	Initiator	Solvent	Temp	Time		Refs.
H	Bu	AIBN	neat	190°	70 h	(30)	21
EtO_2C	$CH_3(O(CH_2)_2)_2O(CH_2)_3$	Et_3B, O_2	benzene	rt	10 min	(60)	122

		*h*ν, $Cu(dap)_2Cl$, MeCN, rt, 6 h	 (68)	47

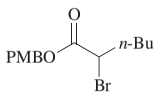


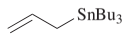


AIBN, benzene, 80°, 3 h

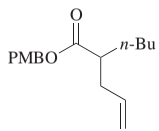


(86) 103

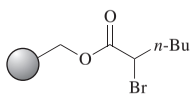


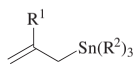


AIBN, benzene, 80°, 14 h

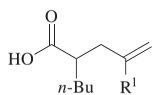


(92) 78





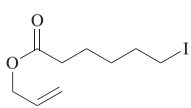
1. AIBN, benzene, 80°, time
2. TFA, $CHCl_3$

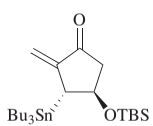


78

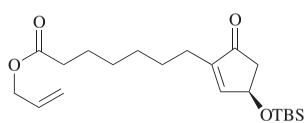
= Wang resin

R^1	R^2	Time (h)	
H	Bu	14	(76)[e]
H	Ph	14	(78)[e]
Me	Bu	—	(66)[e]
MeO_2C	Bu	—	(95)[e]



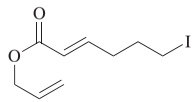
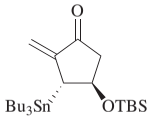
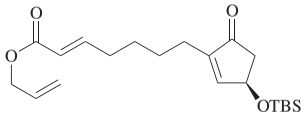
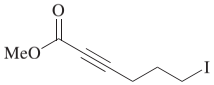
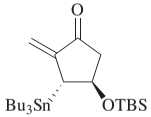
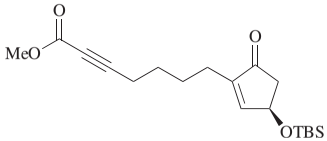
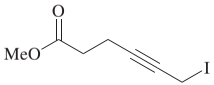
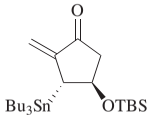
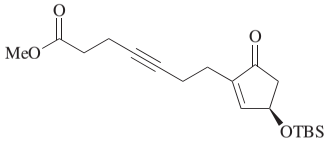
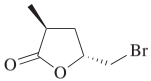
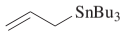
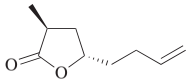
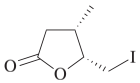
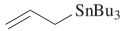
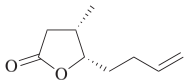
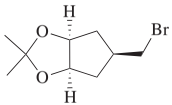
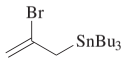
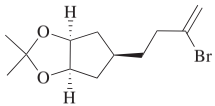


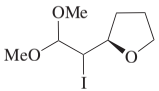
AIBN, benzene, 80°, 3 h

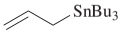


(82) 103

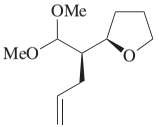
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_6					
		AIBN, benzene, 80°, 3 h		(82)	103
		AIBN, benzene, 80°, 3 h		(86)	103
		AIBN, benzene, 80°, 3 h		(87)	103
		ACCN, toluene, 80°, 22 h		(81)	473a
		AIBN, THF, 60°, 40 h		(63)	474
		AIBN, toluene, 80°, 2–4 h		(50)	430





hν, AIBN, Lewis acid, CH_2Cl_2, rt



I

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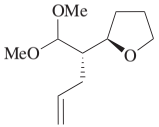

II

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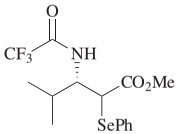
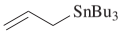
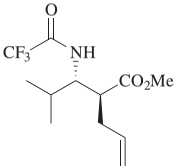
Lewis Acid	**I + II**	**I/II**
none	(50)	1.2:1
$MgBr_2 \bullet OEt_2$	(58)	36:1



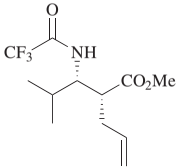


hν, AIBN, CH_2Cl_2 or toluene, –40 or –20°



I

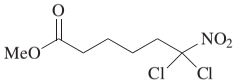
+



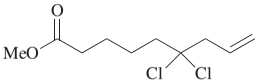
II

188

I + II (79) **I/II** > 49:1



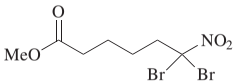
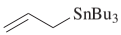
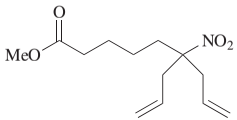
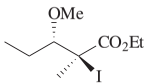
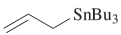
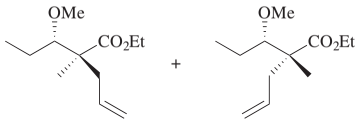
AIBN, toluene, 110°



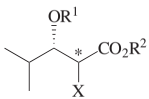
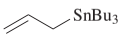
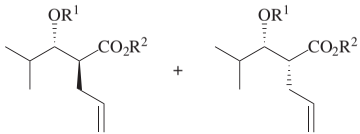
63

R	Time (h)	
Me	6	(70)
Bu	8	(68)
Ph	18	(64)

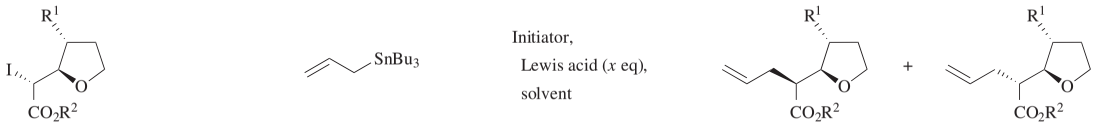
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, toluene, 110°, 8 h	 (70)	63
		Initiator, Lewis acid (*x* eq), solvent	 **I** + **II**	179, 180

Initator	Lewis Acid	*x*	Solvent	Temp	**I + II**	**I/II**
AIBN	none	—	hexanes	reflux	(45)	1:4.8
Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	−78°	(80)	90:1

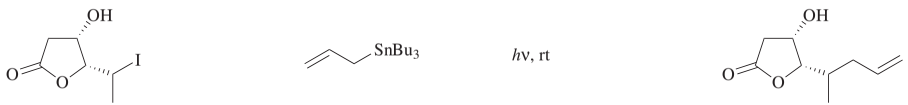
		Conditions, initiator, Lewis acid (*x* eq), solvent	 **I** + **II**	

R^1	R^2	X	*	Conditions	Initiator	Lewis Acid	*x*	Solvent	Temp (°)	**I + II**	**I/II**	
H	Et	Br	(*R*)/(*S*)	*h*ν	$(Bu_3Sn)_2$	none	—	benzene	80	(—)	2.3:1	176
H	Et	Br	(*R*)/(*S*)	—	Et_3B	none	—	benzene	0	(—)	3.2:1	176
Me	Me	I	(*S*)	—	AIBN	none	—	hexane	70	(82)	1:3.3	179, 180
Me	Me	I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	−78	(51)	>100:1	179–181

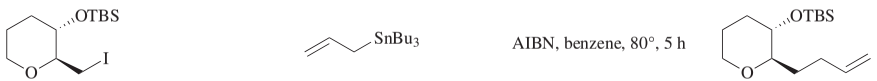


I **II**

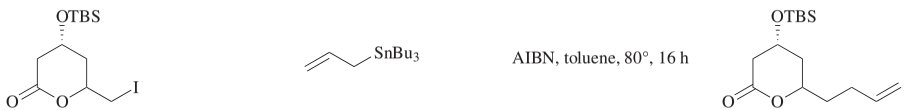
R^1	R^2	Initiator	Lewis Acid	*x*	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
H	Me	AIBN	none	—	hexane	70	—	(90)	1:6	179–181
H	Me	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(91)	4.6:1	179–181
TBSO	Et	AIBN	none	—	hexane	70	—	(74)	1:51	179, 180, 475
TBSO	Et	Et_3B	none	—	toluene	–78	7	(67)	1:>30	475
TBSO	Et	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(80)	6.3:1	179, 180



(68) dr = 1.6:1 — 4



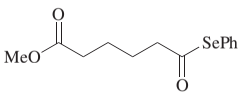
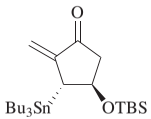
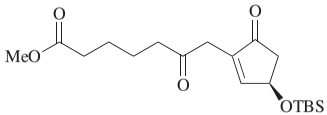
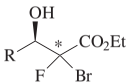
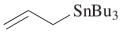
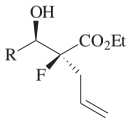
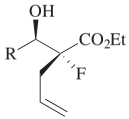
(70) — 422



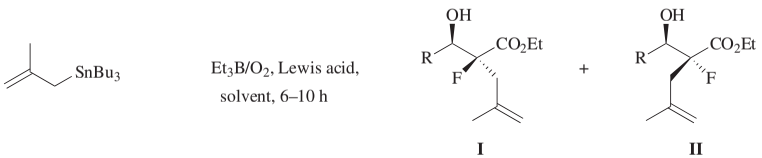
(40) — 476, 477

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_6 		AIBN, benzene, 80°, 3 h	 (19)	103
C_{6-10} 		Et_3B/O_2, Lewis acid, solvent, 6–10 h	 **I** +  **II**	184

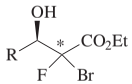
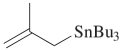
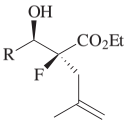
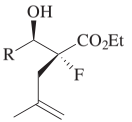
R	*(*R*)/(*S*)	Lewis Acid	Solvent	Temp (°)	**I + II**	**I/II**
n-Pr	1:1.5	none	*i*-PrOH	–78	(75)	1:4.3
n-Pr	1:1.5	Me_3Al	CH_2Cl_2	–15	(72)	19:1
i-Pr	1:2.3	none	*i*-PrOH	–78	(66)	1:9
i-Pr	1:2.3	Me_3Al	CH_2Cl_2	–15	(80)	15.7:1
n-C_6H_{13}	1:1.6	Me_3Al	CH_2Cl_2	–15	(86)	9:1
Ph	1:1.6	none	*i*-PrOH	–78	(80)	1:11.5
Ph	1:1.6	Me_3Al	CH_2Cl_2	–15	(79)	24:1
4-$MeOC_6H_4$	1:1.3	none	*i*-PrOH	–78	(84)	1:10.1
4-$MeOC_6H_4$	1:1.2	Me_3Al	CH_2Cl_2	–15	(73)	19:1
4-$MeOC_6H_4$	1:1.5	Me_3Al	CH_2Cl_2	–15	(73)	13.3:1
4-MeC_6H_4	1:1.5	none	*i*-PrOH	–78	(85)	1:10.1



184

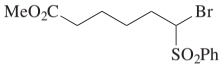
R	*(*R*)/(*S*)	Lewis Acid	Solvent	Temp (°)	**I + II**	**I/II**
n-Pr	1:1.5	none	*i*-PrOH	–78	(89)	1:6.1
n-Pr	1:1.5	Me_3Al	CH_2Cl_2	–15	(86)	9:1
i-Pr	1:2.3	none	*i*-PrOH	–78	(86)	1:10.1
i-Pr	1:2.3	Me_3Al	CH_2Cl_2	–15	(75)	8.1:1
MeCH=CH	1:1.4	none	THF	–78	(81)	1:4.6
MeCH=CH	1:1.4	Me_3Al	CH_2Cl_2	–15	(74)	4.9:1
2-furyl	1:1.4	Me_3Al	CH_2Cl_2	–15	(64)	13.3:1
n-C_6H_{13}	1:1.6	Me_3Al	CH_2Cl_2	–15	(94)	9:1
Ph	1:1.3	Et_3Al	CH_2Cl_2	–15	(67)[k]	15.7:1
Ph	1:1.5	*i*-Bu_3Al	CH_2Cl_2	–15	(56)[l]	3.3:1
Ph	1:1.6	none	toluene	–15	(83)	1.04:1
Ph	1:1.6	none	CH_2Cl_2	–15	(82)	1.04:1
Ph	1:1.6	none	MeCN	–15	(77)	1:2.1
Ph	1:1.6	none	Et_2O	–15	(80)	1:3.2
Ph	1:1.6	none	DME	–78	(88)	1:5.3
Ph	1:1.6	none	THF	–78	(85)	1:13.3

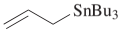
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
Continued from previous page.				
C_{6-10}				
		Et_3B/O_2, Lewis acid, solvent, 6–10 h	 **I** +  **II**	184

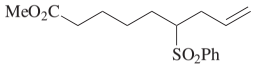
R	*(*R*)/(*S*)	Lewis Acid	Solvent	Temp (°)	**I + II**	**I/II**
Ph	1:1.6	none	THF	–15	(95)	1:49
Ph	1:1.6	none	*i*-PrOH	–15	(79)	1:32
Ph	1:1.6	BuLi	CH_2Cl_2	–15	(24)	1.1:1
Ph	1:1.6	Et_2Zn	CH_2Cl_2	–15	(69)	1.04:1
Ph	1:1.6	Me_3Al	CH_2Cl_2	–15	(83)	19:1
Ph	1:1.6	Me_3Al	CH_2Cl_2	–30	(79)	7.3:1
Ph	1:1.6	Me_3Al	toluene	–15	(80)	7.3:1
Ph	1:1.6	Me_3Al	THF	–15	(76)	1:2.3
Ph	>99:1	Me_3Al	CH_2Cl_2	–15	(81)	>99:1
Ph	1:>99	Me_3Al	CH_2Cl_2	–15	(79)	8.1:1
4-FC_6H_4	1:1.6	none	THF	–78	(88)	1:49
4-FC_6H_4	1:1.6	Me_3Al	CH_2Cl_2	–15	(78)	10.1:1
4-ClC_6H_4	1:1.6	none	THF	–78	(80)	1:49
4-ClC_6H_4	1:1.6	Me_3Al	CH_2Cl_2	–15	(77)	7.3:1
4-$MeOC_6H_4$	1:1.3	none	THF	–78	(93)	1:49
4-$MeOC_6H_4$	1:1.2	Me_3Al	CH_2Cl_2	–15	(85)	15.7:1
4-MeC_6H_4	1:1.5	none	THF	–78	(91)	1:49
4-MeC_6H_4	1:1.5	Me_3Al	CH_2Cl_2	–15	(90)	7.3:1

C_6



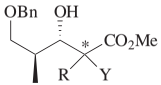


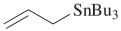
AIBN, benzene, 80°, 2 h



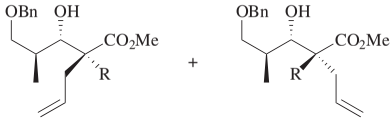
(75) 89

C_{6-7}





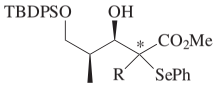
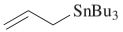
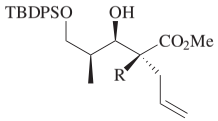
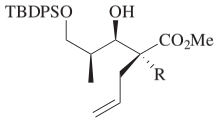
Et_3B/O_2,
Lewis acid (x eq),
CH_2Cl_2, 3.5–9 h



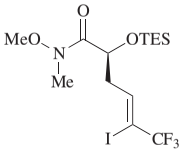
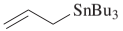
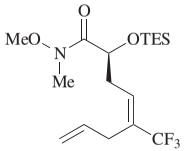
I **II**

R	Y	*	Lewis Acid	x	Temp	**I + II**	**I/II**	
H	PhSe	(*R*)	none	—	–78° to rt	(0)	—	186
H	PhSe	(*R*)	BF_3•OEt_2	1.1	–78° to 0	(69)	3:1	186
H	PhSe	(*R*)	$MgBr_2$•OEt_2	5	–40° to 0	(62)	>20:1	185, 186
H	PhSe	(*R*)	$MgBr_2$•OEt_2	5	–40°	(35)[m]	>20:1	185, 186
H	PhSe	(*R*)	Me_2AlCl	2.5	–78°	(90)	>20:1	185, 186
H	PhSe	(*R*)	Me_2AlCl	3.5	–40°	(52)[m]	>20:1	185, 186
H	PhSe	(*R*)	Me_2AlCl	3.5	–40°	(85)[m,n]	>20:1	185, 186
H	PhSe	(*R*)	$AlMe_3$	2.5	–78°	(80)	>20:1	185, 186
H	PhSe	(*S*)	Me_2AlCl	2.5	–78°	(53)	2:1	186
H	PhSe	(*S*)	$AlMe_3$	2.5	–40°	(60)	6:1	186
Me	PhSe	(*R*)	$TiCl_4$	1.1	0°	(0)	—	186
Me	PhSe	(*R*)	Me_2AlCl	2.5	0°	(55)	8:1	186
Me	PhSe	(*R*)	Me_2AlCl	3.5	0°	(52)[m,n]	>20:1	186
Me	PhSe	(*R*)	$AlMe_3$	2.5	0°	(58)	>20:1	186
Me	Br	(*R*,*S*)	$MgBr_2$•OEt_2	5	rt	(40)	>20:1	186
Me	Br	(*R*)	$AlMe_3$	2.5	0°	(61)	>20:1	186
Me	Br	(*S*)	$AlMe_3$	2.5	0°	(60)	>20:1	186

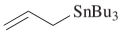
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{6-7}				
		Et_3B/O_2, Me_2AlCl, CH_2Cl_2, 4–6 h	 **I** +  **II**	186

R	*	Temp (°)	**I + II**	**I/II**
H	(*R*)	–40	(76)	>20:1
H	(*S*)	–40	(85)	>20:1
H	(*R*/*S*)	–40	(40)[o]	10:1
Me	(*R*)	0	(50)	>20:1
Me	(*S*)	0	(70)	>20:1
Me	(*R*/*S*)	0	(55)[o]	14:1

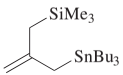
C_6				
		AIBN, benzene, 80°, 6 h	 (74)	105

C_7

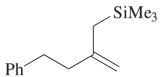


Conditions, AIBN, benzene

X	Conditions	Temp (°)	Time (h)		
Cl	—	80	—	(68)	37
Cl	*hν*	22	5	(36)	37
Cl	—	—	—	(0)[a]	91
Br	*hν*	—	20	(43)[a]	21
Br	—	80	—	(86)	37
Br	*hν*	22	5	(56)	37

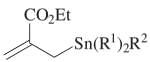


Conditions, initiator, solvent

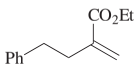


429

Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	benzene	80	13	(19)
hν	none	DME	25	2.5	(46)

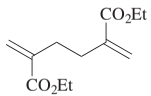


AIBN, benzene, 80°



I

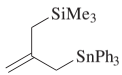
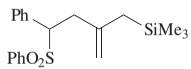
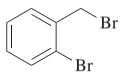
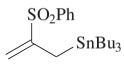
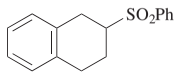
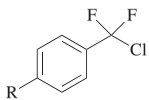
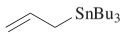
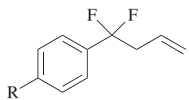
+

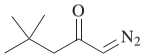
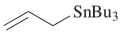
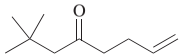
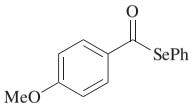
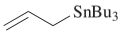
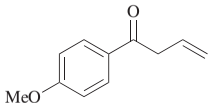
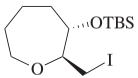
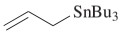
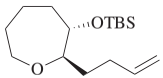
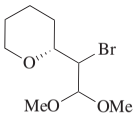
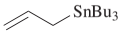
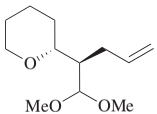
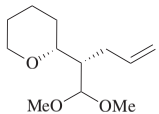


II

R^1	R^2	Time (h)	**I**	**II**	
Cl	Br	12	(8)	(72)	128
$(TMS)_2N$	Br	6	(73)	(—)	127, 128
Bu	Bu	—	(76)	(—)	44
Bu	Bu	12	(74)	(—)	128

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		*h*ν, AIBN, DME, 15–20°, 25 h	 (43)	36
		1. AIBN, benzene, 80° 2. AIBN, Bu_3SnH	 (88)[e]	135
	 *x* eq	AIBN, solvent		

		AIBN, benzene, 80°, 3 h		(72)	64
		AIBN, Bu_3SnH (cat.), benzene, 80°		(23)	111
		AIBN, benzene, 80°, 5 h		(70)	422
		*hν*, AIBN, Lewis acid, CH_2Cl_2, rt	 **I** +  **II**		193

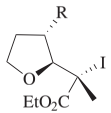
Lewis Acid	**I + II**	**I/II**
—	(60)	1:1.5
$MgBr_2 \bullet OEt_2$	(87)	6.7:1

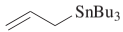
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

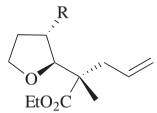
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_7



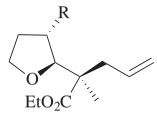


Initiator, Lewis acid, solvent



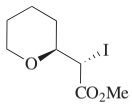
I

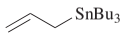
+



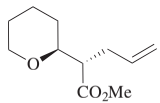
II

R	Initiator	Solvent	Lewis Acid	Temp	**I + II**	**I/II**	
H	AIBN	hexanes	none	reflux	(81)	1:10	179, 180
H	Et_3B	CH_2Cl_2	$MgBr_2{\bullet}OEt_2$	–78°	(82)	1:1	179, 180
TBSO	AIBN	hexanes	none	reflux	(65)	1:16	179, 180, 475
TBSO	Et_3B	toluene	none	–78°	(0)	—	475
TBSO	Et_3B	CH_2Cl_2	$MgBr_2{\bullet}OEt_2$	–78°	(70)	7:1	179, 180



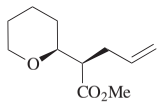


Initiator, Lewis acid, solvent



I

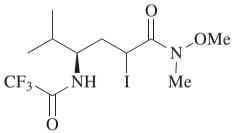
+

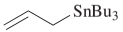


II

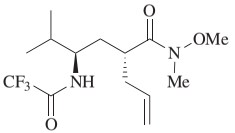
179–181

Initiator	Solvent	Lewis Acid	Temp	**I + II**	**I/II**
AIBN	hexanes	none	reflux	(89)	1:10
Et_3B	CH_2Cl_2	$MgBr_2{\bullet}OEt_2$	–78°	(84)	18:1





$h\nu$, AIBN,
toluene or CH_2Cl_2,
–40 to –20°



I

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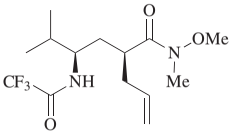
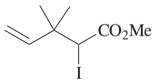
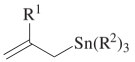


II

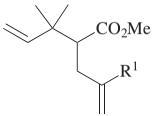
I + II (83) **I/II** = 7.3:1

188



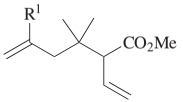


AIBN, benzene, 80°



I

+



II

R^1	R^2	**I + II**	**I/II**
H	Bu	(60)	10.1:1
Me	Bu	(53)	>19:1
MeO_2C	Bu	(27)	2.2:1
MeO_2C	Ph	(65)	1.7:1
Me_3Sn	Me	(—)	>19:1

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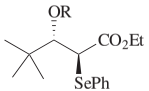
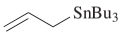
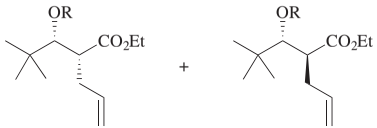
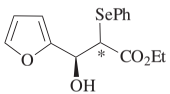
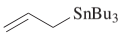
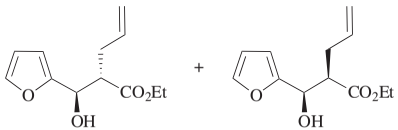
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

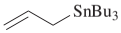
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		*h*ν, AIBN, solvent, –78°	 **I** + **II**	177

R	Solvent	**I + II**	**I/II**
H	THF	(75)	1:4.9
H	toluene	(90)	1:32
Ac	THF	(82)	8.1:1
Ac	toluene	(82)	8.1:1

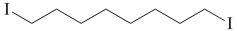
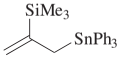
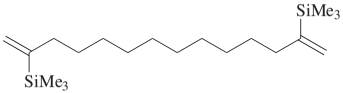
		*h*ν, AIBN, Lewis acid, 10°	 **I** + **II**	183

*	Lewis Acid	**I + II**	**I/II**
(*R*)	none	(94)	3.4:1
(*R*)	Me_3Al	(62)	8.1:1
(*S*)	none	(90)	3.3:1
(*S*)	Me_3Al	(66)	12:1

C_8

n-$C_8H_{17}X$  Conditions, initiator, solvent

X	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
Br	—	AIBN	benzene	80	—	(96)	37
Br	$h\nu$	none	neat	22	5	(90)	37
I	—	AIBN	toluene	80	—	(68)[c]	4
I	—	—	tetrahydropyran	—	—	(—)	479



AIBN, benzene, 80°, 8 h

(82) 39

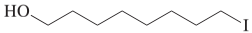
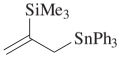
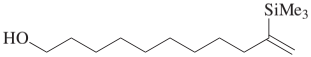
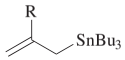
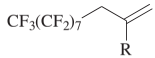
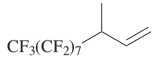
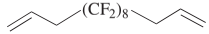
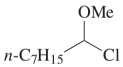
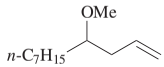
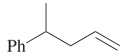


AIBN, benzene, 80°, 8 h

(75) 39

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
$CF_3(CF_2)_7I$		Conditions, initiator, solvent		

R	Conditions	Initiator	Solvent	Temp	Time (h)		Refs.
H	—	AIBN	hexanes	reflux	2	(83)[p]	96
H	—	AIBN	hexanes	reflux	5	(82)[q]	97
H	*h*ν	none	CH_2Cl_2	—	4	(78)	480
H	*h*ν	none	CH_2Cl_2	—	1	(81)	95
Me	—	AIBN	hexanes	reflux	2	(81)[p]	96
Me	—	AIBN	hexanes	reflux	5	(69)[q]	97
Ph	—	AIBN	hexanes	reflux	5	(93)[q]	97

		AIBN, hexanes, reflux, 4 h		(69)[p]	96
$I(CF_2)_8I$		*h*ν, CH_2Cl_2, 0°, 5 h		(52)	481
		$ZnCl_2 \cdot OEt_2$, CH_2Cl_2, –78°		(60)	51
		$ZnCl_2 \cdot OEt_2$, CH_2Cl_2, –78°		(99)	51

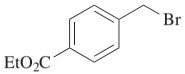
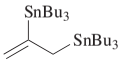
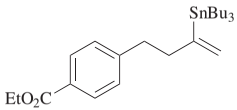
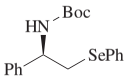
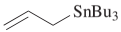
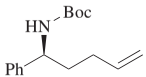
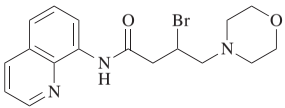
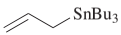
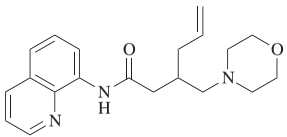
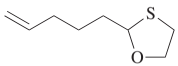
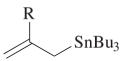
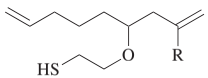
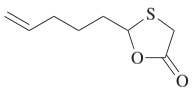
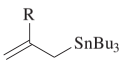
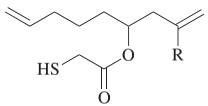
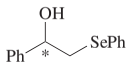
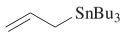
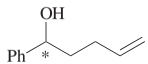
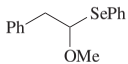
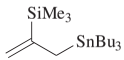
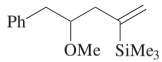
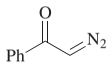
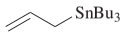
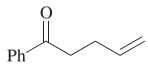
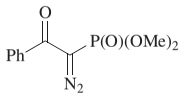
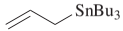
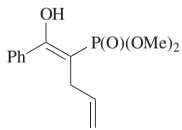
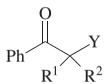
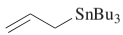
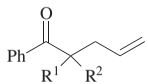
		$h\nu$, $(Bu_3Sn)_2$, toluene, 60°, 2 h		(37)[b]	426
		AIBN, benzene, 80°, 4 h		(90)	482
		AIBN, benzene, 80°, 3 h		(75)	483
		AIBN, benzene, 80°		R H (—) Me (—)	484
		AIBN, benzene, 80°		R H (—) Me (—)	484

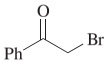
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

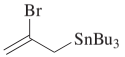
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, benzene, 80°, 5 h	 * (*R*) (66) (*S*) (55)	485
		*hν*, AIBN, benzene, 10°	 (63)	61
		AIBN, benzene, 80°, 3 h	 (75)	64
		*hν*, Hantzsch ester, TBAB, DCE, 25°, 8 h	 (—)	486
C_{8-10}				
		Conditions, initiator, solvent		

R^1	R^2	Y	Conditions	Initiator	Solvent	Temp (°)	Time (h)		Refs.
H	H	F	—	none	benzene	61	53	(0)[c]	59
H	H	F	—	AIBN	benzene	61	53	(95)[c]	59
H	H	Cl	*hν*	none	benzene	22	1	(54)	37
H	H	Cl	*hν*	$Cu(dap)_2Cl$	MeCN	rt	5	(85)	47
H	H	Cl	—	none	benzene	61	53	(30)[c]	59
H	H	Cl	—	AIBN	benzene	61	53	(95)[c]	59

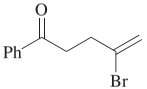
H	H	Cl	—	AIBN	benzene	80	3	(51)	37
H	H	Cl	—	AIBN	benzene	80	5	(59)	440
H	H	Br	*h*ν	$Cu(dap)_2Cl$	MeCN	rt	3	(80)	47
H	H	Br	*h*ν	none	MeCN	rt	3	(0)	47
H	H	Br	*h*ν	none	MeCN	rt	24	(30)	47
H	H	Br	—	none	benzene	61	53	(39)[c]	59
H	H	Br	—	AIBN	benzene	61	53	(95)[c]	59
H	H	PhO	—	none	benzene	61	53	(0)[c]	59
H	H	PhO	—	AIBN	benzene	61	53	(tr)[c]	59
H	H	BzO	—	none	benzene	61	53	(14)[c]	59
H	H	BzO	—	AIBN	benzene	61	53	(83)[c]	59
H	Me	Br	—	none	benzene	61	53	(0)[c]	59
H	Me	Br	—	AIBN	benzene	61	53	(99)[c]	59
Me	Me	Br	—	none	benzene	61	53	(0)[c]	59
Me	Me	Br	—	AIBN	benzene	61	53	(tr)[c]	59

C_8

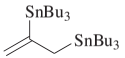




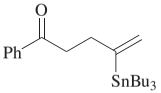
AIBN, toluene, 80°, 2–4 h



(71) 430



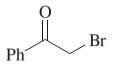
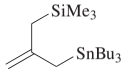
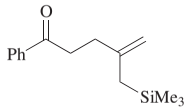
*h*ν, $(Bu_3Sn)_2$, toluene



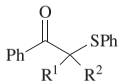
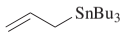
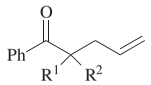
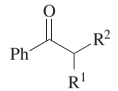
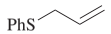
426

Temp	Time (min)	
rt	10	(77)
60°	30	(81)[b]

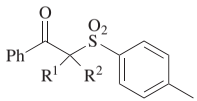
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

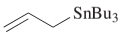
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		Conditions, initiator, solvent		429

Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	benzene	80	12	(51)
*h*ν	AIBN	DME	0	2.5	(74)
*h*ν	none	benzene	0	2.5	(46)

C_{8-10}				
		Initiator, benzene, 61°, 48 h	 **I** +  **II** +  **III**	59

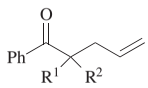
R^1	R^2	Initiator	**I**[c]	**II**[c]	**III**[c]
H	H	none	(0)	(2)	(4)
H	H	AIBN	(6)	(41)	(39)
Me	Me	AIBN	(0)	(tr)	(tr)





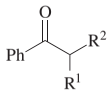
x eq

Initiator, benzene, 61°, 48 h



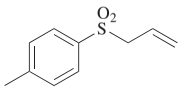
I

+



II

+



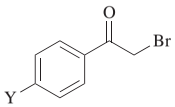
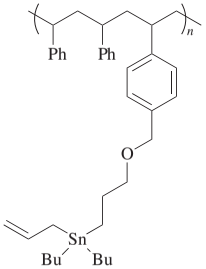
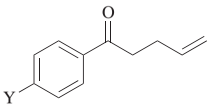
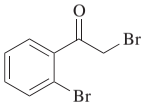
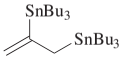
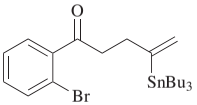
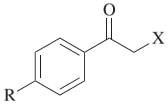
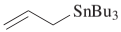
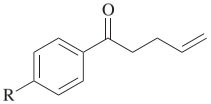
III

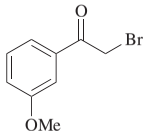
59

R^1	R^2	*x*	Initiator	**I**[c]	**II**[c]	**III**[c]
H	H	1	none	(0)	(1)	(3)
H	H	1	AIBN	(0)	(78)	(78)
H	H	2	none	(0)	(32)	(31)
H	H	2	AIBN	(0)	(89)	(89)
H	Me	2	none	(0)	(4)	(3)
H	Me	2	AIBN	(0)	(79)	(87)
Me	Me	2	none	(0)	(4)	(8)
Me	Me	2	AIBN	(0)	(96)	(92)

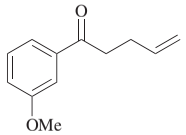
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, benzene, 80°		116
			Y / Time (h): H / 12 (68); Br / 2 (68)	
		$h\nu$, $(Bu_3Sn)_2$, toluene, 60°, 0.5 h	 (43)[b]	426
		$h\nu$, $Cu(dap)_2Cl$, MeCN, rt		47
			X / R / Time (h): Cl / MeO / 5 (79); Br / MeO / 4.5 (74); Br / O_2N / 4 (74)	

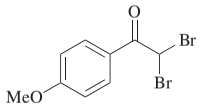


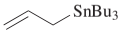
$h\nu$, BTF, 25°



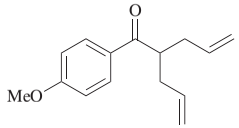
123

R	Time (h)	
$CF_3(CF_2)_3(CH_2)_2$	72	(—)
$CF_3(CF_2)_5(CH_2)_2$	72	(—)
$CF_3(CF_2)_3(CH_2)_3$	8	(67)
$CF_3(CF_2)_3(CH_2)_3$	8	(92)[p]
$CF_3(CF_2)_5(CH_2)_3$	3	(76)



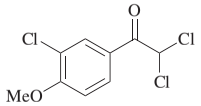


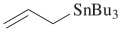
$h\nu$, $Cu(dap)_2Cl$, MeCN, rt, 7 h



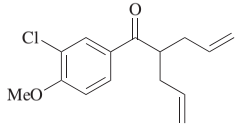
(89)

47





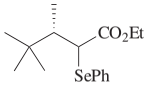
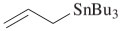
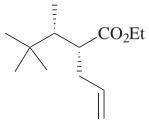
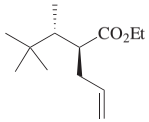
$h\nu$, $Cu(dap)_2Cl$, MeCN, rt, 5.5 h



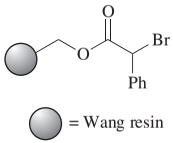
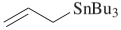
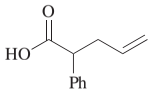
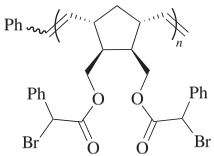
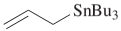
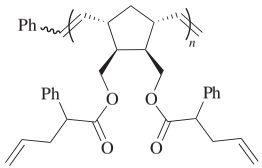
(80)

47

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		Conditions, AIBN, solvent	 **I** +  **II**	177

Conditions	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**
—	benzene	80	—	(65)	1.5:1
*h*ν	THF	–78	39	(69)	1.6:1

 = Wang resin		1. AIBN, benzene, 80°, 14 h 2. TFA, $CHCl_3$	 (76)[e]	78
		AIBN, benzene, 80°	 (76)	441

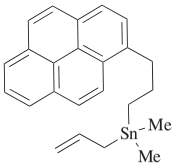
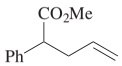
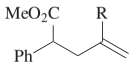
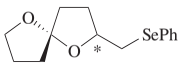
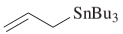
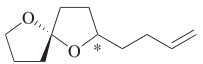
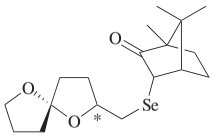
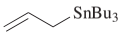
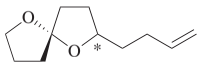
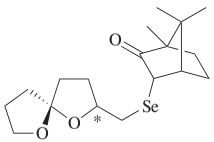
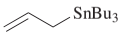
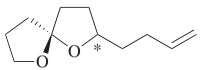
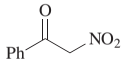
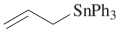
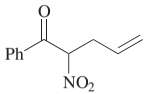
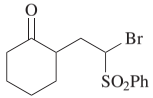
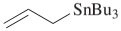
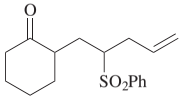
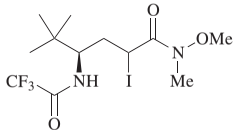
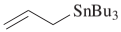
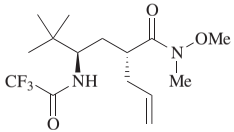
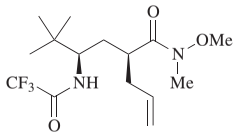
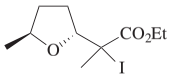
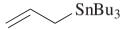
		AIBN, benzene, 80°, 5 h		(86)	126
		AIBN, benzene, 80°, 8 h		R NC– (62) EtO_2C (74)	127
		AIBN, benzene, 80°, 3 h		* (*R*) (60) (*S*) (65)	487
		AIBN, benzene, 80°, 6 h		* (*R*) (80) (*S*) (68)	487
		AIBN, benzene, 80°, 6 h		* (*R*) (73) (*S*) (77)	487

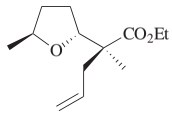
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		$Mn(OAc)_3$, AcOH, 60°, 5 min	 (34)	66
		AIBN, benzene, 80°, 3 h	 (90) dr = 1.5:1	89
		*hν*, AIBN, toluene or CH_2Cl_2, –40° or –20°	 **I** +  **II** **I + II** (72) **I/II** = 8.1:1	188



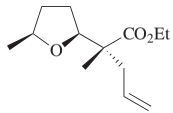


AIBN, hexane, reflux, 12 h



I

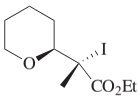
+

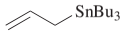


II

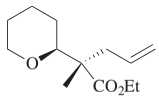
488

I + **II** (66) **I/II** = 1.5:1



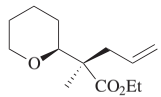


Initiator, Lewis acid, solvent



I

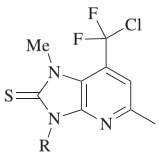
+

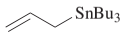


II

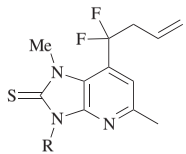
179, 180

Initiator	Solvent	Lewis Acid	Temp	**I + II**	**I/II**
AIBN	hexanes	none	reflux	(77)	1:18
Et_3B	CH_2Cl_2	$MgBr_2 \cdot OEt_2$	–78°	(54)	27:1





AIBN, benzene, 80°, 16 h



R	
Me	(69)
Ph	(55)

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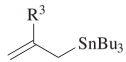
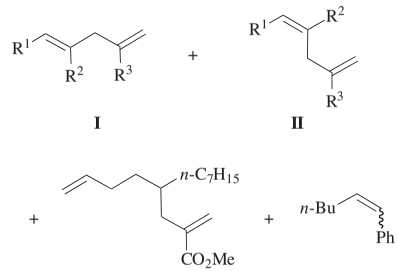
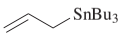
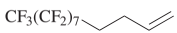
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

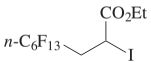
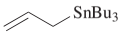
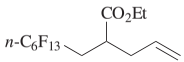
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{9-12}				
		Initiator, benzene		104

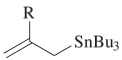
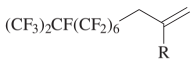
R^1	R^2	R^3	Initiator	Temp (°)	Time (h)	**I + II**	**I/II**	**III**	**IV**
Ph(HO)CH	H	MeO_2C	AIBN	80	1	(59)	2.2:1	(—)	(—)
Ph(HO)CH	H	MeO_2C	Et_3B	25	6	(40)	2:1	(—)	(—)
Ph(HO)CH^r	H	MeO_2C	AIBN	80	1	(52)	2.1:1	(—)	(—)
Ph(HO)CH^r	H	MeO_2C	Et_3B	25	6	(40)	2:1	(—)	(—)
Ph(TBSO)CH	H	MeO_2C	AIBN	80	1	(57)	3.3:1	(—)	(—)
Ph(TBSO)CH	H	MeO_2C	Et_3B	25	6	(58)	2.8:1	(—)	(—)
t-Bu	*n*-Bu	MeO_2C	AIBN	80	1	(71)	13.3:1	(—)	(—)
t-Bu	*n*-Bu	MeO_2C	Et_3B	25	2	(78)	15.7:1	(—)	(—)
t-Bu	*n*-Bu	NC–	AIBN	80	1	(63)	11.5:1	(—)	(—)
t-Bu	*n*-Bu	NC–	Et_3B	25	24	(48)	15.7:1	(—)	(—)
H	*n*-$C_{10}H_{21}$	MeO_2C	AIBN	80	2	(60)	—	(—)	(—)
H	*n*-$C_{10}H_{21}$	NC–	AIBN	80	2	(53)	—	(—)	(—)
n-Bu	Ph	H	AIBN	80	24	(5)	6.1:1	(—)	(4)
n-Bu	Ph	MeO_2C	AIBN	80	4	(86)	6.7:1	(—)	(—)
n-Bu	Ph	MeO_2C	Et_3B	25	24	(70)	11.5:1	(—)	(—)

n-Bu	Ph	NC–	AIBN	80	1	(70)	8.1:1	(—)	(—)
n-Bu	Ph	NC–	Et_3B	25	24	(57)	10.1:1	(—)	(—)
t-Bu	Ph	MeO_2C	AIBN	80	1	(76)	>99:1	(—)	(—)
t-Bu	Ph	MeO_2C	Et_3B	25	24	(83)	>99:1	(—)	(—)
t-Bu	Ph	NC–	AIBN	80	1	(72)	>99:1	(—)	(—)
t-Bu	Ph	NC–	Et_3B	25	24	(66)	>99:1	(—)	(—)
n-C_5H_{11}	*n*-C_5H_{11}	MeO_2C	AIBN	80	1	(76)	1.1:1[g]	(—)	(—)
n-C_5H_{11}	*n*-C_5H_{11}	MeO_2C	Et_3B	25	24	(77)	1.1:1[g]	(—)	(—)
n-$C_{10}H_{21}$	H	MeO_2C	AIBN	80	1	(34)	1.3:1	(4)	(—)
n-$C_{10}H_{21}$	H	MeO_2C	Et_3B	25	3	(55)	1.3:1	(1)	(—)

C_9

$CF_3(CF_2)_7CH_2I$  ACCN, BTF, reflux, 6 h  (56) 95

  Et_3B, CH_2Cl_2, rt, 3 h  (79) 490

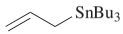
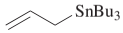
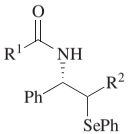
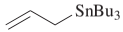
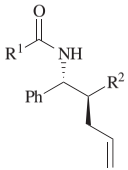
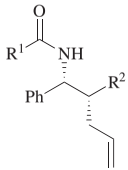
$(CF_3)_2CF(CF_2)_6I$  AIBN, hexanes, reflux 

R	Time (h)		
H	2	(86)[p]	96
H	5	(86)[q]	97
Me	2	(82)[p]	96
Me	5	(84)[q]	97
Ph	5	(86)[q]	97

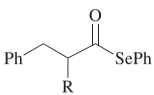
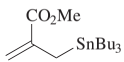
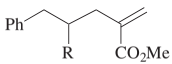
AIBN, hexanes, reflux, 4 h (74)[p] 96

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
t-$BuCH_2OSO_2(CF_2)_2O(CF_2)_2I$		AIBN, hexanes, 65°, 8 h	*t*-$BuCH_2OSO_2(CF_2)_2O(CF_2)_2$ (—)	491
$CF_3(CF_2)_3CH_2OSO_2(CF_2)_2O(CF_2)_2I$		AIBN, hexanes, 65°, 8 h	$CF_3(CF_2)_3CH_2OSO_2(CF_2)_2O(CF_2)_2$ (—)	491
		*hν*, AIBN, solvent	 +  **I** **II**	188

R^1	R^2	Solvent	Temp (°)	**I + II**	**I/II**
CF_3	Me_2NCO	toluene	–40	(76)	>49:1
CF_3	Me_2NCO	toluene	30	(—)	>49:1
CF_3	Me_2NCO	DMSO	—	(76)	1.2:1
CF_3	MeO_2C	toluene	–40	(—)	>49:1
CF_3	MeO_2C	DMSO	—	(—)	1:3.2
t-Bu	MeO_2C	toluene	–40	(—)	>49:1
t-Bu	MeO_2C	DMSO	—	(—)	1:4
t-Bu	NC–	toluene	–40	(—)	3.2:1

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		AIBN, benzene, 80°, 3 h	 R: BocHN (58); PhthN (53)	113

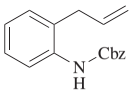
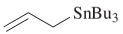
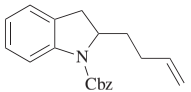
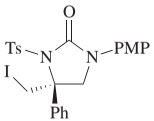
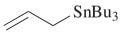
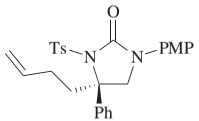
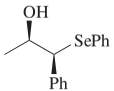
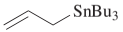
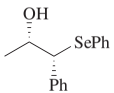
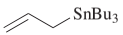
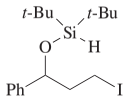
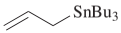
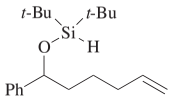
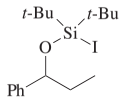
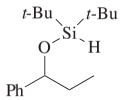
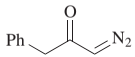
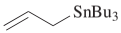
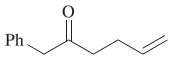
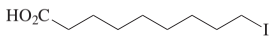
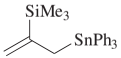
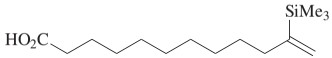
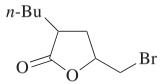
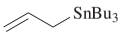
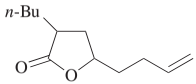
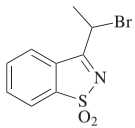
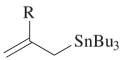
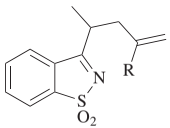
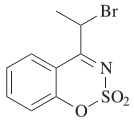
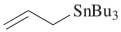
		1. PhthN–SePh, CH_2Cl_2 2. Allylstannane, AIBN, toluene, 110°		(76)[e]	464
		AIBN, benzene, 80°, 3 h		(60)	492
		AIBN, benzene, 80°, 23 h			485
			I **I + II** (64) **I/II** = 1:1 **II**		
		AIBN, benzene, 80°, 23 h			485
			I **I + II** (56) **I/II** = 1:1 **II**		

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

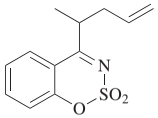
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		AIBN, benzene, 80°	 (43)[c]	437
			+  (44)[c] +  (5)[c]	
		AIBN, benzene, 80°, 3 h	 (70)	64
		AIBN, benzene, 80°, 8 h	 (65)	39
		AIBN, benzene, 80°	 (83)	493
		*h*ν, initiator, MeCN, rt, 12 h		405

R	Initiator	
H	erythrosin B	(87)
Me	$Ru(bpy)_3(PF_6)_2$	(71)

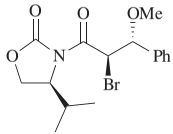


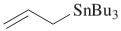


hν, erythrosin B, MeCN, rt, 12 h

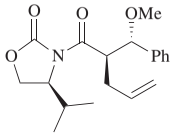


(81) 405

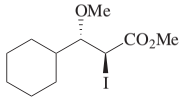


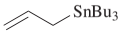


hν, $Cu(dap)_2Cl$, MeCN, rt, 15 h

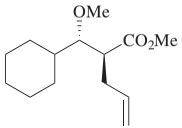


(75) dr = 3:1 47





Initiator, Lewis acid, solvent



I

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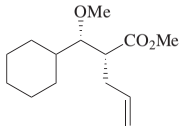


II

179, 180

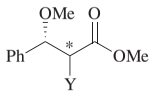
Initiator	Solvent	Lewis Acid	Temp	**I + II**	**I/II**
AIBN	hexanes	none	reflux	(84)	1:3.5
Et_3B	CH_2Cl_2	$MgBr_2 \cdot OEt_2$	−78°	(95)	>100:1

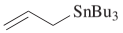
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

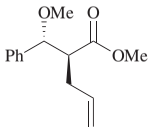
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_9



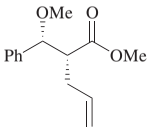


Conditions, initiator, Lewis acid (*x* eq), solvent



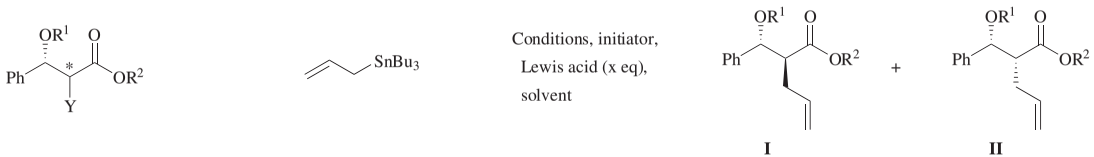
I

+



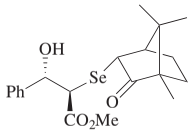
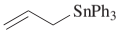
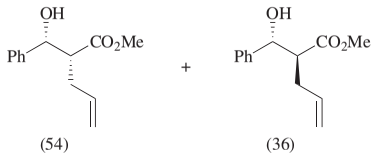
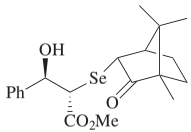
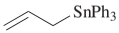
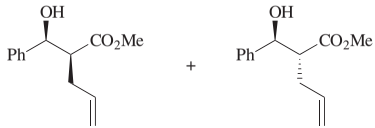
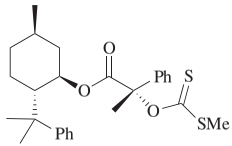
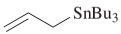
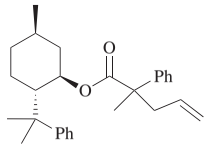
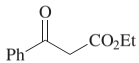
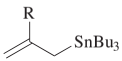
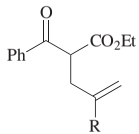
II

Y	*	Conditions	Initiator	Lewis Acid	*x*	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
Br	(*R*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(82)	1:6	179
Br	(*R*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(80)	20:1	179, 181
Br	(*S*)	—	AIBN	none	—	benzene	80	—	(87)	1:4	177
Br	(*S*)	*h*ν	AIBN	none	—	THF	–78	—	(88)	1:9	177
Br	(*S*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(73)	1:5	179
Br	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(78)	19:1	179–181
I	(*R*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(84)	1:6	179
I	(*R*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(69)	5:1	179–181
I	(*S*)	—	AIBN	none	—	hexane	69	5	(82)	1:5	180, 181, 475
I	(*S*)	—	Et_3B	none	—	toluene	–78	6	(75)	1:17	179, 475
I	(*S*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(82)	1:5	179
I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	0.25	CH_2Cl_2	–78	—	(—)	1.6:1	181
I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	1	CH_2Cl_2	–78	—	(—)	7:1	181
I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(80)	38:1	179–181
PhSe	(*R*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(86)	1:6	179
PhSe	(*R*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(76)	38:1	179
PhSe	(*S*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(63)	1:5	179
PhSe	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(90)	65:1	179–181



R^1	R^2	Y	*	Conditions	Initiator	Lewis Acid	x	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
H	Me	Br	(*S*)	*hν*	AIBN	none	—	THF	–78	—	(91)	1:6.7	177
H	Me	Br	(*S*)	*hν*	AIBN	none	—	toluene	–78	—	(79)	1:1.2	177
Bn	Me	I	(*S*)	—	AIBN	none	—	hexanes	69	7	(73)	1:5	475
Bn	Me	I	(*S*)	—	Et_3B	none	—	toluene	–78	4	(87)	1:22	475
Bn	Me	I	(*S*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(60)	1:10	179
Bn	Me	I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(52)	5:1	179, 180
TMS	Me	I	(*S*)	—	AIBN	none	—	hexanes	69	—	(84)	1:3	179
TMS	Me	I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(78)	1:4	179
TBS	Me	Br	(*S*)	*hν*	AIBN	none	—	CH_2Cl_2	32	2	(100)	1:3.4	460
TBS	Me	Br	(*S*)	*hν*	AIBN	$Eu(fod)_3$	0.1	CH_2Cl_2	32	2	(88)	1:4	460
TBS	Me	Br	(*S*)	*hν*	AIBN	$Eu(fod)_3$	1.1	CH_2Cl_2	32	2	(77)	1:4	460
TBS	Me	I	(*S*)	—	Et_3B	none	—	CH_2Cl_2	–78	—	(86)	1:13	179–181
TBS	Me	I	(*S*)	—	Et_3B	$MgBr_2{\bullet}OEt_2$	3	CH_2Cl_2	–78	—	(90)	1:8	179–181
TBS	Et	Br	(*S*)	*hν*	AIBN	none	—	CH_2Cl_2	32	2	(100)	1:3	460
TBS	Et	Br	(*S*)	*hν*	AIBN	$Eu(fod)_3$	0.1	CH_2Cl_2	32	2	(91)	1:4.1	460
TBS	Et	Br	(*S*)	*hν*	AIBN	$Eu(fod)_3$	1.1	CH_2Cl_2	32	2	(94)	1:4.8	460
TBDPS	Et	Br	(*R*)/(*S*)	—	$(Bu_3Sn)_2$	none	—	benzene	80	—	(—)	1.5:1	176

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		AIBN, benzene, 80°, 7 h	 (54) + (36)	494
		AIBN, benzene, 80°, 7 h	 (33) + (27)	494
		*h*ν, AIBN, toluene, –78°	 (36) dr > 99:1[g]	208
		*h*ν, $Ru(bpy)_3Cl_2$, air, K_2CO_3, $Ph_3C^+BF_4^-$, DMF, rt, 24–48 h	 R: H (28); Me (72); EtO_2C (64); Ph (42)	68

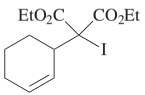
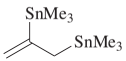
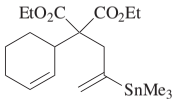
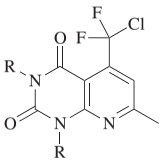
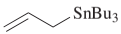
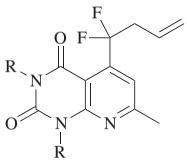
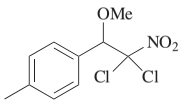
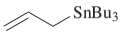
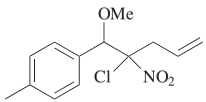
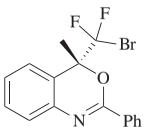
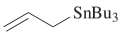
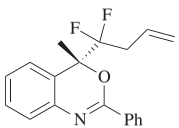
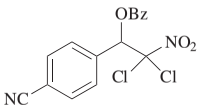
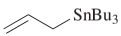
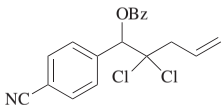
		AIBN, benzene, 80°, 8 h		(62)	41
		AIBN, benzene, 80°, 16 h		R H (29) Me (43)	94
		AIBN, toluene, 120°, 9 h		(55)	495
		AIBN, benzene, 90°, o/n		(91)	489
		AIBN, toluene, 120°, 9 h		(70)	496

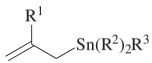
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

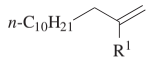
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

C_{10}

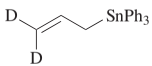
n-$C_{10}H_{21}X$



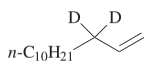
Initiator, benzene

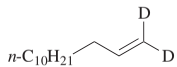


X	R^1	R^2	R^3	Initiator	Temp	Time		Refs.
Br	H	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	AIBN	80°	16 h	(68)	121
Br	EtO_2C	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	AIBN	80°	16 h	(60)	121
Br	EtO_2C	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	Et_3B, O_2	rt	10 min	(71)	121
Br	EtO_2C	$(TMS)_2N$	Br	AIBN	80°	8 h	(56)	127
I	EtO_2C	Bu	Bu	AIBN	80°	—	(70)	44



AIBN, benzene, 80°



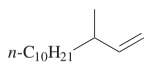
I + 

II — 44

X	Time (h)	**I + II**	**I/II**
Cl	36	(4)	1:1
Br	24	(16)	3:1
I	12	(45)	>10:1

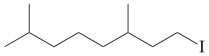
n-$C_{10}H_{21}Br$

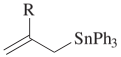
Initiator, solvent, 8 h



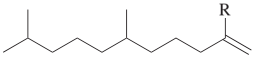
I + n-$C_{10}H_{22}$ **II** — 139

Initiator	Solvent	Temp (°)	**I**	**II**
AIBN	toluene	80	(0)	(0)
$(t\text{-BuO})_2$	chlorobenzene	131	(0)	(52)



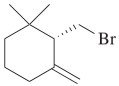


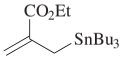
AIBN, benzene, 80°



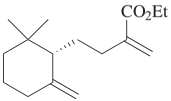
39

R	Time (h)	
H	8	(74)
TMS	4	(94)





AIBN, benzene, 80°, 30 h

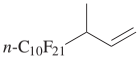


(87)

497

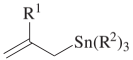
n-$C_{10}F_{21}I$

AIBN, hexane, 69°, 4 h

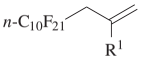


(73)[p]

96

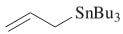
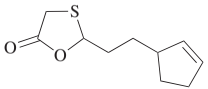
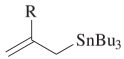
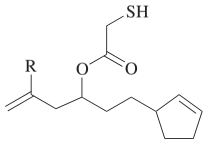
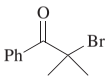
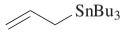
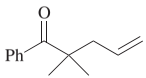
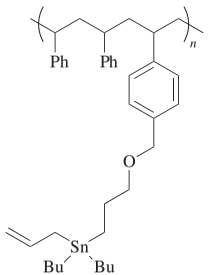
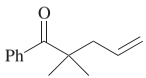


Conditions, initiator, solvent

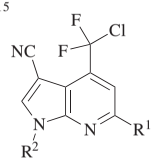


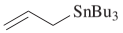
R^1	R^2	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
H	Bu	$h\nu$	none	neat	rt	2	(80)	472
H	Bu	—	AIBN	hexane	69	2	(90)[p]	96
H	Bu	—	AIBN	hexane	69	5	(97)[q]	97
H	$CF_3(CF_2)_5(CH_2)_3$	—	AIBN	BTF	80	2–5	(75)	123
Me	Bu	—	AIBN	hexane	69	2	(87)[p]	96
Me	Bu	—	AIBN	hexane	69	5	(89)[q]	97
Ph	Bu	—	AIBN	hexane	69	5	(90)[q]	97

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

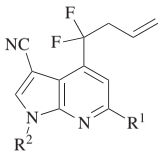
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_{10}				
$ArOSO_2(CF_2)_2O(CF_2)_2I$		AIBN, hexane, 65°, 8 h	$ArOSO_2(CF_2)_2O(CF_2)_2$	491
			Ar / (—): Ph; 4-$O_2NC_4H_4$; 2,4-$F_2C_4H_3$	
		None reported		484
			R / (—): H; Me	
		AIBN, benzene, 80°	 (0)	116
		AIBN, benzene, 80°, 48 h	 (50)	116

C_{10-15}





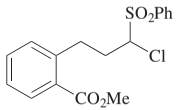
AIBN, benzene, 80°, 16 h

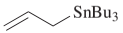


94

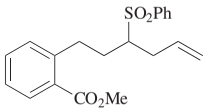
R^1	R^2	
Me	*t*-Bu	(68)
Me	PMB	(61)
4-ClC_6H_4	*t*-Bu	(68)
4-ClC_6H_4	PMB	(68)

C_{10}





AIBN, benzene, 80°, 2 h



(82)

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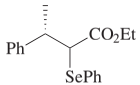
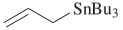
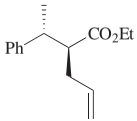


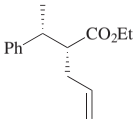


Conditions, AIBN, solvent



I

+

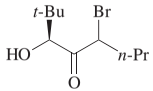
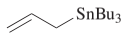
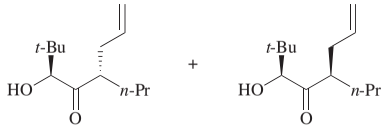


II

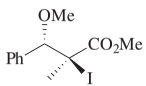
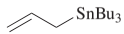
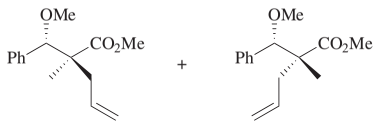
177

Conditions	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**
—	benzene	80	—	(70)	2:1
*h*ν	THF	–78	39	(86)	2.8:1

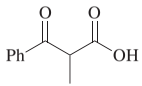
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

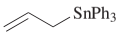
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
		Initiator, Lewis acid, solvent	 **I** + **II**	187

