CHAPTER 1

THE JULIA–KOCIENSKI OLEFINATION

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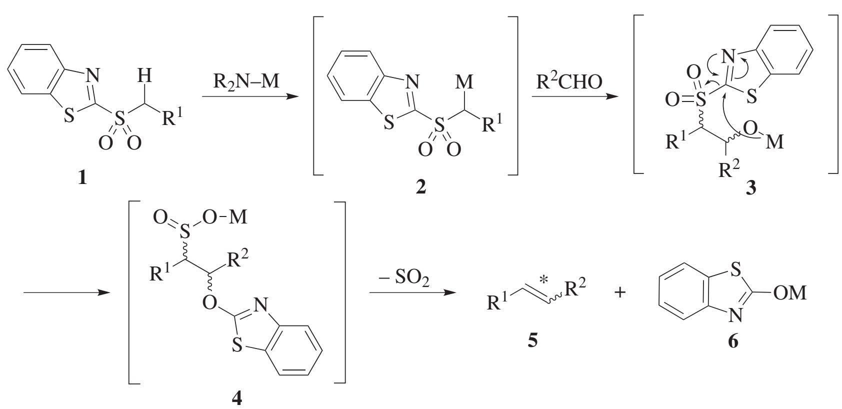
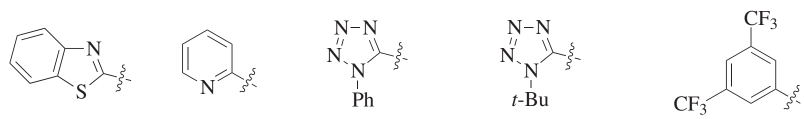
INTRODUCTION

The Julia–Kocienski olefination, also known as the modified Julia olefination, or the one-pot Julia olefination, is a connective synthesis of alkenes involving the reaction of an α-metalated aryl alkyl sulfone (sulfone anion) such as **2** with a carbonyl compound (Scheme 1).[1] The aryl group is necessary to permit *ipso* substitution next to the sulfonyl moiety such that the initially generated addition adduct **3** may undergo a spontaneous Smiles rearrangement (i.e., **3** to **4**).[2] The elimination of sulfur dioxide and an aryloxide anion from the Smiles rearrangement product **4** affords alkene **5** and metalated benzothiazole **6**. The reaction was first described using benzothiazol-2-yl (BT) sulfones (**1** in Scheme 1),[1] but it has since been extended to include a variety of



Scheme 1

alternative aromatic activating groups, each of which has its own merits (Figure 1).[3−6] To avoid confusion, it is worth noting at the outset that the Julia–Kocienski olefination (discovered by S. A. Julia)[1] is distinct from the older Julia–Lythgoe olefination (discovered by M. Julia),[7] which is an indirect alkene synthesis that involves the addition of phenyl sulfone anions to carbonyl compounds followed by a separate reductive desulfonylation step (see "Comparison with Other Methods").[8−12] Throughout this review an asterisk indicates the site of a newly introduced alkene.



benzothiazol-2-yl (BT) | pyrid-2-yl (PYR) | 1-phenyl-1*H*-tetrazol-5-yl (PT) | 1-*tert*-butyl-1*H*-tetrazol-5-yl (TBT) | 3,5-bis(trifluoromethyl)phenyl (BTFP)

Figure 1. Five aromatic activators (Act) commonly used in the Julia–Kocienski olefination.

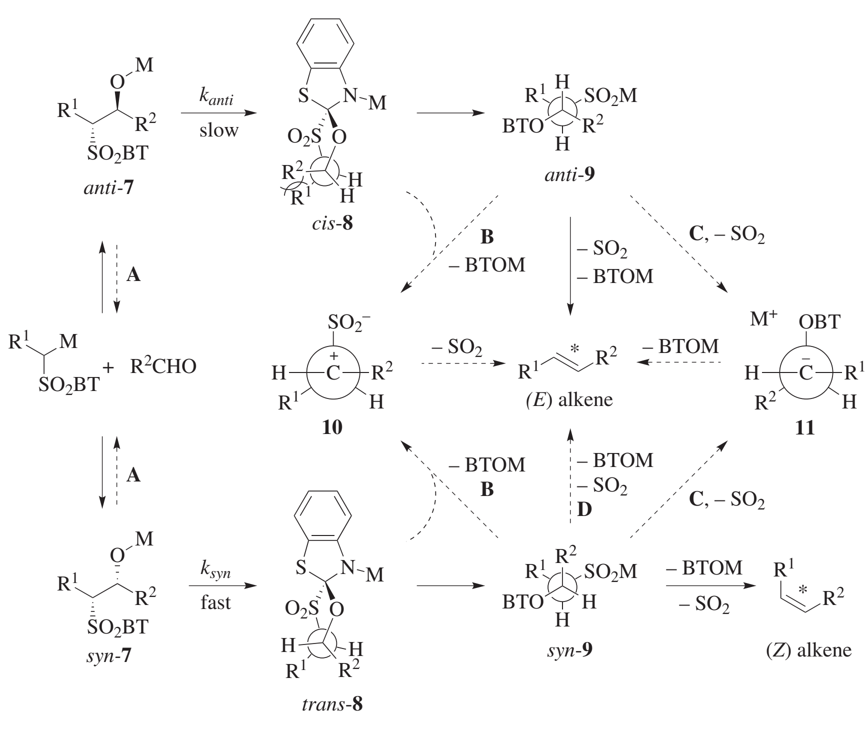
The outcome of the Julia–Kocienski olefination is sensitive to all variables, and an informed selection of coupling partner types (sulfone and carbonyl component, choice of bond disconnection in polyenes, type of activator) and reaction conditions (protocol for sulfone anion generation, type of base, base countercation, solvent, additives) is critical to obtain a high yielding alkene synthesis with the desired configuration. Providing that the coupling of interest is optimized and properly executed, the Julia–Kocienski olefination is capable of generating a wide variety of complex alkene targets, in which it is especially well suited to the production of *trans*-1,2-disubstituted double bonds. The olefination process itself and the methods available for installing the activating sulfone moiety generally exhibit broad functional-group tolerance, and consequently, the Julia–Kocienski reaction has enjoyed widespread adoption as a reliable tool for the coupling of multifunctional sulfone and carbonyl compounds during total synthesis efforts. This review focuses on how to achieve optimal results from the Julia–Kocienski olefination by a consideration of its theoretical and operational aspects, in what situations it is best applied, and when an alternative carbonyl olefination tactic is perhaps better suited. Notable variants of the process leading to non-alkene targets are also briefly surveyed. The Julia–Kocienski olefination has been previously reviewed, and these accounts should be consulted for discourse on the historical development of the process.[2,9,11−14]

MECHANISM AND STEREOCHEMISTRY

The broader aspects of the mechanism for the Julia–Kocienski olefination are well understood; however, a rigorous framework to fully explain the influence of substituents and other parameters on the stereochemical outcome of the process is not yet available. Nonetheless, extensive experimental findings reveal substrate-dependent stereoselectivity traits, most of which can be rationalized on at least an empirical level.[3] A more complete understanding of the mechanistic origin of stereoselectivity in some special cases has been obtained by a combination of control experiments and computational studies.[13,15−18]

Mechanism

The current mechanistic understanding of the Julia–Kocienski olefination is summarized below and illustrated for the synthesis of a 1,2-disubstituted alkene from a metalated BT-sulfone and an aldehyde (Scheme 2; solid arrows depict the default pathway that is followed when R^1 and R^2 are non-conjugating substituents). Analogous pathways will be followed for alternative activators and for substrates leading to other classes of alkenes. Addition of the metalated sulfone nucleophile to the carbonyl electrophile generates the expected pair of diastereomeric *syn* and *anti* β-alkoxy sulfone intermediates **7**; diastereoselectivity for this step is strongly dependent on reaction conditions and activator type. The initial adducts, *syn*-**7** and *anti*-**7**, are formed irreversibly if the sulfone anion is not stabilized (e.g., R^1 = alkyl) but are capable of equilibration via a retroaddition/re-addition mechanism (pathway **A**) if the sulfone anion is equipped with an anion-stabilizing group (e.g., R^1 = vinyl, aryl, carbonyl, etc.). Smiles rearrangement occurs by way of spirocyclic intermediates *trans*-**8** and *cis*-**8** (an example of which has been isolated),[19] which open to generate *syn* and *anti* β-aryloxy sulfinates **9**, respectively. Spirocyclization occurs more rapidly from *syn*-**7** than from *anti*-**7** because the spirocycle derived from the latter isomer (*cis*-**8**) exhibits higher strain.[15] This accounts for the observation of (*Z*)-selective Julia–Kocienski olefination in certain cases, in which the initial addition reaction is reversible and the



Scheme 2

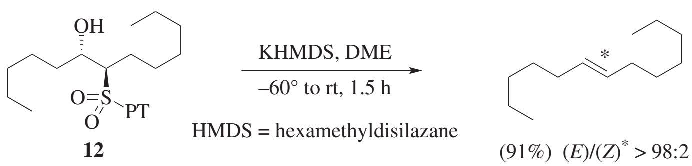
Curtin–Hammett principle operates (i.e., equilibration between *syn*-**7** and *anti*-**7** is faster than spirocyclization).

A variety of mechanistic pathways have been identified, or at least inferred by indirect evidence, for the production of alkenes from β-aryloxy sulfinates **9**. Loss of the aryloxide anion (BTOM) and sulfur dioxide from sulfinates **9** is stereospecific only when R^1 and R^2 are non-conjugating substituents (e.g., simple alkyl); in such cases, elimination is a concerted E2-like process occurring from the illustrated conformers, wherein the β-C–OAct and α-C–SO_2^- bonds have an antiperiplanar alignment, and *anti*-**9** leads to the (*E*) alkene whereas *syn*-**9** affords the (*Z*) alkene. The validity of this pathway for the reaction of metalated $PTSO_2Et$ with acetaldehyde is supported by a recent DFT computational study, albeit whether spirocycle **8** is a true intermediate along the reaction coordinate or merely a transition structure was questioned.[18] Unsaturation in either R^1 or R^2 potentially enables the non-stereospecific conversion of β-aryloxy sulfinate isomers **9** to alkene products: where R^2 is a cation-stabilizing substituent (aryl, vinyl, etc.), the suggestion of an E1-type elimination (from **9** or **8**) via zwitterion **10** was noted in Julia's original work (pathway **B**),[3] and when R^1 is a strongly electron-withdrawing group (e.g., carbonyl), an E1cB-type elimination via carbanion **11** (i.e., an enolate) is consistent with some relevant data (pathway **C**).[14,16,20] Conformational relaxation via rotation about the central C–C bond in intermediates **10** and **11** prior to respective electrofuge (SO_2) or nucleofuge (BTO^-) release leads preferentially to the (*E*) alkene in both cases. More recent work casts doubt on the veracity of Julia's ad hoc zwitterion (**10**) hypothesis, at the very least for reactions involving R^2 = aryl; a concerted *syn* E2-like elimination mechanism from *syn*-**9** (R^2 = aryl) via a conformation with synperiplanar β-C–OAct and α-C–SO_2^- bonds (not illustrated) was identified computationally and suggested by experiment (pathway **D**).[17] Related *syn* elimination pathways from spirocycles **8** that bypass β-aryloxy sulfinate intermediates altogether and lead directly to alkene products have been located by computational studies for reactions involving 3,5-bis(trifluoromethyl)phenyl (BTFP) sulfonyl acetates.[16] Results that support the various mechanistic pathways posited above and the relationship between the substituent and other parameters on the stereochemical outcome of the Julia–Kocienski olefination are now considered.

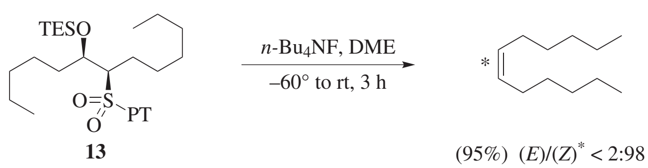
Factors Influencing Stereoselectivity

Substituent effects play a major role in determining the stereochemical outcome of the Julia–Kocienski olefination, and intrinsic selectivity trends can be accentuated or sometimes reversed by the use of different activators. Selectivity is further influenced in most cases by the base used to form the sulfone anion, the countercation, solvents, and any added cosolvents or cation-complexing agents. The presence or absence of conjugation in each coupling partner has the most profound effect on stereoselectivity, and reactions are usefully divided into four substrate pair classes according to this principle.[3] Examples within the same class share related stereochemical behaviors that can be rationalized within the mechanistic framework advanced above (Scheme 2). The four classes are: (I) reactions of sulfone anions that are not β,γ-unsaturated with carbonyl compounds that are not α,β-unsaturated, (II) reactions of sulfone anions that are β,γ-unsaturated with carbonyl compounds that are not α,β-unsaturated, (III) reactions of sulfone anions that are not β,γ-unsaturated with carbonyl compounds that are α,β-unsaturated, and (IV) reactions of sulfone anions that are β,γ-unsaturated with carbonyl compounds that are α,β-unsaturated. These broad reaction classes are now considered in turn within the context of 1,2-disubstituted alkene synthesis. Similar principles apply for tri- and tetrasubstituted alkene synthesis, but these types of products generally cannot be obtained with high levels of stereoselectivity via the Julia–Kocienski olefination because the steric interactions that differentiate the competing diastereomeric pathways are less energetically distinguished in higher-substituted cases (see "Scope and Limitations").

Stereoselectivity in Type I Reactions: Neither Component Conjugated. The stereochemical outcome of a Type I reaction is determined by the kinetic diastereoselectivity in the initial addition step: the formation of β-alkoxy sulfone intermediates **7** is irreversible in such cases, and their subsequent breakdown to alkene products is stereospecific. This fact was established experimentally for alkyl BT, pyrid-2-yl (PYR), and 1-phenyl-1*H*-tetrazol-5-yl (PT) sulfones by studying the base-mediated elimination of alkyl-substituted, stereodefined β-alkoxy sulfones.[15,21] For example, treatment of *anti* β-hydroxy sulfone **12** (generated from *trans*-7-tetradecene oxide by ring-opening with PTSH followed by oxidation of the resulting thioether) with KHMDS (HMDS = hexamethyldisilazane) leads exclusively to (*E*)-7-tetradecene (Scheme 3). By contrast, in situ generation of the corresponding *syn* β-alkoxy sulfone anion via desilylation of *syn* β-silyloxy-PT-sulfone **13** with TBAF provides exclusively (*Z*)-7-tetradecene (Scheme 4).[21]

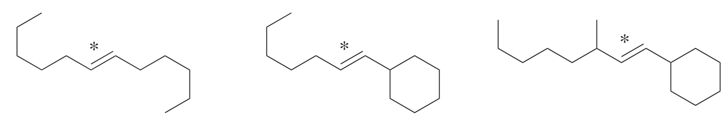


Scheme 3



Scheme 4

Type I reactions generally result in poor stereoselectivity under the reaction conditions for olefination that were first described by Julia and coworkers (BT or PYR sulfones, LDA, THF, –78° to room temperature).[3] The inference of low diastereoselectivity in the sulfone anion addition step was confirmed in the case of lithiated alkyl PYR sulfones by the isolation of β-hydroxy sulfones with dr ∼50:50 directly from reactions with non-conjugated aldehydes.[15] Early efforts to apply the nascent Julia–Kocienski olefination to target-directed syntheses revealed that variations in base countercation and solvent polarity markedly affect stereoselectivity.[22−24] Building on these findings, Kocienski and coworkers systematically investigated the role of base countercation, solvent polarity, and aromatic activator on the stereochemical outcome of simple Type I reactions.[4] Conditions that promote the dissociation of the metal cation from the sulfone anion (e.g., K^+ countercation in a polar solvent) favor (*E*) alkene products, which is particularly pronounced when PT sulfones are employed. As seen in Figure 2, an excellent level of *trans* selectivity can be obtained using PT sulfones, regardless of the degree of chain branching, using KHMDS as base in 1,2-dimethoxyethane.[4] Other reaction conditions that also favor a "naked" PT sulfone anion have the same effect; for example, LiHMDS in dimethylformamide with hexamethylphosphoramide as the cosolvent,[25] and KHMDS in tetrahydrofuran with added 18-crown-6.[26]



Act = BT	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*
	Li	THF	60:40	Li	THF	66:34	Li	THF	72:28
	K	DME	75:25	K	DME	76:24	K	DME	36:64

Act = PT	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*	M	Solvent	(*E*)/(*Z*)*
	Li	THF	75:25	Li	THF	69:31	Li	THF	53:47
	K	DME	94:6	K	DME	99:1	K	DME	99:1

Figure 2. Stereoselectivity of alkene formation via addition of R^1CHMSO_2Act to R^2CHO (−78° or −60°, increasing to rt); sulfone anions are generated via premetalation with $(TMS)_2NM$ bases; the group to the left of the double bond originated from the sulfone (R^1).

A credible stereocontrol model has been proposed to account for the high *anti* diastereoselectivity (and ultimately the (*E*)-selective olefination) for the addition of metalated sulfones to aldehydes under conditions favoring cation dissociation.[14] An extension of the model to explain both high and low stereoselectivity scenarios is now delineated. Sulfones do not stabilize adjacent negative charge density by 2p–3d π-bonding resonance, but rather by a combination of inductive, polarization, and hyperconjugative effects.[27,28] Solid-state and solution-phase studies of alkyl aryl sulfone metalates indicate the existence of species such as **14** or comparable dimers (Figure 3), wherein the metal cation is associated with the sulfone oxygen atoms, and a pyramidalized sp^3-hybridized carbanion is oriented to allow for $n_C \rightarrow \sigma^*_{S-Ar}$ orbital overlap.[29] For addition reactions in which the cation is expected to be tightly bound to the metalated sulfone, e.g., M = Li and tetrahydrofuran (or a less coordinating solvent), closed chair-like transition states **15** and **16** are more likely the dominant species (Scheme 5).[30,31] There is little to differentiate energetically between these two assemblies because significant 1,3-diaxial interactions do not exist to distinguish the axial disposition of R^1 in **16** from its equatorial placement in **15**. The observation of poor stereocontrol for Type I olefinations under Julia's original reaction conditions (LDA, THF, –78° to rt) is understandable on this basis. By contrast, protocols that favor cation dissociation, e.g., M = K and 1,2-dimethoxyethane solvent or M = Li and dimethylformamide–hexamethylphosphoramide solvent, allow for open transition states such as **18** and **19**. The second transition state (**19**) is of lower energy because it lacks the gauche interaction between R^1 and R^2 that is present in the alternative transition state (**18**). Progression of the olefination process via the favored transition state **19** leads to *anti* β-alkoxy sulfone **17** and thence to the (*E*) alkene. Thus, a plausible hypothesis is at hand to account for the finding of high *trans* selectivity under conditions involving "naked" sulfone anions. A recent DFT computational study draws a similar conclusion and offers additional insights.[18] In addition, the reason why PT sulfones offer intrinsically higher *anti* selectivity than BT sulfones has been the source of speculation;[14] however, no definitive conclusion can yet be drawn. Taken as a whole, the mechanistic origin of diastereoselectivity in the addition of sulfone anions to carbonyl compounds warrants further studies.

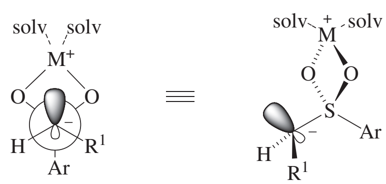


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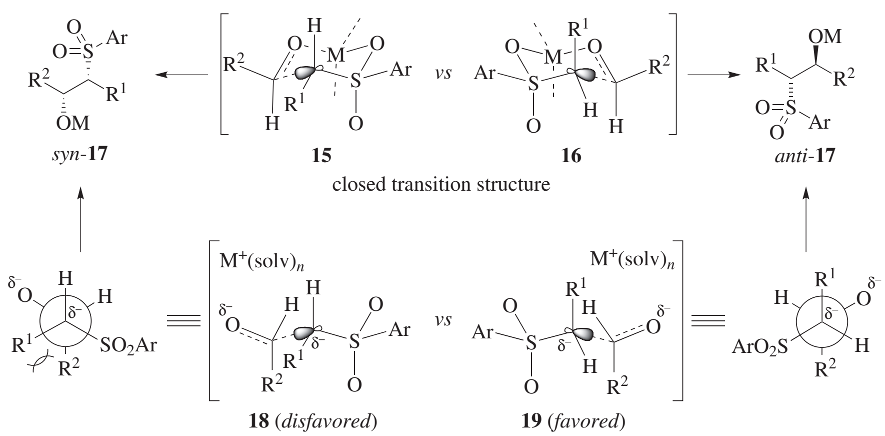
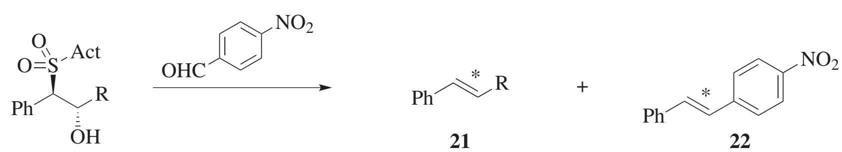
Figure 3. The structure of an alkyl aryl sulfone metalate.



Scheme 5

Stereoselectivity in Type II Reactions: Conjugated Sulfone Anions. The use of stabilized (e.g., R^1 = carbonyl) or semi-stabilized (e.g., R^1 = vinyl, alkynyl, aryl) conjugated sulfone anions provides the possibility of equilibration between intermediate β-alkoxy sulfones **7** via a retroaddition/re-addition mechanism (pathway **A**, Scheme 2). Conditions under which retroaddition operates in the case of metalated benzylic BT and PT sulfones have been identified experimentally using crossover experiments with 2-sulfonyl-2-phenylethanols **20** (Scheme 6).[13,17,21,32] Treatment of β-hydroxy sulfones **20** with base in the presence of 4-nitrobenzaldehyde generates the direct elimination product **21** if no fragmentation of the alkoxide anion occurs. However, if the intermediate alkoxide undergoes retroaddition, a competition will exist between re-addition of the resulting sulfone anion $PhCHMSO_2Act$ to RCHO or to 4-nitrobenzaldehyde. The isolation of the "crossover" product **22** therefore provides evidence that some degree of retroaddition occurs. In the case of *anti* β-hydroxy sulfones **20** (R = Ph), lithium alkoxides of both BT and PT variants experience significant retroaddition between –78° and room temperature.[13,21] In the case of the less-substituted BT sulfone **20** (R = H), retroaddition from the derived lithium alkoxide does not occur to any measureable extent at –60°, in which the inducement of significant fragmentation requires generation of the potassium alkoxide in the presence of potassium-selective complexing agents such as 18-crown-6 or tris[2-(2-methoxyethoxy)ethyl]amine (TDA).[32] The potassium alkoxide of the analogous PT sulfone **20** (R = H) exhibits a much higher propensity to fragment under the same reaction conditions.



20 **21** *direct product* **22** *cross-over product*

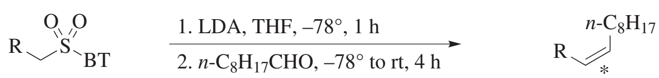
R	Act	Base	Solvent	Temp	Direct Product Yield (%)	Direct Product (*E*)/(*Z*)*	Cross-Over Product Yield (%)	Cross-Over Product (*E*)/(*Z*)*
Ph	BT	LDA	THF	–78° to rt	40	≥98:2	60	92:8
Ph	PT	LDA	THF	–78° to rt	35	87:13	60	69:31
H	BT	LiHMDS	DMF–HMPA (3:1)	–60°	>98[a]	na	<2[a]	—
H	BT	KHMDS	18-crown-6, DMF	–55°	34[a]	na	66[a]	—
H	BT	KHMDS	DMF–TDA (3:1)	–60°	22[a]	na	72	—
H	PT	KHMDS	DMF–TDA (3:1)	–60°	<2[a]	na	93	—

[a]Based on HPLC analysis.

TDA = tris[2-(2-methoxyethoxy)ethyl]amine
na = not applicable

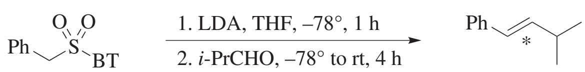
Scheme 6

In Type II reactions in which a retroaddition mechanism operates, the ultimate stereochemical outcome of olefination is not a simple consequence of diastereoselectivity in the initial step. Furthermore, because *syn* β-alkoxy sulfone intermediates **7** cyclize faster than their *anti* counterparts, the preferred formation of *cis* alkenes is anticipated in cases where retroaddition is more facile than spirocyclization, and the elimination from β-aryloxysulfinates **9** follows a stereospecific *anti* pathway (see Scheme 2). Indeed, potentially useful (*Z*) selectivity has been documented for many Type II reactions, particularly for examples involving propargylic sulfones (Scheme 7);[3] however, this outcome is by no means certain, and the *cis* bias is generally overridden when α-branched aldehydes are utilized (Scheme 8).[3] Less reactive aromatic activators such as PYR[3] and 1-*tert*-butyl-1*H*-tetrazol-5-yl (TBT)[5] raise the energy barrier for the Smiles rearrangement (by lower activator electrophilicity in the former, and by increased steric hindrance to *ipso* substitution in the latter), thereby promoting (*Z*) selectivity by enhancing equilibration between *syn* and *anti* β-alkoxy sulfone intermediates. As illustrated in Scheme 9, this kind of activator effect can be significant enough to result in the reversal in stereoselectivity.[5]



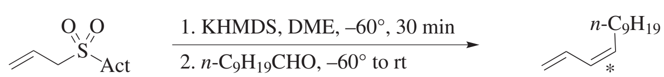
R	Yield (%)	(*E*)/(*Z*)*
Ph	81	37:63
CH_2=CH	66	40:60
n-C_4H_9—≡	26	<1:99

Scheme 7



(51%) (*E*)/(*Z*)* = 90:10

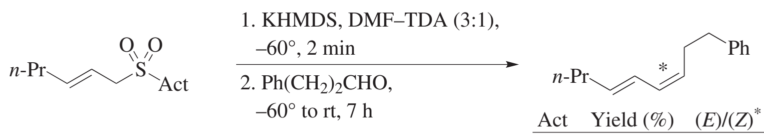
Scheme 8



Act	Yield (%)	(*E*)/(*Z*)*
PT	39	67:33
TBT	60	4:96

Scheme 9

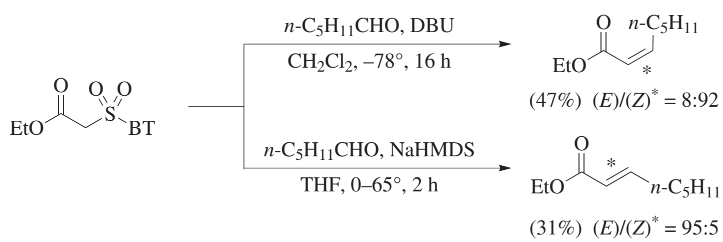
An alternative strategy to enhance (*Z*) selectivity from semi-stabilized sulfone anions utilizes the more common BT or PT activators under the reaction conditions noted above in Scheme 6 for optimal retroaddition (Scheme 10).[32] The presence of α-branching on the aldehyde leads to (*E*) alkenes, which has been ascribed to the difficulty of generating *syn* β-alkoxy sulfones via an open transition state (**18**, Scheme 5) in which R^2 is bulky.[32] Steric effects are evidently not the only cause of losing *cis* selectivity, because non-branched α-oxygenated aldehydes also afford (*E*) alkene products under these conditions.[32]



Act	Yield (%)	(*E*)/(*Z*)*
BT	73	17:83
PT	40	13:87

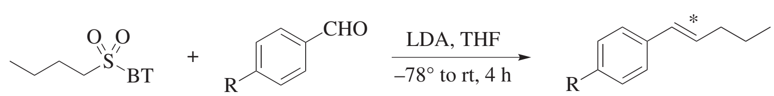
Scheme 10

Type II reactions involving highly stabilized sulfone anions (e.g., R^1 = carbonyl) follow the same trends highlighted above for semi-stabilized cases; thus, (*Z*) α,β-unsaturated carbonyl compounds can be prepared from non-conjugated unbranched aldehydes, but (*E*) selectivity is observed in all other cases.[20] The sense of stereoselectivity is dependent on reaction temperature, in which any inherent (*Z*) selectivity is accentuated at low temperature, and (*E*) selectivity is obtained upon heating (Scheme 11).[20] It has been suggested that at higher temperatures, loss of SO_2 and the aryloxide anion from β-aryloxy sulfinates **9** is non-concerted and follows an E1cB-type mechanism via **11** (pathway **C**, Scheme 2).[14] In this case (i.e., R^1 = carbonyl or with other strongly electron-withdrawing groups), the formation of the (*E*) alkene would be anticipated if the stabilized carbanion (enolate) **11** eliminates $ActO^-$ from the lower-energy conformer. The synthesis of α,β-unsaturated carbonyl compounds and related alkenes, including fluorinated examples,[33] is discussed in more detail below (see "Scope and Limitations").



Scheme 11

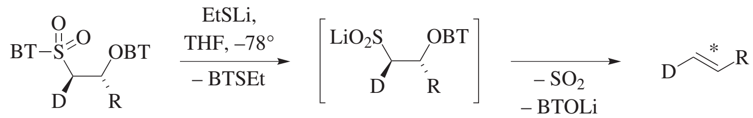
Stereoselectivity in Type III Reactions: Conjugated Carbonyl Compounds. Julia–Kocienski olefinations involving non-conjugated primary BT or PT sulfone anions and α,β-unsaturated aldehydes (including aryl aldehydes) result in the preferential formation of (*E*)-configured 1,2-disubstituted alkenes in a vast majority of cases.[3] The level of stereoselectivity obtained is usually high [(*E*)/(*Z*) ratios well in excess of 4:1 are typical], and the stereochemical outcome is not particularly sensitive to solvent, cation, or additive effects, making these kinds of reactions reliable and easy to perform. As is the case for Type II reactions, kinetic diastereoselectivity in the initial addition step is not the determinant of alkene configuration in Type III reactions,[15] but for the latter type, this fact is attributed to the mechanistic complexity of the elimination from β-aryloxy sulfinate intermediates rather than to issues of reversibility.[17] Prompted by the (*E*) selectivity in Type III reactions and the correlation between product (*E*)/(*Z*) ratio and the electron richness of substituted benzaldehyde substrates (Scheme 12), Julia and coworkers proposed the zwitterionic pathway outlined in Scheme 2 (pathway B).[3] It was reasoned that zwitterionic intermediates **10** can be formed in cases where R^2 is capable of stabilizing an adjacent carbocation; loss of SO_2 from the lower-energy conformer of **10** leads to the (*E*) alkene regardless of the original *syn* or *anti* configuration of the precursor β-aryloxy sulfinate **9**. Substituents that can stabilize the positively charged center are anticipated to promote the zwitterionic pathway and so accentuate the stereoselectivity of the reaction. Although the zwitterion hypothesis has predictive value, experimental proof has not been forthcoming, and its validity is dubious given the poor nucleofugality of aryloxide anions (e.g., BTO^-) and the expected high energy of zwitterions **10** in the relatively non-polar ethereal solvent media.