Initiator	Lewis Acid	Solvent	Temp (°)	**I + II**	**I/II**
AIBN	none	benzene	80	(90)	4:1
Et_3B, O_2	none	CH_2Cl_2	–78	(33)	5:1
Et_3B, O_2	none	CH_2Cl_2	0	(23)	3:1
Et_3B, O_2	none	CH_2Cl_2	25	(40)	3:1
Et_3B, O_2	$ZnCl_2$	CH_2Cl_2, THF	–78	(76)	100:1
Et_3B, O_2	$ZnCl_2$	CH_2Cl_2, THF	0	(75)	6:1
Et_3B, O_2	$MgBr_2{\bullet}OEt_2$	CH_2Cl_2, Et_2O	–78	(81)	100:1
Et_3B, O_2	$MgBr_2{\bullet}OEt_2$	CH_2Cl_2, Et_2O	0	(91)	6:1
Et_3B, O_2	$Yb(OTf)_3$	CH_2Cl_2	–78	(48)	9:1
Et_3B, O_2	$Yb(OTf)_3$	CH_2Cl_2	0	(66)	5:1

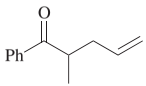
		Initiator, Lewis acid, solvent	 **I** + **II**	179, 180, 383

Initiator	Lewis Acid	Solvent	Temp (°)	**I + II**	**I/II**
AIBN	none	hexanes	69	(75)	1:16
Et_3B	$MgBr_2{\bullet}OEt_2$	CH_2Cl_2	–78	(76)	>100:1

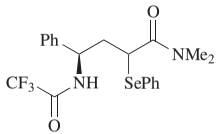


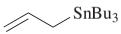


Mn(pic)$_3$, DMF, rt, 110 h

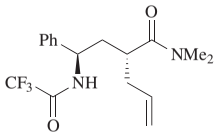


(63) 67



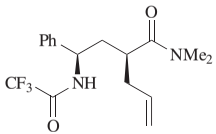


*h*ν, AIBN, solvent



I

+

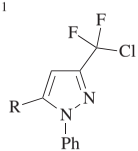


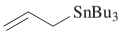
II

188

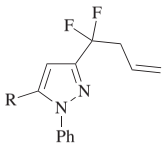
Solvent	Temp (°)	**I + II**	**I/II**
toluene	–40	(97)	1.6:1
DMSO	—	(—)	1:1

C_{10-11}





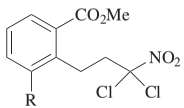
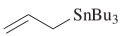
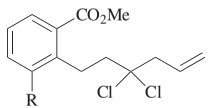
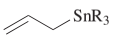
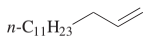
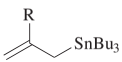
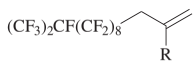
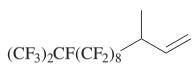
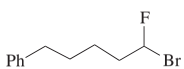
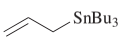
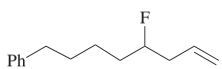
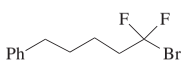
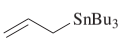
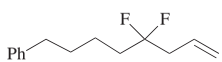
AIBN, benzene, 80°, 16 h

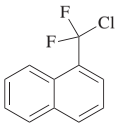


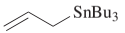
R	
H	(38)
Me	(40)

94

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

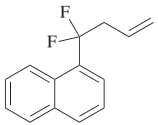
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_{10}				
		AIBN, toluene, 110°, 8 h	 R: H (70); MeO (68)	63
C_{11}				
n-$C_{11}H_{23}I$	 R = $(CH_2)_3(CF_2)_5CF_3$	AIBN, BTF, 80°, 2–5 h	 (75)	123
$(CF_3)_2CF(CF_2)_8I$		AIBN, hexane, reflux, 2 h	 R: H (91)[p]; Me (95)[p]	96
		AIBN, hexane, reflux, 4 h	 (78)[p]	96
		AIBN, toluene, 90°, 2 h	 (70)	498
		AIBN, toluene, 90°, 2 h	 (53)	499





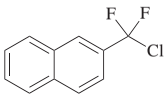
x eq

Initiator, benzene

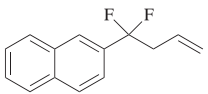


91

Initiator	*x*	
AIBN	1.2	(33)[c]
$(PhCO_2)_2$	1.2	(36)[c]
AIBN, Bu_3SnH	1.2	(44)[c]
AIBN	5	(93)[c]



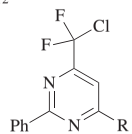
AIBN, benzene

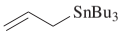


(96)[c]

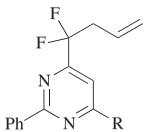
91

C_{11-12}





AIBN, benzene, 80°, 16 h



R	
H	(29)
Me	(45)

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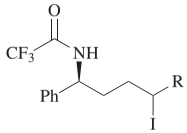
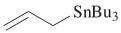
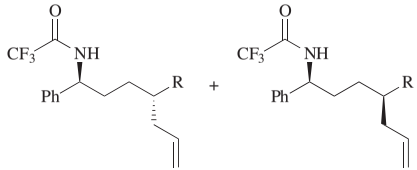
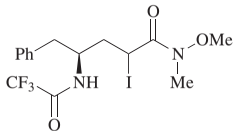
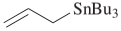
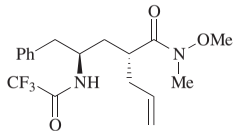
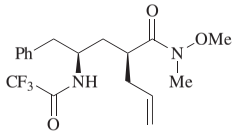
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11}				
		*hν*, AIBN, solvent, –40°, 10 h	 **I** + **II**	188

R	Solvent	**I + II**	**I/II**
MeO_2C	toluene	(—)	1.9:1
Me_2NCO	CH_2Cl_2	(79)	6.1:1
NC–	toluene	(—)	1:1

		*hν*, AIBN, toluene, –25°, 9 h	 **I** +  **II** **I + II** (82) **I/II** = 6.7:1	188

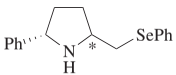
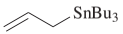
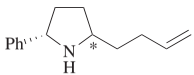
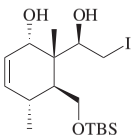
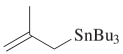
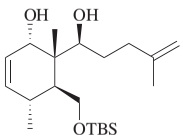
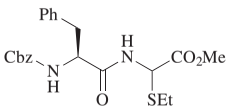
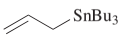
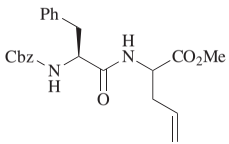
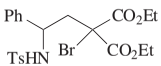
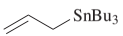
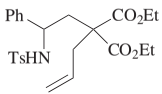
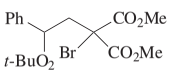
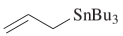
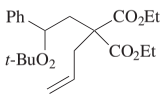
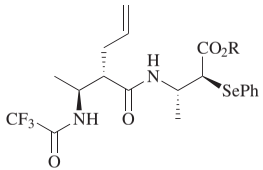
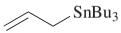
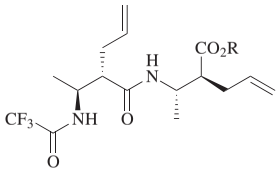
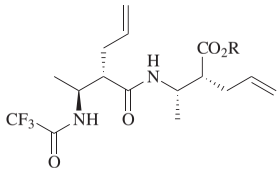
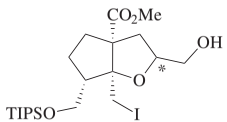
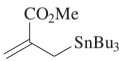
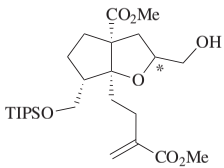
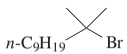
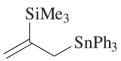
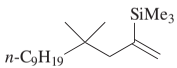
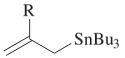
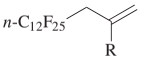
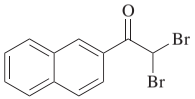
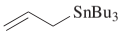
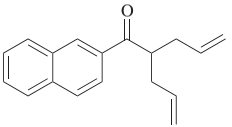
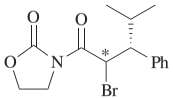
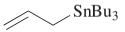
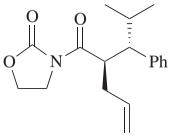
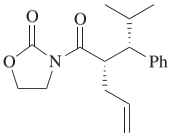
		AIBN, benzene, 80°, 4 h		* (*R*) (65) (*S*) (68)	73
		ACCN, benzene, 80°, 6 h		(58)	500
		AIBN, benzene, 80°, 1 h		(62) dr = 1:1	501
		AIBN, benzene, 80°, 2 h		(91)	502
		AIBN, benzene, 80°, 2 h		(76)	503

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

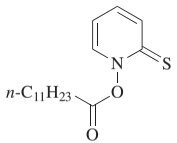
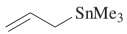
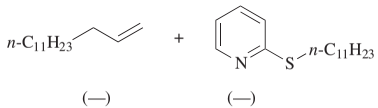
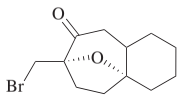
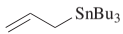
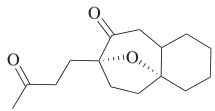
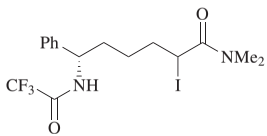
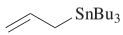
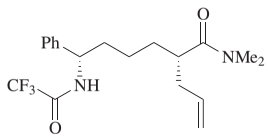
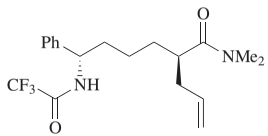
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11}				
 R = $(CH_2)_2SiMe_3$		*h*ν, AIBN, toluene, –40°, 5 h	 **I** +  **II** **I** + **II** (91) **I/II** > 49:1	188
 *dr = 1:1		AIBN, benzene, 80°, 2.5 h	 (59) *dr = 1:1	504
C_{12}				
		AIBN, benzene, 80°, 8 h	 (97)	39

n-$C_{12}F_{25}I$		AIBN, hexane, 69°, 5 h		R H (89)[g] Me (75)[g] Ph (90)[g]	97
	 2 eq	$h\nu$, $Cu(dap)_2Cl$, MeCN, rt, 6 h		(78)	47
		Et_3B, O_2, $Mg(ClO_4)_2$, ligand, CH_2Cl_2, –78°	 **I** +  **II**		119

*	Ligand	**I + II**	**I/II**
(*R*)	—	(87)	5:1
(*R*)	(*S*,*R*,*R*,*S*)-**L10**	(83)	12:1
(*R*)	(*R*,*S*,*S*,*R*)-**L10**	(87)	8:1
(*S*)	—	(84)	6:1
(*S*)	(*S*,*R*,*R*,*S*)-**L10**	(82)	7:1
(*S*)	(*R*,*S*,*S*,*R*)-**L10**	(84)	13:1

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}				
		*h*ν, benzene, 50°, 5 min	 (—) (—)	12
		1. AIBN, toluene, 80°, 7 h 2. $PdCl_2$, CuI, O_2, DMF, H_2O, rt, 24 h	 (70)[e]	505
		*h*ν, AIBN, CH_2Cl_2, –40°, 10 h	 **I** +  **II** **I + II** (72) **I/II** = 2.8:1	188

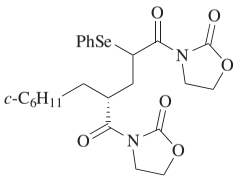
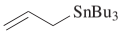
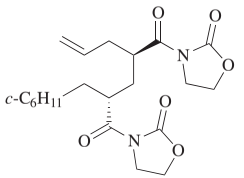
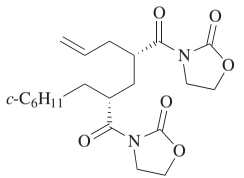
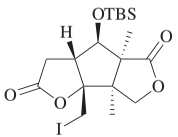
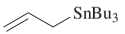
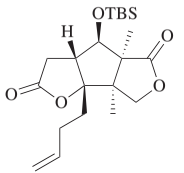
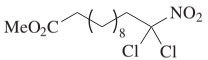
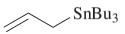
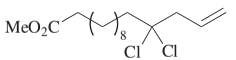
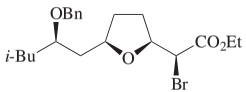
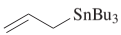
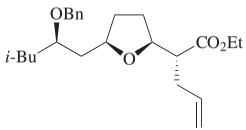
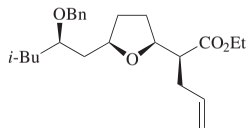
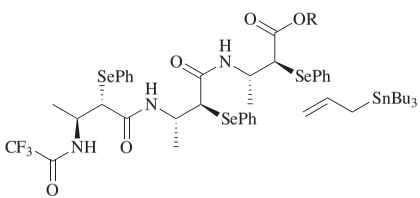
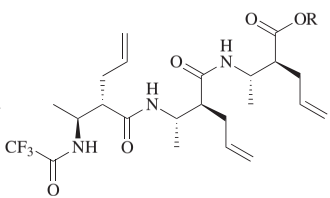
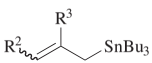
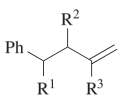
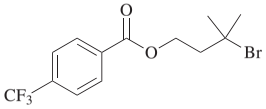
		Toluene	 **I** +  **II**	**I + II** (82) **I/II** = 6.1:1	506
		AIBN, benzene		(75)	74
		AIBN, toluene, 110°, 8 h		(62)	63

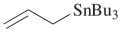
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

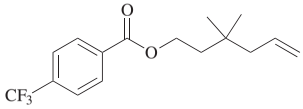
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}				
		*hν*, AIBN, toluene, –78°, 4 h	 **I** +  **II** **I** + **II** (65) **I/II** > 19:1	507
 R = $(CH_2)_2SiMe_3$		*hν*, AIBN, CH_2Cl_2, –40°, 9 h	 (80)	188
C_{13}				
		$ZnCl_2$•OEt_2, CH_2Cl_2, –78°		

R^1	R^2	R^3		
c-C_6H_{11}	H	H	(30)	51
Ph	H	H	(91)	50, 51
Ph	Me	H	(88)	51
Ph	Me	Me	(90)	51

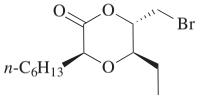


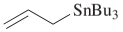


AIBN, toluene, 80°, 8 h

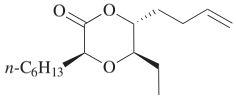


(64) 508

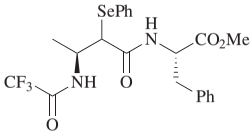




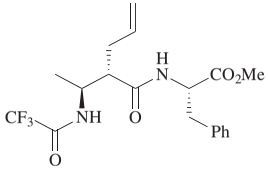
AIBN, benzene, 80°



(89) 509



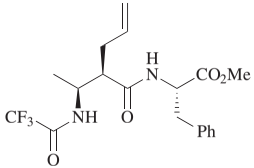
$h\nu$, AIBN, toluene, –40°



I

188

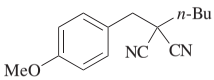
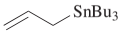
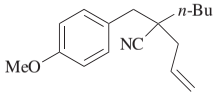
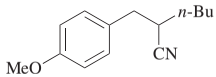
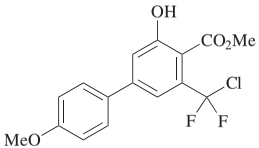
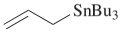
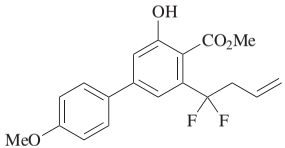
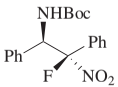
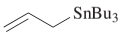
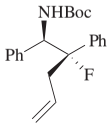
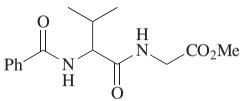
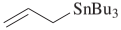
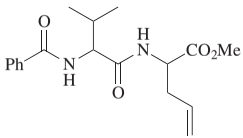
+



II

I + **II** (96) **I**/**II** > 49:1

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{14}				
		*t*-BuO_2*t*-Bu, 4 Å MS, 120°, 16 h	 (57) +  (21)	510
		AIBN, benzene, 80°, 16 h	 (90)	511
 dr = 4.8:1		AIBN, benzene, 80°, 3 h	 (53) dr > 10:1	512
		1. *hν*, NBS, CH_2Cl_2, 40° 2. *hν*, 25°	 (33)[e] dr = 3:1	434

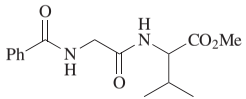
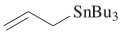
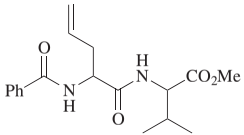
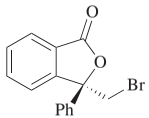
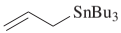
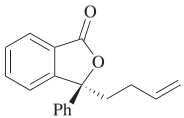
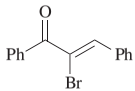
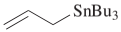
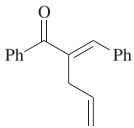
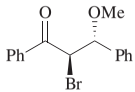
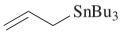
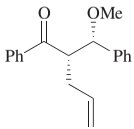
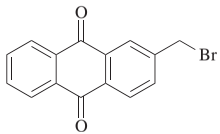
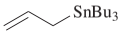
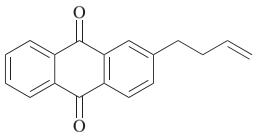
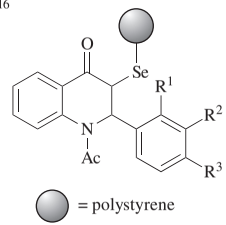
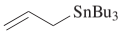
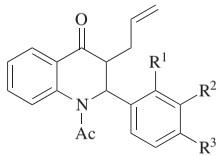
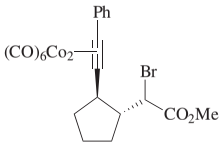
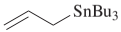
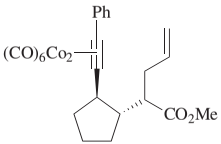
		1. *h*ν, NBS, CH_2Cl_2, 40° 2. *h*ν, 25°		(35)[e] dr = 1:1	434
C_{15} 		AIBN, benzene, 80°, 24 h		(63)	516
 (*E*)/(*Z*) = 1:7.3		*h*ν, [Ir{dF(CF_3)ppy}$_2$ (dtbbpy)]PF_6, DMF, rt, 5 h		(72) (*E*)/(*Z*) = 8.1:1	513
		*h*ν, Cu(dap)$_2$Cl, MeCN, rt, 12 h		(72) dr = 5.7:1	47
		AIBN, dioxane, 101°, 24 h		(49)	514

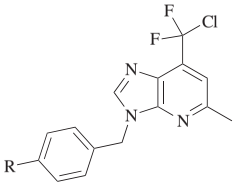
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

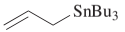
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{15-16} 		AIBN, toluene, 90°, 2 h		515

R^1	R^2	R^3	
H	H	H	(>90)
H	H	F	(>85)
H	H	MeO	(>85)
H	H	Br	(>80)
H	MeO	H	(>90)
H	Br	H	(>85)
Br	H	H	(>80)
H	H	CF_3	(>85)

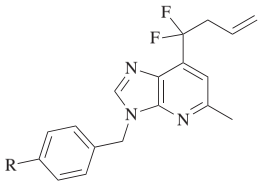
C_{15} 		Conditions, initiator		517

Conditions	Initiator	
—	$(Bu_3Sn)_2$	(0)
—	AIBN	(0)
hν	vitamin B_{12}, Zn	(0)



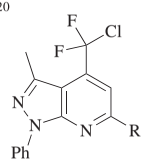


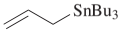
AIBN, benzene, 80°, 16 h



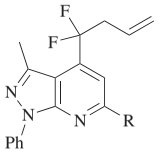
R		
Cl	(98)	94
MeO	(59)	

C_{15-20}



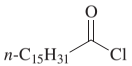


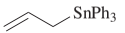
AIBN, benzene, 80°, 16 h



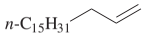
R		
Me	(95)	94
4-ClC_6H_4	(72)	
4-$MeOC_6H_4$	(65)	

C_{16}



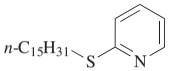


DMAP, xylene, 142°, 1 h



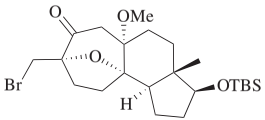
(50)

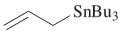
+



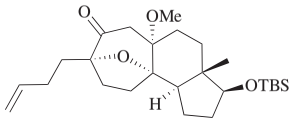
(30)

65



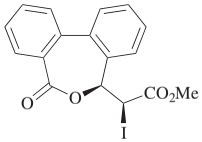
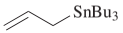
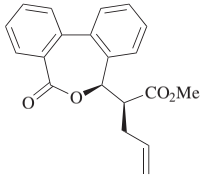
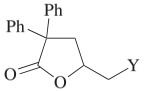
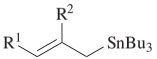
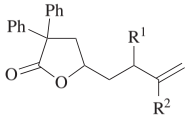
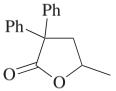


AIBN, benzene, 80°, 18 h

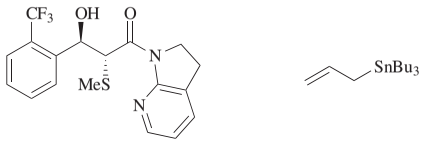


(78) 505

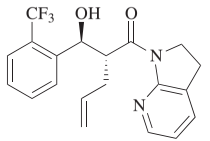
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{16} 		AIBN, benzene, 80°, 4.5 h	 (50)	518
C_{17} 		Conditions, initiator, solvent	 **I** +  **II**	

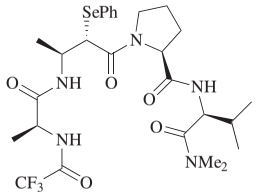
Y	R^1	R^2	Conditions	Initiator	Solvent	Temp	Time (h)	**I**	**II**	
Br	H	H	—	AIBN	benzene	80°	10	(88)	(0)	3, 4
Br	H	H	*h*ν	none	benzene	rt	8	(82)	(0)	3, 4
Br	H	Me	—	AIBN	benzene	80°	10	(97)	(0)	4
Br	Me	H	—	AIBN	toluene	80°	8	(0)	(0)	139
Br	Me	H	*h*ν	none	toluene	25°	2	(0)	(0)	139
Br	Me	H	—	$(t\text{-BuO})_2$	xylene	140°	8	(0)	(78)	139
Br	Me	H	—	$(t\text{-BuO})_2$	chlorobenzene	131°	8	(0)	(70)	139
PhS	H	H	—	AIBN	benzene	80°	10	(0)	(0)	4
PhS	H	H	*h*ν	none	benzene	rt	8	(0)	(0)	4
PhSe	H	H	—	AIBN	benzene	80°	10	(79)	(0)	3, 4
PhSe	H	H	*h*ν	none	benzene	rt	8	(75)	(0)	3, 4

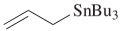


AIBN, benzene, 80°, 24 h

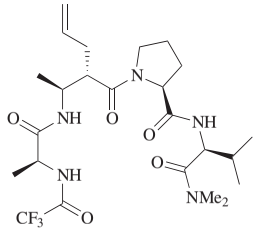


(85) 519



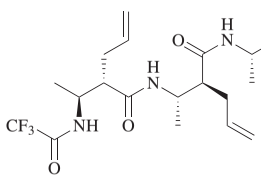


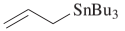
hν, AIBN, CH_2Cl_2, 0°



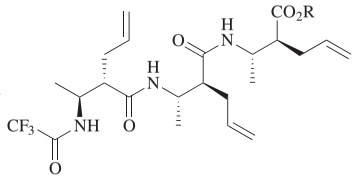
(58) 457

C_{18}





hν, AIBN, toluene, –40°, 5 h

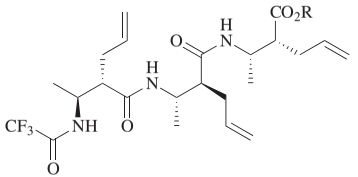


188

R = $(CH_2)_2SiMe_3$

I

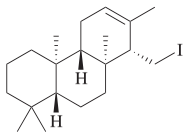
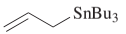
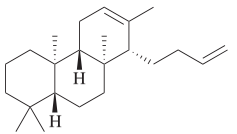
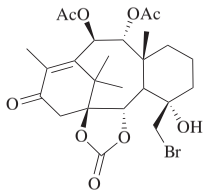
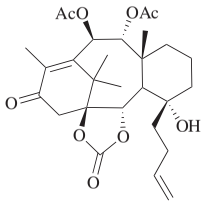
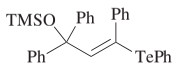
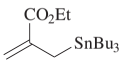
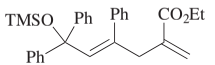
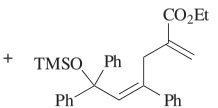
+

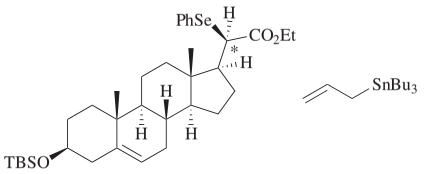


II

I + **II** (58) **I/II** > 49:1

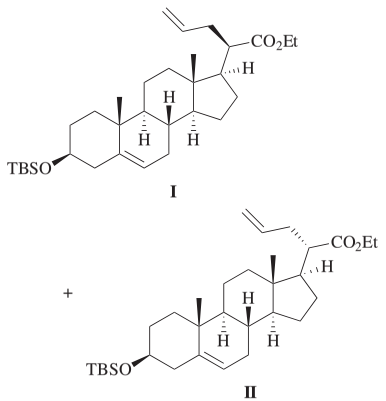
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{20} 		Not reported	 (0)	520, 521
		AIBN, benzene, 80°, 2 h	 (63)	522
C_{21} 		AIBN, neat, 80°, 3 h	 **I** +  **II** **I + II** (78) **I/II** = 24:1	523



*(*R*)/(*S*) = 18:1

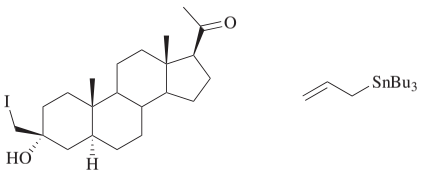
Conditions, AIBN, solvent



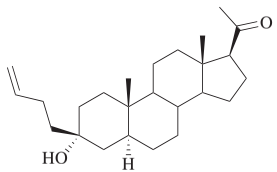
177, 524

Conditions	Solvent	Temp (°)	**I + II**	**I/II**
—	benzene	80	(88)	6:1
*h*ν	THF	–60	(90)	9:1

C_{22}



AIBN, benzene, 80°, 3.5 h

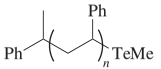
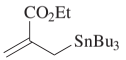
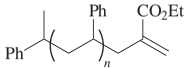
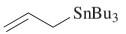


(35)

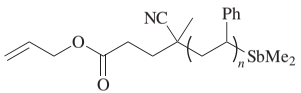
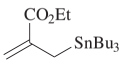
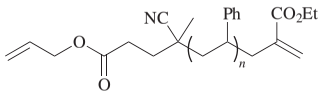
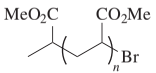
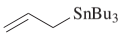
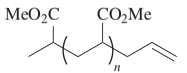
525

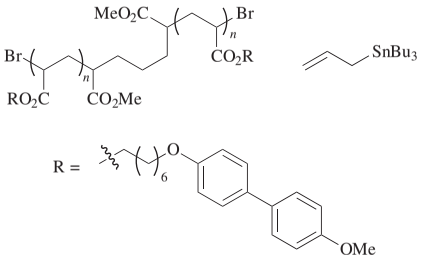
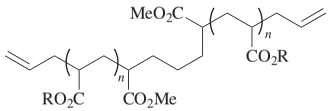
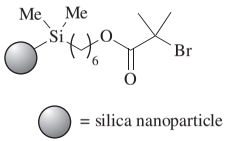
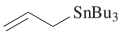
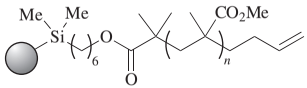
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

A. ACYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_n				
		AIBN, BTF, 80°, 6 h	 (61)	526
		Initiator, solvent		527

Initiator	Solvent	Temp (°)	Time (d)	
AIBN	benzene	80	4	(10)
Co(III), Mg	THF	65	12	(50)

		AIBN, BTF, 80°, 4 h	 (—)	528
		Benzene, 80°, 8 h	 (—)	529

		Not reported		(—)	530
		1. Methyl methacrylate, CuCl, dNbpy, 70°, 0.5 h 2. Allylstannane (0.1 eq), 70 °, 24 h		(—)	455

[a] The yield was determined by NMR spectroscopy.

[b] This is the overall yield for a one-pot, two-step process where the allylstannane is first formed by reaction of phenyl propargyl ether with Bu_3SnH and $Pd(PPh_3)_4$.

[c] The yield was determined by GC.

[d] This is the yield for two steps after removal of the THP protecting group.

[e] This is the overall yield for two steps.

[f] The yield was determined by NMR spectroscopy or GC.

[g] The configurations of the products were not definitively established.

[h] Exact yields were not reported.

[i] The solvent was CH_2Cl_2.

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
A. ACYCLIC SUBSTRATES (*Continued*)

[j] An identical yield and diastereomer ratio was obtained in CH_2Cl_2 at –20°.

[k] The reduction product was also isolated in 4% yield.

[l] The reduction product was also isolated in 19% yield.

[m] This is the overall yield for a one-pot, two-step process where the substrate for the allylation was formed in a $MgBr_2$•OEt_2-promoted Mukaiyama reaction.

[n] Acetic acid was added with the Lewis acid before the radical reaction.

[o] This is the overall yield for a one-pot, two-step process where the substrate for the allylation was formed in a Me_2AlCl-promoted Mukaiyama reaction.

[p] The product was purified by chromatography using fluorous reverse-phase silica.

[q] The product was purified using fluorous solvent to elute from normal-phase silica.

[r] The (*Z*)-isomer was used.

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES

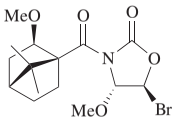
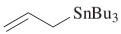
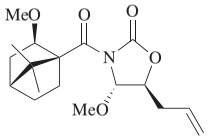
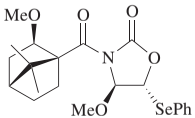
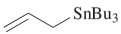
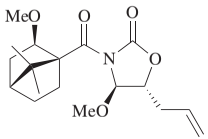
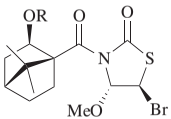
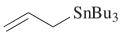
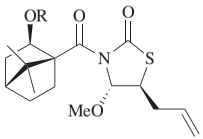
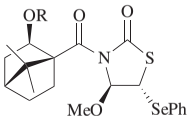
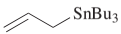
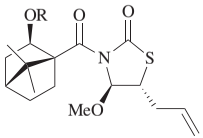
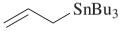
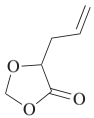
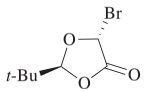
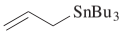
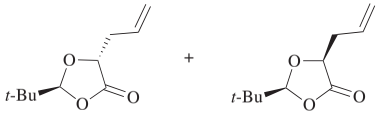
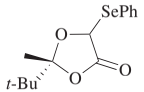
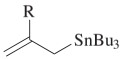
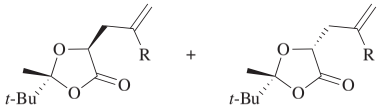
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
		$h\nu$, Et_2O, 2 h	 (71)	531, 532
		$h\nu$, Et_2O, 2 h	 (71)	531, 532
		AIBN, benzene, 80°, 2 h	 R: Me (74); $MeO(CH_2)_2$ (74)	533
		AIBN, benzene, 80°, 2 h	 R: Me (75); $MeO(CH_2)_2$ (85)	533
		$h\nu$, AIBN, benzene, 23°	 (75)	99

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
		*h*ν, AIBN, benzene, 23°	 **I** **I + II** (68) **I/II** = 2:1 **II**	99
		*h*ν, solvent	 **I** **II**	165

R	Solvent	Temp (°)	**I + II**	**I/II**
H	benzene	80	(78)	3.5:1
H	benzene	40	(30)	1.8:1
H	toluene	110	(80)	4.5:1
H	toluene	80	(65)	3.3:1
H	toluene	50	(70)	2.5:1
H	toluene	30	(55)	1.6:1
H	toluene	–10	(50)	1.4:1
H	toluene	–80	(5)	1:1
H	1,2-dichlorobenzene	180	(30)	7:1
MeO_2C	benzene	80	(87)	11.5:1
MeO_2C	benzene	40	(43)	16:1
Me_3Si	benzene	80	(85)	9.2:1
Me_3Si	benzene	40	(27)	6.8:1

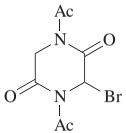
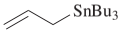
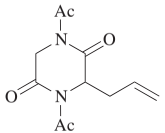
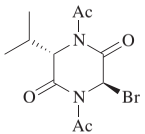
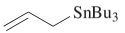
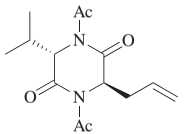
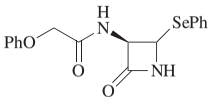
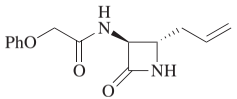
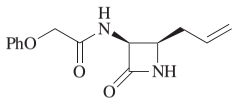
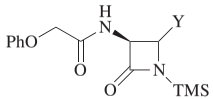
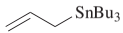
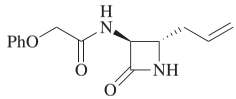
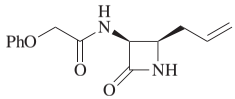
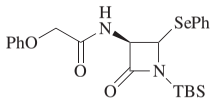
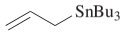
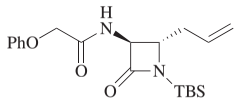
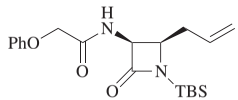
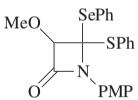
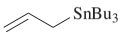
		Benzene, 80°		(66)	534
		AIBN, benzene, 80°, 6 h		(60)	535
C_3 		AIBN, DME, 85°, 1 h	 **I** +  **II**	**I + II** (55) **I/II** = 2:1	58

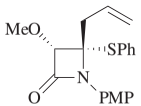
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3 		AIBN, benzene, 80°, 1 h	 **I** +  **II**	58
			Y / **I + II** / **I/II**: PhS (30) 2:1; PhSO (0) —; $PhSO_2$ (0) —; PhSe (61) 2:1	
		AIBN, benzene, 80°, 3 h	 **I** +  **II**	58
			I + II (72) **I/II** = 2:1	





AIBN, benzene, 80°, 8 h



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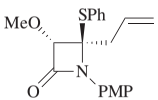
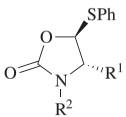
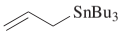


536

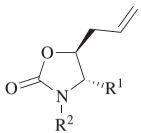
I **I + II** (67) **I/II** = 1.8:1 **II**

C_{3-9}



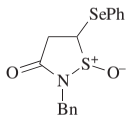
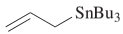
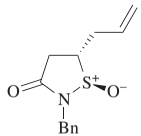
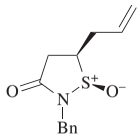


*h*ν, $(Bu_3Sn)_2$,
toluene/MeCN (7:3), rt

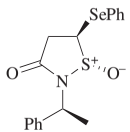
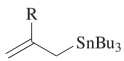
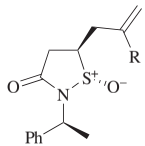
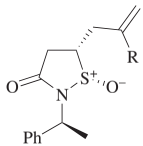


R^1	R^2	Time (h)		
Me	H	24	(45)	162
Me	Ac	24	(62)	162
Me	Boc	24	(72)	162
$AcOCH_2$	Boc	6	(81)	537
$MeCH(OEt)OCH_2$	Boc	6	(76)	537
CH_2=CH	Boc	24	(60)	162
CH_2=CH	Boc	24	(20)[a]	162
(*R*)-Me(AcO)CH	Boc	6	(75)	537
(*S*)-Me(AcO)CH	Boc	6	(81)	537
i-Bu	H	24	(71)	162
i-Bu	Boc	24	(76)	162
s-Bu	Ac	24	(81)	162
s-Bu	Ac	24	(30)[a]	162
s-Bu	Boc	—	(80)	538
Bn	H	24	(55)	162
Bn	Boc	24	(81)	162

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

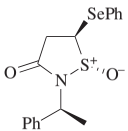
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		AIBN, additive (x eq), solvent, 55°, 24 h	 **I** +  **II** (—)	174

Additive	x	Solvent	**I**	**I/II**
none	—	benzene	(59)	5.3:1
none	—	EtOH	(63)	9.8:1
CF_3CH_2OH	1	benzene	(61)	7.1:1
CF_3CH_2OH	5	benzene	(63)	10.3:1
A2	0.25	benzene	(70)	7:1
A2	0.5	benzene	(72)	11.3:1
A2	1	benzene	(72)	14.1:1

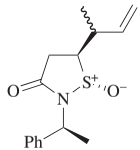
		Conditions, initiator, solvent	 **I** +  **II** (—)	132

R	Conditions	Initiator	Solvent	Temp	Time (h)	**I**	**I/II**
H	—	AIBN, Bu_3SnH	benzene	80°	24	(75)	6.8:1
H	$h\nu$	AIBN, Bu_3SnH	benzene	rt	7	(82)	9.6:1
H	$h\nu$	AIBN	c-C_6H_{12}/DME (7:1)	rt	3	(83)	9:1

H	*hν*	AIBN	DME	rt	2.5	(79)	10:1
H	*hν*	AIBN	EtOH	rt	2	(82)	17.5:1
H	*hν*	AIBN	CF_3CH_2OH	rt	0.33	(89)	50:1
Me	—	AIBN, Bu_3SnH	benzene	80°	4	(64)	6.8:1
Me	*hν*	AIBN, Bu_3SnH	benzene	rt	19	(69)	12.8:1
n-Bu	*hν*	AIBN	benzene	rt	5	(79)	9.6:1
n-Bu	*hν*	AIBN	*i*-PrOH	rt	8	(63)	14.4:1
n-Bu	*hν*	AIBN	EtOH	rt	5	(82)	17.2:1
n-Bu	*hν*	AIBN	CF_3CH_2OH	rt	—	(0)	—
BnO_2C	—	AIBN	benzene	80°	3	(62)	3.8:1
BnO_2C	*hν*	AIBN	benzene	rt	1	(90)	7.9:1
BnO_2C	*hν*	AIBN	EtOH	rt	1	(79)	12.6:1
BnO_2C	*hν*	AIBN	CF_3CH_2OH	rt	1	(87)	22.8:1

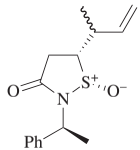


hν, AIBN, Bu_3SnH, benzene, rt, 19 h



I

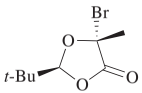
+

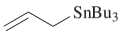


II

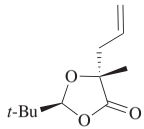
132

I + **II** (40) **I/II** = 10:1



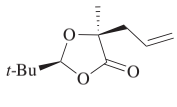


hν, AIBN, benzene, 23°



I

+

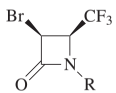
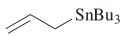
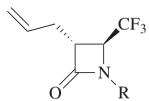
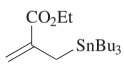
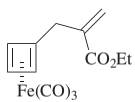
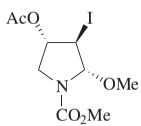
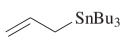
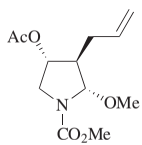
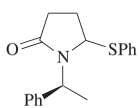
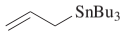
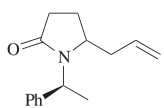
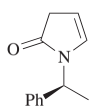
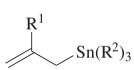
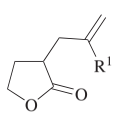


II

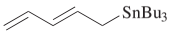
99

I + **II** (72) **I/II** = 7:1

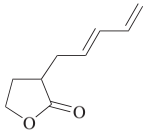
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		AIBN, toluene, 80°	 R: PMP (79); PMB (57); Bn (62)	539
		AIBN, benzene, 80°, 50 h	 (39)	130
		AIBN, benzene, 80°, 4 h	 (91)	540, 541
		AIBN, toluene, 80°, 16 h	 (8) dr = 53:47 +  (—)	101
		Conditions, initiator, solvent		

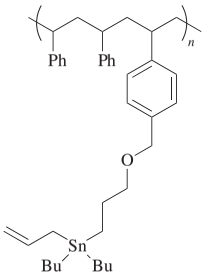
Y	R^1	R^2	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
Br	H	Bu	—	AIBN	benzene	80	2	(85)	124
Br	H	$CF_3(CF_2)_5(CH_2)_3$	—	AIBN	benzene	80	2–5	(89)	123
Br	H	$CF_3(CF_2)_5(CH_2)_3$	—	AIBN	BTF	80	2–5	(94)	123
Br	Me_3SiCH_2	Bu	—	AIBN	benzene	80	14	(70)	429
Br	Me_3SiCH_2	Bu	*hν*	none	benzene	0	—	(95)	429
Br	Me_3Sn	Me	—	AIBN	benzene	80	18	(72)	41
Br	Bu_3Sn	Bu	*hν*	$(Bu_3Sn)_2$	toluene	rt	0.5	(78)	426
Br	Bu_3Sn	Bu	*hν*	$(Bu_3Sn)_2$	toluene	60	1	(75)[b]	426
PhSe	H	Bu	*hν*	$(Bu_3Sn)_2$	benzene	—	1	(90)	77, 542
PhSe	Me	Bu	*hν*	none	benzene	—	0.5	(91)	129



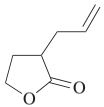
hν, benzene, 2 h



(72) 129

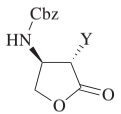
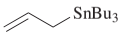
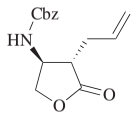
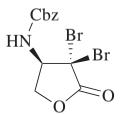
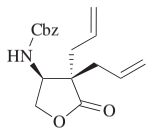
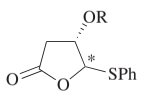
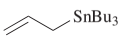
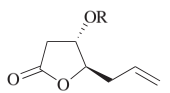
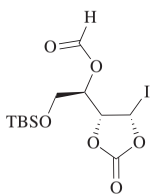
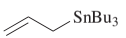
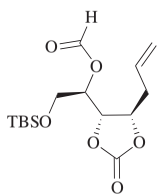
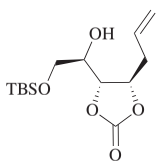


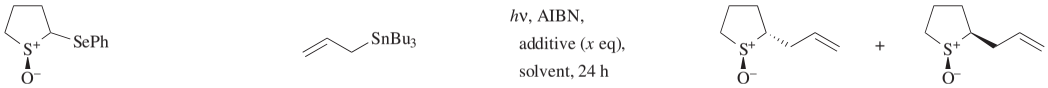
AIBN, benzene, 80°, 4 h



(73) 116

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

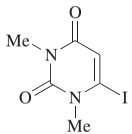
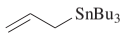
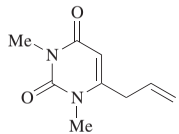
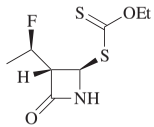
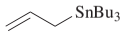
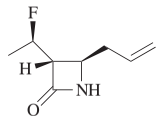
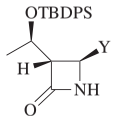
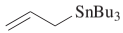
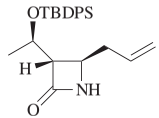
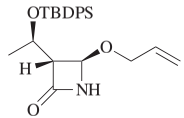
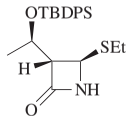
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		AIBN, benzene, 80°	 Y / Time (h) Br / — / (82) SePh / 16 / (55)	543
		AIBN, benzene, 80°	 (86)	543
		*h*ν, $(Bu_3Sn)_2$, toluene, MeCN, 30 h	 R / * / Ac / (*R*) / (58) Ac / (*S*) / (55) *t*-Bu / (*S*) / (50)	544
		AIBN, benzene, 80°, 3 h	 (45) +  (29)	545



I **II**

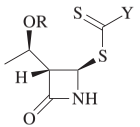
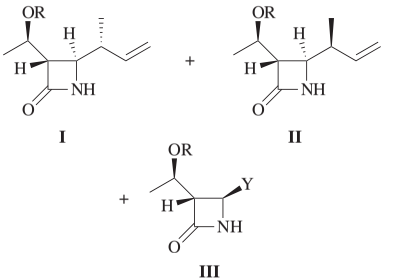
Additive	x	Solvent	Temp (°)	**I + II**	**I/II**	
none	—	CH_2Cl_2	10	(63)	4.6:1	173
none	—	CH_2Cl_2	10	(63)[c]	4.6:1	173
none	—	EtCN	10	(88)	3.3:1	173
none	—	benzene	10	(78)	2.3:1	173
none	—	benzene	10	(49)[c]	2.3:1	173
none	—	THF	10	(44)	2.2:1	173
none	—	EtOH	10	(87)	4.9:1	173
none	—	CF_3CH_2OH	10	(83)	8.1:1	173
none	—	AcOH	10	(51)	6.7:1	173
$Eu(dpm)_3$	1.1	CH_2Cl_2	10	(55)	8.1:1	173
Et_2AlCl	1.1	CH_2Cl_2	10	(21)	3.3:1	173
$Ti(O\textit{i}\text{-}Pr)_3Cl$	1.1	CH_2Cl_2	10	(28)	6.1:1	173
TBAP	1.1	CH_2Cl_2	10	(88)	4.3:1	173
MAP	1.1	CH_2Cl_2	10	(78)	13.3:1	173
MAD	1.1	CH_2Cl_2	10	(80)	66:1	173
MAD	1.1	CH_2Cl_2	10	(69)[c]	66:1	173
MAD	0.1	CH_2Cl_2	10	(63)	5.7:1	173
MABR	1.1	CH_2Cl_2	10	(57)	49:1	173
MABR	0.1	CH_2Cl_2	10	(66)	9:1	173
$ZnBr_2$	1.1	THF	10	(58)	7.3:1	173
$BF_3{\bullet}OEt_2$	1.1	THF	10	(75)	4.6:1	173
LiCl	1.1	THF	10	(29)	5.3:1	173
$t\text{-}BuCO_2H$	1.1	benzene	10	(79)	3.5:1	173
A2	0.2	benzene	15	(57)	3.8:1	174
A2	0.6	benzene	15	(72)	5.7:1	174
A2	1.0	benzene	15	(81)	75:1	174
$LiClO_4$	1.1	EtCN	10	(84)	9:1	173

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

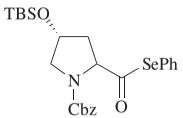
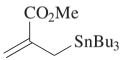
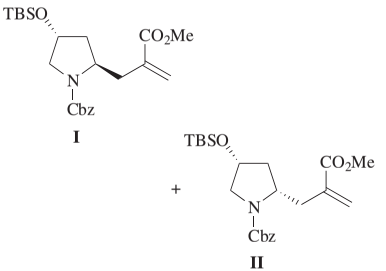
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		$h\nu$, MeCN/H_2O (10:1), 10 h	 (80)	546, 106
C_5				
		Toluene, 90°, 20 h	 (67)	25
		Conditions, initiator, solvent	 **I** +  **II** +  **III**	25

Y	Conditions	Initiator	Solvent	Temp (°)	Time (h)	**I**	**II**	**III**
AcO	—	AIBN	toluene	90	20	(12)	(25)	(—)
AcO	*h*ν	none	—	—	48	(30)	(6)	(—)
AcO	—	none	toluene	90	20	(0)	(—)	(—)
EtS	—	AIBN	toluene	90	24	(11)	(—)	(—)
EtS	*h*ν	none	—	—	20	(0)	(—)	(—)
EtS	—	none	toluene	90	20	(0)	(—)	(—)
EtSO	—	AIBN	toluene	90	24	(17)	(—)	(—)
EtSO	*h*ν	none	—	—	24	(14)	(—)	(—)
EtSO	—	none	toluene	90	24	(0)	(—)	(—)
EtO(S)CS	—	AIBN	toluene	90	24	(72)	(—)	(—)
EtO(S)CS	*h*ν	none	—	—	24	(62)	(—)	(—)
EtO(S)CS	—	none	toluene	90	24	(0)	(—)	(—)
EtS(S)CS	—	AIBN	toluene	90	24	(79)	(—)	(—)
EtS(S)CS	*h*ν	none	—	—	24	(66)	(—)	(30)
EtS(S)CS	—	none	toluene	90	48	(23)	(—)	(23)

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		Initiator, toluene, 90°, 20 h	 **I** + **II** + **III**	25

R	Y	Initiator	**I + II**	**I/II**	**III**
TBS	EtS	none	(42)	5:1	(27)
TBDPS	EtO	AIBN	(30)	10:1	(20)

		AIBN, benzene, 80°, 3 h	 **I** + **II**	113

I + II (69) **I/II** = 1.7:1

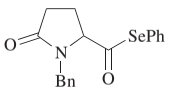
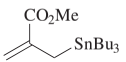
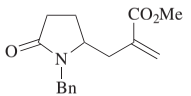
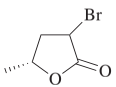
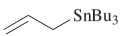
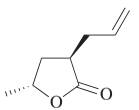
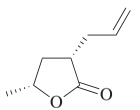
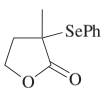
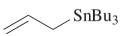
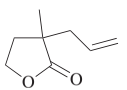
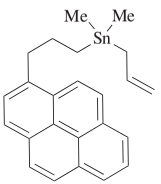
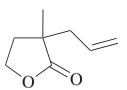
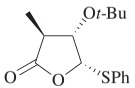
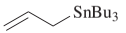
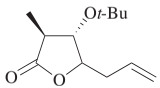
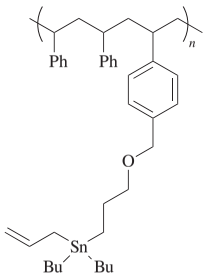
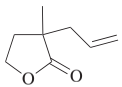
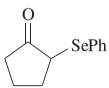
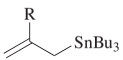
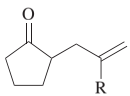
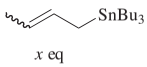
		AIBN, benzene, 80°, 3 h		(62)	113
		AIBN, benzene, 80°, 3 h	 +  **I** **II**	**I** + **II** (95) **I/II** = 4:1	124
		*hν*, benzene, 2.5 h		(64)	77
		AIBN, benzene, 80°, 5 h		(86)	126

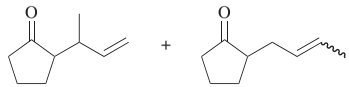
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		*h*ν, $(Bu_3Sn)_2$, toluene, MeCN	 (—) dr = 1:1	544
		AIBN, benzene, 80°, 12 h	 (73)	116
		Conditions, initiator, benzene		

R	Conditions	Initiator	Temp (°)	Time (h)		Refs.
H	*h*ν	none	—	1	(80)	77
Me	*h*ν	none	—	1	(80)	129
EtO_2C	—	AIBN	80	4	(92)	547



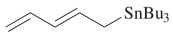
*h*ν, benzene



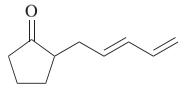
I **II**

129

x	Time (h)	**I + II**	**I/II**
2	2	(77)	1.9:1
5	1	(95)	3:1

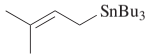


*h*ν, benzene, rt, 1.5 h

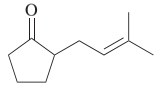


(82)

129

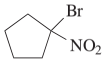


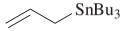
*h*ν, benzene



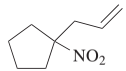
(63)

129





AIBN, 100°, 24 h



(55)

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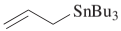
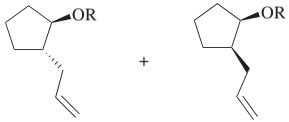
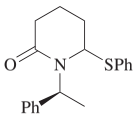
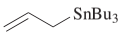
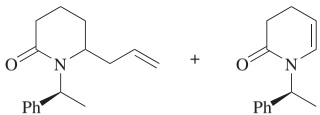
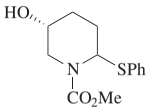
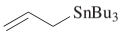
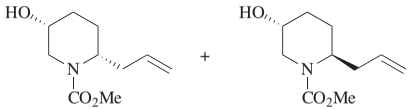
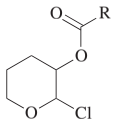
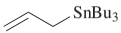
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		Conditions, initiator, benzene	 **I** + **II**	4

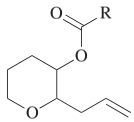
R	Conditions	Initiator	Temp	**I** + **II**[d]	**I/II**
H	—	AIBN	80°	(71)	—
H	*h*ν	none	rt	(67)	10:1
TBS	*h*ν	none	rt	(—)	7:1
TBDPS	*h*ν	none	rt	(—)	11:1
Bz	*h*ν	none	rt	(—)	7:1

		AIBN, toluene, 80°, 16 h	 (38) dr = 1.2:1 + (—)	101
		AIBN, toluene, 110°	 **I** + **II** **I** + **II** (33) **I/II** = 5:1	548

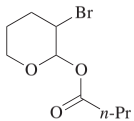


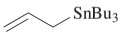


AIBN, benzene, 80°, 12 h

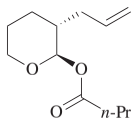


R		dr	
n-Pr	(22)	1:1	100
t-Bu	(38)	1:1	



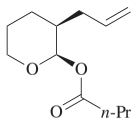


AIBN, benzene, 80°, 7 h



I

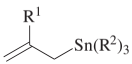
+



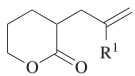
II

100

I + **II** (47) **I/II** = 3.7:1

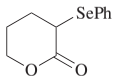
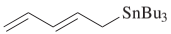
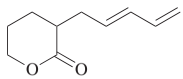
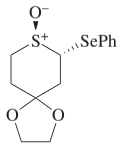
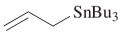
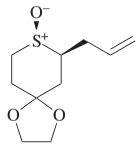
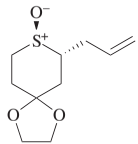
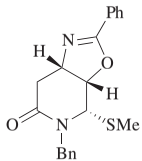
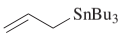
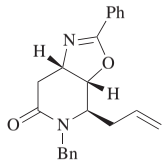
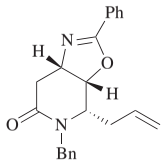
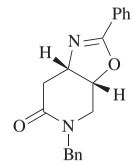
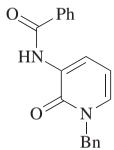


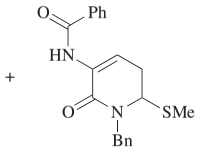
*h*ν, initiator, solvent



Y	R^1	R^2	Initiator	Solvent	Temp (°)	Time (h)		
Br	Me_3SiCH_2	Ph	AIBN	DME	15–20	12	(81)	36
PhSe	H	Bu	none	benzene	—	1	(81)	77
PhSe	Me	Bu	none	benzene	—	0.5	(90)	129

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

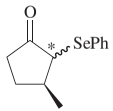
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		*hν*, benzene, 2 h	 (87)	129
		AIBN, benzene, 80°	 **I** +  **II**	175
			I + **II** (82) **I/II** = 9:1	
	 *x* eq	Conditions, initiator (*x* eq), solvent	 **I** +  **II**	
			+  **III** +  **IV**	

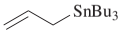


V

Conditions	Initiator	x	Solvent	Temp (°)	Time (h)	**I**	**II**	**III**	**IV**	**V**	
—	AIBN	2	toluene	80	8	(0)	(0)	(0)	(20)	(23)	549
$h\nu$	$(Bu_3Sn)_2$	4	toluene/MeCN (7:3)	20	43	(29)	(15)	(23)	(0)	(0)	549
$h\nu$	$(Bu_3Sn)_2$	6	toluene/MeCN (7:3)	20	43	(32)	(16)	(18)	(0)	(0)	549
$h\nu$	none	6	toluene/MeCN (7:3)	20	70	(40)	(21)	(15)	(0)	(0)	549, 550
$h\nu^e$	none	6	toluene/MeCN (7:3)	20	70	(36)	(18)	(20)	(0)	(0)	549

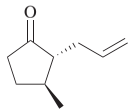
C_6



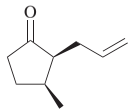


x eq

$h\nu$, benzene



I

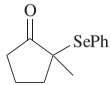
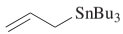
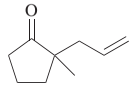
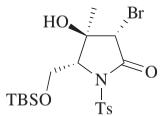
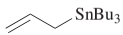
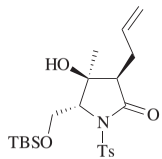
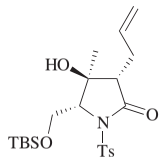
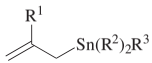
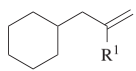
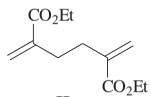


II

551

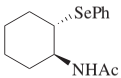
*Config	x	Time (h)	**I + II**[d]	**I/II**
trans	1.5	1	(76)	3.3:1
trans	2.0	1	(93)	3.5:1
trans	3.0	0.5	(98)	3.5:1
cis	1.5	1	(83)	3.5:1
cis	2.0	1	(94)	3.5:1

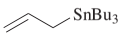
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		*h*ν, benzene, 4.5 h	 (63)	77
		AIBN, toluene, 110°, 3 h	 **I** +  **II** **I + II** (75) **I/II** = 3:1	555
		Conditions, initiator, solvent	 **I** +  **II**	

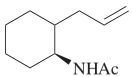
Y	R^1	R^2	R^3	Conditions	Initiator	Solvent	Temp (°)	Time (h)	**I**	**II**	
Br	H	Bu	Bu	—	AIBN	toluene	80	—	(88)[d]	(—)	4
Br	H	Bu	Bu	—	AIBN	benzene	80	—	(86)	(—)	37
Br	H	Bu	Bu	*h*ν	none	neat	22	5	(84)	(—)	37
Br	H	Bu	Bu	—	$ZnCl_2 \bullet OEt_2$	CH_2Cl_2	–78	—	(0)	(—)	51
ClHg	H	Bu	Bu	*h*ν	none	benzene, DMSO	40	23	(12)[d]	(—)	331
Br	H	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	—	AIBN	benzene	80	16	(70)	(—)	121
I	H	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	—	AIBN	benzene	80	16	(78)	(—)	121
Br	Me	Bu	Bu	—	AIBN	toluene	80	—	(72)[d]	(—)	4
Br	EtO_2C	Bu	Bu	—	AIBN	benzene	80	16	(74)	(—)	436
Br	EtO_2C	Cl	Br	—	AIBN	benzene	80	12	(12)	(75)	128

Cl	EtO_2C	$(TMS)_2N$	Br	—	AIBN	benzene	80	8	(0)	(71)	127, 128
Br	EtO_2C	$(TMS)_2N$	Br	—	AIBN	benzene	80	8	(71)	(16)	127, 128
I	EtO_2C	$(TMS)_2N$	Br	—	AIBN	benzene	80	8	(78)	(6)	127, 128
PhSe	EtO_2C	$(TMS)_2N$	Br	—	AIBN	benzene	80	8	(76)	(11)	127, 128
EtO(S)CS	EtO_2C	$(TMS)_2N$	Br	—	AIBN	benzene	80	8	(54)	(34)	127, 128
Br	EtO_2C	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	—	AIBN	benzene	80	16	(70)	(—)	121
Br	EtO_2C	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	—	Et_3B, O_2	benzene	rt	0.17	(78)	(—)	121
I	EtO_2C	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	—	AIBN	benzene	80	16	(80)	(—)	121
I	EtO_2C	Bu	$CH_3(O(CH_2)_2)O(CH_2)_3$	—	Et_3B, O_2	benzene	rt	0.17	(85)	(—)	121
Br	Me_3SiCH_2	Bu	Bu	—	AIBN	benzene	80	16	(49)	(—)	429
Br	Me_3SiCH_2	Bu	Bu	$h\nu$	none	benzene	0	5	(45)	(—)	429

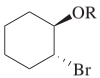


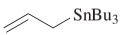


AIBN, toluene, 80°, 1 h

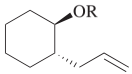


(—) 454



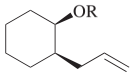


Conditions, initiator, solvent



I

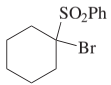
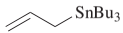
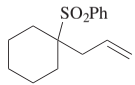
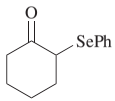
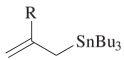
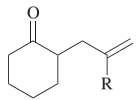
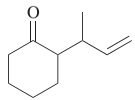
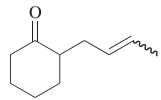
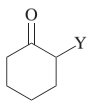
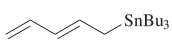
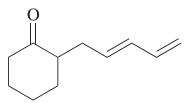
+

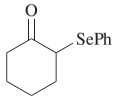


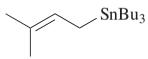
II

R	Conditions	Initiator	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	
H	—	AIBN	toluene	80	8	(74)	3.7:1	4
H	$h\nu$	none	toluene	rt	26	(74)	4:1	4
TBS	$h\nu$	none	toluene	rt	26	(—)	2:1	4
TBDPS	$h\nu$	none	toluene	rt	26	(—)	2:1	4
n-PrCO	—	AIBN	benzene	80	12	(50)	3.2:1	100
Bz	$h\nu$	none	toluene	rt	26	(—)	3:1	4

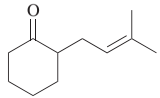
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, benzene, 80°, 2 h	 (85)	89
		*h*ν, benzene		
			R — Time (h)	
			H — 1.5 — (81)	77
			Me — 2.5 — (93)	129
	x eq	*h*ν, benzene	 +  **I** **II**	129
			x — Time (h) — **I + II** — **I/II**	
			2 — 3 — (45) — 1:1.2	
			5 — 1 — (61) — 1.1:1	
		*h*ν, benzene		
			Y — Time (h)	
			PhS — 10 — (49)	129
			PhSe — 0.8 — (78)	