R	Yield (%)	(*E*)/(*Z*)*
H	68	94:6
MeO	95	99:1
Cl	51	77:23

Scheme 12

Recently performed calculations also fail to locate zwitterions as credible intermediates in Type III (or Type IV) reactions and reveal stereoconvergence in the elimination of β-aryloxy sulfinates **9** (M = Li, R^1 = Me, R^2 = Ph) such that both possible diastereoisomers preferentially generate the (*E*) alkene product but via distinct, concerted mechanisms.[17] The lowest-energy pathway for loss of SO_2 and BTOLi from *anti*-**9** (M = Li, R^1 = Me, R^2 = Ph) is via antiperiplanar elimination, whereas for *syn*-**9** (M = Li, R^1 = Me, R^2 = Ph), the synperiplanar elimination pathway is lower in energy (pathway D, Scheme 2). Lending credence to the major conclusions of this important computational study, generation of stereodefined, isotopically labeled β-aryloxy sulfinates **24** from sulfones **23** leads predominantly to (*E*)-alkene products **25** predicted by a *syn* elimination pathway (Scheme 13).[17] Given that the (*E*)- and (*Z*)-alkene products **25** in this case differ only by isotopic substitution, these findings are incompatible with the zwitterionic pathway hypothesis, which would afford alkenes **25** with (*E*)/(*Z*) ~ 50:50. Significantly, the dependence of the (*E*)/(*Z*) ratio on the aryl moiety mirrors the trend found previously for Type III Julia–Kocienski olefinations involving aryl aldehydes (c.f., Scheme 12), indicating that electron-releasing R^2 substituents stabilize the transition state of the synperiplanar elimination pathway (which is precluded for *anti* β-aryloxy sulfinates **7** with non-trivial substituents because of an eclipsing interaction between R^1 and R^2). It waits to be seen whether or not stereoconvergence is also the cause of (*E*) selectivity in Type III olefinations involving non-aromatic α,β-unsaturated aldehydes.

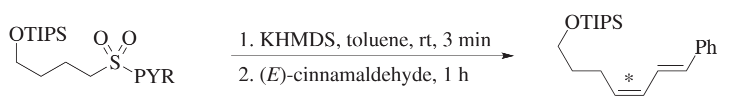


23 **24** **25**

R	Yield (%)	(*E*)/(*Z*)*
Ph	92	90:10
4-MeOC$_6$H$_4$	87	94:6
4-ClC$_6$H$_4$	89	81:19

Scheme 13

Although most Type III reactions are (*E*)-selective, some exceptions are known. For example, in a limited focus study, it was found that the potassium metalate of a non-conjugated PYR sulfone reacts with (*E*)-configured α,β-unsaturated aldehydes to provide the (*E,Z*)-diene products (Scheme 14).[34,35] The mechanistic origin of selectivity for this reaction is unknown, as is its potential generality for the synthesis of conjugated (*Z*)-configured alkenes.



(70%) (*E*)/(*Z*)* = 8:92

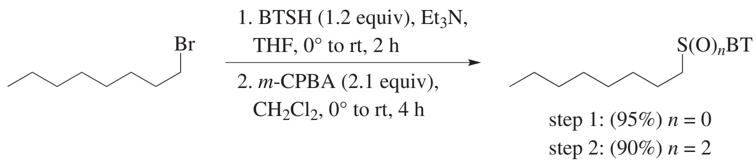
Scheme 14

Stereoselectivity in Type IV Reactions: Both Components Conjugated. For scenarios in which both R[1] and R[2] are conjugating substituents, all of the mechanistic possibilities discussed above for Type II and Type III reactions come into play. Prediction of the stereochemical outcome of Type IV olefination reactions is difficult unless one has knowledge of the behavior of closely related examples. Some specific cases are discussed below.

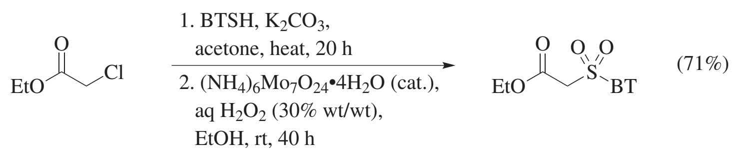
SCOPE AND LIMITATIONS

Methods for Introducing Sulfone Activators

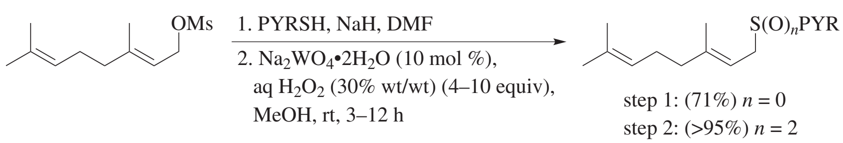
Via Oxidation of Intermediate Thioethers. An attractive feature of the Julia–Kocienski olefination is the ease with which the activating sulfone moiety can be introduced into a fragment of interest. Sulfones are generally prepared via oxidation of the corresponding thioethers which are, in turn, typically produced by the alkylation of the appropriate thiol ActSH (Act = BT, PT, PYR, etc.) via an S_N2 substitution. It is worth noting from the standpoint of operational convenience that the heterocyclic thiols most commonly employed as starting materials are odorless solids. For simple R groups (R = primary or secondary alkyl), thioether formation is most economically achieved by direct alkylation of the thiol with an alkyl halide or alkyl sulfonate ester in the presence of a base (e.g., step 1, Schemes 15–17).[20,34–36]



Scheme 15

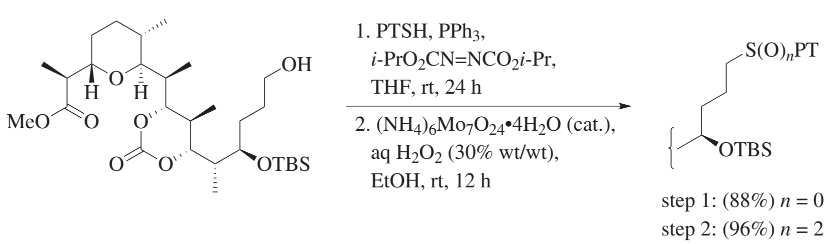


Scheme 16

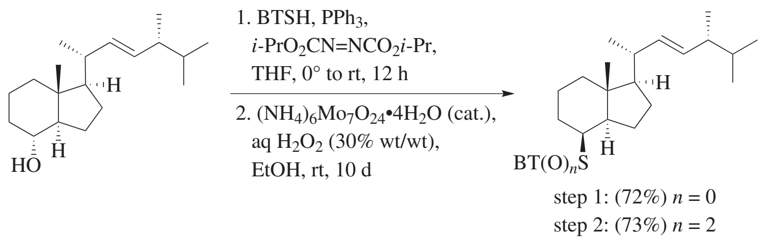


Scheme 17

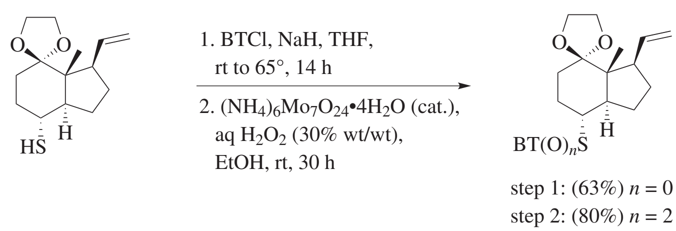
For more complex R groups, wherein preparation of the alkyl halide or sulfonate would necessitate unwelcome additional operations, thioethers are conveniently produced from alcohol precursors with ActSH using the Mitsunobu reaction.[37] The Mitsunobu method is compatible with a wide range of aprotic functional groups (including common protecting groups), and it has been successfully applied to the synthesis of many late-stage polyfunctional intermediates en route to natural product targets (Scheme 18).[38] As expected, thioetherification of stereogenic secondary alcohols proceeds with inversion of configuration (Scheme 19).[39] An alternative and less-explored approach to thioethers to prepare Julia–Kocienski reagents involves an S_NAr reaction of a substrate thiol with an ActX type species (Scheme 20).[40]



Scheme 18



Scheme 19



Scheme 20

A wide variety of oxidants are capable of converting thioethers into the corresponding sulfones (e.g., *m*-CPBA, Oxone, transition-metal oxo complexes etc.); however, before implementing a particular method one must consider any relevant chemoselectivity issues. For example, the use of peroxyacid reagents (e.g., *m*-CPBA) may result in competitive alkene epoxidation during the attempted conversion of an alkenyl thioether into a sulfone. Protocols based on the use of transition-metal oxo complexes are available that achieve chemoselective oxidation at sulfur while minimizing unwanted transformations at other sites. An ammonium molybdate hydrate catalyst [$(NH_4)_6Mo_7O_{24}\bullet 4H_2O$] in the presence of aqueous hydrogen peroxide (30 wt %) as the terminal oxidant has enjoyed widespread use for the synthesis of sulfones for the Julia–Kocienski olefination (e.g., step 2, Schemes 18–20).[38–40] Finally, catalytic thioether oxidation with sodium tungstate dihydrate has been reported to be superior to molybdenum(VI) catalysts for sulfone production with particularly sensitive substrates (Scheme 17).[34,35]

Regardless of the oxidation procedure employed, it should be noted that the conversion of thioethers to sulfones is an indirect process that proceeds via intermediate sulfoxides. Production of the sulfoxide from the thioether is rapid, and further oxidation of the sulfoxide to the sulfone is considerably slower. Monitoring the extent of oxidation by TLC analysis is recommended, since it is generally found that the sulfoxide is more polar than the thioether, and that the sulfone has a polarity between those of the thioether and the sulfoxide (usually closer to the thioether than to the sulfoxide). The NMR signature of the α-methylene unit in compounds $ActS(O)_nCH_2CH_2R$ (where R is achiral) undergoes diagnostic changes as the oxidation state increases.[41] For the thioether ($n = 0$), a simple triplet ($\delta_H \sim 3.25$ ppm) characteristic of a first order A_2X_2 spin system is observed. For the sulfoxide ($n = 1$), the stereogenic center at sulfur results in the emergence of an ABXY spin system with clearly differentiated chemical shift values for each individual diastereotopic α-H atom. Further oxidation to the sulfone ($n = 2$) results in loss of stereogenicity at sulfur; however, the NMR signature of the α-methylene unit can be quite different in appearance to that seen in the symmetry-related thioether. Thus, in the case of the sulfone, the multiplet observed ($\delta_H \sim 3.50$ ppm) is often not a simple triplet but instead a complex pattern characteristic of a second order AA'BB' spin system (Figure 4).[41,42]

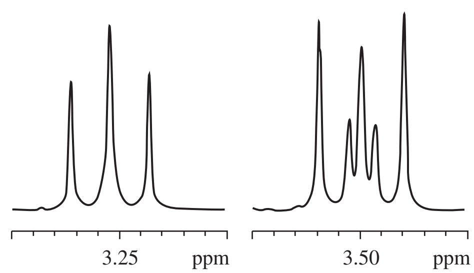
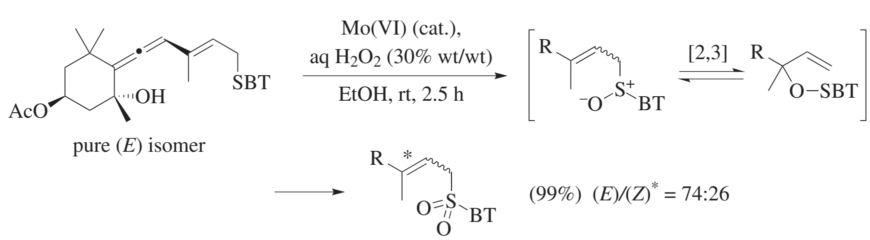
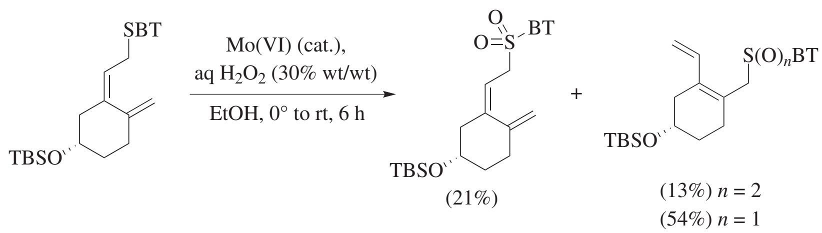


Figure 4. ^{1}H NMR spectral signature for the α-CH_2 group in $BTSCH_2Et$ (left) and $BTSO_2CH_2Et$ (right). Reproduced from ref. 41 with permission from the Royal Society of Chemistry.

The synthesis of allylic sulfones via oxidation of allylic thioethers can be complicated by [2,3]-sigmatropic rearrangement[43] of the intermediate allylic sulfoxide. For example, synthesis of an allylic BT sulfone en route to the carotenoid peridinin from the corresponding isomerically pure (*E*)-configured thioether results in significant (*E*)/(*Z*) isomerization as a consequence of [2,3]-sigmatropy of the intermediate sulfoxide (Scheme 21).[44] In a more dramatic example, consecutive [2,3]-sigmatropic rearrangements are responsible for relocation of the activating BT sulfone unit during an attempted synthesis of a vitamin D_2 A-ring precursor (Scheme 22).[39]

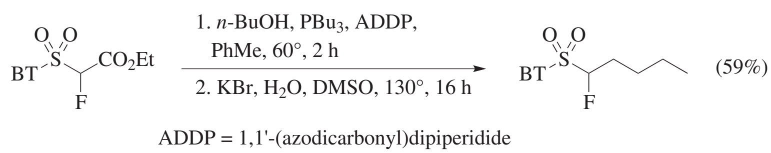


Scheme 21

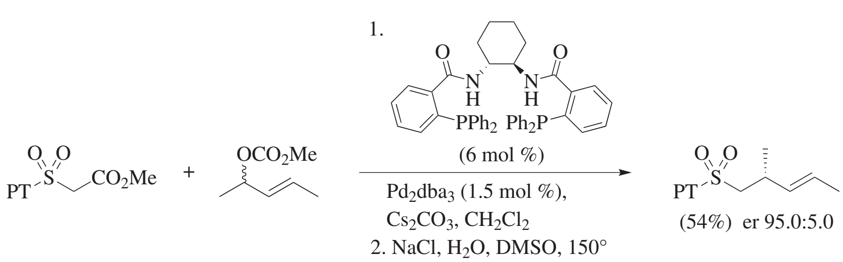


Scheme 22

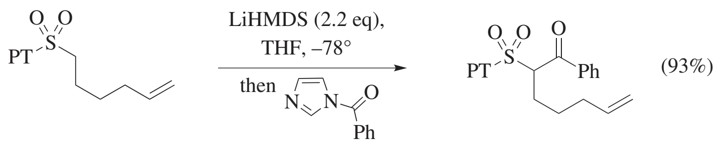
Via Sulfone Derivatization. Sulfones for Julia–Kocienski olefination are also potentially available by derivatization of simpler sulfone-containing precursors, providing that the chemistry involved does not induce any kind of unwanted sulfone degradation or premature olefination. β-Alkoxy carbonyl sulfones are versatile precursors in this regard since the α position is readily derivatized (cf. malonate chemistry) and the auxiliary ester group can be removed later if desired by Krapcho dealkoxycarbonylation[45,46] (Schemes 23 and 24).[47,48] The example in Scheme 24 is notable in that sulfone synthesis is achieved in an enantioselective manner. More recently, chiral iridum(I) catalysts have been used in related asymmetric allylic alkylations of sulfonyl acetates using generic linear allylic carbonates, resulting in scalemic branched sulfone products.[49] β-Alkoxy carbonyl sulfones or β-keto sulfones can also be prepared via a Claisen condensation type process involving acylation of sulfone metalates (Scheme 25).[50]



Scheme 23

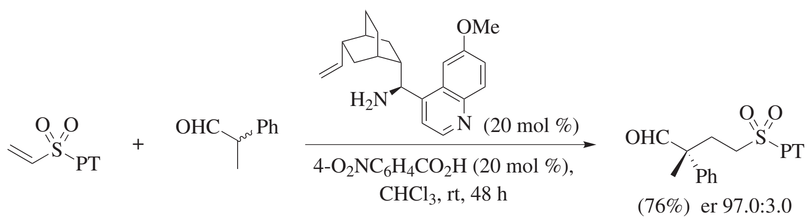


Scheme 24

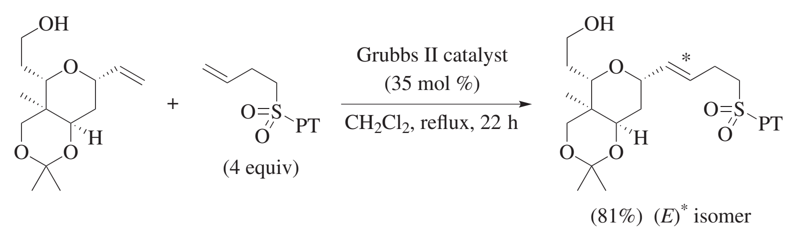


Scheme 25

Conjugate addition to vinyl sulfones has also been employed for the synthesis of Julia–Kocienski olefination reagents. For example, β-alkoxy[51] and β-amino[52] sulfones can be obtained by conjugate addition of heteroatom nucleophiles, and enantioselective organocatalysis through the addition of carbon nucleophiles (Scheme 26).[53] Other types of reactions are likewise compatible with acceptor aryl sulfones and allow for efficient derivatization. Notable in this regard is the feasibility of alkene cross-metathesis (Scheme 27).[54]



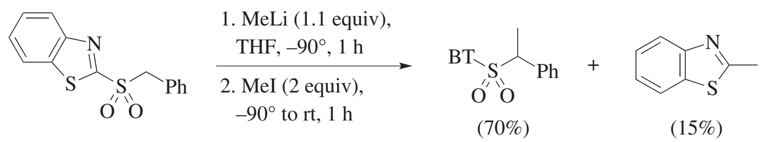
Scheme 26



Scheme 27

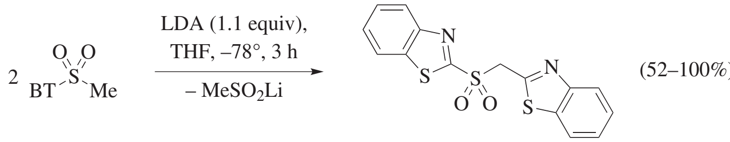
Generation of Sulfone Anions and Strategies to Avoid Self-Condensation

The electron-accepting nature of the aromatic activators found in Julia–Kocienski olefination reagents means that sulfone anion generation is best conducted with a non-nucleophilic base to avoid premature *ipso* substitution of the sulfinate nucleofuge. With the notable exception of PYR sulfones, which can be cleanly metalated with *n*-butyllithium,[3] the use of alkyllithiums for deprotonation is not recommended because some degree of nucleophilic attack will also occur (Scheme 28).[3] The pK_a of the α-hydrogen atoms in simple alkyl aryl sulfones is comparable to that found in esters (ca. 30 in DMSO);[55] accordingly, the hindered, alkali-metal amides,[56] such as lithium diisopropylamide (LDA) and the commercially available hexamethyldisilazides (LiHMDS, NaHMDS, and KHMDS), are sufficiently strong to effect deprotonation, and these types of reagents are used in a majority of Julia–Kocienski olefination reactions. For instance, quantitative metalation within 15 minutes is generally observed at –78° in ethereal solvents. Curiously, metal amide bases are ineffective for olefination reactions using BTFP sulfones, and these compounds are instead treated either with potassium hydroxide in tetrahydrofuran at room temperature or a Schwesinger phosphazene base[57] such as 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene) (P4-*t*-Bu) in tetrahydrofuran at –78°.[58] When sulfone coupling partners are equipped with electron-withdrawing R groups, weaker bases such as DBU or cesium carbonate are sufficiently basic to facilitate for successful olefination.



Scheme 28

The problem of premature *ipso* substitution is not necessarily confined to the metalation stage of the olefination process because the sulfone anions themselves are capable of pairwise intermolecular self-condensation.[3,5] The propensity for self-condensation is dependent on the net electrophilicity of the aromatic activator and the size of the substituent R associated with the sulfone; BT and PT sulfones are particularly susceptible because R is of low steric demand. For example, incubating the lithiate of $BTSO_2Me$ for a short time in tetrahydrofuran at –78° results in extensive self-condensation and affords the anticipated sulfone-linked bis(heterocyclic) adduct (Scheme 29).[3,50] By contrast, PYR, TBT, and BTFP sulfone metalates are more resistant to self-condensation than the BT or PT derived species due to lower intrinsic electrophilicity of the aromatic activator (PYR and BTFP)[58] and/or steric protection of the electrophilic center (cf. TBT versus PT).[5] Metalate stability in a series of benzylic sulfones has been quantified by exposure to various basic reaction conditions followed by protonolysis and assessment of percent recovery of the non-decomposed starting material (Figure 5).[58] In addition to revealing the heightened stability of TBT and BTFP sulfone metalates, the data indicate that lithiated sulfones are more stable than other types of sulfone anion and that, despite earlier assertions to the contrary,[4] PT sulfone metalates are not necessarily more stable that their BT congeners.[59]



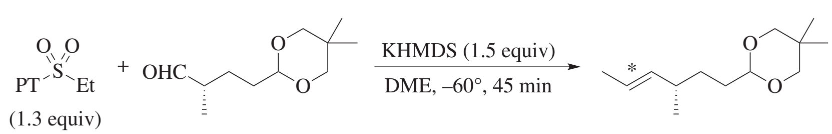
Scheme 29

Conditions	BTFP–SO_2–CH_2Ph	TBT–SO_2–CH_2Ph	PT–SO_2–CH_2Ph	BT–SO_2–CH_2Ph
LDA, THF, –78°, 24 h	(>95%)	(>95%)	(>95%)	(>95%)
KHMDS, DME, –60°, 24 h	(75%)	(99%)	(50%)	(84%)
phosphazene P4-*t*-Bu, THF, –78°, 24 h	(88%)	(78%)	(64%)	(73%)
KOH, Bu_4NBr, THF, rt, 24 h	(32%)	(0%)	(0%)	(5%)

phosphazene P4-*t*-Bu = 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene)

Figure 5. Percent recovery of benzylic sulfones following exposure to basic reaction conditions and then reprotonation with H_2O.

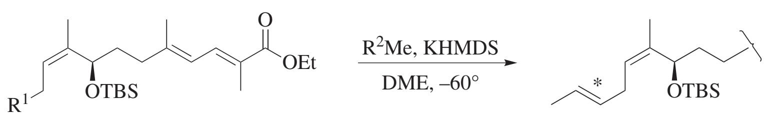
For sulfone metalates of low kinetic stability, the problem of self-condensation can often be ameliorated by adoption of a so-called 'Barbier' protocol wherein the base is added to a mixture of the sulfone and carbonyl compound rather than a more conventional 'premetalation' protocol that involves addition of the latter only after complete sulfone deprotonation. Presumably, under Barbier conditions the sulfone anion is consumed by the carbonyl compound as soon as it is formed and thus self-condensation of the sulfone coupling partner is minimized. The possibility of an enolizable aldehyde or ketone being adversely affected by a Barbier protocol is a legitimate concern; however, a great many results attest to the effectiveness of the approach even in cases where chemical intuition suggests that it should fail. For example, Scheme 30 depicts the attempted synthesis of an (*E*)-configured 1,2-disubstituted alkene using an enantioenriched α-substituted enolizable aldehyde and a sterically unencumbered PT sulfone.[60,21] This reaction results in an unacceptably low yield via a premetalation protocol because the sulfone metalate undergoes self-condensation. An otherwise identical experiment that involves premixing of the sulfone and aldehyde prior to the introduction of KHMDS results in a dramatically improved olefination yield without detectable aldehyde racemization. In general, it is suggested that a premetalation



Procedure	Yield (%)	(*E*)/(*Z*)*
premetalation [sulfone + KHMDS, then aldehyde]	93	93:7
Barbier [sulfone + aldehyde, then KHMDS]	15	>90:10

Scheme 30

protocol be evaluated initially and then Barbier conditions be tested subsequently if a problem is encountered with the first approach. In some cases, a poor outcome due to sulfone metalate instability is best tackled by investigating alternative aryl activators and/or a strategic reversal in sulfone and carbonyl component selection (Scheme 31).[61]

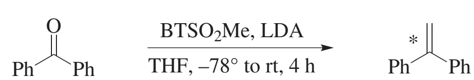


Procedure	R^1	R^2	Yield (%)	(*E*)/(*Z*)*
Barbier	OHC	PTO_2SCH_2	26	—
premetalation	PTO_2SCH_2	OHC	90	86:14

Scheme 31

Optimal Targeting of Different Classes of Alkene

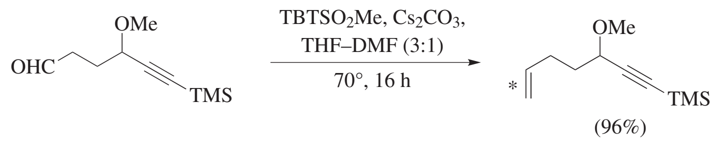
Monosubstituted and 1,1-Disubstituted Alkenes. Julia–Kocienski olefination can be used to generate these classes of alkenes either by methylenation of an aldehyde or a ketone with a methyl sulfone reagent ($ActSO_2Me$) or by the use of formaldehyde as the carbonyl component. Both strategies have been successfully implemented although the former approach is far more common. Given the problem of self-condensation for sterically unencumbered sulfone metalates (cf. Scheme 29), the yield of methylenation is generally higher if the olefination reaction is performed under Barbier conditions (Scheme 32).[3] Although favorable outcomes have been described with BT and PT methyl sulfones, the more robust TBT,[62] BTFP,[58] and *N*-alkylbenzimidazolyl[63] methyl sulfones may offer superior results, particularly for the methylenation of hindered ketones. Methylenation with $TBTSO_2Me$ can be conveniently achieved by using cesium carbonate as the base in a mixture of tetrahydrofuran and dimethylformamide at 70° (Scheme 33). However, these reaction conditions result in partial racemization/epimerization of α-substituted carbonyl compounds and, in such cases, a more conventional protocol (NaHMDS, THF, –78°) should be employed.[62] Readily prepared *N*-alkylbenzimidazolyl methyl sulfones methylenate aldehydes and ketones in high yield using potassium *tert*-butoxide as the base in dimethylformamide at room temperature; the *N*-isopropyl variant



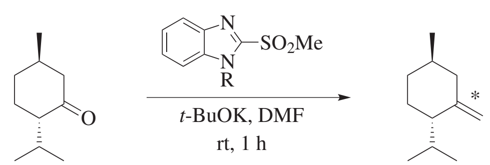
Procedure	Yield (%)
Barbier	55
premetalation	11

Scheme 32

offers better results than its *N*-methyl congener (Scheme 34).[63] In one of the few examples of the Julia–Kocienski olefination using formaldehyde, 4-nitrophenyl (NP) sulfonyl acetates engage with formalin in the presence of cesium carbonate to afford methylidene esters directly via the usual mechanism (Scheme 35).[64]

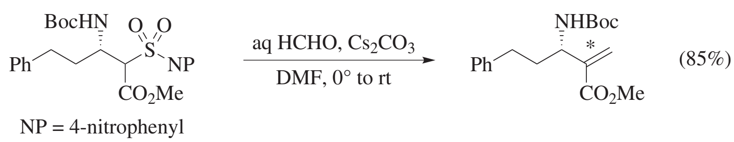


Scheme 33



R	Yield (%)
Me	60
i-Pr	76

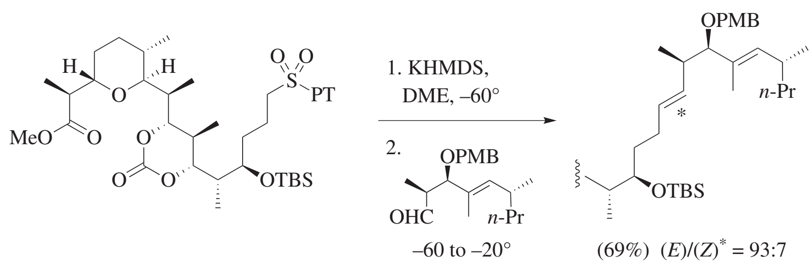
Scheme 34



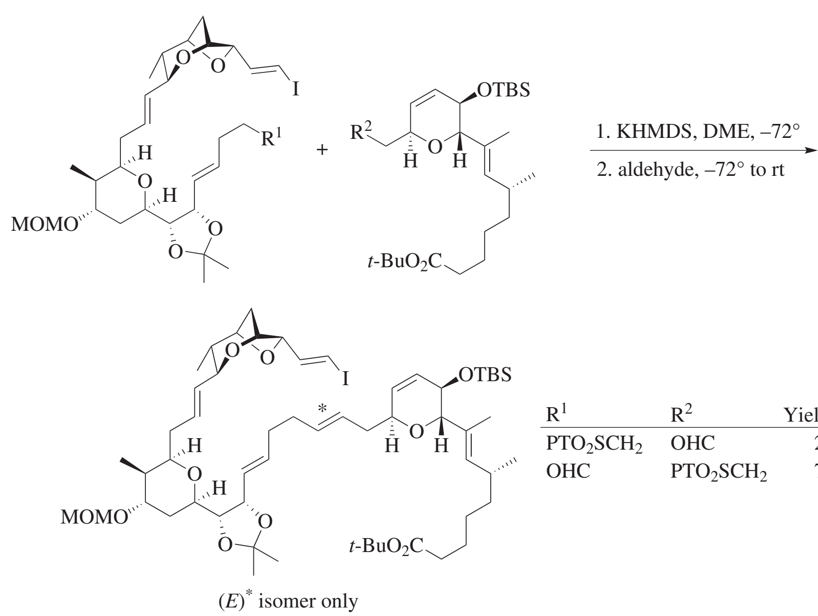
Scheme 35

Non-Conjugated 1,2-Disubstituted Alkenes. The Julia–Kocienski olefination has enjoyed its most widespread application for the synthesis of non-conjugated 1,2-disubstituted alkenes. This popularity exists because the process is high yielding and that under appropriate reaction conditions, (*E*)-alkene isomers are formed preferentially with a synthetically useful level of stereoselectivity. The ability to prepare *trans* alkenes in the absence of intrinsic steric or electronic biasing elements in either coupling partner stands in contrast to other common carbonyl olefination processes.[12] Significantly, the Julia–Kocienski olefination to form non-conjugated 1,2-disubstituted alkenes is stereocomplementary to the standard Wittig reaction, which remains optimal for the synthesis of *cis* alkenes (see "Comparison with Other Methods").