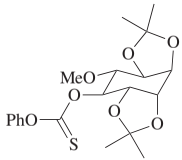


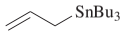


hν, benzene

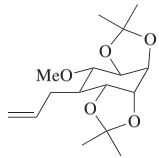


(55) 129



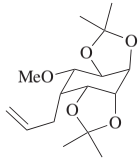


AIBN, toluene, 110°, 4 h



I

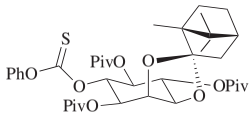
+

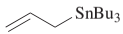


II

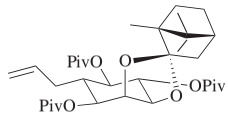
552

I + II (56) **I/II** > 9:1

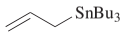




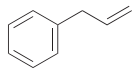
AIBN, toluene, 110°, 18 h



(61) 553

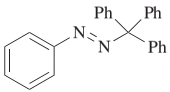
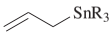
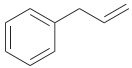
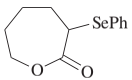
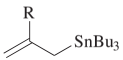
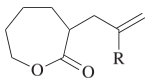
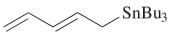
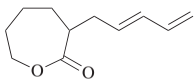
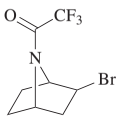
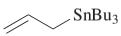
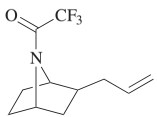


Conditions, initiator, solvent



X	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
Cl	—	AIBN	benzene	80	—	(0)	37
Cl	*hν*	none	neat	22	25	(0)	37
Br	—	AIBN	benzene	80	—	(58)	37
Br	*hν*	none	toluene	22	5	(58)	37
I	—	AIBN	benzene	80	—	(35)	37
I	—	AIBN	toluene	80	—	(57)[d]	4
I	*hν*	none	benzene	22	24	(18)	37

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		Benzene, 80°	 + Ph—Ph **I** **II** R / **I** / **II** Me (50) (0) Bu (50) (10)	37
		*hν*, benzene	 R / Time (h) H 3 (76) Me 1.3 (80)	77 129
		*hν*, benzene, 2 h	 (57)	129
		AIBN, toluene, 80°, 9 h	 (13)	554

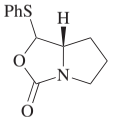
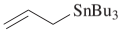
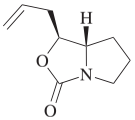
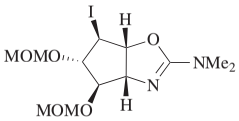
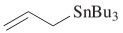
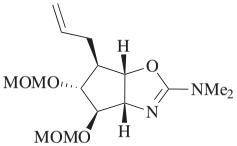
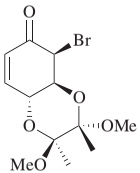
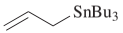
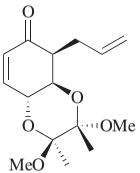
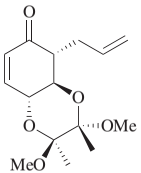
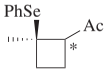
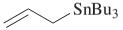
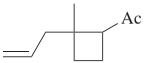
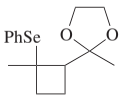
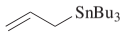
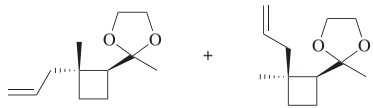
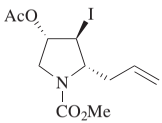
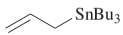
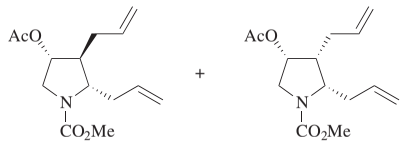
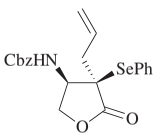
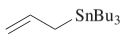
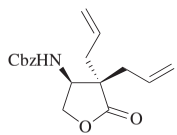
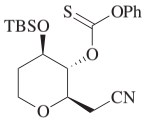
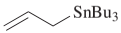
 *trans*/*cis* = 2.4:1		*h*ν, $(Bu_3Sn)_2$, toluene/MeCN (7:3), rt, 40 h		(57)	162
		AIBN, benzene, 80°, 18 h		(81)	75
		AIBN, toluene, 80°, 18 h	 **I**	+  **II**	556
			I + **II** (74) **I**/**II** = 9:1		
C_7 		AIBN, benzene, 80°, 4 h		* dr (*R*) (58) 2:1 (*S*) (86) 2:1	557

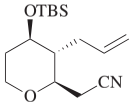
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		AIBN, benzene, 80°, 4 h	 **I** + **II** (48) **I/II** = 9:1	557
		AIBN, benzene, 80°, 4 h	 **I** + **II** (92) **I/II** = 99:1	541
		AIBN, benzene, 80°, 1.45 h	 (84)	543



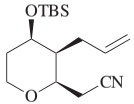


$h\nu$, benzene, rt, 26 h



I

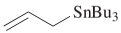
+



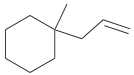
II

558, 559

I + II (83) **I/II** = 6:1

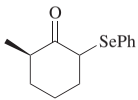


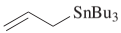
AIBN, toluene, 80°



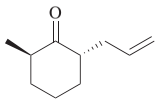
(90)[d]

3, 4



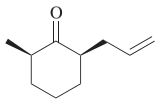


$h\nu$, benzene



I

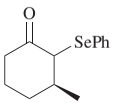
+



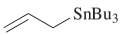
II

551

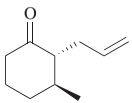
trans/*cis*	Time (h)	**I + II**[d]	**I/II**
trans	1	(85)	6.1:1
cis	3	(62)	6.1:1
1:1	1	(82)	6.1:1



trans/*cis* = 1:1

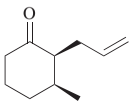


$h\nu$, benzene, 2.5 h



I

+

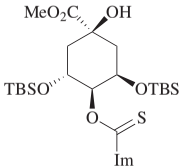
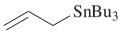
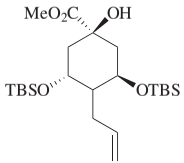
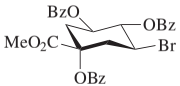
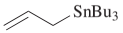
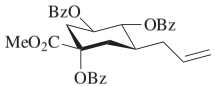
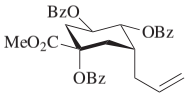
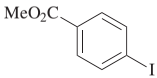
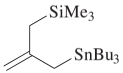
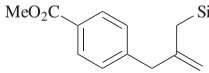
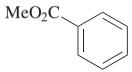
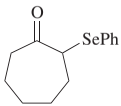
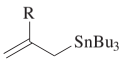
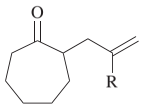


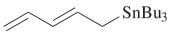
II

551

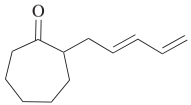
I + II (70)[d] **I/II** = 2:1

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		AIBN, benzene, 80°, 6 h	 (60) dr = 2.3:1	560, 561
		AIBN, benzene, 50°, 12 h	 **I** +  **II** **I** + **II** (86) **I/II** = 32:1	562
		*h*ν, ACCN, DME, rt, 24 h	 (51)[h] +  (47)[h]	36
		*h*ν, benzene		
			R / Time (h): H / 1.5 / (79)	77
			Me / 1 / (85)	129

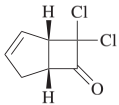


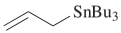
Conditions, initiator, solvent



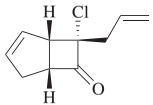
129

Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	toluene	80	18	(48)
$h\nu$	none	benzene	—	0.8	(78)



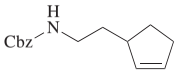


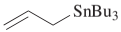
AIBN, benzene, 80°



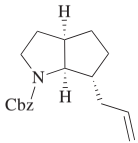
(78)

83, 84



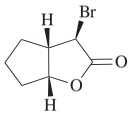


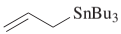
1. PhthN-SePh, CH_2Cl_2
2. Allylstannane, AIBN, toluene, 110°



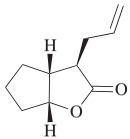
(82)[f,g]

464





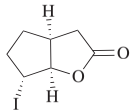
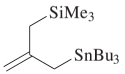
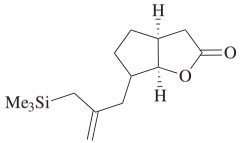
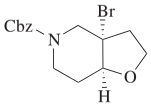
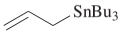
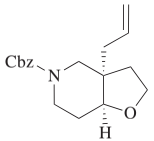
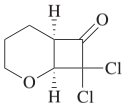
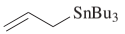
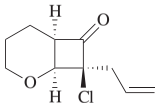
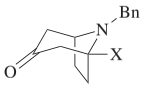
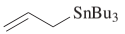
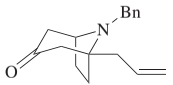
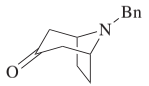
AIBN, 4-methylTHP, 90°, 2 h



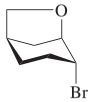
(76) dr > 20:1

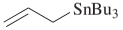
563

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

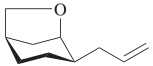
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		*hν*, benzene, 15–20°, 15 h	 (68) dr = 9.3:1	36
		AIBN, benzene, 4 Å MS, 80°, 1 h	 (92)	564
		AIBN, benzene, 80°	 (55)	83, 84
	 *x* eq	ACCN (*y* eq), toluene, 85°, o/n	 **I** +  **II**	565

X	x	y	**I**	**II**
Cl	2	1.2	(24)	(47)
Cl	10	1.2	(52)	(—)
Br	2	0.2	(5)	(—)
Br	10	0.2	(71)	(—)
Br	10	1.2	(76)	(—)





$h\nu$, benzene, rt, 8 h



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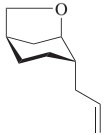
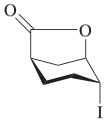
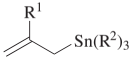


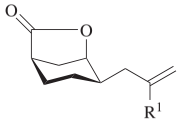
4

I **I + II** (66) **I/II** = 1.7:1 **II**





Conditions, initiator, benzene



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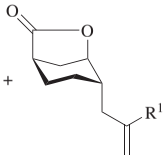
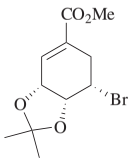
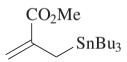
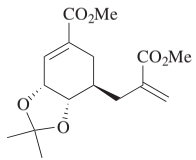
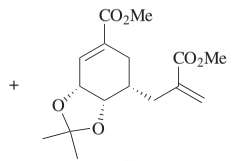
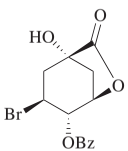
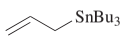
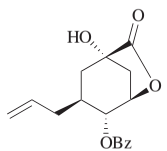
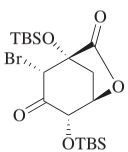
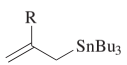
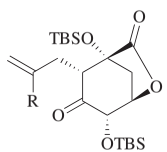


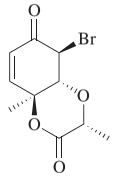
I **II**

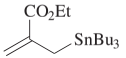
R^1	R^2	Conditions	Initiator	Temp (°)	Time (h)	**I + II**	**I/II**	
H	Bu	—	AIBN	80	10	(65)	1.7:1	4
H	Bu	$h\nu$	none	rt	8	(81)	1.7:1	4
Me_3Sn	Me	—	AIBN	80	12	(53)	—	41

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

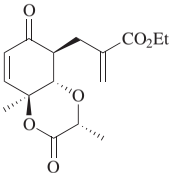
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		AIBN, toluene, 110°, 3 h	 **I** +  **II** **I + II** (65) **I/II** = 3.2:1	566
		AIBN, benzene, 80°	 (82)	567
		AIBN, toluene, 14 h		

R	Temp (°)		
H	80	(99)	568, 569
Me	90	(96)	569



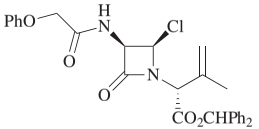


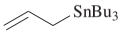
AIBN, benzene, 80°, 12 h



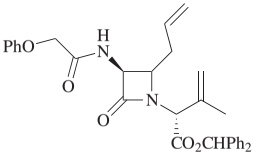
(81) 570

C_8





AIBN, benzene, 80°, 2.5 h



(0) 58

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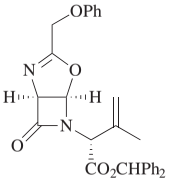
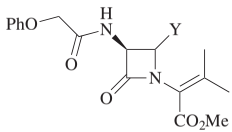
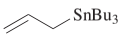
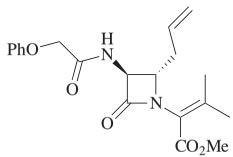
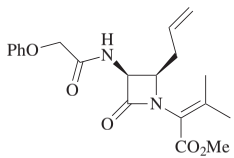
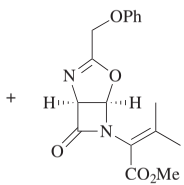
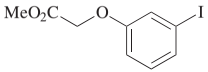


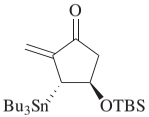
(—)

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

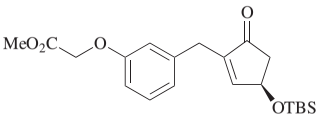
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8 		AIBN, benzene, 80°	 **I** +  **II** +  **III**	58

Y	Time (h)	**I + II**	**I/II**	**III**
Cl	2.5	(0)	—	(—)
PhSe	2	(49)	2:1	(0)

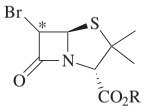


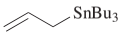


AIBN, benzene, 80°, 3 h

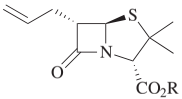


(10) 103

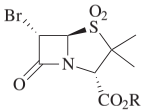


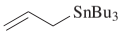


AIBN, solvent

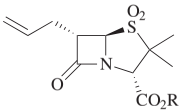


R	*	Solvent	Temp (°)	Time (h)		
Me	(*S*)	benzene	80	5	(87)	80, 81
All	(*S*)	benzene	80	5	(85)	81
PMB	(*S*)	benzene	80	5	(81)	81
PNB	(*S*)	benzene	80	5	(0)	81
Ph_2CH	(*R*)	toluene	65	0.75	(95)	571
Ph_2CH	(*S*)	toluene	65	0.75	(95)	571





AIBN, solvent



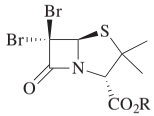
R	Solvent	Temp (°)	Time (h)		
Me	benzene	80	5	(93)	80, 81
All	benzene	80	5	(69)	81
PMB	benzene	80	5	(76)	81
Ph_2CH	—	—	—	(79)	307

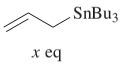
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

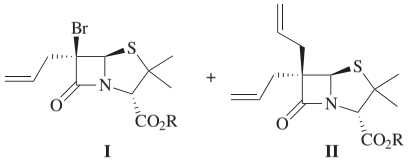
C_8





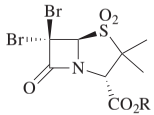
x eq

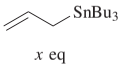
AIBN, solvent



I **II**

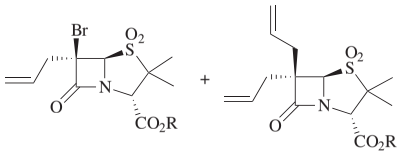
R	*x*	Solvent	Temp (°)	Time (h)	**I**	**II**	
Me	1.7	benzene	80	4	(54)	(13)	80, 81
Me	3	benzene	80	6	(0)	(84)	80, 81
All	1.7	benzene	80	4	(55)	(—)	81
All	3	benzene	80	6	(0)	(76)	81
Ph_2CH	2	toluene	65	0.25	(60)	(22)	571





x eq

AIBN, solvent



I **II**

R	*x*	Solvent	Temp (°)	Time (h)	**I**	**II**	
All	1.3	benzene	80	4	(55)	(0)	81
All	3	benzene	80	6	(0)	(72)	81
Ph_2CH	1.1	toluene	110	6	(72)	(0)	572
Ph_2CH	—	—	110	1	(—)	(—)	573

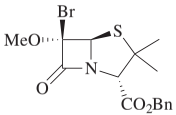
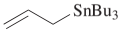
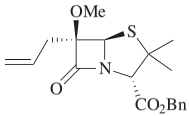
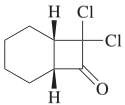
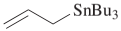
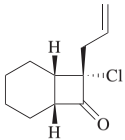
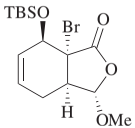
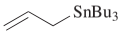
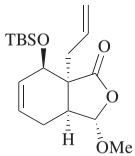
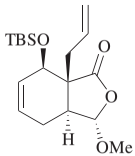
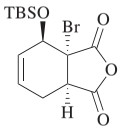
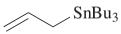
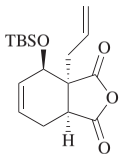
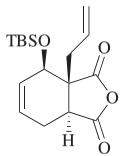
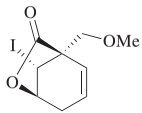
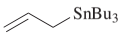
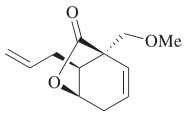
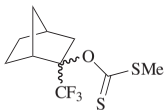
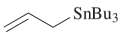
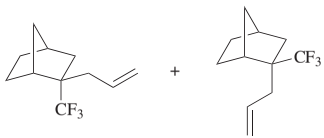
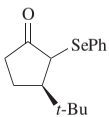
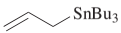
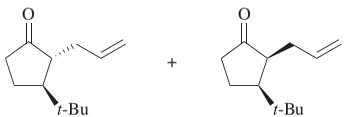
		AIBN, benzene, 80°, 29 h		(22)	291
		AIBN, benzene, 80°		(51)	83, 84
		AIBN, toluene, 80°, 8 h	 +  **I** **II** **I** + **II** (93) **I/II** = 2.1:1		171
		AIBN, MW, toluene, 90°, 0.75 h	 +  (65) (23)		574

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, benzene, 80°	 (66)	575
		Et_3B, neat, 25°	 **I** + **II** (84) **I/II** = 24:1	170
C_9				
	 *x* eq	Conditions, initiator, benzene	 **I** + **II**	551

trans/cis	Conditions	Initiator	*x*	Temp (°)	Time (h)	**I + II**[d]	**I/II**
trans	—	AIBN	2	80	2	(88)	4.9:1
trans	*h*ν	none	2	—	2	(95)	3.8:1
cis	*h*ν	none	1.5	—	2	(72)	3.5:1
cis	*h*ν	none	2	—	1	(91)	3.8:1

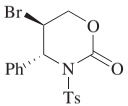
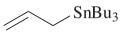
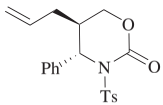
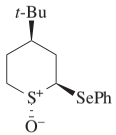
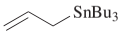
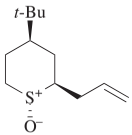
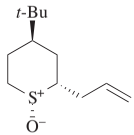
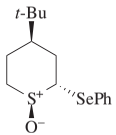
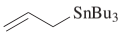
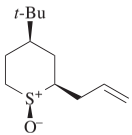
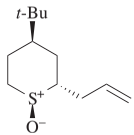
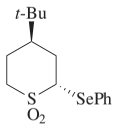
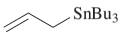
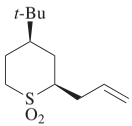
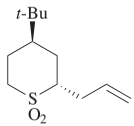
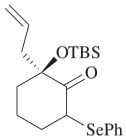
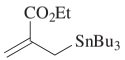
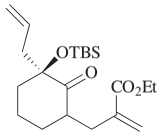
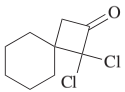
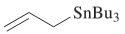
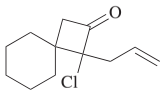
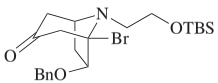
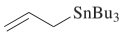
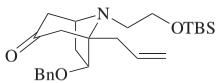
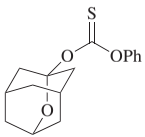
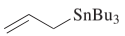
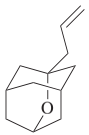
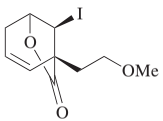
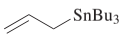
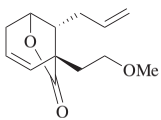
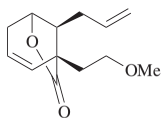
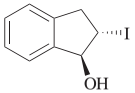
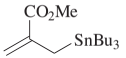
		AIBN, benzene, 85°, 36 h	 (89)	576
		AIBN, benzene, 80°	 **I** +  **II** **I + II** (92) **I/II** = 1.5:1	175
		AIBN, benzene, 80°	 **I** +  **II** **I + II** (58) **I/II** = 2.3:1	175
		AIBN, benzene, 80°	 **I** +  **II** **I + II** (70) **I/II** = 5.2:1	175

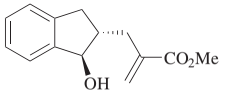
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		AIBN, benzene, 80°, 3 h	 (80) dr = 1:1	577
		AIBN, toluene, 80°	 (50)	83, 84
		ACCN, toluene, 85°, 18 h	 (78)	565, 578
		AIBN, benzene, 80°, 6 h	 (64)	579
		AIBN, benzene, 80°	 +  **I** **II** **I + II** (68) **I/II** = 24:1	580



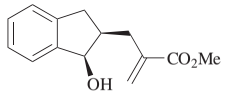


$h\nu$, AIBN, Lewis acid, CH_2Cl_2, 10°, 5 h



I

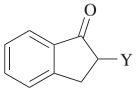
+

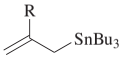


II

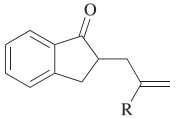
163

Lewis Acid	**I + II**	**I/II**
none	(67)	1.2:1
MAD	(69)	100:1



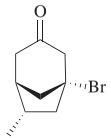
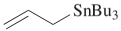
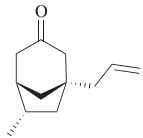
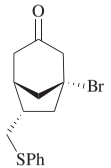
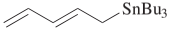
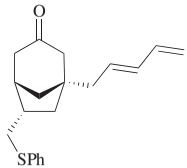
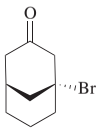
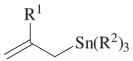
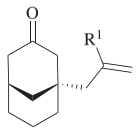
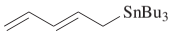
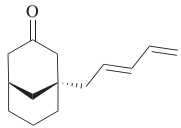


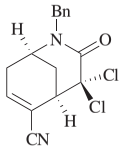
Conditions, initiator, benzene

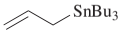


Y	R	Conditions	Initiator	Temp (°)	Time (h)		
PhSe	H	$h\nu$	none	—	1	(72)	542
PhSe	H	$h\nu$	$(Bu_3Sn)_2$	—	0.5	(71)	542
Br	Me_3SiCH_2	—	AIBN	80	2	(68)	36
Br	Me_3SiCH_2	$h\nu$	none	15–20	3	(86)	36

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

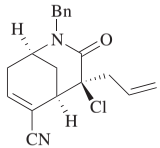
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_9				
		AIBN	 (61)	71
		Vitamin B_{12}, Zn	 (82)	581
		AIBN	 R^1 / R^2: H / Bu (86); Me_3Sn / Me (65)	71
		AIBN	 (48)	71



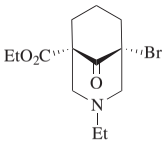


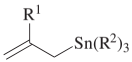
2.3 eq

AIBN, benzene, 80°, 7 h

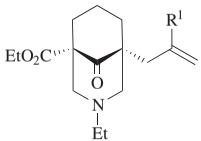


(63) 582



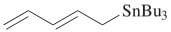


AIBN

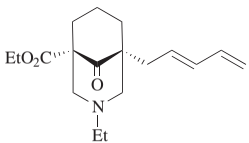


71

R^1	R^2	
H	Bu	(90)
Me	Bu	(85)
Me_3Sn	Me	(50)



Vitamin B_{12}, Zn, Et_3N, DMF, H_2O, rt, 20 h



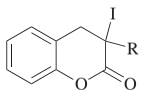
(61) 583

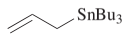
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

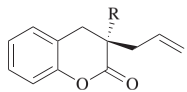
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{9-10}



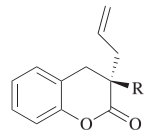


Et_3B, Lewis acid (*x* eq), ligand (*y* eq), additive, solvent, –78°



I

+

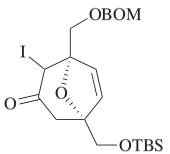
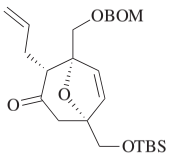
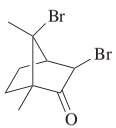
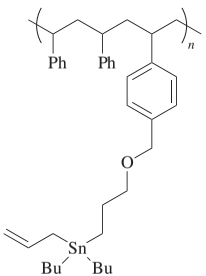
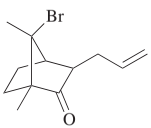
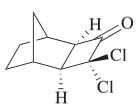
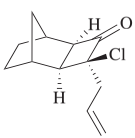
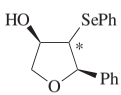
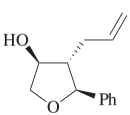


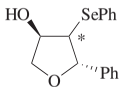
II

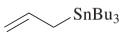
R	Lewis Acid	*x*	Ligand	*y*	Additive	Solvent	Time (h)	**I + II**	**I/II**	
H	none	—	(*R*)-**L11**	1.2	none	CH_2Cl_2	1	(63)	1:1.5	219
Me	Me_3Al	0.1	(*R*)-**L8b**	0.1	Et_2O	toluene	3	(83)	6.1:1	217
Me	Me_3Al	0.2	(*R*)-**L8b**	0.2	Et_2O	toluene	3	(81)	9:1	217
Me	Me_3Al	0.5	(*R*)-**L8b**	0.5	Et_2O	toluene	3	(82)	9.5:1	217
Me	Me_3Al	1	(*R*)-**L8b**	1	Et_2O	toluene	3	(84)	9.5:1	217
Me	Me_3Al	1	(*R*)-**L8b**	1	none	toluene	3	(72)	1.7:1	217
$MeOCH_2$	none	—	(*R*)-**L8a**	1.2	none	CH_2Cl_2	1	(72)	1.1:1	219
$MeOCH_2$	none	—	(*R*)-**L8b**	1.2	none	CH_2Cl_2	1	(71)	1:1	219
$MeOCH_2$	none	—	(*R*,*R*)-**L3c**	1.2	none	CH_2Cl_2	1	(72)	1.4:1	219
$MeOCH_2$	none	—	(*R*,*R*)-**L3d**	1.2	none	CH_2Cl_2	1	(68)	1.02:1	219
$MeOCH_2$	none	—	(*R*)-**L11**	1.2	none	CH_2Cl_2	1	(75)	1:1.9	219
$MeOCH_2$	none	—	(*R*)-**L11**	1.2	none	CH_2Cl_2	1	(71)[i]	1:1.8	219
$MeOCH_2$	none	—	(*R*)-**L11**	1.2	none	CH_2Cl_2	3	(—)[j]	1:1.6	219
$MeOCH_2$	none	—	(*R*)-**L11**	1.2	none	toluene	1	(50)[k]	1:1.1	219
$MeOCH_2$	none	—	(*R*)-**L11**	1.2	none	toluene	1	(69)	1:1.2	219
$MeOCH_2$	Me_3Al	0.1	(*R*)-**L8b**	0.1	Et_2O	toluene	3	(76)	6.77:1	217
$MeOCH_2$	Me_3Al	0.2	(*R*)-**L8b**	0.2	Et_2O	toluene	3	(78)	9:1	217
$MeOCH_2$	Me_3Al	0.5	(*R*)-**L8b**	0.5	Et_2O	toluene	3	(81)	9.5:1	217

R	Lewis Acid	*x*	Ligand	*y*	Additive	Solvent	Time (h)	**I + II**	**I/II**	
$MeOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	Et_2O	toluene	3	(85)	10.1:1	217
$MeOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	*i*-Pr_2O	toluene	3	(83)	2.5:1	217
$MeOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	THF	toluene	3	(71)	2:1	217
$MeOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	*N*-Me-pyrrolidine	toluene	3	(59)	1.1:1	217
$MeOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	none	toluene	3	(75)	1:1.2	217
$MeOCH_2$	Et_2AlCl	1	(*R*,*R*)-**L3c**	1	none	toluene	3	(29)	1.1:1	218
$MeOCH_2$	Me_3Al	1	(*R*,*R*)-**L3c**	1	none	toluene	3	(50)	1.1:1	218
$EtOCH_2$	none	—	(*R*)-**L11**	1.2	none	CH_2Cl_2	1	(77)	1:1.4	219
$EtOCH_2$	Me_3Al	0.1	(*R*)-**L8b**	0.1	Et_2O	toluene	3	(74)	5.7:1	217
$EtOCH_2$	Me_3Al	0.2	(*R*)-**L8b**	0.2	Et_2O	toluene	3	(79)	10.8:1	217
$EtOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	Et_2O	toluene	3	(85)	12.3:1	217
$EtOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	none	toluene	3	(77)	1:1.1	217
$BnOCH_2$	none	—	(*R*,*R*)-**L3c**	1.2	none	CH_2Cl_2	1	(75)	1.2:1	219
$BnOCH_2$	none	—	(*R*,*R*)-**L3c**	1.2	none	CH_2Cl_2	3	(—)[j]	1.2:1	219
$BnOCH_2$	none	—	(*R*)-**L11**	1.2	none	CH_2Cl_2	1	(68)	1:1.2	219
$BnOCH_2$	Me_3Al	0.1	(*R*)-**L8b**	0.1	Et_2O	toluene	3	(78)	5.9:1	217
$BnOCH_2$	Me_3Al	0.2	(*R*)-**L8b**	0.2	Et_2O	toluene	3	(73)	10.2:1	217
$BnOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	Et_2O	toluene	3	(76)	21:1	217
$BnOCH_2$	Me_3Al	1	(*R*)-**L8b**	1	none	toluene	3	(72)	1:1.1	217
$BnOCH_2$	Et_2AlCl	1	(*R*,*R*)-**L3c**	1	none	toluene	3	(19)	1:1	218
$BnOCH_2$	Me_3Al	1	(*R*,*R*)-**L3c**	1	none	toluene	3	(75)	1.7:1	218
$BnOCH_2$	*i*-Bu_3Al	1	(*R*,*R*)-**L3c**	1	none	toluene	3	(62)	1.4:1	218
$BnOCH_2$	Me_3Al	1	(*R*,*R*)-**L3d**	1	none	toluene	3	(76)	1:1.3	218
$BnOCH_2$	*i*-Bu_3Al	1	(*R*,*R*)-**L3d**	1	none	toluene	3	(68)	1:2.4	218
$BnOCH_2$	Me_3Al	2	(*R*,*R*)-**L3e**	0.5	none	toluene	3	(72)	3.3:1	218
$BnOCH_2$	Me_3Al	1.5	(*R*,*R*)-**L3e**	1	none	toluene	3	(73)	3.3:1	218
$BnOCH_2$	Me_3Al	3	(*R*,*R*)-**L3e**	0.5	none	toluene	3	(75)	1.2:1	218
$BnOCH_2$	Me_3Al	2	(*R*,*R*)-**L3e**	1	none	toluene	3	(76)	3.1:1	218
$BnOCH_2$	*i*-Bu_3Al	2	(*R*,*R*)-**L3e**	0.5	none	toluene	3	(72)	2.2:1	218
$BnOCH_2$	*i*-Bu_3Al	2	(*R*,*R*)-**L3e**	1	none	toluene	3	(75)	2.5:1	218
$BnOCH_2$	Et_2AlCl	1.5	(*R*,*R*)-**L3e**	1	none	toluene	3	(76)	1.1:1	218

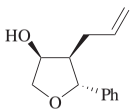
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		AIBN, benzene, 80°, 24 h	 (91)	584
		AIBN, benzene, 80°, 12 h	 (66)	116
		AIBN, benzene, 80°	 (64)	83, 84
C_{10}				
		AIBN, benzene, 80°, 3 h	 * (*R*) (70) (*S*) (65)	585



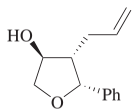


AIBN, benzene, 80°, 3 h



I

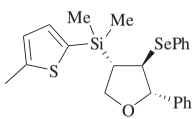
+

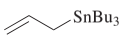


II

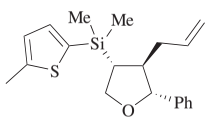
585

*	**I**	**II**
(*R*)	(28)	(25)
(*S*)	(23)	(20)



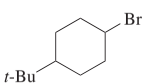


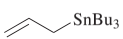
AIBN, benzene, 80°, 7 d



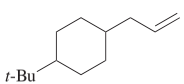
(55)

586



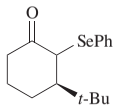
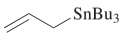
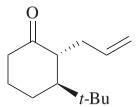
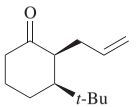


Conditions, AIBN, solvent

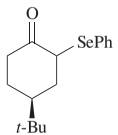
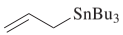
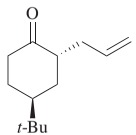
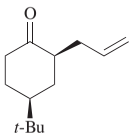


Conditions	Solvent	Temp (°)	Time (h)		*trans*/*cis*	
hν	—	—	12	(46)	—	21
—	benzene	80	72	(27)	1:1	100

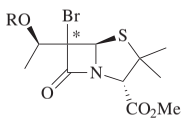
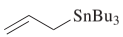
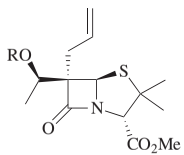
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10} 		Conditions, initiator, benzene	 **I** +  **II**	551

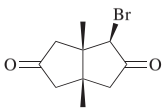
trans/cis	Conditions	Initiator	Temp (°)	Time (h)	**I + II**[d]	**I/II**
trans	—	AIBN	80	2	(91)	2.7:1
trans	*h*ν	none	—	1	(67)	1.9:1
cis	—	AIBN	80	2	(82)	2.6:1
cis	*h*ν	none	—	1	(54)	1.9:1

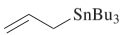
		*h*ν, benzene, 1 h	 **I** +  **II**	551

trans/cis	**I + II**[d]	**I/II**
trans	(72)	5.7:1
cis	(60)	6.7:1

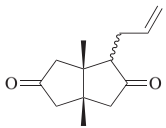
		AIBN, benzene, 80°		

R	*	Time (h)		
H	(*R*)	4	(81)	80
H	(*S*)	35	(82)	81
TMSO	(*S*)	4	(75)	81
TBSO	(*R*)	1.5	(75)	80

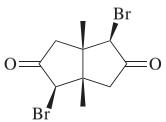


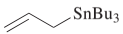


AIBN, toluene, 80°, 16 h

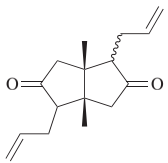


(49) 587

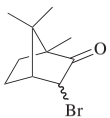


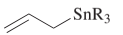


AIBN, toluene, 80°, 37 h



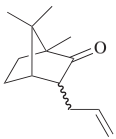
(31) 587



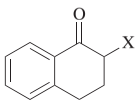


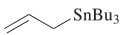
R = $CH_3(O(CH_2)_2)O(CH_2)_3$

AIBN, benzene, 80°, 16 h

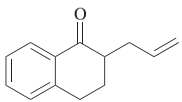


(45) 121



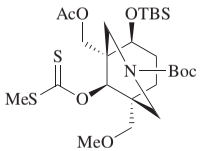
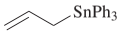
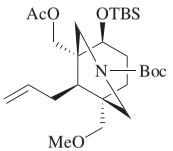
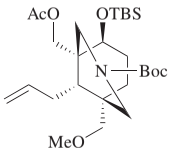
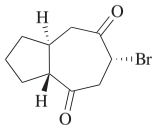
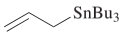
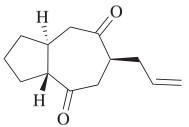
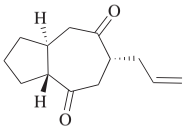
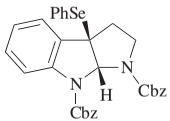
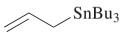
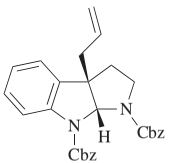
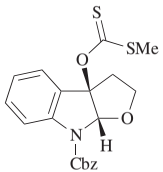
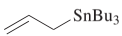
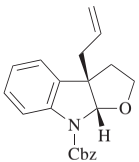


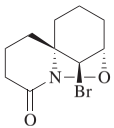
*h*ν, $Cu(dap)_2Cl$, MeCN, rt

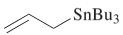


X	Time (h)		
Cl	6	(63)	47
Br	7	(70)	

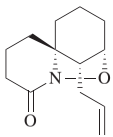
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
	 4 eq	ACCN, neat, 130°, 18 h	 (36) +  (32)	588
		AIBN, toluene, 80°, 9 h	 **I** +  **II** **I** + **II** (76) **I/II** = 28:1	589
		AIBN, toluene, 110°, 15 h	 (56)	76
		*h*ν, benzene	 (87)	590



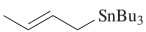


Conditions, initiator, solvent

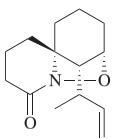


3, 4, 308

Conditions	Initiator	Solvent	Temp (°)	Time (h)	
—	AIBN	benzene	80	5	(88)
*h*ν	none	toluene	rt	6	(70)



AIBN, toluene, 80°, 8 h

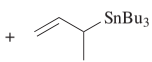


(0)

139

I

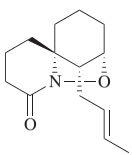
+



II

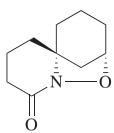
I/II = 1.5:1

AIBN, toluene, 80°, 8 h



III

+

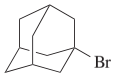
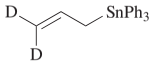
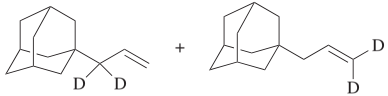
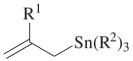
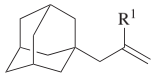


IV

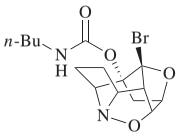
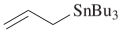
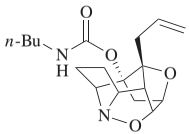
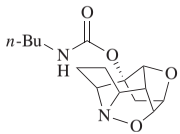
III + IV (66) **III/IV** = 1:1

4, 139

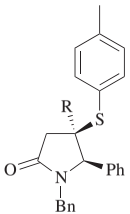
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

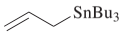
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
		AIBN, benzene, 80°, 12 h	 **I** + **II** (88) **I/II** > 10:1	44
		Conditions, initiator, solvent		

R^1	R^2	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
H	Bu	—	AIBN	benzene	80	58	(57)	69
H	Bu	—	$ZnCl_2$•OEt_2	CH_2Cl_2	–78	—	(91)	51
H	$CF_3(CF_2)_5(CH_2)_3$	*hν*	none	neat	25	3–30	(89)	123
t-BuHNCO	Bu	—	AIBN	benzene	80	—	(76)	44
EtO_2C	Bu	—	AIBN	benzene	80	—	(70)	44

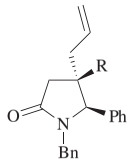
		AIBN, benzene, 85°, 15 h	 (71)		591, 592
			+  (27)		

C_{11}



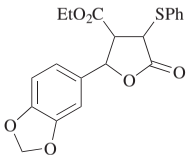


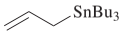
AIBN, toluene, 110°, 3 h



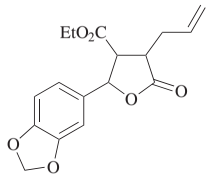
R	
MeO_2C	(0)
NC–	(99)

593



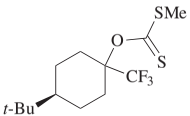


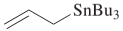
Not reported



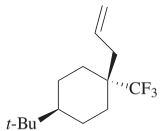
(58)

594



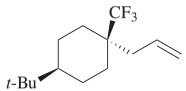


Et_3B, neat, 25°



I

+

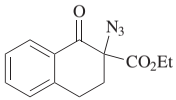
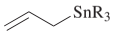
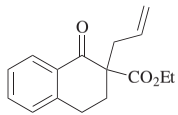
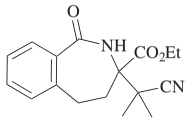
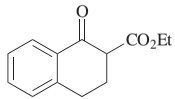


II

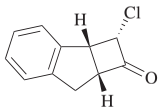
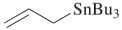
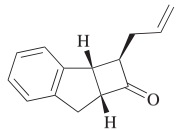
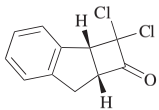
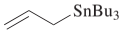
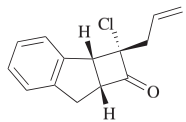
I + II (82) **I/II** = 3.5:1

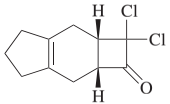
170

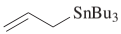
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11}				
		AIBN, benzene, 80°	 **I** +  **II** +  **III**	118

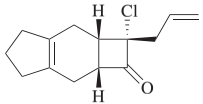
R	Time (h)	**I**	**II**	**III**
Bu	4.5	(5)	(48)	(22)
Ph	4	(63)	(14)	(0)

		AIBN	 (52)	85
		AIBN, benzene, 80°	 (67)	83, 84

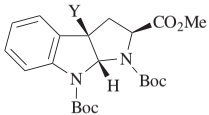


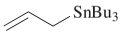


AIBN, benzene, 80°

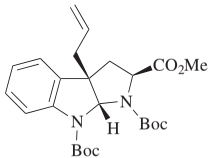


(42) 83, 84

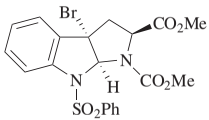


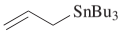


Conditions, initiator, solvent

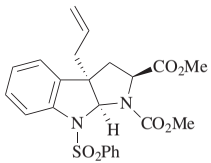


Y	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
Br	—	AIBN	benzene	80	—	(90)	595
PhSe	*hν*	$(Bu_3Sn)_2$	toluene	23	9	(94)[l]	76





AIBN, benzene, 80°, 18 h



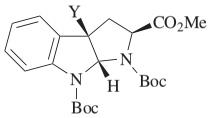
(80) 309

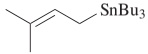
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

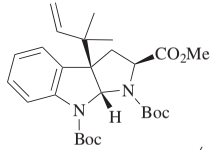
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{11}



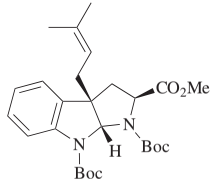


Conditions, initiator, solvent



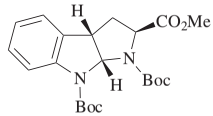
I

+



II

+



III

Y	Conditions	Initiator	Solvent	Temp (°)	**I + II**	**III**	**I/II**	
Br	—	AIBN	benzene	80	(—)	(0)	1.5:1	595
PhSe	*h*ν	$(Bu_3Sn)_2$	toluene	23	(0)	$(—)^l$	—	76

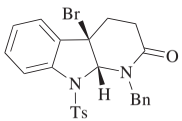
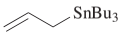
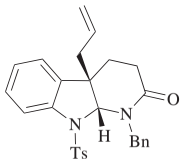
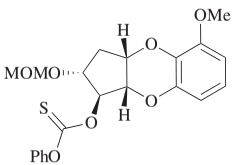
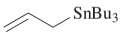
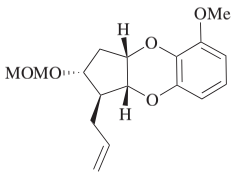
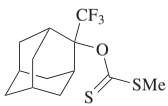
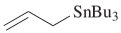
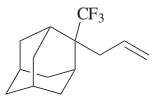
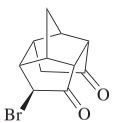
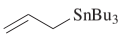
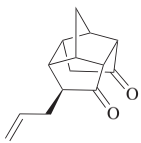
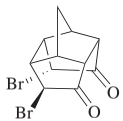
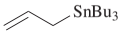
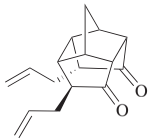
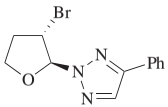
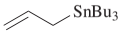
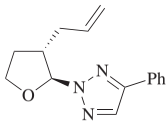
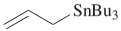
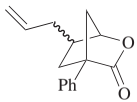
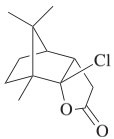
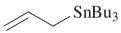
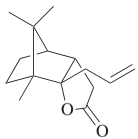
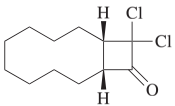
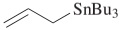
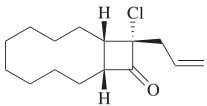
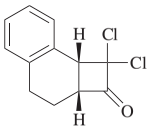
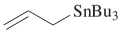
		AIBN, toluene, 110°, 7 h		(80)	596
		*hν*, benzene, 10 h		(75)	597
		Et_3B, neat, 25°		(56)	170
		AIBN, toluene, 80°, 2 h		(75)	82

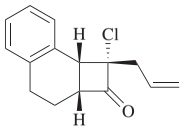
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11}				
		AIBN, toluene, 80°, 2 h	 (76)	82
C_{12}				
		AIBN, benzene, 90°, 12 h	 (82)[m]	598
		AIBN, benzene, 80°, 4.5 h	 (53) dr = 5:1	599
		AIBN, benzene, 80°, 16 h	 (46)	600
		AIBN, benzene, 80°	 (58)	84

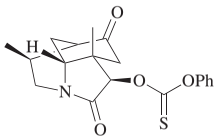


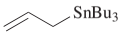


AIBN, benzene, 80°

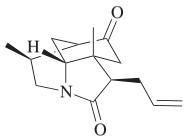


(44) 84

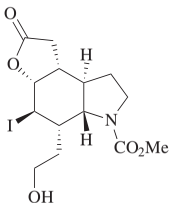


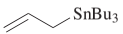


AIBN, toluene, 90°, o/n

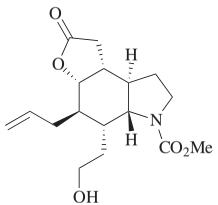


(72) 601

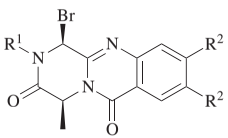


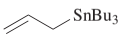


AIBN, benzene, 80°, 1 h

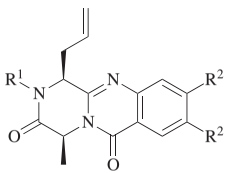


(83) 311, 602





AIBN, benzene, 80°, 1.5 h



R^1	R^2	
Me	H	(85)
Bn	MeO	(60)

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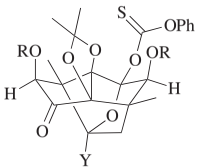
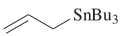
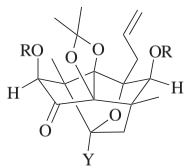
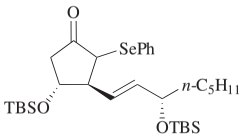
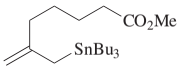
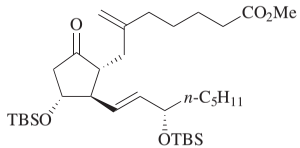
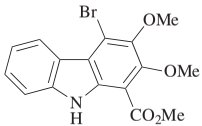
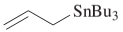
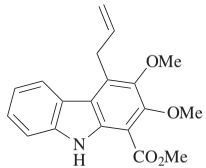
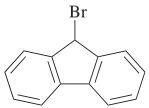
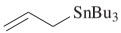
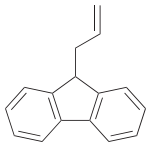
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}				
		AIBN, benzene, 80°		
			R / Y / Time (h)	
			MOM / BnO / 13 (70)	319, 579
			TBS / H / 3 (66)	320
C_{13}				
		$h\nu$, benzene, 2 h	 (76)	77
		AIBN, benzene, 80°, 1 h	 (89)	604





Initiator (x eq), solvent



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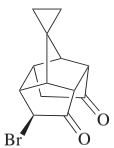
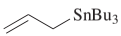
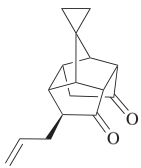
Initiator	x	Solvent	Temp (°)	
none	—	benzene	80	(28)
AIBN	0.1	benzene	80	(50)
$ZnCl_2 \bullet OEt_2$	1	CH_2Cl_2	−78 to rt	(64)
$ZnCl_2 \bullet OEt_2$	0.1	CH_2Cl_2	−78 to rt	(73)



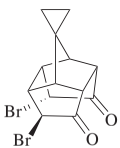


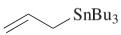
AIBN, toluene, 80°, 2 h



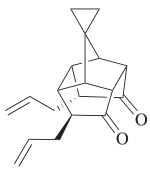
(64)

82





AIBN, toluene, 80°, 2 h



(75)

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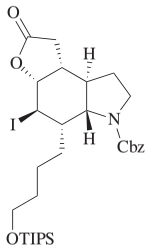
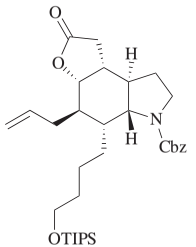
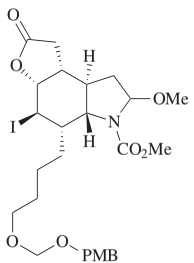
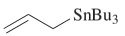
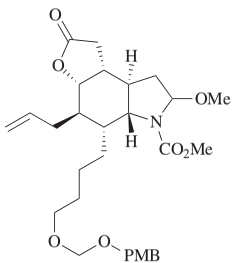
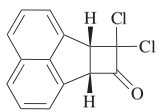
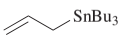
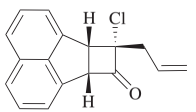
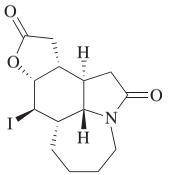
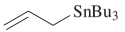
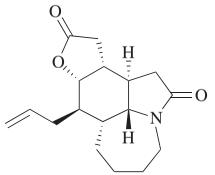
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{14} 		AIBN, neat, 80°, 12 h	 (90)	312
		AIBN, toluene, 80°, 4 h	 (80)	313
		AIBN, benzene, 80°	 (54)	84



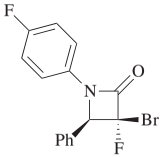


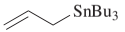
AIBN, benzene, 80°



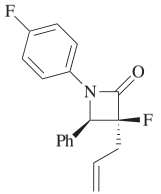
Time (h)		
6	(59)	314, 315
22	(93)	316, 317

C_{15}





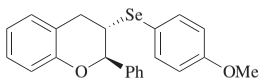
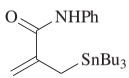
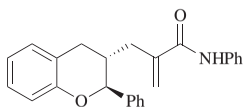
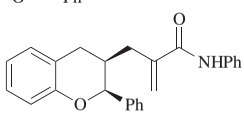
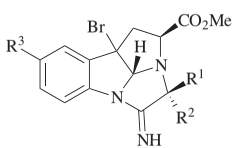
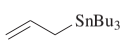
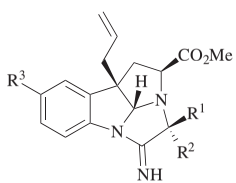
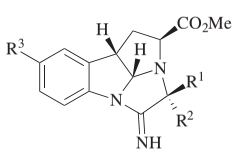
Initiator, solvent



605

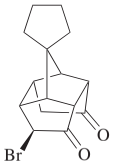
Initiator	Solvent	Temp (°)	Time		dr
Et_3B, O_2	CH_2Cl_2/THF (4:1)	–78 to –40	0.25 h; then o/n	(92)	>99:1
AIBN	benzene	80	o/n	(89)	95:5

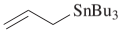
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{15} 		V-70, benzene, 30°, 24 h	 (59) +  (32)	606
C_{15-18} 		AIBN, xylene, 130°	 **I** +  **II**	

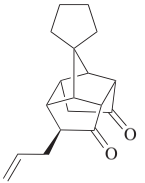
R^1	R^2	R^3	Time (h)	**I**	**II**^{n}	
Me	Me	H	2	(36)	(11–30)	607
Me	Me	Br	2	(26)	(11–30)	607
$-(CH_2)_2NBn(CH_2)_2-$		H	2	(57)	(11–30)	607
$-(CH_2)_2NBn(CH_2)_2-$		Br	2	(28)	(11–30)	607
$-(CH_2)_5-$		H	48	(70)	(11–30)	608
$-(CH_2)_5-$		Br	48	(65)	(11–30)	608

C_{15}

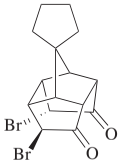


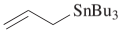


AIBN, toluene, 80°, 2 h

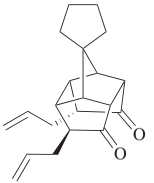


(84) 82



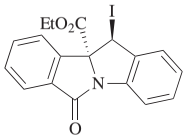
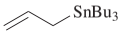
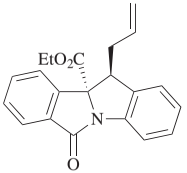
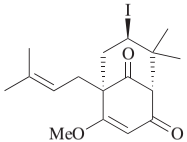
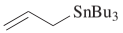
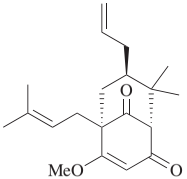
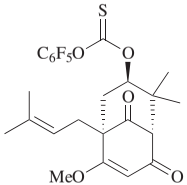
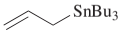
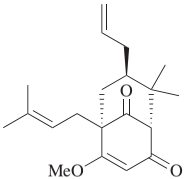
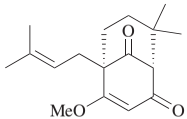


AIBN, toluene, 80°, 2 h

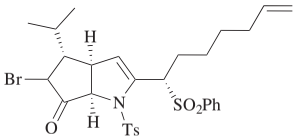


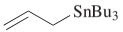
(70) 82

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

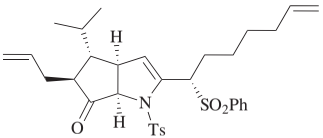
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{16}				
		$Cu(OTf)_2$, Cu^0, dtbbpy, benzene, 75°	 (47) dr > 20:1	609
		AIBN, benzene, 80°	 (84)	610
		Et_3B, air, benzene, rt, 1.25 h	 (56) +  (11)	611

C_{17}

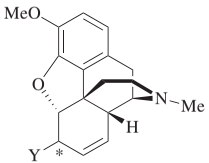


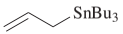


AIBN, toluene, 100°

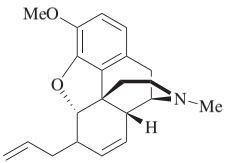


(52) 172





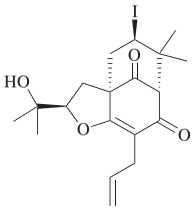
AIBN, toluene, 80°

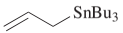


612

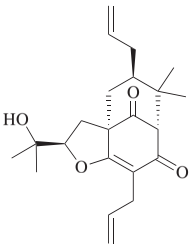
Y	*	
Br	(*R*)	(0)
Im(S)CO	(*S*)	(0)

C_{19}



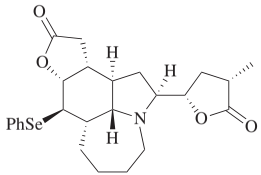
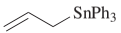
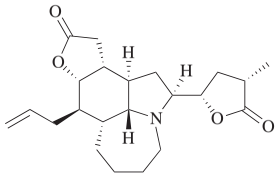
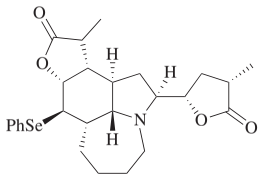
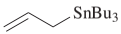
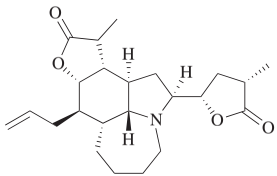
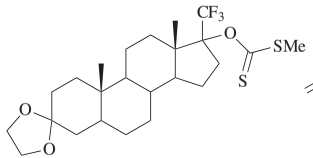
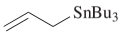
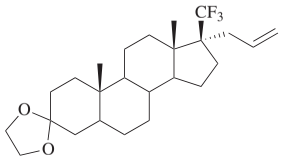


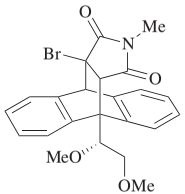
AIBN, benzene, 80°, 2 h

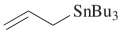


(82) 310

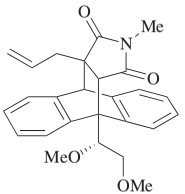
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{19} 	 $SnPh_3$	AIBN, solvent		
			Solvent / Temp (°) / Time (h): neat / 95 / — / (70)	318
			BTF / 100 / 14 / (70)	120
C_{20} 	 $SnBu_3$	AIBN, BTF, 95°	 (70)	120
	 $SnBu_3$	Et_3B, neat, –20°	 (7)	170



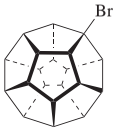


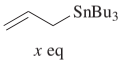
AIBN, benzene, 80°, 24 h



(98)

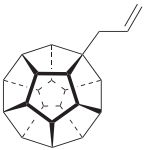
613, 614





x eq

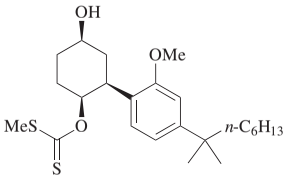
*h*ν



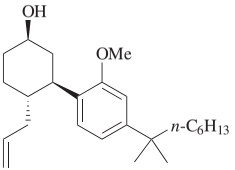
x	
20	(0)
200	(30)

70

C_{21}

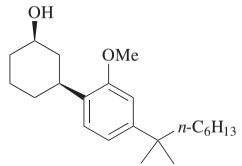


AIBN, benzene, 80°, 12 h



I

+

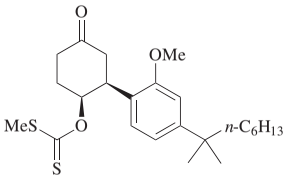
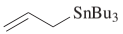
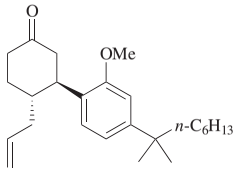
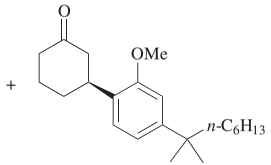
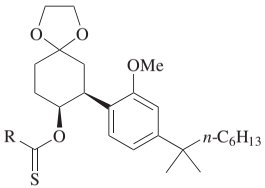
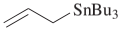
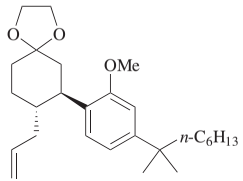


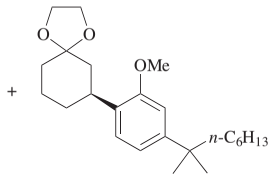
II

I + **II** (80) **I**/**II** = 1.6:1

615

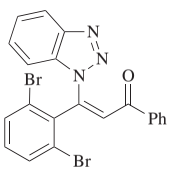
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

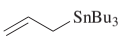
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{21} 		AIBN, benzene, 80°, 12 h	 **I**  **II** **I + II** (20) **I/II** = 2.4:1	615
		AIBN, solvent, 80°, 12 h	 **I**	615



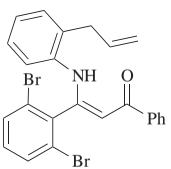
II

R	Solvent	**I + II**	**I/II**
PhO	toluene	(53)	1:1.2
C_6F_5O	toluene	(35)	1:1.2
Im	toluene	(32)	1:1.4
MeS	toluene	(60)	1:1.2
MeS	benzene	(66)	1.1:1



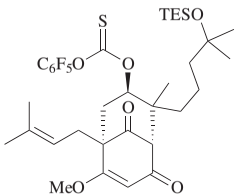
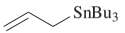
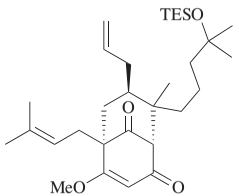
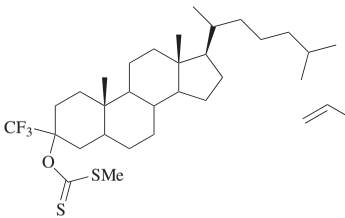
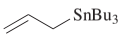
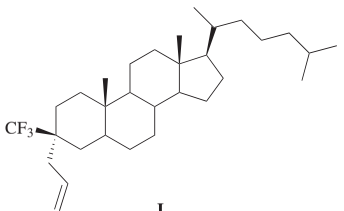
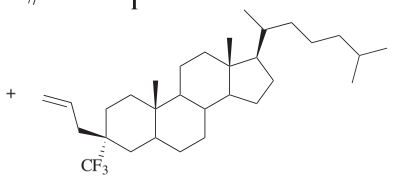


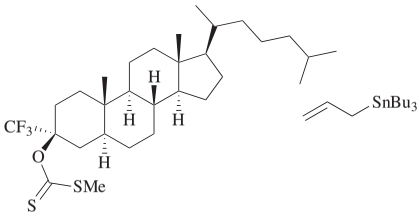
$h\nu$, Hantzsch ester, MeCN, rt, 8 h



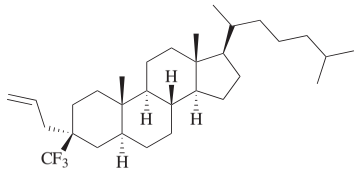
(—) 616

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
B. CYCLIC SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{21} 		Et_3B, air, benzene, rt, 70 min	 (72)	617
C_{28} 		Et_3B, neat, –20°	 **I** +  **II** **I + II** (55) **I/II** = 2.7:1	170



Et_3B, O_2, neat, –30°, 1 h



(55) dr = 2.5:1

618

[a] The *cis* isomer of the substrate was used.

[b] This is the overall yield for a one-pot, two-step process where the allylstannane is formed first by reaction of phenyl propargyl ether with Bu_3SnH and $Pd(PPh_3)_4$.