As detailed above ("Factors Influencing Stereoselectivity"), the use of PT sulfones under reaction conditions that favor a "naked" sulfone anion species (i.e., polar/dipolar aprotic solvent, non-coordinating countercations and/or cation complexation agents) generally leads to maximal (*E*) selectivity for Type I reactions. In most cases, the use of BT sulfones provides lower *trans* selectivities within this target class, particularly if the original reaction conditions are employed (LDA, THF, –78°).[3] By contrast, the use of Kocienski's reaction conditions with PT sulfones (KHMDS, DME, –55°)[4] has proven effective in many different and complex scenarios (Schemes 36 and 37).[38,65] The urge to substitute tetrahydrofuran for the advocated solvent 1,2-dimethoxyethane should be resisted when using this protocol, because stereoselectivity will be compromised to some degree; however, excellent (*E*) selectivity can be obtained if 18-crown-6 is added in conjunction with tetrahydrofuran.[26] Replacing the KHMDS base with NaHMDS or LiHMDS in an ethereal solvent will also generally result in a lower (*E*)/(*Z*) ratio, although such a change is often accompanied by an increase in yield because potassiated sulfones are more prone to decomposition than their less reactive sodium or lithium counterparts.



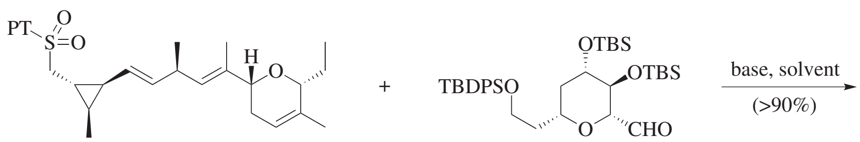
Scheme 36

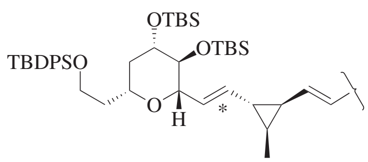


R1	R2	Yield (%)
PTO_2SCH_2	OHC	28
OHC	PTO_2SCH_2	79

Scheme 37

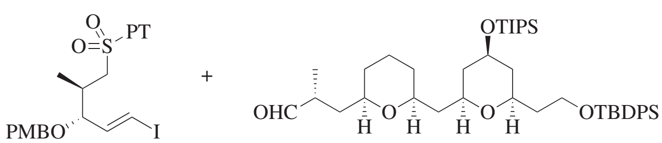
High (*E*) selectivity can be obtained with lithiated PT sulfones if blended solvent media containing strong dipolar aprotic components are employed, for example THF–HMPA, DMF–HMPA, or DMF–DMPU (Scheme 38).[25] Although cyclopropylmethyl sulfones often provide variable selectivities in Julia–Kocienski olefination reactions (see below), the excellent *trans* stereoselectivity seen in Scheme 38 is quite general and extends to other types of PT sulfones. Indeed, because this protocol avoids potentially unstable potassiated sulfones, it has proven superior in cases wherein Kocienski's conditions afford unsatisfactorily low yields (Scheme 39).[66]

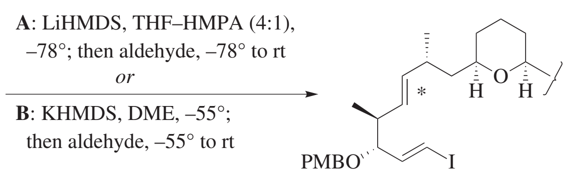




Base	Solvent	Temp (°)	(*E*)/(*Z*)*
NaHMDS	THF	–78	11:89
KHMDS	DME	–60	50:50
LiHMDS	THF–HMPA (4:1)	–60	75:25
LiHMDS	DMF–HMPA (4:1)	–35	>97:3

Scheme 38

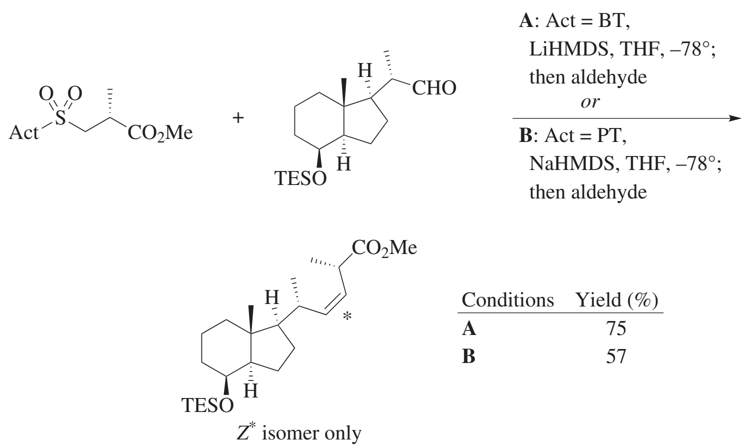




Conditions	Yield (%)	(*E*)/(*Z*)*
A	80	94:6
B	11	93:7

Scheme 39

As alluded to above, anomalous stereoselectivity has been noted for certain Type I olefination reactions. For example, the preferential formation of (*Z*)-configured alkenes from cyclopropylmethyl sulfones under certain reaction conditions was observed early on,[24] and it has been encountered numerous times since, including in the example shown above in Scheme 38 (note the high proportion of (*Z*) alkene generated when either NaHMDS or KHMDS is employed in an ethereal solvent).[25] Another notable exception is the exclusive formation of a (*Z*)-alkene product in the reaction of a branched β-sulfonyl ester with an α-branched CD-ring steroid derived aldehyde (Scheme 40).[67] This example is remarkable in that both BT and PT sulfones produce only the (*Z*) product using a variety of different bases and solvents (including KHMDS and 1,2-dimethoxyethane). Other olefination reactions employing similar steroid derived aldehydes and β-branched sulfones also favor formation of the (*Z*) alkene.[68,69]



Conditions	Yield (%)
A	75
B	57

Scheme 40

In summary, while occasional deviations from *trans* stereoselectivity in the synthesis of non-conjugated 1,2-disubstituted alkenes have been encountered, the Julia–Kocienski olefination is typically (*E*)-selective in this context when properly tuned. As such, it should not be strategically applied to target non-conjugated 1,2-disubstituted (*Z*) alkenes. When contemplating the synthesis of an (*E*)-configured non-conjugated 1,2-disubstituted alkene, it is recommended that a PT sulfone is first evaluated and its reactivity explored with the aldehyde of choice utilizing either KHMDS in 1,2-dimethoxyethane or LiHMDS in THF–HMPA (or DMF–HMPA) via a premetalation protocol. In the event of an unfavorable outcome, a Barbier protocol should be tested, and then the sulfone/aldehyde component reversal be investigated before alternative reaction variations are considered. Schemes 31 and 37 illustrate the dramatic difference that component reversal can have on the outcome.[61,65]

Conjugated 1,2-Disubstituted Alkenes. The Julia–Kocienski olefination has been broadly applied to the synthesis of conjugated 1,2-disubstituted alkenes. Component selection is particularly critical within this context because the manner in which the conjugated system is disconnected determines whether the olefination is of Type II or III (or IV in the case of extended conjugated systems), and this single factor has a dominant impact on whether (*E*) or (*Z*) stereoselectivity is likely to be obtained (see "Factors Influencing Stereoselectivity"). If the generation of an (*E*)-configured conjugated alkene is desired, it is logical to select an α,β-unsaturated aldehyde and a non-conjugated sulfone anion (i.e., Type III, Figure 6). Conversely, a (*Z*)-configured conjugated alkene could potentially be targeted by employing a conjugated sulfone anion and a non-conjugated aldehyde (Type II). In the second case, *cis* selectivity is possible if the aldehyde in question is non-branched, and the tactics highlighted above (in Schemes 9 and 10)[5,32] are used to enhance the existing bias towards the (*Z*) alkene product.

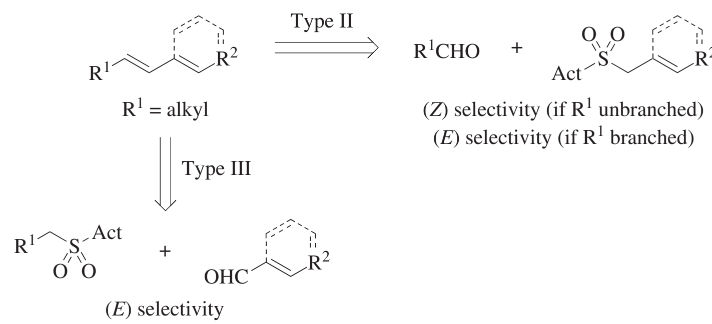
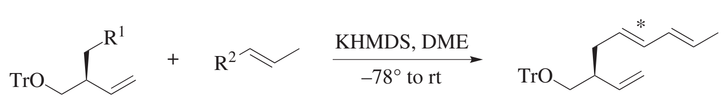


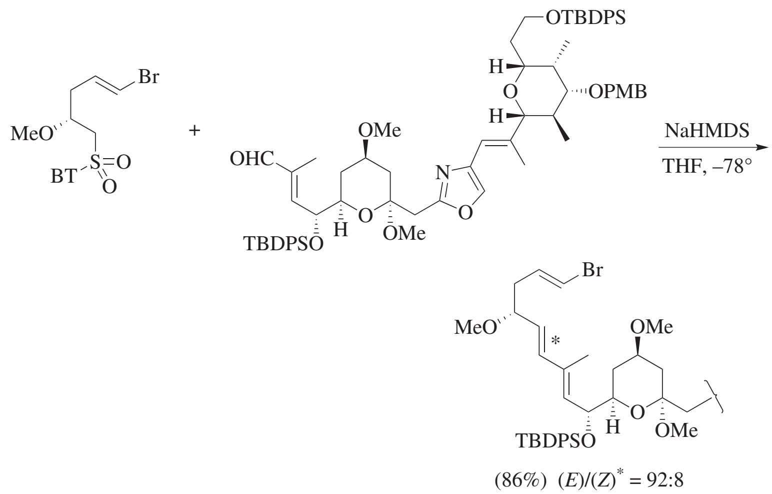
Figure 6. Disconnection strategies for a conjugated 1,2-disubstituted alkene and expected stereochemical bias.

The synthesis of (*E*) alkenes in conjugated diene systems has been extensively explored. Providing that the generally superior Type III component selection is made (Scheme 41 shows a direct comparison of Type II and Type III reactions),[70] high *trans* selectivity is readily achieved, and the olefination outcome is not overly sensitive to reaction conditions. BT and PT sulfones are often equivalent in this regard, and olefination using either LiHMDS or NaHMDS in tetrahydrofuran usually affords excellent results (Schemes 42 and 43).[71,72] The same behavior is observed during the synthesis of (*E*)-configured styryl systems, which are best obtained by a Type III reaction involving a non-conjugated sulfone anion and an aryl aldehyde (Scheme 44).[73] The scale of the latter example—a reaction used in the manufacture of a next-generation statin drug—is notable, as is the fact that quenching the reaction mixture at −80° (rather than at −10°) results in a significantly lower (*E*)/(*Z*) ratio (94:6 instead of >99:1). Schemes 42 and 44 also highlight the fact that β-alkoxy sulfones are often largely resistant to β-elimination during Julia–Kocienski olefination.

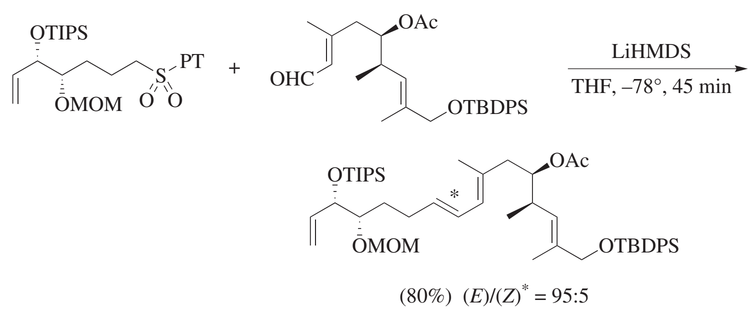


Type	R^1	R^2	Yield (%)	(*E*)/(*Z*)*
II	OHC	PTO_2SCH_2	81	63:37
III	PTO_2SCH_2	OHC	69	94:6

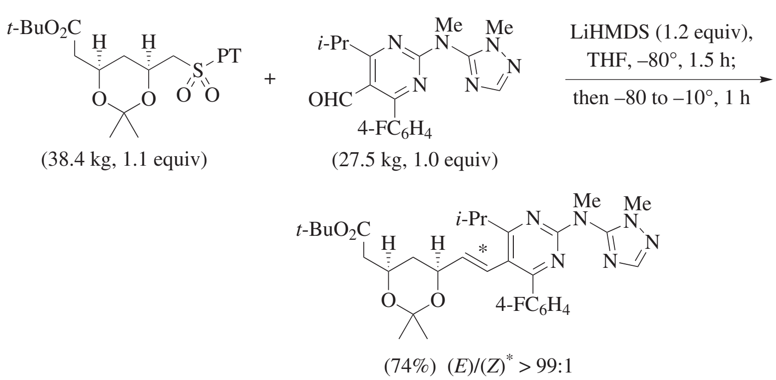
Scheme 41



Scheme 42

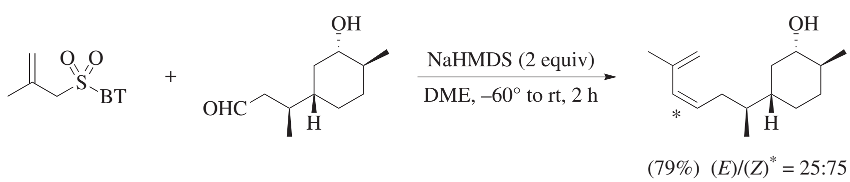


Scheme 43

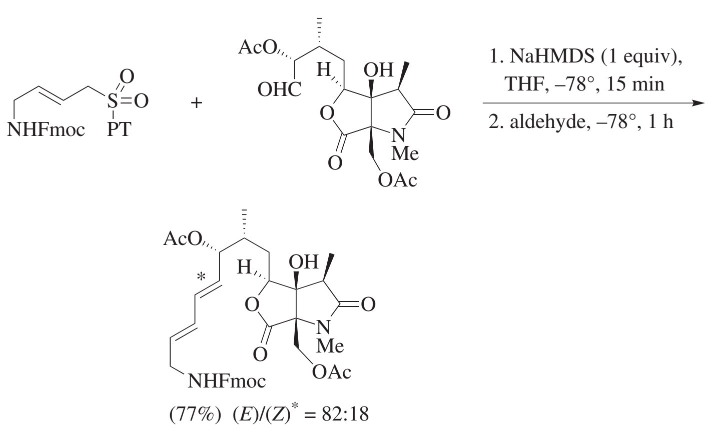


Scheme 44

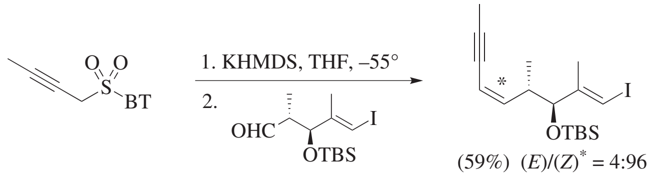
Type II olefination reactions toward (*Z*) alkenes within conjugated diene systems have rarely been deliberately exploited, and the tactics described above (see "Stereoselectivity in Type II Reactions") to facilitate (*Z*) selectivity through enhanced β-alkoxy sulfone diastereoisomer equilibration have yet to enter common usage. Nonetheless, providing that the aldehyde lacks significant chain branching about the carbonyl group, even quite standard reactions conditions will lead to (*Z*)-conjugated alkenes with reasonable stereoselectivity (Scheme 45).[74] When the aldehyde is β-branched, Type II reactions are less predictable and may provide low stereoselectivity. By contrast, α-branched aldehydes afford (*E*) alkenes with good selectivity (Scheme 46),[75] albeit not as high as that routinely achieved via a Type III process. Certain types of conjugated sulfone anions afford high levels of (*Z*) selectivity regardless of the degree of branching within the aldehyde and without recourse to special activators or reaction conditions. Propargylic sulfones reliably generate (*Z*) enynes in Julia–Kocienski olefination reactions (Scheme 47).[76]



Scheme 45

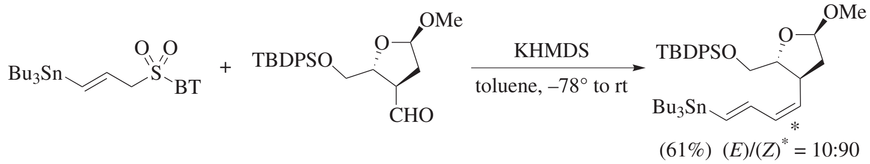


Scheme 46



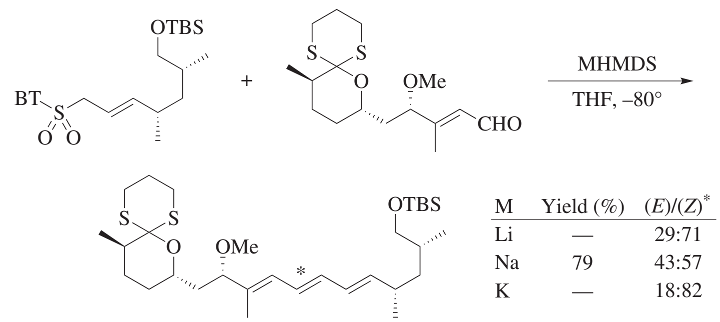
Scheme 47

More recently, it has been discovered that Type II (and Type IV) reactions using γ-stannyl allylic sulfones[77,78] also result in uniformly high *cis* selectivity (Scheme 48).[79]



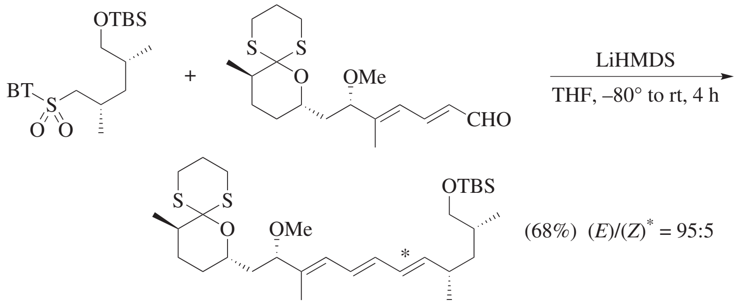
Scheme 48

Conjugated trienes and higher-order systems of concatenated double bonds can be disconnected into components that reflect Type II, III, or IV olefinations. Electing to pursue the last option offers the greatest degree of convergency because the system may then be disconnected down the middle; however, this strategic advantage will come at the expense of predictability since the stereochemical outcomes of Type IV olefinations are variable. Selecting a Type II or III approach requires a sacrifice in convergency, but prediction of stereochemical bias can then be made with a greater degree of confidence. An early application of the Julia–Kocienski olefination to the synthesis of the (*E,E,E*)-triene system of rapamycin is exemplary (Schemes 49 and 50).[22] In this case, high stereoselectivity is not achievable via the Type IV olefination approach, and the required (*E,E,E*)-triene system is never the major isomer produced (Scheme 49). The more reliable Type III olefination approach delivers the (*E,E,E*)-triene in a satisfactory manner (Scheme 50); however, in this case the aldehyde coupling partner requires a more elaborate synthesis. Type IV olefinations have been most extensively studied during the convergent assembly of the polyolefinic regions of light-harvesting cartenoids such as peridinin.[44,80–83] In constructing these extended conjugated π-systems, (*Z*) stereoselectivity is generally observed (Scheme 51).[81]

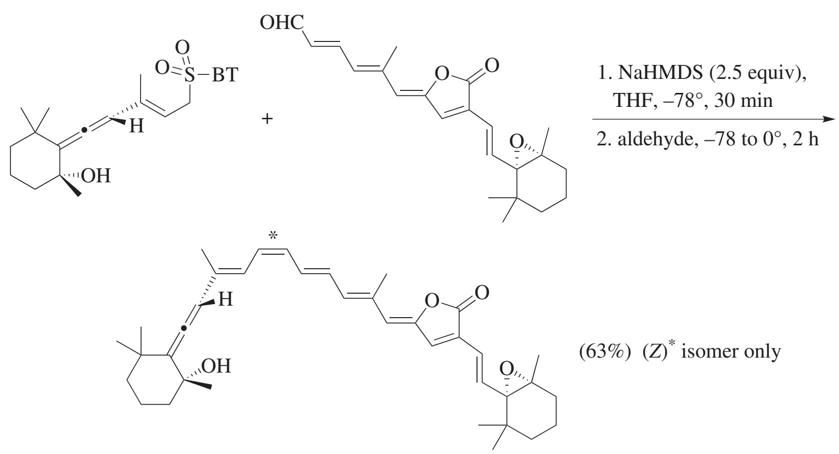


M	Yield (%)	(*E*)/(*Z*)*
Li	—	29:71
Na	79	43:57
K	—	18:82

Scheme 49

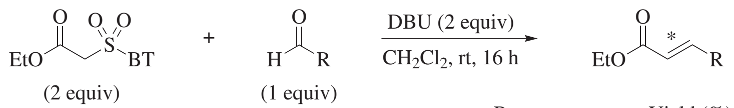


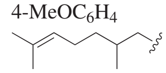
Scheme 50



Scheme 51

The synthesis of α,β-unsaturated carbonyl compounds from β-carbonyl sulfone species represents a special case of Type II (or IV) reactivity because an E1cB pathway is potentially involved in the generation of the alkene (see "Factors Influencing Stereoselectivity"). The relevant sulfone anions in this case are highly stabilized and, as a result, strong bases are not necessarily required for olefination. At the reaction temperatures usually employed (room temperature and above), alkene formation is typically (*E*)-selective, although non-branched aldehydes may yield (*Z*) alkenes, as observed for other Type II olefinations. Ethyl (benzothiazol-2-ylsulfonyl)acetate affords good yields of conjugated enoates when allowed to react with aryl aldehydes in the presence of DBU in dichloromethane at room temperature; however, the olefination of enolizable aldehydes leads to variable results under the same conditions (Scheme 52).[20] The comparable BTFP sulfone reagent provides low yields with enolizable aldehydes but again performs better with aryl aldehydes (Scheme 53).[16] Weinreb amides analogous to the BT and BTFP sulfonylacetate reagents react in the expected manner to afford *trans* α,β-unsaturated enamides.[16,84] (*E*)-Chalcones have likewise been generated by reaction of α-BT sulfonyl acetophenones with aldehydes.[85] In an extension of this chemistry, the 2-hydroxyacetophenone sulfone derivative leads directly to flavanones via spontaneous intramolecular hetero-Michael addition following the intermolecular Julia–Kocienski olefination reaction (Scheme 54).[85]

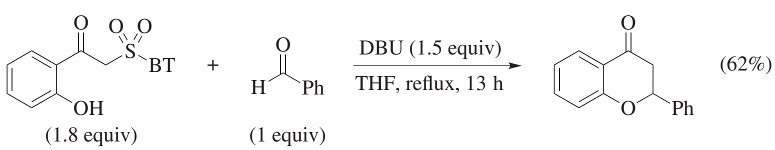


R	Yield (%)	(*E*)/(*Z*)*
n-C_5H_{11}	41	19:81
c-C_6H_{11}	80	80:20
4-$MeOC_6H_4$	93	92:8
	64	30:70

Scheme 52

R	Yield (%)	(*E*)/(*Z*)*
c-C_6H_{11}	15	75:25
4-$MeOC_6H_4$	45	>99:1
4-$CF_3C_6H_4$	74	>99:1
n-C_9H_{19}	14	68:32

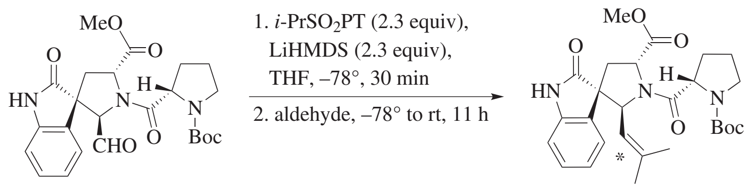
Scheme 53



Scheme 54

Trisubstituted and Tetrasubstituted Alkenes. Comparatively few examples of the synthesis of (all-carbon) tri- and tetrasubstituted alkenes have been reported using the Julia–Kocienski olefination. Although the method is reasonably effective at producing such alkenes (particularly trisubstituted alkenes), stereoselectivity is modest at best. Product isomeric ratios seldom exceed 3:1, and the usual stereochemical traits for Type I–IV olefinations are only weakly followed.

Trisubstituted alkenes are successfully generated from both the union of secondary alkyl sulfone anions with aldehydes and the alternative coupling mode employing a primary alkyl sulfone anion with a ketone. When symmetric secondary alkyl sulfones are involved, stereoselectivity is not an issue, and for this reason, isopropyl PT sulfone has become a popular tool for the generation of prenyl groups from aldehyde substrates (Scheme 55).[86] Another symmetrical secondary alkyl sulfone, cyclopropyl TBT sulfone, is effective for generating substituted methylenecyclopropanes from aldehydes (Scheme 56).[87] Cyclopropyl pentachlorophenyl sulfones, formed in situ by base-mediated cyclization of 3-halopropyl sulfones, can be similarly employed.[88]



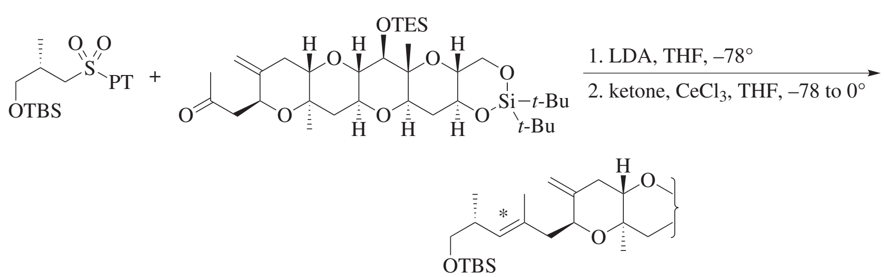
(78%)

Scheme 55

R	Yield (%)
4-PhC_6H_4	76
$TBSO(CH_2)_3$	43

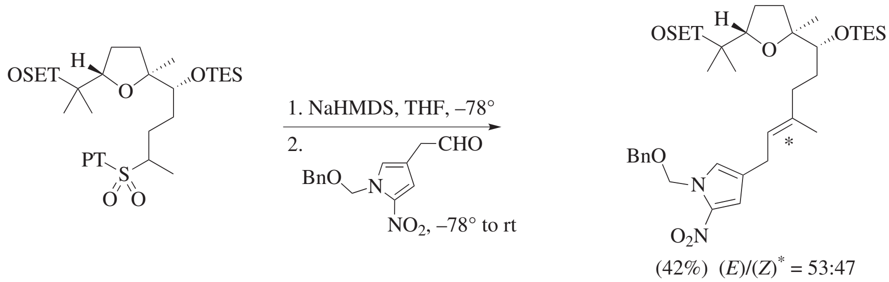
Scheme 56

In the case of Type I couplings to make non-symmetrical methyl-group-bearing trisubstituted alkenes, the addition of a primary alkyl sulfone anion to a methyl ketone generally results in higher (*E*) selectivity versus the reversed component selection (Scheme 57 versus Scheme 58).[89,90] The first of these examples is notable in that pre-complexation of the ketone with anhydrous cerium(III) chloride significantly increases the yield of the coupling, presumably by minimizing proton exchange between the lithiated sulfone and the enolizable ketone. The same approach has been applied to a more complex methyl ketone in the final stages of a total synthesis of gambieric acid A.[91]



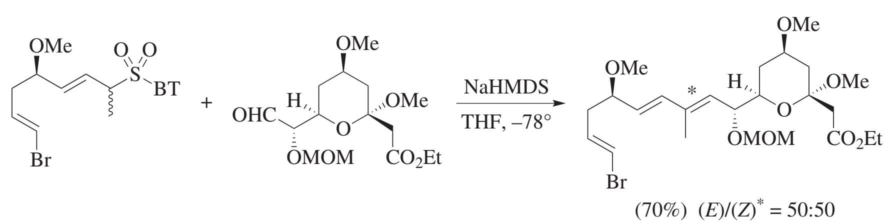
(76%) (*E*)/(*Z*)* = 76:24

Scheme 57

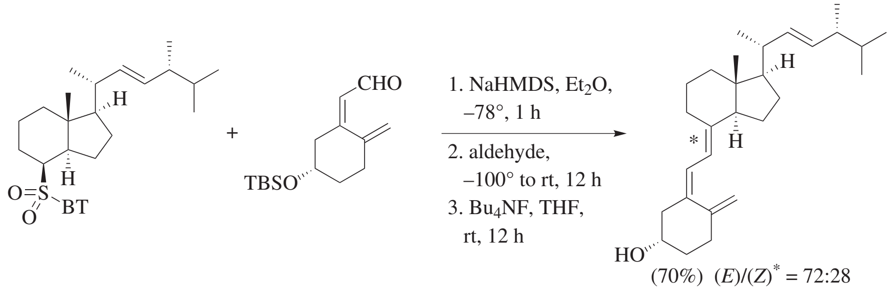


Scheme 58

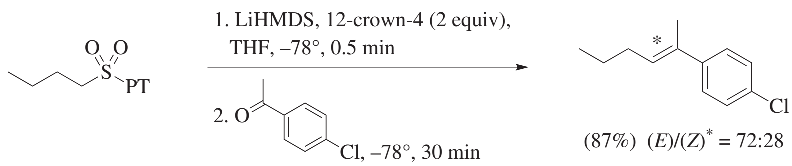
The use of conjugated sulfone anions in Type II olefinations toward trisubstituted alkenes has yet to be thoroughly investigated; however, the limited data available suggest that such reactions do not offer generally useful levels of stereoselectivity (Scheme 59).[92] Better outcomes have been realized from Type III olefinations, and modest (*E*) selectivity is typically obtained when either conjugated aldehydes (Scheme 60)[39] or conjugated ketones (Scheme 61)[26] are employed as substrates. The highest stereoselectivities observed for the synthesis of trisubstituted alkenes via the Julia–Kocienski olefination involve a Type IV reaction to make simple (*Z*)-configured stilbene derivatives (Scheme 62).[93] The generality of this result as it may pertain to other Type IV olefinations en route to trisubstituted alkenes has not been fully established.