[c] The pure *cis* starting material was used.

[d] The yield was determined by GC.

[e] The substrate with the opposite stereochemistry of the SMe group was used.

[f] This is the overall yield for the two-step process.

[g] The configuration of the products was not definitively established.

[h] The yield was determined by NMR spectroscopy.

[i] Excess allyltributyltin was used.

[j] Initiation was done with *hν*, AIBN instead of Et_3B.

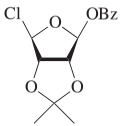
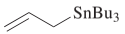
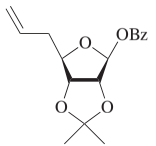
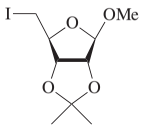
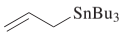
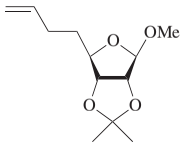
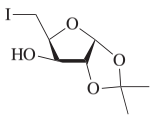
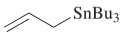
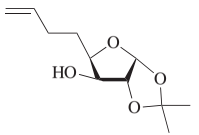
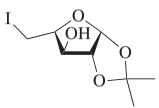
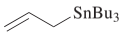
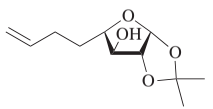
[k] The reaction was carried out at –50°.

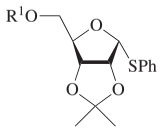
[l] Both the starting material and the product contained a 5:1 mixture of the *exo*/*endo* stereoisomers.

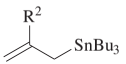
[m] The reaction was carried out in a sealed tube.

[n] Specific yields were not given.

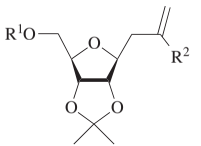
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		AIBN, benzene, 80°, 4 h	 (85)	619, 620
C_5				
		AIBN, benzene, 80°, 18 h	 (64)	621
		AIBN, solvent, 80°		
			Solvent / Time (h)	
			benzene / 18 (55)	621
			benzene / — (—)	622
			toluene / — (45)	623
		AIBN, benzene, 80°, 18 h	 (58)	624





$h\nu$, solvent, rt



I

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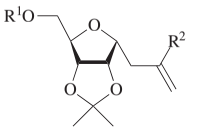
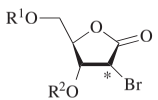
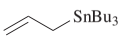


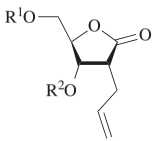
II

R^1	R^2	Solvent	**I + II**	**I/II**	
TBDPS	H	—	(76)	4:1	4
TBS	Me	toluene	(79)	1.5:1	625
TBDPS	Me	toluene	(86)	4.9:1	4, 625





AIBN, benzene, 80°



I

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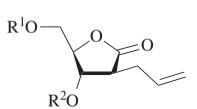
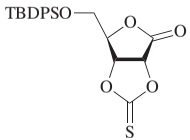
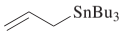
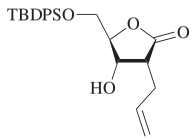
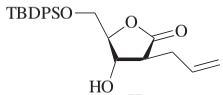
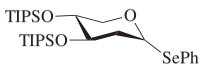
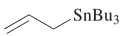
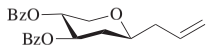
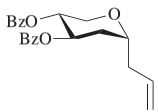


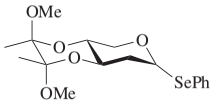
II

124

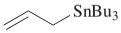
R^1	R^2	*	Time (h)	**I + II**	**I/II**
H	H	(*S*)	3	(85)	1:1.2
TBS	TBS	(*R*)/(*S*) (1:2)	0.75	(88)	2:1
H	TBS	(*S*)	2	(90)	2.3:1
H	TBS	(*R*)	2	(92)	2.1:1
TBDPS	H	(*S*)	3	(92)	2:1

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

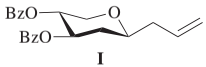
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_5 		AIBN, benzene, 80°, 0.75 h	 **I** +  **II** **I + II** (85) **I/II** = 1.6:1	124
 α/β = 1:1		1. AIBN, benzene, 80° 2. TBAF 3. BzCl, DMAP, pyridine	 **I** +  **II** **I + II** (34)[a] **I/II** = 1.2:1	169



α/β = 1:1

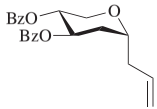


1. AIBN, benzene, 80°
2. TFA, H_2O
3. BzCl, DMAP, pyridine



I

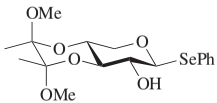
+

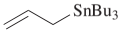


II

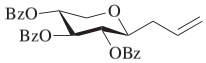
I + **II** (74)[a] **I**/**II** = 1:49

169



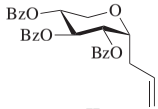


1. AIBN, benzene, 80°
2. TFA, H_2O
3. BzCl, DMAP, pyridine



I

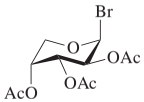
+

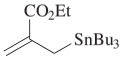


II

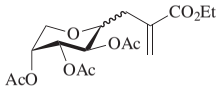
I + **II** (69)[a] **I**/**II** = 1:10.1

169





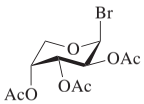
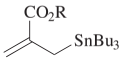
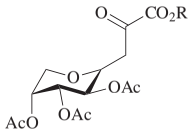
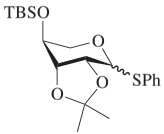
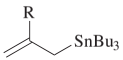
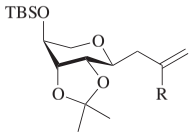
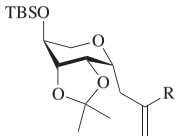
AIBN, benzene, 80°, 3.5 h



(76) dr = 1:1

626

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		1. AIBN, benzene, 80°, 3.5 h 2. O_3	 R — dr Et — (50)[b,c] — 1:1 *t*-Bu — (67)[b] — 1:1	626, 627 627
		*hν*, toluene, rt	 **I** +  **II** R — **I + II** — **I/II** H — (82) — 9:1 Me — (87) — 11.5:1	4, 423, 625

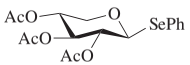
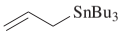
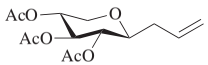
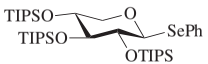
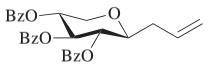
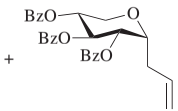
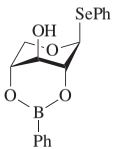
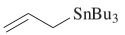
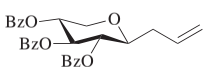
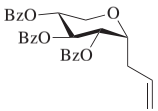
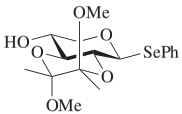
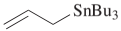
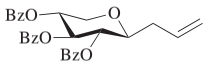
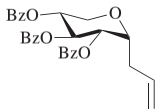
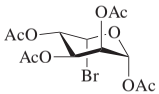
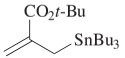
		AIBN, benzene, 80°		(0)	169
		1. AIBN, benzene, 80° 2. TBAF 3. BzCl, DMAP, pyridine	 **I** +  **II** **I + II** (26)[a] **I/II** = 99:1 + (61)		169
		1. AIBN, benzene, 80° 2. $HO(CH_2)_3OH$, acetone 3. BzCl, DMAP, pyridine	 **I** +  **II**	**I + II** (61)[a] **I/II** = 99:1	169

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

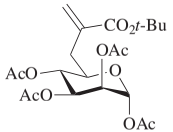
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_5 		1. AIBN, benzene, 80° 2. TFA, H_2O 3. BzCl, DMAP, pyridine	 **I** +  **II** **I + II** (73)[a] **I/II** = 1:5.7	169

R	Conditions	Initiator	Solvent	Temp (°)	Time		Refs.
MeS	—	AIBN	toluene	80	o/n	(13)	4, 423
MeS	*hν*	none	benzene	rt	—	(62)	4, 423
PhO	*hν*	none	toluene	rt	65 h	(80)	4, 423, 628
Im	—	AIBN	toluene	80	—	(27)	3, 4, 423
Im	*hν*	none	toluene	rt	—	(55)	3, 4, 423



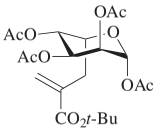


AIBN, benzene, 80°, 1.5 h



I

+

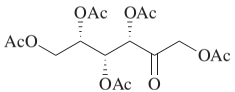


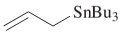
II

I + **II** (68) **I/II** = 3:1

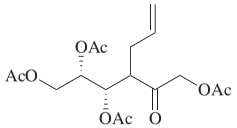
629

C_6



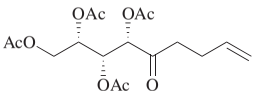


AIBN, benzene, 80°



I dr = 4:3

+

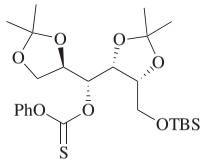
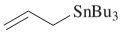
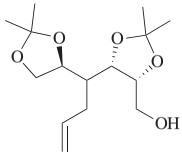
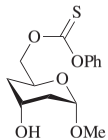
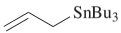
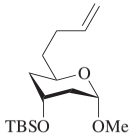
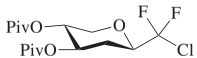
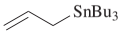
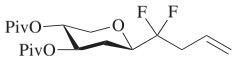
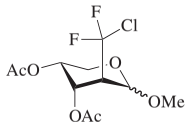
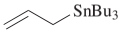
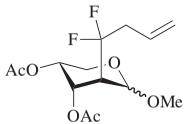
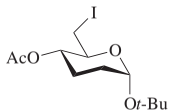
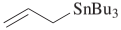
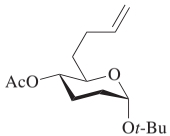


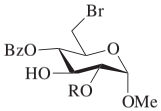
II

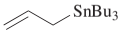
I + **II** (—) **I/II** = 2:1

56

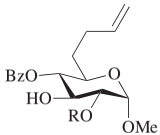
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		1. *h*ν, toluene, 75–85°, 6 h 2. Et_4NF, THF, 50°, 4 h	 (78)[b] dr = 1:1	630
		1. *h*ν, toluene, rt, 7 h 2. TBSCl, imidazole, DMF	 (82)[b]	631
		*h*ν, EtOAc, 2–3 h	 (62)	632
		*h*ν, EtOAc, 2–3 h	 (64)	632
		AIBN, benzene, 80°, 5 h	 (51)	621

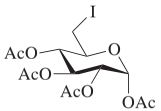


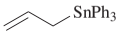


Conditions, initiator, solvent

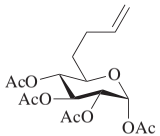


R	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
H	—	AIBN	toluene	80	14	(92)	4
H	*h*ν	none	toluene/EtOAc (2.7:1)	rt	18	(91)	4
Ts	—	AIBN	toluene	80	8	(74)	3, 4
Ts	*h*ν	none	toluene	rt	5	(60)	3, 4

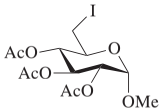


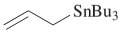


*h*ν, AIBN, benzene, 20°, 7 h

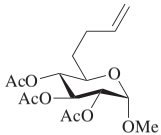


(68) 633



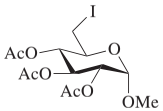
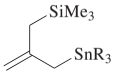
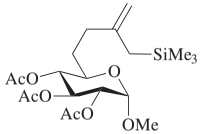
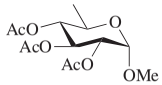
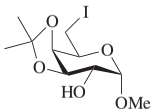
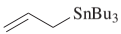
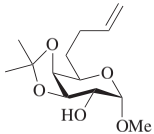
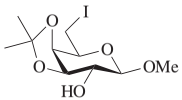
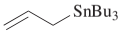
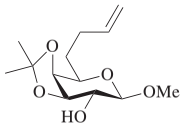
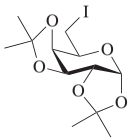
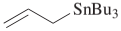
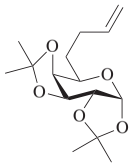


AIBN, benzene, 80°, 18 h



(64) 621

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_6				
		*hν*, DME, 15–20°	 **I** +  **II**	36
			R / Time (h) / **I** / **II**: Bu / 9 / (45) / (51); Ph / 20 / (42) / (52)	
		AIBN, benzene, 80°, 18 h	 (57)	621
		AIBN, benzene, 80°	 (—)	622
		AIBN, benzene, 80°, 18 h	 (65)	621

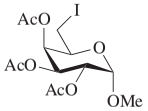
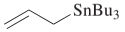
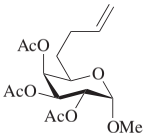
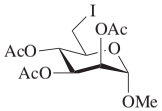
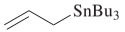
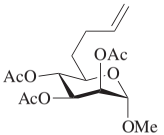
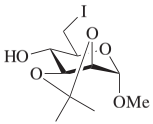
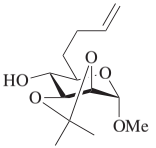
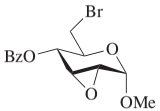
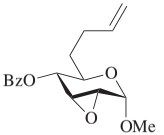
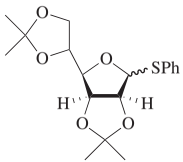
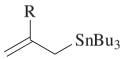
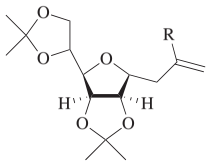
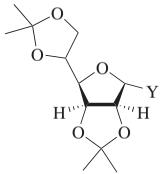
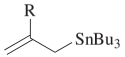
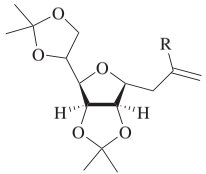
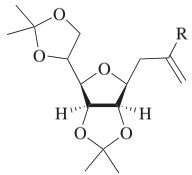
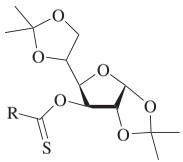
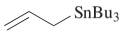
		AIBN, benzene, 80°, 18 h		(60)	621
		AIBN, benzene, 80°, 18 h		(58)	621
		AIBN, benzene, 80°, 18 h		(53)	621
		AIBN, benzene, 80°, 10 h		(76)	3, 4

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

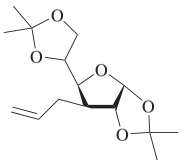
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6 		*h*ν, toluene, rt	 R: H (91); Me (72)	4
		Conditions, initiator, toluene	 **I** +  **II**	

Y	R	Conditions	Initiator	Temp	**I + II**	**I/II**	
Cl	H	—	AIBN	80°	(79)	>99:1	3, 4
Cl	H	*h*ν	none	rt	(68)	>99:1	3, 4
PhS	Me	*h*ν	none	rt	(91)	99:1	625



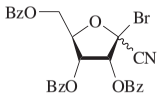


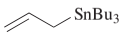
Conditions, initiator, solvent



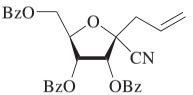
634

R	Conditions	Initiator	Solvent	Temp (°)	Time (h)	
PhO	*h*ν	none	benzene	10	40	(80)
MeS	—	AIBN	toluene	110	0.5	(35)



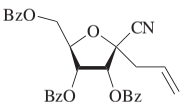


AIBN, THF, 65°, 16 h



I

+

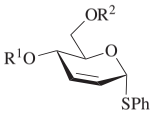
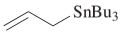
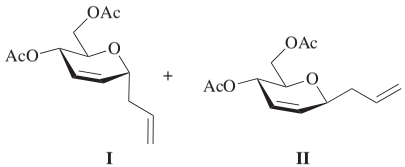
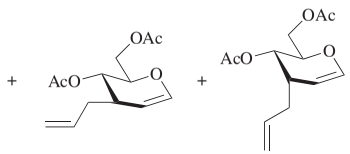


II

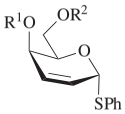
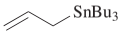
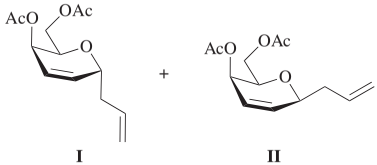
I + **II** (42) **I/II** = 5:1

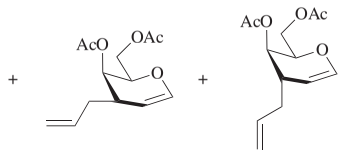
635

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		*hν*, toluene, rt, 18–24 h	 **I** + **II**  **III** + **IV**	636

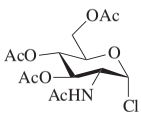
R^1	R^2	**I**	**II**	**III + IV**	**III/IV**
H	H[d]	(12)	(8)	(16)	1.3:1
H	TBS[e]	(17)	(10)	(20)	1:1
Ac	Ac	(13)	(11)	(16)	2:1
TBS	TBS[e]	(13)	(13)	(18)	1:1

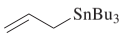
		*hν*, toluene, rt, 18–24 h	 **I** + **II**	636



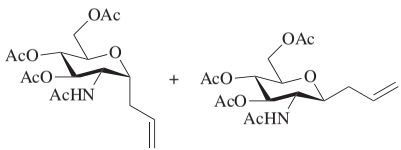
III **IV**

R^1	R^2	**I**	**II**	**III + IV**	**III/IV**
H	TBS[e]	(13)	(9)	(15)	>99:1
Ac	Ac	(14)	(11)	(17)	4.2:1

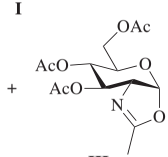




AIBN, solvent



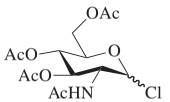
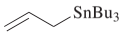
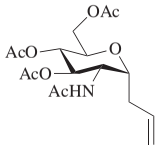
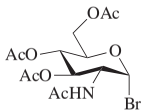
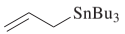
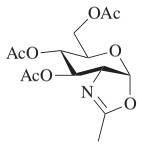
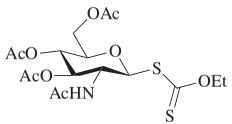
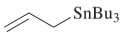
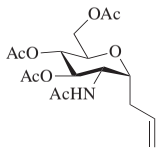
I **II**

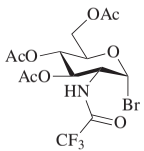


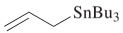
III

Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	**III**	
toluene	85	8	(69)	33.5:1	(5)	637
THF	65	1	(66)	10:1	(0)	638
THF	55–68	3	(73)	12:1	(0)	639

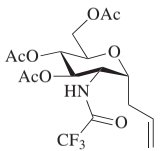
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, THF, MW (10 W) 100°, 10 min	 (51)	640
		AIBN, toluene, DME, 80°, 18 h	 (88)	637
		AIBN, toluene, 80°, 24 h	 (25)	637



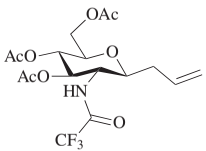


AIBN, toluene, 85°, 6 h



I

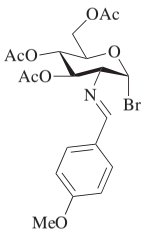
+

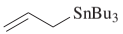


II

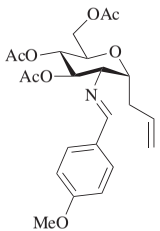
637

I + **II** (65) **I**/**II** = 12:1



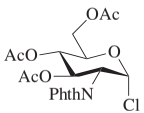


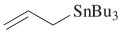
AIBN, toluene, 90°, 24 h



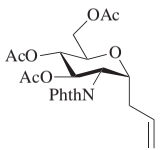
(45)

637





AIBN, toluene, 85°, 24 h



(0)

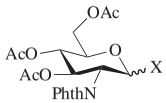
637

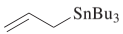
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

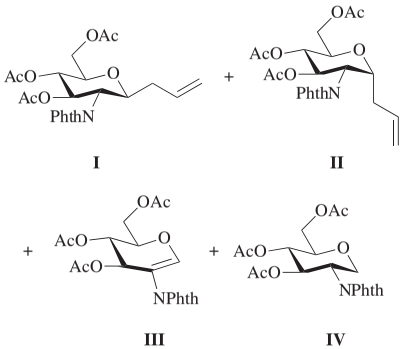
C_6



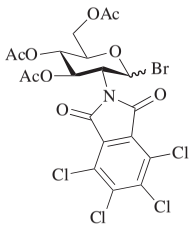


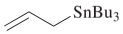
x eq

AIBN, solvent



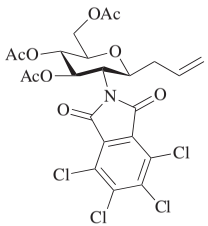
X	*x*	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**	**III**	**IV**	
Cl	12	benzene	80	12	(0)	—	(0)	(0)	638
Cl	12	toluene	110	12	(0)	—	(—)	(0)	638
Br	2	toluene	85	24	(40)[f]	>99:1	(16)	(8)	637
Br	3	benzene	80	12	(30)	—	(—)	(0)	638
Br	12	benzene	80	12	(71)	10:1	(0)	(0)	638





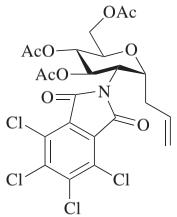
12 eq

AIBN, benzene, 80°, 18 h



I

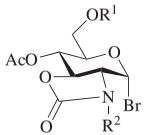
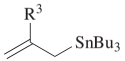
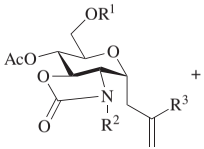
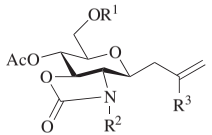
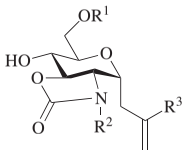
+



II

I + **II** (77) **I/II** > 20:1 638

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6 	 12 eq	AIBN, benzene, 80°, 12 h	 **I** +  **II** 641 +  **III**	

R^1	R^2	R^3	**I + II**	**III**	**I/II**
Ac	H	H	(<14)	(—)	—
Ac	Ac	H	(76)	(—)	>99:1
Ac	Ac	H	(35)[g]	(—)	>99:1
Ac	Ac	Me	(59)	(—)	>99:1
Ac	Bn	H	(84)	(0)	15.7:1
Bn	Ac	H	(41)	(—)	>99:1
Bn	Bn	H	(56)	(19)	13.3:1
TBDPS	Bn	H	(26)	(47)	>91:9

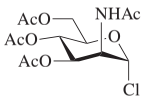
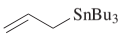
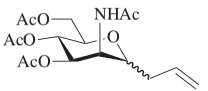
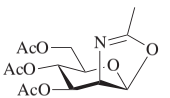
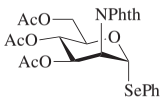
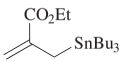
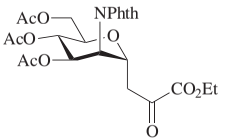
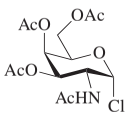
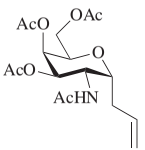
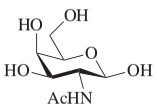
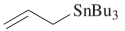
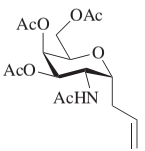
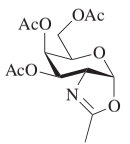
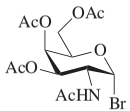
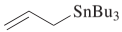
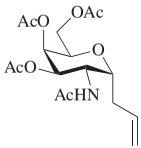
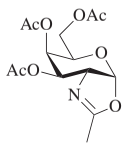
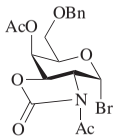
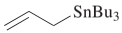
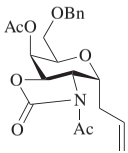
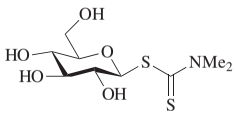
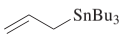
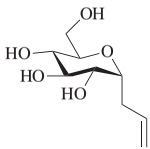
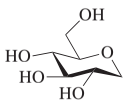
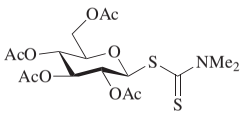
		AIBN, toluene, 85°, 6 h	 (0) +  (82)	637
		1. — 2. O_3	 (80)[b]	627
		AIBN, toluene, 85°, 7 h	 (56)	637, 642
		1. AcCl, HCl, 30° 2. Allylstannane, AIBN, toluene, 85°	 (14)[b] +  (—)	639

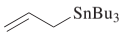
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, toluene, 85°	 (0) +  (—)	639
		AIBN, benzene, 80°, 12 h	 (65)	641
	 *x* eq	AIBN, solvent, 75°	 **I** +  **II**	643

x	Solvent	Time (h)	**I + II**[h]	**I/II**
3	2-propanol	21	(75)	1:1.1
5	ethanol	4	(100)	1:1
5	acetonitrile	6	(90)	1.3:1
5	1,4-dioxane	4	(100)	1.3:1
10	1,4-dioxane	2	(100)	1.9:1
15	1,4-dioxane	1.5	(100)	1.5:1

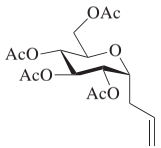


x M



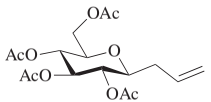
5 eq

AIBN, toluene, 75°



I

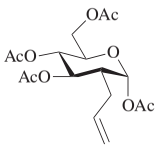
+



II

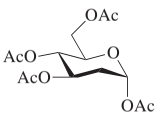
643

+



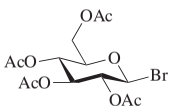
III

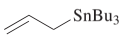
+



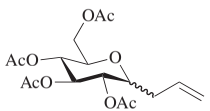
IV

x	Time (h)	**I + II + III + IV**[h]	**I/II**	**(I + II)/III/IV**
0.05	4	(100)	6:1	1:4.7:1
0.25	24	(90)	4:1	6:2:1





Conditions, initiator, benzene

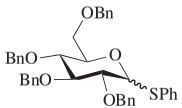
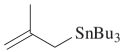
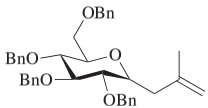
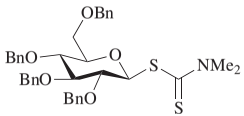
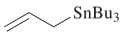
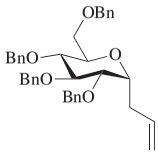
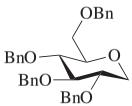
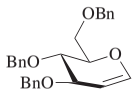
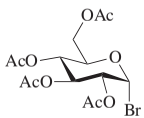
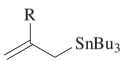
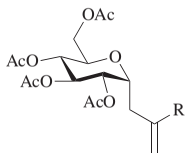
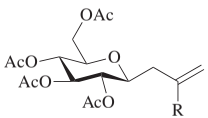


4

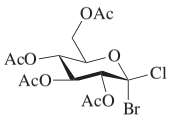
Conditions	Initiator	Temp	
—	AIBN	80°	(64)
hν	none	rt	(52)

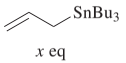
TABLE 1. DIRECT ALLYLATIONS (*Continued*)

C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		*hν*, toluene, rt	 (—) dr = 1:1	625
	 8 eq	AIBN, toluene, 75°, 24 h	 **I** +  **II** +  **III** **I + II + III** (90)[h] **I/II/III** = 3.7:1:1.3	643
		Conditions, AIBN, benzene	 **I** +  **II**	

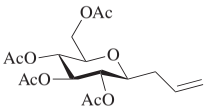
R	Conditions	Temp (°)	Time (h)	**I + II**	**I/II**	
EtO_2C	—	80	4	(84)	>99:1	626
Me_3Si	*h*ν	10	—	(70)	5:1	61



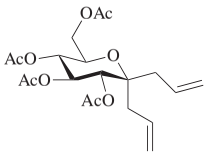


x eq

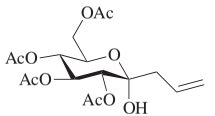
*h*ν, AIBN, benzene



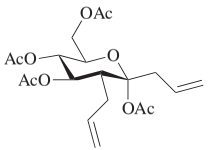
I

+ 

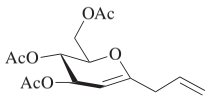
II

+ 

III

+ 

IV

+ 

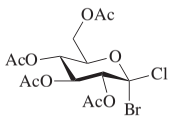
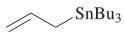
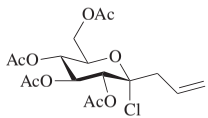
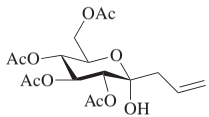
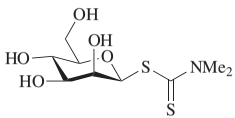
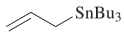
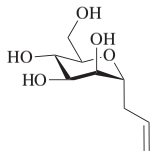
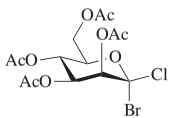
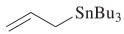
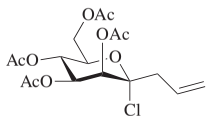
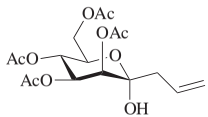
V

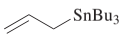
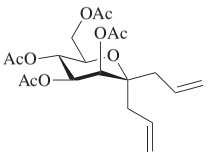
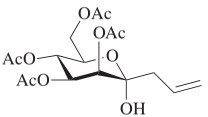
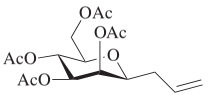
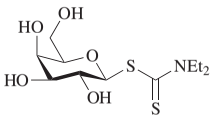
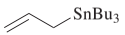
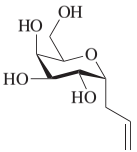
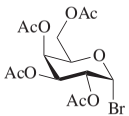
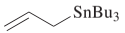
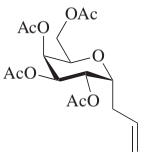
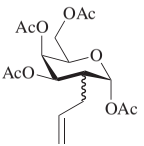
644

x	Temp (°)	Time (h)	**I**	**II**	**III**	**IV**	**V**
2; then 3	80	2; then 2	(7)	(10)	(0)	(0)	(64)
6	35	—	(11)	(37)	(14)	(0)	(5)
2; then 4	35	0.3; then 2.3	(12)	(40)	(2)	(0)	(6)
4; then 2	35	0.3; then 2.3	(17)	(24)	(19)	(0)	(15)
2; then 4	0	—	(10)	(24)	(0)	(8)	(tr)

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

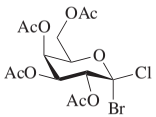
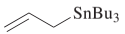
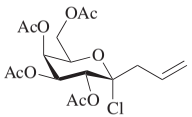
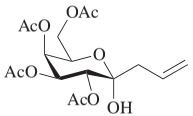
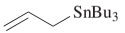
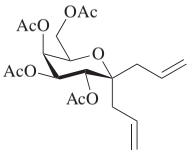
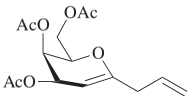
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

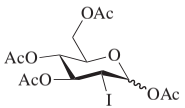
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
	 2 eq	*hν*, AIBN, benzene, 25°, 0.5 h	 (86)	645, 646
			+  (7.5)	
	 10 eq	AIBN, 1,4-dioxane, 75°, 3 h	 (65)[h]	643
	 2 eq	*hν*, AIBN, benzene, 25°, 0.5 h	 (31)	645, 646
			+  (8)	

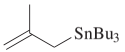
	 4 eq	$h\nu$, AIBN, benzene, 35°, 2.5 h		(34)	644, 647
			+ 	(11)	
			+ 	(1)	
	 10 eq	AIBN, 1,4-dioxane, 75°, 3 h		(67)[h]	643
		Et_3B, O_2, CH_2Cl_2, rt, 18 h	 **I** +  **II**		648

I + **II** (70) **I/II** = 15.7:1

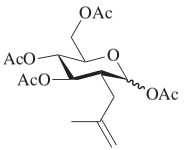
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
	 2 eq	*h*ν, AIBN, benzene, 25°, 0.5 h	 (51)	645, 646
			+  (23)	
	 2; then 4 eq	*h*ν, AIBN, benzene, 35°, 25 min; then 2.8 h	 (24)	644, 647
			+  (7)	



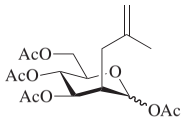


AIBN, benzene, 80°, 3 h



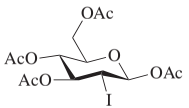
(70)

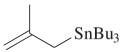
+



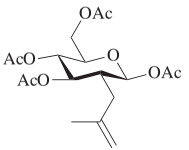
(<5)

649



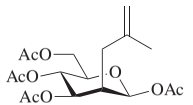


AIBN, benzene, 80°



I

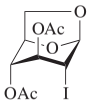
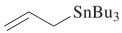
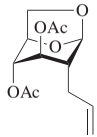
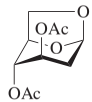
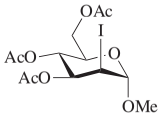
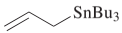
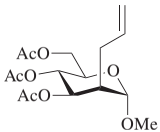
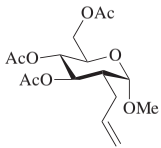
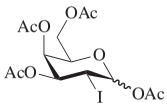
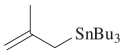
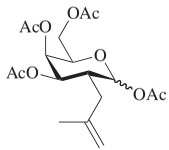
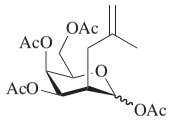
+

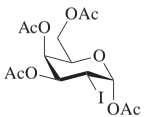


II

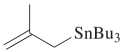
Time (h)	**I**	**II**	**I + II**	**I/II**	
o/n	(—)	(—)	(70)	6:1	650
4	(66)	(13)	(—)	—	651
4	(94)	(—)	(—)	—	652

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

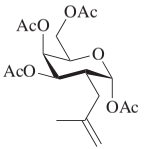
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, benzene, 80°, 3 h	 (65) +  (tr)	653
		AIBN, toluene, 110°, 1.5 h	 **I** +  **II** **I + II** (64) **I/II** = 1.5:1	321, 322, 654
		AIBN, benzene, 80°, 3 h	 (68) +  (<5)	649



α/β = 13:1

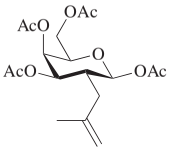


AIBN, benzene, 80°, 80 min



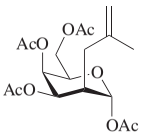
I

+



II

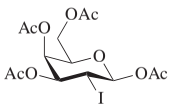
+

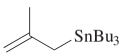


III

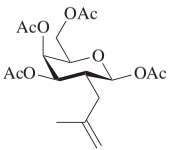
I + II + III (62) **I/II/III** = 4.4:1:8.3

655



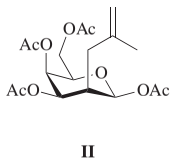


AIBN, benzene, 80°



I

+



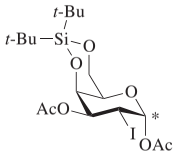
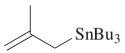
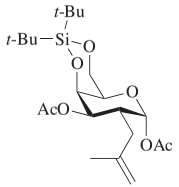
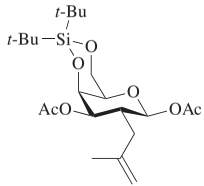
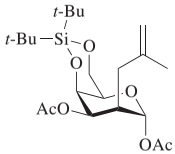
II

Time	**I**	**II**	**I + II**	**I/II**
o/n	(—)	(—)	(65)	6.7:1
4 h	(90)	(—)	(—)	(—)

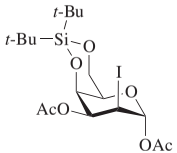
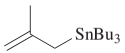
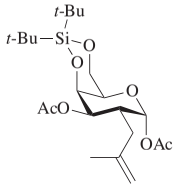
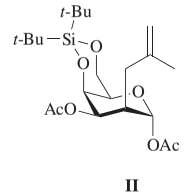
650

652

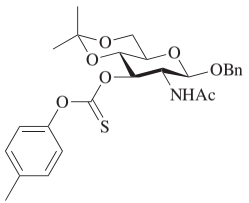
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

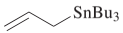
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_6				
		AIBN, benzene, 80°, 80 min	 **I** +  **II** +  **III**	655

*α/β	I + II + III	I/II/III
1.2:1	(97)	1:2.9:0.26
13:1	(89)	10.2:1:2.4

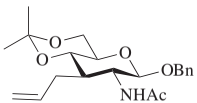
		AIBN, benzene, 80°, 80 min	 **I** +  **II**	655

I + II (89) **I/II** = 4.2:1

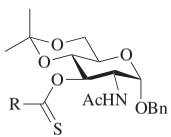


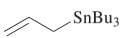


AIBN, toluene, 110°, 6 h



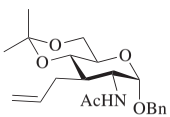
(60) 656





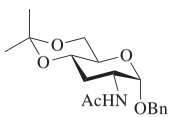
x eq

AIBN, solvent



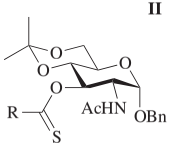
I

+



II

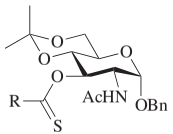
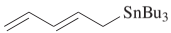
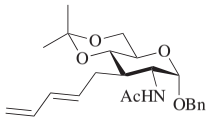
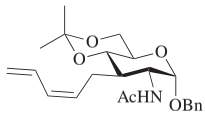
+



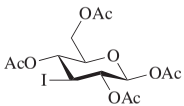
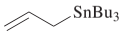
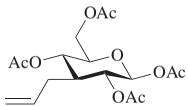
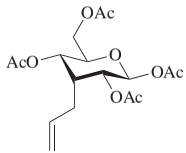
III

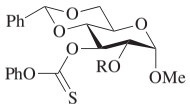
R	*x*	Solvent	Temp (°)	Time (h)	**I**	**II**	**III**	
PhO	5	toluene	110	6	(50)	(—)	(0)	656
PhO	5	toluene	80	6	(60)	(—)	(0)	656
PhO	5	benzene	80	6	(72)	(<10)	(0)	656
4-MeC_6H_4O	5	toluene	110	6	(50)	(—)	(0)	656
4-MeC_6H_4O	5	toluene	80	6	(60)	(—)	(0)	656
4-FC_6H_4O	5	toluene	110	6	(60)	(—)	(0)	656
4-FC_6H_4O	5	toluene	80	6	(30)	(—)	(0)	656
MeS	2.4	toluene	110	12	(45)	(30)	(15)	656–658
MeS	5	toluene	110	—	(60)	(—)	(0)	656

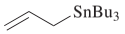
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6 	 (E)/(Z) = 4:1	AIBN, solvent	 **I** +  **II**	656

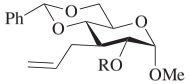
R	Solvent	Temp (°)	Time (h)	**I** + **II**	**I**/**II**
PhO	toluene	95	3	(81)	6.5:1
PhO	toluene	80	—	(70)	9:1
PhO	benzene	80	—	(75)	9:1
4-MeC_6H_4O	toluene	80	—	(50)	9:1
4-FC_6H_4O	toluene	80	—	(70)	9:1
MeS	toluene	80	—	(50)	5:1

		AIBN, benzene, 80°, 8 h	 **I** +  **II** **I** + **II** (71) **I**/**II** = 5.7:1	633

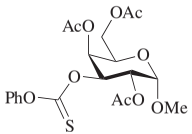


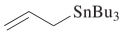


AIBN, toluene, 110°

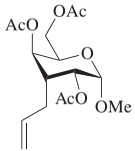


R	Time (h)		
Bn	24	(62)	321, 322, 654
Bz	4	(77)	659





AIBN, benzene, 80°, 1.5 h



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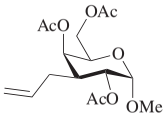
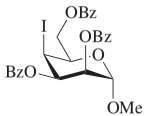
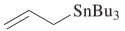


322, 654

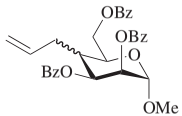
I **II**

I + II (64) **I/II** = 1.7:1



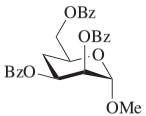


AIBN or DLP,
toluene, 110°, 72 h



(—)

+

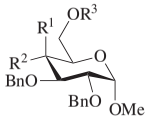
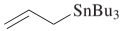
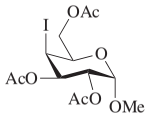
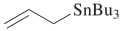
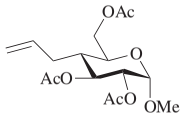
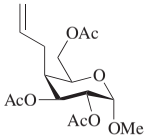
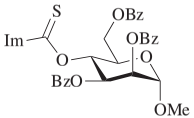
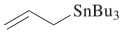
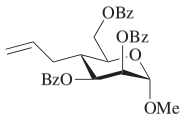


(—)

660

TABLE 1. DIRECT ALLYLATIONS (*Continued*)

C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6 		AIBN, heat or *h*ν, $(Bu_3Sn)_2$	"complex mixtures"	322
R^1 / R^2 / R^3: I / H / Bn; H / ImC(S)O / Bn; H / PhOC(S)O / Bn; H / ImC(S)O / TIPS; H / PhOC(S)O / TIPS				
		AIBN, toluene, 110°, 4 h	 +  **I** **II** **I + II** (75) **I/II** = 6:1	321, 322, 654
		DLP, benzene, 80°, o/n	 (79)	660

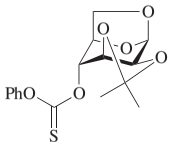
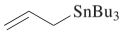
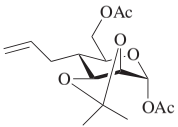
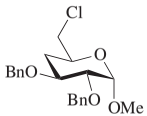
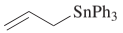
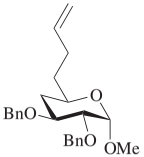
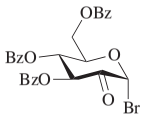
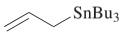
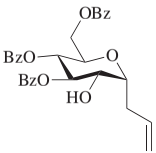
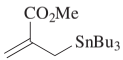
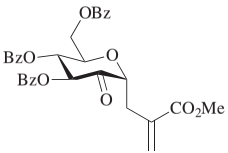
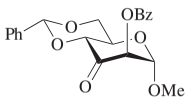
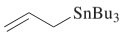
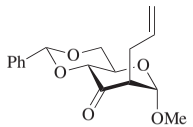
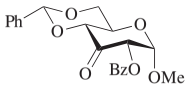
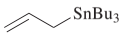
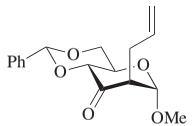
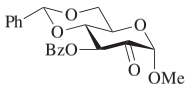
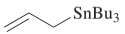
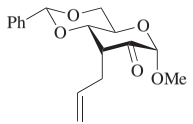
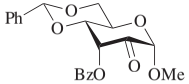
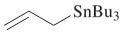
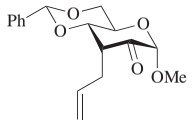
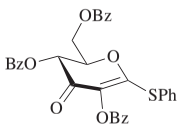
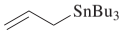
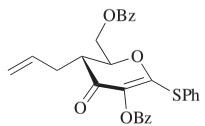
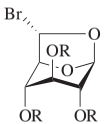
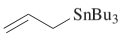
		1. *h*ν, toluene, EtOAc, 75–85°, 6 h 2. Ac_2O, TFA, 0°, 80 min		(71)[b]	630
		Sealed tube, ACCN, toluene, 150°, 1 h		(52)	661
		1. AIBN, benzene, 80°, 7 h 2. BH_3, pyridine, THF, –78°, 0.5 h		(26)[b]	662
		AIBN, benzene, 80°, 8 h		(52)	662

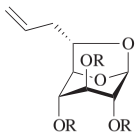
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, benzene, 80°	 (100)	56
		AIBN, benzene, 80°	 (100)	56
		AIBN, benzene, 80°	 (87)	56
		AIBN, benzene, 80°	 (87)	56
		AIBN, benzene, 80°	 (80)	56

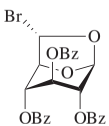


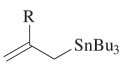


AIBN, solvent

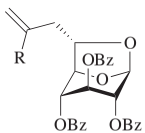


R	Solvent	Temp (°)	Time (h)		
Ac	—	—	—	(—)	663
Bz	toluene	100	36	(47)	134

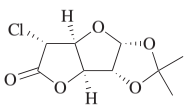


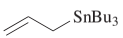


1. AIBN, toluene, 100°, 36 h
2. BzCl, pyridine, CH_2Cl_2

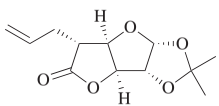


R		
Me	(48)[b]	134
$BnOCH_2$	(46)[b]	



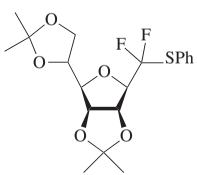


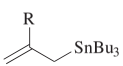
AIBN, benzene, 80°, 10 h



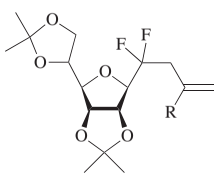
(92) 664, 665

C_7



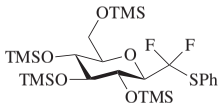
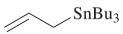
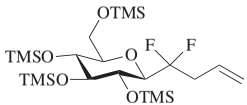
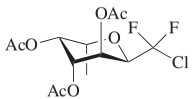
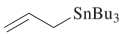
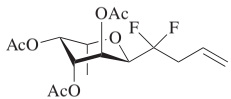
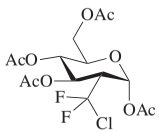
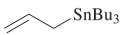
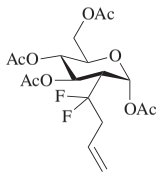
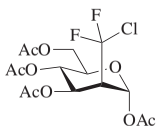
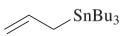
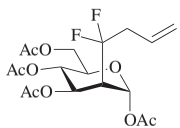
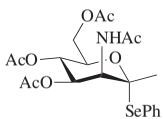
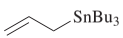
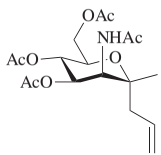


AIBN, toluene

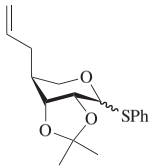


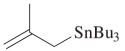
R		
H	(77)	666
EtO_2C	(36)	

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

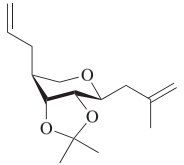
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		AIBN, toluene	 (60)	666
		*h*ν, EtOAc, 2–3 h	 (73)	632
		*h*ν, EtOAc, 2–3 h	 (73)	632
		*h*ν, EtOAc, 2–3 h	 (48)	632
		AIBN, benzene, 80°, 12 h	 (51)	667

C_8

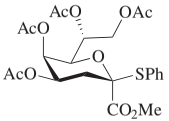


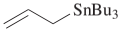


*h*ν, toluene, rt

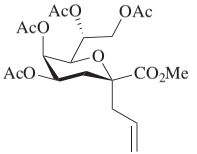


(tr) 423





*h*ν, toluene



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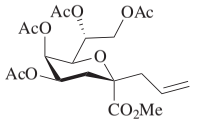
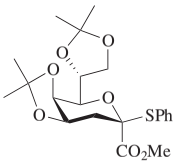
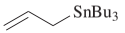


668

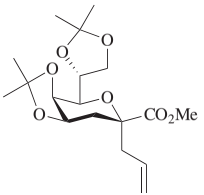
I **II**

I + **II** (30) **I/II** = 1:1





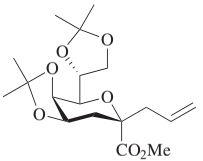
*h*ν, toluene



I + **II** (30) **I/II** = 9:1 668

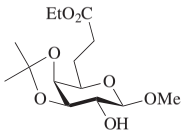
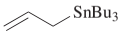
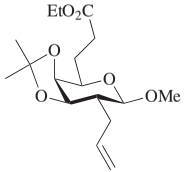
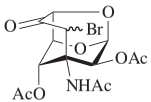
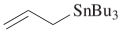
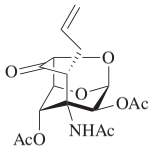
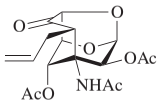
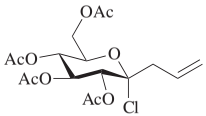
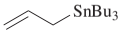
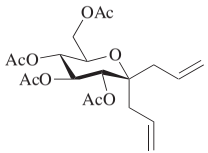
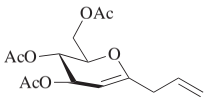
I

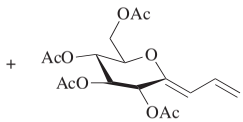
+



II

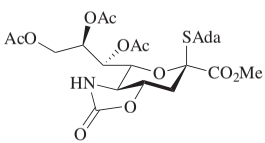
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

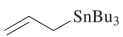
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		1. NHS, PhOC(S)Cl 2. AIBN	 (80)[b]	323, 654
		AIBN, benzene, 80°, 7.5 h	 **I** +  **II** **I** + **II** (68) **I**/**II** = 4:1	669, 670
C_9				
	 *x* eq	Initiator, benzene, 80°	 **I** +  **II**	644



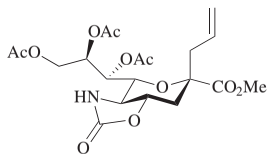
III

x	Initiator	**I**	**II**	**III**
1	AIBN	(0)	(0)	(60)
4	—	(0)	(0)	(63)
4	AIBN	(0)	(80)	(0)



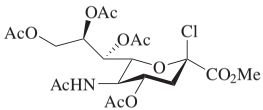
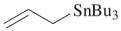
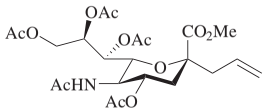
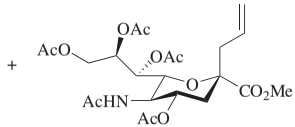


$h\nu$, $(Bu_3Sn)_2$,
toluene, rt, 48 h

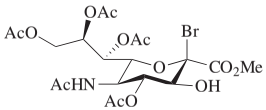


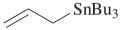
(33) dr = 1:1 671

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

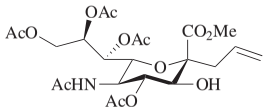
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9 		Conditions, initiator, solvent	 **I** +  **II**	

Conditions	Initiator	Solvent	Temp	Time	**I + II**	**I/II**	
—	AIBN	THF	60°	20 h	(93)	1:1.8	672
*h*ν	$(Bu_3Sn)_2$	toluene	rt	18 h	(65)	1:1	673
*h*ν	$(Bu_3Sn)_2$	toluene	rt	5–7 d	(—)[i]	1:1	674
*h*ν	$(Bu_3Sn)_2$	toluene/THF (1:1)	rt	5–7 d	(—)[i]	1:2	674
*h*ν	$(Bu_3Sn)_2$	THF	rt	5–7 d	(—)[i]	1:2	674



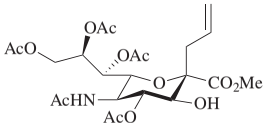


AIBN, THF, 60°, 14 h



I

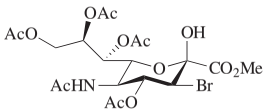
+

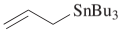


II

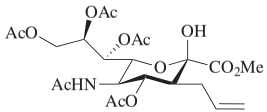
I + **II** (69) **I**/**II** = 3:1

672





hν, THF, rt, 20 h



(34)

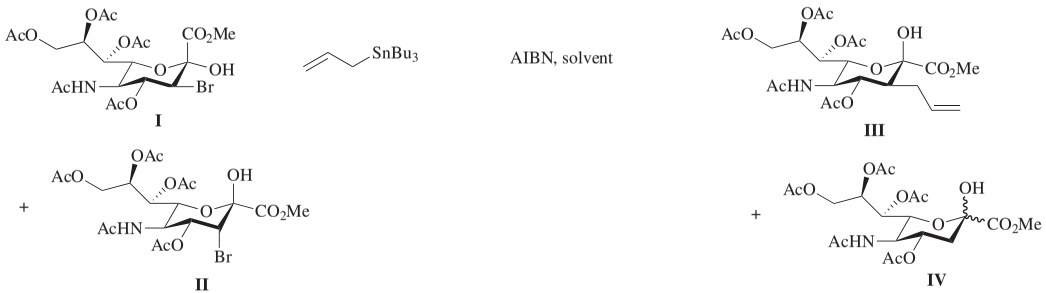
672

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
C. CARBOHYDRATES AND RELATED SUBSTRATES (*Continued*)

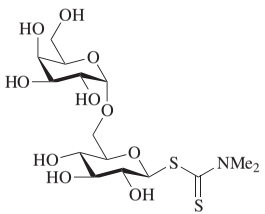
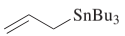
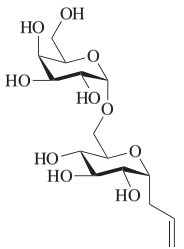
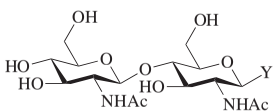
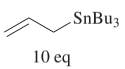
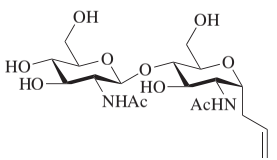
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_9



I/II	Solvent	Temp (°)	Time (h)	**I + II**	**III**	**IV**	
I only	THF	60	—	(—)	(5)	(—)	675
I only	toluene	100	8	(—)	(57)	(—)	676
I only	toluene	100	8	(—)	(62)	(30)	675
II only	toluene	100	8	(—)	(66)	(—)	677
1:2	THF	60	10	(5)	(8)	(80)	677
1:2	DCE	80	10	(18)	(26)	(40)	677
1:2	MeCN	80	10	(15)	(40)	(35)	677
1:2	benzene	80	10	(0)	(79)	(8)	677
1:2	1,4-dioxane	100	8	(10)	(20)	(35)	677
1:2	toluene	100	8	(0)	(68)	(22)	677, 678

C_{12}		 10 eq	AIBN, ethanol, 75°, 3 h		(70)[h]	643
	 Y = SC(S)NMe$_2$	 10 eq	AIBN, ethanol/DMF (1:1), 75°, 9 h		(63)[h]	643

[a] This is the overall yield for the three-step process.

[b] This is the overall yield for the two-step process.

[c] The yield of the first step was 76%.

[d] This is the overall yield for a two-step process involving photolysis followed by acetylation.

[e] This is the overall yield for a three step-process involving photolysis followed by desilylation and acetylation.

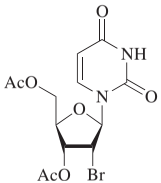
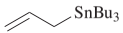
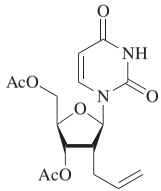
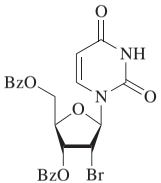
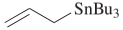
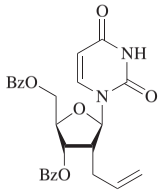
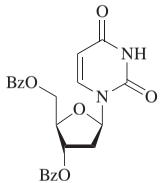
[f] The starting material was the pure α-bromo anomer.

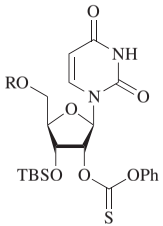
[g] Two equivalents of allyltributylstannane were used.

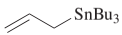
[h] The yield was determined by NMR spectroscopy.

[i] For one set of conditions, unspecified, isolated yields were 17% and 34% for **I** and **II**, respectively.

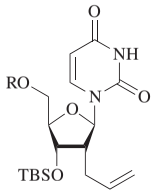
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
D. NUCLEOSIDES AND RELATED SUBSTRATES

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		AIBN, toluene, 110°, 5 d	 (28)	679
		AIBN, benzene, 80°, 2 h	 (54) +  (18)	680





AIBN, toluene, 110°



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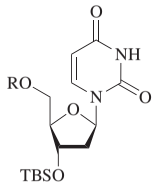
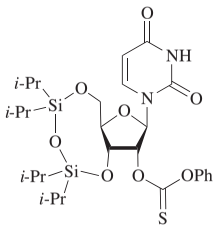
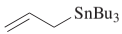


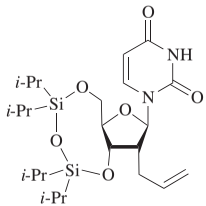
I **II**

R	Time (h)	**I**	**II**	
DMT	10	(70)	(15)	681
TBS	3	(65)	(—)	682



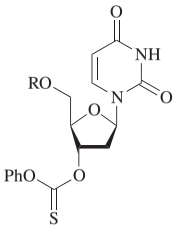
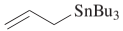
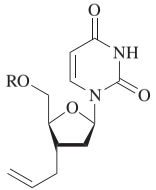
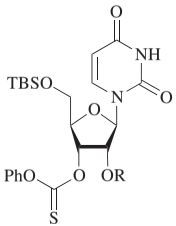
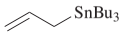
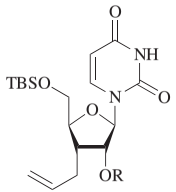


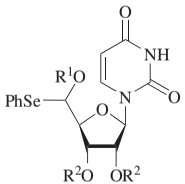
Conditions, initiator, solvent

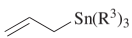


Conditions	Initiator	Solvent	Temp (°)	Time (h)		
*h*ν	none	toluene	—	6	(72)	679
*h*ν	AIBN	benzene	25	9	(84)	683
—	AIBN	toluene	—	—	(72)	684
—	AIBN	—	—	—	(67)	685
—	AIBN	toluene	110	10	(80)	681
—	$(BzO)_2$	toluene	110	8	(68)	681

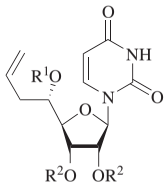
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
D. NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_9				
		AIBN, toluene		
			R / Temp (°) / Time (h): TBS / 80 / 24 (50)	686
			TBDPS / — / — (—)	687
		AIBN, toluene, 80°, 6 h		
			R: Me (70); TBS (75)	688



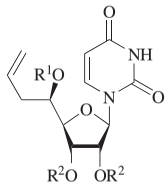


Conditions, initiator, solvent



I

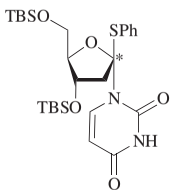
+



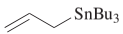
II

689, 690

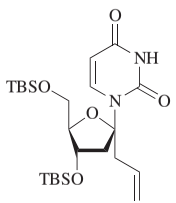
R^1	R^2	R^3	Conditions	Initiator	Solvent	Temp	Time	**I + II**	**I/II**
Ac	Ac	Bu	—	AIBN	benzene	80°	o/n	(36)	1.05:1
Ac	TBS	Bu	*h*ν	$(Bu_3Sn)_2$	benzene	rt	5 h	(56)	6:1
Ac	TBS	Bu	—	Et_3B, O_2	THF	rt	72 h	(0)	—
Ac	TBS	Bu	—	AIBN	benzene	80°	o/n	(84)	3:1
Ac	TBS	Ph	—	AIBN	benzene	80°	o/n	(96)	3.6:1
Bz	TBS	Bu	*h*ν	$(Bu_3Sn)_2$	toluene	0°	4 h	(66)	12.7:1
Bz	TBS	Bu	*h*ν	$(Bu_3Sn)_2$	benzene	rt	4 h	(67)	10.2:1
Bz	TBS	Ph	*h*ν	$(Bu_3Sn)_2$	benzene	rt	4 h	(70)	9.9:1
Bz	TBS	Bu	—	AIBN	benzene	80°	o/n	(70)[a]	6.6:1



*dr = 85:15

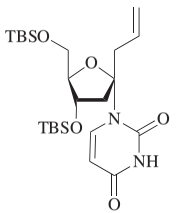


AIBN, benzene, 80°, 2 h



I

+



II

691

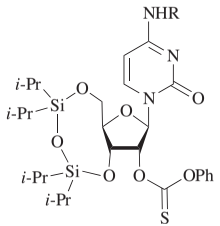
I + II (82)[b] **I/II** = 2.1:1

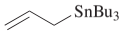
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
D. NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

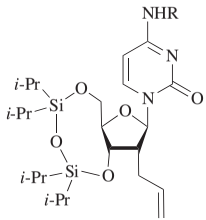
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_9

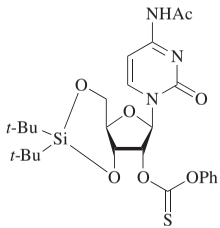


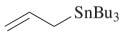


Conditions, initiator, toluene

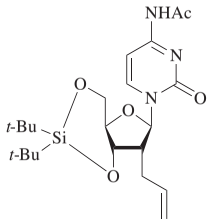


R	Conditions	Initiator	Temp (°)	Time (h)		Refs.
H	*h*ν	none	—	96	(71)	679
Ac	—	AIBN	110	10	(50)	681
Ac	—	$(BzO)_2$	110	8	(15)	681
i-PrC(O)	—	$(BzO)_2$	110	8	(0)	681



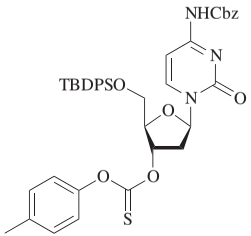


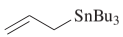
AIBN, solvent



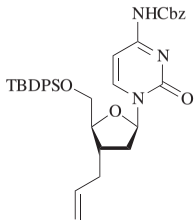
692

Solvent	Temp (°)	Time (h)	
toluene	110	6	(59)
benzene	80	4	(65)



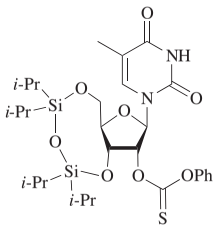


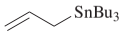
AIBN, benzene, 80°



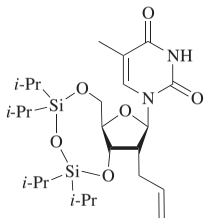
(49) 693

C_{10}





$h\nu$, AIBN, benzene



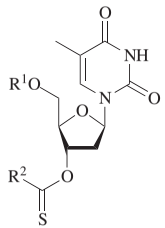
Temp (°)	Time (h)		
25	9	(90)	683
—	—	(94)	694

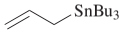
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
D. NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

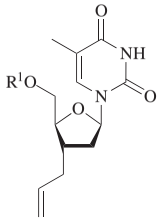
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{10}





Conditions, initiator, solvent



R^1	R^2	Conditions	Initiator	Solvent	Temp (°)	Time (h)		
TBS	PhO	—	AIBN	toluene	80	4–6	(84)	695
TBS	PhO	—	AIBN	toluene	80	48	(74)	686
TBS	PhO	*hν*	none	toluene	—	—	(76)[c]	696
TBS	Im	—	AIBN	toluene	80	—	(<76)	696
TBS	Im	—	AIBN	benzene	80	1	(79)	697
TBS	Im	—	AIBN	benzene	80	6	(50)	698
TBDPS	MeS	—	AIBN	benzene	80	96	(22)	53
TBDPS	PhO	—	AIBN	benzene	80	12	(85)	54
TBDPS	PhO	—	AIBN	benzene	80	70	(32)	53
TBDPS	PhO	—	AIBN	toluene	—	—	(—)	687
TBDPS	4-MeC_6H_4O	—	AIBN	benzene	80	15	(84)	55
TBDPS	4-MeC_6H_4O	—	AIBN	benzene	80	20	(82)	699
TBDPS	4-MeC_6H_4O	—	AIBN	toluene	80	24	(93)	700
TBDPS	C_6F_5O	—	AIBN	benzene	80	2	(90)	53
TBDPS	Im	—	AIBN	benzene	80	7	(77)	53
Tr	PhO	—	AIBN	toluene	80	48	(64)[d]	701

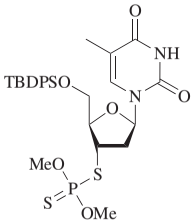
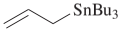
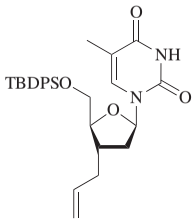
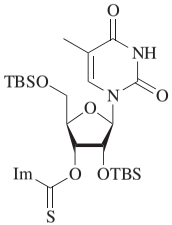
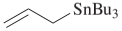
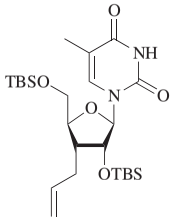
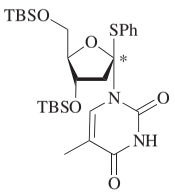
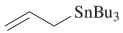
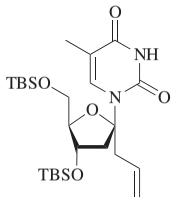
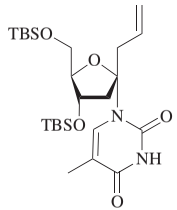
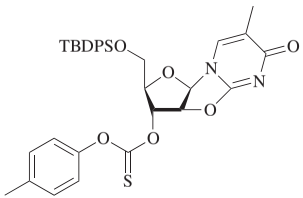
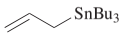
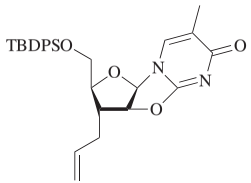
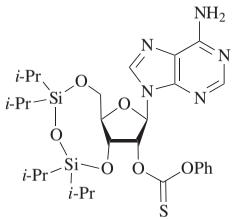
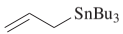
		AIBN, benzene, 80°, 12 h		(72)	702
		*hν*, AIBN, benzene/CH_2Cl_2 (3:2), 3 h		(40)	694

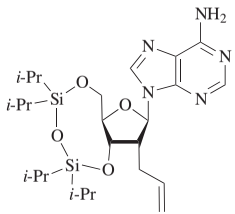
TABLE 1. DIRECT ALLYLATIONS (*Continued*)
D. NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_{10}  *dr = 94:6		AIBN, benzene, 80°, 4 h	 **I** +  **II** **I** + **II** (81) **I**/**II** = 2.1:1	691
		AIBN, benzene, 80°, 20 h	 (79)	324

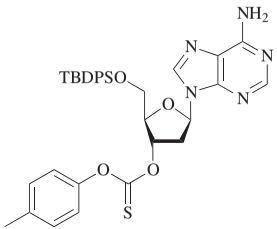


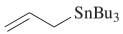


$h\nu$, initiator, toluene

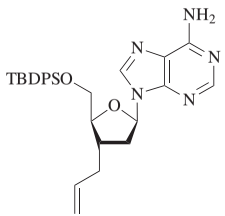


Initiator	Temp	Time (h)		
AIBN	rt	15	(85)	703
none	—	96	(78)	679



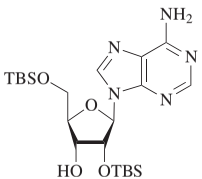
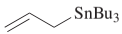
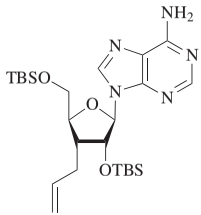
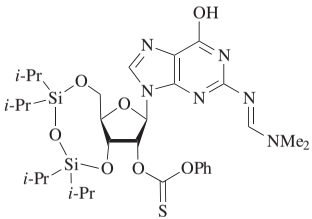
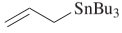
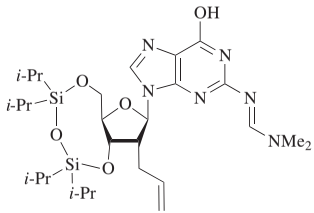
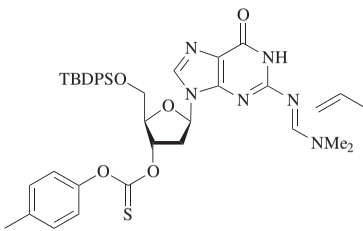
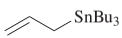
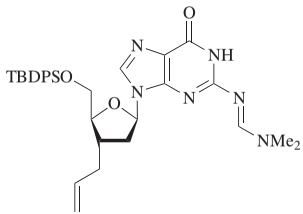


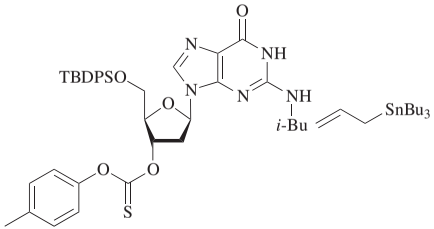
AIBN, benzene, 80°



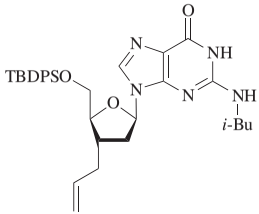
(90) 693

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
D. NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

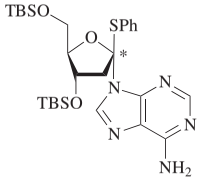
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_{10}				
		1. PhOC(S)Cl, DMAP, CH_2Cl_2 2. AIBN, chlorobenzene, reflux, 1 h	 (71)[e]	704
		$h\nu$, toluene, 96 h	 (71)	679
		AIBN, benzene, 80°	 (57)	693



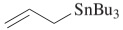
AIBN, toluene, 80°, 24 h



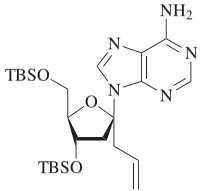
(60) 700



*dr = 76:24



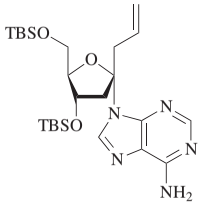
AIBN, benzene, 80°, 24 h



I

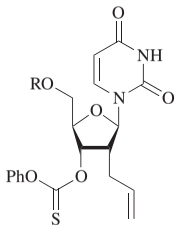
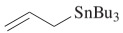
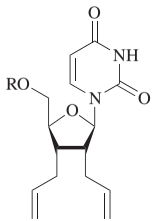
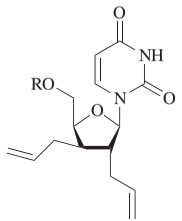
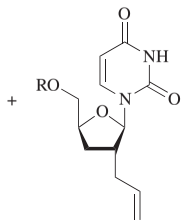
I + **II** (72) **I**/**II** = 2.4:1 691

+



II

TABLE 1. DIRECT ALLYLATIONS (*Continued*)
D. NUCLEOSIDES AND RELATED SUBSTRATES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}  R = TBDPS		AIBN, benzene, 80°, 14 h	 **I** +  **II** **I** + **II** (51) **I/II** = 3:1 +  (6)	705

[a] The reduction product was also isolated in 14% yield.

[b] The starting material was a mixture of epimers with an 85:15 ratio of the SPh group α/β.

[c] The reduction product was also isolated in 10–20% yield.

[d] The reduction product was also isolated in 19% yield.

[e] This is the overall yield for the-two step process.

TABLE 2. MULTICOMPONENT REACTIONS
A. THREE-COMPONENT PROCESSES

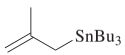
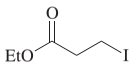
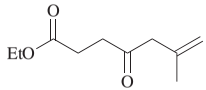
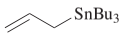
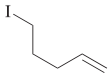
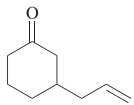
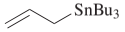
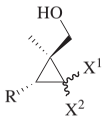
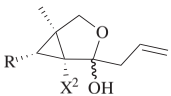
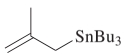
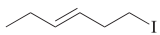
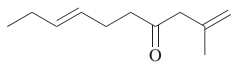
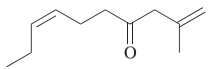
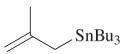
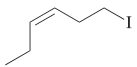
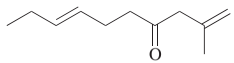
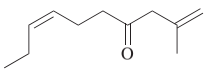
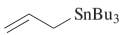
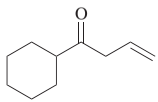
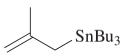
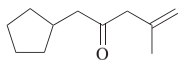
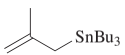
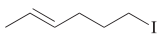
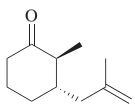
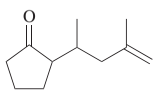
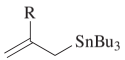
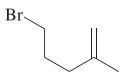
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_1					
CO 10 atm			AIBN, benzene, 80°, 12 h	 (65)	152
5 atm			AIBN, benzene, 80°, 8 h	 (67)	156
40 atm			AIBN, benzene, 80°, 24 h		706
				X^1 / X^2 / R Cl / Cl / H (38) Br / Cl / H (68) Br / Cl / Ph (35)	
10 atm			AIBN, benzene, 80°, 12 h	 **I** +  **II** **I** + **II** (71), **I/II** = 7.3:1	152

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

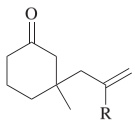
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_1					
CO *x* atm			AIBN, benzene, 80°, 12 h	 **I** +  **II** *x* / **I + II** / **I/II** 10 / (68) / 3:1 30 / (69) / 1.1:1	152 152, 153
10 atm			AIBN, benzene, 80°, 12 h	 (70)	152
10 atm			AIBN, benzene, 80°, 12 h	 (66)	152
10 atm			AIBN, benzene, 80°, 12 h	 +  **I** **II** **I + II** (64), **I/II** = 15.7:1	152

50 atm





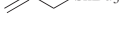
AIBN, benzene, 80°, 12 h



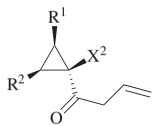
R	
H	(85)
Me	(86)

156

40 atm



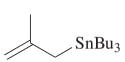
AIBN, benzene, 80°, 24 h



706

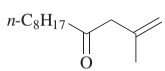
X^1	X^2	R^1	R^2	
Cl	Cl	$-(CH_2)_4-$		(54)
Cl	Cl	Ph	H	(51)
Cl	Cl	n-C_6H_{11}	H	(47)
Cl	Cl	$-(CH_2)_6-$		(48)
Br	Br	$-(CH_2)_4-$		(17)
Br	Cl	$-(CH_2)_4-$		(64)
Br	Cl	Ph	H	(58)
Br	Cl	n-C_6H_{11}	H	(53)
Br	Cl	$-(CH_2)_6-$		(54)

x atm



n-$C_8H_{17}I$

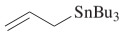
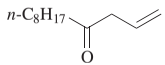
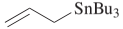
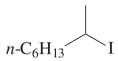
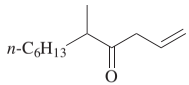
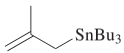
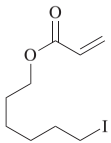
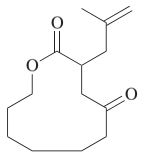
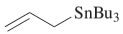
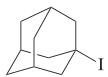
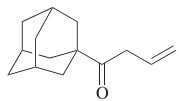
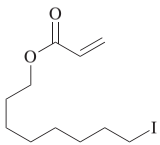
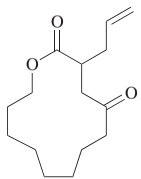
AIBN, benzene, 80°, 12 h



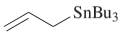
x	
2	(58)
5	(69)
10	(74)

152

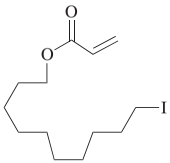
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_1					
CO 10 atm		n-$C_8H_{17}I$	AIBN, benzene, 80°, 12 h	 (73)	152
x atm			AIBN, benzene, 80°, 12 h		152
				x / (%) 10 (45) 30 (62)	
20 atm			AIBN, benzene, 80°, 8 h	 (47)	154
30 atm			AIBN, benzene, 80°, 12 h	 (60)	152
20 atm			AIBN, benzene, 80°, 8 h	 (56)	154

20 atm

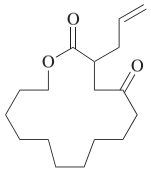


x eq



y M

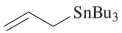
AIBN, benzene, 80°, 8 h

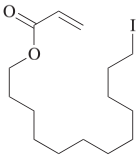


x	*y*	
2	0.100	(12)[a]
2	0.025	(29)[a], (23)
3	0.010	(46)[a]
6	0.005	(64)[a]
10	0.005	(72)[a], (61)

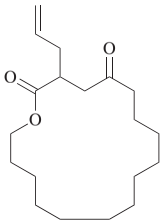
154

20 atm





AIBN, benzene, 80°, 8 h



(70)

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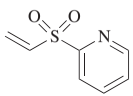
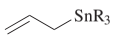
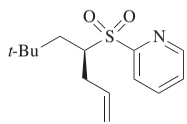
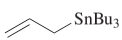
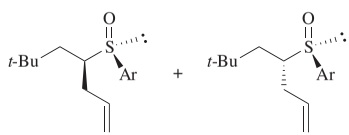
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

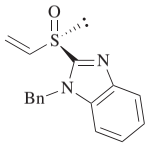
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_2					
		*t*-BuI	Et_3B, $Zn(OTf)_2$, ligand, CH_2Cl_2, –78°		216

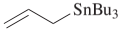
R	Ligand	Time (h)		er
Bu	(*S*,*S*)-**L9a**	2	(36)	73.0:27.0
Bu	(*S*,*S*)-**L9c**	0.5	(60)	55.0:45.0
Bu	(*S*,*S*)-**L9d**	2	(47)	52.0:48.0
Ph	(*S*,*S*)-**L9a**	1.5	(82)	75.0:25.0

		*t*-BuI	Et_3B, Lewis acid, CH_2Cl_2, rt	 **I** + **II**	707

Ar	Lewis Acid	Time (h)	**I + II**	**I/II**
1-methylimidazol-2-yl	none	5	(0)	—
1-methylimidazol-2-yl	$ZnBr_2$	0.5	(60)	2.6:1
1-methylimidazol-2-yl	$Zn(OTf)_2$	1	(98)	19:1
2-C_5H_4N	none	24	(<5)	—
2-C_5H_4N	$ZnBr_2$	1	(38)	1.1:1
2-C_5H_4N	$Zn(OTf)_2$	1	(62)	2.6:1
Ph	none	15	(51)	1:1

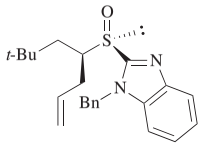
4-MeC_6H_4	none	24	(22)	1:1
2,4,6-$Me_3C_6H_2$	none	24	(0)	—
1-methylbenzimidazol-2-yl	none	24	(<5)	—
1-methylbenzimidazol-2-yl	$ZnBr_2$	0.5	(42)	5.7:1
1-methylbenzimidazol-2-yl	$Zn(OTf)_2$	0.2	(54)	19:1
1-benzylbenzimidazol-2-yl	none	24	(<5)	—
1-benzylbenzimidazol-2-yl	$Zn(OTf)_2$	0.5	(61)	19:1





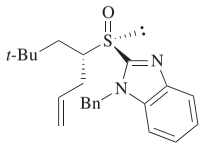
t-BuI

Et_3B, $Zn(OTf)_2$, CH_2Cl_2, –78°



I

+



II

I + **II** (96), **I/II** > 19:1

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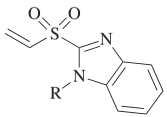
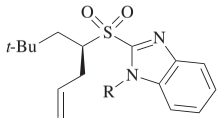
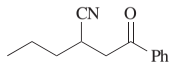
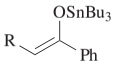
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

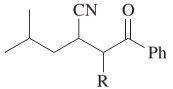
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_2 	"Allyl tin" *x* eq	*t*-BuI	Et_3B, $Zn(OTf)_2$, ligand, CH_2Cl_2, –78°		216

R	Allyl Tin	*x*	Ligand	Time (min)		er
Me	$AllylBu_3Sn$	—	(*S*,*S*)-**L9a**	120	(35)	81.0:19.0
Me	$AllylPh_3Sn$	—	(*S*,*S*)-**L9a**	90	(88)	62.0:38.0
Bn	$AllylBu_3Sn$	—	(*S*,*S*)-**L9a**	120	(35)	90.0:10.0
Bn	$AllylPh_3Sn$	—	(*S*,*S*)-**L9a**	180	(49)	58.0:42.0
Bn	$Allyl_4Sn$	—	(*S*,*S*)-**L9a**	120	(87)	75.5:24.5
Bn	$Allyl_2Bu_2Sn$	—	(*S*,*S*)-**L9a**	120	(74)	75.0:25.0
Bn	$Allyl_2Bu_2Sn$	5	(*S*,*S*)-**L9a**	50	(86)	89.0:11.0
Bn	$Allyl_2Bu_2Sn$	10	(*S*,*S*)-**L9a**	20	(80)	92.0:8.0
Bn	$Allyl_2Bu_2Sn$	—	(*S*,*R*,*R*,*S*)-**L10**	15	(18)	52.0:48.0
Bn	$AllylBu_2SnCl$	—	(*S*,*S*)-**L9a**	180	(85)	58.5:41.5

C_3			AIBN, benzene, 80°, 4 h		(88)	142

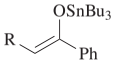


AIBN, benzene, 80°, 4 h



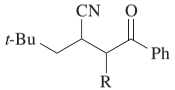
R		dr
H	(90)	—
Me	(87)	1.04:1

142



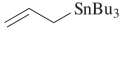
t-BuI

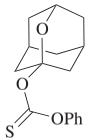
AIBN, benzene, 80°, 4 h



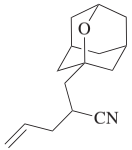
R		dr
H	(85)	—
Me	(92)	1.3:1

142





ACCN, benzene, 80°, 8 h



(43)

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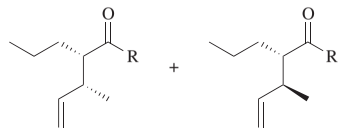
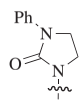
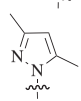
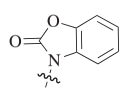
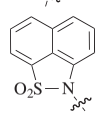
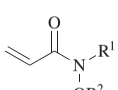
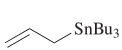
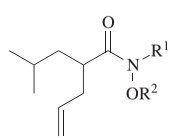
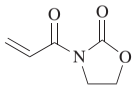
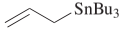
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_3					
			Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (2:1), –78°, 3 h	 **I** + **II**	26
				R / **I + II** / **I/II**	
				(78) 3.7:1	
				 (56) 3.7:1	
				 (79) 1.5:1	
				 (51) 1.4:1	
				 (30) 2.3:1	
			Et_3B, $Zn(OTf)_2$, (*R*,*S*,*S*,*R*)-**L10**, CH_2Cl_2, –78°, 3–10 h		708

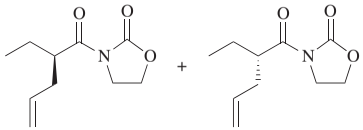
R^1	R^2		er
Me	Bn	(57)	65.0:35.0
Me	2-naphthylmethyl	(5)	50.0:50.0
2-naphthylmethyl	Me	(40)	53.5:46.5





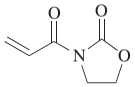
MeI

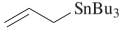
Et_3B, O_2,
$Zn(OTf)_2$ (x eq),
(R,R)-**L9a** (x eq),
CH_2Cl_2, pentane, –78°



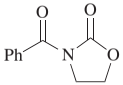
I **II** 210

x	**I + II**	**I/II**
0.2	(60–90)[b]	1:1.6
0.6	(60–90)[b]	1:3.5
1	(60–90)[b]	1:4.1
2	(60–90)[b]	1:5.1



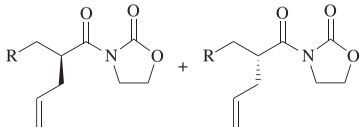


RI



Addend A

Et_3B, O_2,
$Y(OTf)_3$ (0.3 eq),
(S)-**L12a** (0.3 eq),
addend, CH_2Cl_2, –78°



I **II** 212

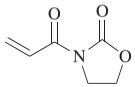
R	Addend	**I + II**	**I/II**
$ClCH_2$	—	(56)	2.4:1
n-Pr	—	(57)	4:1
i-Pr	—	(50)	3.5:1
i-Pr	A	(67)	5.3:1
n-Bu	—	(41)	2.2:1

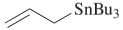
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.

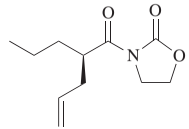
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_3



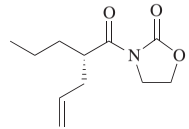


Et_3B, O_2,
Lewis acid (*x* eq),
ligand (*x* eq),
addend, solvent, –78°

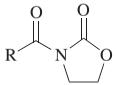


I

+



II



Addend	R
A	Ph
B	Me

Lewis Acid	*x*	Ligand	Addend	Solvent	**I + II**	**I/II**	
$Zn(OTf)_2$	0.2	(*R*,*R*)-**L9a**	—	CH_2Cl_2, pentane	(60–90)[b]	1:1.9	210
$Zn(OTf)_2$	0.6	(*R*,*R*)-**L9a**	—	CH_2Cl_2, pentane	(60–90)[b]	1:4.3	210
$Zn(OTf)_2$	1	(*R*,*R*)-**L9a**	—	CH_2Cl_2, pentane	(60–90)[b]	1:5.5	210
$Zn(OTf)_2$	2	(*R*,*R*)-**L9a**	—	CH_2Cl_2, pentane	(60–90)[b]	1:7	210
$Y(OTf)_3$	0.3	(*S*,*S*)-**L13a**	A	CH_2Cl_2	(72)	1.4:1	212
$Y(OTf)_3$	0.3	(*S*,*S*)-**L13a**	4 Å MS	CH_2Cl_2	(48)	1.2:1	212
$Y(OTf)_3$	0.3	(*S*,*S*)-**L13a**	—	CH_2Cl_2	(46)	1:1	212
$Yb(OTf)_3$	0.3	(*S*,*S*)-**L13a**	—	CH_2Cl_2	(48)	1.2:1	212
$Y(NTf_2)_3$	0.3	(*S*,*S*)-**L13a**	—	CH_2Cl_2	(30)	1.1:1	212
$Sm(OTf)_3$	0.3	(*S*,*S*)-**L13a**	—	CH_2Cl_2	(60)	1.5:1	212
$Y(OTf)_3$	0.3	(*S*,*S*)-**L13b**	—	CH_2Cl_2	(41)	1.1:1	212
$Yb(OTf)_3$	0.3	(*S*,*S*)-**L13b**	—	CH_2Cl_2	(14)	1.1:1	212
$Sm(OTf)_3$	0.3	(*S*,*S*)-**L13b**	—	CH_2Cl_2	(34)	1.1:1	212
$Y(OTf)_3$	0.3	(*S*,*R*,*R*,*S*)-**L14**	—	CH_2Cl_2	(78)	1.6:1	212
$Yb(OTf)_3$	0.3	(*S*,*R*,*R*,*S*)-**L14**	—	CH_2Cl_2	(62)	1.1:1	212

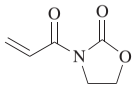
$Sm(OTf)_3$	0.3	(*S*,*R*,*R*,*S*)-**L14**	—	CH_2Cl_2	(73)	1.6:1	212
$La(OTf)_3$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(56)	1:1	212
$Ce(OTf)_4$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(53)	1:1	212
$Sm(OTf)_3$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(35)	3.2:1	212
$Er(OTf)_3$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(35)	2.2:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(61)	5.7:1	212
$Y(OTf)_3$	1	(*S*)-**L12a**	—	CH_2Cl_2	(46)	4.9:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12a**	4 Å MS	CH_2Cl_2	(50)	1.5:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12a**	A	CH_2Cl_2	(71)	9:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12a**	B	CH_2Cl_2	(69)	8.5:1	212
$Yb(OTf)_3$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(45)	3:1	212
$Y(NTf_2)_3$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(22)	1.2:1	212
$Sc(OTf)_3$	0.3	(*S*)-**L12a**	—	CH_2Cl_2	(10)	1.2:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12b**	—	CH_2Cl_2	(59)	5.1:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12c**	—	CH_2Cl_2	(73)	3.3:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12d**	—	CH_2Cl_2	(63)	1.9:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12e**	—	CH_2Cl_2	(59)	1.1:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12f**	—	CH_2Cl_2	(52)	6.4:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12g**	—	CH_2Cl_2	(60)	6.4:1	212

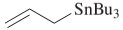
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

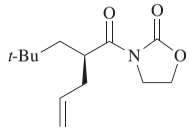
C_3



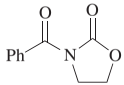


t-BuI

Et_3B, O_2,
Lewis acid (*x* eq),
ligand (*y* eq),
addend, solvent, –78°

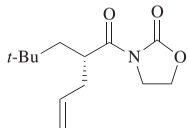


I



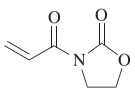
Addend A

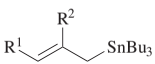
+

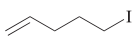


II

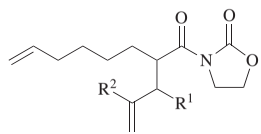
Lewis Acid	*x*	Ligand	*y*	Addend	Solvent	**I + II**	**I/II**	
$Y(OTf)_3$	0.3	(*S*)-**L12a**	0.3	—	CH_2Cl_2	(40)	1.6:1	212
$Y(OTf)_3$	0.3	(*S*)-**L12a**	0.3	A	CH_2Cl_2	(46)	2.4:1	212
$Y(OTf)_3$	1	(*S*)-**L12a**	1	—	CH_2Cl_2	(48)	1.6:1	212
$Zn(OTf)_2$	0.2	(*R*,*R*)-**L9a**	0.2	—	CH_2Cl_2, pentane	(60–90)[b]	1:3.3	210
$Zn(OTf)_2$	0.6	(*R*,*R*)-**L9a**	0.6	—	CH_2Cl_2, pentane	(60–90)[b]	1:11.5	210
$Zn(OTf)_2$	1	(*R*,*R*)-**L9a**	1	—	CH_2Cl_2, pentane	(60–90)[b]	1:15	210
$Zn(OTf)_2$	1	(*R*,*R*)-**L9a**	1.2	—	CH_2Cl_2, pentane	(92)	1:19	209
$Zn(OTf)_2$	1	(*S*,*S*)-**L9a**	1.2	—	CH_2Cl_2, pentane	(78)	15.7:1	209
$Zn(OTf)_2$	2	(*R*,*R*)-**L9a**	2	—	CH_2Cl_2, pentane	(60–90)[b]	1:19	210
$Zn(OTf)_2$	2	(*R*,*R*)-**L9a**	2.1	—	ether	(55)	1:15.7	209



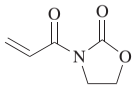


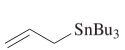


Et_3B, O_2, $Yb(OTf)_3$,
CH_2Cl_2/THF (2:1),
–78°, 4 h

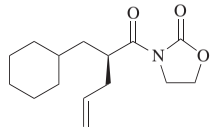


709



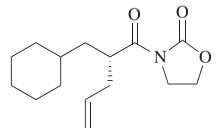


Et_3B, O_2,
Lewis acid (x eq),
ligand (y eq),
solvent, –78°



I

+

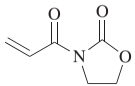
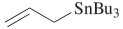
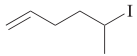
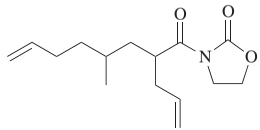
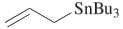
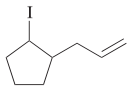
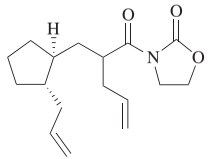
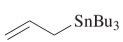
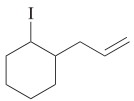
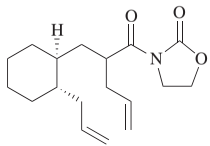


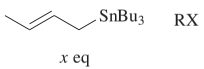
II

R^1	R^2		dr
H	H	(49)	—
H	Me	(47)	—
Me	H	(50)	2:1

Lewis Acid	x	Ligand	y	Solvent	**I + II**	**I/II**	
$Zn(OTf)_2$	1	(S,S)-**L9a**	1	CH_2Cl_2	(62)	3:1	209
$Zn(OTf)_2$	1	(S,S)-**L9a**	1	ether	(90)	4.6:1	209
$Zn(OTf)_2$	2	(S,S)-**L9a**	2	ether	(61)	9:1	209
$Zn(OTf)_2$	1	(R,R)-**L9a**	1.2	CH_2Cl_2, pentane	(62)	1:5.3	209
$Zn(OTf)_2$	2	(R,R)-**L9a**	2.4	CH_2Cl_2, pentane	(92)	1:6.1	209
$Zn(OTf)_2$	1	(S,S)-**L9b**	1	CH_2Cl_2	(60)	1:1	209
$Zn(OTf)_2$	1	(S,S)-**L15**	1	CH_2Cl_2	(63)	2:1	209
$Zn(OTf)_2$	0.2	(R,R)-**L9a**	0.2	CH_2Cl_2, pentane	(60–90)[b]	1:2	210
$Zn(OTf)_2$	0.6	(R,R)-**L9a**	0.6	CH_2Cl_2, pentane	(60–90)[b]	1:7.3	210
$Zn(OTf)_2$	1	(R,R)-**L9a**	1	CH_2Cl_2, pentane	(60–90)[b]	1:8.1	210
$Zn(OTf)_2$	2	(R,R)-**L9a**	2	CH_2Cl_2, pentane	(60–90)[b]	1:9	210
$Y(OTf)_3$	0.3	(S)-**L12a**	0.3	CH_2Cl_2	(53)	1.9:1	212

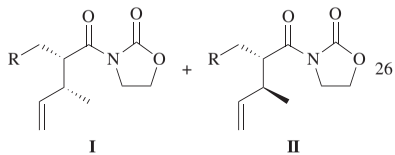
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_3					
			Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (2:1), –78°, 4 h	 (51) dr = 1:1	709
			Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (2:1), –78°, 4 h	 (19) dr = 1:1	709
			Et_3B, O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (2:1), –78°, 4 h	 (14) dr = 1:1	709



RX

Et_3B, O_2,
Lewis acid, (y eq),
CH_2Cl_2/THF (2:1),
–78°, 3 h



26

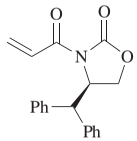
x	R	X	Lewis Acid	y	**I + II**	**I/II**
2	Et	I	$Yb(OTf)_3$	2	(55)	3.6:1
3	Et	I	none	—	(<5)	—
5	$MeOCH_2$	Br	$Yb(OTf)_3$	1	(48)	2.0:1
5	Et	I	$Yb(OTf)_3$	1	(68)	3.5:1
5	Et	I	$Yb(OTf)_3$	0.3	(70)	3.5:1
5	Et	I	$Zn(OTf)_2$	1	(19)	2.3:1
5	Et	I	$Mg(ClO_4)_2$	1	(22)	3.2:1
5	Et	I	$Hf(OTf)_4$	1	(45)	3.4:1
5	*i*-Pr	I	$Yb(OTf)_3$	1	(63)	3.0:1
5	Bu	I	$Yb(OTf)_3$	1	(58)	3.4:1
5	*i*-Bu	I	$Yb(OTf)_3$	1	(63)	2.6:1
5	*t*-Bu	I	$Yb(OTf)_3$	1	(75)	5.4:1
5	*c*-C_6H_{11}	I	$Yb(OTf)_3$	1	(62)	3.5:1
5	1-adamantyl	I	$Yb(OTf)_3$	1	(69)	5.6:1

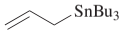
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

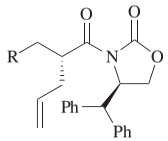
C_3





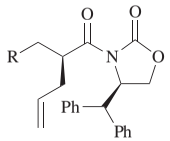
RX

Et_3B, O_2,
Lewis acid (x eq),
CH_2Cl_2, –78°, 2 h



I

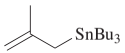
+



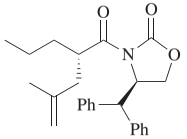
II

204

R	X	Lewis Acid	x	**I + II**	**I/II**
Me	I	$MgBr_2$	2	(82)	>100:1
$MeOCH_2$	Br	$MgBr_2$	2	(50)	1.8:1
$MeOCH_2$	Br	$Yb(OTf)_3$	1	(70)	58:1
Et	I	none	—	(90)	1:1
Et	I	$BF_3{\bullet}Et_2O$	2	(90)	1:1.8
Et	I	ZnI_2	2	(85)	2.2:1
Et	I	$ZnCl_2$	2	(90)	4.1:1
Et	I	$Zn(OTf)_2$	2	(85)	1.3:1
Et	I	$MgBr_2{\bullet}Et_2O$	2	(93)	>100:1
Et	I	$Yb(OTf)_3$	1	(90)	>100:1
Et	I	$Sm(OTf)_3$	1	(90)	>100:1
Et	I	$La(OTf)_3$	1	(71)	>100:1
Ac	Br	$MgBr_2$	2	(55)	50:1
i-Pr	I	$MgBr_2$	2	(85)	>100:1
t-Bu	I	$MgBr_2$	2	(94)	>100:1
c-C_6H_{11}	I	$MgBr_2$	2	(93)	>100:1
Bz	Br	$MgBr_2$	2	(90)	50:1

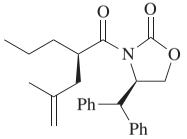


Et_3B, O_2, $Yb(OTf)_3$,
CH_2Cl_2/THF (2:1), –78°



I

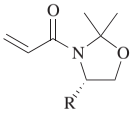
+



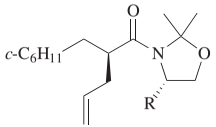
II

I + II (—) **I/II** > 20:1

131

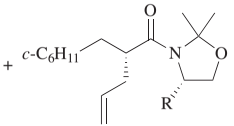


AIBN, benzene,
80°, 9 h



I

+



II

R	**I + II**	**I/II**
i-Pr	(—)	4:1
t-Bu	(33)	25:1

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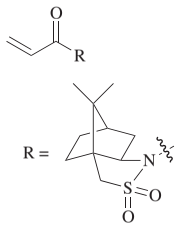
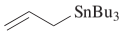
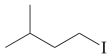
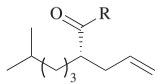
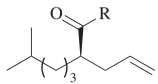
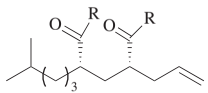
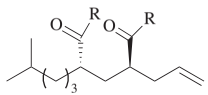
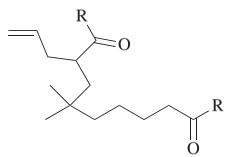
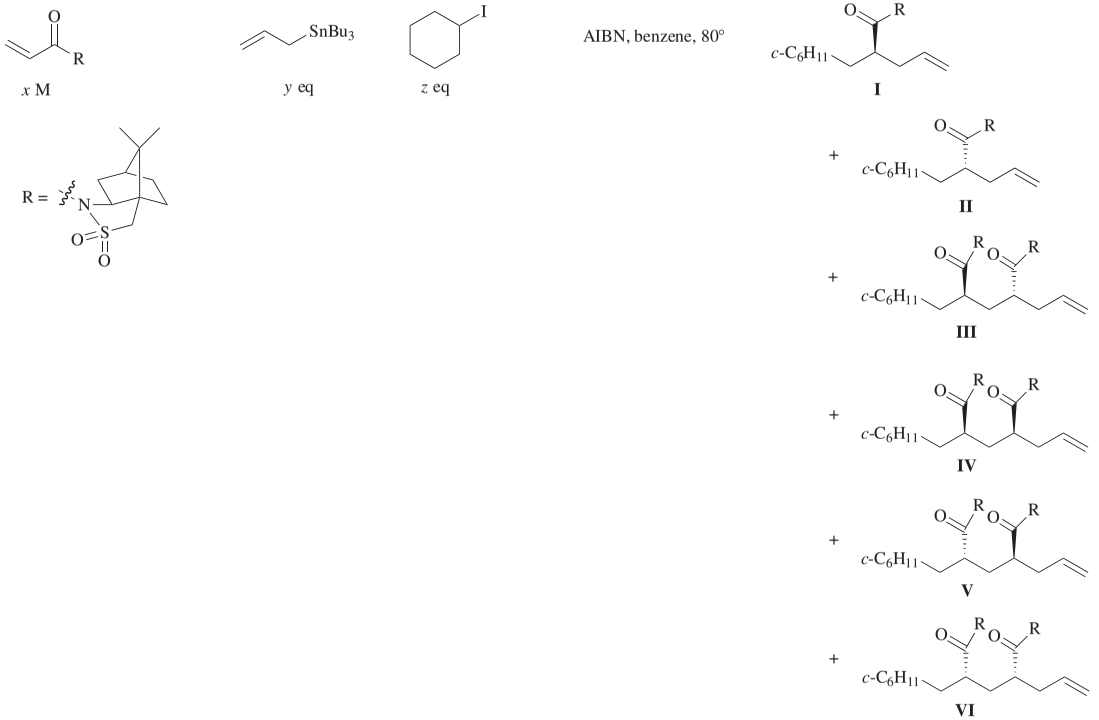
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_3					
			AIBN, benzene 80°, 9 h	 **I** +  **II**	710
				+  **III**	
				+  **IV**	
				I + **II** (17) **I/II** = 7:1; **III** + **IV** (18) **III/IV** = 1.2:1	
				+ 	(11)



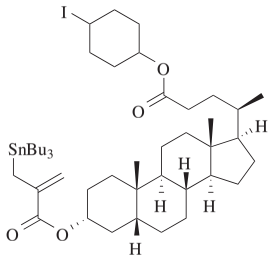
x	y	z	Time (h)	**I + II**	**I/II**	**III + IV + V + VI**	**III/IV/V/VI**	
0.29	1.9	0.53	7	(59)	—	(18)	36:46:10:8	146, 200
0.50	2.5	1	6	(81)	11.5:1	(13)	—	711

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

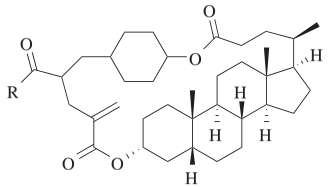
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.

Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_3



Conditions, benzene, rt



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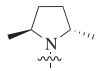
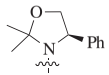
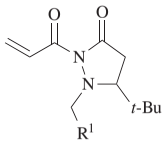
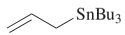
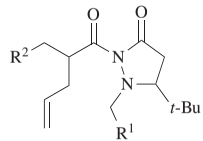
R	Conditions	Time (h)	
	Et_3B/O_2	4	(51)
	*h*v, $(BuSn)_2$	3	(51)
	*h*v, $(BuSn)_2$	3	(29)
	*h*v, $(BuSn)_2$	3	(31)





R^2I

Et_3B, O_2,
Lewis acid (x eq),
solvent, –78°, 3–5 h



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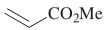
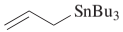
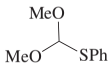
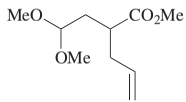
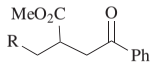
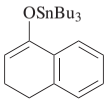
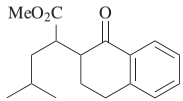
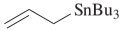
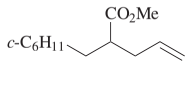
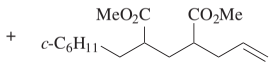
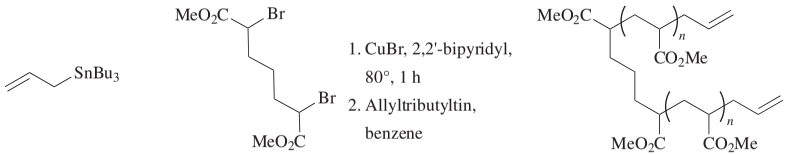
R^1	R^2	Lewis Acid	x	Solvent		dr
Ph	Me	$Y(OTf)_3$	2	CH_2Cl_2, THF	(81)	7.3:1
Ph	Et	$Y(OTf)_3$	2	CH_2Cl_2, THF	(84)	6.7:1
Ph	*i*-Pr	$Y(OTf)_3$	2	CH_2Cl_2, THF	(89)	6.7:1
Ph	*t*-Bu	none	—	CH_2Cl_2	(20)	1.3:1
Ph	*t*-Bu	$Mg(ClO_4)_2$	2	CH_2Cl_2	(84)	4.0:1
Ph	*t*-Bu	$Mg(ClO_4)_2$	1	CH_2Cl_2	(40)	2.6:1
Ph	*t*-Bu	$Mg(ClO_4)_2$	0.5	CH_2Cl_2	(26)	2.3:1
Ph	*t*-Bu	$Mg(NTf)_2$	2	CH_2Cl_2	(75)	1.8:1
Ph	*t*-Bu	$Mg(OTf)_2$	2	CH_2Cl_2	(38)	1.3:1
Ph	*t*-Bu	$MgBr_2{\bullet}OEt_2$	2	CH_2Cl_2	(72)	1.9:1
Ph	*t*-Bu	$Cu(OTf)_2$	2	CH_2Cl_2	(21)	1.3:1
Ph	*t*-Bu	$Zn(OTf)_2$	2	CH_2Cl_2	(32)	2.2:1
Ph	*t*-Bu	$Sc(OTf)_3$	2	CH_2Cl_2, THF	(50)	2.6:1
Ph	*t*-Bu	$Yb(OTf)_3$	2	CH_2Cl_2, THF	(56)	4.0:1
Ph	*t*-Bu	$Yb(OTf)_3$/4 Å MS	2	CH_2Cl_2, THF	(63)	15.7:1
Ph	*t*-Bu	$Y(OTf)_3$	2	CH_2Cl_2, THF	(84)	15.7:1
Ph	*t*-Bu	$Y(OTf)_3$/4 Å MS	2	CH_2Cl_2, THF	(72)	15.7:1
Ph	*t*-Bu	$Sm(OTf)_3$	2	CH_2Cl_2, THF	(65)	13.3:1
Ph	*t*-Bu	$Ni(ClO_4)_2$	2	CH_2Cl_2	(39)	1.3:1
Ph	*c*-C_6H_{11}	$Y(OTf)_3$	2	CH_2Cl_2, THF	(87)	7.3:1
1-naphthyl	*t*-Bu	$Y(OTf)_3$	2	CH_2Cl_2, THF	(10)	4.6:1
2-naphthyl	*t*-Bu	$Y(OTf)_3$	2	CH_2Cl_2, THF	(31)	10.1:1
1-mesityl	*t*-Bu	$Y(OTf)_3$	2	CH_2Cl_2, THF	(32)	4.9:1

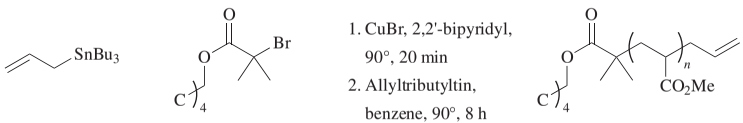
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_3					
			*h*ν, $(Bu_3Sn)_2$, benzene, rt, 12 h	 (42)	143
		RI	AIBN, benzene, 80°, 4 h	 R: Et (68); *i*-Pr (78); *t*-Bu (73)	142
			AIBN, benzene, 80°, 4 h	 (91) dr = 64:36	142
			AIBN, benzene, 80°, 6 h	 (58) +  (19) dr = 1:1	146



(—) $n \approx 5–30$

150

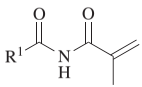
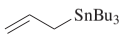
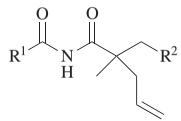
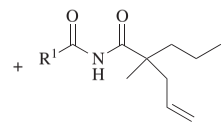


(—) $n \approx 5–20$

"4-armed star telechelics"

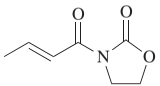
150

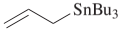
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_4					
		R^2I	Et_3B/O_2, Lewis acid (x eq), ligand, CH_2Cl_2, –78°, 12 h	 **I** +  **II**	214

R^1	R^2	Lewis Acid	x	Ligand	**I**	er **I**	**II**
i-Pr	*i*-Pr	$Yb(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(46)	55.0:45.0	(—)
t-Bu	Et	$Yb(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(55)	57.5:42.5	(—)
t-Bu	Et	$Y(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(64)	61.0:39.0	(—)
t-Bu	*i*-Pr	$Yb(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(64)	85.0:15.0	(—)
t-Bu	*i*-Pr	$Yb(OTf)_3$	0.5	(*S*,*R*,*R*,*S*)-**L14**	(62)	81.5:18.5	(—)
t-Bu	*i*-Pr	$Yb(OTf)_3$	0.3	(*S*,*R*,*R*,*S*)-**L14**	(59)	76.0:24.0	(—)
t-Bu	*i*-Pr	$Y(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(72)	78.5:21.5	(—)
t-Bu	*i*-Pr	$Sm(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(52)	56.0:44.0	(—)
t-Bu	*i*-Pr	$Sc(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(37)	62.5:37.5	(—)
t-Bu	*i*-Pr	$Yb(OTf)_3$	1	(*S*,*S*)-**L13a**	(63)	59.5:40.5	(—)
t-Bu	*i*-Pr	$Yb(OTf)_3$	1	(*S*,*S*)-**L13b**	(34)	50.5:49.5	(—)
t-Bu	*i*-Pr	$Yb(OTf)_3$	1	(*S*,*S*)-**L13c**	(51)	50.5:49.5	(—)
t-Bu	*i*-Pr	$Yb(OTf)_3$	1	(*R*,*S*,*S*,*R*)-**L16**	(55)	59.5:40.5	(17)
t-Bu	*i*-Pr	$Y(OTf)_3$	1	(*R*,*S*,*S*,*R*)-**L16**	(54)	63.5:36.5	(17)
t-Bu	*i*-Pr	$Yb(OTf)_3$	1	(*S*,*S*)-**L17**	(50)	69.5:30.5	(—)

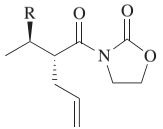
t-Bu	*i*-Pr	$Mg(ClO_4)_2$	1	(*S*,*S*)-**L17**	(84)	54.0:46.0	(—)
t-Bu	*i*-Pr	$Ni(ClO_4)_2$	1	(*S*,*S*)-**L17**	(35)	54.0:46.0	(—)
t-Bu	*i*-Pr	MgI_2	1	(*S*,*R*,*R*,*S*)-**L10**	(22)	70.5:29.5	(16)
t-Bu	*i*-Pr	$Mg(ClO_4)_2$	1	(*S*,*R*,*R*,*S*)-**L10**	(32)	55.0:45.0	(14)
t-Bu	*i*-Pr	$Ni(ClO_4)_2$	1	(*S*,*R*,*R*,*S*)-**L10**	(36)	70.5:29.5	(4)
t-Bu	*n*-Bu	$Yb(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(38)	59.0:41.0	(—)
t-Bu	*n*-Bu	$Y(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(55)	60.0:40.0	(—)
t-Bu	*t*-Bu	$Yb(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(46)	82.0:18.0	(—)
t-Bu	*t*-Bu	$Y(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(64)	86.5:13.5	(—)
t-Bu	*c*-C_5H_9	$Y(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(58)	62.0:38.0	(—)
t-Bu	*c*-C_6H_{11}	$Y(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(63)	82.0:18.0	(—)
Ph	*i*-Pr	$Yb(OTf)_3$	1	(*S*,*R*,*R*,*S*)-**L14**	(42)	54.5:45.5	(—)





RI

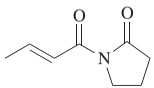
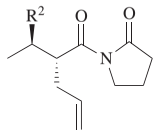
Et_3B/O_2, $Mg(ClO_4)_2$,
(*S*,*R*,*R*,*S*)-**L10**,
CH_2Cl_2, –78°



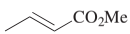
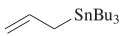
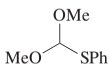
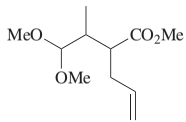
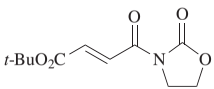
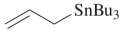
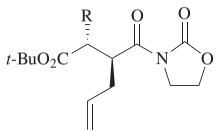
119

R		dr	er
Et	(83)	4:1	80.5:19.5
c-C_6H_{11}	(83)	4:1	81.0:19.0

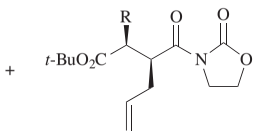
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_4					
		R^2X	Et_3B/O_2, Lewis acid, (*S*,*R*,*R*,*S*)-**L10**, CH_2Cl_2, –78°		119

R^1	R^2	X	Lewis Acid		dr	er
Bu	$MeOCH_2$	Br	$Mg(ClO_4)_2$	(83)	2.4:1	76.5:23.5
Bu	Et	I	$Mg(ClO_4)_2$	(83)	7:1	83.0:17.0
Bu	*i*-Pr	I	$Mg(ClO_4)_2$	(84)	7:1	88.0:12.0
Bu	*t*-Bu	I	$Mg(ClO_4)_2$	(85)	19:1	96.0:4.0
Bu	*c*-C_6H_{11}	I	$Mg(ClO_4)_2$	(84)	7:1	84.5:15.5
Ph	*i*-Pr	I	$Cu(OTf)_2$	(95)	10:1	12.0:88.0
Ph	*t*-Bu	I	$Cu(OTf)_2$	(66)	50:1	8.5:91.5

			*h*ν, $(Bu_3Sn)_2$, benzene, rt, 12 h	 (46) dr = 2:1	143
		RI	Et_3B/O_2, Lewis acid, CH_2Cl_2/THF (2:1), –78°	 **I/II** 99:1	147

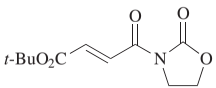
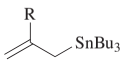
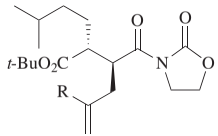
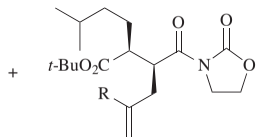
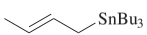
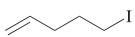
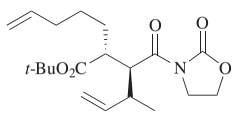
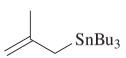
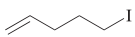
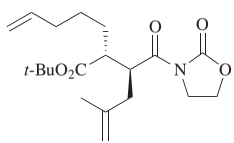
I



II

R	Lewis Acid	Time (h)	**I + II**
Et	$Y(OTf)_3$	—	(85)
Et	$Sm(OTf)_3$	—	(87)
i-Pr	$Y(OTf)_3$	—	(80)
i-Pr	$Sm(OTf)_3$	—	(82)
i-Bu	none	4	(44)
i-Bu	MgI_2	6	(26)
i-Bu	$Mg(ClO_4)_2$	4	(70)
i-Bu	$Mg(OTf)_2$	2	(58)
i-Bu	$Al(OTf)_3$	4	(41)
i-Bu	$In(OTf)_3$	4	(43)
i-Bu	$Sc(OTf)_3$	4	(56)
i-Bu	$Y(OTf)_3$	2	(91)
i-Bu	$Sm(OTf)_3$	2	(85)
i-Bu	$Yb(OTf)_3$	4	(67)
t-Bu	$Y(OTf)_3$	—	(62)
t-Bu	$Sm(OTf)_3$	—	(64)
$CH_2{=}CH(CH_2)_3$	$Y(OTf)_3$	—	(66)
$CH_2{=}CH(CH_2)_3$	$Sm(OTf)_3$	—	(63)
$Ph(CH_2)_3$	$Y(OTf)_3$	—	(72)
$Ph(CH_2)_3$	$Sm(OTf)_3$	—	(74)
1-adamantyl	$Y(OTf)_3$	—	(15)
1-adamantyl	$Sm(OTf)_3$	—	(22)

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_4					
			Et_3B, O_2, $Y(OTf)_3$, CH_2Cl_2/THF (2:1), –78°	 **I** +  **II**	**I/II** ≥ 99:1	147
			Et_3B, O_2, $Y(OTf)_3$, CH_2Cl_2/THF (2:1), –78°, 4 h		(49) dr = 2:1	709
			Et_3B, O_2, $Y(OTf)_3$, CH_2Cl_2/THF (2:1), –78°, 4 h		(47)	709

R	**I + II**
Me	(77)
$AcOCH_2$	(28)

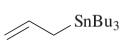
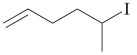
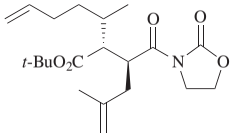
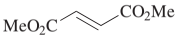
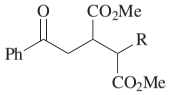
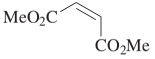
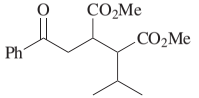
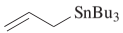
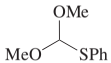
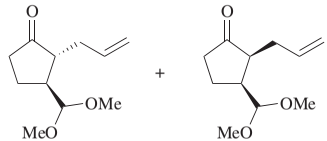
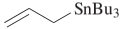
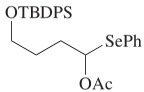
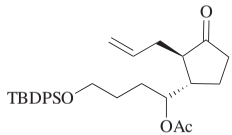
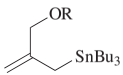
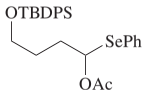
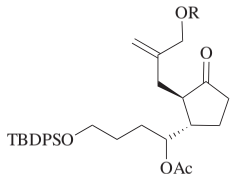
			Et_3B, O_2, $Y(OTf)_3$, CH_2Cl_2/THF (2:1), –78°, 4 h		(72) dr = 1:1	709
		RI	AIBN, benzene, 80°, 4 h			142
				R / dr: Et (95) 2.8:1; *i*-Pr (100) 4.3:1; *t*-Bu (85) >99:1		
			AIBN, benzene, 80°, 4 h		(93) dr = 4.3:1	142

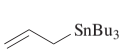
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_5					
			Conditions, $(Bu_3Sn)_2$, solvent, 12 h	 **I** + **II**	143

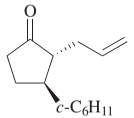
Conditions	Solvent	**I + II**	**I/II**
*h*ν (sunlamp)	benzene	(69)	8:1
*h*ν (sunlamp)	toluene	(67)	—
*h*ν (450W Hanovia)	benzene	(55)	—

		AIBN, benzene, 80°, 3 h	 (68)	712
		ACCN, toluene, 110°, 3 h		712

R	
Ac	(59)
TBDPS	(68)



$h\nu$, benzene, 3.5 h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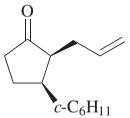
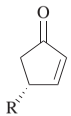
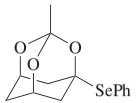


542

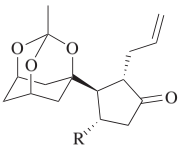
I **II**

I + II (55) **I/II** = 10.1:1

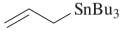
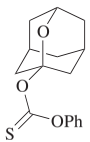




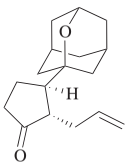
ACCN, toluene, 110°, 8 h



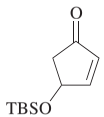
R		
H	(75)	144, 713
TBSO	(77)	

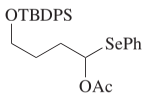



ACCN, toluene, 110°, 8 h

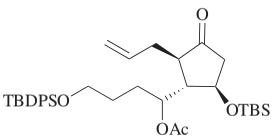


(56) 579



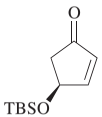
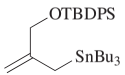
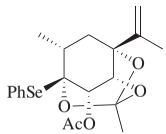
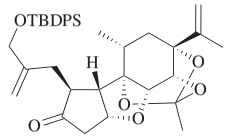
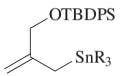
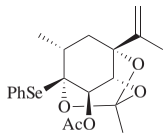
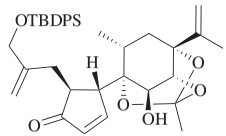
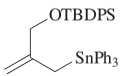
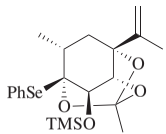
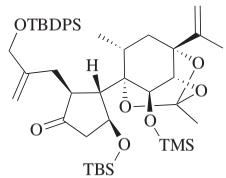


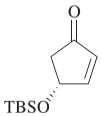
AIBN, toluene, 110°, 3 h

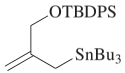


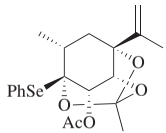
(46) 712

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

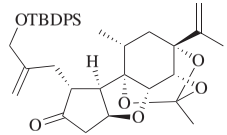
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_5					
			1. ACCN, chlorobenzene, 130°, 0.5 h 2. K_2CO_3, CH_3OH, rt, 3 h	 (9)[c]	325, 714
			1. ACCN, chlorobenzene, 130°, 0.5 h 2. K_2CO_3, CH_3OH, rt, 3 h		
				R Bu (27)[c] Ph (33)[c]	325, 713, 714 325
			ACCN, chlorobenzene, 130°, 0.5 h	 (52)	325



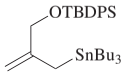


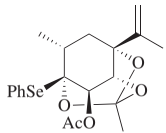


1. ACCN, chlorobenzene, 130°, 0.5 h
2. K_2CO_3, CH_3OH, rt, 3 h

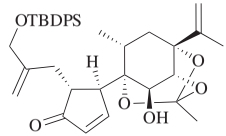


(36)[c] 714



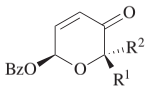


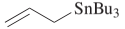
1. ACCN, chlorobenzene, 130°, 0.5 h
2. K_2CO_3, CH_3OH, rt, 3 h



(56)[c] 713, 714

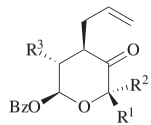
C_{5-6}





R^3I

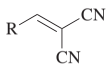
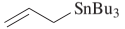
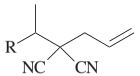
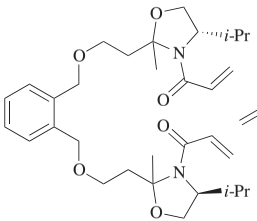
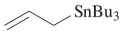
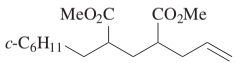
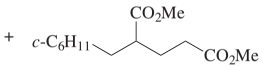
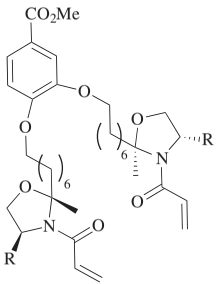
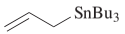
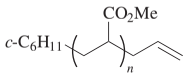
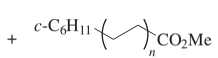
AIBN, benzene, 80°, 2 h



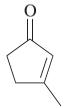
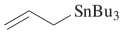
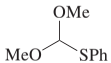
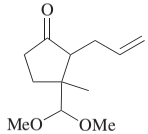
715

R^1	R^2	R^3		dr[d]
H	H	Et	(45)	7.3:1
H	H	*i*-Pr	(65)	13.3:1
H	H	*t*-Bu	(60)	15.7:1
H	H	*c*-C_5H_9	(48)	49:1
H	H	*c*-C_6H_{11}	(59)	9:1
H	Me	*i*-Pr	(52)	32:1
Me	H	*i*-Pr	(38)	32:1

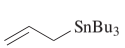
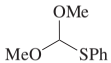
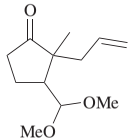
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_{6-8} 		MeI	AIBN, benzene, 80°, 12 h	 R: Et (60); *n*-Bu (61)	19
C_6 			1. AIBN, benzene, 80° 2. 4 N HCl/dioxane (1:1), reflux 3. CH_2N_2	 **I** dr = 2:1 +  **II** **I** + **II** (—) **I/II** = 1:1	149
			1. AIBN, benzene, 80° 2. 4 N HCl/dioxane (1:1), reflux 3. CH_2N_2	 **I** (*n* = 1); **II** (*n* = 2); **III** (*n* = 3); **IV** (*n* = 4) +  **V** (*n* = 1); **VI** (*n* = 2)	149

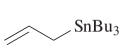
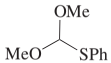
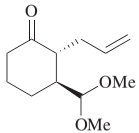
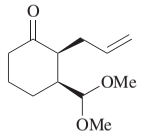
R	I/II/III/IV/V/VI	II	dr II
i-Pr	10:65:3:10:2:10	(—)	3:1
t-Bu	11:72:6:9:0.5:0.7	(30)[e]	22:1

$h\nu$, $(Bu_3Sn)_2$, benzene, 12 h — (28) dr = 3:1 — 143

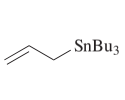
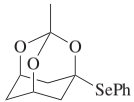