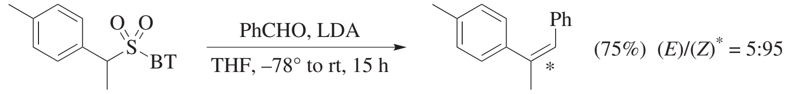
Scheme 59



Scheme 60

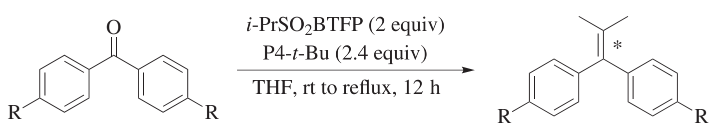


Scheme 61



Scheme 62

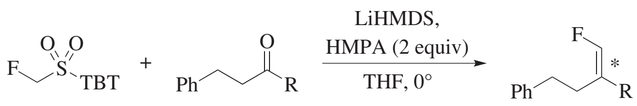
The synthesis of a tetrasubstituted alkene requires the addition of a secondary alkyl sulfone anion to a ketone. Given the comparatively low reactivity of each coupling partner, the steric compression present in the initial addition adduct, and the high level of allylic strain found in the product alkene, this feat is not easy to accomplish;[94] nonetheless, some success has been reported using robust BTFP sulfone anions. For example, isopropyl BTFP sulfone is somewhat effective in the generation of symmetrical tetrasubstituted olefins from diaryl ketones (Scheme 63).[95] Nevertheless, an attempt to apply this method to access a 1,1,2-triarylpropene from propylphen-1-yl BTFP sulfone failed.[95]



R	Yield (%)
H	40
MeO	10
Cl	71

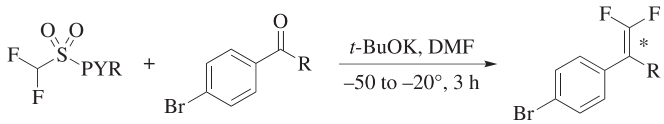
Scheme 63

Vinyl Halides. All types of haloalkenes have been successfully prepared via the Julia–Kocienski olefination, and the process has found a particular niche for the synthesis of structurally varied vinyl fluorides.[33] Terminal fluoromethylene and difluoromethylene alkenes are accessed from aldehydes and ketones by base-mediated reactions with TBT and PYR sulfones (Schemes 64 and 65).[96,97] Substituted α-fluoroalkyl sulfones are also effective for the synthesis of internal fluoroalkenes, and in many cases the stereoselectivity traits expected for Type I (Scheme 66),[98] Type II (Scheme 67),[99] and Type III (Scheme 68)[98] olefinations have been observed. Note that in these examples, the fluorine atom has the highest priority for the purposes of configurational assignment, and so the (*Z*) fluoroalkene is a *trans*-like system and the (*E*) isomer is a *cis*-like system. In a related fashion, 1-substituted fluoroethene derivatives are prepared in good to excellent yields by the reaction of α-fluoroalkyl BT sulfone anions with paraformaldehyde,[100] and the analogous reactions with ketones lead to fully substituted fluoroalkenes.[98]



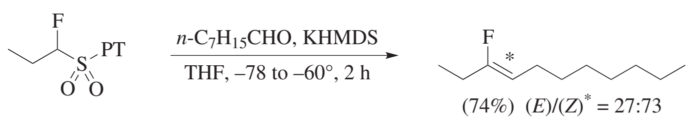
R	Yield (%)	(*E*)/(*Z*)*
H	51	48:52
Me	75	30:70

Scheme 64

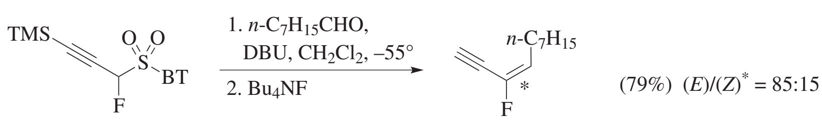


R	Yield (%)
H	72
Me	77

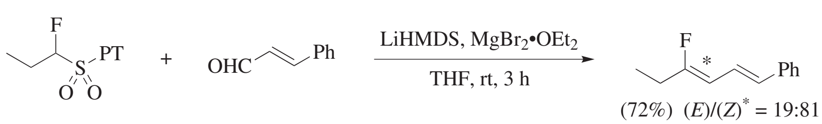
Scheme 65



Scheme 66

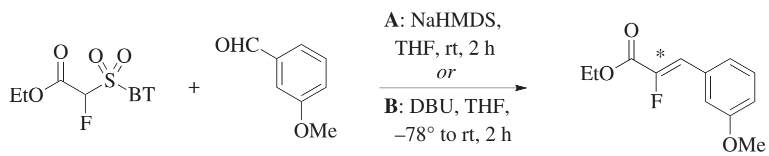


Scheme 67



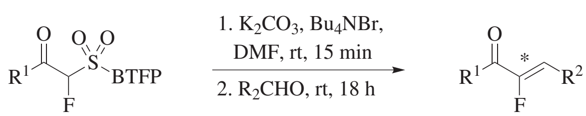
Scheme 68

α-Fluorosulfonyl acetates and acetamides, as well as related activated (i.e., low pK_a) α-fluorosulfones, are highly effective in the Julia–Kocienski olefination.[33,101−103] In the cases that have been examined, such reagents are more reactive than the corresponding non-fluorinated sulfones, possibly due to an α-effect.[101] As with non-fluorinated sulfonyl acetates,[20] varying the temperature and base can reverse the sense of stereoselectivity (Scheme 69).[102] BT α-fluorosulfonyl acetamides and acetonitriles generate *trans*-like [(*Z*)-configured] products, as would be expected with the corresponding non-fluorinated starting materials.[103,104] BTFP fluorosulfonyl acetates and acetamides are similarly used to good effect and universally favor the *trans*-like [(*Z*)-configured] product under the illustrated reaction conditions (Scheme 70).[105]



Conditions	Yield (%)	(*E*)/(*Z*)*
A	75	15:85
B	74	85:15

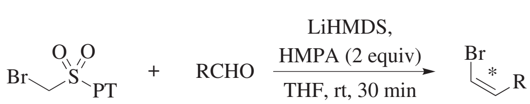
Scheme 69



R^1	R^2	Yield (%)	(*E*)/(*Z*)*
MeO	Ph	95	7:93
MeO	*c*-C_6H_{11}	71	7:93
MeO(Me)N	Ph	83	0:100
MeO(Me)N	*c*-C_6H_{11}	65	0:100

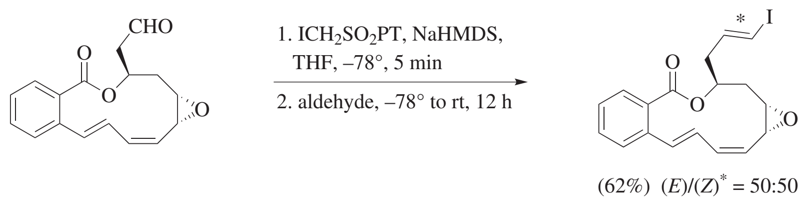
Scheme 70

Other types of vinyl halides (particularly bromides and iodides) are valuable substrates in transition-metal-catalyzed cross-coupling reactions, and a few useful protocols for their synthesis via the Julia–Kocienski olefination have been developed. Chloro- and bromomethyl PT sulfones generate predominantly (*Z*) haloalkenes upon reaction with aryl, alkenyl, and alkyl aldehydes (Scheme 71).[106] In some cases, replacing hexamethylphosphoramide with magnesium bromide diethyl etherate in an otherwise identical procedure results in the production of (*E*) chloroalkenes from aryl aldehydes and chloromethyl PT sulfone.[106] Iodomethyl PT sulfone has not been well investigated; in an isolated example, a non-stereoselective reaction is observed with a complex non-conjugated alkyl aldehyde (Scheme 72).[107]



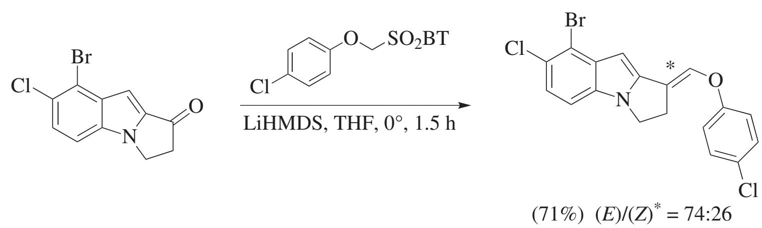
R	Yield (%)	(*E*)/(*Z*)*
4-$MeOC_6H_4$	70	5:95
(*E*)-PhCH=CH	69	8:92
$Ph(CH_2)_2$	73	23:77

Scheme 71

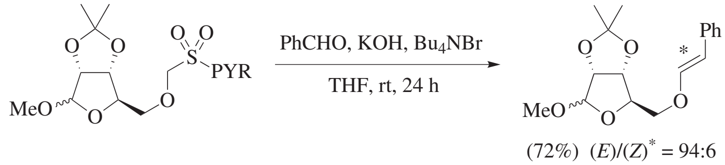


Scheme 72

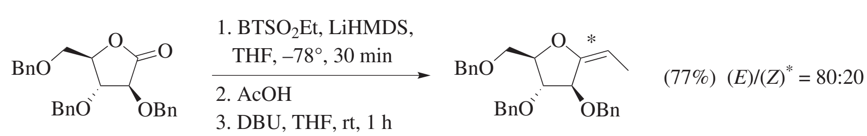
Miscellaneous Alkene Classes. Beyond vinyl halides, various other types of heteroatom-substituted alkenes are prepared via the Julia–Kocienski olefination. Of these, the generation of enol ethers has received the greatest attention, and two distinct approaches have been developed: first, by the addition of alkoxymethyl sulfone anions to aldehydes and ketones (Schemes 73 and 74),[108,109] and second, by a multi-step process involving addition of alkyl sulfone anions to lactones followed by DBU-mediated elimination (Scheme 75).[110,111] In general, neither route is highly stereoselective, but each provides a potentially useful and nonconventional approach to enol ethers, which are challenging motifs to prepare via conventional methods. The first approach has also been extended to the synthesis of enamine-like compounds as illustrated in Scheme 76.[112] Interestingly, the benzotriazolylmethyl PT thioether precursor to the sulfone shown is prepared by a 1,3-dipolar cycloaddition of azidomethyl PT thioether to benzyne.



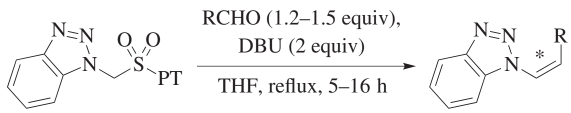
Scheme 73



Scheme 74



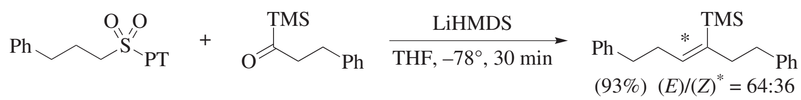
Scheme 75



R	Yield (%)	(*E*)/(*Z*)*
2-$MeOC_6H_4$	57	15:85
2-FC_6H_4	83	11:89
Et_2CH	50	3:97

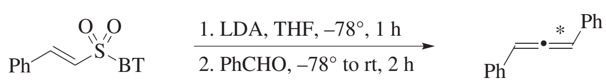
Scheme 76

Acyl silanes are compatible with the Julia–Kocienski olefination process, providing an interesting, albeit not particularly stereoselective, synthesis of vinyl silanes (Scheme 77).[113]



Scheme 77

Lastly, a vinyl BT sulfone anion can be used in an olefination reaction to generate an allene product (Scheme 78). This approach to allenes has yet to be further investigated.[3]

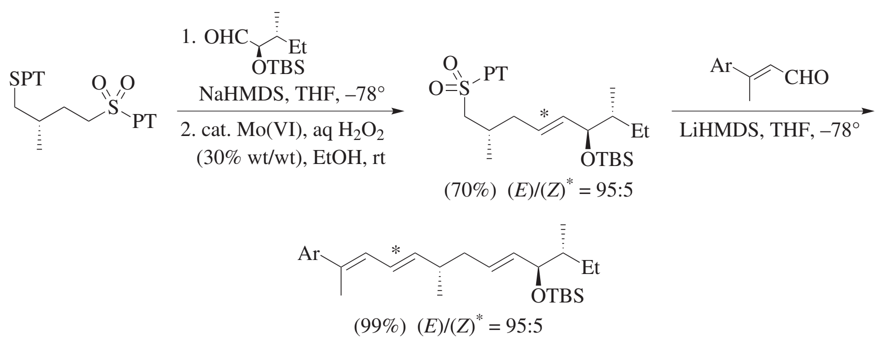


Scheme 78

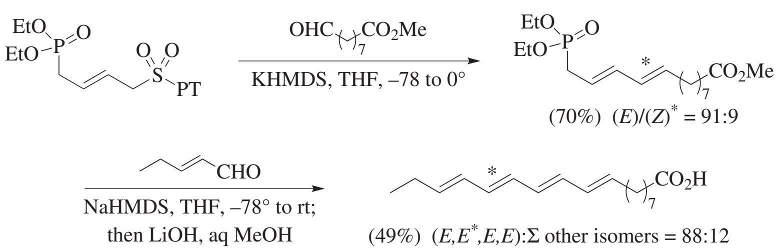
Functional-Group Tolerance of Olefination and Epimerization Possibilities

Even a cursory glance at the transformations shown above (and the many more found in the Tabular Surveys) reveals that the Julia–Kocienski olefination is broadly compatible with a wide variety of functional groups. For example, the process typically tolerates preexisting unsaturated carbon–carbon bonds (including vinyl halides and vinyl boronates), epoxides, esters, and common protecting groups for alcohols (such as silyl ethers) and amines (such as Boc and Fmoc carbamates). Furthermore, a small number of unprotected protic sites can be accommodated within the coupling partners, providing that an additional equivalent of base is used to account for each available proton (Schemes 45, 51, and 55). Despite the risk of β-elimination, sulfones containing β-oxygenated functionality often perform quite well, especially when Barbier conditions are employed to minimize the lifetime of the sulfone anion (Schemes 42, 44, and 82). Sulfones and aldehydes (or ketones) bearing functionality primed for multiple olefination events have also been successfully engaged, and they enable the rapid assembly of polyunsaturated materials (Schemes 79–81).[114–116] Scheme 79 exemplifies deployment of a sulfonyl thioether linchpin reagent to facilitate sequential Julia–Kocienski olefination reactions.[114] The same strategy can be applied with sulfonyl thioether reagents containing a mixture of different activators.[117] In the sequence depicted in Scheme 80, it is notable that

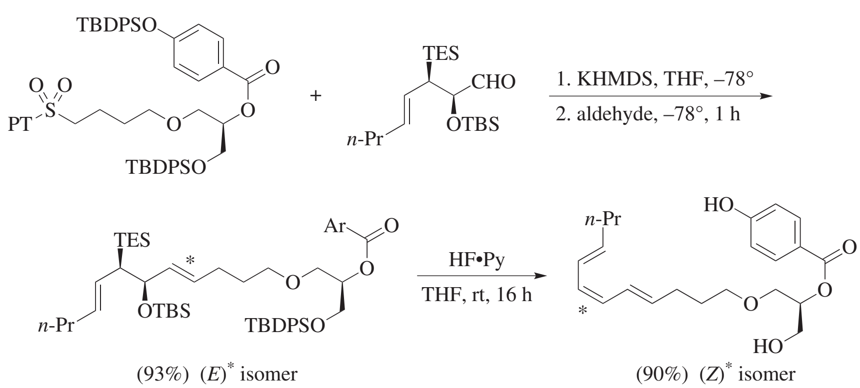
Julia–Kocienski olefination is triggered before the Horner–Wadsworth–Emmons reaction.[115] Scheme 81 shows a deft combination of Julia–Kocienski olefination with a stereospecific Peterson elimination[118] for the generation of the (*E,Z,E*)-triene system found in bretonin B.[116]



Scheme 79

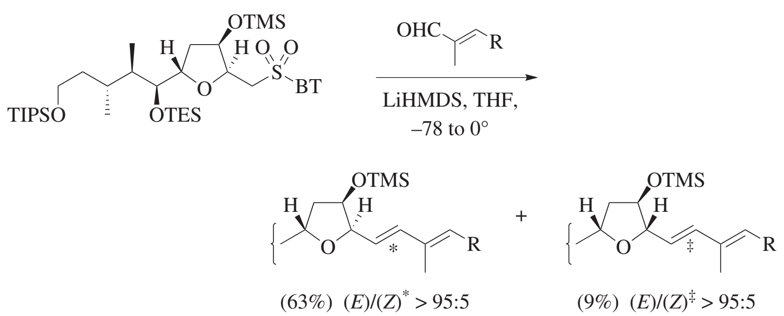


Scheme 80

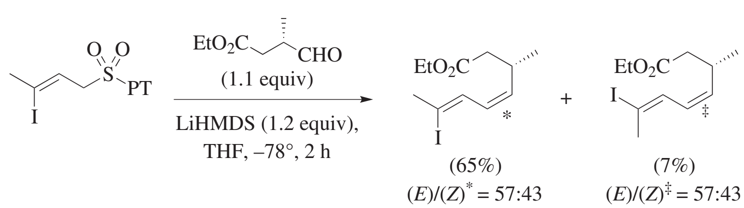


Scheme 81

Epimerization at preexisting stereogenic sites within either the sulfone or the carbonyl compound is rarely encountered, but some notable examples of unwanted isomerization have been documented. As outlined above, although the possibility of epimerizing enolizable α-substituted aldehydes or ketones is an obvious concern, in reality, stereochemical integrity is typically well maintained at such positions even if Barbier conditions are employed. In such cases where this is problematic, PT sulfones result in less epimerization than the corresponding BT sulfones.[119] Epimerization of a complex tetrahydrofurylmethyl sulfone is observed in the synthesis of the pectenotoxins (Scheme 82).[120] In this case, the mechanistic origin of epimerization is β-elimination from the sulfone anion followed by re-addition of the resulting alkoxide to the putative vinyl sulfone intermediate. The same epimerization phenomenon occurs in simpler tetrahydrofurylmethyl sulfones.[121] Unwanted isomerization is also observed in Type II olefinations employing allylic sulfones (Scheme 83).[122]

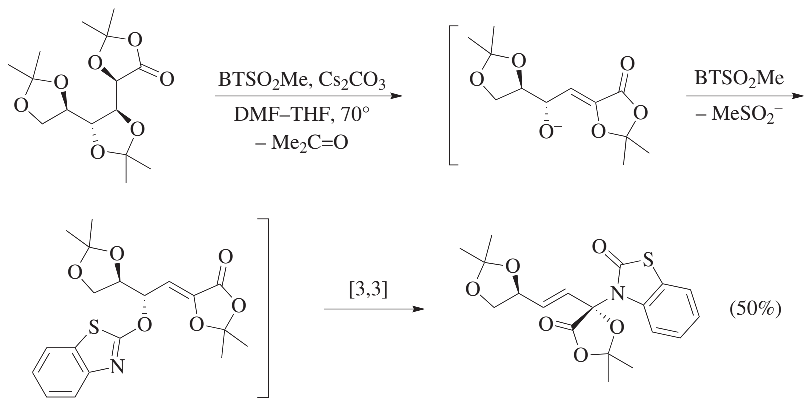


Scheme 82

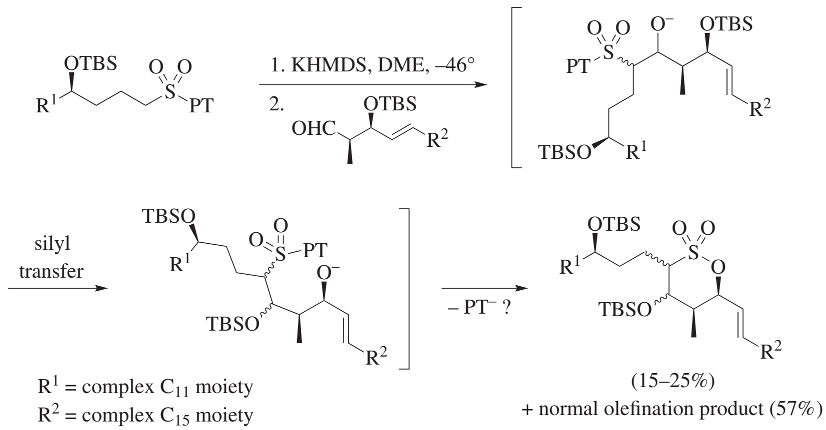


Scheme 83

On occasion, more exotic and unanticipated side-reactions are encountered. For instance, in an attempt to methylenate a lactone carbonyl group using methyl BT sulfone, the basic reaction conditions cause E1cB elimination and then *ipso* attack by the revealed alkoxide anion on the sulfone reagent (Scheme 84).[123] The resulting allylic BT ether experiences a spontaneous Overman-type [3,3]-sigmatropic rearrangement to yield the illustrated final product. Another example of a side-reaction involving an unintentionally generated alkoxide anion is observed during the synthesis of the complex macrolide oasomycin A (Scheme 85).[124] In this case, spirocyclization is complicated by a second process that involves the transfer of a *tert*-butyldimethylsilyl protecting group to the alkoxide anion produced from the initial addition event. The resulting δ-alkoxy sulfone species leads to the generation of a sultone product via direct attack of the new alkoxide anion at sulfur with expulsion of a putative phenyltetrazolyl anion nucleofuge. No sultone formation is observed when LiHMDS is used as the base instead of KHMDS, but then (*E*) selectivity is significantly reduced [(*E*)/(*Z*) = 88:12 with KHMDS versus (*E*)/(*Z*) = 66:34 with LiHMDS].[124]



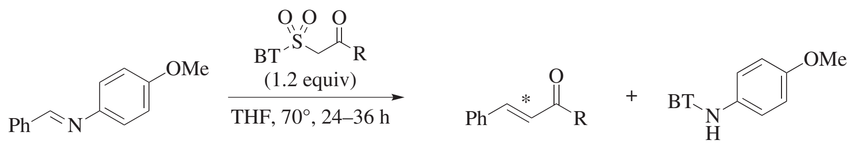
Scheme 84



Scheme 85

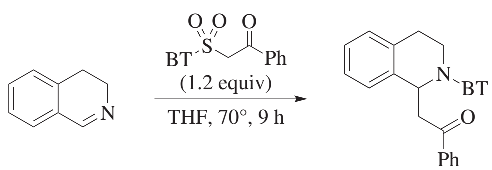
Reaction Variants

The pivotal Smiles rearrangement/elimination cascade that lies at the heart of the Julia–Kocienski olefination has been employed creatively in other types of useful transformations. In one of the more straightforward variants of the basic process, imines are substituted for the usual carbonyl electrophiles and react with β-alkoxy, β-amino and β-arylcarbonyl BT sulfones (Schemes 86–88).[125] Reactions with simple acyclic imines lead to alkene products (Scheme 86), but in the case of cyclic imine substrates, the 2-aminobenzothiazole moiety (that is normally lost in the elimination stage) is now tethered, and it engages in an intramolecular conjugate addition reaction with the incipient α,β-unsaturated carbonyl moiety to generate cyclic amine products (Scheme 87).[125] Along similar lines, α,β-unsaturated imine substrates lead to vicinal difunctionalization on either side of the electrophilic alkene moiety via a reaction cascade that begins with conjugate addition and proceeds via a Smiles rearrangement involving an intermediate enamine (Scheme 88).[125] In all of these reactions, the imine substrate itself serves to deprotonate the acidic β-oxo sulfone, which circumvents the necessity to employ an exogenous base.



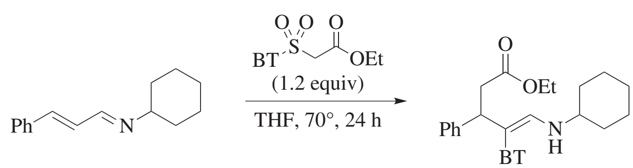
R	Yield (%)	(*E*)/(*Z*)*
EtO	88	>99:1
H_2N	90	>99:1
Ph	84	>99:1

Scheme 86



(94%)

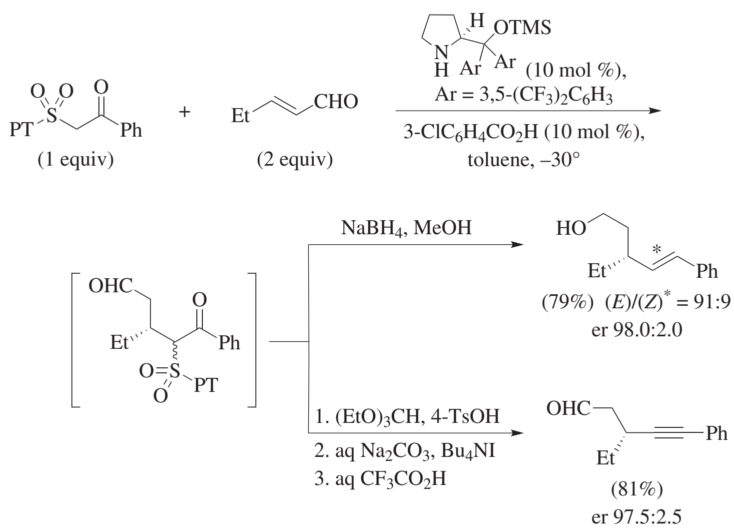
Scheme 87



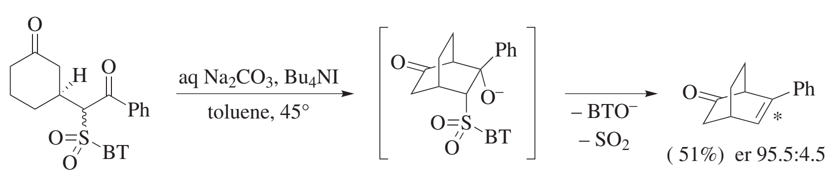
(63%)

Scheme 88

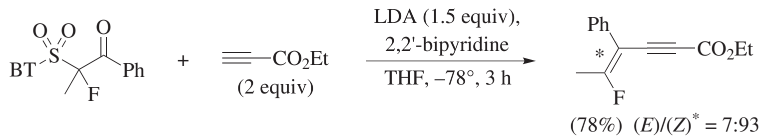
A number of interesting reaction sequences have been reported that involve the enantioselective organocatalytic Michael addition of β-keto sulfones to α,β-unsaturated carbonyl compounds and subsequent Smiles rearrangement from the resulting adducts.[126] For example, addition of the illustrated β-keto PT sulfone to 2-pentenal affords the expected addition adduct in high enantioselectivity when mediated by a proline-derived secondary amine catalyst (Scheme 89).[127] In situ reduction of this intermediate results in the generation of a β-alkoxy sulfone moiety that forms an alkene via the usual elimination mechanism. Alternatively, after protection of the aldehyde group as an acetal, the β-keto sulfone intermediate is converted to the alkyne by treatment with sodium carbonate and tetrabutylammonium iodide (TBAI).[127] The conversion of the enolates of such keto sulfones to alkynes presumably occurs via the Smiles rearrangement/elimination sequence;[126] regardless of the mechanism, this kind of alkynylation process warrants further development. In a related reaction, the conjugate addition adduct formed with cyclohexenone evolves in a different manner when treated with sodium carbonate and TBAI (Scheme 90).[128] In this case, an intramolecular aldol reaction from the distal ketone enolate competes with alkyne formation from the thermodynamically favored β-keto sulfone enolate. The resulting aldol adduct (as shown) contains a β-alkoxy sulfone system which expels sulfur dioxide and the benzothiazolone anion to yield the observed bicyclo[2.2.2]octenone product. More recently, β-keto sulfone adducts such as that shown in Scheme 89 have been further processed in a similar fashion via *N*-heterocyclic carbene catalyzed benzoin cyclization leading to cyclopentenones.[129] Along the same lines, addition of acetylides and enolates to non-enolizable α-fluoro-β-keto sulfones is highly effective for the stereoselective synthesis of tetrasubstituted fluoroalkenes (Scheme 91).[130] Taken together, the aforementioned results (Schemes 90 and 91) indicate that, as a class, β-keto BT and PT sulfones can be regarded as vinyl cation equivalents, provided that their enolization does not interfere with nucleophilic addition.



Scheme 89

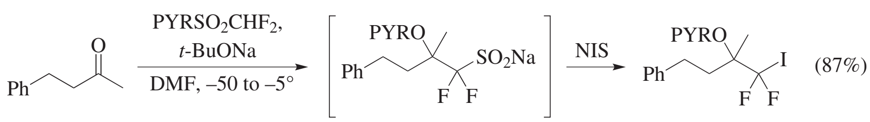


Scheme 90



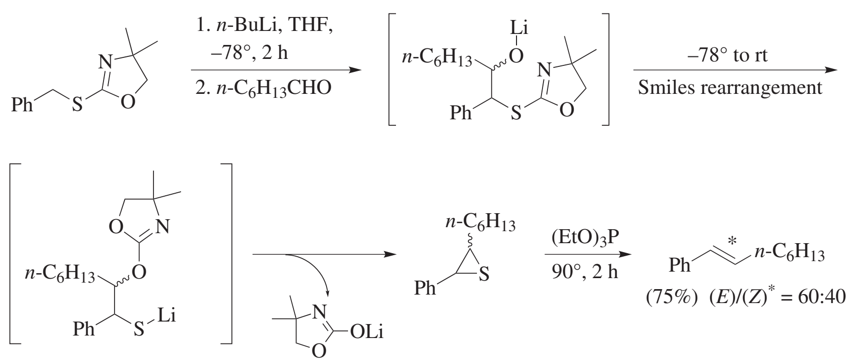
Scheme 91

Transformations in which Smiles rearrangement is not followed by the canonical elimination process have also found utility. For example, the reaction of difluoromethyl PYR sulfone anions with aldehydes or ketones proceeds as far as the Smiles rearrangement stage, but the intermediate sulfinate does not spontaneously eject PYRO⁻; interception of the sulfinate with electrophilic halogen sources results in a net halodifluoromethylation of the carbonyl compound (Scheme 92).[131] Finally, divergence from the familiar mechanism is also seen in an antecedent of the Julia–Kocienski method that involves the addition of α-metalated 2-alkylthio-2-oxazolines to aldehydes and ketones (Scheme 93).[132] The primary products of this olefination are thiiranes, which are generated by Smiles rearrangement of the initial adduct followed by a cyclization event rather than loss of elemental sulfur. Desulfurization of the thiiranes with triphenylphosphine or triethyl phosphite leads to the net product of carbonyl olefination.