$h\nu$, $(Bu_3Sn)_2$, benzene, 12 h — (51) dr = 3:1 — 143

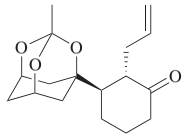





I + **II** — 143

Inititator	I + II	I/II
$(Bu_3Sn)_2$	(33)	4:1
—	(11)	—

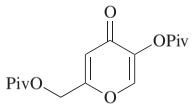
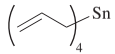
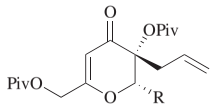
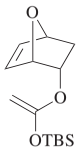
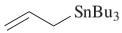
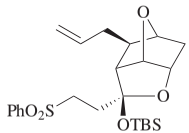
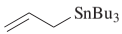
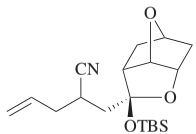
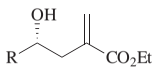
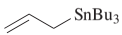
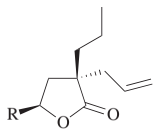
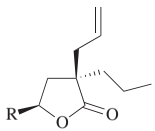



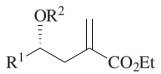
ACCN, toluene, 110°, 8 h

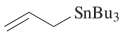


(32) — 144

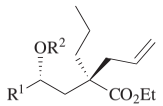
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_6					
		RI	Et_3B, O_2, (*R*,*R*)-**A1** (0.5 eq), CH_2Cl_2, –78°		716
				R / dr[d] / er *i*-Pr (77) 99:1 85.0:15.0 *c*-C_5H_9 (90) 99:1 84.5:15.5	
C_8					
			AIBN, benzene, 80°, 12 h	 (38)	145
			AIBN, benzene, 80°, 12 h	 (35)	145
C_{8-11}					
			Et_3B/O_2, Et_2AlCl (*x* eq), CH_2Cl_2, 0°	 **I** +  **II**	717



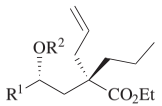


Et_3B, O_2,
Lewis acid (x eq),
CH_2Cl_2, co-solvent, 0°



I

+



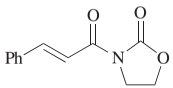
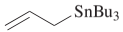
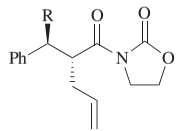
II

717

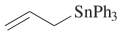
R	x	**I + II**	**I/II**
i-Pr	1.1	(72)	>99:1
t-Bu	1.2	(73)	>99:1
Ph	1.1	(27)	3.2:1

R^1	R^2	Lewis Acid	x	Co-Solvent	**I + II**	**I/II**
i-Pr	H	$MgBr_2$	3	—	(31)	>99:1
i-Pr	MOM	$MgBr_2$	3	—	(56)	>99:1
i-Pr	MOM	Et_2AlCl	1.2	—	(66)	1.5:1
t-Bu	H	$MgBr_2$	3	—	(44)	>99:1
t-Bu	MOM	$MgBr_2$	3	—	(63)	>99:1
t-Bu	MOM	Et_2AlCl	1.1	—	(74)	2.2:1
Ph	H	none	—	—	(0)	—
Ph	H	$MgBr_2$	3	—	(60)	3.3:1
Ph	Me	none	—	—	(0)	—
Ph	Me	$MgBr_2 \bullet OEt_2$	3	—	(53)[f]	12.2:1
Ph	Me	$MgBr_2$	3	—	(53)	6.3:1
Ph	Bn	none	—	—	(0)	—
Ph	Bn	$MgBr_2 \bullet OEt_2$	3	—	(66)	16.7:1
Ph	Bn	$MgBr_2$	3	—	(54)	7.9:1
Ph	Bn	$MgBr_2$	3	Et_2O	(65)	12.5:1
Ph	Bn	Et_2AlCl	1.2	—	(31)	1:1
Ph	MOM	$MgBr_2$	3	—	(48)	5.5:1

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

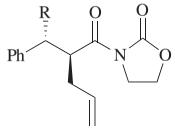
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_9					
		RX	Et_3B, O_2, Lewis acid (x eq), (S,R,S)-**L10**, CH_2Cl_2		119

R	X	Lewis Acid	x	Temp (°)		er	dr
$MeOCH_2$	Br	MgI_2	0.3	–78	(80)	6.1:1	20:1
Et	I	MgI_2	0.3	–78	(79)	7.7:1	32:1
i-Pr	I	MgI_2	1	–78	(82)	13.3:1	19:1
i-Pr	I	MgI_2	0.3	–78	(93)	28:1	37:1
i-Pr	I	MgI_2	0.3	–40	(70)	4.7:11	36:1
i-Pr	I	$MgBr_2$	0.3	–78	(90)	19:1	30:1
i-Pr	I	$Mg(ClO_4)_2$	0.3	–78	(91)	14.4:1	40:1
t-Bu	I	MgI_2	0.3	–78	(84)	66:1	99:1
c-C_6H_{11}	I	MgI_2	0.3	–78	(80)	24:1	60:1



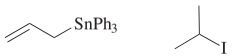
RI

Et_3B, O_2,
$Cu(OTf)_2$ (x eq),
(S,R,R,S)-**L10**,
CH_2Cl_2, –78°

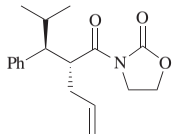


119

R	x		er	dr
i-Pr	0.3	(93)	8.5:1	30:1
i-Pr	1	(84)	7.3:1	30:1
t-Bu	0.3	(90)	49:1	99:1

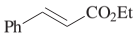


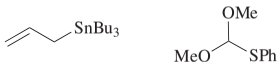
Et_3B/O_2, MgI_2,
(S,R,R,S)-**L10**,
CH_2Cl_2, –78°



(82) er = 21:1, dr = 36:1

119





AIBN, benzene,
80°, 12 h

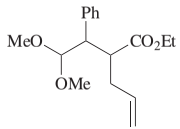


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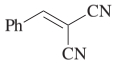
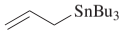
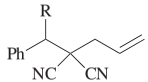
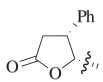
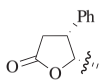
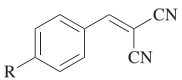
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)

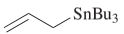
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_{10}					
		RI	Conditions, initiator, benzene		19

R	Conditions	Initiator	Temp	Time (h)	
Me	—	AIBN	80°	6	(85)
Me	*h*ν	none	rt	12	(65)
n-Pr	—	AIBN	80°	12	(51)
n-Pr	*h*ν	none	rt	12	(50)
i-Pr	—	AIBN	80°	12	(65)
i-Pr	*h*ν	none	rt	12	(75)
$CH_2{=}CHCH_2$	—	AIBN	80°	10	(73)
n-Bu	—	AIBN	80°	11	(67)
n-Bu	*h*ν	none	rt	11	(92)
t-Bu	—	AIBN	80°	24	(25)
t-Bu	*h*ν	none	rt	38	(46)
$HO(CH_2)_4$	*h*ν	none	rt	12	(40)
$Ac(CH_2)_2$	—	AIBN	80°	12	(55)
$Cl(CH_2)_4$	*h*ν	none	rt	18	(75)
$Br(CH_2)_4$	*h*ν	none	rt	20	(91)
c-C_6H_{11}	—	AIBN	80°	12	(47)
Ph	—	AIBN	80°	48	(13)
n-C_7H_{15}	—	AIBN	80°	15	(76)
$PhCH_2$	—	AIBN	80°	6	(82)
	—	AIBN	80°	—	(60)
	*h*ν	none	rt	—	(54)

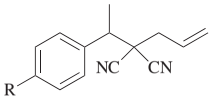
C_{10-11}





MeI

Conditions, initiator, benzene



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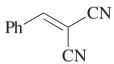
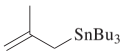
R	Conditions	Initiator	Temp	Time (h)	
Cl	—	AIBN	80°	6	(90)
Cl	*h*ν	none	rt	12	(66)
MeO	—	AIBN	80°	24	(29)
Me	—	AIBN	80°	12	(66)
NC–	—	AIBN	80°	6	(88)
NC–	*h*ν	none	rt	6	(60)

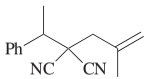
C_{10}





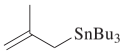
MeI

AIBN, benzene, 80°, 12 h

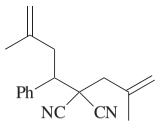


(87)

19

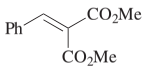


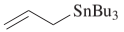
AIBN, benzene, 80°, 12 h



(65)

19





MeI

AIBN, benzene, 80°, 60 h

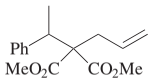


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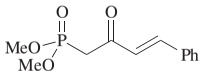
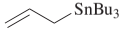
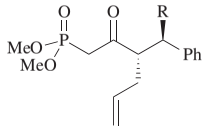
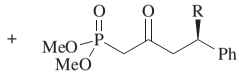
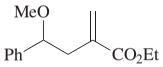
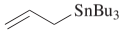
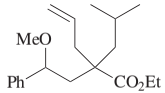
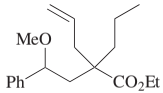
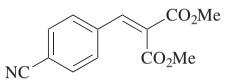
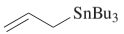
TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
A. THREE-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
C_{10}					
		RI	Et_3B, O_2, $Zn(OTf)_2$, (*S*,*R*,*S*)-**L18**, Et_2O, –78°	 **I** +  **II**	220

R	Time (h)	**I**	er **I**	dr **I**	**II**	er **II**
i-Pr	12–36	(71)	95.5:4.5	20:1	(7)	79.0:21.0
t-Bu	12–36	(76)	99.5:0.5	>50:1	(10)	83.0:17.0
	12–36	(71)	98.5:1.5	>50:1	(7)	85.5:14.5
	24	(70)	97.0:3.0	>50:1	(—)	—

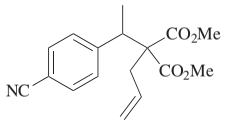
C_{11}					
			Et_3B, O_2, $MgBr_2$•OEt_2, CH_2Cl_2, –78°	 (30) +  (26)	717





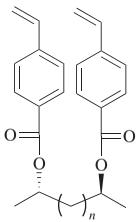
MeI

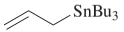
AIBN, benzene, 80°, 60 h



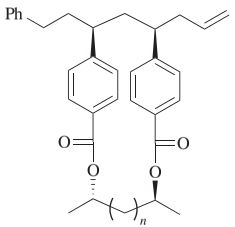
(39) 19

C_{22-24}





AIBN, toluene, 80°, 6 h



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n		(*R*,*R*)/(*R*,*S*)/(*S*,*R*)/(*S*,*S*)
0	(2)	48:39:41:1
1	(5)	130:57:146:1
2	(4)	50:28:46:1

[a] The yield was determined by gas chromatography.

[b] Specific yields were not given.

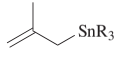
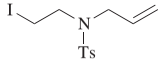
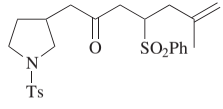
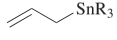
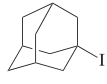
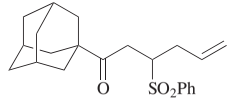
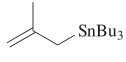
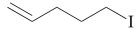
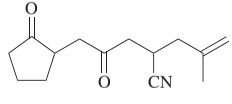
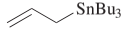
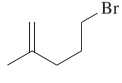
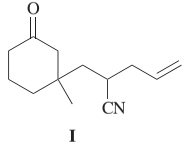
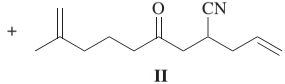
[c] This is the yield for the two-step process.

[d] The configuration of the minor product was not determined.

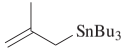
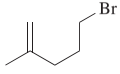
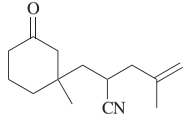
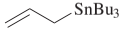
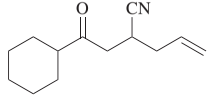
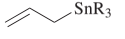
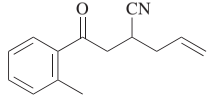
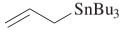
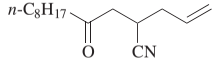
[e] This is the yield for the three-step process.

[f] There was also a 10% yield of the product resulting from bromine atom transfer instead of allyl transfer.

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
B. FOUR-COMPONENT PROCESSES

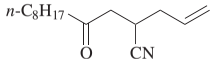
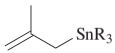
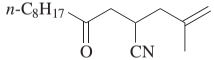
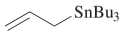
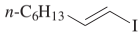
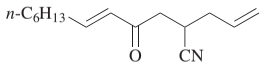
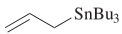
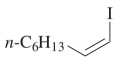
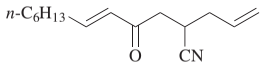
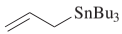
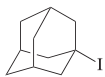
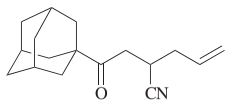
Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_2					
	 R = n-$C_6F_{13}(CH_2)_3$		ACCN, BTF, CO (80–90 atm), 100°, 12 h	 (65) dr = 1:1	719
	 R = n-$C_6F_{13}(CH_2)_3$		ACCN, BTF, CO (80–90 atm), 80°, 12 h	 (60)	719
C_3					
			AIBN, benzene, CO (80 atm), 80°	 (62) dr = 1:1	153
x M			AIBN, benzene, CO (80 atm), 80°, 12 h	 **I** +  **II**	156

x	**I**	dr **I**	**II**
0.03	(50)	1.3:1	(3)
0.1	(40)	1.3:1	(7)

			AIBN, benzene, CO (80 atm), 80°, 12 h		(65) dr = 1.3:1	156
			AIBN, benzene, CO (50 atm), 80°, 8 h		(67)	155
	 R = n-$C_6F_{13}(CH_2)_3$		AIBN, BTF, CO (80–90 atm), 80°, 12 h		(56)	719
		n-$C_8H_{17}X$	AIBN, benzene, CO (x atm), 80°, 8 h			155

X	x	
Br	20	(66)
I	10	(72)

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
B. FOUR-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_3					
	R = n-$C_6F_{13}(CH_2)_3$	n-$C_8H_{17}I$	ACCN, BTF, CO (80–90 atm), 100°, 12 h	 (68)	719
	 R = n-$C_6F_{13}(CH_2)_3$	n-$C_8H_{17}I$	AIBN, BTF, CO (80–90 atm), 80°, 12 h	 (61)	719
			AIBN, benzene, CO (30 atm), 80°, 8 h	 (66) (*E*)/(*Z*) = 8.1:1	155
			AIBN, benzene, CO (50 atm), 80°, 8 h	 (70) (*E*)/(*Z*) = 9:1	155
			AIBN, benzene, CO (80 atm), 80°, 8 h	 (61)	155

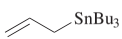
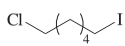
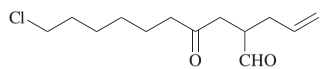
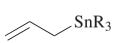
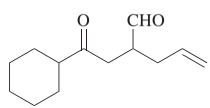
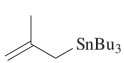
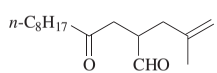
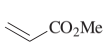
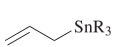
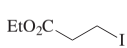
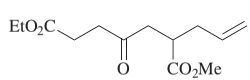
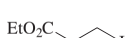
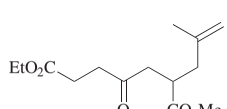
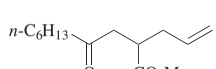
			AIBN, benzene, CO (20 atm), 80°, 8 h	 (70)		155
	 R = n-$C_6F_{13}(CH_2)_3$		AIBN, BTF, CO (80–90 atm), 80°, 12 h		(66)	719
		n-$C_8H_{17}I$	AIBN, benzene, CO (20 atm), 80°, 8 h		(74)	155
	 R = n-$C_6F_{13}(CH_2)_3$		AIBN, BTF, CO (80–90 atm), 80°, 12 h		(71)	719
			AIBN, benzene, CO (20 atm), 80°, 8 h		(67)	155
		n-$C_6H_{13}I$	AIBN, benzene, CO (20 atm), 80°, 8 h		(72)	155

TABLE 2. MULTICOMPONENT REACTIONS (*Continued*)
B. FOUR-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Radical Precursor	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*					
C_3					
CO_2Me	SnR_3 R = n-$C_6F_{13}(CH_2)_3$	n-$C_8H_{17}I$	AIBN, BTF, CO (80–90 atm), 80°, 12 h	n-C_8H_{17}, O, CO_2Me	(60)	719
CO_2Et 0.03 M	$SnBu_3$	Br	AIBN, benzene, CO (80 atm), 80°, 12 h	O, CO_2Et	(47) dr = 1.2:1	156
CO_2Et	$SnBu_3$	Br	AIBN, benzene, CO (80 atm), 80°, 12 h	O, CO_2Et	(60) dr = 1.2:1	156
	$SnBu_3$	I	AIBN, benzene, CO (50 atm), 80°, 8 h	O, CO_2Et	(65)	155
O, O	$SnBu_3$	O, O, Br	AIBN, benzene, CO (50 atm), 80°, 8 h	O, O, O, O	(60)	155

C_4

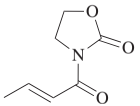
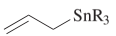
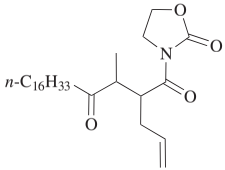
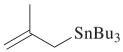
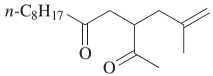
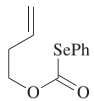
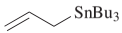
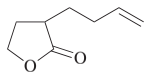
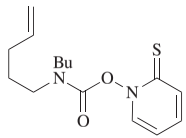
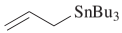
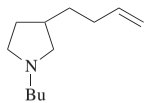
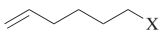
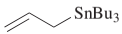
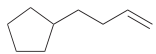
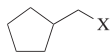
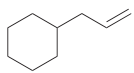
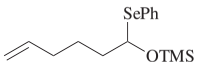
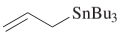
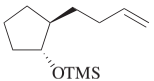
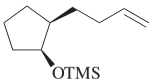
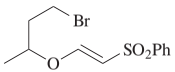
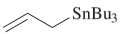
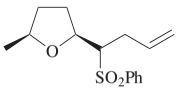
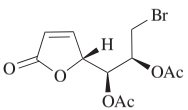
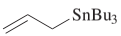
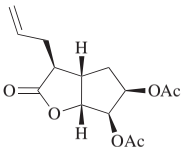
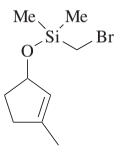
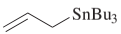
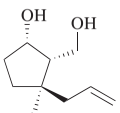
	 R = n-$C_6F_{13}(CH_2)_3$	n-$C_{16}H_{33}Br$	AIBN, BTF, CO (80–90 atm), 80°, 12 h		(67) dr = 1:1	719
		n-$C_8H_{17}I$	AIBN, benzene, CO (20 atm), 80°, 8 h		(77)	155

TABLE 3. ALLYLATIONS FOLLOWING CYCLIZATIONS

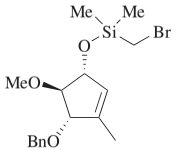
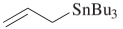
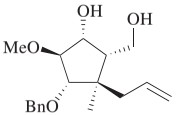
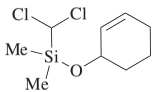
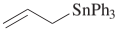
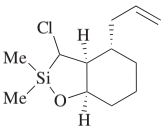
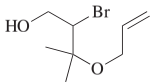
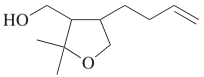
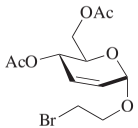
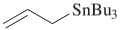
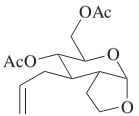
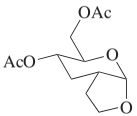
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		AIBN, benzene, 80°, 1 h	 (76)	232
		*h*ν, MeCN, rt	 (0)	238
C_6				
		AIBN, solvent	 +  **I** **II** + **III** +  **IV**	

X	Solvent	Temp (°)	Time (h)	**I + II + III + IV**	**I/II/III/IV**	
Br	—	80	15	(80)[a]	100:0:0:0	12
I	—	80	—	(—)	1:5:0:0	12
I	neat	190	70	(32)	80:0:15:5	2, 21

		AIBN, benzene, 80°, 12 h	 +  **I** **I + II** (67) **I/II** = 7:1 **II**	720
		Et_3B/air, benzene, 25°, 2 h	 (91) dr = 1.4:1	222, 223
C_7 		AIBN, EtOAc, reflux, 24 h	 (78)	224
		1. Conditions, initiator 2. H_2O_2, KF, $KHCO_3$, reflux		230

Conditions	Initiator	Temp (°)	
hν	$(Bu_3Sn)_2$	—	$(45)^b$
hν	AIBN	—	$(0)^b$
—	AIBN	80	$(0)^b$

TABLE 3. ALLYLATIONS FOLLOWING CYCLIZATIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		1. Conditions, initiator, solvent 2. H_2O_2, KF, $KHCO_3$, MeOH, THF, 80°		
		Conditions: *hν*; Initiator: $(Bu_3Sn)_2$; Solvent: benzene; Temp (°): —	(0)[b]	230
		Conditions: —; Initiator: ACCN; Solvent: heptane; Temp (°): 100	(50)[b]	229, 230
		*hν*, benzene, 16 h	 (65)	721
C_8				
		AIBN, benzene, 80°, 20 h	 (37)	221
		AIBN, benzene, 80°, 16 h	 (56) +  (27)	17, 18

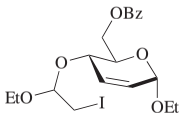
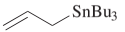
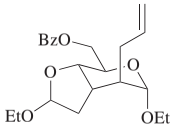
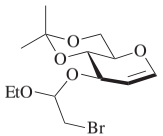
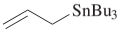
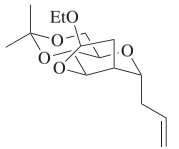
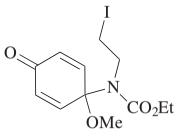
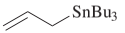
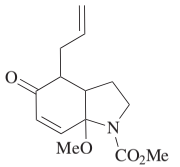
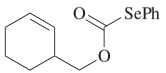
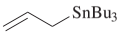
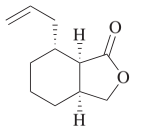
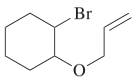
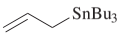
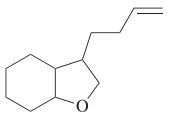
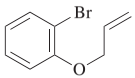
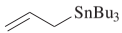
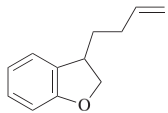
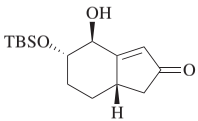
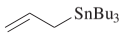
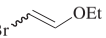
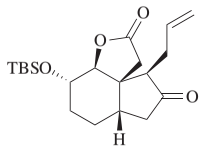
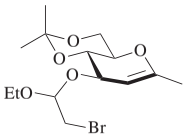
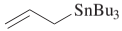
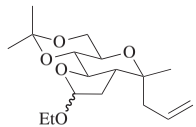
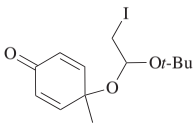
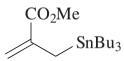
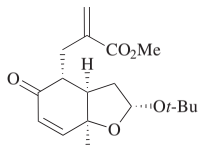
		AIBN, benzene, 80°, 16 h		(84)	17, 18
		AIBN, benzene, 80°, 36 h		(68)	297, 722
		AIBN, toluene, 110°, 24 h		(61)	225
		$h\nu$, $(Bu_3Sn)_2$, benzene, 24 h		(72)	723, 724
		AIBN, benzene, 80°, 20 h		(49)	221

TABLE 3. ALLYLATIONS FOLLOWING CYCLIZATIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		AIBN, benzene, 80°	 (—)	221
		1.  , CSA, PPTS, rt, 6 h 2. AIBN, benzene, 80°, 12 h 3. MCPBA, BF_3•OEt_2, CH_2Cl_2, –40°, 1 h	 (65)[b]	326
		AIBN, toluene, 80°, 48 h	 (64)	725
		AIBN, benzene, 80°	 **I** + uncharacterized isomer(s) **II**	**I** + **II** (68) **I/II** = 4.3:1 726, 727

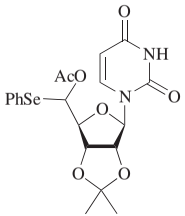
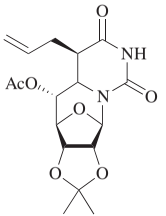
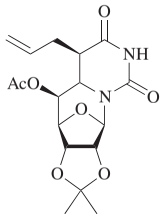
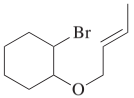
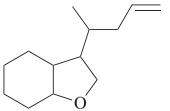
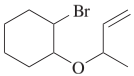
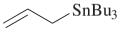
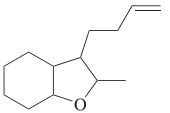
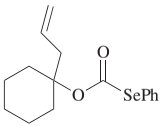
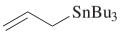
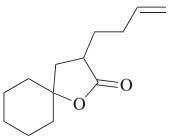
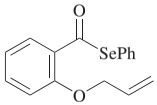
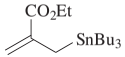
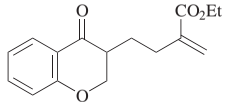
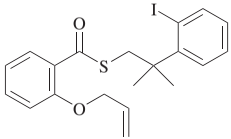
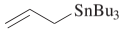
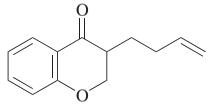
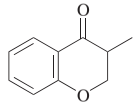
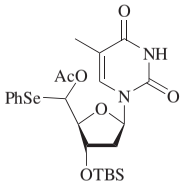
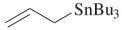
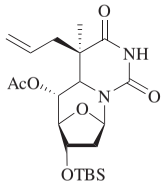
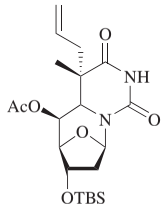
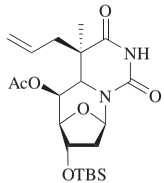
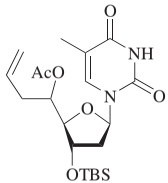
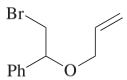
		$h\nu$, $(Bu_3Sn)_2$, benzene, rt, 3 h	 (78) +	 (7)	689, 690
C_{10}					
		AIBN, benzene, 80°, 20 h		(43)	221
		AIBN, benzene, 80°, 20 h		(48) 2 isomers	221
		AIBN, benzene, 80°, 1 h		(73)	232

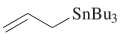
TABLE 3. ALLYLATIONS FOLLOWING CYCLIZATIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
		AIBN, benzene, 80°, 15 h	 (23)	233, 234
		AIBN, benzene, 80°, 10 h	 (56) +  (10)	235
		Conditions, initiator, benzene	 **I** +  **II** +  **III** +  **IV**	690

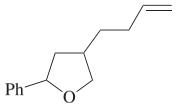
Conditions	Initiator	Temp	Time (h)	**I**	**II**	**III**	**IV**
hν	$(Bu_3Sn)_2$	rt	3	(43)	(10)	(5)	(10)
—	AIBN	80°	4	(55)	(16)	(8)	(9)

C_{11}

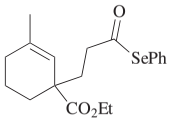


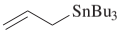


AIBN, benzene, 80°, 20 h

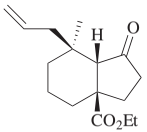


(35) 221



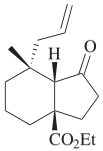


ACCN, heptane, reflux, 6.5 h



(55)

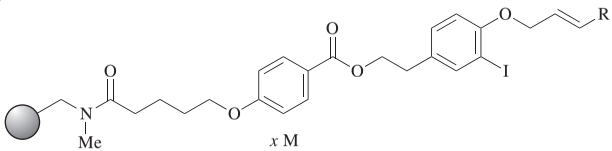
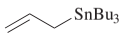
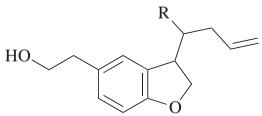
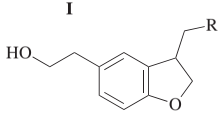
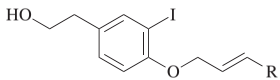
+



(5)

231

TABLE 3. ALLYLATIONS FOLLOWING CYCLIZATIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11-17} 	 *y* eq	1. AIBN, benzene, 80°, 46 h 2. NaOMe, MeOH/dioxane (1:4), rt, 24 h	 **I** +  **II** +  **III**	228

R	*x*	*y*	**I/II/III**
H	0.025	25	49:10:41
H	0.05	10	70:24:6
H	0.05	15	78:22:0
H	0.05	25	37:10:53
Me	0.05	15	49:22:29
Ph	0.05	15	10:10:80

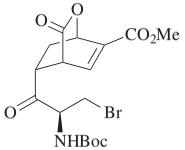
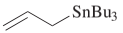
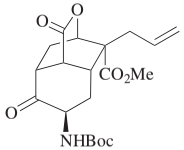
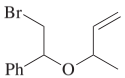
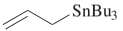
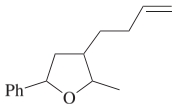
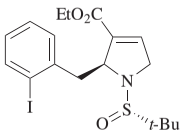
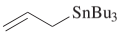
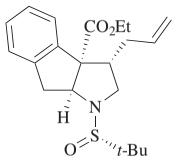
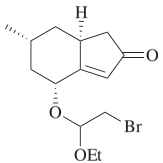
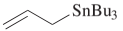
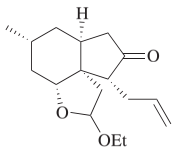
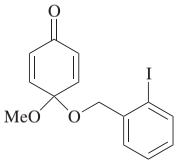
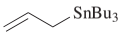
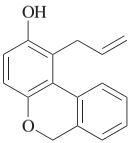
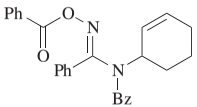
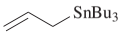
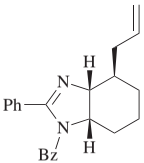
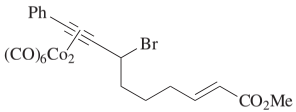
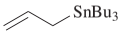
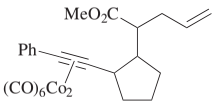
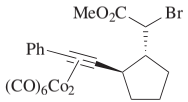
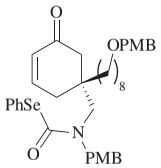
C_{11}			Et_3B, air, benzene, 75°, 5 h		(59)	327
C_{12}			AIBN, benzene, 80°, 20 h		(25)	221
			AIBN, benzene, 80°, 3 h		(78)	728
			AIBN, benzene, 80°, 2.5 h		(85)	729

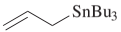
TABLE 3. ALLYLATIONS FOLLOWING CYCLIZATIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{13}				
		1. AIBN, toluene, 110°, 34 h 2. TsOH•H_2O, CH_2Cl_2, acetone, rt, o/n	 (72)[b]	226, 227
		ACCN, toluene, 110°	 (68)	237
C_{15}				
		*h*ν, $(Bu_3Sn)_2$, *or* AIBN, *or* vitamin B_{12}/Zn	 (0)	517
			+  (—)	

C_{16}

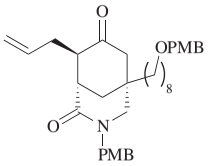


x M



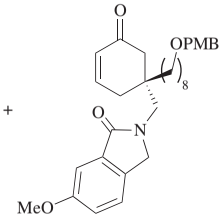
4 eq

Initiator, solvent



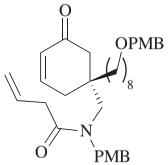
I

+



II

+

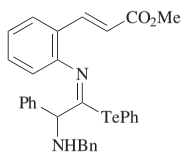
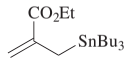
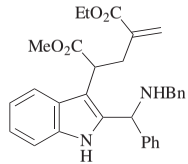
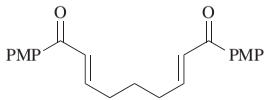
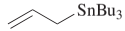
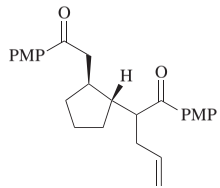


III

730

x	Initiator	Solvent	Temp (°)	Time (h)	**I**	**II**	**III**
0.1	AIBN	benzene	80	7	(21)	(9)	(11)
0.02	AIBN	benzene	80	7	(19)	(13)	(0)
0.02	ACCN	benzene	110[c]	7	(55)	(18)	(0)
0.02	ACCN	chlorobenzene	110	7	(60)	(26)	(0)
0.02	ACCN	benzene	130	2	(67)	(8)	(0)
0.02	ACCN	chlorobenzene	130	2	(73)	(13)	(0)
0.02	ACCN	chlorobenzene	150	2	(63)	(15)	(0)

TABLE 3. ALLYLATIONS FOLLOWING CYCLIZATIONS (*Continued*)

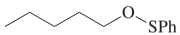
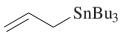
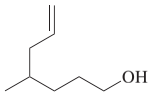
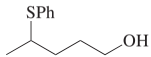
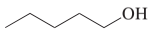
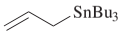
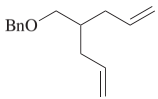
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{17} 		AIBN, benzene, 80°, 48 h	 (59)	236
C_{21} 		*hν*, organocatalyst **A3** (0.2 eq), [fac-Ir(ppy)$_3$] (1 mol %), MeCN, rt, 3 h	 (48)	731

[a] The yield was determined by GC.

[b] This is the overall yield for the two- or three-step process.

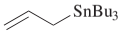
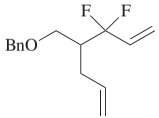
[c] The reaction was conducted in a sealed tube.

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS

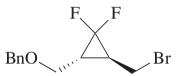
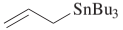
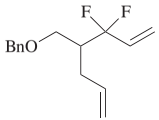
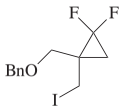
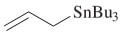
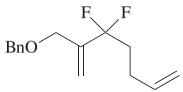
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_5				
 *x* M		*h*ν, benzene	 **I** +  **II** +  **III**	732
		AIBN, benzene, 80°, 12 h	 (70)	249, 250

x	**I**	**II**	**III**
0.02	(15)	(0)	(0)
0.25	(10)	(54)	(27)

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
	 *x* eq	AIBN (*y* eq), solvent, 80°, 12 h		733

x	*y*	Solvent	
2	3.6	benzene	(5)[a]
2	25	benzene	(25)
6	5	benzene	(68)
7	5	benzene	(84)
7	5	toluene	(62)
8	5	benzene	(89)
8	5	benzene	(89)[b]
10	5	benzene	(71)

		AIBN, benzene, 80°, 12 h	 (90)	734
		AIBN, benzene, 80°, 12 h	 (76)	734

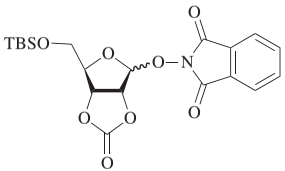
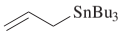
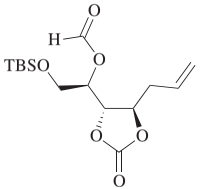
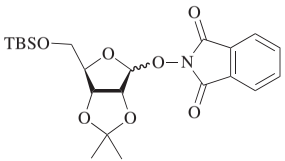
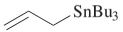
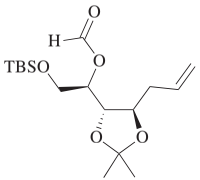
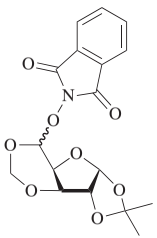
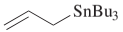
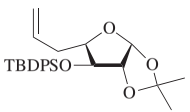
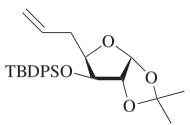
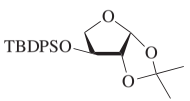
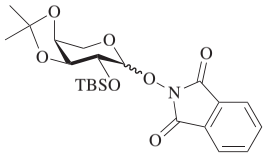
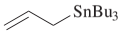
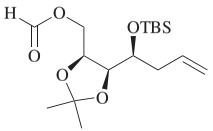
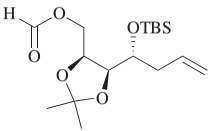
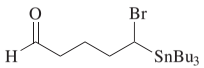
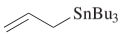
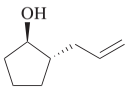
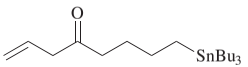
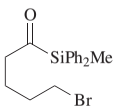
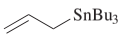
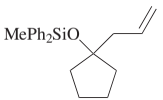
		AIBN, benzene, 80°, 2 h	 (81)	246
		AIBN, benzene, 80°, 3.5 h	 (65)	246
		1. AIBN, benzene, 80°, 5 h 2. Imidazole, 80°, 15 h 3. Imidazole, TBDPSCl, rt, 23 h	 **I** +  **II** **I + II** (33)[c] **I/II** = 15.7:1 +  (7)[c]	246

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5 		AIBN, benzene, 80°, 2.5 h	 **I** +  **II** **I + II** (76) **I/II** = 1.2:1	246
		*h*ν, $(Bu_3Sn)_2$, benzene, rt, 12 h	 (35) +  (tr)	241, 242
		AIBN, benzene, 80°, 8 h	 (61)	240

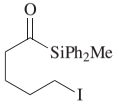
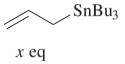
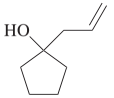
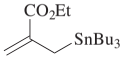
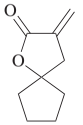
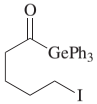
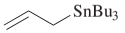
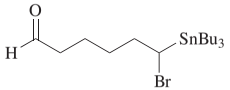
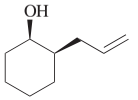
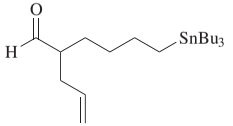
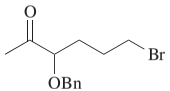
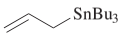
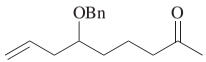
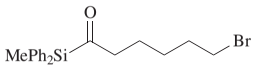
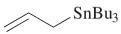
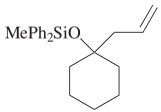
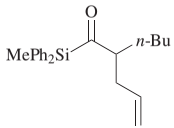
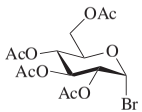
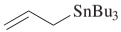
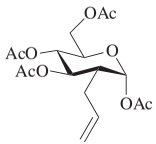
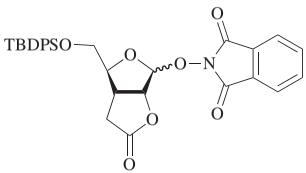
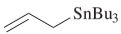
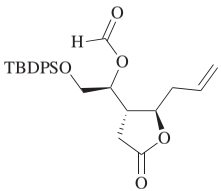
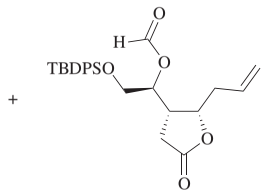
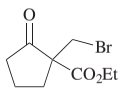
	 x eq	1. AIBN, benzene, 80°, 8 h 2. F^-		x 1 (23)[c] 2 (39)[c]	240
		1. AIBN, benzene, 80° 2. F^-		(39)[c]	240
		AIBN, benzene, 80°, 8 h		(—)	240
C_6 		$h\nu$, $(Bu_3Sn)_2$, benzene, rt, 8 h		(10)	241, 242
			+ 	(50)	

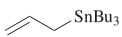
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, Bu_3SnH (2.2 mol %), benzene, 80°, 1.5 h	 (47)	735
		AIBN, benzene, 80°	 (60) +  (17)	240
		AIBN, benzene, 80°	 (—)	736
C_7				
		AIBN, benzene, 80°, 1.5 h	 **I**	246

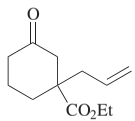


I + II (80) **I/II** = 7.3:1



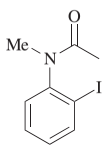


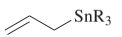
AIBN, benzene, 80°, 8 h



(48) 243

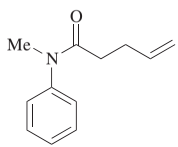
C_8



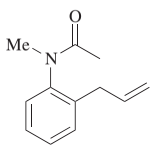


R = n-$C_6F_{13}(CH_2)_3$

$h\nu$, benzene, 25°, 3–30 h



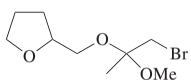
I

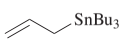


II

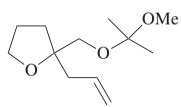
I + II (63) **I/II** = 1.6:1

123



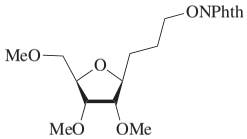
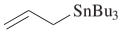
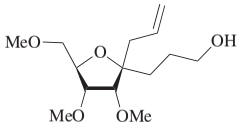
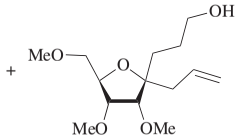
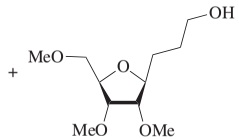


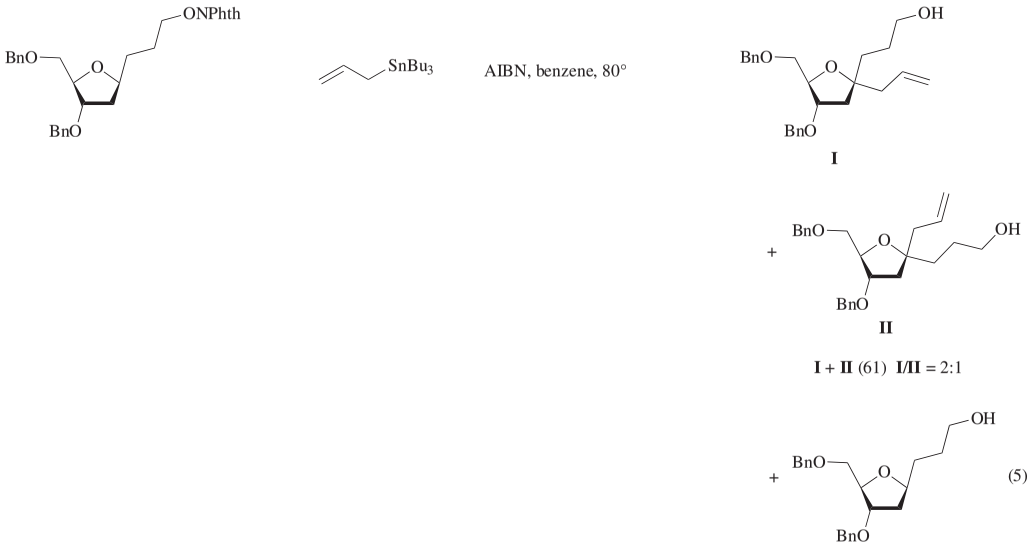
AIBN, benzene, 80°, 5 h



(29) 737

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

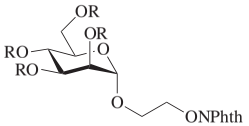
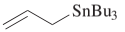
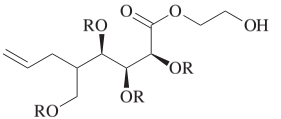
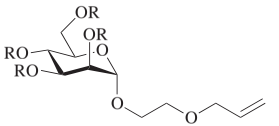
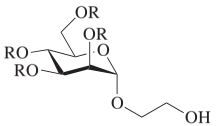
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, benzene, 80°	 **I**  **II** **I** + **II** (56) **I/II** = 3.5:1  (9)	251


ONPhth
BnO
O
BnO
SnBu3
AIBN, benzene, 80°
OH
BnO
O
BnO
I
+
BnO
O
OH
BnO
II
I + II (61) I/II = 2:1
+
OH
BnO
O
BnO

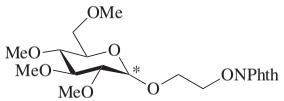
251

(5)

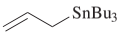
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8 		AIBN, benzene, 80°	 **I** +  **II** +  **III**	252

R	Time (h)	**I**	**I** dr	**II**	**III**
Me	4	(48)	1.1:1	(0)	(10)
Ac	3	(0)	—	(33)	(0)

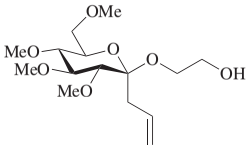


x M



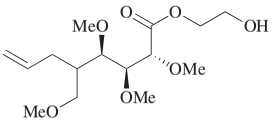
y eq

AIBN, benzene, 80°



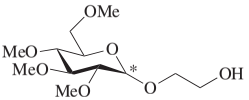
I

+



II

+

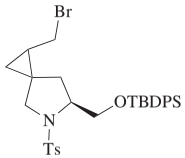
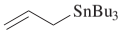
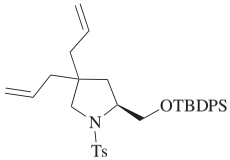
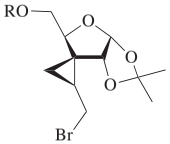
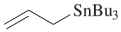
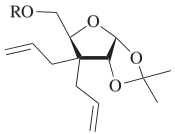
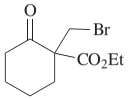
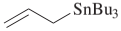
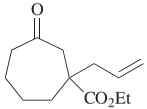


III

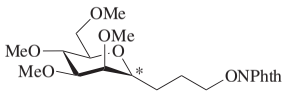
252

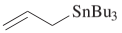
*	*x*	*y*	Time (h)	**I**	**II**	**II** dr	**III**
α	0.03	5	7	(—)	(50)	1.5:1	(3–10)
α	0.1	5	3	(7)	(36)	1.5:1	(3–10)
α	0.1	10	7	(13)	(40)	1.5:1	(3–10)
β	0.1	10	2.5	(20)	(46)	1.5:1	(3–10)

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

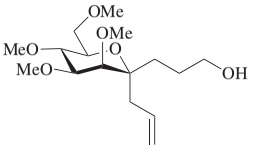
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, benzene, 80°, 12 h	 (66)	250
		AIBN, benzene, 80°, 12 h		
			R	
			Me (72)	249
			TBDPS (80)	249, 250
		AIBN, benzene, 80°, 8 h	 (50)	243

C_9



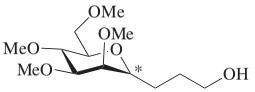


AIBN, benzene, 80°



I

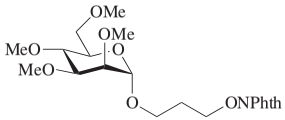
+

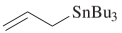


II

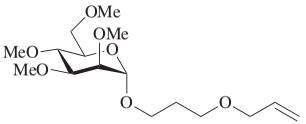
*	**I**	**II**
α	(42)	(7)
β	(54)	(10)

251



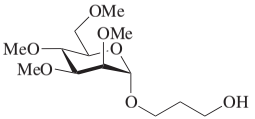


AIBN, benzene, 80°, 8 h



(20)

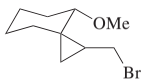
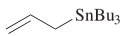
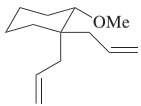
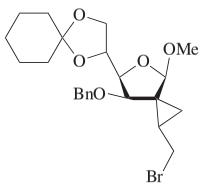
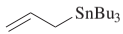
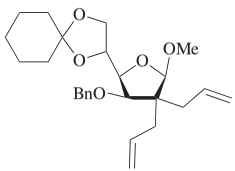
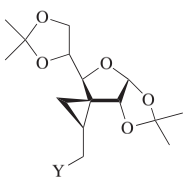
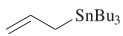
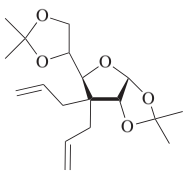
+



(39)

252

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		AIBN, benzene, 80°, 12 h	 (75)	249, 250
		AIBN, benzene, 80°, 12 h	 (63)	249, 250
		AIBN, benzene, 80°, 12 h		
			Y	
			Br (76)	249, 250
			MeS(S)CO (62)	250

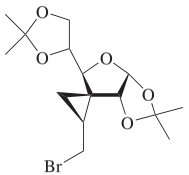
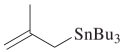
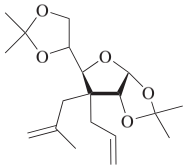
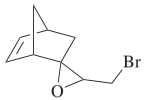
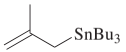
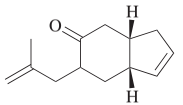
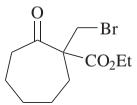
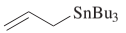
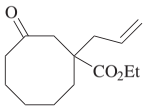
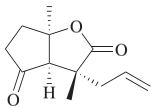
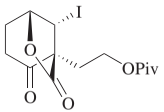
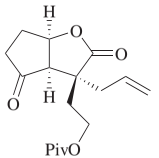
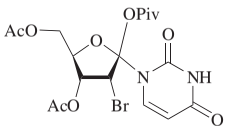
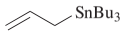
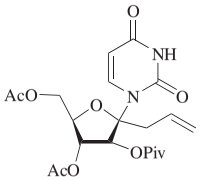
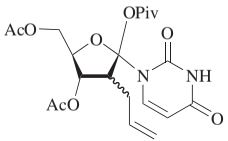
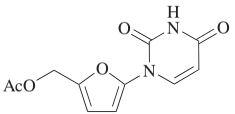
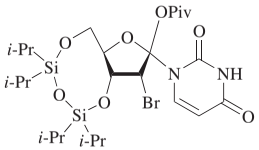
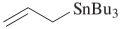
		AIBN, benzene, 80°, 12 h		(52)	250
		AIBN, benzene, 80°		(59)	738
		AIBN, benzene, 80°, 8 h		(46)	243
		AIBN, benzene, 80°, 16 h		(37)	739
		AIBN, benzene, 80°, 16 h		(94)	739

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

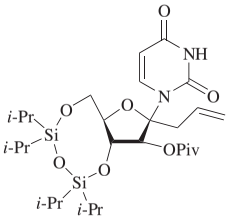
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		Conditions, initiator, benzene	 **I** +  **II** +  **III**	

Conditions	Initiator	Temp	**I**	**II**	**III**	
*h*ν	$(Bu_3Sn)_2$	rt	(62)	(10)	(0)	248
—	AIBN	80°	(46)	(0)	(37)	740



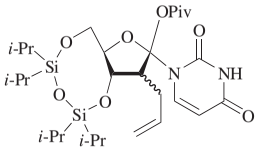


Conditions, initiator, benzene



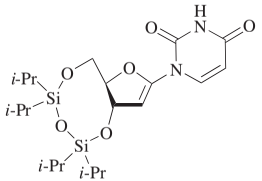
I

+



II

+

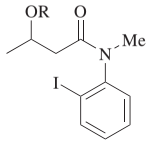
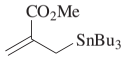
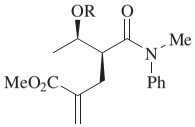
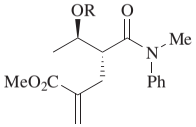
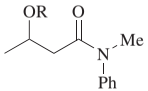
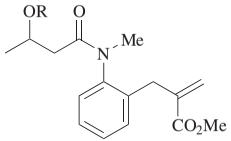


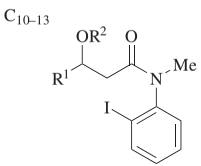
III

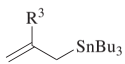
248, 740

Conditions	Initiator	Temp	Time (h)	**I**	**II**	**III**
*h*ν	$(Bu_3Sn)_2$	rt	4	(66)	(6)	(0)
—	AIBN	80°	2	(52)	(0)	(11)

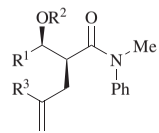
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10} 		*h*v, $(Me_3Sn)_2$, neat, 80°, 2 h	 **I** +  **II** +  **III** +  **IV**	125



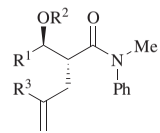


Conditions, initiator, benzene



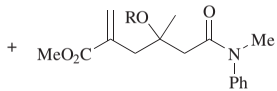
I

+



II

+



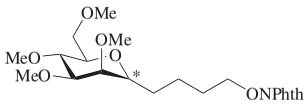
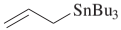
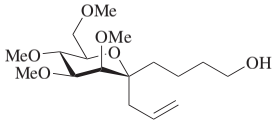
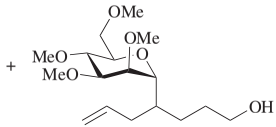
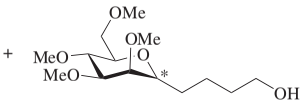
V

R	I + II + III + IV + V	I/II/III/IV/V
H	(—)	tr:54:35:11:tr
Ac	(26)	43:11:35:11:tr

125

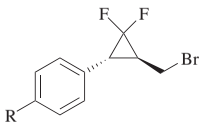
R^1	R^2	R^3	Conditions	Initiator	Temp (°)	Time (h)	I + II	I/II
Me	TBS	H	—	AIBN	80	—	(0)	—
Me	TBDPS	H	—	AIBN	80	—	(0)	—
t-Bu	H	H	*h*ν	none	25	48	(64)	1:13.3
t-Bu	H	H	—	AIBN	80	10	(72)	1:6.7
t-Bu	H	MeO_2C	—	AIBN	80	—	(61)	1:>9
t-Bu	TBS	H	—	AIBN	80	—	(0)	—
t-Bu	Ac	H	*h*ν	none	25	24	(41)	4.3:1
t-Bu	Ac	H	—	AIBN	80	26	(38)	6.7:1
t-Bu	Ac	MeO_2C	—	AIBN	80	14.5	(87)	3:1
t-Bu	CF_3CO	H	—	AIBN	80	—	(0)	—

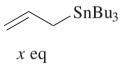
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
		AIBN, benzene, 80°	 **I**  **II**  **III**	251

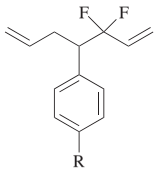
*	**I**	**II**	**II** dr	**III**
α	(35)	(4)	1.5:1	(28)
β	(58)	(0)	—	(15)

C_{10-11}



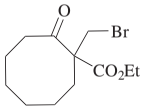


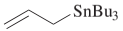
AIBN, benzene, 80°, 12 h



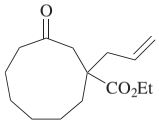
R	*x*		
H	8	(45)	
H	16	(71)	733
H	16	(72)[d]	
F	16	(84)	
Cl	16	(89)	
Br	16	(84)	
MeO	16	(25)	
Me	16	(90)	

C_{10}

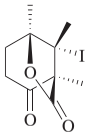


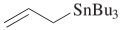


AIBN, benzene, 80°, 8 h

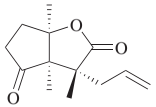


(45) 243



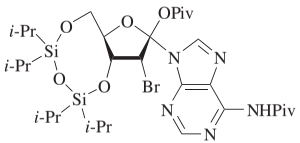
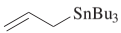
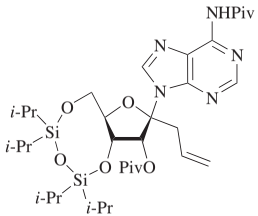
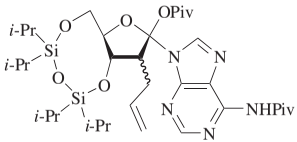


AIBN, benzene, 80°, 24 h



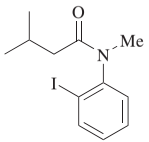
(18) 739

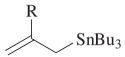
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
	 *x* eq	*h*ν, $(Bu_3Sn)_2$, benzene, rt, 4 h	 **I** +  **II**	248

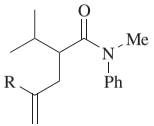
x	**I**	**II**
1.5	(60)	(5)
2.5	(52)	(11)
5.0	(42)	(24)

C_{11}



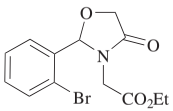


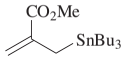
Conditions, initiator, benzene



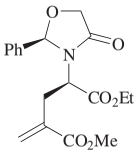
125

R	Conditions	Initiator	Temp (°)	Time (h)	
H	—	AIBN	80	24	(tr)
H	*h*ν	$(Me_3Sn)_2$	25	48	(57)
MeO_2C	*h*ν	AIBN	80	22	(63)



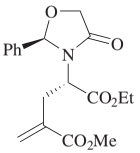


Conditions, AIBN, benzene



I

+

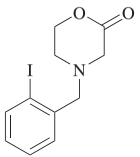
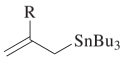
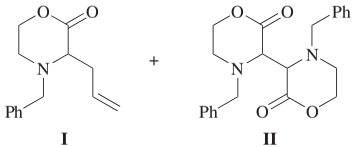
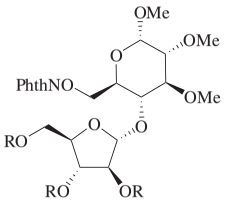
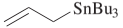
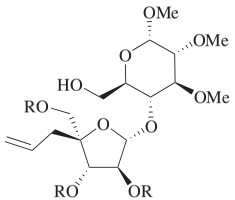
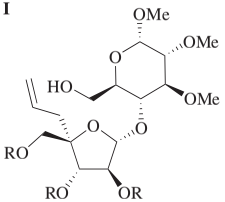


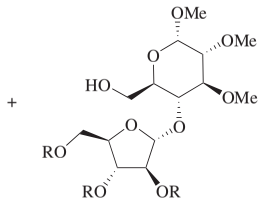
II

254

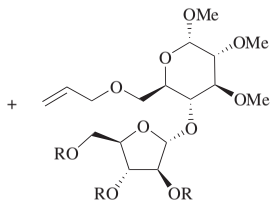
Conditions	Temp (°)	Time (h)	**I + II**	**I/II**
*h*ν	10	24	(61)	5.3:1
—	80	18	(59)	1.9:1

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11}				
		AIBN, benzene, 80°, 14 h	 **I** + **II**	741
			R / **I** / **II**: H (0) (75); Me (0) (92)	
		AIBN, benzene, 80°	 **I** +  **II**	252



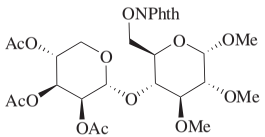
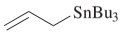
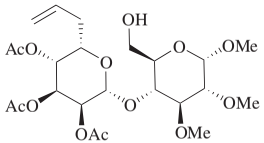
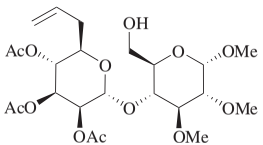
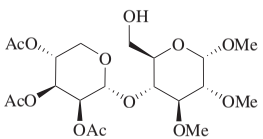
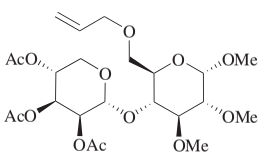
III



IV

R	Time (h)	**I**	**II**	**III**	**IV**
Me	4	(36)	(15)	(22)	(21)
Ac	5	(25)	(27)	(12)	(0)

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11} 		AIBN, benzene, 80°, 3 h	 **I** +  **II** **I + II** (29) **I/II** = 6.3:1 +  (29) +  (17)	252

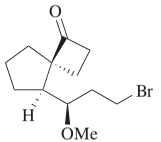
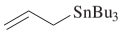
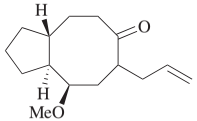
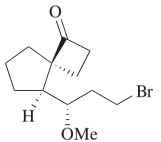
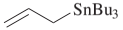
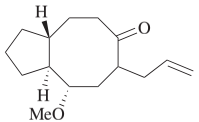
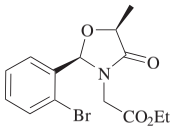
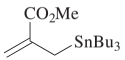
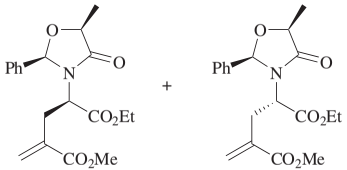
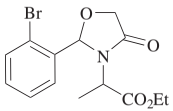
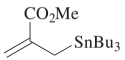
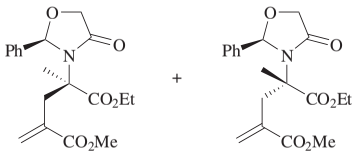
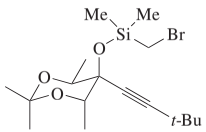
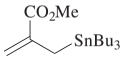
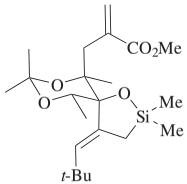
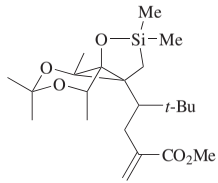
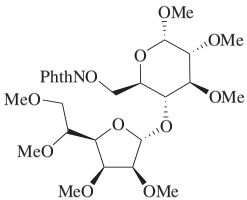
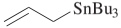
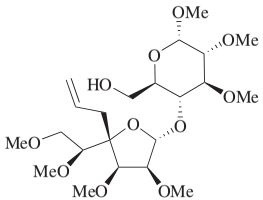
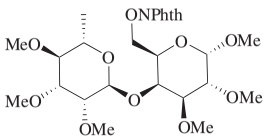
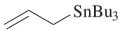
		AIBN, benzene, 80°, 6 h		(52) dr = 5:1	244, 245
		AIBN, benzene, 80°, 6 h		(70) dr = 7:1	244, 245
C_{12}					
		AIBN, benzene, 80°, 18 h	 **I** + **II** (85) **I/II** = 2.6:1		254
		AIBN, benzene, 80°, 18 h	 **I** + **II** (74) **I/II** = 49:1		254

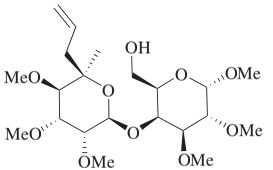
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}				
		AIBN, benzene, 80°, 13 h	 (32) +  (20) dr = 2:1	255
		AIBN, benzene, 80°, 2 h	 **I**	252



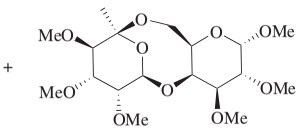


AIBN, benzene, 80°, 4 h



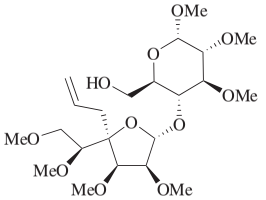
(51) 252

+



(36)

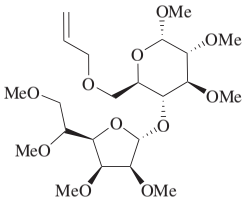
+



II

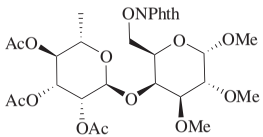
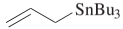
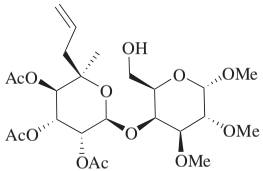
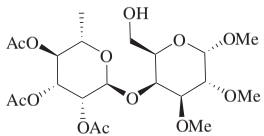
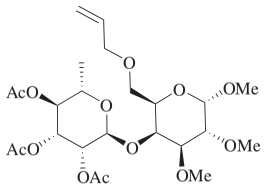
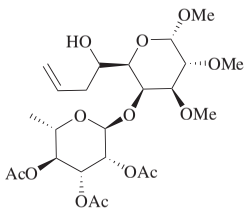
I + **II** (52) **I**/**II** = 1:1

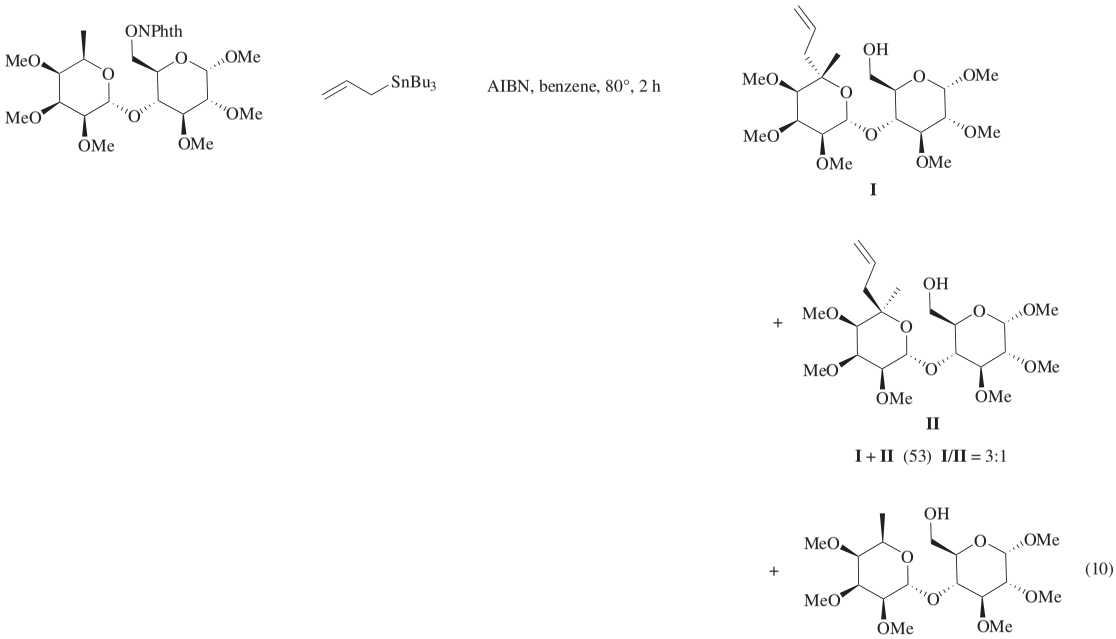
+



(22)

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}				
		AIBN, benzene, 80°, 4 h	 (42)	252
			+  (14)	
			+  (11)	
			+  (10)	

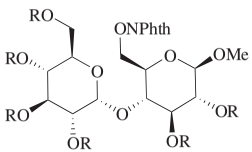
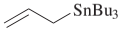
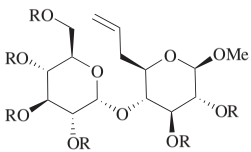
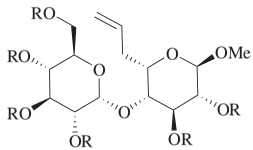
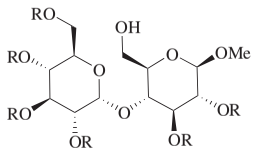


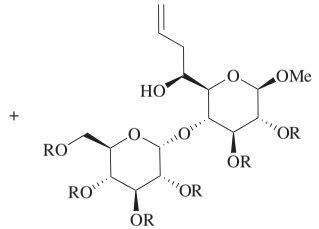
I + II (53) I/II = 3:1

(10)

252

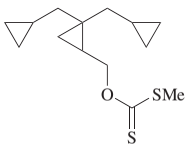
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

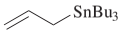
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12} 		AIBN, benzene, 80°	 **I** +  **II** +  **III**	252



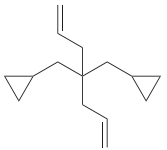
IV

R	Time (h)	**I + II**	**I/II**	**III**	**IV**
Me	5	(35)	2.3:1	(9)	(44)
Ac	4.5	(68)	2.5:1	(11)	(0)





AIBN, benzene, 80°, 12 h



(42)

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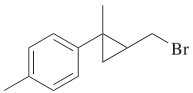
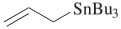
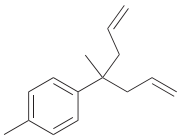




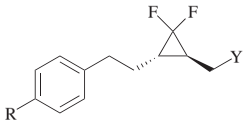
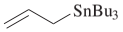
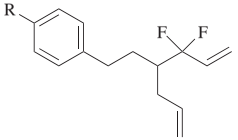
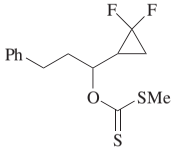
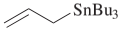
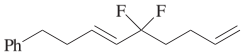
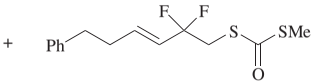
AIBN, toluene, 110°, 12 h



(72)

743

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}				
		AIBN, benzene, 80°, 12 h		733
			R / Y H / Br (77) H / MeS(S)CO (50) MeO / Br (68)	
	 *x* eq	Initiator (*y* eq), benzene, 80°, 12 h	 **I** +  **II**	733

x	Initiator	*y*	**I**	**II**
0	AIBN	0.25	(0)	(tr)
0.5	AIBN	0.4	(15)	(70)
0.5	ACCN	0.4	(14)	(74)
1	AIBN	0.25	(25)	(65)
4	AIBN	0.1	(50)[a]	(35)[a]
8	AIBN	0.1	(55)[a]	(22)[a]
16	AIBN	0.1	(75)	(15)

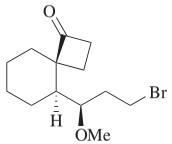
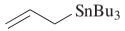
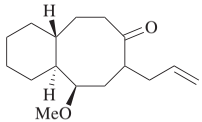
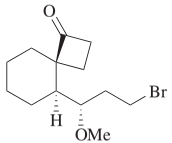
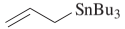
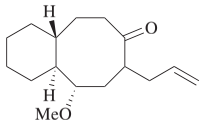
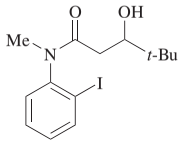
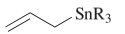
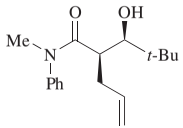
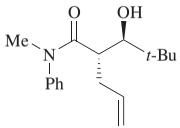
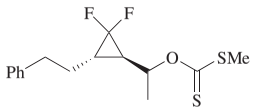
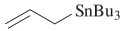
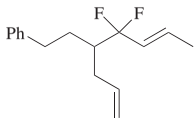
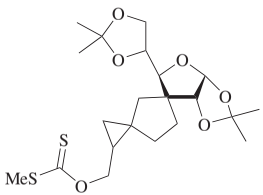
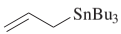
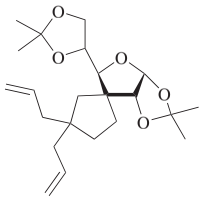
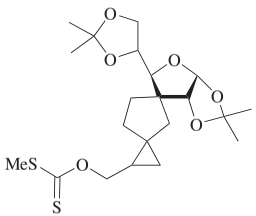
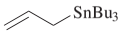
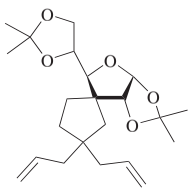
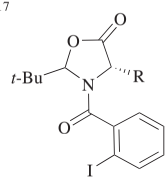
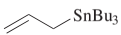
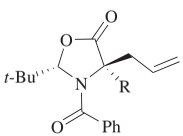
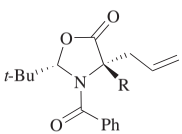
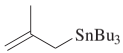
		AIBN, benzene, 80°, 6 h		(95) dr = 6:1	244
		AIBN, benzene, 80°, 6 h		(96) dr = 6:1	244, 245
C_{13} 	 R = n-$C_6F_{13}(CH_2)_3$	$h\nu$, BTF, 25°, 3–30 h	 +  **I** **II** **I** + **II** (63) **I**/**II** = 1:6.7		123
		AIBN, benzene, 80°, 12 h		(70) (E)/(Z) = 4.9:1	733

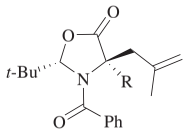
TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{13}				
		AIBN, benzene, 80°, 12 h	 (34)	250
		AIBN, benzene, 80°, 12 h	 (—)	250
$C_{14–17}$				
		*h*ν, AIBN, benzene, 25°, 8 h	 **I** +  **II**	253

R	I + II	I/II
H	(42)	>99:1
Me	(64)	4:1
i-Pr	(5)	>99:1

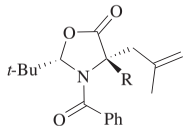


*h*ν, AIBN, benzene, 25°, 8 h



I

+

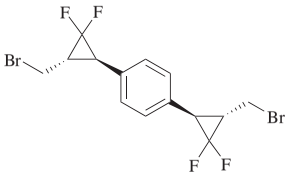


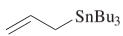
II

253

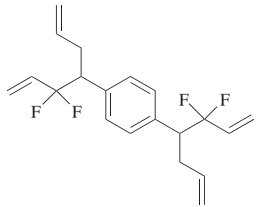
R	I + II	I/II
H	(43)	**I** only
Me	(39)	1.6:1
i-Pr	(3)	1.6:1

C_{14}





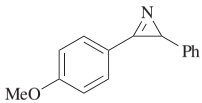
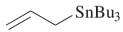
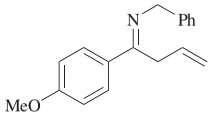
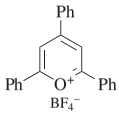
AIBN, benzene, 80°, 12 h



(72)

733

TABLE 4. ALLYLATIONS FOLLOWING OTHER REARRANGEMENTS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{14}				
		*h*ν, catalyst, solvent, 25°	 (—)	
			Catalyst / Solvent / Time (h)	
			Mes-Acr$^+$BF$_4^-$ / CH_2Cl_2 / o/n	744
			 / MeCN / 24	745

[a] The yield was determined by NMR spectroscopy.

[b] The *trans* isomer of the substrate was used.

[c] This is the overall yield for the two- or three-step process.

[d] The *cis* isomer of the substrate was used.

TABLE 5. INTRAMOLECULAR TRAPPING BY A STANNANE
A. SIMPLE CYCLIZATIONS

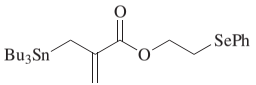
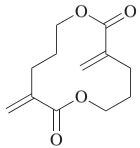
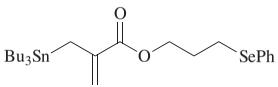
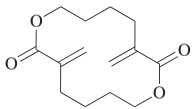
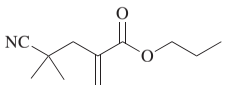
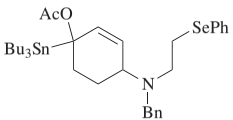
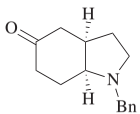
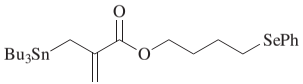
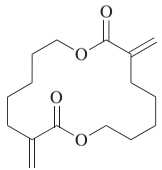
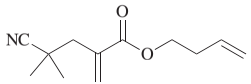
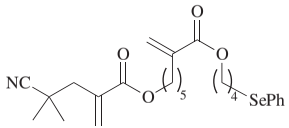
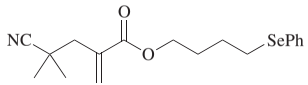
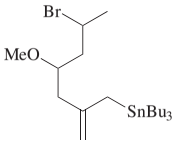
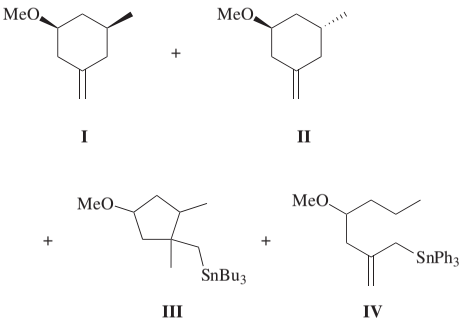
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_6			
	AIBN, Bu_3SnH (cat.), benzene, 80°, 48 h	 (34)	262, 263
C_7			
	AIBN, Bu_3SnH (cat.), benzene, 80°, 48 h	 (25)[a] +  (5)[a]	262, 263
C_8			
	1. AIBN, Bu_3SnH 2. SiO_2	 (—)	258

TABLE 5. INTRAMOLECULAR TRAPPING BY A STANNANE (*Continued*)
A. SIMPLE CYCLIZATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_8			
	AIBN, Bu_3SnH (cat.), benzene, 80°, 48 h	 (30)[a] +  (5)[a]	262, 263
		+  (5)[a]	
		+  (5)[a]	



A. Ph_3SnH, AIBN, C_6D_6; *or*
B. *h*ν, $(Me_3Sn)_2$, Ph_2CO, C_6D_6



I + **II** + **III** + **IV**

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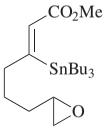
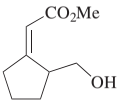
Conditions	Temp (°)	**I + II + III + IV**	**(I + II)/III/IV**	**I/II**
A	80	(—)	1.5:<0.2:1	1.6:1
B	40	(89)[a]	100:0:0	1.7:1



Cp_2TiCl, THF, rt



(83) (*E*)/(*Z*) 1:>49

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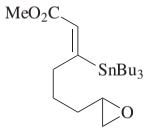
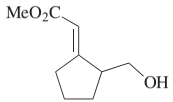
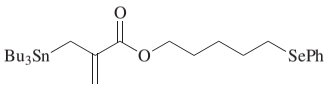
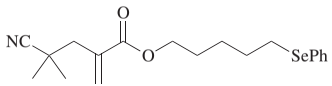
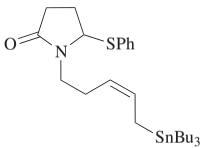
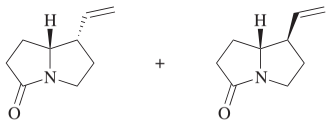
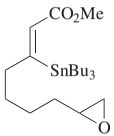
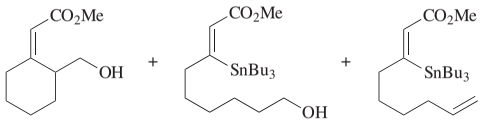
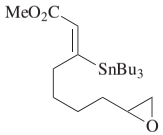
TABLE 5. INTRAMOLECULAR TRAPPING BY A STANNANE (*Continued*)

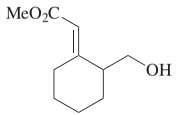
A. SIMPLE CYCLIZATIONS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_8 	Cp_2TiCl, THF, rt	 (86) (*E*)/(*Z*) > 49:1	301
C_9 	AIBN, Bu_3SnH (cat.), benzene, 80°, 48 h	 (21)	262, 263
	*h*ν, toluene, rt, 6 h	 **I** + **II** (45), **I**/**II** = 11.3:1	256, 257
	Cp_2TiCl, solvent	 **I** **II** **III**	301

Solvent	Temp	**I**	**II**	**III**
THF	rt	(0)	(—)	(0)
benzene	80°	(0)	(0)	(—)

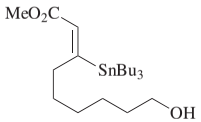


Cp_2TiCl, solvent



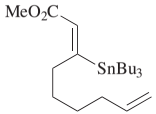
I

+



II

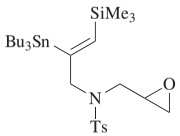
+



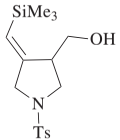
III

Solvent	Temp	**I**	**II**	**III**
THF	rt	(0)	(—)	(0)
benzene	80°	(0)	(0)	(—)

301



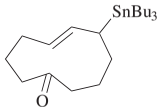
1. Cp_2TiCl, THF, rt, 0.5 h
2. H^+, H_2O



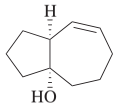
(78)[b] (*E*)/(*Z*) = 5:1

746

C_{10}

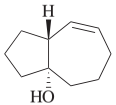


Conditions, solvent



I

+



II

Conditions	Solvent	Temp (°)	Time (min)	**I**	**II**
Na, naphthalene	THF	25	3	(56)	(0)
SmI_2	MeOH, THF	25	5	(51)	(13)
AIBN, Bu_3SnH	benzene	80	—	(—)	(—)

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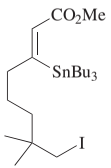
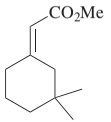
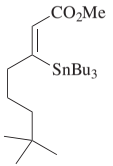
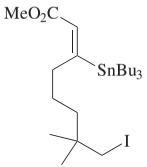
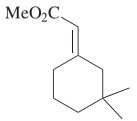
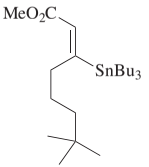
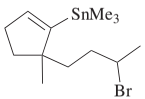
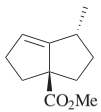
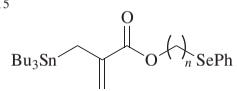
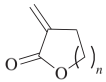
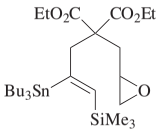
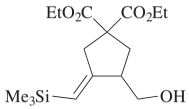
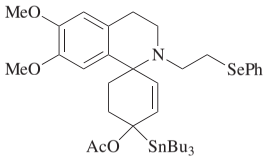
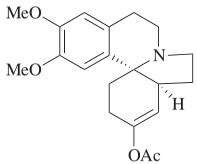
TABLE 5. INTRAMOLECULAR TRAPPING BY A STANNANE (*Continued*)
A. SIMPLE CYCLIZATIONS (*Continued*)

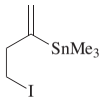
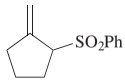
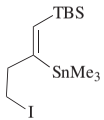
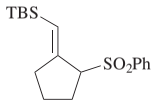
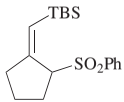
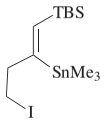
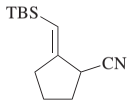
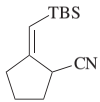
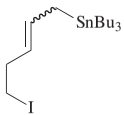
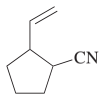
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{10} 	AIBN, Bu_3SnH, benzene, 85°	 +  (35) (*E*)/(*Z*) = 1:14 (—)	299
	AIBN, Bu_3SnH, benzene, 85°	 +  (48) (*E*)/(*Z*) = 77:1 (—)	299
	AIBN, Bu_3SnH, benzene, 80°, 10 h	 (90)	300

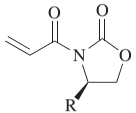
C_{10-15}		AIBN, Bu_3SnH (cat.), benzene, 80°, 48 h		*n* (%) 6 (54) 7 (46) 8 (61) 9 (50) 10 (80) 11 (72)	262, 263
C_{12}		1. Cp_2TiCl, THF, rt, 0.5 h 2. H^+, H_2O		(73)[b] (*E*)/(*Z*) = 1.7:1	746
C_{16}		AIBN, Bu_3SnH		(65)	258

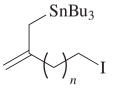
[a] The yield was determined by NMR spectroscopy.

[b] This is the overall yield for the two-step process.

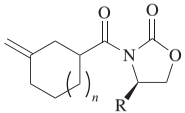
TABLE 5. INTRAMOLECULAR TRAPPING BY A STANNANE (*Continued*)
B. TWO-COMPONENT PROCESSES

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_2				
		AIBN, Bu_3SnH, benzene, 80°	 (0)	302
		AIBN, Bu_3SnH, benzene, 80°	 +  **I** **II**	302
			I + **II** (57) **I/II** = 32:1	
C_3				
		AIBN, Bu_3SnH, benzene, 80°	 +  **I** **II**	302
			I + **II** (56) **I/II** = 8.1:1	
		AIBN, Bu_3SnH, benzene, 80°	 (20–25)[a] dr = 1:1	302





Et_3B, O_2, Lewis acid,
CH_2Cl_2/THF (5:1), –78°



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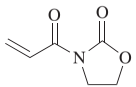
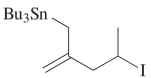
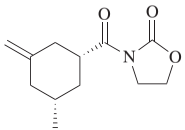
R	*n*	Lewis Acid		dr[b]
H	1	none	(66)	—
H	1	$Yb(OTf)_3$	(77)	—
H	1	$Y(OTf)_3$	(67)	—
H	1	$Sc(OTf)_3$	(36)	—
H	1	$Sm(OTf)_3$	(71)	—
H	1	$Zn(OTf)_2$	(72)	—
H	1	MgI_2	(<10)	—

R	*n*	Lewis Acid		dr[b]
H	1	$MgBr_2$	(<10)	—
H	1	$Mg(ClO_4)_2$	(33)	—
Ph	1	$Yb(OTf)_3$	(91)	1.5:1
Ph_2CH	1	$Yb(OTf)_3$	(83)	>99:1
H	2	$Yb(OTf)_3$	(61)	—
H	2	$Zn(OTf)_2$	(56)	—



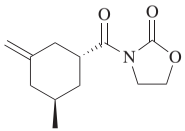


Et_3B, O_2, $Yb(OTf)_3$,
CH_2Cl_2/THF (5:1), –78°



I

+



II

I + **II** (68) **I**/**II** = 7:1

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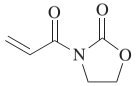
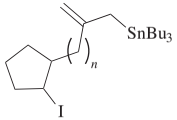
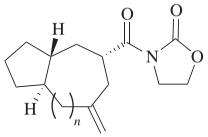
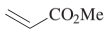
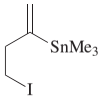
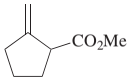
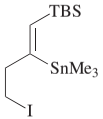
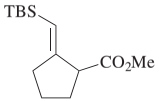
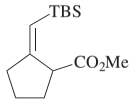
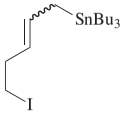
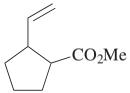
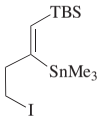
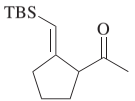
TABLE 5. INTRAMOLECULAR TRAPPING BY A STANNANE (*Continued*)
B. TWO-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Et_3B,O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (5:1), –78°	 *n* (dr[c]): 0 (65) 5.2:1; 1 (80) 9:1	264
		AIBN, Bu_3SnH, benzene, 80°	 (0)	302
		AIBN, Bu_3SnH, benzene, 80°	 **I** +  **II** **I** + **II** (56) **I/II** = 98:1	302
		AIBN, Bu_3SnH, benzene, 80°	 (20–25)[a] dr = 1:1	302

C_4

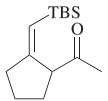


AIBN, Bu_3SnH, benzene, 80°



I

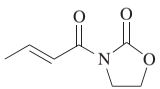
+

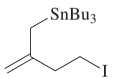


II

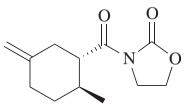
302

I + II (53) **I/II** = 32:1



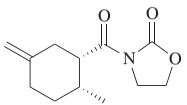


Et_3B, O_2, Lewis acid,
CH_2Cl_2/THF (5:1), –78°



I

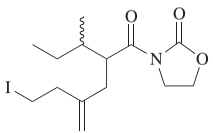
+



II

264

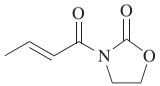
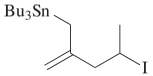
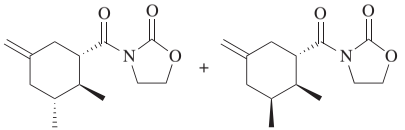
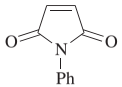
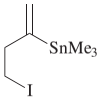
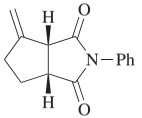
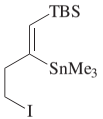
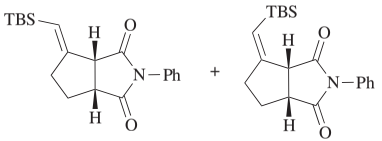
+

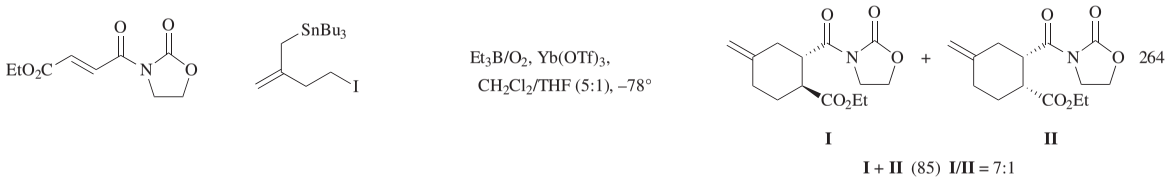


III

Lewis Acid	**I + II**	**I/II**	**III**
$Sc(OTf)_3$	(63)	20:1	(—)
$Yb(OTf)_3$	(10)	—	(>30)

TABLE 5. INTRAMOLECULAR TRAPPING BY A STANNANE (*Continued*)
B. TWO-COMPONENT PROCESSES (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		Et_3B/O_2, $Yb(OTf)_3$, CH_2Cl_2/THF (5:1), –78°	 **I** + **II** (85) **I/II** = 1.5:1	264
		AIBN, Bu_3SnH, benzene, 80°	 (59)	302
		AIBN, Bu_3SnH, benzene, 80°, 6 h	 **I** + **II** (57) **I/II** = 4:1	302

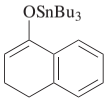
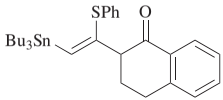
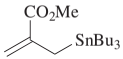
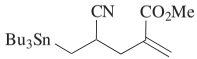
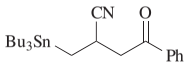
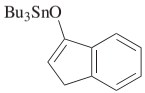
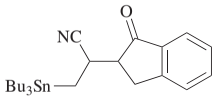
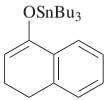
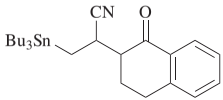
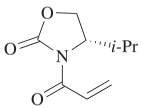
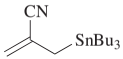
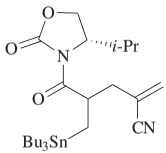


[a] Specific yields were not given.

[b] The major diastereomer was not identified

[c] The configuration of the minor product was not determined.

TABLE 6. ALLYLSTANNYLATION REACTIONS

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_2				
		AIBN, benzene, 80°, 4 h	 (16)	270
C_3				
		AIBN, benzene, 80°, 4 h	 (83)	265, 266
		AIBN, benzene, 80°	 (31)	270
		AIBN, benzene, 80°, 5 h	 (62) dr = 1.1:1	270
		AIBN, benzene, 80°, 5 h	 (62) dr = 1.04:1	270
		AIBN, benzene, 80°, 1 h	 (78) dr = 2.6:1	266

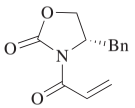
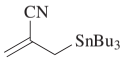
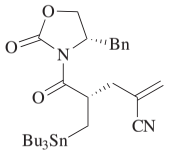
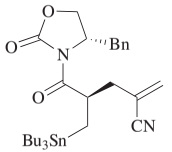
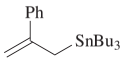
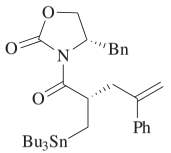
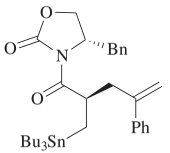
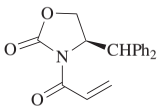
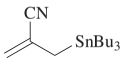
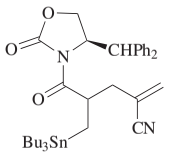
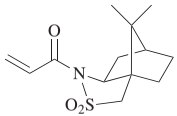
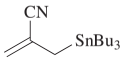
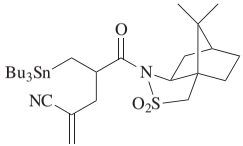
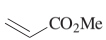
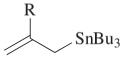
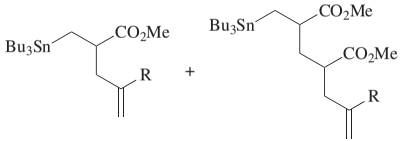
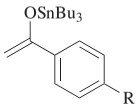
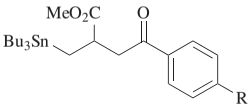
		AIBN, benzene, 80°, 1 h	 (49) +  (22)	266
		AIBN, benzene, 80°, 4 h	 **I** +  **II** **I + II** (78) **I/II** = 1.9:1	266
		AIBN, benzene, 80°, 1 h	 (61) dr = 1.6:1	266

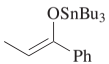
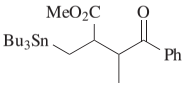
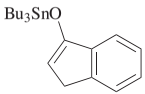
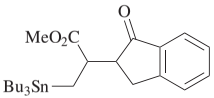
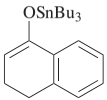
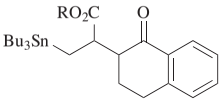
TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		AIBN, benzene, 80°, 24 h	 (0)	266
	 *x* eq	AIBN, benzene, 80°	 **I** + **II**	265, 266

R	*x*	Time (h)	**I**	**II**	**II** dr
H	4	4	(13)	(40)	1.5:1
Me	4	2	(21)	(47)	1.5:1
MeO_2C	2	—	(77)	(0)	—
MeO_2C	4	1	(88)	(0)	—
NC–	4	2	(81)	(0)	—
Ph	4	2	(69)	(<3)	—
Me_3Si	4	4	(48)	(33)	1.5:1

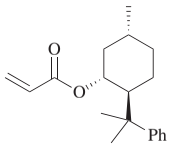
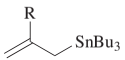
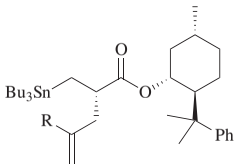
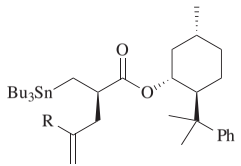
		AIBN, benzene, 80°		270

R	Time (h)	
H	—	(40)
F	2	(39)
MeO	3	(0)

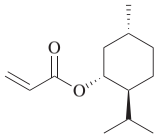
		AIBN, benzene, 80°, 2 h	 (33) dr = 1.9:1	270
		AIBN, benzene, 80°, 2 h	 (48) dr = 1.8:1	270
		AIBN, benzene, 80°, 3 h	 dr = 1.9:1	270

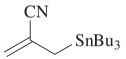
R	
Me	(72)
c-C_6H_{11}	(76)

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

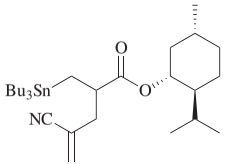
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Initiator, solvent	 **I** +  **II**	266

R	Initiator	Solvent	Temp (°)	Time (h)	**I + II**	**I/II**
Me	AIBN	benzene	80	4	(39)	1.7:1
MeO_2C	AIBN	benzene	80	4	(68)	2.3:1
MeO_2C	Et_3B/air	hexane	25	24	(68)	6.7:1
NC–	AIBN	EtOAc	77	4	(82)	4.9:1
NC–	AIBN	THF	67	4	(47)	4.9:1
NC–	AIBN	hexane	69	4	(69)	6.1:1
NC–	Et_3B/air	hexane	25	24	(72)	9:1
NC–	Et_3B/air	hexane	–78	10	(38)	10.1:1
Ph	AIBN	benzene	80	4	(81)	5.3:1
Ph	Et_3B/air	hexane	25	24	(39)	6.7:1

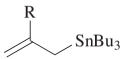




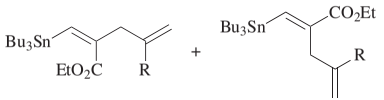
AIBN, benzene, 80°, 4 h



(79) dr = 1.7:1 266

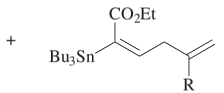


AIBN, benzene, 80°



266, 268

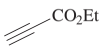
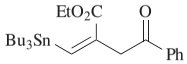
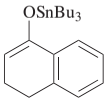
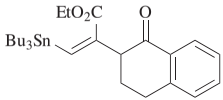
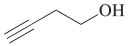
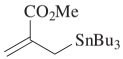
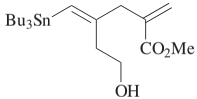
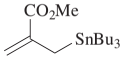
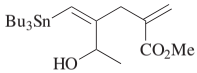
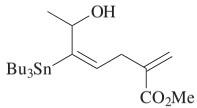
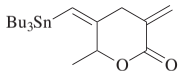
I **II**



III

R	Time (h)	**I**	**II + III**	**II/III**
H	4	(12)[a]	(<1)	66:34[a]
Me	2	(27)[a]	(<2)	75:25[a]
MeO_2C	1	(70)	(<15)	73:27[a]
NC–	1	(66)	(11)	>99:1[a]
Me_3Si	2	(38)	(<2)	50:50[a]
Ph	1	(61)	(<5)	34:66[a]

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		AIBN, benzene, 80°, 5 h	 (26)	270
		AIBN, benzene, 80°, 5 h	 (66) (*E*)/(*Z*) = 1:4.6	270
C_4				
		AIBN, benzene, 80°, 2 h	 (69)	266, 268
		AIBN, benzene, 80°, 2 h	 **I**	266, 268
			+  **II**	
			I + II (39) **I/II** = 6.8:1	
			+  (< 4)	

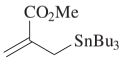
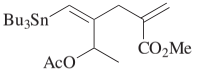
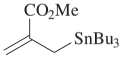
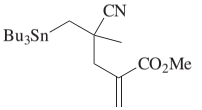
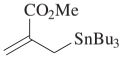
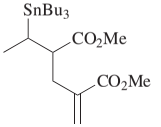
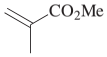
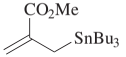
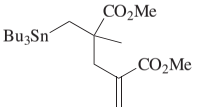
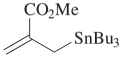
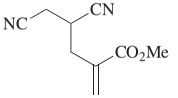
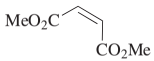
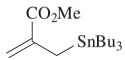
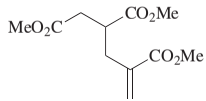
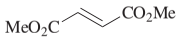
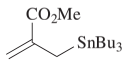
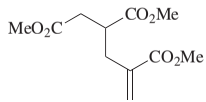
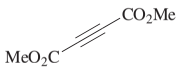
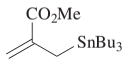
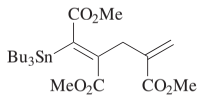
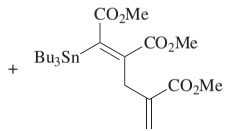
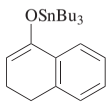
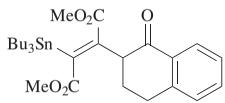
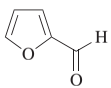
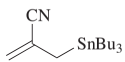
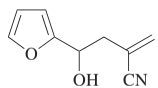
		AIBN, benzene, 80°, 2 h		(62)	266, 268
		AIBN, benzene, 80°, 4 h		(62)	265, 266
		AIBN, benzene, 80°		(0)	265, 266
		AIBN, benzene, 80°, 2 h		(63)	265, 266
		1. AIBN, benzene, 80°, 4 h 2. HCl, MeCN, rt		(76)[b]	265, 266

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_4				
		1. AIBN, benzene, 80°, 4 h 2. HCl, MeCN, rt	 (67)[b]	265, 266
		1. AIBN, benzene, 80°, 2 h 2. HCl, MeCN, rt	 (40)[b]	265, 266
		AIBN, benzene, 80°, 1 h	 (85) +  (<1)	266, 268
		AIBN, benzene, 80°, 4 h	 (41)	270
C_5				
		1. AIBN, benzene, 80°, 8 h 2. DBU; then silica	 (53)[b]	266

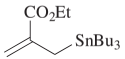
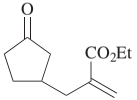
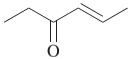
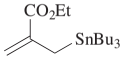
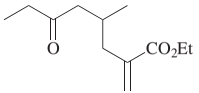
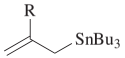
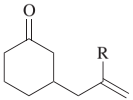
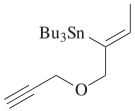
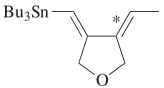
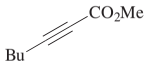
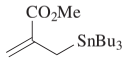
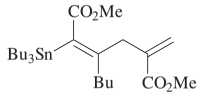
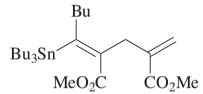
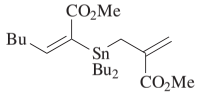
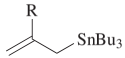
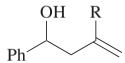
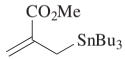
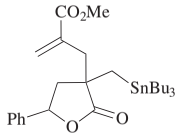
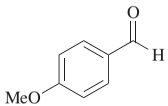
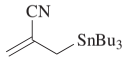
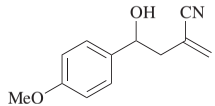
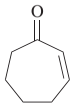
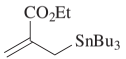
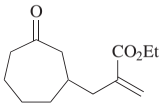
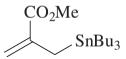
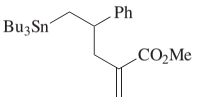
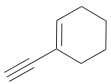
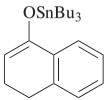
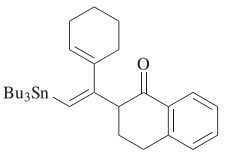
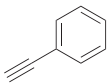
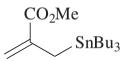
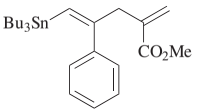
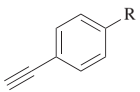
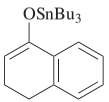
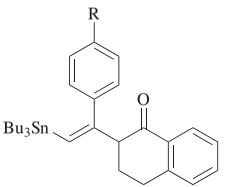
			AIBN, benzene, 80°, 10 h		(58)	271
C_6			AIBN, benzene, 80°, 10 h		(65)	271
			AIBN, benzene, 80°		R / Time (h): H / 24 / (0); EtO_2C / 10 / (61)	271
C_7	 (*E*)/(*Z*) = 1:24	—	AIBN, Bu_3SnH (0.4 eq), benzene, 80°, 3 h		(48) *dr = 4.6:1	276

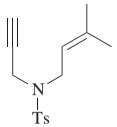
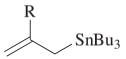
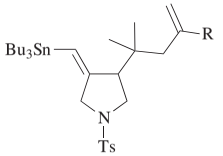
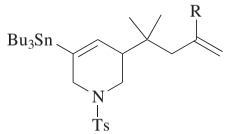
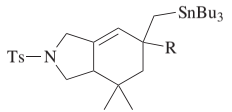
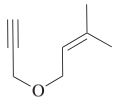
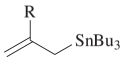
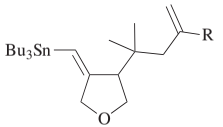
TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		AIBN, benzene, 80°, 2 h	 (38)	266, 268
			+  (15)	
			+  (7) (*E*)/(*Z*) = 6.7:1	
		1. AIBN, benzene, 80°, 8 h 2. DBU; then silica	 R: H (0)[b]; NC– (59)[b]	266
		1. AIBN, benzene, 80°, 8 h 2. DBU; then silica	 (45)[b] dr = 13.3:1	266
		1. AIBN, benzene, 80°, 8 h 2. DBU; then silica	 (35)[b]	266

			AIBN, benzene, 80°, 10 h	 (67)	271
C_8					
			AIBN, benzene, 80°, 2 h	 (40)	265, 266
			AIBN, benzene, 80°, 5 h	 (50)	270
			AIBN, benzene, 80°, 1 h	 (94)	266, 268
C_{8-9}					
			AIBN, benzene, 80°		270

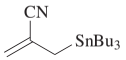
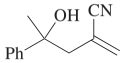
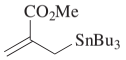
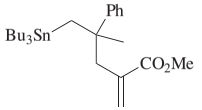
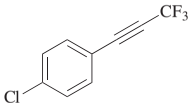
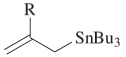
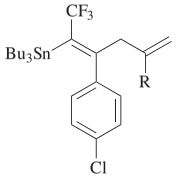
R	Time (h)	
H	4	(70)
Me	5	(69)

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, benzene, 80°	 **I** +  **II** +  **III** dr = 13.3:1	32
		AIBN, benzene, 80°		32

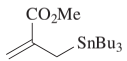
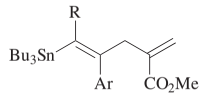
R	Time (h)	**I**	**II + III**	**II/III**
MeO_2C	2	(77)	(9)	>99:1
NC–	7	(51)	(17)	1:1.4
Ph	8	(71)	(7)	>99:1

R	Time (h)	
MeO_2C	6	(70)
Ph	10	(75)

		1. AIBN, benzene, 80°, 8 h 2. DBU; then silica		(29)[b]	266
C_9					
		AIBN, benzene, 80°, 2 h		(7)	265, 276
		Initiator, benzene, 80°, 2 h			269

R	Initiator	
H	AIBN	(tr)[a]
H	air	(0)[a]
Me	AIBN	(tr)[a]
Me	air	(0)[a]
MeO_2C	AIBN	(60)
MeO_2C	air	(92)
NC–	AIBN	(67)[a]
NC–	air	(37)[a]

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{9-11}				
		Initiator, benzene, 80°		269

R	Ar	Initiator	Time (h)	
CF_3	Ph	AIBN	2	(79)[a]
CF_3	Ph	air	12	(90)
CF_3	2-ClC_6H_4	AIBN	2	(85)[a]
CF_3	2-ClC_6H_4	air	2	(83)
CF_3	3-ClC_6H_4	AIBN	2	(81)[a]
CF_3	3-ClC_6H_4	air	12	(83)
CF_3	4-ClC_6H_4	AIBN	2	(60)
CF_3	4-ClC_6H_4	air	12	(92)
CF_3	4-$MeOC_6H_4$	AIBN	2	(84)[a]
CF_3	4-$MeOC_6H_4$	air	12	(86)
CF_3	4-MeC_6H_4	AIBN	2	(91)[a]
CF_3	4-MeC_6H_4	air	12	(94)
CF_3	4-$EtO_2CC_6H_4$	AIBN	2	(90)[a]
CF_3	4-$EtO_2CC_6H_4$	air	12	(86)
CF_3	4-$MeOC_6H_4CH_2$	AIBN	2	(44)
CF_3	4-$MeOC_6H_4CH_2$	air	12	(0)[a]
CHF_2	4-ClC_6H_4	AIBN	2	(99)
CHF_2	4-ClC_6H_4	air	22	(73)[a]
$CHF_2CF_2CF_2$	4-ClC_6H_4	AIBN	2	(78)
$CHF_2CF_2CF_2$	4-ClC_6H_4	air	12	(28)[a]

C_9

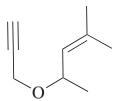
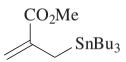
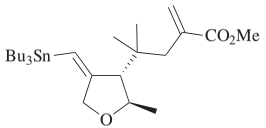
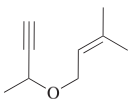
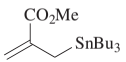
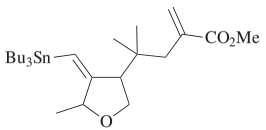
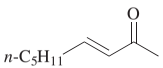
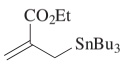
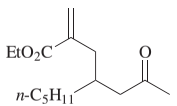
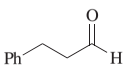
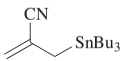
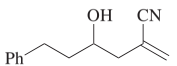
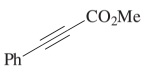
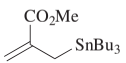
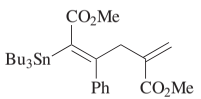
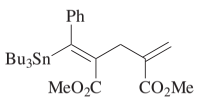
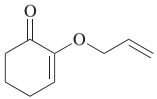
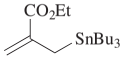
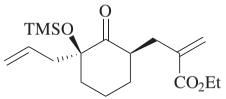
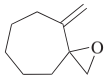
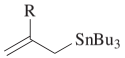
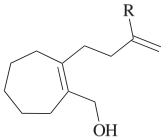
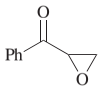
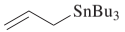
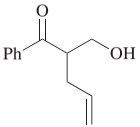
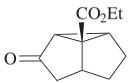
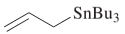
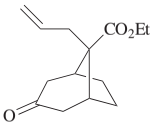
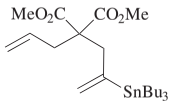
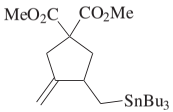
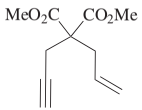
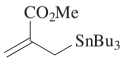
		AIBN, benzene, 80°, 6 h		(75)	32
		AIBN, benzene, 80°, 6 h		(68) dr = 1.6:1	32
		AIBN, benzene, 80°, 10 h		(63)	271
		1. AIBN, benzene, 80°, 8 h 2. DBU; then silica		(0)[b]	276
		AIBN, benzene, 80°, 1 h		(84)	266, 268
			+ 	(2)	

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

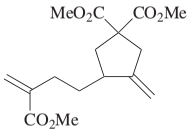
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_9				
		1. AIBN, benzene, 80°, 12 h 2. TMSCl	 (40)[b]	577
		AIBN, toluene, 80°, 2 h	 R: EtO_2C (63); NC– (87)	275
		AIBN, benzene, 80°, 2 h	 (81)	274
		AIBN, benzene, 80°, 16 h	 (94)	272, 273
	—	AIBN, Bu_3SnH (0.1 eq), benzene, 80°, 3 h	 (19)	276



x M

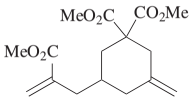


1. AIBN, benzene, 80°, time
2. HCl, MeCN, rt, 10 min



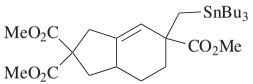
I

+



II

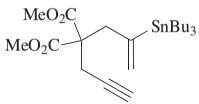
+



III

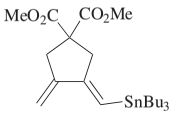
x	Time (h)	**I + II**	**I/II**	**III**
0.2	5	(55)[b]	61:39	(2)[b]
0.02	7	(70)[b]	18:82	(0)[b]

32



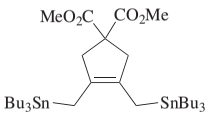
—

AIBN, Bu_3SnH (0.1 eq), benzene, 80°, 3 h



(0)

+



(5)

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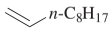
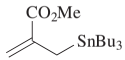
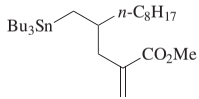
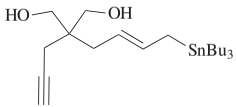
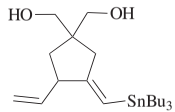
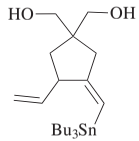
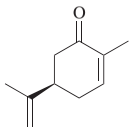
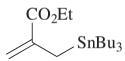
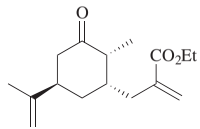
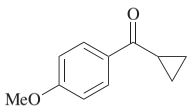
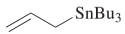
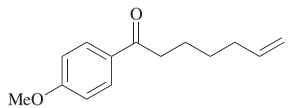
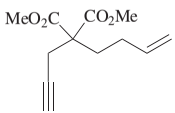
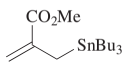
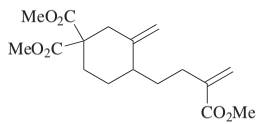
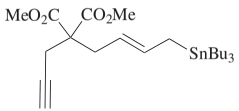
TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

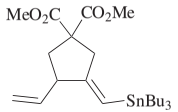
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
		AIBN, benzene, 80°, 24 h	 (0)	265, 266
 (*E*)/(*Z*) = 4:1	—	AIBN, Bu_3SnH (0.1 eq), benzene, 80°, 3 h	 (84) +  (9)	276
		AIBN, benzene, 80°, 10 h	 (69)	271
		AIBN, benzene, 80°, 24 h	 (24)	272
		1. AIBN, benzene, 80°, 5 h 2. HCl, MeCN, rt, 10 min	 (60)[b]	32



(*E*)/(*Z*) = 4.3:1

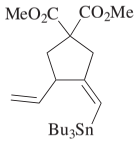
—

AIBN, Bu_3SnH (*x* eq), benzene, 80°, 3 h



I

+

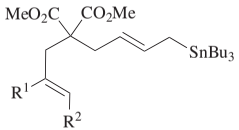


II

276

x	**I**	**II**
0	(<10)	(—)
0.1	(82)	(6)

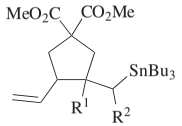
C_{10-16}



(*E*)/(*Z*) ≈ 4:1

—

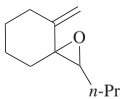
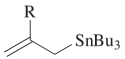
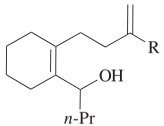
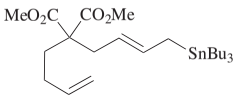
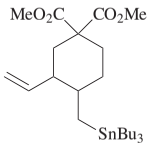
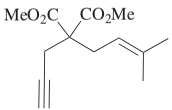
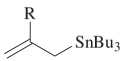
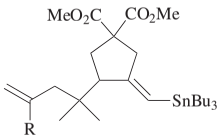
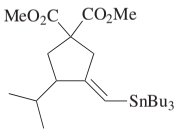
AIBN, Bu_3SnH (0.1 eq), benzene, 80°, 3 h

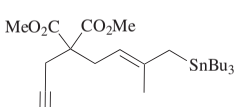


276

R^1	R^2		*cis*/*trans*
H	H	(88)	4.6:1
H	Me	(0)	—
Me	H	(90)	1:1.4
NC–	H	(96)	2.1:1
Ph	H	(100)	1.2:1

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

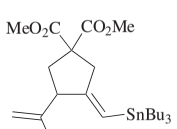
Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11}				
		AIBN, toluene, 80°, 2 h	 R: H (0); Me (0); EtO_2C (70); NC– (86)	275
 (*E*)/(*Z*) ≈ 4:1	—	AIBN, Bu_3SnH (0.1 eq), benzene, 80°, 3 h	 (0)	276
		AIBN, benzene, 80°	 **I** +  **II**	32



dr = 1.8:1

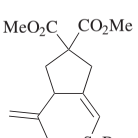
—

AIBN, Bu_3SnH (0.1 eq),
benzene, 80°, 3 h



(81)

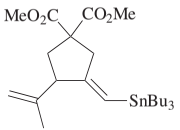
+



(9)

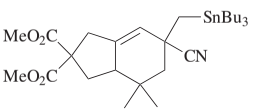
276

+



III

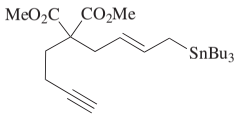
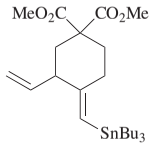
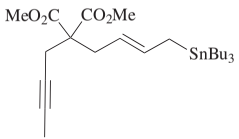
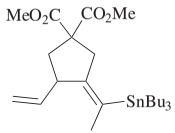
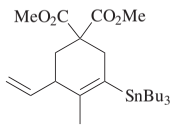
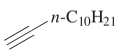
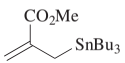
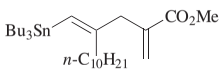
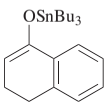
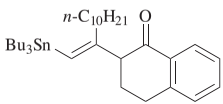
+



IV

R	Time (h)	**I + II + III**	**I/II/III**	**IV**
H	10	(39)	80:11:9	(0)
Me	10	(38)	70:17:13	(0)
MeO_2C	3	(87)	**I** only	(0)
NC–	5	(59)	**I** only	(19)
Me_3Si	10	(63)	**I** only	(0)
Ph	5	(78)	**I** only	(0)

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{11}				
 (*E*)/(*Z*) = 4:1	—	AIBN, Bu_3SnH (0.1 eq), benzene, 80°, 3 h	 (68)	276
 (*E*)/(*Z*) = 4.3:1	—	AIBN (*x* eq), Bu_3SnH (*y* eq), benzene, 80°, 3 h	 **I** +  **II**	276
C_{12}				
		AIBN, benzene, 80°, 6 h	 (44)	266, 268
		AIBN, benzene, 80°, 5 h	 (15)	270

x	*y*	**I + II**	**I/II**
0.05	0.1	(22)	3.2:1
0.2	0.4	(65)	3.2:1

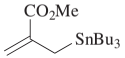
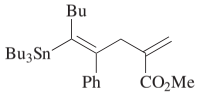
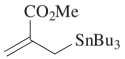
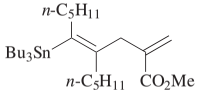
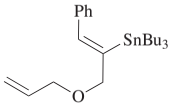
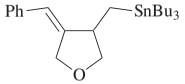
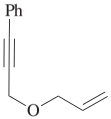
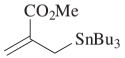
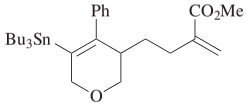
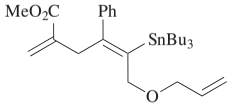
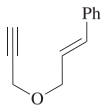
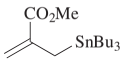
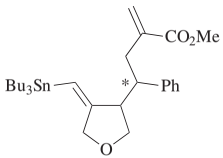
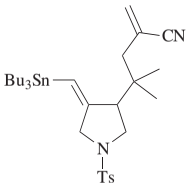
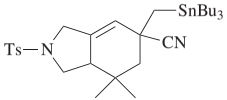
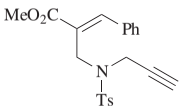
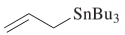
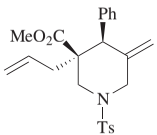
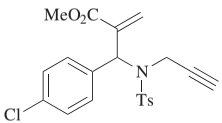
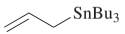
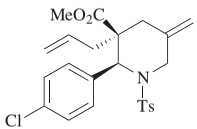
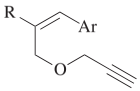
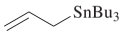
		AIBN, benzene, 80°, 6 h		(19)	266, 268
		AIBN, benzene, 80°, 24 h		(0)	266, 268
	—	AIBN, Bu_3SnH (0.1 eq), benzene, 80°, 3 h		(73) (*E*)/(*Z*) = 1:3.3	276
		AIBN, benzene, 80°, 10 h		(34)	32
			+ 	(22)	

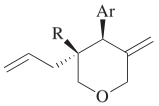
TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{12}				
		AIBN, benzene, 80°, 10 h	 (70) *dr = 6.1:1	32
	—	AIBN, Bu_3SnH (0.2 eq), benzene, 80°, 10 h	 (52) dr = 13.3:1	32
C_{13}				
		1. AIBN, neat, 80°, 1 h 2. HCl, Et_2O, 0–25°, 1 h	 (79)[b]	747
		1. AIBN, neat, 80°, 1 h 2. HCl, Et_2O, 0–25°, 1 h	 (63)[b]	747



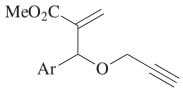


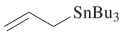
1. AIBN, neat, 80°, 1 h
2. HCl, Et_2O, 0–25°, 1 h



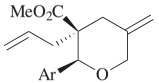
R	Ar	
$HOCH_2$	Ph	(0)[b]
MeO_2C	Ph	(82)[b]
MeO_2C	4-ClC_6H_4	(81)[b]
NC–	Ph	(<5)[b]

747





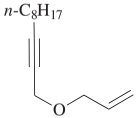
1. AIBN, neat, 80°, 1 h
2. HCl, Et_2O, 0° to 25°, 1 h

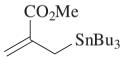


Ar	
Ph	(75)[b]
4-ClC_6H_4	(88)[b]

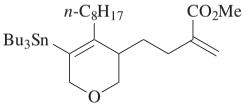
747

C_{14}





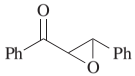
AIBN, benzene, 80°, 10 h

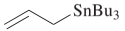


(0)

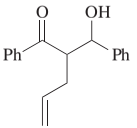
32

C_{15}





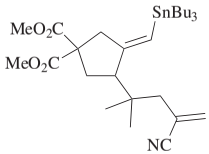
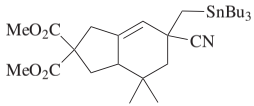
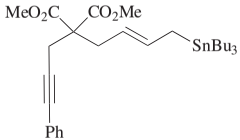
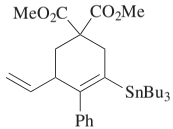
AIBN, benzene, 80°, 2 h



(69) dr = 1:1

274

TABLE 6. ALLYLSTANNYLATION REACTIONS (*Continued*)

Substrate	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{15} 	—	AIBN, Bu_3SnH (0.2 eq), benzene, 80°, 3 h	 (64) dr = 5.7:1	32
C_{16}  (*E*)/(*Z*) = 76:24	—	AIBN (*x* eq), Bu_3SnH (*y* eq), benzene, 80°, 3 h	 *x* / *y* / (%): 0.05 / 0.1 / (20); 0.2 / 0.4 / (87)	276

[a] The yield or ratio was determined by NMR spectroscopy.

[b] This is the overall yield for the two-step process.