NIS = *N*-iodosuccinimide

Scheme 92



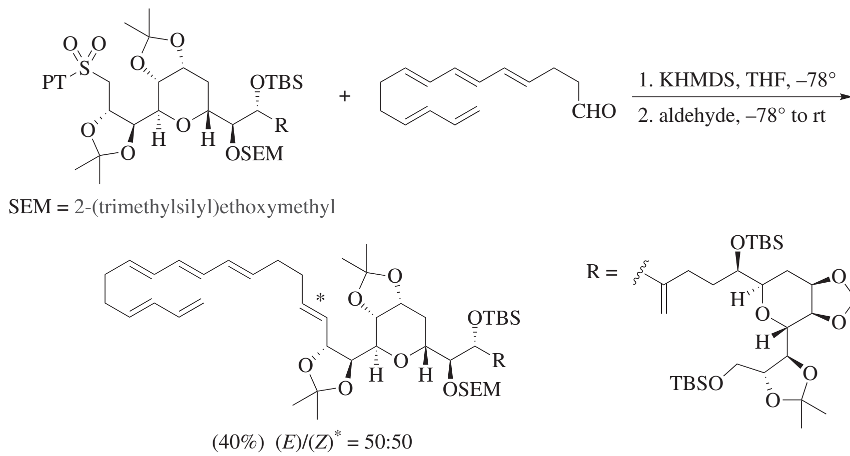
Scheme 93

COMPARISON WITH OTHER METHODS

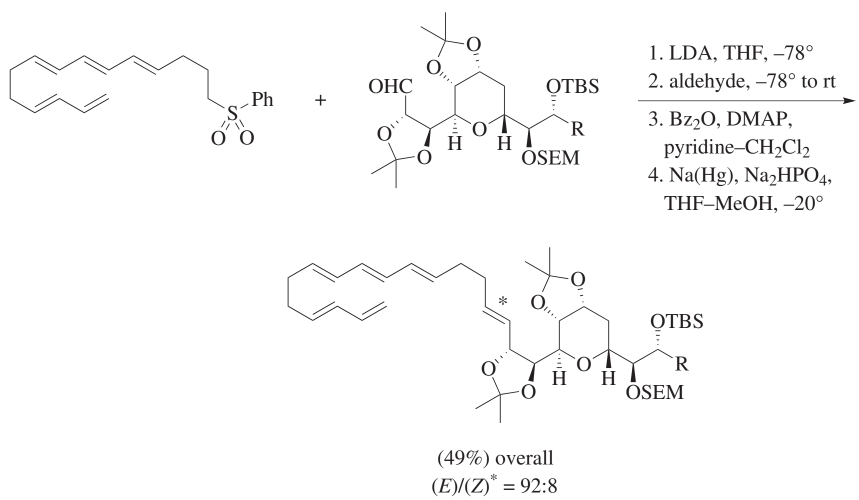
The Julia–Kocienski olefination belongs to the broader class of connective, alkene-forming reactions that involve the addition of a carbanion (or ylide) stabilized by an adjacent oxyphilic group to a carbonyl compound.[12] Typically, an ensuing cascade of fundamental steps then leads to the spontaneous formation of the alkene with the concomitant extrusion of an oxidized form of the activating group. Other well-known processes conforming to this general paradigm include the organophosphorus-based Wittig,[133−135] Horner–Wittig,[136] and Horner–Wadsworth–Emmons reactions,[133,137] and the organosilicon-based Peterson olefination.[118,138] The Julia–Lythgoe olefination[8,10,11] is a little different in that a separate reduction step is necessary to initiate elimination, but like the other carbonyl olefination methods listed, it also provides the capability to splice together fragments with stereocontrol about a newly forged carbon–carbon double bond. In principle, all of the aforementioned processes offer the same strategic approach to alkene synthesis, but one method may be favored over another in a given context for reasons of optimal yield, stereoselectivity, or general efficiency and convenience (including ease of precursor synthesis). Alternative approaches to access alkene-containing materials that are quite distinct from carbonyl olefination may also offer advantages to solve a particular synthesis problem. For example, transition-metal-catalyzed processes involving the conversion of alkenes of one type into another type are of ever-increasing importance (e.g., cross-coupling, olefin metathesis); however, one should not lose sight of the fact that carbonyl olefination is often involved in the manufacture of the precursors for such transformations. A brief selection of cogent examples comparing the Julia–Kocienski olefination to other common carbonyl olefination tactics and to an assortment of different reactions for alkene synthesis, are now surveyed.

Julia–Lythgoe Olefination

The Julia–Lythgoe procedure for the olefination of carbonyl compounds using phenyl sulfone anions requires multiple synthetic operations to generate an alkene product.[7,10] Nonetheless, it offers reliably high (*E*) selectivity in various scenarios because of the radical nature of the reductive elimination stage,[139,140] and it continues to enjoy occasional application. For example, in a synthesis of a C31–C67 subunit of amphidinol 3, the Julia–Kocienski olefination fails to produce the target skipped polyene in a stereoselective manner (Scheme 94) whereas the Julia–Lythgoe method (albeit with a different component polarization) succeeds in generating the desired (*E*) alkene with high stereoselectivity (Scheme 95).[141] Interestingly, other workers report the stereocontrolled synthesis of a closely related (*E*) alkene (80%, (*E*)/(*Z*) > 95:5) using the same aldehyde depicted in Scheme 94 and a very similar PT sulfone under otherwise identical Julia–Kocienski reaction conditions.[142]

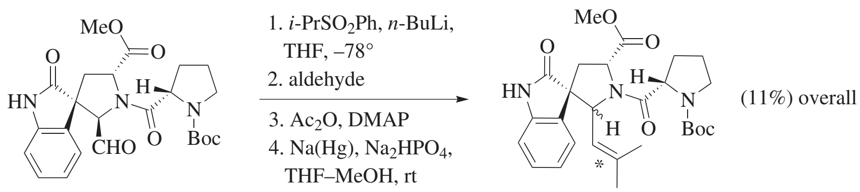


Scheme 94

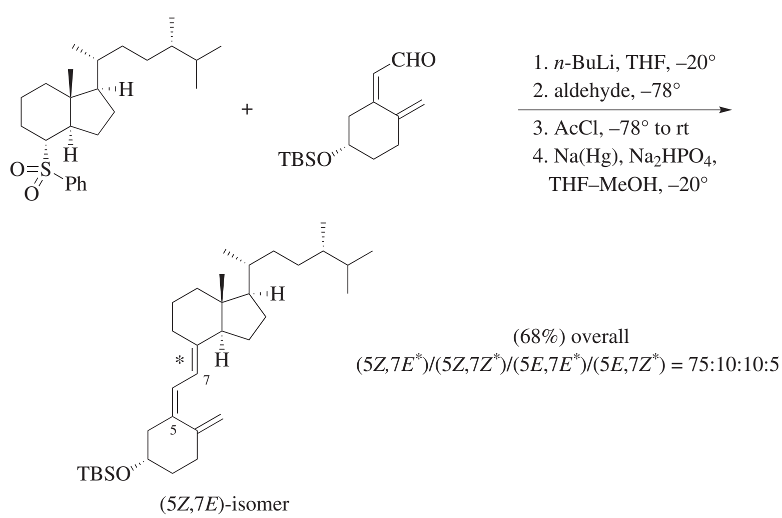


Scheme 95

Although a few examples of the Julia–Lythgoe olefination out-performing the Julia–Kocienski olefination are documented, in a majority of cases in which the two processes have been directly compared, the latter method usually provides the superior outcome. For example, in a synthesis of spirotryprostatin B, conversion of a complex aldehyde to the corresponding isopropylidene derivative via the Julia–Lythgoe olefination results in a low yield and is accompanied by extensive epimerization of the aldehyde α-stereocenter (Scheme 96).[86] By contrast, the same product is accessed without detectable epimerization and in 78% yield by application of the Julia–Kocienski olefination using isopropyl PT sulfone (Scheme 55). The early development of the Julia–Lythgoe olefination was motivated by the need for new protocols capable of delivering the delicate conjugated triene system of the D vitamins with the natural (5*Z*,7*E*)-configuration.[143,144] In this context, contemporary work also reveals that the Julia–Kocienski olefination offers generally better results than the older method. Thus, condensation of a CD-ring BT sulfone with an A-ring dienal, followed by silyl ether deprotection, affords vitamin D_2 in a 70% yield as a mixture of only two stereoisomers, favoring the desired (5*Z*,7*E*)-isomer over the (5*Z*,7*Z*)-isomer by 72:28 (Scheme 60).[39] A comparable synthesis of vitamin D_4 employing an analogous CD-ring phenyl sulfone via the Julia–Lythgoe protocol results in significant epimerization of the preexisting (*Z*) alkene within the dienal and produces the target triene as a mixture of all four possible stereoisomers (Scheme 97).[145]



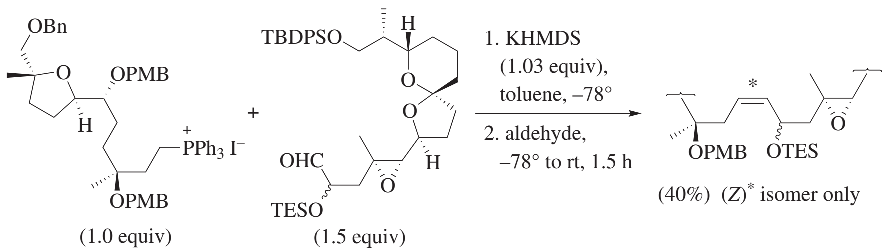
Scheme 96



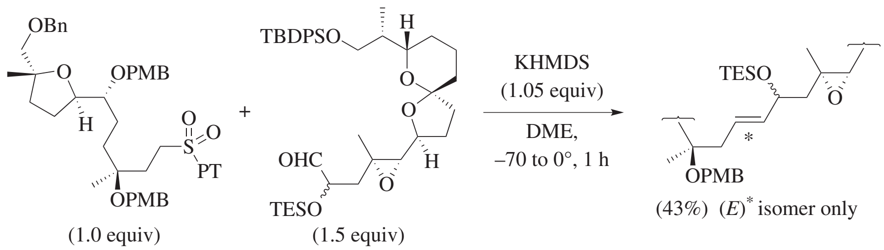
Scheme 97

Wittig Reaction and Other Phosphorus-Based Olefination Methods

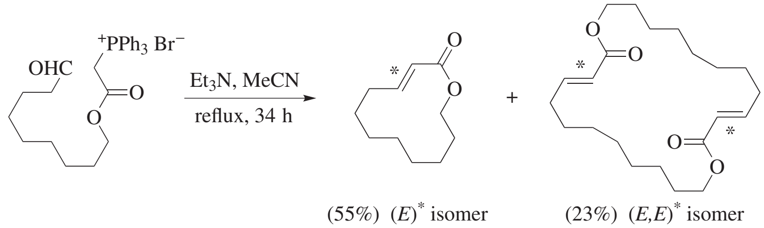
The venerable Wittig reaction[134] and the Julia–Kocienski olefination share a stereocomplementary relationship that can be confidently exploited. Thus, the well-known (albeit over-simplified) maxim for the Wittig reaction posits that non-stabilized phosphoranes preferentially yield (*Z*) alkenes, whereas stabilized phosphoranes afford (*E*) alkenes.[146] The stereochemical outcome can be approximately reversed when Julia–Kocienski reactions using comparable non-stabilized and stabilized sulfone anions are considered. For example, while evaluating different fragment linkage tactics en route to pectenotoxin-2, closely related Wittig (Scheme 98) and Julia–Kocienski (Scheme 99) olefinations employing non-stabilized nucleophilic components were observed to proceed with similar efficiencies but affording the opposite geometrical isomer.[147] Also in line with expectation, the synthesis of α,β-unsaturated macrolactones by intramolecular olefination using stabilized nucleophilic components leads preferentially to the formation of (*E*) macrolides and (*E*,*E*)-diolides by the Wittig reaction (Scheme 100),[148] and to formation of (*Z*) macrolides and (*Z*,*Z*) diolides via the Julia–Kocienski olefination (Scheme 101).[149]



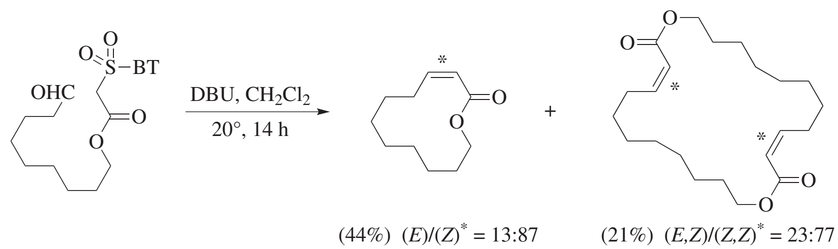
Scheme 98



Scheme 99

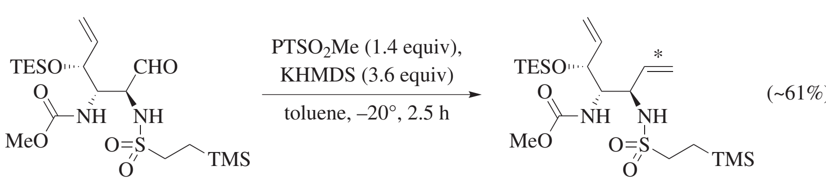


Scheme 100



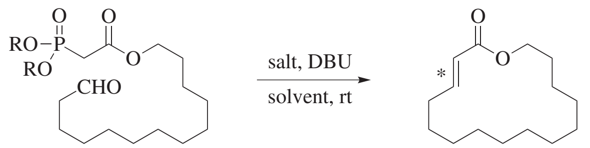
Scheme 101

The Wittig reaction and the Julia–Kocienski olefination do not necessarily proceed with equal efficiency, and in cases in which the stereochemical outcome is not a prime consideration, both methods are worthy of consideration. In particular, the sulfone-based method is competitive with the Wittig reaction for carbonyl methylenations. For example, in a synthesis of agelastatin A, methylenation of the illustrated aldehyde is unexpectedly difficult, and the desired transformation was successfully achieved using methyl PT sulfone (Scheme 102) after the reaction failed with methylenetriphenylphosphorane and a number of other methylenation procedures (including Peterson and Tebbe methods).[150]



Scheme 102

The Horner–Wadsworth–Emmons reaction[137] is narrower in scope than the Julia–Kocienski olefination, but it provides generally superior results for the synthesis of α,β-unsaturated carbonyl compounds. Furthermore, the Still–Gennari[151] or Ando[152] variants of this phosphonate-based method can be used if (*Z*)-configured products are desired rather than the more typically generated (*E*)-configured products. For example, the synthesis of α,β-unsaturated macrolactones using the Horner–Wadsworth–Emmons reaction is far more efficient and stereoselective than the Julia–Kocienski approach seen above (Scheme 101),[149] in which (*E*) or (*Z*) enoates are available by selection of the appropriate reaction conditions and phosphonate substitution (Scheme 103).[153]

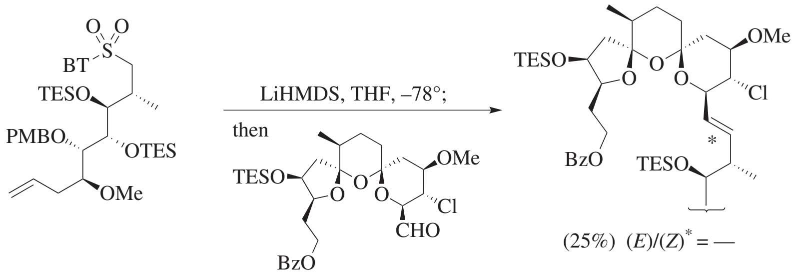


R	Salt	Solvent	Yield (%)	(*E*)/(*Z*)*
Et	LiCl	MeCN	82	98:2
2-*t*-BuC_6H_4	NaI	THF	93	6:94

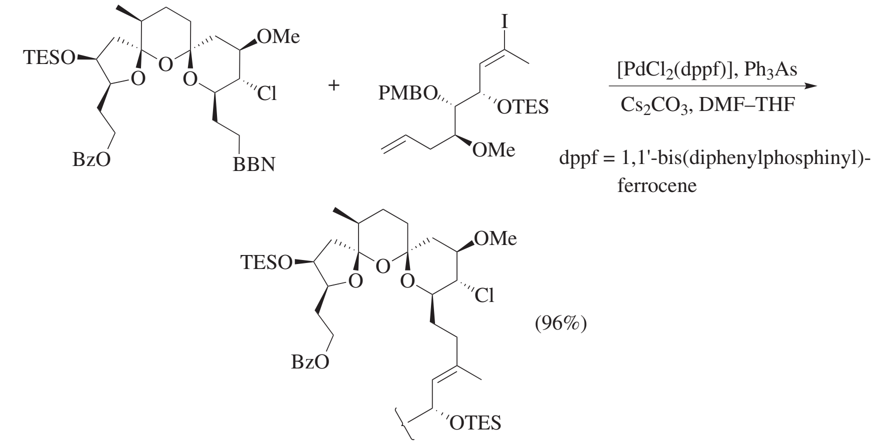
Scheme 103

Miscellaneous Methods for Alkene Synthesis

In relevant scenarios, palladium-catalyzed cross-coupling processes such as the Stille[154] and Suzuki–Miyaura[155] reactions may offer an alternative to the Julia–Kocienski olefination or a comparable, fragment-linking transformation. For example, a plan to access spirastrellolide A by the Julia–Kocienski olefination was abandoned when it was discovered that the requisite union between the illustrated BT sulfone and aldehyde could not be achieved in a high yield because of an extreme level of steric hindrance near the carbonyl group (Scheme 104).[156] Since olefination is used purely to conjoin advanced fragments (i.e., the alkene formed was to be removed by subsequent hydrogenation), the approach was reworked to target an adjacent bond disconnection. To this end, a *B*-alkyl Suzuki coupling was employed, which resulted in a vastly superior result (Scheme 105).[156]

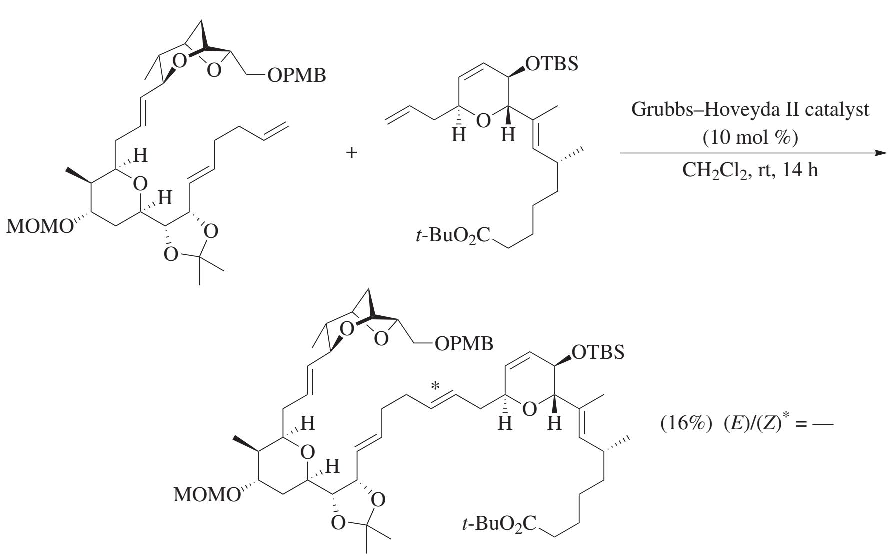


Scheme 104



Scheme 105

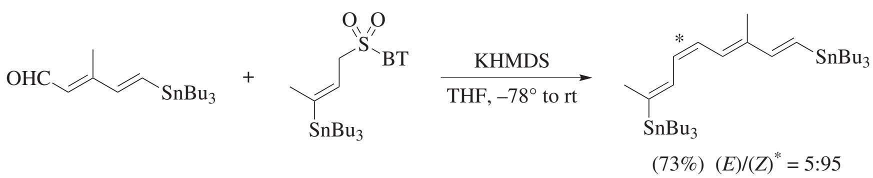
Olefin cross-metathesis has more recently emerged as a popular strategy to rival carbonyl olefination as an advanced-fragment-linkage tool.[157] Its advantage over a process like the Julia–Kocienski olefination is that precursor synthesis is trivial (i.e., the requisite terminal alkene adducts can often be present from the outset of the synthesis). However, only certain pairs of alkene-containing reactants can be efficiently converted to the desired crossed adducts using this technique, and one of the components must typically be used in a significant excess to bias the alkene shuffling toward the target.[158] A case in point is seen in a total synthesis of sorangicin A that incorporates a late-stage olefin cross-metathesis between two complex terminal alkenes (Scheme 106).[159] In this example, the desired



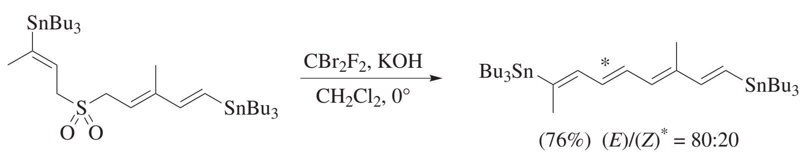
Scheme 106

1,2-disubstituted (*E*)-configured alkene crossed adduct is obtained in low yield. By contrast, a closely related advanced-fragment linkage of even greater complexity is successfully realized with the more controllable Julia–Kocienski olefination (Scheme 37).[65,159]

Finally, Julia–Kocienski olefinations offer a stereocomplementary outcome to the Ramberg–Bäcklund reaction[160] for the synthesis of α,ω-distannylated conjugated trienes, tetraenes, and pentaenes (Schemes 107 and 108).[78] The high (*Z*) selectivity realizable in this kind of Type IV Julia–Kocienski olefination is notable, and it has been encountered in other scenarios (Scheme 51).[81]



Scheme 107

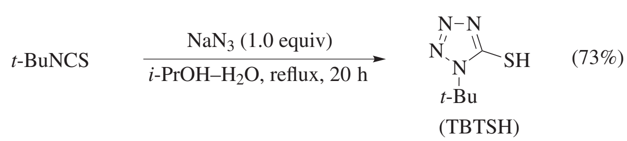


Scheme 108

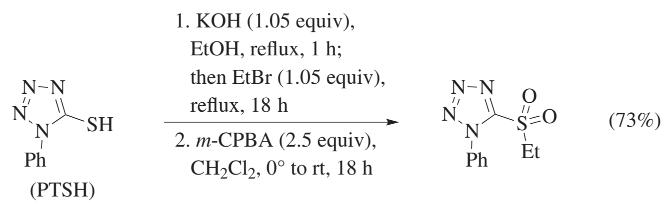
EXPERIMENTAL CONDITIONS

The Julia–Kocienski olefination typically calls for standard experimental techniques necessary to perform reactions under anaerobic, anhydrous, and low-temperature conditions. In the most commonly encountered scenario in which a metal amide base is employed to deprotonate the sulfone, reactions should be conducted in anhydrous solvent under an inert atmosphere of N_2 or Ar at an initial temperature of −78° (dry ice/acetone cold bath), or slightly warmer for solvents that may freeze at this temperature (n.b., the melting point for 1,2-dimethoxyethane is −58°). Dry and deoxygenated ethereal solvents (e.g., Et_2O, THF, and DME) are best obtained by traditional distillation from sodium benzophenone ketyl, whereas solvents such as DMF or HMPA are dried by distillation from CaH_2 at reduced pressure and stored over 4 Å molecular sieves.[161] Alternatively, anhydrous solvents collected from modern solvent purification systems that employ activated drying columns perform perfectly well, obviating the need for potentially dangerous distillation procedures.[162] Olefination reactions utilizing stabilized sulfone anions do not require any special precautions and can often be conducted without protection from air and in reagent-grade solvents used as received. Commercially available solutions of LiHMDS, NaHMDS, or KHMDS (all three bases are widely available at 1.0 M in toluene or THF) can be used directly as received, but the solvent that the base is dispensed from should match, or have a similar polarity to, that called for in the olefination procedure since the net polarity of the overall reaction medium may affect stereoselectivity. Each of the aforementioned hexamethyldisilazide bases can also be purchased in solid form (the solids are flammable but non-pyrophoric), and thus custom stock solutions in any compatible solvent desired can be prepared, e.g., a solution of KHMDS in 1,2-dimethoxyethane is preferable for the preparation of *trans* alkenes using the Kocienski procedure.[4,163] With regard to the stereoselectivity of the product formation, LiHMDS and LDA are essentially interchangeable; however, if the latter is used, it is best freshly prepared by the addition of a solution of *n*-BuLi (1.5 to 2.5 M in hexanes, 1.0 equiv) to anhydrous diisopropylamine (distilled from CaH_2, 1.1 equiv) in the appropriate ethereal solvent (typically anhydrous THF) at ca. –20° under an inert atmosphere.[56] The olefination process does not necessarily reach completion at –78° (reaction mixtures are commonly allowed to warm somewhat before quenching with saturated aqueous NH_4Cl solution), and therefore, TLC analysis of a low-temperature reaction mixture can be misleading since the sampled aliquot will warm before it is spotted on the TLC plate.

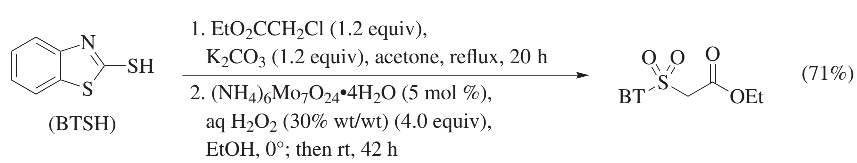
EXPERIMENTAL PROCEDURES



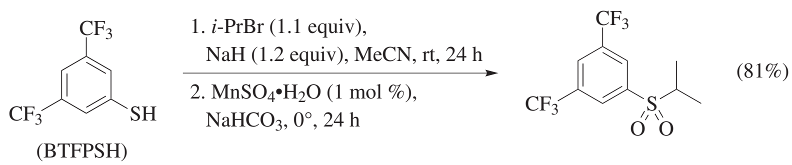
1-*tert*-Butyl-1*H*-tetrazole-5-thiol [Preparation of TBTSH].[5,62,164] *tert*-Butyl isothiocyanate (10.0 g, 86.8 mmol) in *i*-PrOH (25 mL) was added dropwise over 30 min via an addition funnel to a stirred solution of NaN_3 (*CAUTION! Toxic and shock sensitive*, 5.64 g, 86.8 mmol) in H_2O (25 mL) at rt. The resulting mixture was stirred at reflux for 20 h, then it was cooled in an ice bath and treated cautiously with concentrated aqueous HCl (15 mL). The acidified mixture was concentrated under vacuum, and the residue was stored at 0° overnight, which resulted in the precipitation of a solid. The solid material was triturated with ice-cold H_2O (20 mL), was removed by filtration, and then was dissolved in CH_2Cl_2 (50 mL). The organic phase was washed with brine (20 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was recrystallized from cyclohexane to afford the title compound (10.03 g, 63.4 mmol, 73%) as a colorless solid: mp 97–98° (cyclohexane); ^1H NMR (360 MHz, $CDCl_3$) δ 1.83 (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 162.8 (0), 63.6 (0), 27.6 (3C, 3).



5-Ethylsulfonyl-1-phenyl-1*H*-tetrazole [Sulfone Preparation via Alkylation/Oxidation: PTSH, RBr, KOH/*m*-CPBA].[60] To a suspension of powdered KOH (3.3 g, 58.9 mmol) in EtOH (100 mL) was added 1-phenyl-1*H*-tetrazole-5-thiol (PTSH, 10.0 g, 56.2 mmol), and the resulting mixture was stirred at reflux for 1 h. After this time, ethyl bromide (4.4 mL, d = 1.47 g/mL, 6.42 g, 58.9 mmol) was added dropwise, and the reaction mixture was stirred at reflux for a further 18 h. The solvent was then removed under vacuum, and the residue was partitioned between H_2O (100 mL) and Et_2O (100 mL). The layers were then separated, and the organic phase was washed with saturated aqueous $NaHCO_3$ (2 × 75 mL) and brine (75 mL). After drying ($MgSO_4$), the solvent was removed under vacuum to yield essentially pure 5-ethylthio-1-phenyl-1H-tetrazole (PTSEt, 9.86 g, 47.9 mmol, 86%) as a brown oil. A mechanically stirred suspension of the thioether (9.86 g, 47.9 mmol) and solid $NaHCO_3$ (20 g, 238 mmol) in CH_2Cl_2 (200 mL) was treated portion-wise with 3-chloroperoxybenzoic acid (*m*-CPBA, 41.0 g, 50 wt %, 119 mmol) and then was stirred vigorously for 18 h. After this time, the reaction mixture was poured into saturated aqueous $NaHCO_3$–$Na_2S_2O_3$ (1:1, 200 mL) and was stirred vigorously for 3 h. The layers were then separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were then washed with saturated aqueous $NaHCO_3$ (3 × 75 ml) and brine (75 mL). The washed organic layer was dried ($MgSO_4$) and then concentrated under vacuum. The residue was purified by column chromatography on silica gel (Et_2O/hexanes, 40:60 to 55:45) to yield the title compound (8.33 g, 35.0 mmol, 73% over two steps) as a colorless solid: mp 70–71° (hexanes/EtOAc, 90:10); ^1H NMR (360 MHz, $CDCl_3$) δ 7.71–7.65 (m, 2H), 7.64–7.55 (m, 3H), 3.75 (q, J = 7.4 Hz, 2H), 1.52 (t, J = 7.4, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 153.2 (0), 133.1 (0), 131.6 (1), 129.8 (2C, 1), 125.2 (2C, 1), 50.9 (2), 7.0 (3).

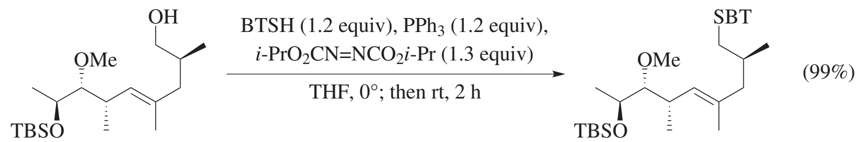


Ethyl (Benzothiazol-2-ylsulfonyl)acetate [Sulfone Preparation via Alkylation/Oxidation: BTSH, RCl, K_2CO_3/Mo(VI), H_2O_2].[20] A stirred suspension of 2-mercapto-1,3-benzothiazole (BTSH, 10.0 g, 59.8 mmol) and K_2CO_3 (9.9 g, 72 mmol) in acetone (100 mL) was treated with neat ethyl chloroacetate (7.6 mL, d = 1.16 g/mL, 8.8 g, 72 mmol). The mixture was heated at reflux for 20 h. After being allowed to cool, the mixture was filtered. Concentration of the filtrate under vacuum yielded 15.3 g of crude ethyl (benzothiazol-2-ylsulfanyl)acetate as a brown oil. A stirred solution of this material in EtOH (50 mL) at 0° was treated with $(NH_4)_6Mo_7O_{24}\bullet4H_2O$ (3.7 g, 3.0 mmol) followed by aq H_2O_2 (23.1 mL, d = 1.18 g/mL, 27.2 g, 30 wt %, 240 mmol). The resulting solution was allowed to warm slowly to rt and then was stirred at rt for 42 h. After this time, the bulk of the EtOH solvent was removed under vacuum, and the residue was partitioned between EtOAc (50 mL) and H_2O (50 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (2 × 25 mL). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4), and concentrated under vacuum to yield 16.1 g of the title sulfone as an off-white solid (>90% purity as judged by ^{1}H NMR analysis). Recrystallization from *tert*-butyl methyl ether (TBME) afforded analytically pure ethyl (benzothiazol-2-ylsulfonyl)acetate (12.1 g, 42.4 mmol, 71%) as colorless prisms: mp 58–59° (TBME); IR (neat) 3461, 2983, 1736, 1470, 1273, 1152, 1026, 910, 853, 770, 614 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.1, 1.8 Hz, 1H), 8.04 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.67 (td, *J* = 7.2, 1.6 Hz, 1H), 7.62 (td, *J* = 7.3, 1.6 Hz, 1H), 4.58 (s, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (0), 161.7 (0), 152.5 (0), 137.1 (0), 128.4 (1), 127.9 (1), 125.7 (1), 122.5 (1), 62.9 (2), 58.9 (2), 13.9 (3); MS (ES) (*m/z*): 286 $(M + H)^+$. Anal. Calcd for $C_{11}H_{11}NO_4S_2$: C, 46.30; H, 3.89; N, 4.91; found: C, 46.40; H, 4.00; N, 4.95.

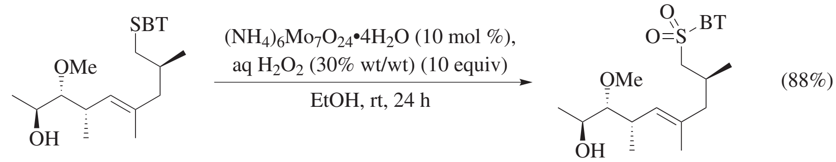


3,5-Bis(trifluoromethyl)phenyl Isopropyl Sulfone [Sulfone Preparation via Alkylation/Oxidation: BTFPSH, RBr, NaH/Mn(II), H_2O_2].[95] A mixture of 3,5-bis(trifluoromethyl)benzenethiol (BTFPSH, 1.23 g, 5.0 mmol) and NaH (150 mg, 95 wt %, 6.0 mmol) in MeCN (15 mL) at rt under Ar was treated with isopropyl bromide (677 mg, 5.5 mmol). After stirring for 24 h at rt, H_2O (20 mL) was added, and the mixture was extracted with EtOAc (2 × 20 mL). The combined organic phases were dried (Na_2SO_4) and then were concentrated under vacuum to afford the crude intermediate thioether (BTFPS*i*-Pr, 1.23 g, 4.27 mmol, 85%) as a yellow oil. Portions of the thioether (288 mg, 1.0 mmol) and $MnSO_4\bullet H_2O$ (2 mg, 0.012 mmol) were dissolved in MeCN (23 mL), and this solution was added dropwise to a stirred mixture of 30 wt % aq H_2O_2 (0.52 mL) and aq $NaHCO_3$ (17 mL, 0.20 M) at 0°. After stirring for 24 h at 0°, the reaction mixture was treated with brine (30 mL) and was extracted with EtOAc (2 × 20 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under vacuum, and then the residue was recrystallized from hexanes to afford the title compound (304 mg, 0.95 mmol, 95%) as a colorless solid: mp 80–83° (hexanes); IR 3091, 2989, 2937, 1621, 1363, 1286, 1136 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 2H), 8.17 (s, 1H), 3.28 (septet,

J = 6.8 Hz, 1H), 1.35 (d, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1 (0), 133.0 (q, $^2J_{CF}$ = 34.8 Hz, 2C), 129.3, 127.3 (1), 122.3 (q, $^1J_{CF}$ = 273.3 Hz, 2C), 55.8 (1), 15.4 (2C, 3) ppm; HRMS (EI) (*m/z*): $(M - F)^+$ calcd for $C_{11}H_{10}F_5O_2S$, 301.0322; found, 301.0325.

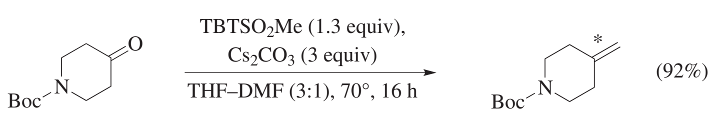


(*E*,2*S*,6*S*,7*R*,8*S*)-1-(1,3-Benzothiazol-2-ylsulfanyl)-8-(*tert*-butyldimethylsilyloxy)-7-methoxy-2,4,6-trimethylnon-4-ene [Mitsunobu Thioetherification].[60] To a stirred solution of the illustrated alcohol (1.47 g, 4.27 mmol) in anhydrous THF (25 mL) at rt under N_2 was added 2-mercaptobenzothiazole (BTSH, 0.86 g, 5.15 mmol) and triphenylphosphine (1.34 g, 5.11 mmol). The resulting solution was cooled to 0° and diisopropyl azodicarboxylate (DIAD, 1.10 mL, d = 1.03 g/mL, 1.13 g, 5.59 mmol) was added dropwise. The cooling bath was then removed, and the mixture was stirred at rt for 2 h. After this time, the solvent was removed under vacuum, and the residue was further purified by column chromatography on silica gel (hexanes/EtOAc, 97:3) to yield the title thioether (2.08 g, 4.21 mmol, 99%) as a colorless oil: $[\alpha]_D$ + 0.3 (*c* 0.65, $CHCl_3$); IR (neat) 2956, 2928, 2894, 2856, 1461, 1428, 1255, 1103, 995, 836, 775, 755 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.86 (dm, J = 8.1 Hz, 1H), 7.75 (dm, J = 8.0 Hz, 1H), 7.41 (ddd, J = 8.5, 7.3, 1.3 Hz, 1H), 7.29 (ddd, J = 8.1, 7.4, 1.2 Hz, 1H), 5.06 (dm, J = 9.9 Hz, 1H), 3.87 (dq, J = 6.2, 3.4 Hz, 1H), 3.54 (s, 3H), 3.45 (dd, J = 12.9, 5.3 Hz, 1H), 3.12 (dd, J = 12.9, 7.5 Hz, 1H), 2.88 (dd, J = 7.9, 3.4 Hz, 1H), 2.47 (ddq, J = 9.9, 7.8, 6.7 Hz, 1H), 2.27–2.10 (m, 2H), 1.93 (dd, J = 12.8, 8.0 Hz, 1H), 1.62 (d, J = 1.2 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H), 1.03 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 167.6 (0), 153.4 (0), 135.3 (0), 132.2 (0), 130.7 (1), 126.1 (1), 124.2 (1), 121.5 (1), 121.0 (1), 90.3 (1), 70.4 (1), 61.5 (3), 47.2 (2), 40.4 (2), 35.3 (1), 31.5 (1), 26.0 (3C, 3), 19.4 (3), 18.2 (0), 17.7 (3), 17.2 (3), 16.1 (3), –4.3 (3), –4.7 (3); MS (CI) (*m/z*): M^+ 493 (10), 446 (6), 436 (4), 330 (47), 203 (97), 159 (33), 123 (63), 73 (100). Anal. Calcd for $C_{26}H_{43}NO_2S_2Si$: C, 63.23; H, 8.78; N, 2.84. Found: C, 63.36; H, 8.84; N, 2.82.

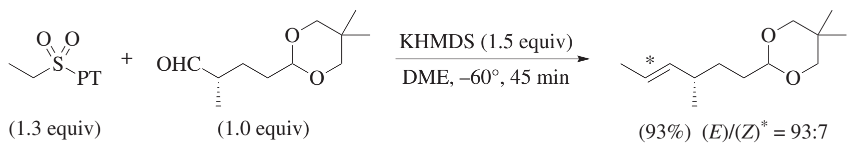


(*E*,2*S*,6*S*,7*R*,8*S*)-1-(1,3-Benzothiazol-2-ylsulfonyl)-7-methoxy-2,4,6-trimethylnon-4-en-8-ol [Thioether Oxidation: Catalytic Mo(VI), H_2O_2].[60] To a stirred solution of the illustrated thioether (870 mg, 2.30 mmol) in EtOH

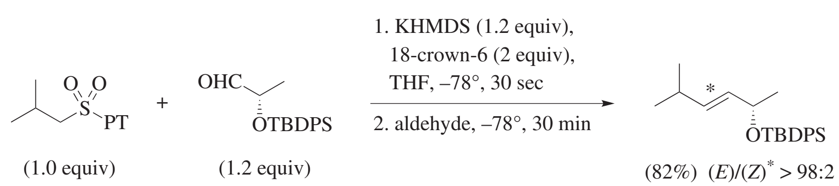
(20 mL) at rt was added dropwise a yellow solution of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}$•$4H_2O$, 280 mg, 0.23 mmol] in aq H_2O_2 (2.60 g, 30 wt %, 22.9 mmol). The resultant mixture was stirred vigorously for 24 h and then was partitioned between Et_2O (30 mL) and H_2O (20 mL). The layers were shaken and then were separated, and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with H_2O (2 × 20 mL), dried ($MgSO_4$), and then concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 60:40) to yield the title compound (835 mg, 2.03 mmol, 88%) as a colorless oil: $[\alpha]_D$ – 24.0 (*c* 1.09, $CHCl_3$); IR (neat) 3447, 2962, 2929, 1472, 1458, 1318, 1146, 1097, 763, 731, 632 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.19 (dm, J = 7.8 Hz, 1H), 8.01 (dm, J = 8.1 Hz, 1H), 7.63 (ddd, J = 8.1, 7.2, 1.4 Hz, 1H), 7.58 (ddd, J = 7.9, 7.2, 1.4 Hz, 1H), 5.02 (dm, J = 9.9 Hz, 1H), 3.79 (dq, J = 6.4, 3.8 Hz, 1H), 3.58 (dd, J = 14.4, 3.7 Hz, 1H), 3.50 (s, 3H), 3.23 (dd, J = 14.4, 8.7 Hz, 1H), 2.92 (dd, J = 8.0, 3.8 Hz, 1H), 2.50–2.39 (m, 2H), 2.07 (ddd, J = 13.4, 7.9, 1.1 Hz, 1H), 1.98 (dd, J = 13.6, 6.8 Hz, 1H), 2.00–1.80 (br s, OH), 1.49 (d, J = 1.3 Hz, 3H), 1.10 (d, J = 6.4 Hz, 6H), 1.01 (d, J = 6.7 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 166.7 (0), 152.8 (0), 136.8 (0), 131.6 (0), 131.3 (1), 128.2 (1), 127.8 (1), 125.5 (1), 122.5 (1), 89.4 (1), 69.2 (1), 61.4 (3), 60.0 (2), 47.4 (2), 35.5 (1), 26.6 (1), 20.2 (3), 17.6 (3), 17.5 (3), 15.9 (3); MS (CI) (*m/z*) 412 (100), 380 (26), 362 (42), 322 (54). Anal. Calcd for $C_{20}H_{29}NO_4S_2$: C, 58.36; H, 7.10; N, 3.40. Found: C, 58.17; H, 7.15; N, 3.42.



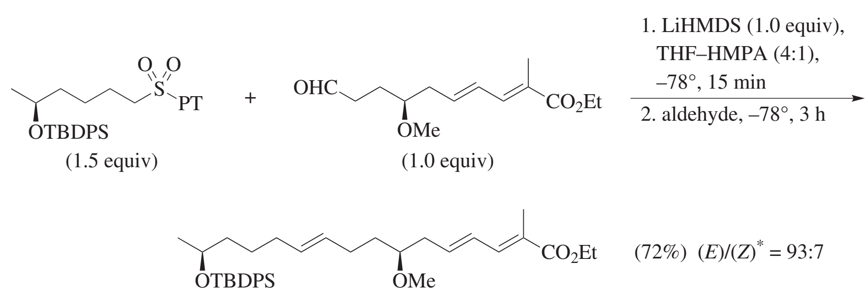
***N*-(*tert*-Butoxycarbonyl)-4-methylenepiperidine [Methylenation of a Ketone: TBT Sulfone, Barbier, Cs_2CO_3, THF–DMF].[62]** A suspension of Cs_2CO_3 (248 mg, 0.760 mmol), *N*-Boc-4-piperidinone (50 mg, 0.251 mmol), and 1-*tert*-butyl-1*H*-tetrazol-5-yl methyl sulfone ($TBTSO_2Me$, 67 mg, 0.326 mmol) in anhydrous THF/DMF (3:1, 2.5 mL) was stirred at 70° under Ar for 16 h. After this time, the reaction mixture was cooled to rt, treated with saturated aqueous NH_4Cl (10 mL), and extracted with TBME (20 mL). The combined organic extracts were washed with brine (10 mL), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 87.5:12.5) to yield the title compound (46 mg, 0.233 mmol, 92%) as a colorless oil: IR (neat) 3074, 3006, 2978, 2941, 2909, 2864, 1699, 1652, 1365, 1238, 1171, 991, 892, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 2H), 3.42 (t, J = 6.0 Hz, 4H), 2.18 (t, J = 5.8 Hz, 4H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 145.6, 109.2, 79.7, 45.6 (2C), 34.7 (2C), 28.6 (3C); MS (EI) (*m/z*): M^+ 197 (10), 141 (33), 124 (11), 96 (15), 82 (12), 57 (100). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71. Found: C, 66.84; H, 9.33.



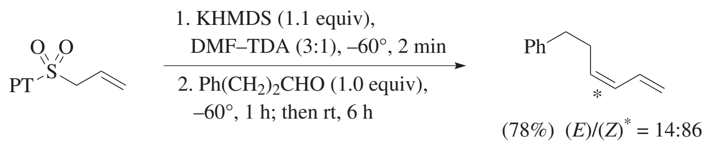
5,5-Dimethyl-2-[(*E*,*S*)-3-methylhex-4-enyl]-1,3-dioxane [Synthesis of a Non-Conjugated 1,2-Disubstituted (*E*) Alkene: PT Sulfone, Barbier, KHMDS, DME].[60] A stirred solution of ethyl (1-phenyl-1*H*-tetrazol-5-yl) sulfone (5.95 g, 25.0 mmol) and (*S*)-4-(5,5-dimethyl-1,3-dioxan-2-yl)-2-methylbutanal (3.82 g, 19.1 mmol) in anhydrous DME (80 mL) at −60° (bath temperature) was treated dropwise via cannula with a solution of KHMDS (7.00 g, 80 wt %, 28.1 mmol) in anhydrous DME (40 mL) over 45 min. After this time, H_2O (10 mL) was added, and the mixture was allowed to warm to rt. The reaction mixture was diluted with Et_2O (150 mL) and H_2O (80 mL), and the layers were separated. The aqueous phase was extracted with Et_2O (3 × 50 mL), and the combined organic phases were washed with H_2O (3 × 50 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/Et_2O, 100:0 to 90:10) to yield the title compound (3.76 g, 17.7 mmol, 93%, (*E*)/(*Z*) = 93:7) as a colorless oil: $[\alpha]_D$ + 7.2 (*c* 1.01, $CHCl_3$); IR (neat) 2956, 1454, 1394, 1122, 1044, 1020, 966 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.40 (ddq, *J* = 15.2, 6.2, 0.7 Hz, 1H), 5.26 (ddq, *J* = 15.2, 7.6, 1.3 Hz, 1H), 4.39 (t, *J* = 5.1 Hz, 1H), 3.60 (d, *J* = 9.9 Hz, 2H), 3.42 (d, *J* = 10.6 Hz, 2H), 2.04 (septet, *J* = 7.0 Hz, 1H), 1.70–1.52 (m, 2H), 1.63 (dm, *J* = 6.3 Hz, 3H), 1.44–1.27 (m, 2H), 1.19 (s, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.72 (s, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 137.1 (1), 123.5 (1), 102.6 (1), 77.4 (2C, 2), 36.9 (1), 33.0 (2), 31.3 (2), 30.3 (0), 23.1 (3), 22.0 (3), 21.0 (3), 18.1 (3). Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.36; H, 11.13.



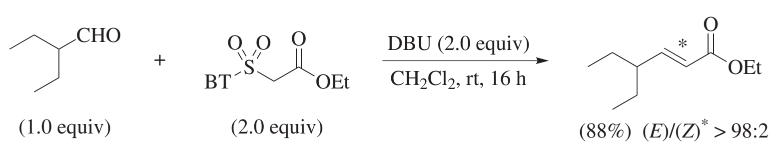
(*S,E*)-*tert*-Butyldiphenyl(5-methylhex-3-en-2-yloxy)silane [Synthesis of a Non-Conjugated 1,2-Disubstituted (*E*) Alkene: PT Sulfone, Premetalation, KHMDS, 18-crown-6, THF].[26] A stirred solution of isobutyl (1-phenyl-1*H*-tetrazol-5-yl) sulfone (50 mg, 0.188 mmol) and 18-crown-6 (99.4 mg, 0.376 mmol) in anhydrous THF (2 mL) at −78° was treated dropwise with KHMDS (0.451 mL, 0.5 M in toluene, 0.226 mmol) over 10 sec. After 30 sec, a solution of (*S*)-2-(*tert*-butyldiphenylsilyloxy)propanal (73 mg, 0.234 mmol) in anhydrous THF (0.5 mL) was added and stirring was continued for 30 min at –78°. Saturated aqueous NH_4Cl (10 mL) was added, and the mixture was extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 100:0 to 95:5) to yield the title compound (54.4 mg, 0.154 mmol, 82%, (*E*)/(*Z*) > 98:2) as a colorless oil: IR (neat) 3032, 2958, 2925, 2871, 2495, 2455, 967 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72–7.33 (m, 10H), 5.42 (ddd, *J* = 15.6, 6.3, 0.5 Hz, 1H), 5.32 (dd, *J* = 15.5, 6.2 Hz, 1H), 4.26 (quintet, *J* = 6.2 Hz, 1H), 2.18 (m, 1H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.08 (s, 9H), 0.92 (d, *J* = 6.2 Hz, 3H), 0.90 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 136.2, 136.1, 135.0, 131.5, 129.5, 127.6, 127.5, 70.8, 30.7, 27.2, 24.8, 22.5, 22.4, 19.4; MS (CI) (*m/z*): 353 (10), 352 (28), 351 (100), 251 (24), 229 (22).



Ethyl (2*E*,4*E*,7*S*,10*E*,15*S*)-15-(*tert*-Butyldiphenylsilyloxy)-7-methoxy-2-methylhexadeca-2,4,10-trienoate [Synthesis of a Non-Conjugated 1,2-Disubstituted (*E*) Alkene: PT Sulfone, Premetalation, LiHMDS, THF–HMPA].[165] A solution of the sulfone (615 mg, 1.12 mmol) in anhydrous THF/HMPA (4:1, 4.0 mL) at –78° under Ar was treated with LiHMDS (0.75 mL, 1.0 M in THF, 0.75 mmol) and stirred for 15 min. After this time, a solution of the aldehyde (190 mg, 0.75 mmol) in THF/HMPA (4:1, 1.0 mL) was added dropwise, and the resulting mixture was stirred at –78° for 3 h. Saturated aqueous NH_4Cl (20 mL) was then added, and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 96:4 to 94:6) to afford the title compound (310 mg, 0.537 mmol, 72%, (*E*)/(*Z*)* = 93:7) as a colorless oil: $[\alpha]_D$ – 9.4 (*c* 2.46, $CHCl_3$); IR (neat) 3620, 3404, 2929, 2360, 1704, 1365, 1219, 1105, 769, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76–7.57 (m, 4H), 7.46–7.31 (m, 6H), 7.19 (m, 1H), 6.41 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.08 (m, 1H), 5.42–5.25 (m, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.93–3.78 (m, 2H), 3.61 (m, 1H), 3.35 (s, 3H) 3.26 (m, 1H), 2.40 (t, *J* = 6.6 Hz, 2H), 2.12–1.77 (m, 8H), 1.94 (s, 3H), 1.58–1.21 (m, 9H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 138.6, 135.9, 134.8, 131.4, 129.7, 129.4, 127.6, 127.5, 127.4, 125.1, 79.8, 69.5, 68.9, 60.5, 56.8, 55.9, 39.0 (2C), 38.4, 37.3, 33.7, 32.5, 29.7, 28.4, 27.1, 25.2, 23.8, 23.2, 19.3, 14.3, 12.6; MS (ES) (*m/z*): 578 (100); HRMS (ES) (*m/z*): $[M + 2H]^+$ calcd for $C_{36}H_{54}O_4Si$, 578.3791; found, 578.3767.

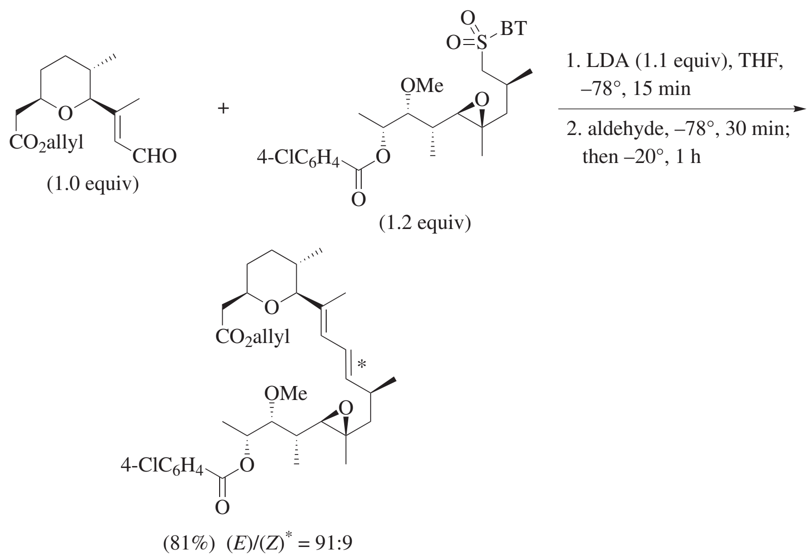


(*Z*)-6-Phenyl-1,3-hexadiene [Synthesis of a Conjugated 1,2-Disubstituted (*Z*) Alkene via a Type II Olefination: PT Sulfone, Premetalation, KHMDS, DMF–TDA].[32] To a stirred solution of allyl (1-phenyl-1*H*-tetrazol-5-yl) sulfone (250 mg, 1.00 mmol) in DMF–tris[2-(2-methoxyethoxy)ethyl]amine (TDA, 10 mL, 3:1) at –60° was added KHMDS (1.83 mL, 0.6 M in toluene, 1.10 mmol) over 10 sec. The resulting mixture was stirred for 2 min, and then a solution of dihydrocinnamaldehyde (131 μL, d = 1.02 g/mL, 134 mg, 1.00 mmol) in DMF (0.2 mL) was added dropwise. Stirring at –60° was continued for 1 h, and then the mixture was allowed to warm to rt. After being stirred for 6 h at rt, saturated aqueous NH_4Cl (10 mL) was added, and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 98:2) to afford the title compound (123 mg, 0.777 mmol, 78%, (*E*)/(*Z*) = 14:86) as a pale-yellow oil: IR (neat) 3031, 2956, 2887, 1524, 1487, 1334, 1001, 906, 800, 746, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37–7.28 (m, 2H), 7.26–7.15 (m, 3H), 6.65 (dtd, *J* = 16.9, 10.6, 1.0 Hz, 1H), 6.06 (t, *J* = 10.9 Hz, 1H), 5.53 (dt, *J* = 10.5, 7.7 Hz, 1H), 5.22 (dd, *J* = 16.9, 1.7 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 2.80–2.67 (m, 2H), 2.55 (dd, *J* = 15.3, 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 137.4, 134.5, 132.3, 131.8, 129.9, 128.6, 128.5, 126.1, 117.5, 36.0, 29.8; HRMS (EI) (*m/z*): M^+ calcd for $C_{12}H_{14}$, 158.1096; found, 158.1094.

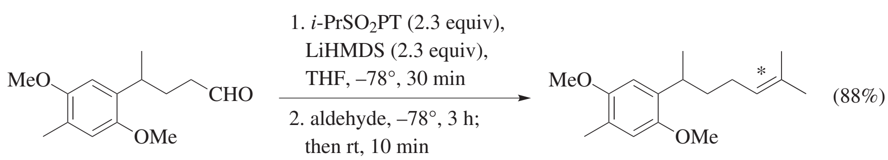


Ethyl (*E*)-4-Ethylhex-2-enoate [Synthesis of a Conjugated 1,2-Disubstituted (*E*) Enoate via a Type II Olefination: BT Sulfone, Barbier, DBU, CH_2Cl_2].[20] A solution of ethyl (benzothiazol-2-ylsulfonyl)acetate (228 mg, 0.80 mmol) in CH_2Cl_2 (5 mL) was treated sequentially with DBU (0.12 mL, d = 1.02 g/mL, 122 mg, 0.80 mmol) and 2-ethylbutanal (40 mg, 0.40 mmol), and the resulting reaction mixture was stirred at rt for 16 h. After this time, saturated aqueous NH_4Cl

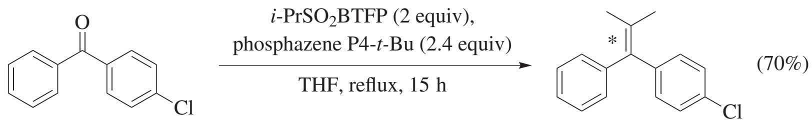
(5 mL) was added, and the layers were shaken and separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic phases were washed with brine (10 mL), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 95:5 to 80:20) to yield the title compound (60 mg, 0.353 mmol, 88%, (*E*)/(*Z*) > 98:2) as a colorless oil: IR (neat) 2930, 1731, 1461 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 15.7, 9.2 Hz, 1H), 5.79 (dm, *J* = 15.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.98 (dtt, *J* = 9.2, 8.3, 6.0 Hz, 1H), 1.57–1.41 (m, 2H), 1.39–1.24 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0 (0), 153.5 (1), 121.5 (1), 60.3 (2), 46.2 (1), 27.0 (2C, 2), 14.5 (3), 11.8 (2C, 3).



18-*O*-(4-Chlorobenzoyl)herboxidiene, Allyl Ester [Synthesis of a Conjugated 1,2-Disubstituted (*E*) Alkene via a Type III Olefination: BT Sulfone, Premetalation, LDA, THF].[60] To a stirred solution of the illustrated sulfone (331 mg, 0.58 mmol) in anhydrous THF (6 mL) at –78° under N_2 was added dropwise a solution of freshly prepared lithium diisopropylamide (LDA, 1.3 mL, 0.41 M in THF, 0.53 mmol), and the resulting deep-yellow solution was stirred for 15 min. A solution of the the aldehyde (131 mg, 0.49 mmol) in anhydrous THF (2 mL) was then added dropwise. The color of the reaction mixture lightened immediately. The mixture was stirred for 30 min at –78° and then was allowed to warm to –20° over 1 h. Saturated aqueous NH_4Cl (2 mL) was added to the colorless solution at –20°, and the resulting mixture was allowed to warm to rt with vigorous stirring. To the product solution were added EtOAc (15 mL) and H_2O (15 mL), and the layers were shaken and separated. The aqueous phase was extracted with EtOAc (3 × 5 mL), and the combined organic extracts were washed with brine (5 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 85:15) to yield the title compound (246 mg, 0.399 mmol, 81%, (*E*)/(*Z*)* = 91:9) as a colorless oil: $[\alpha]_D$ – 25 (*c* 0.40, $CHCl_3$); IR (neat) 2927, 1720, 1091 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.22 (dd, *J* = 15.0, 10.9 Hz, 1H), 5.94–5.82 (m, 1H), 5.88 (dm, *J* = 10.4 Hz, 1H), 5.42 (dd, *J* = 15.0, 8.9 Hz, 1H), 5.30 (dm, *J* = 17.9 Hz, 1H), 5.27 (quintet, *J* = 6.9 Hz, 1H), 5.20 (dm, *J* = 10.5, 1H), 4.58 (d, *J* = 5.5 Hz, 2H), 3.83–3.74 (m, 1H), 3.52 (s, 3H), 3.37 (dd, *J* = 6.9, 3.9 Hz, 1H), 3.31 (d, *J* = 9.9 Hz, 1H), 2.62 (d, *J* = 9.7 Hz, 1H), 2.61 (dd, *J* = 15.1, 6.5 Hz, 1H), 2.47–2.34 (m, 1H), 2.43 (dd, *J* = 15.2, 6.5 Hz, 1H), 1.91 (dd, *J* = 13.5, 4.6 Hz, 1H), 1.88–1.80 (m, 1H), 1.72–1.65 (m, 1H), 1.69 (s, 3H), 1.57–1.46 (m, 2H), 1.40–1.15 (m, 3H), 1.29 (d, *J* = 6.5 Hz, 3H), 1.24 (s, 3H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.64 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 171.2 (0), 165.3 (0), 139.4 (1), 139.4 (0), 135.3 (0), 132.3 (1), 131.2 (2C, 1), 129.3 (0), 128.8 (2C, 1), 128.3 (1), 125.3 (1), 118.0 (2), 90.8 (1), 84.7 (1), 74.0 (1), 73.3 (1), 66.0 (1), 65.1 (2), 61.5 (3), 60.9 (0), 47.1 (2), 41.6 (2), 35.4 (1), 35.2 (1), 32.4 (2), 32.2 (1), 31.8 (2), 22.3 (3), 17.7 (3), 16.8 (3), 16.8 (3), 12.0 (3), 10.8 (3); HRMS (CI) (*m/z*): M^+ calcd for $C_{35}H_{49}ClO_7$, 616.3167; found, 616.3169.



1,4-Dimethoxy-2-methyl-5-(6-methylhept-5-en-2-yl)benzene [Synthesis of a Trisubstituted Alkene: PT Sulfone, LiHMDS, THF].[166] A solution of the sulfone (4.30 g, 17.0 mmol) in anhydrous THF (100 mL) at –78° under Ar was treated dropwise with LiHMDS (10.8 mL, 1.60 M in THF, 17.3 mmol), and the solution was stirred for 30 min. The resulting yellow solution of sulfone anion was added in one portion via a precooled syringe to a stirred solution of 4-(2,5-dimethoxy-4-methylphenyl)pentanal (1.77 g, 7.50 mmol) in anhydrous THF (100 mL). The reaction mixture was stirred at –78° for 3 h, and then it was allowed to warm to rt over 10 min. After this time, H_2O (100 mL) was added, and the mixture was extracted with Et_2O (2 × 200 mL). The combined organic phases were washed with brine (50 mL) and then were concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexanes/EtOAc, 95:5) to yield the title compound (1.73 g, 6.59 mmol, 88%) as a colorless oil: IR (neat) 2927, 2852, 1504, 1465, 1398, 1208, 1049 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 2H), 5.12 (t, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.14 (sextet, *J* = 7.6 Hz, 1H), 2.20 (s, 3H), 2.00–1.85 (m, 2H), 1.67 (s, 3H), 1.67–1.48 (m, 2H), 1.54 (s, 3H), 1.18 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9 (0), 150.8 (0), 133.9 (0), 130.9 (0), 124.8 (1), 124.1 (0), 114.2 (1), 109.7 (1), 56.2 (3), 55.9 (3), 37.3 (2), 31.9 (1), 26.3 (2), 25.6 (3), 21.2 (3), 17.5 (3), 16.0 (3); HRMS (ES) (*m/z*): $[M + Na]^+$ calcd for $C_{17}H_{26}NaO_2$, 285.1831; found, 285.1839.