TABLE 7. ADDITIONS TO STANNYL ENOLATES

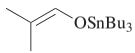
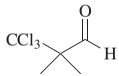
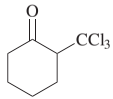
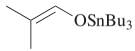
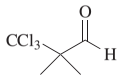
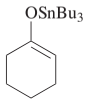
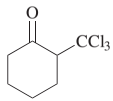
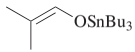
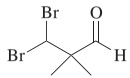
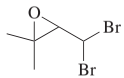
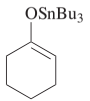
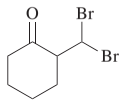
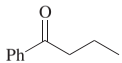
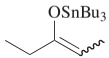
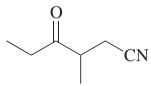
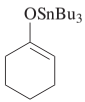
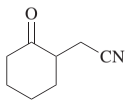
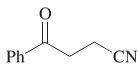
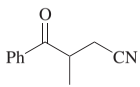
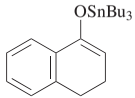
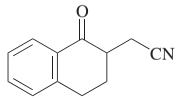
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_1				
CCl_4		$h\nu$, CCl_4, 35°, 2 h	 (54)[a]	140
		$h\nu$, CCl_4, 35°, 2 h	 (59)[a]	140
CCl_3Br		$h\nu$, CCl_3Br, 35°, 5 min	 (48)[a]	140
		$h\nu$, CCl_3Br, 35°, 3 h	 (64)[a]	140
$CHBr_3$		$h\nu$, $CHBr_3$, 35°, 3 h	 (18)[a] +  (6)[a]	140
		$h\nu$, $CHBr_3$, 35°, 1 h	 (29)[a]	140

TABLE 7. ADDITIONS TO STANNYL ENOLATES (*Continued*)

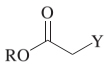
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
		AIBN, benzene, 80°, 4 h	 (79)	142
		Initiator, solvent		142
		Initiator / Solvent / Temp / Time (h)		
		Et_3B, air / hexane / rt / 9	(72)	
		AIBN / benzene / 80° / 4	(90)	
		Et_3B, air, hexane, rt, 9 h	 (98)	142
		AIBN, benzene, 80°, 4 h	 (89)	142
	(Z)/(E) > 49:1	AIBN, benzene, 80°, 4 h	 (95)	142



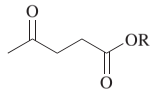
AIBN, benzene, 80°, 4 h



(100) 142

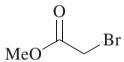


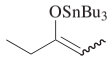
Conditions, initiator, benzene



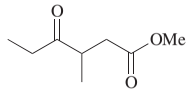
141

R	Y	Conditions	Initiator	Temp	Time (h)	
Me	PhS	*hν*	none	rt	1	(65)
Me	PhSe	*hν*	none	rt	1	(81)
Me	PhSe	—	AIBN	80°	2	(54)
Et	Br	*hν*	none	rt	1	(50)
Et	I	*hν*	none	rt	1	(74)





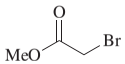
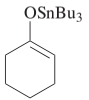
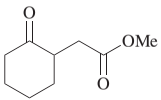
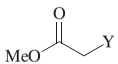
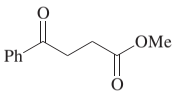
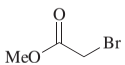
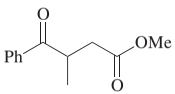
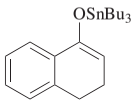
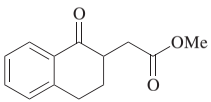
Initiator, solvent



142

Initiator	Solvent	Temp	Time (h)	
Et_3B, air	hexane	rt	9	(80)
AIBN	benzene	80°	4	(88)

TABLE 7. ADDITIONS TO STANNYL ENOLATES (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_2				
		Initiator, solvent		142
			Initiator / Solvent / Temp / Time (h): Et_3B, air / hexane / rt / 9 (90); AIBN / benzene / 80° / 4 (69)	
		AIBN, benzene, 80°, 4 h	 Y: Br (94); PhO(S)CO (88); PhS (42)	142
	(*Z*)/(*E*) > 49:1	AIBN, benzene, 80°, 4 h	 (95)	142
		AIBN, benzene, 80°, 4 h	 (100)	142

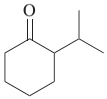
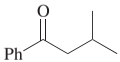
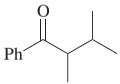
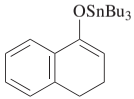
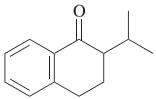
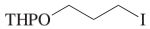
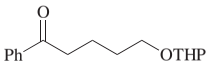
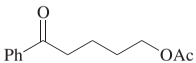
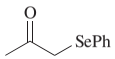
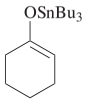
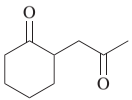
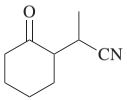
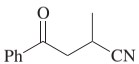
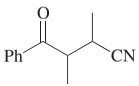
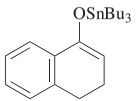
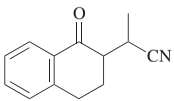
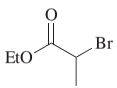
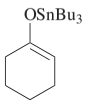
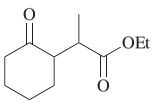
C_3					
		AIBN, benzene, 80°		(0)	142
		AIBN, benzene, 80°, 4 h		Y Br (89) I (97) PhO(S)CO (63)	142
	 (Z)/(E) > 49:1	AIBN, benzene, 80°, 4 h		(19)	142
		AIBN, benzene, 80°, 4 h		(46)	142
		AIBN, benzene, 80°, 4 h		(70)	142
		AIBN, benzene, 80°, 4 h		(81)	142

TABLE 7. ADDITIONS TO STANNYL ENOLATES (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		*h*ν, benzene, rt, 2 h	 (76)	141
		Et_3B, air, hexane, rt, 9 h	 (26)	142
		AIBN, benzene, 80°, 4 h	 (100)	142
	(*Z*)/(*E*) > 49:1	AIBN, benzene, 80°, 4 h	 (95)	142
		AIBN, benzene, 80°, 4 h	 (100)	142
		Et_3B, air, hexane, rt, 9 h	 (15)	142

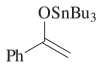
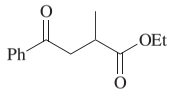
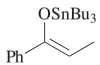
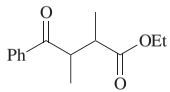
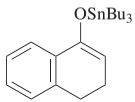
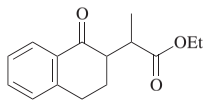
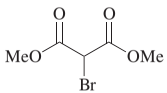
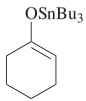
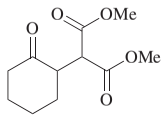
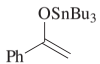
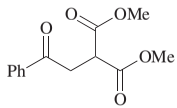
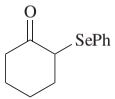
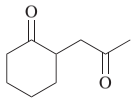
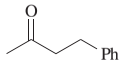
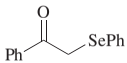
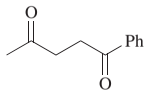
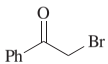
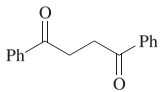
		AIBN, benzene, 80°, 4 h		(95)	142
	 (Z)/(E) > 49:1	AIBN, benzene, 80°, 4 h		(95)	142
		AIBN, benzene, 80°, 4 h		(100)	142
		Et_3B, air, hexane, rt, 9 h		(95)	142
		AIBN, benzene, 80°, 4 h		(100)	142

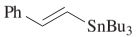
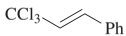
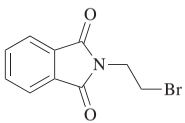
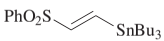
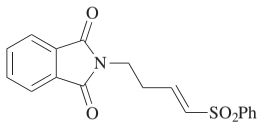
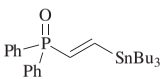
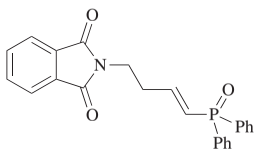
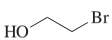
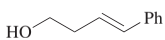
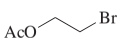
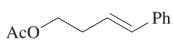
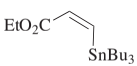
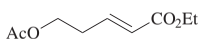
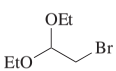
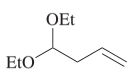
TABLE 7. ADDITIONS TO STANNYL ENOLATES (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_4				
t-BuI	OSnBu$_3$	AIBN, benzene, 80°	O, *t*-Bu (0)	142
	OSnBu$_3$, Ph	AIBN, benzene, 80°, 4 h	O, Ph, *t*-Bu (100)	142
SePh, O, O	OSnBu$_3$	*h*ν, benzene, rt, 1 h	O, O, O (80)	141
O, RO, Y	OSnBu$_3$	*h*ν, benzene, rt	O, OR, O	141
			R / Y / Time (h): Me / I / 12 (0); Et / PhSe / 10 (0)	
C_5				
O, SePh	OSnBu$_3$	*h*ν, benzene, rt, 3 h	O, O (82)	141

C_6			*h*ν, benzene, rt, 1.5 h	 (71)	141
C_7			*h*ν, benzene, rt, 6 h	 (45)	141
C_8			*h*ν, benzene, rt, 2 h	 (80)	141
			AIBN, benzene, 80°, 4 h	 (85)	142

[a] The yield was determined by NMR spectroscopy.

TABLE 8. VINYLATION REACTIONS

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_1				
CCl_4		*h*ν, CCl_4, 35°, 38 h	 (62)[a] (*E*)/(*Z*) = 19:1	292
C_2				
		*h*ν, AIBN, benzene, rt, 12 h	 (77)	294
		*h*ν, AIBN, benzene, rt, 12 h	 (58) (*E*)/(*Z*) = 10:1	294
		AIBN, toluene, 86°, 24–36 h	 (32)	288
		AIBN, toluene, 86°, 24–36 h	 (41)	288
		AIBN, toluene, 86°, 24–36 h	 (43)	288
		AIBN, toluene, 86°	 (0)	288

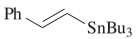
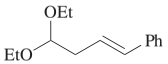
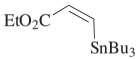
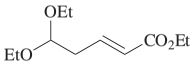
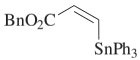
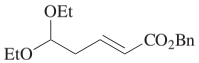
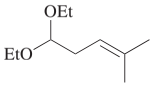
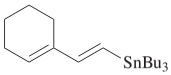
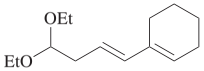
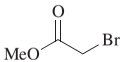
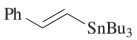
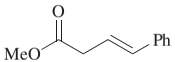
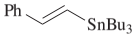
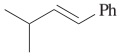
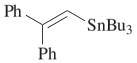
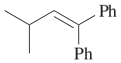
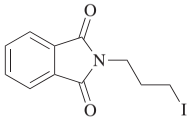
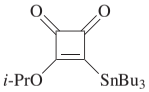
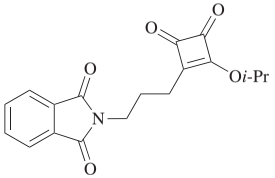
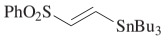
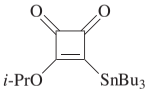
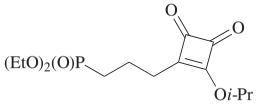
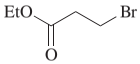
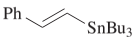
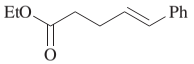
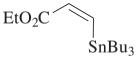
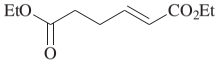
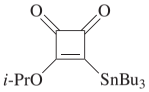
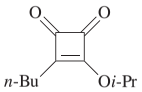
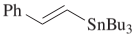
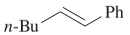
		AIBN, toluene, 86°, 24–36 h		(52)	288
		AIBN, toluene, 86°, 24–36 h		(52)	288
		AIBN, toluene, 86°, 24–36 h		(34)	288
		AIBN, toluene, 86°		(0)	288
		AIBN, toluene, 86°, 1–10 d		(0)	288
		$h\nu$, benzene, 35°, 44 h		(38)[a] $(E)/(Z) = 5:1$	292

TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		Conditions, initator, benzene		

Y	Conditions	Initiator	Temp (°)	Time (h)		(*E*)/(*Z*)	
I	*hν*	none	35	15	(18)[a]	—	292
ClHg	*hν*	none	35	18	(86)	11.5:1	62, 292
ClHg	—	AIBN	80	16	(73)	15.6:1	62, 292
ClHg	dark	none	50	24	(0)	—	62, 292
ClHg	—	AIBN	70	12	(90)[b]	—	285

		*hν*, benzene, 28 h		(73)[a]	62, 292
		ACCN, toluene, 110°, 46 h		(39)	295
		*hν*, AIBN, benzene, rt, 12 h		(66)	294
		ACCN, toluene, 110°, 24 h		(40)	295

		AIBN, toluene, 86°, 24–36 h		(22)	288
		AIBN, toluene, 86°, 24–36 h		(63)	288
C_4					
n-BuBr		AIBN, toluene, 95°, 22 h		(7)	295
n-BuY		*h*ν, benzene, 35°			

Y	Time (h)		(*E*)/(*Z*)	
I	30	(62)[a]	7:1	292
ClHg	40	(46)[a]	6.1:1	62, 292

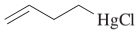
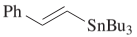
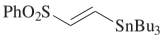
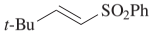
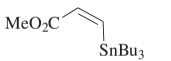
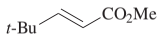
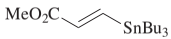
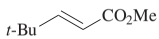
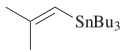
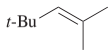
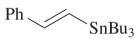
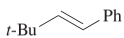
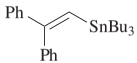
		*h*ν, benzene, 35°, 36 h		(45)[a] (*E*)/(*Z*) = 7.3:1	62, 292
t-BuHgCl		*h*ν, benzene/DMSO, 2 h		(<10)[a]	62
		*h*ν, DMSO, 3 h		(100)[a] (*E*)/(*Z*) > 50:1	62

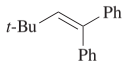
TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_4				
t-BuHgCl		*h*ν, benzene, 5 h	 (49)[a] (*E*)/(*Z*) > 50:1	20, 62
		*h*ν, benzene, 5 h	 (36)[a] (*E*)/(*Z*) > 50:1	20, 62
		*h*ν, benzene, 18 h	 (0)[a]	62
t-BuY		Conditions, initiator, benzene		

Y	Conditions	Initiator	Temp (°)	Time (h)		(*E*)/(*Z*)	
Br	*h*ν	none	35	—	(0)[a]	—	292
Br	—	AIBN	80	—	(0)[a]	—	292
ClHg	*h*ν	none	35	14	(83)[a]	49:1	62, 292



*h*ν, benzene



Y	Temp (°)	Time (h)		
Br	—	—	(0)[a]	292
ClHg	35	72	(78)[a]	62

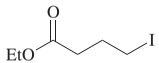
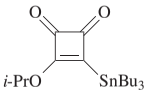
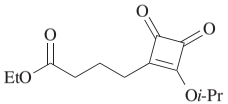
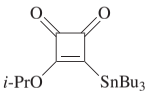
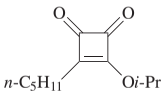
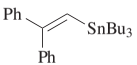
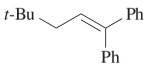
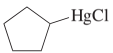
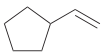
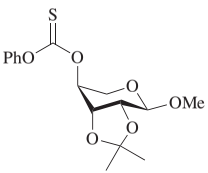
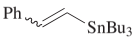
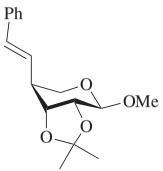
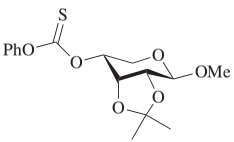
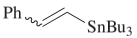
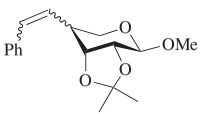
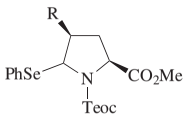
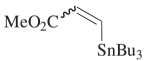
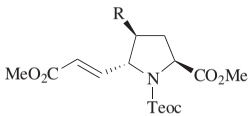
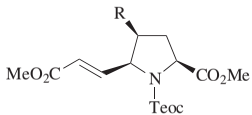
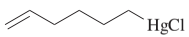
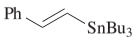
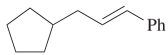
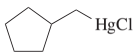
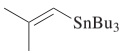
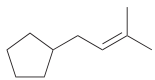
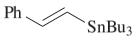
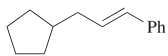
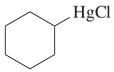
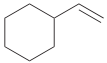
			ACCN, toluene, 110°, 22 h		(56)	295
C_5	n-$C_5H_{11}I$		AIBN, toluene, 85°, 46 h		(52)	295
			$h\nu$, benzene, 72 h		(10)[a]	62
			$h\nu$, benzene, 24 h		(10)[a]	62
			AIBN, benzene, 80°, 12 h		(62)	748
			AIBN		(0)	749

TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
		$h\nu$, $(Bu_3Sn)_2$, benzene	 **I** +  **II**	
			R / Time (h) / **I + II** / **I/II**: H / 8 / (65) / 3:1	290
			AcO / 4 / (67) / >99:1	289, 290
C_6				
		$h\nu$, benzene, 35°, 32 h	 (55)[a] $(E)/(Z) = 7.3:1$	62
		$h\nu$, benzene, 96 h	 (0)[a]	62
		$h\nu$, benzene, 35°, 48 h	 (52)[a] $(E)/(Z) = 5.7:1$	62, 292

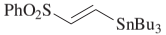


*h*ν, DMSO, 24 h

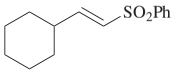


(8)[a]

62

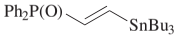


*h*ν, AIBN, benzene, rt, 12 h

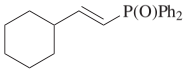


Y	
Br	(79)
PhO(S)CO	(83)

294

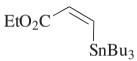


*h*ν, AIBN, benzene, rt, 12 h

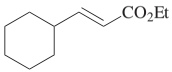


294

Y		(*E*)/(*Z*)
Br	(61)	(*E*) only
PhO(S)CO	(75)	12:1

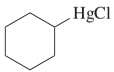


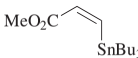
AIBN, toluene, 86°, 24–36 h



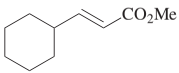
(57) (*E*)/(*Z*) = 3.4:1

288





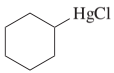
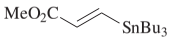
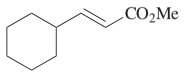
Conditions, solvent



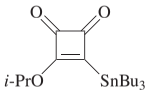
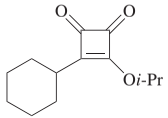
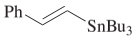
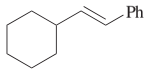
20, 62

Conditions	Solvent	Time (h)		(*E*)/(*Z*)
sunlamp	benzene	2	(34)[a]	2.5:1
UV	benzene/DMSO	5	(70)[a]	2.1:1

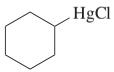
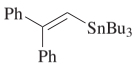
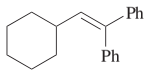
TABLE 8. VINYLATION REACTIONS (*Continued*)

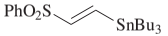
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		Conditions, solvent		20, 62

Conditions	Solvent	Time (h)		(*E*)/(*Z*)
sunlamp	benzene	2	(20)[a]	36:1
UV	benzene/DMSO	5	(66)[a]	23:1

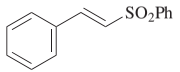
		ACCN, toluene, 110°, 22 h	 (21)	295
		Conditions, initiator, solvent		

Y	Conditions	Initiator	Solvent	Temp (°)	Time (h)		(*E*)/(*Z*)	
Br	—	AIBN	toluene	86	24–36	(51)	—	288
ClHg	*h*ν	none	DMSO	—	16	(88)[a]	19:1	62
ClHg	*h*ν	none	benzene	—	18	(77)[a]	19:1	62

		*h*ν, DMSO, 32 h	 (76)[a]	62

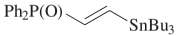


*h*ν, AIBN, benzene, rt, >12 h

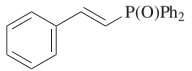


X		(*E*)/(*Z*)
Br	(45)	6:1
I	(82)	8:1

294



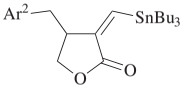
*h*ν, AIBN, benzene, rt, >12 h



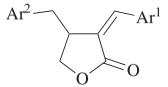
(42) (*E*)/(*Z*) = 6:1

294

Ar^1I

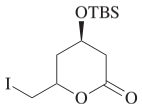


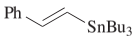
AIBN, benzene, 80°, 5 h



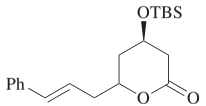
296

Ar^1	Ar^2	
Ph	Ph	(44)
2,3-$OCH_2OC_6H_3$	Ph	(56)
2,3-$OCH_2OC_6H_3$	2,3-$OCH_2OC_6H_3$	(58)





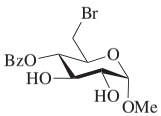
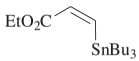
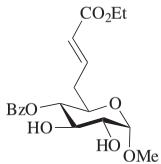
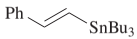
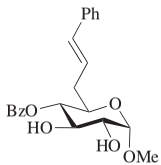
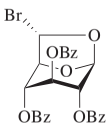
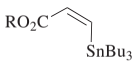
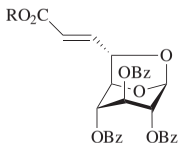
AIBN, toluene, 80°



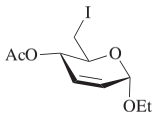
(40)

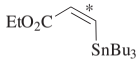
476, 477

TABLE 8. VINYLATION REACTIONS (*Continued*)

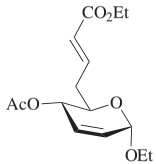
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
		AIBN, toluene, 86°, 24–36 h	 (74)	288
		AIBN, toluene, 86°, 24–36 h	 (82)	288
		AIBN, toluene, 100°, 36 h		134

R		(*E*)/(*Z*)
Me	(59)	1.5:1
Et	(54)	1.4:1



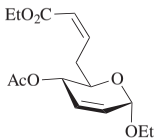


AIBN, toluene, 85°



I

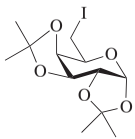
+

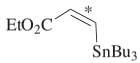


II

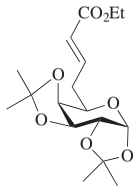
293, 750

*(*E*)/(*Z*)	Time (d)	**I**	**II**
1:>99	2	(66)	(22)
>99:1	7	(72)	(0)
1:1.4	3	(51)	(17)
1:1.1	4	(59)	(20)
6:1	3	(60)	(26)



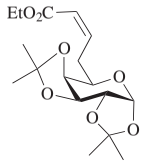


AIBN, toluene, 85°



I

+



II

293

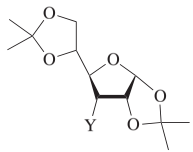
*(*E*)/(*Z*)	Time (d)	**I**	**II**
1:>99	1.5	(76)	(18)
>99:1	3	(79)	(0)
1:1.3	2	(63)	(7)

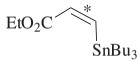
TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

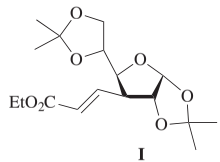
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_6



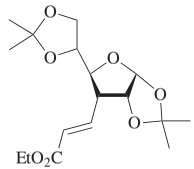


AIBN, toluene



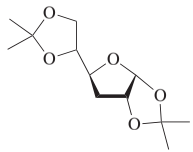
I

+



II

+



III

Y	*(*E*)/(*Z*)	Temp (°)	Time (d)	**I**	**II**	**III**	
I	1:>99	85	1.7	(72)	(11)	(0)	293
I	>99:1	85	4	(19)	(10)	(0)	293
I	1:1.3	85	3	(49)	(14)	(0)	293
MeS(S)CO	1:>99	105–110	—	(30)	(0)	(30)	288

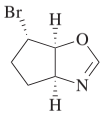
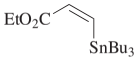
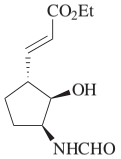
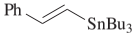
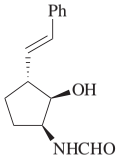
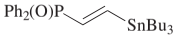
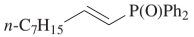
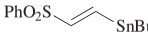
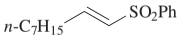
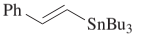
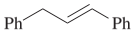
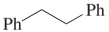
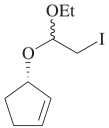
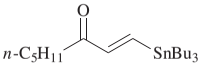
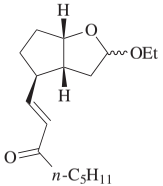
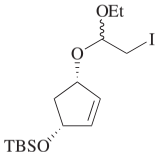
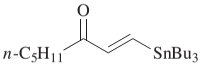
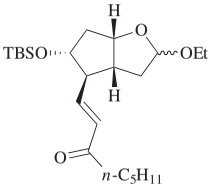
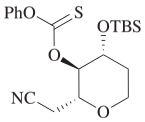
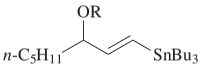
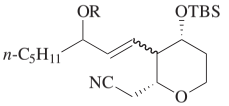
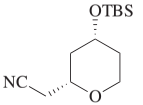
			1. AIBN, toluene, 86°, 24–36 h 2. AcOH, H_2O, THF		(79)[c] (*E*)/(*Z*) = 2.3:1	288, 751
			1. AIBN, toluene, 86°, 24–36 h 2. AcOH, H_2O, THF		(70)[c]	288
C_7						
	n-$C_7H_{15}I$		*h*ν, AIBN, benzene, rt, 12 h		(78) (*E*)/(*Z*) = 8:1	294
			*h*ν, AIBN, benzene, rt, 12 h		(76)	294
			*h*ν, benzene, 15 h	 +  (18)[a] (*E*)/(*Z*) = 10.1:1	(—)	62
			ACCN, toluene, 110°, 10 h		(74)	298

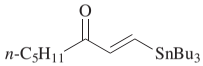
TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		Initiator, toluene		298

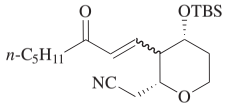
Initiator	Temp (°)	Time (h)	
AIBN	65	—	(tr)
AIBN	80	10	(43)
ACCN	110	10	(72)

		Conditions, initiator, solvent	 (0) +  (—)	559

R	Conditions	Initiator	Solvent	Temp
H	—	AIBN	benzene	80°
H	—	AIBN	toluene	110°
H	*hν*	none	benzene	rt
TBS	—	AIBN	benzene	80°
TBS	—	AIBN	toluene	110°
TBS	*hν*	none	benzene	rt

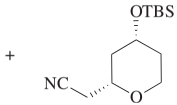


Conditions, initiator, solvent



(0)

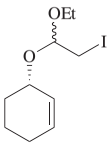
559

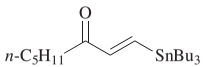


(—)

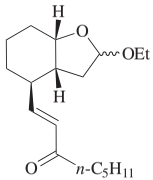
Conditions	Initiator	Solvent	Temp
—	AIBN	benzene	80°
—	AIBN	toluene	110°
$h\nu$	none	benzene	rt

C_8





ACCN, toluene, 110°, 10 h



(60)

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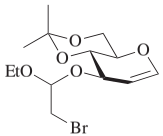
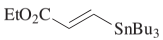
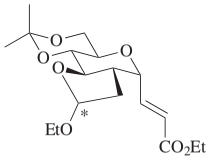
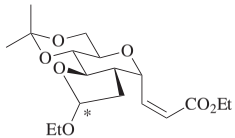
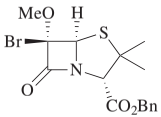
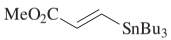
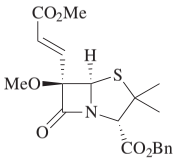
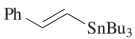
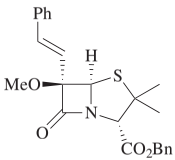
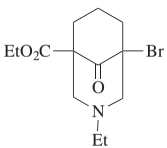
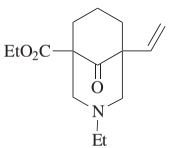
TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_8				
	 (E)/(Z) = 3:1	AIBN, toluene, 80°, 24 h	 (63) *dr = 1:1	297
			+  (8) *dr = 1:1	
		AIBN, benzene, 80°, 52 h	 (31)	291
		AIBN, benzene, 80°, 72 h	 (51)	291
C_9				
		AIBN	 (27)	71

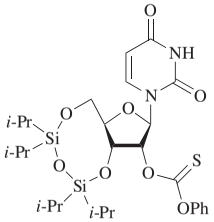
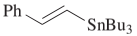
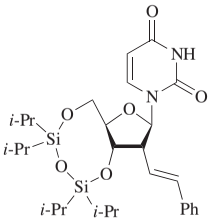
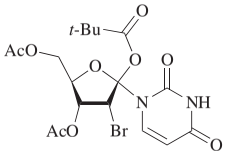
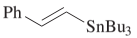
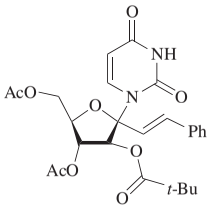
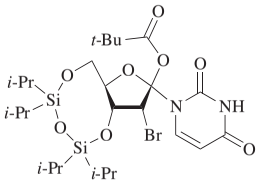
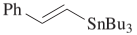
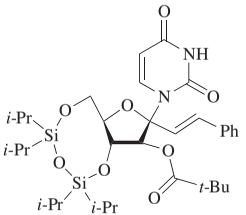
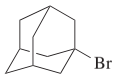
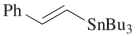
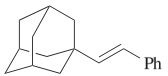
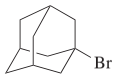
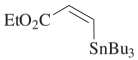
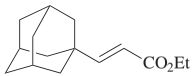
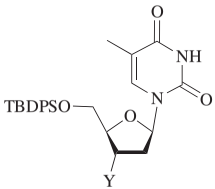
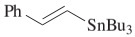
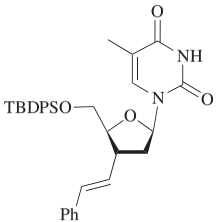
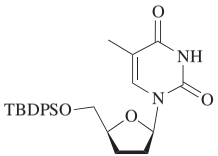
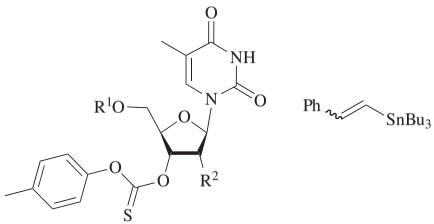
			AIBN, benzene, 80°, 40 h		(58)	683
			$h\nu$, $(Bu_3Sn)_2$, benzene, rt, 4 h		(71) $(E)/(Z) = 10:1$	248
			$h\nu$, $(Bu_3Sn)_2$, benzene, rt, 4 h		(76)	248
C_{10}			AIBN, toluene, 86°, 24–36 h		(42)	288

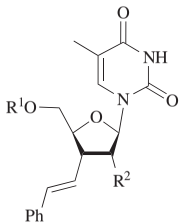
TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_{10} 		AIBN, toluene, 86°, 24–36 h	 (49)	288
		AIBN, benzene, 80°	 **I** +  **II**	

Y	Time (h)	**I**	**II**	
I	3	(25)	(30)	752
PhO(S)CO	35	(70)	(10)	752
PhO(S)CO	72	(24)	(—)	753
4-$MeC_6H_4O(S)CO$	—	(70)	(—)	754

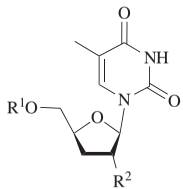


AIBN, benzene, 80°



I

+

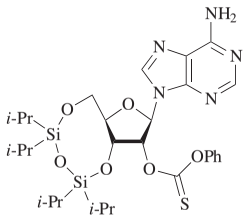
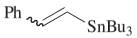
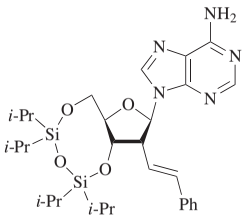
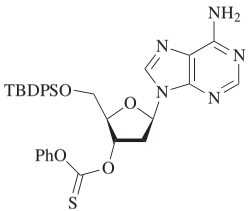
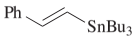
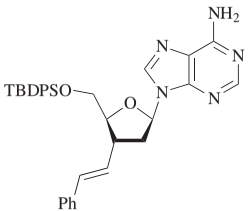
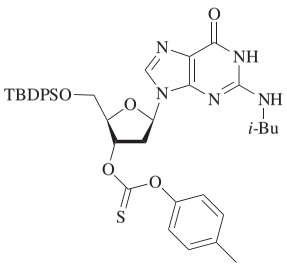
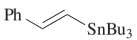
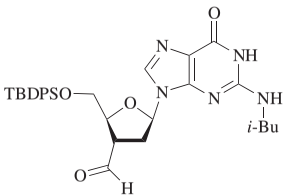


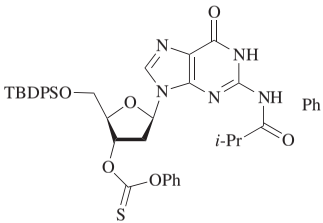
II

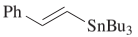
755

R^1	R^2	**I**	**II**
DMT	MeO	(45)	(10)
TBDPS	F	(—)	(—)

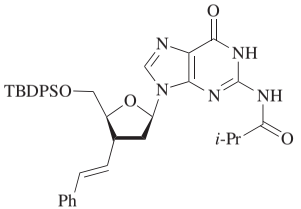
TABLE 8. VINYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{10}				
		AIBN, benzene, 80°, 50 h	 (42)	756
		AIBN, benzene, 80°, 75 h	 (43)	757
		1. AIBN, toluene, 80°, 48 h 2. OsO_4, NMO, dioxane, rt, 2 h 3. $NaIO_4$, 20°, 3 h	 (28)[d]	758

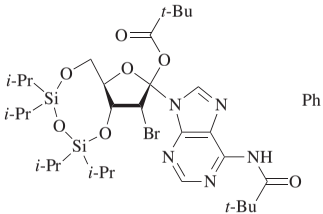


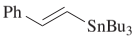


AIBN, benzene, 80°, 16 h

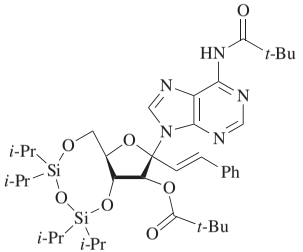


(45) 757





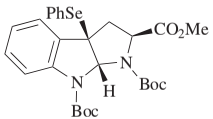
$h\nu$, $(Bu_3Sn)_2$, benzene, rt, 4 h

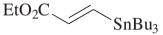


(65) $(E)/(Z) = 2.4:1$

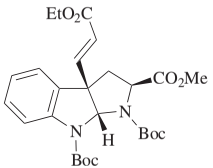
248

C_{11}



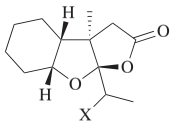
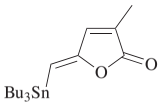
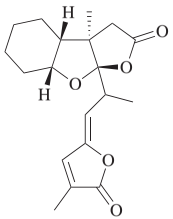
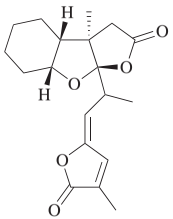


$h\nu$, $(Bu_3Sn)_2$, toluene, 23°, 10 h



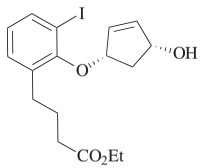
(21) 76

TABLE 8. VINYLATION REACTIONS (*Continued*)

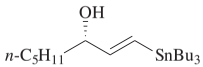
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{13}				
		Initiator, additive, solvent	 **I** +  **II**	759

X	Initiator	Additive	Solvent	Temp (°)	**I + II**[a]	**I/II**
Br	AIBN	none	toluene	80	(0)	—
Br	AIBN	Bu_3SnH	toluene	80	(0)	—
Br	AIBN	Bu_3SnH	BTF	80	(0)	—
Br	AIBN	Bu_3SnH	benzene	80	(0)	—
Br	Et_3B, O_2	none	Et_2O	—	(0)	—
I	AIBN	none	toluene	86	(tr)	—
I	AIBN	Bu_3SnH	toluene	80	(66)	1.4:1
I	AIBN	Bu_3SnH, 4 Å MS	toluene	80	(75)	1.2:1

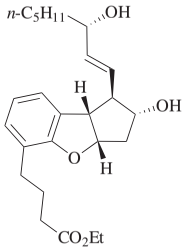
C_{15}



racemic



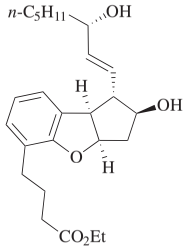
AIBN, toluene, 130°, 16 h



(21)

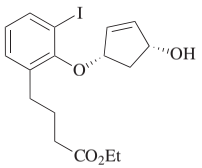
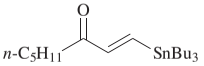
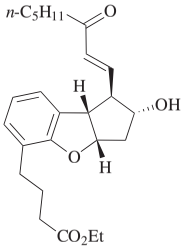
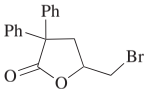
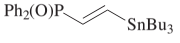
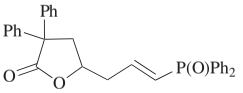
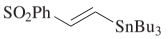
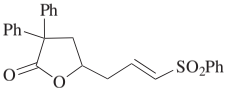
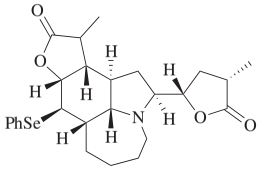
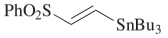
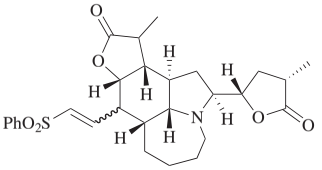
760

+

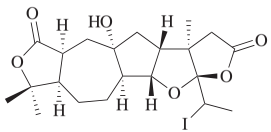


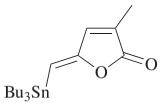
(20)

TABLE 8. VINYLATION REACTIONS (*Continued*)

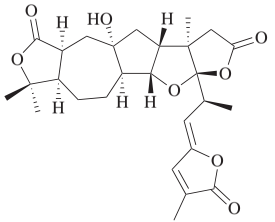
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{15}				
		AIBN, toluene, 90°, 12 h	 (80)	760
C_{17}				
		*h*ν, AIBN, benzene, rt, 12 h	 (46) (*E*)/(*Z*) = 8:1	294
		*h*ν, AIBN, benzene, rt, 12 h	 (73)	294
C_{20}				
		—	 (tr)	120

C_{21}



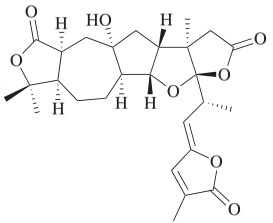


AIBN, Bu_3SnH,
4 Å MS, toluene, 100°, 4 h



(36) 759, 761

+



(9)

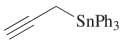
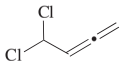
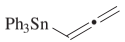
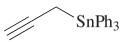
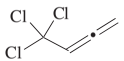
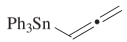
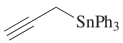
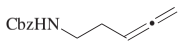
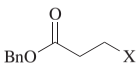
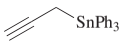
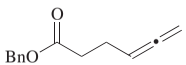
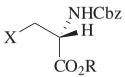
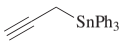
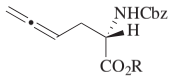
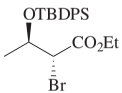
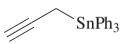
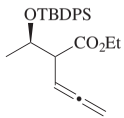
[a] The yield was determined by NMR spectroscopy.

[b] The yield was determined by GC or NMR spectroscopy; the method used was not further specified.

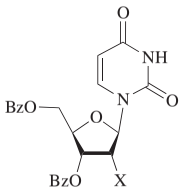
[c] This is the overall yield for the two-step process.

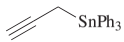
[d] This is the overall yield for the three-step process.

TABLE 9. ALLENYLATION REACTIONS

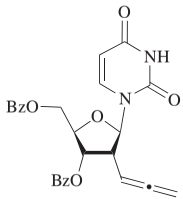
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_1				
$CHCl_3$		AIBN, benzene, 70°, 8 h	 (31)[a] +  (12)[a]	140
CCl_4		AIBN, benzene, 70°, 8 h	 (46)[a] +  (24)[a]	140
C_2				
		AIBN, benzene, 80°, 24 h	 (46)	305
C_3				
		AIBN, benzene, 80°, 24 h	 X: Cl (<5); I (55)	305
		AIBN, benzene, 80°, 24 h	 X, R: Br, Bn (55); I, Bn (60); I, PMB (55)	305
C_4				
		Not reported	 (17) dr = 1.9:1	176

C_9



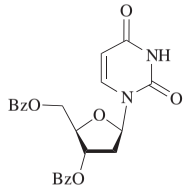


AIBN, benzene, 80°, 5 h



I

+

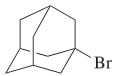


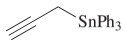
II

680

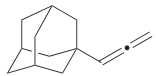
X	**I**	**II**
Br	(54)	(8)
I	(65)	(9)

C_{10}



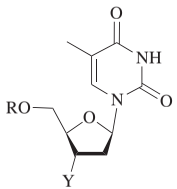


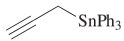
AIBN, benzene, 80°, 24 h



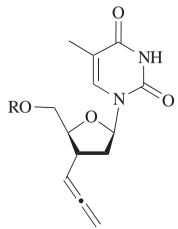
(45)

305



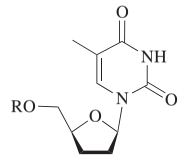


Initiator, solvent



I

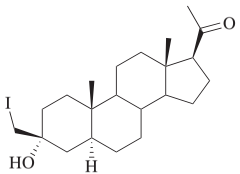
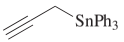
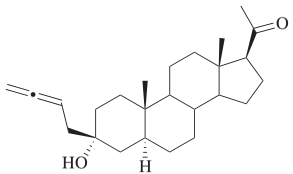
+



II

Y	R	Initiator	Solvent	Temp (°)	**I**	**II**	
Br or I	Bz	AIBN	benzene	80	(62–68)[b]	(13–16)[b]	762, 763
Br or I	Bz	Et_3B	benzene	25	(62–68)[b]	(13–16)[b]	762, 763
PhO(S)CO	TBS	AIBN	toluene	110	(0)	(0)	762

TABLE 9. ALLENYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{22} 		AIBN, benzene, 80°, 2 h	 (11)	525

[a] The yield was determined by NMR spectroscopy.

[b] The reference did not specify which yields corresponded to which substrates and conditions.

TABLE 10. ALKYNYLATION AND PROPARGYLATION REACTIONS

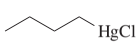
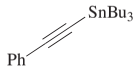
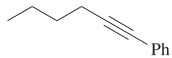
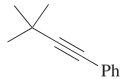
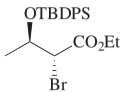
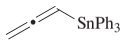
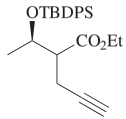
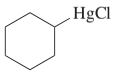
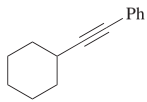
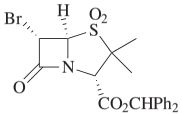
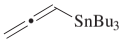
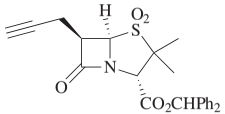
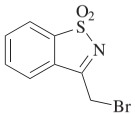
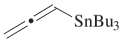
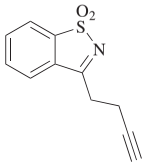
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_4				
		*h*ν, benzene, 35°, 30 h	 (13)[a]	62, 306
		*h*ν, benzene, 35°, 30 h	 (61)[a]	62, 306
		—	 (6)	176
C_6				
		*h*ν, benzene, 35°, 30 h	 (43)[a]	62, 306

TABLE 10. ALKYNYLATION AND PROPARGYLATION REACTIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, toluene, 16 h	 (50)	307
		$h\nu$, $Ru(bpy)_3(PF_6)_2$, MeCN, rt, 12 h	 (39)	405

[a] The yield was determined by GC.

TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS
A. ALLYLATIONS

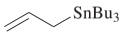
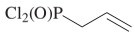
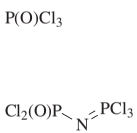
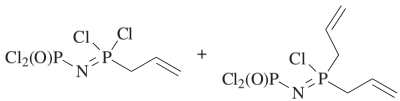
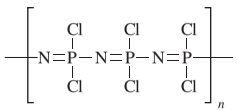
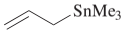
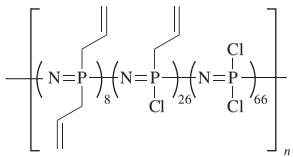
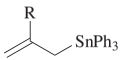
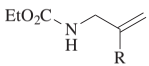
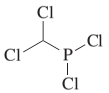
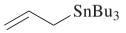
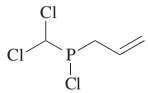
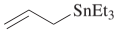
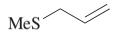
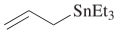
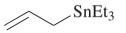
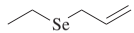
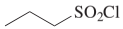
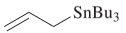
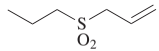
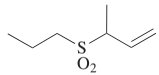
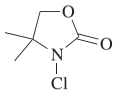
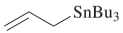
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_0				
PCl_3		*h*ν, toluene	(75)	286
$P(O)Cl_3$		*h*ν, toluene	 (85)	286
	*x* eq	*h*ν	 **I** + **II**	287
			R / *x* / **I** / **II**: Me / 1.1 / (81) / (8); Bu / 2.2 / (0) / (85)	
		*h*ν	 (—)	287
C_1				
EtO_2CN_3		AIBN, benzene, 80°, 9 h	 R / (%): H / (74); Me / (78)	280

TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)
A. ALLYLATIONS (*Continued*)

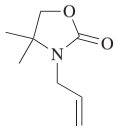
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_1				
		*h*ν, toluene	 (92)	286
MeSH	 *x* eq	*h*ν, 45°, 12 h	 *x*: 2 (12)[a]; 1 (7.5)[a]; 0.5 (2.7)[a]; 0.33 (0.3)[a]	764
C_2				
		*h*ν, 45°, 10 h	Y: H (8)[a]; D (10)[a]	764
		*h*ν, 45°, 10 h	 (0)[a]	764
C_3				
		*h*ν, benzene, 6 h	 (74)	140
		*h*ν, benzene, 3 min	 (46)[b]	140

C_5



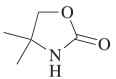


Initiator, 80°



I

+

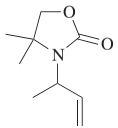


II

278

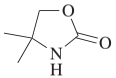
Initiator	Time (h)	**I**	**II**
AIBN	5	(25)	(33)
$(PhCO_2)_2$	15	(13)	(42)

$(PhCO_2)_2$, 80°, 15 h



(9)

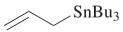
+



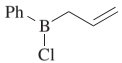
(52)

278

C_6



*h*ν, toluene

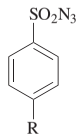
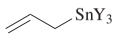
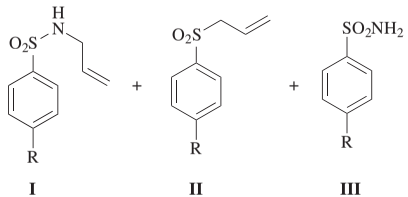


(90)

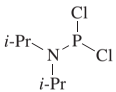
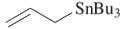
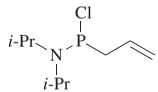
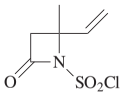
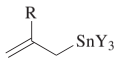
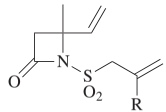
286

TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)

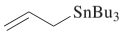
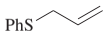
A. ALLYLATIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{6-7}				
		AIBN, benzene, 80°, 3 h	 **I** + **II** + **III**	280

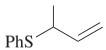
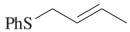
R	Y	**I**[b]	**II**[b]	**III**	R	Y	**I**[b]	**II**[b]	**III**
H	Ph	(91)	(5)	(4)	F	Me	(72)	(20)	(8)
H	Me	(81)	(12)	(7)	F	Bu	(14)	(21)	(65)
H	Bu	(6)	(30)	(64)	O_2N	Ph	(15)	(<1)	(<1)
MeO	Ph	(86)	(10)	(4)	O_2N	Bu	(0)	(0)	(0)
MeO	Me	(82)	(14)	(4)	Me	Ph	(89)	(8)	(3)
MeO	Bu	(4)	(37)	(59)	Me	Me	(83)	(11)	(6)
F	Ph	(83)	(12)	(5)	Me	Bu	(7)	(32)	(61)

C_6				
		*h*ν, toluene	 (85)	286
		Et_3B, O_2, toluene, –78°, 1 h		284

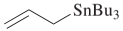
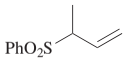
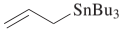
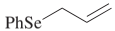
R	Y	
H	Ph	(36)
Me	Bu	(32)
MeO_2C	Bu	(0)

PhSSPh		*h*ν, benzene		

Temp	Time (h)		
rt	4	(63)[c]	285
—	6	(77)	140

		*h*ν, benzene, 2 h	 + 	140

I **I + II** (—) **I/II** = 1:1 **II**

$PhSO_2Cl$		*h*ν, benzene, 6 h	(76)	140
		*h*ν, benzene, 9 min	 (72)[b]	140
PhSePh		*h*ν, benzene		

Temp	Time (h)		
rt	4	(56)[c]	285
—	6	(94)[b]	140

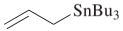
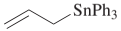
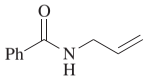
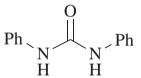
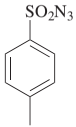
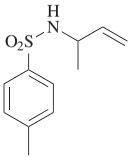
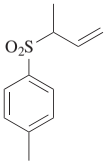
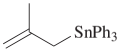
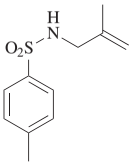
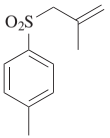
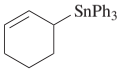
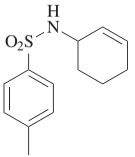
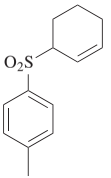
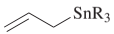
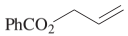
PhTePh		*h*ν, benzene, rt, 12 h	(<2)[c]	285

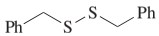
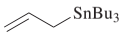
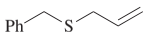
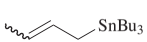
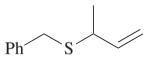
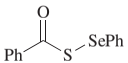
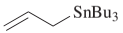
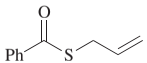
TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)

A. ALLYLATIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
		AIBN, benzene, 80°, 2.5 h	 (0) +  (—)	280
		AIBN, benzene, 80°, 3 h	 (0) +  (0)	280
		AIBN, benzene, 80°, 3 h	 (86) +  (9)	280
		AIBN, benzene, 80°, 3 h	 (0) +  (0)	280

$(PhCO_2)_2$		Benzene, 80°	 **I** + $PhCO_2SnR_3$ **II**	37

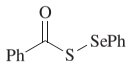
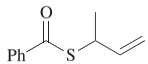
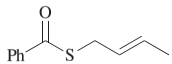
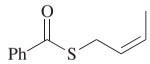
R	**I**	**II**
Me	(30)	(40)
Bu	(18)	(40)

		*h*ν, benzene, 6 h	 (77)	140
		*h*ν, benzene, 1.5 h	 (34)[b]	140
		Conditions, initiator, benzene		281

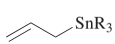
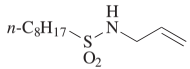
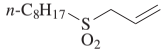
Conditions	Initiator	Temp (°)	Time (h)	
—	AIBN	80	2	(86)
*h*ν	none	—	1.5	(84)

TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)

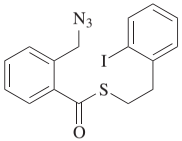
A. ALLYLATIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_7				
	$(E)/(Z) = 3:1$	Conditions, initiator, benzene	 **I** +  **II** +  **III**	281

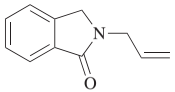
Conditions	Initiator	Temp (°)	Time (h)	**I + II + III**	**I/II/III**
—	AIBN	80	2	(89)	79:14:7
$h\nu$	none	—	0.6	(79)	77:17:6

C_8				
n-$C_8H_{17}SO_2N_3$		AIBN, benzene, 80°, 3 h	 **I** +  **II** + n-$C_8H_{17}SO_2NH_2$ **III**	280

R	**I**	**II**	**III**
Bu	(9)	(36)	(55)
Ph	(56)	(42)	(2)

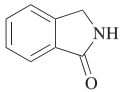


AIBN, benzene, 80°, 8 h



I

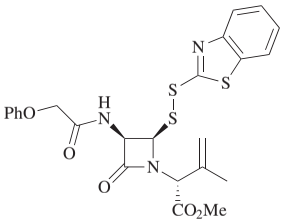
+

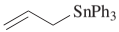


II

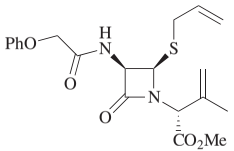
279

R	**I**	**II**
Bu	(40)	(45)
Ph	(60)	(25)



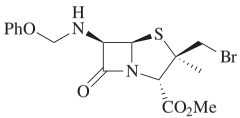


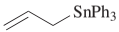
AIBN, benzene, 80°, 16 h



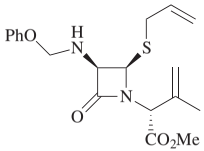
(83)

282, 283





AIBN, benzene, 80°, 3 h



(94)

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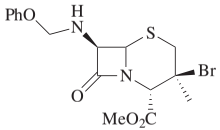
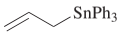
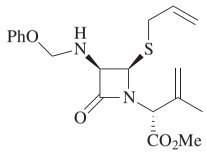
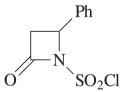
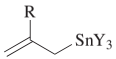
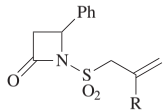
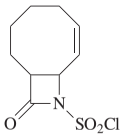
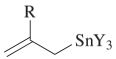
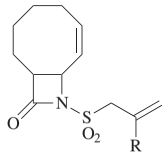
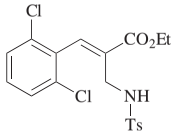
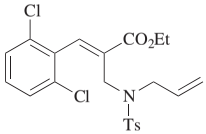
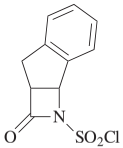
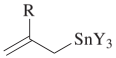
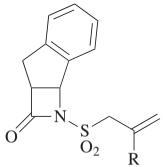
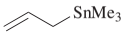
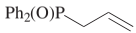
TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)
A. ALLYLATIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8				
		AIBN, benzene, 80°, 3 h	 (91)	282, 283
C_9				
		Et_3B, O_2, toluene, rt, 1 h		284
			R / Y / (%): H / Ph / (73); Me / Bu / (100); MeO_2C / Bu / (40)	
		Et_3B, O_2, toluene, rt, 1 h		284
			R / Y / (%): H / Ph / (72); Me / Bu / (99); MeO_2C / Bu / (75)	

C_{10}			$h\nu$, $Ru(bpy)_3Cl_2$, NaOH, $CHCl_3$, 25°, 12 h		(—)	765
			Et_3B, O_2, toluene, rt, 1 h			284
				R / Y: H / Ph (92); Me / Bu (77); MeO_2C / Bu (44)		
C_{12}	$Ph_2P(O)Cl$		$h\nu$, toluene		(95)	286

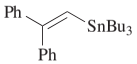
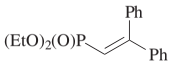
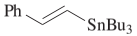
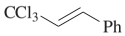
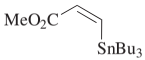
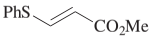
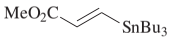
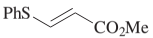
[a] The yield was determined by GC.

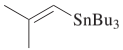
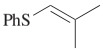
[b] The yield was determined by NMR spectroscopy.

[c] The yield was determined by GC or NMR spectroscopy; the method used was not specified.

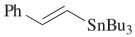
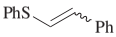
TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)

B. VINYLATIONS

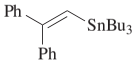
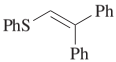
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_0				
$(EtO)_2P(O)Y$		*h*ν, DMSO, 35°		292, 303, 766
			Y / Time (h): ClHg / 24 / (65)[a]; $(EtO)_2(O)PHg$ / 20 / (14)[a]	
C_1				
CCl_3SO_2Cl		*h*ν, benzene, 35°, 24 h	 (48)[b]	303
C_6				
PhSY		Conditions, initiator, solvent		303
			Y / Conditions / Initiator / Solvent / Temp (°) / Time (h): PhS / *h*ν / none / benzene / 35 / 4 / (91); PhS / — / AIBN / benzene / 80 / 4 / (82); PhSHg / *h*ν / none / DMSO / — / 20 / (45)[a]	
PhSSPh		*h*ν, benzene, 35°, 8 h	 (91)[a] (*E*)/(*Z*) = 3.7:1	20, 303
		*h*ν, benzene, 35°, 8 h	 (79)[a] (*E*)/(*Z*) = 3.8:1	303

PhSY  Conditions, initiator, solvent  303

Y	Conditions	Initiator	Solvent	Temp (°)	Time (h)	
PhS	$h\nu$	none	benzene	35	2	(74)
PhS	AIBN	AIBN	benzene	80	2	(97)[a]
PhSHg	$h\nu$	none	DMSO	—	20	(56)[a]

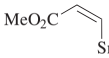
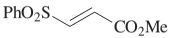
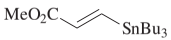
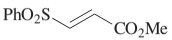
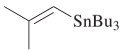
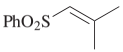
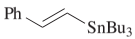
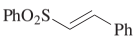
PhSSPh  Conditions, initiator 

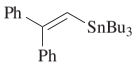
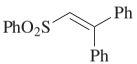
Conditions	Initiator	Temp (°)	Time (h)		
—	AIBN	70	20	(95)[c]	285
$h\nu$	none	35	4	(86)	303

PhSY  $h\nu$, solvent  303

Y	Solvent	Temp (°)	Time (h)	
PhS	benzene	35	2	(93)[a]
PhSHg	DMSO	—	20	(66)[a]

TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)
B. VINYLATIONS (*Continued*)

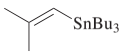
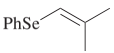
Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_6				
$PhSO_2Y$		*h*ν, solvent		303
		Y / Solvent / Temp (°) / Time (h): Cl / benzene / 35 / 6 (89); $PhSO_2Hg$ / DMSO / — / 4 (tr)		
$PhSO_2Cl$		*h*ν, benzene, 35°, 10 h	 (76)[a] (*E*)/(*Z*) > 50:1	20, 303
		*h*ν, benzene, 35°, 10 h	 (68)[a] (*E*)/(*Z*) > 50:1	20, 303
$PhSO_2Y$		*h*ν, solvent, 4 h		303
		Y / Solvent / Temp (°): Cl / benzene / 35 / (90)[a]; $PhSO_2Hg$ / DMSO / — / (38)		
$PhSO_2Cl$		*h*ν, benzene, 35°, 4 h	 (88) (*E*)/(*Z*) > 50:1	303

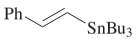
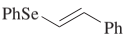
$PhSO_2Y$  *hν*, solvent  303

Y	Solvent	Temp (°)	Time (h)	
Cl	benzene	35	4	(76)[a]
$PhSO_2Hg$	DMSO	—	4	(63)[a]

PhSeY *hν*, solvent 303

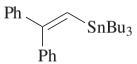
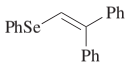
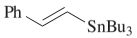
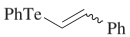
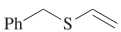
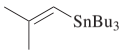
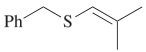
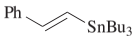
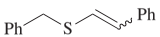
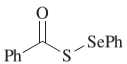
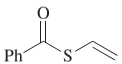
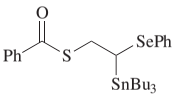
Y	Solvent	Temp (°)	Time (h)	
PhSe	benzene	35	24	(0)[b]
PhSeHg	DMSO	—	20	(64)[a]

PhSePh  *hν*, benzene, 35°, 4 h  (0)[a] 303

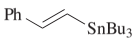
PhSeY  Conditions, initiator 

Y	Conditions	Initiator	Temp	Time (h)		(*E*)/(*Z*)	
PhSe	—	AIBN	70°	12	(<2)[c]	—	285
PhSe	*hν*	none	rt	12	(<2)[c]	—	285
PhSe	*hν*	none	35°	24	(0)[b]	—	303
Ts	*hν*	none	35°	6	(84)	>50:1	303

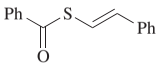
TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)
B. VINYLATIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*				
C_6				
$(PhSe)_2Hg$		*hν*, DMSO, 20 h	 (92)[a]	303
PhTePh		Conditions, initiator, benzene, 12 h		285
			Conditions / Initiator / Temp: — / AIBN / 80° (<2)[c]; *hν* / none / rt (<2)[c]	
C_7				
		hν, benzene, 35°, 2 h	 (82)	303
		*hν*, benzene, 35°, 2 h	 (84)[a]	303
		*hν*, benzene, 35°, 10 h	 (85)	303
		Conditions, initiator, benzene	 **I** +  **II**	281

Conditions	Initiator	Temp (°)	Time (h)	**I**	**II**
—	AIBN	80	2	(0)	(60)
hν	none	—	1.5	(0)	(60)



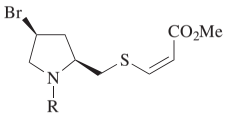
Conditions, initiator, benzene



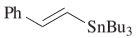
281

Conditions	Initiator	Temp (°)	Time (h)	
—	AIBN	80	7.5	(92)
hν	none	—	1	(95)

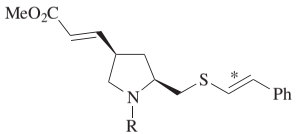
C_8



(*E*)/(*Z*) = 1:1.5

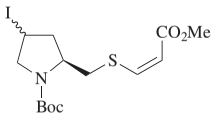


ACCN, toluene, 105°, 7 h

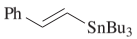


304

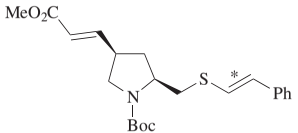
R		(*E*)/(*Z*)*
Boc	(84)	9:1
Ts	(78)	11.5:1



(*E*)/(*Z*) = 1:1.5



ACCN, toluene, 105°, 4 h



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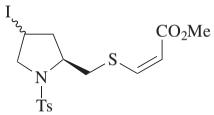
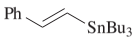
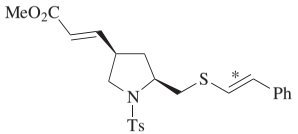
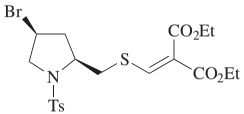
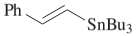
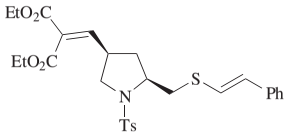
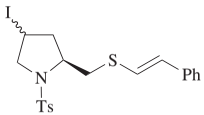
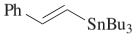
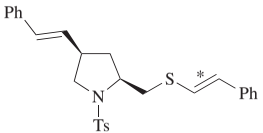
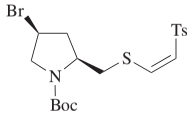
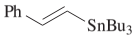
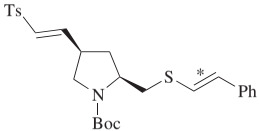
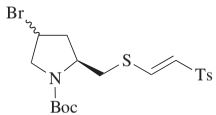
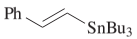
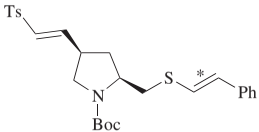
(86) (*E*)/(*Z*)* = 7.3:1

TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)
B. VINYLATIONS (*Continued*)

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_8  (*E*)/(*Z*) = 1:1.25		ACCN, toluene, 105°, 4 h	 (69) (*E*)/(*Z*)* = 11.5:1	304
C_9 		ACCN, toluene, 105°, 7 h	 (89) (*E*)/(*Z*) = 6.7:1	304
C_{13}  (*E*)/(*Z*) = 2:1		ACCN, toluene, 105°, 4 h	 (82) (*E*)/(*Z*)* = 11.5:1[d]	304

C_{14} 		ACCN, toluene, 105°, 7 h	 (89) (*E*)/(*Z*)* = 9:1	304
		ACCN, toluene, 105°, 7 h	 (86) (*E*)/(*Z*)* = 13.3:1	304

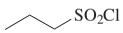
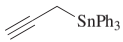
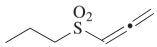
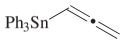
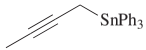
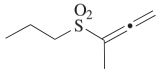
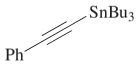
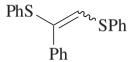
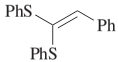
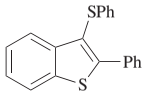
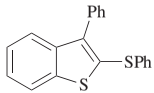
[a] The yield was determined by NMR spectroscopy.

[b] The yield was determined by GC.

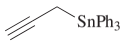
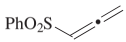
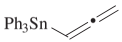
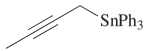
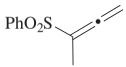
[c] The yield was determined by GC or NMR spectroscopy; the method used was not specified.

[d] About 2% of the 4-(*Z*-styryl) derivative was also observed.

TABLE 11. REACTIONS OF HETEROATOM-CENTERED RADICALS (*Continued*)
C. ALLENYLATIONS AND ALKYNYLATIONS

Radical Precursor	Stannane Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
		AIBN, benzene, 70°, 8 h	 (31)[a] +  (43)[a]	140
		*hν*, benzene, 35°, 38 h	 (31)[a]	140
C_6				
PhSR		*hν*, solvent	**I** +  **II** +  **III** +  **IV** +  **V**	303

R	Solvent	Time (h)	**I**	**II + III + IV + V**
PhS	benzene	12	(60)[b]	(8)[b]
PhSHg	DMSO, benzene	24	(35)[b]	(13)[b]

$PhSO_2Cl$		AIBN, benzene, 70°, 8 h	 (36)[a]	+	 (36)[a]	140
		$h\nu$, benzene, 35°, 35 h		(42)[a]		140

[a] The yield was determined by NMR spectroscopy.

[b] The yield was determined by GC.

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SUPPLEMENTAL REFERENCES

Table 1. Direct Allylations

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Table 3. Allylations Following Cyclizations

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Table 11. Reactions of Heteroatom-Centered Radicals

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