1-(4-Chlorophenyl)-2-methyl-1-phenylpropene [Synthesis of a Tetrasubstituted Alkene: BTFP Sulfone, Barbier, P4-*t*-Bu, THF].[95] A stirred solution of 3,5-bis(trifluoromethyl)phenyl isopropyl sulfone (*i*-$PrSO_2$BTFP, 96 mg, 0.30 mmol) and 4-chlorobenzophenone (32 mg, 0.15 mmol) in anhydrous THF (6 mL) at rt under Ar was treated dropwise with phosphazene base P4-*t*-Bu (0.36 mL, 1.0 M in *n*-hexane, 0.36 mmol). The resulting mixture was heated to reflux. After stirring for 15 h at reflux, the reaction mixture was cooled to rt and then was concentrated under vacuum. Water (5 mL) was added, and the mixture was extracted with pentane (2 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under vacuum, and the residue was purified by column chromatography on silica gel (hexanes) to yield the title compound (25.5 mg, 0.105 mmol, 70%) as a colorless oil: IR (neat) 3083, 3064, 3026, 2983, 2918, 2848, 1649, 1600, 1568, 1482, 1450, 1401, 1369 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.03 (m, 9H), 1.79 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 141.6, 135.8, 131.7, 131.2, 129.8, 128.0, 127.9, 126.2, 22.5, 22.4; HRMS (EI) (*m/z*): M^+ calcd for $C_{16}H_{15}Cl$, 242.0862; found, 242.0871.

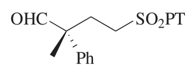
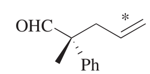
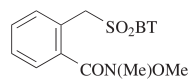
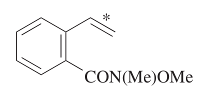
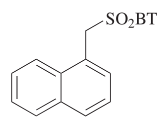
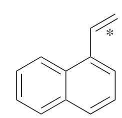
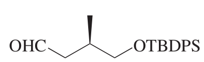
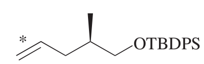
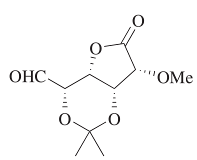
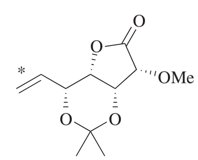
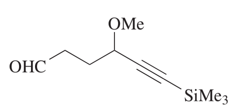
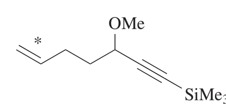
TABULAR SURVEY

Tables 1–18 are organized by the carbonyl component of the olefination reaction according to the number of skeletal carbon atoms; carbon atoms found in any heteroatom-linked subdomains or protecting groups are excluded from the count. Unless otherwise stated, the sulfone should be assumed to be the first component added to the reaction mixture. Use of a premetalation protocol is indicated by reaction conditions written as “1. base, 2. add aldehyde/ketone”; otherwise, a Barbier protocol (i.e., sulfone and carbonyl compound premixed before addition of base) is involved. For each example an asterisk (*) clearly identifies the site of the newly introduced alkene in the product, and the given (*E*)/(*Z*) ratios are for this double bond, unless otherwise stated. Reaction stoichiometry is noted only when it differs significantly from the typical values seen in the experimental procedures given above. In general, the more valuable reaction coupling partner (sulfone or carbonyl compound) is used as the limiting reagent and a slight excess (1.1 to 1.5 equivalents) of the other component is employed. The quantity of base commonly used at least equals the amount of sulfone in the reaction mixture; when other protic sites are present (e.g., free hydroxyl groups, amide NH), an additional equivalent of base is used to accommodate each effective source of proton. The tables contain all examples published in the primary peer-reviewed literature through the first quarter of 2016 as retrieved by SciFinder Scholar and Reaxys substructure, keyword, and citation searches.

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

Act	Activator group
ADDP	1,1′-(azodicarbonyl)dipiperidide
BEMP	2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine
BHT	2,6-di(*tert*-butyl)-4-methylphenol
BOM	benzyloxymethyl
BT	benzothiazol-2-yl
BTFP	3,5-bis(trifluoromethyl)phenyl
c-C_5H_9	cyclopentyl
c-C_6H_{11}	cyclohexyl
CSA	camphorsulfonic acid
DMB	3,4-dimethoxybenzyl
HMDS	hexamethyldisilazane
IM	1-methylimidazol-2-yl
IQ	isoquinolin-1-yl
MPM	(4-methoxyphenyl)methyl
MS	molecular sieves
NAP	2-naphthylmethyl
NP	4-nitrophenyl
m-NPT	1-(3-nitrophenyl)-1*H*-tetrazol-5-yl
p-NPT	1-(4-nitrophenyl)-1*H*-tetrazol-5-yl
P2-Et	1-ethyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene)
P4-*t*-Bu	1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene)
^{F}PMB	variable fluorine-containing 4-methoxybenzyl groups to encode stereochemistry
PMP	4-methoxyphenyl
PNB	4-nitrobenzoate
PS	polystyrene
PT	1-phenyl-1*H*-tetrazol-5-yl
PYM	pyrimidin-2-yl
PYR	pyrid-2-yl
SEM	2-(trimethylsilyl)ethoxymethyl
SES	trimethylsilylethylsulfonyl
TBDPS	*tert*-butyldiphenylsilyl
TBT	1-*tert*-butyl-1*H*-tetrazol-5-yl
TDA	tris[2-(2-methoxyethoxy)ethyl]amine
TES	triethylsilyl
TMG	*N*,*N*,*N*′,*N*′-tetramethylguanidine
TZ	4-methyl-1,2,4-triazol-3-yl

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED ALKENES

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
CH_2O		1. Ethylene glycol, 4-TsOH, benzene, reflux, overnight 2. Aldehyde (30 eq), KHMDS, DME, –78° 3. 4 M HCl, THF, 50°	 (30)	53
$[CH_2O]_n$		Paraformaldehyde (1.5 eq), sulfone (1 eq), NaH (1.2 eq), DMF, 0° to rt, 3 h	 (92)	167
		Cs_2CO_3, CH_2Cl_2, rt, 15 h	 (58)	100
C_5				
	$MeSO_2PT$	LiHMDS, THF, –78°, 3 h; then rt	 (81)	168
C_6				
	$MeSO_2PT$	LiHMDS, DMF/HMPA –35 to 35°, 12 h	 (6)	169
	$MeSO_2TBT$	Cs_2CO_3, THF/DMF, 70°, 16 h	 (96)	62

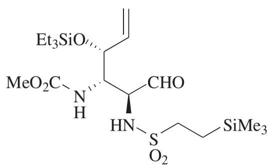
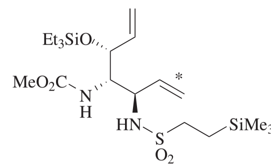
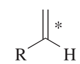
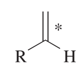
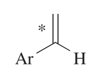
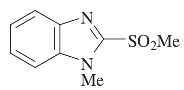
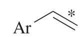
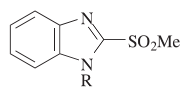
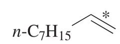
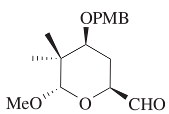
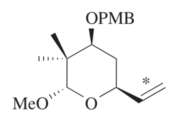
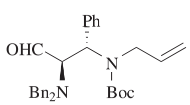
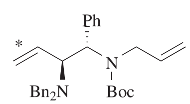
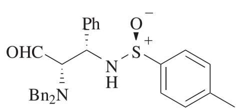
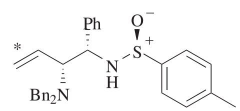
	$MeSO_2PT$	KHMDS, THF/toluene, –20°		(>36)	150
C_{7-10}					
RCHO	$MeSO_2BT$	LDA, THF, –78°, 3 h; then rt, 1 h		R: 4-$MeOC_6H_4$ (64); 4-$Me_2NC_6H_4$ (44); *n*-C_9H_{19} (20)	3
C_{7-11}					
RCHO	$MeSO_2BTFP$	**A**: KOH, *n*-Bu_4NBr, THF, rt, 16 h *or* **B**: P4-*t*-Bu, THF/HMPA, 0° to rt, 16 h		R, Conditions: 4-$MeOC_6H_4$, **A** (60); $Ph(CH_2)_2$, **B** (30); (*E*)-PhCH=CH, **A** (50); 6-MeO-2-naphthyl, **A** (80); 6-MeO-2-naphthyl, **B** (82)	58
C_{7-13}					
ArCHO	$MeSO_2TBT$	**A**: NaHMDS, THF, –78° to rt, 16 h *or* **B**: Cs_2CO_3, THF/DMF, 70°, 16 h		Ar, Conditions: 3,4-$(MeO)_2$-5-BrC_6H_2, **B** (92); 2,6-$(PMBO)_2C_6H_3$, **A** (93); 4-$MeO_2CC_6H_4$, **B** (80); 4-PhC_6H_4, **B** (93)	62

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED ALKENES (*Continued*)

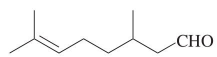
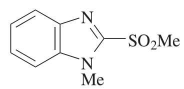
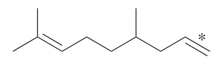
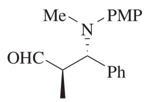
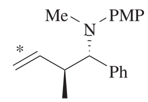
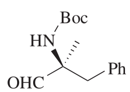
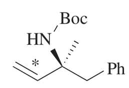
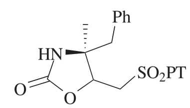
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-11}				
ArCHO		Aldehyde (1.0 eq), sulfone (*x* eq), base (*y* eq), DMF		63

Ar	*x*	Base	*y*	Temp/Time	
4-ClC_6H_4	1.1	*t*-BuOK	3	rt, 1 h	(93)
3,4-$(MeO)_2C_6H_3$	1.0	NaHMDS	1.3	–55°, 5 min; to rt, 2 h; rt, 2 h	(97)
3,4-$(MeO)_2C_6H_3$	1.2	*t*-BuOK	2.6	rt	(92)
1-naphthyl	1.0	NaHMDS	1.3	–55°, 5 min; to rt, 2 h; rt, 2 h	(90)
1-naphthyl	1.1	*t*-BuOK	3.0	rt, 1 h	(91)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
n-C_7H_{15}CHO		Aldehyde (1.0 eq), sulfone (*x* eq), *t*-BuOK (*y* eq), DMF, rt, 1 h		63
	$MeSO_2PT$	KHMDS, THF/toluene, –78°, 4 h; then rt, 24 h	 (>44)	170
C_9				
	$MeSO_2PT$	1. KHMDS, THF, –20° 2. Aldehyde	 (88)	171
	$MeSO_2PT$	1. KHMDS, THF, –20° 2. Aldehyde	 (≥70)	172

R	*x*	*y*	
Me	1.5	2.6	(74)
i-Pr	—	—	(75)

C_{10}

		Aldehyde (1.0 eq), sulfone (1.1 eq), *t*-BuOK (2.6 eq), DMF, rt, 1 h	 (97)	63
	$MeSO_2PT$	KHMDS, toluene, –20°, 1.5 h	 (90)	173
	$MeSO_2PT$	1. $M(SiMe_3)_2$, THF, –20° 2. Aldehyde, time	 **I** +  **II** "substantial amounts"	174

M	Time (h)	**I**
Li	3	(25)
Na	24	(52)
K	19	(40)

C_{11}

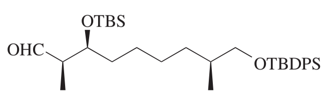
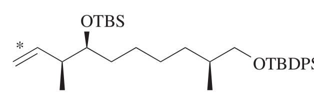
	$MeSO_2PT$	1. Sulfone (1 eq), NaHMDS (1 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –78°, 2 h; then to rt, 4 h	 (74)	175

TABLE 1. SYNTHESIS OF MONOSUBSTITUTED ALKENES (*Continued*)

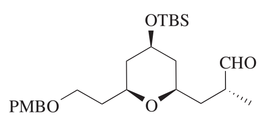
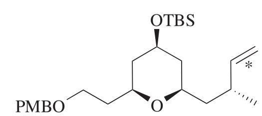
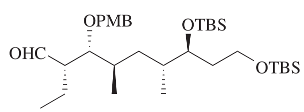
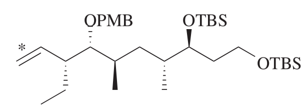
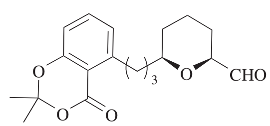
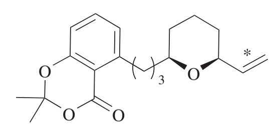
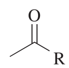
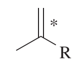
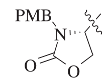
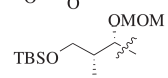
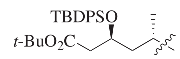
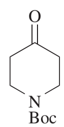
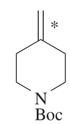
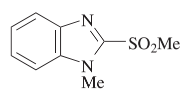
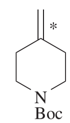
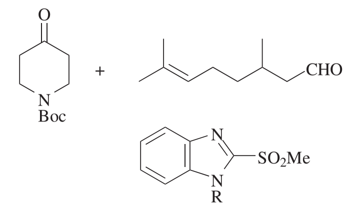
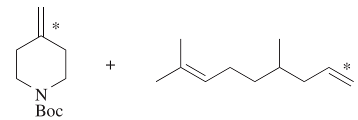
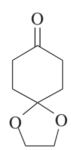
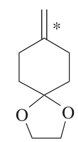
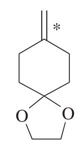
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{11} 	$MeSO_2PT$	1. Sulfone (3 eq), NaHMDS (2 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –79°; then to rt; then rt, 12 h		(80), two steps	176
C_{13} 	$MeSO_2PT$	1. Sulfone (3 eq), NaHMDS (2 eq), THF, –78°, 1 h 2. Aldehyde (1 eq), –78°; then to rt; then rt, 18 h		(78), 2 steps	177
C_{16} 	$MeSO_2PT$	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 4 h		(93)	178 179

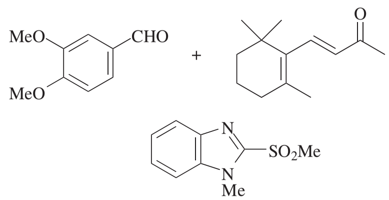
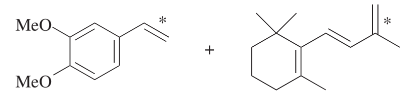
TABLE 2. SYNTHESIS OF 1,1-DISUBSTITUTED ALKENES

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-8}				
	$MeSO_2TBT$	NaHMDS, THF, –78° to rt, 16 h	 R:  (85);  (77);  (90)	62
C_5				
	$MeSO_2TBT$	**A**: NaHMDS, THF, –78° to rt, 16 h *or* **B**: Cs_2CO_3, THF/DMF, 70°, 16 h	 Conditions: **A** (92); **B** (93)	62
		Ketone (1.0 eq), sulfone (*x* eq), base (*y* eq), DMF		63

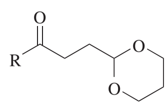
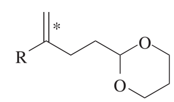
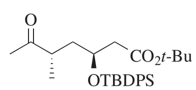
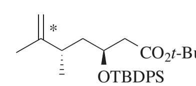
x	Base	*y*	Temp/Time	
1.0	NaHMDS	1.7	55°, 5 min; to rt, 2 h; rt, 2 h	(95)
1.2	*t*-BuOK	3.0	rt, 1 h	(99)

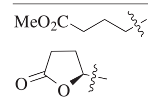
Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_5 + C_{10}$			
	Ketone (1 eq), aldehyde (1 eq), sulfone (1 eq), *t*-BuOK (2.6 eq), DMF, 1 h	 **I** + **II** R / Temp (°) / **I** / **II** / **I/II** Me / 0 / (62) / (—) / 88:12 Me / rt / (—) / (54) / 42:58 *i*-Pr / 0 / (66) / (—) / 88:12	63
C_6			
 $MeSO_2BTFP$	P4-*t*-Bu, THF/HMPA, 0° to rt, 16 h	 (41)	58
$MeSO_2TBT$	**A**: NaHMDS, THF, –78° to rt, 16 h *or* **B**: Cs_2CO_3, THF/DMF, 70°, 16 h	 Conditions **A** (90) **B** (84)	62

$C_7 + C_{13}$

Substrate	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		Aldehyde (1 eq), ketone (1 eq), sulfone (1 eq), t-BuOK (2.6 eq), DMF, 0°, 1 h	 **I** (89) + **II**; **I/II** = 97:3	63

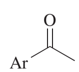
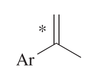
C_8

Substrate	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
	$MeSO_2TBT$	NaHMDS, THF, –78° to rt, 16 h		62
	$MeSO_2TBT$	NaHMDS, THF, –78° to rt, 16 h	 (90)	62



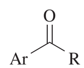
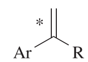
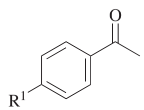
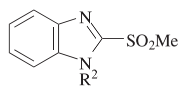
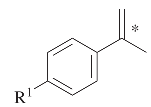
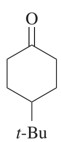
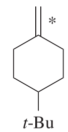
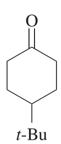
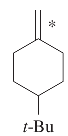
R	Conditions	Yield (%)
$MeO_2C(CH_2)_3$	**A**	(99)
lactone	**A**	(59)
lactone	**B**	(93)[a]

C_{8-9}

Substrate	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
	$MeSO_2TBT$	**A**: NaHMDS, THF, –78° to rt, 16 h *or* **B**: Cs_2CO_3, THF/DMF, 70°, 16 h		62

Ar	Conditions	Yield (%)
$4\text{-}MeOC_6H_4$	**A**	(77)
$4\text{-}MeOC_6H_4$	**B**	(63)
$4\text{-}EtO_2CC_6H_4$	**B**	(71)

TABLE 2. SYNTHESIS OF 1,1-DISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-13}				
	$MeSO_2BT$	**A**: LDA, THF, –78°, 3 h; then rt, 1 h *or* **B**: 1. LDA, THF, –78° 2. Aldehyde, –78° to rt		3
C_8				
		Ketone (1.0 eq), sulfone (*x* eq), base (*y* eq), DMF		63
C_{10}				
	MeSO$_2$BTFP	**A**: KOH, *n*-Bu$_4$NBr, THF, rt, 16 h *or* **B**: P4-*t*-Bu, THF/HMPA, 0° to rt, 16 h		58
	$MeSO_2BT$	LDA, THF, –78°, 3 h; then rt, 1 h	 (21)	3

Ar(C=O)R with $MeSO_2BT$ (ref. 3), product yields:

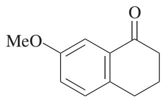
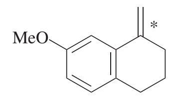
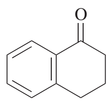
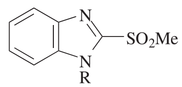
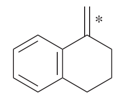
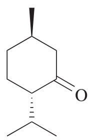
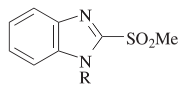
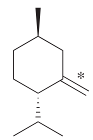
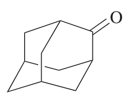
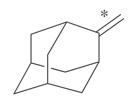
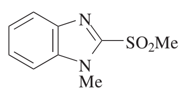
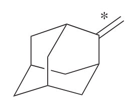
Ar	R	Conditions	Yield (%)
4-MeOC$_6$H$_4$	Me	**A**	(50)
Ph	Ph	**A**	(55)
Ph	Ph	**B**	(11)

Substituted acetophenone with benzimidazole sulfone (ref. 63), product yields:

R^1	R^2	*x*	Base	*y*	Temp/Time	Yield (%)
Br	Me	1.0	NaHMDS	1.7	–55°, 5 min; to rt, 2 h; rt, 2 h	(86)
Br	Me	1.3	*t*-BuOK	4.0	rt, 1 h	(95)
MeO	Me	1.0	LiHMDS	1.3	–78°, 5 min; to rt, 2 h; rt, 2 h	(21)
MeO	Me	1.0	NaHMDS	1.3	–55°, 5 min; to rt, 2 h; rt, 2 h	(54)
MeO	Me	1.0	KHMDS	1.3	–55°, 5 min; to rt, 2 h; rt, 2 h	(25)
MeO	Me	1.2	*t*-BuOK	3.0	rt, 1 h	(92)
MeO	*i*-Pr	—	*t*-BuOK	—	rt, 1 h	(93)

4-*t*-Butylcyclohexanone with MeSO$_2$BTFP (ref. 58), product yields:

Conditions	Yield (%)
A	(10)
B	(74)

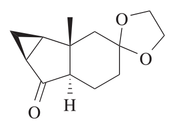
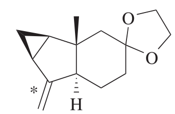
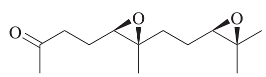
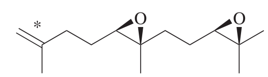
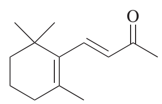
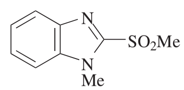
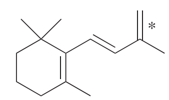
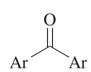
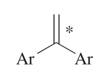
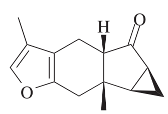
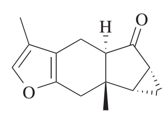
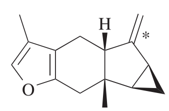
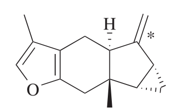
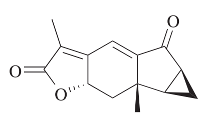
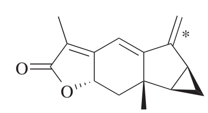
	$MeSO_2TBT$	Cs_2CO_3, THF/DMF, 70°, 16 h	 (45)	62
		Ketone (1.0 eq), sulfone (*x* eq), *t*-BuOK (*y* eq), DMF, rt, 1 h		63
		Ketone (1.0 eq), sulfone (*x* eq), *t*-BuOK (*y* eq), DMF, rt, 1 h		63
	$MeSO_2TBT$	Cs_2CO_3, THF/DMF, 70°, 16 h	 (57)	62
		Ketone (1.0 eq), sulfone (*x* eq), base (*y* eq), DMF		63

R	*x*	*y*	
Me	1.5	3.0	(77)
i-Pr	—	—	(77)

R	*x*	*y*	
Me	2.0	3.0	(60)
i-Pr	—	—	(76)

x	Base	*y*	Temp/Time	
1.0	NaHMDS	1.7	–55°, 5 min; to rt, 2 h; rt, 2 h	(95)
1.2	*t*-BuOK	3.0	rt, 1 h	(96)

TABLE 2. SYNTHESIS OF 1,1-DISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
 $MeSO_2TBT$	NaHMDS, THF, –78° to rt, 12 h	 (79)	180
C_{13}			
 $MeSO_2TBT$	NaHMDS, THF, –78° to rt	 (90)	181
 	Ketone (1.0 eq), sulfone (1.2 eq), *t*-BuOK (3.0 eq), DMF, rt, 1 h	 (91)	63
 $MeSO_2BTFP$	P4-*t*-Bu, THF/HMPA, 0° to rt, 16 h	 Ar: Ph (36); 4-ClC_6H_4 (50)	58
C_{14}			
 +  $MeSO_2TBT$	NaHMDS, THF, –78°	 **I** +  **II** **I** + **II** (65)	182
 $MeSO_2TBT$	Ketone (1 eq), sulfone (1.4 eq), NaHMDS (1.5 eq), THF, –78°, 6 h	 (47)	183

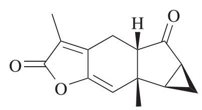
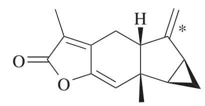
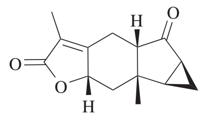
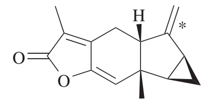
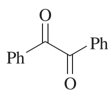
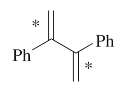
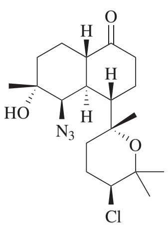
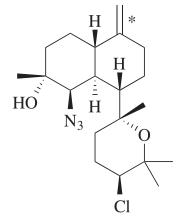
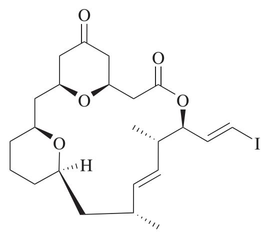
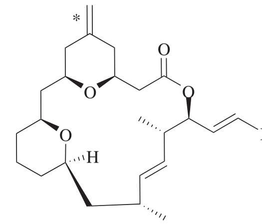
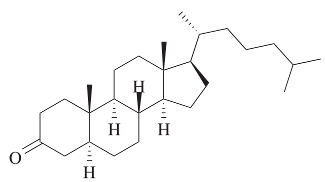
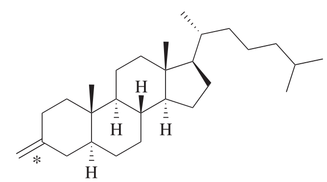
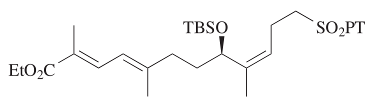
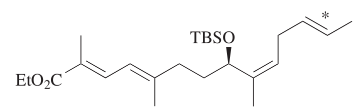
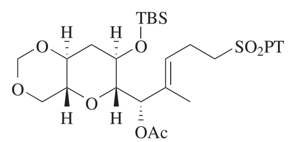
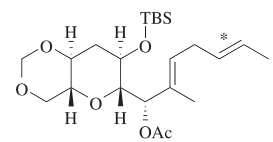
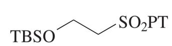
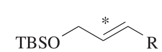
	$MeSO_2TBT$	1. Sulfone (3.0 eq), NaHMDS (2.5 eq), THF, –78°, 1 h 2. Ketone (1.0 eq), –78°; then to –40°, 3 h	 (81)	184
	$MeSO_2TBT$	NaHMDS, THF, –78°, 2.1 h	 (72)	185
	$MeSO_2BTFP$	Sulfone (4 eq), diketone (1 eq) P4-*t*-Bu, THF/HMPA, 0° to rt, 16 h	 (45)	58
C_{19}				
	$MeSO_2BT$	Sulfone (4 eq), LiHMDS, THF, –78°, 3 h	 (88)	186

TABLE 2. SYNTHESIS OF 1,1-DISUBSTITUTED ALKENES (*Continued*)

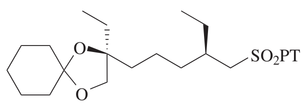
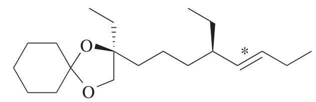
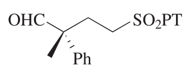
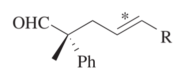
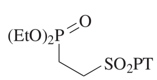
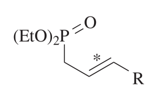
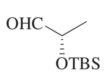
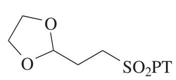
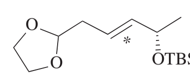
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{23}					
	$MeSO_2TBT$	NaHMDS, THF, −78 to −17°, 1.5 h		(100)	66
C_{27}					
	$MeSO_2TBT$	NaHMDS, THF, −78° to rt, 16 h		(76)	62

[a] Partial racemization from er 97.0:3.0 to er 80.5:19.5 occurred.

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES

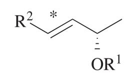
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
MeCHO		1. KHMDS, DME, –60°, 0.33 h 2. Aldehyde, –60° 0.5 h	 (90), (*E*)/(*Z*)* = 86:14	61
		Aldehyde (10 eq), sulfone (1 eq), KHMDS (1.5 eq), THF, –78°, 0.5 h; then to rt	 (32), (*E*)*-isomer	187
C_{2-9}				
RCHO		KHMDS, solvent, –78°, 0.5 h; then rt		188

R	Solvent		(*E*)/(*Z*)*
$BnOCH_2$	THF	(91)	92:8
$TBSO(CH_2)_2$	THF	(88)	98:2
n-Pr	THF	(89)	88:12
$MeO_2C(CH_2)_3$	THF	(89)	96:4
t-Bu	THF	(87)	>99:1
c-C_6H_{11}	THF	(84)	93:7
$Ph(CH_2)_2$	THF	(88)	84:16
$Ph(CH_2)_2$	DME	(83)	91:9

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		LiHMDS, DME	 (74), (*E*)/(*Z*)* = 60:40	189
C_{3-5}				
RCHO		**A**: NaHMDS, DME, –78° *or* **B**: 1. Ethylene glycol, *p*-TsOH, benzene, reflux 2. Aldehyde, KHMDS, DME, –78° 3. HCl, THF, 50°	 R / Conditions / / (*E*)/(*Z*)* Et / **A** / (15) / 67:33 Et / **B** / (45) / 89:11 *i*-Bu / **B** / (48) / 87:13	53
C_{3-9}				
RCHO		1. KHMDS, THF, –78°, 5 min 2. Aldehyde, –78°, 20 min; then 0°, 1 h	 R / / (*E*)/(*Z*)* Et / (77) / 93:7 *i*-Pr / (72) / >95:5 *t*-Bu / (40) / >95:5 *n*-C_5H_{11} / (82) / >95:5 *c*-C_5H_9 / (80) / >95:5 *c*-C_6H_{11} / (79) / >95:5 $Ph(CH_2)_2$ / (85) / >95:5	115
C_3				
		KHMDS, DME, –55 to 0°, 14 h	 (92), (*E*)/(*Z*)* = 95:5	190

A:
1. KHMDS, THF, –78°
2. Aldehyde

or **B**:
1. KHMDS (1.1 eq), 18-crown-6 (2.0 eq), –78° THF, 0.5 min
2. Aldehyde, –78°, 30 min



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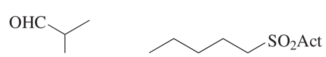
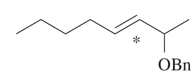
		Conditions **A**		Conditions **B**	
R^1	R^2		$(E)/(Z)^*$		$(E)/(Z)^*$
Bn	Me	(76)	80:20	(75)	95:5
Bn	*n*-Pr	(68)	90:10	(63)	>98:2
Bn	*i*-Pr	(78)	95:5	(75)	>98:2
t-$BuPh_2Si$	*i*-Pr	(81)	95:5	(82)	>98:2



Act = BT or PT

1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h
2. Aldehyde, temp, 3 h; then to rt



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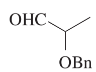
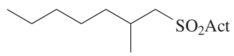
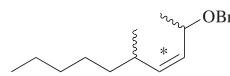
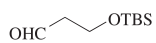
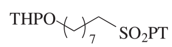
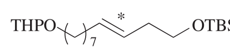
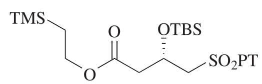
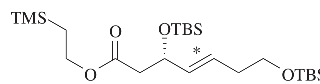
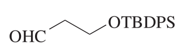
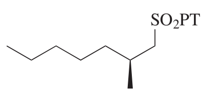
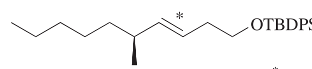
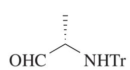
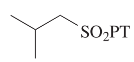
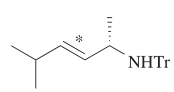
			Act = BT		Act = PT	
M	Solvent	Temp (°)		$(E)/(Z)^*$		$(E)/(Z)^*$
Li	toluene	–78	(2)	50:50	(54)	31:69
Li	Et_2O	–78	(1)	55:45	(31)	35:65
Li	THF	–78	(23)	74:26	(91)	64:36
Li	DME	–60	(<1)	—	(88)	59:41
Na	toluene	–78	(5)	52:48	(100)	49:51
Na	Et_2O	–78	(5)	52:48	(82)	44:56

			Act = BT		Act = PT	
M	Solvent	Temp (°)		$(E)/(Z)^*$		$(E)/(Z)^*$
Na	THF	–78	(32)	64:36	(100)	65:35
Na	DME	–60	(25)	64:36	(96)	68:32
K	toluene	–78	(8)	63:37	(47)	58:42
K	Et_2O	–78	(10)	76:24	(78)	59:41
K	THF	–78	(44)	61:39	(100)	72:38
K	DME	–60	(50)	58:42	(94)	79:21

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 Act = BT or PT	1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h 2. Aldehyde, temp, 3 h; then rt		21

M	Solvent	Temp (°)	Act = BT	$(E)/(Z)^*$	Act = PT	$(E)/(Z)^*$
Li	toluene	–78	(100)	47:53	(—)	43:57
Li	Et_2O	–78	(85)	48:52	(100)	42:58
Li	THF	–78	(89)	54:46	(87)	44:56
Li	DME	–60	(55)	68:32	(90)	45:55
Na	toluene	–78	(72)	61:39	(79)	30:70
Na	Et_2O	–78	(34)	42:58	(100)	28:72
Na	THF	–78	(84)	50:50	(99)	19:81
Na	DME	–60	(94)	57:43	(93)	50:50
K	toluene	–78	(98)	61:39	(71)	64:36
K	Et_2O	–78	(88)	41:59	(48)	34:66
K	THF	–78	(95)	34:66	(66)	45:55
K	DME	–60	(86)	40:60	(37)	80:20

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
		LiHMDS, THF, 0°	 (74), $(E)/(Z)^*$ = —	191
		NaHMDS, THF, –78°	 (35), $(E)/(Z)^*$ = 80:20	193
		KHMDS, DME, –60° to rt, 12 h	 (35), $(E)/(Z)^*$ = 92:8	192
		NaHMDS (2 eq), DME, –55°, 3 h	 (70), $(E)^*$-isomer only	194

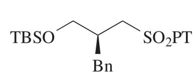
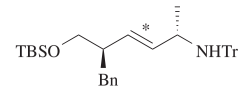
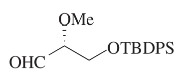
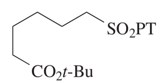
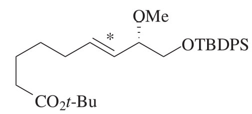
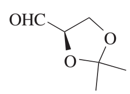
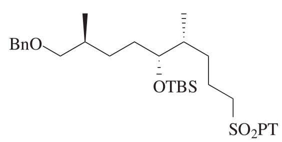
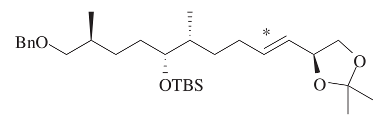
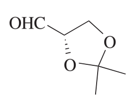
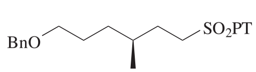
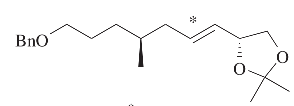
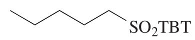
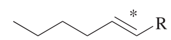
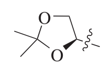
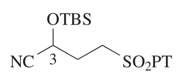
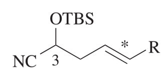
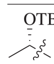
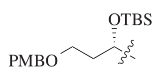
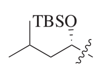
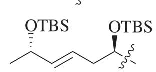
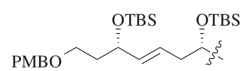
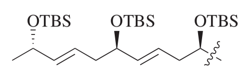
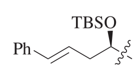
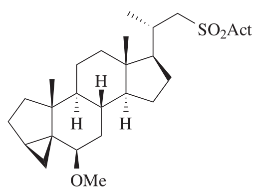
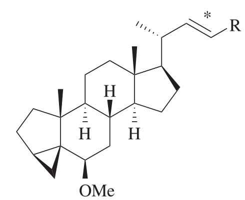
		1. LiHMDS, solvent, –78°, 0.33 h 2. Aldehyde, –78°, 3 h; then rt, 15 h	 Solvent / (E)/(Z)* THF (68) 50:50 THF/HMPA (31) 100:0	195
		1. KHMDS, DME, –78°, 0.5 h 2. Aldehyde, –78° to rt, 3 h	 (76), (*E*)/(*Z*)* = 50:50	196
		1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60°, 2 h; then 0°	 (82), (*E*)*-isomer only	197, 198
		1. Sulfone (1 eq), NaHMDS (1.1 eq), THF/HMPA (4:1), –78°, 1 h 2. Aldehyde (1.1 eq). –78°, 3 h; then to rt; then rt, 2 h	 (62), (*E*)*-isomer	199

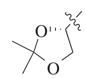
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-7}			
RCHO 	**A**: 1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60° to rt *or* **B**: Cs_2CO_3, THF/DMF, 70°, 16 h		
		R:  Conditions **B** (60) (E)/(Z)* 70:30	62
		R: c-C_6H_{11} Conditions **A** (88) (E)/(Z)* 89:11	5
C_{3-11}			
RCHO 	1. $MN(SiMe_3)_2$, THF, –78°, 0.75 h 2. Aldehyde, –78°; then rt, 3 h		200

R	C-3	M		(E)/(Z)*
	(*R*)	K	(95)	98:2
i-Pr	(*R*)	Na	(96)	95:5
	(*S*)	K	(85)	95:5
	(*S*)	K	(99)	95:5
	(*R*)	K	(83)	95:5
	(*S*)	K	(86)	95:5
	(*R*)	K	(85)	95:5
	(*R*)	K	(88)	95:5
	(*S*)	K	(96)	95:5

C_{3-5}

RCHO		1. NaHMDS, solvent –78°, 0.25 h 2. Aldehyde, –78° to rt		59

R	Act	Solvent		(*E*)/(*Z*)*
	BT	THF/HMPA	(81)	90:10
n-Pr	PT	THF	(39)	50:50
n-Pr	BT	THF	(61)	64:36
n-Pr	BT	THF/HMPA	(65)	80:20
i-Pr	BT	THF/HMPA	(90)	75:25
(*S*)-TBSOCH$_2$(Me)CH	BT	THF/HMPA	(60)	85:15
(*S*)-Me$_2$CH(OBn)CH	BT	THF/HMPA	(82)	94:6
(*R*)-Me$_2$CH(OBn)CH	BT	THF/HMPA	(80)	82:18

C_4

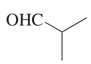
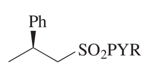
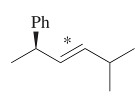
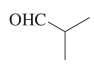
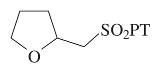
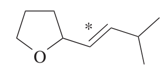
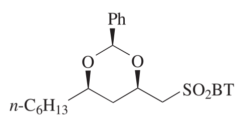
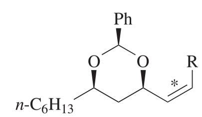
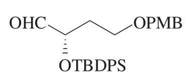
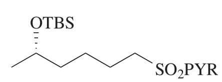
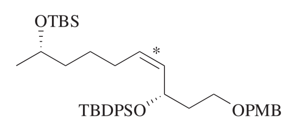
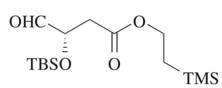
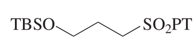
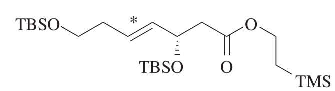
		1. KHMDS, DME, –78°, 3 min 2. Aldehyde, –78°, 2 h		(74), (*E*)/(*Z*)* = 65:35	201

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		1. $MN(SiMe_3)_2$, solvent, temp, 10 min 2. Aldehyde, temp, 1 h; then rt		121
C_{4-9}				
RCHO		NaH, THF, 20°		51
C_4				
		KHMDS, THF, –78°	 (8)[a], $(Z)^*$-isomer	202
		NaHMDS, THF, –78°, 4 h; then rt	 (74), $(E)/(Z)^*$ = 89:11	203

Reference 121 (product of entry 1):

M	Solvent	Temp (°)		$(E)/(Z)^*$
Na	THF	–78	(—)	15:85
Na	DME	–78	(—)	58:42
Na	DMF	–60	(—)	85:15
K	THF	–78	(—)	60:40
K	DME	–78	(—)	85:15
K	DMF	–60	(—)	90:10
K	DMF/HMPA	–78	(—)	93:7

Reference 51 (product of entry 2):

R		$(E)/(Z)^*$
i-Pr	(60)	25:75
$Ph(CH_2)_2$	(70)	25:75

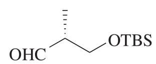
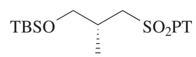
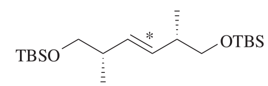
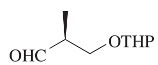
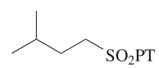
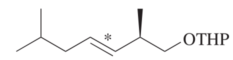
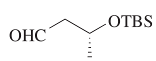
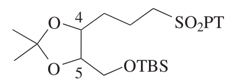
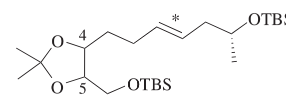
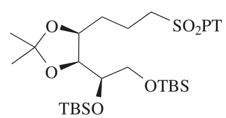
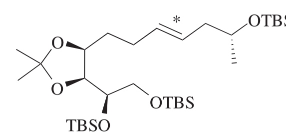
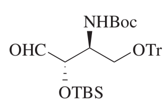
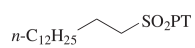
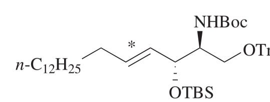
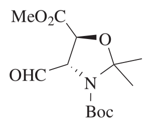
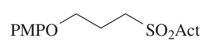
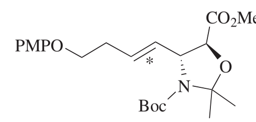
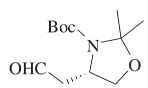
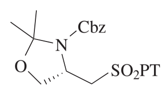
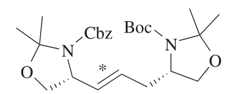
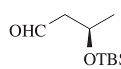
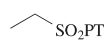
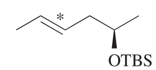
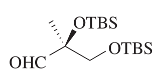
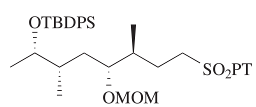
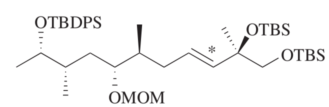
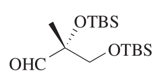
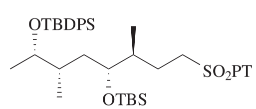
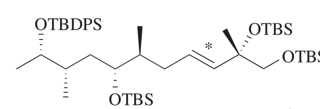
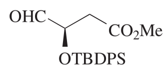
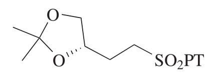
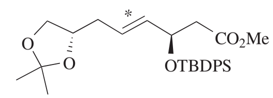
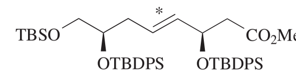
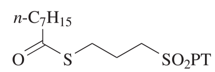
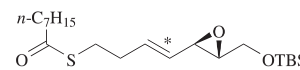
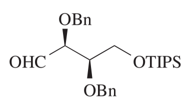
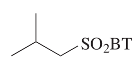
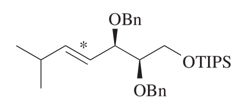
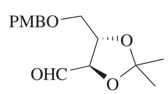
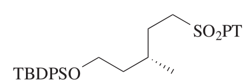
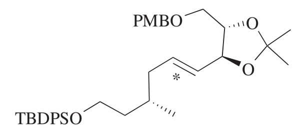
		1. KHMDS, DME, –55°, 1 h 2. Aldehyde, –55° to rt, 12 h		(69), $(E)^*$-isomer only	204
		1. KHMDS, DME, –55°, 1 h 2. Aldehyde, –50°, 1 h; rt, 12 h		(>51), $(E)/(Z)^*$ = 95:5	205
		LiHMDS, THF, –78°		C-4 C-5 $(E)/(Z)^*$ (*S*) (*S*) (84) 73:27 (*R*) (*R*) (72) 71:29	206
		LiHMDS, THF, –78°		(83), $(E)^*$-isomer	206
		1. KHMDS, DME, –56°, 0.5 h 2. Aldehyde; then –50°	 (64), $(E)/(Z)^*$ = 88:12		207

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		Barbier conditions. See table.		208

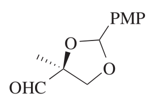
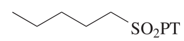
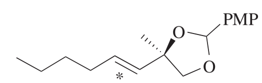
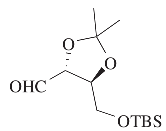
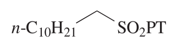
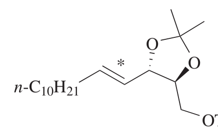
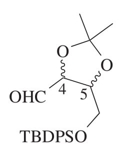
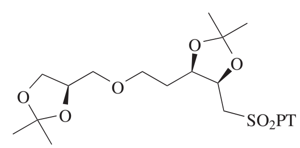
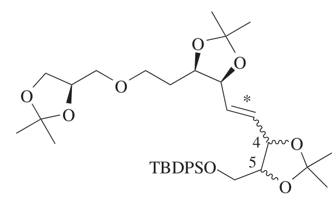
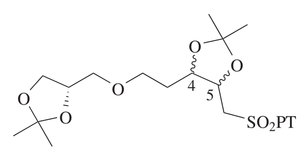
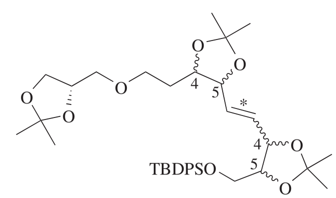
Act	Base	Solvent	Temp (°)	Time (h)		$(E)/(Z)^*$
BT	LDA	THF	–78	17	(42)	55:45
PT	LDA	THF	–78	17	(35)	62:38
PT	NaHMDS	DME	–60	0.5	(58)	64:36
PT	KHMDS	DME	–60	0.75	(67)	73:27

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
		1. NaHMDS, THF, –70° 2. Aldehyde; then rt, 2 h	 (71), $(E)/(Z)^*$ = —	209
		1. KHMDS, THF, –78°, 25 min 2. Aldehyde; then rt	 (56), $(E)^*$-isomer	210
		1. LiHMDS, DMF/HMPA –40°, 10 min 2. Aldehyde, –40° to rt, 24 h	 (91), $(E)/(Z)^*$ = 95:5	211
		1. LiHMDS, DMF/HMPA, –40° 2. Aldehyde	 (50), $(E)/(Z)^*$ >95:5	212

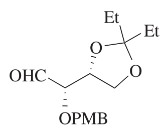
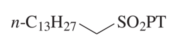
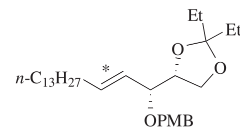
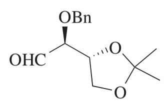
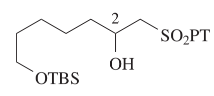
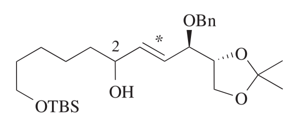
		KHMDS, THF, –78°, 4 h; then rt, 12 h	 (90), $(E)/(Z)^{*}$ = 75:25	213
		KHMDS, THF, –78°, 4 h; then rt, 12 h	 (72), $(E)/(Z)^{*}$ = 80:20	213
		KHMDS, THF, –78°, 1 h; then rt, 5 h	 (45), $(E)/(Z)^{*}$ = 77:23	214
		1. LiHMDS, THF, –78° 2. Aldehyde, –78°, 1 h; then rt	 (>92), $(E)/(Z)^{*}$ >95:5	215
		1. $MN(SiMe_3)_2$, solvent, –78° 2. Aldehyde, rt, time		216

M	Solvent	Time (h)		$(E)/(Z)^{*}$
Li	DMF/DMPU	2	(58)	91:9
Li	DMF/DMPU	6	(68)	91:9
K	DME	2	(38)	84:16
K	DME	6	(40)	84:16
K	DME/HMPA	6	(42)	84:16

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		1. KHMDS, –78° 2. Aldehyde, –78° to rt	 (79), $(E)^*$-isomer only	217
		1. NaHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 2 h	 (65), $(E)/(Z)^*$ = —	218
		1. Sulfone (1 eq), NaHMDS (1.03 eq), THF, –78°, 5 min 2. Aldehyde (1.2 eq), –78°, 0.5 h; then to rt, 1 h	 C-4,5 / / $(E)/(Z)^*$ (*R*,*S*) (68) — (*S*,*R*) (69) —	219
		1. Sulfone (1 eq), NaHMDS (1.03 eq), THF, –78°, 5 min 2. Aldehyde (1.2 eq), –78°, 0.5 h; then to rt, 1 h		219

Aldehyde	Sulfone	(67–69)	$(E)/(Z)^*$
(*R,S*)	(*R,S*)	(67–69)	—
(*R,S*)	(*S,R*)	(67–69)	—
(*R,S*)	(*R,R*)	(68–69)	—
(*S,R*)	(*R,S*)	(67–69)	—
(*S,R*)	(*S,R*)	(67–69)	—

		KHMDS, DME, –55°, 0.5 h; then rt		(52), $(E)/(Z)^*$ = 80:20	220
		1. KHMDS, THF, 0° to rt, 0.33 h 2. Aldehyde, –78°, 3 h; then rt, 12 h			221

C-2		$(E)/(Z)^*$
(*R*)	(66)	99:1
(*S*)	(60)	99:1

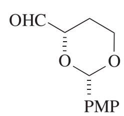
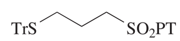
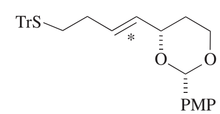
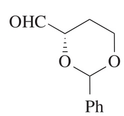
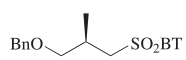
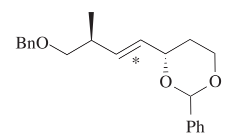
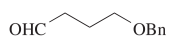
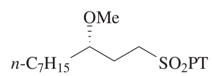
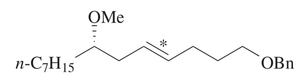
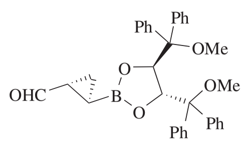
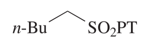
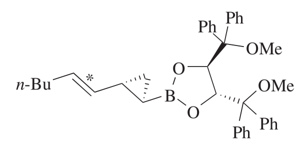
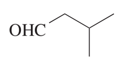
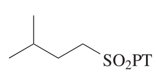
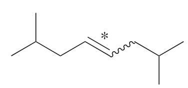
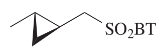
		LiHMDS, DMF, –60°, 2 h; then 0°, 2 h		(66), $(E)/(Z)^*$ = 83:17	222
		1. LiHMDS, THF, –78° 2. Aldehyde, –78 to 50°		(45), $(E)/(Z)^*$ = 72:28	223

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		KHMDS, THF, –78°, 16 h	 (83), $(E)^*$-isomer	224
		**A**: 1. $MN(SiMe_3)_2$ (x eq), DME, temp, 1 h 2. Aldehyde, DME, time *or* **B**: $MN(SiMe_3)_2$ (x eq), DME, temp, time		225, 163
C_5				
		1. Sulfone, MHMDS, solvent, –78°, 0.5 h 2. Aldehyde, –78° to rt, overnight		226

Conditions	M	x	Temp (°)	Time		$(E)/(Z)^*$
A	Na	1.2	–78	15 h	(43)	97:3
A	K	1.2	–60	15 h	(46)	99:1
A	K	1.2	–78	15 h	(20)	99:1
A	K	1.8	–60	10 min	(93)	99:1
A	K	3.0	–78	15 h	(36)	98:2
B	K	1.4	–60	15 h	(54)	99:1
B	K	1.8	–60	15 min	(73)	99:1
B	K	1.8	–78	1 min	(71)	99:1

M	Solvent		$(E)/(Z)$*	M	Solvent		$(E)/(Z)$*	M	Solvent		$(E)/(Z)$*
Li	toluene	(60)	60:40	Na	toluene	(63)	63:37	K	toluene	(88)	88:12
Li	Et_2O	(74)	74:26	Na	Et_2O	(68)	68:32	K	Et_2O	(86)	86:14
Li	THF	(86)	86:14	Na	THF	(87)	87:13	K	THF	(96)	96:4
Li	DME	(90)	89:11	Na	DME	(94)	94:6	K	DME	(99)	99:1

		Barbier conditions. See table.	 (>90)	24

Base	Solvent	Temp (°)	(*E*)/(*Z*)*
NaHMDS	toluene	–78	9:91
NaHMDS	CH_2Cl_2	–78	9:91
NaHMDS	Et_2O	–78	11:89
NaHMDS	THF	–78	52:48
NaHMDS	DME	–60	71:29
NaHMDS	DMF	–60	78:22
KHMDS	toluene	–78	21:79
KHMDS	THF	–78	55:45

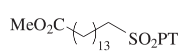
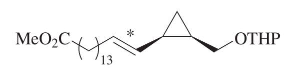
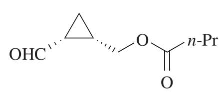
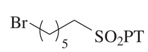
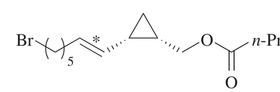
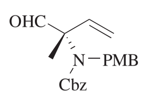
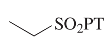
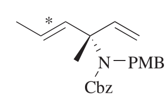
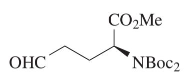
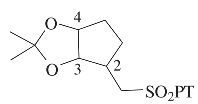
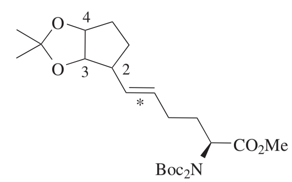
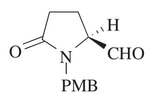
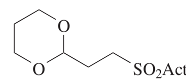
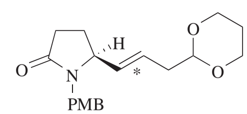
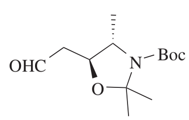
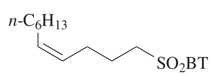
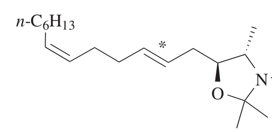
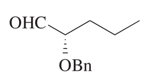
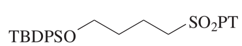
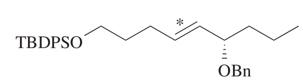
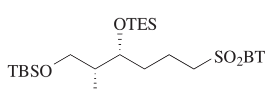
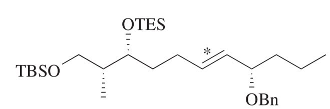
		Aldehyde (1 eq), sulfone (1.3 eq), LiHMDS (1.8 eq), THF, –10°; then to rt	 (89), (*E*)/(*Z*)* = —	227
		LiHMDS, THF, –20° to rt, 16 h	 (78), (*E*)/(*Z*)* = 79:21	228
		KHMDS, DME, –60°	 (75), (*E*)*-isomer only	229

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1–3 h; then rt, 20 h	 C-2 / C-3 / C-4 / (E)/(Z)* (S) (S) (R) (69) 90:10 (R) (R) (S) (71) 80:20	230
		KHMDS, DME	 Act / (E)/(Z)* PT (53) 100:0 BT (0) —	231
		KHMDS, THF	 (70), (E)/(Z)* = 79:21	232
		KHMDS, DME, –78° to rt	 (>82) (E)/(Z)* = 88:12	233
		1. LiHMDS, THF, –78° 2. Aldehyde, –78° to rt	 (80), (E)/(Z)* = 55:45	233

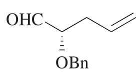
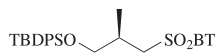
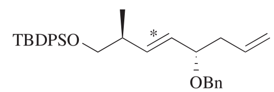
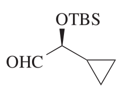
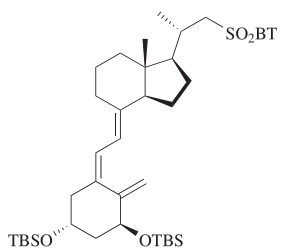
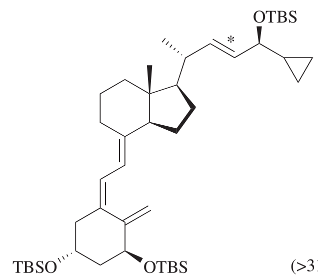
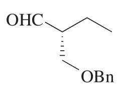
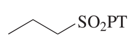
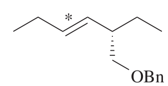
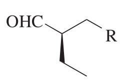
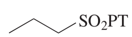
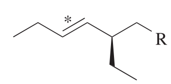
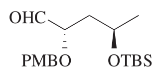
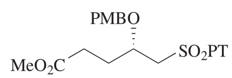
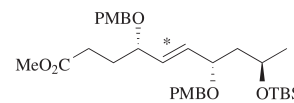
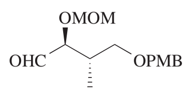
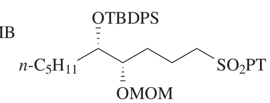
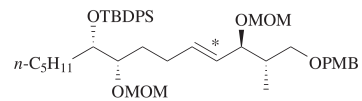
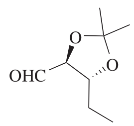
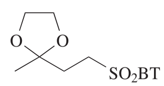
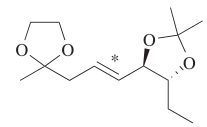
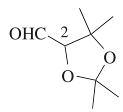
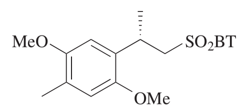
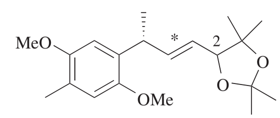
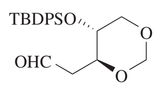
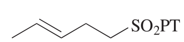
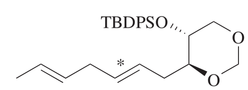
		1. LiHMDS, THF, –78° 0.5 h 2. Aldehyde, –78 to –20°, 2.5 h	 (87), (*E*)/(*Z*)* = 60:40	234
		LiHMDS, DME, –70°, 0.5 h; then rt, 3 h	 (>31), (*E*)/(*Z*)* = —	235
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78° to rt, 18 h	 (64), (*E*)/(*Z*)* >95:5	236
C_{5-6}				
		1. KHMDS, DME, –78°, 3 h 2. Aldehyde, –78° to rt	 R / (*E*)/(*Z*)* TBSO (80) 82:8 $BnOCH_2$ (68) 95:5	237

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		NaHMDS, THF/HMPA, –78°	 (60), (*E*)*-isomer	238
		1. Sulfone (1.0 eq), KHMDS (1.1 eq), THF, –78°, 0.25 h 2. Aldehyde (1.1 eq), –78°; then to rt	 (72), (*E*)/(*Z*)* = 90:10	239
		LiHMDS, THF, –78° to rt, 3 h	 (68), (*E*)*-isomer only	240
		1. NaHMDS, THF, –78°, 0.25 h 2. Aldehyde, –78°, 1 h	 C-2 — (*E*)/(*Z*)* (*S*) (60) 75:25 (*R*) (61) 86:14	241
		1. Sulfone (1.0 eq), KHMDS (1.15 eq), THF, –78°, 65 min 2. Aldehyde (1.15 eq), –78°, 5 min; then to rt, 16 h	 (61), (*E*)*-isomer	242

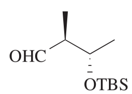
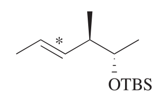
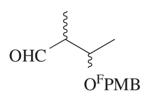
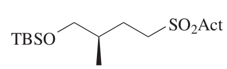
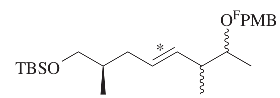
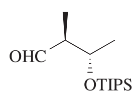
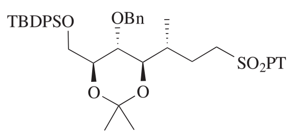
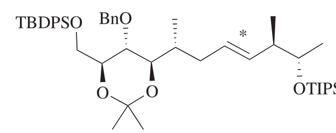
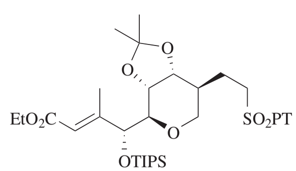
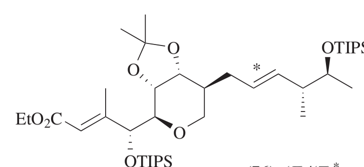
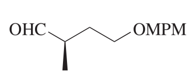
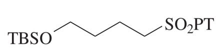
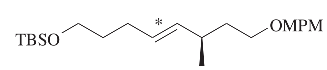
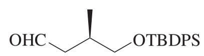
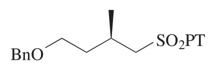
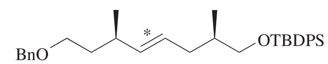
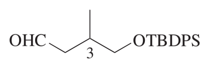
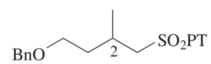
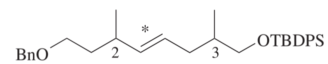
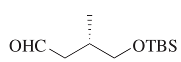
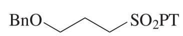
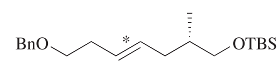
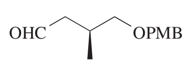
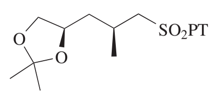
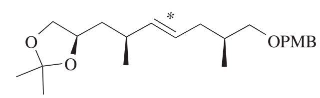
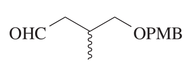
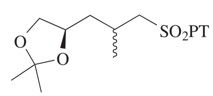
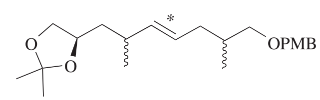
		1. KHMDS, THF, –78°, 25 min 2. Aldehyde, rt	 (65), $(E)^*$-isomer	210
		1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h	 Act — $(E)/(Z)^*$ BT (81) — PT (93) —	119, 243
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°; then rt, 12 h	 (76), $(E)^*$-isomer predominantly	244
		1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 1.5 h; then rt	 (76), $(E)/(Z)^*$ = —	245
		1. Sulfone (1.5 eq), KHMDS (1.5 eq), DME, –55°, 2 h 2. Aldehyde (1.0 eq), –55°, 3 h	 (64), two steps, $(E)/(Z)^*$ >20:1	246

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

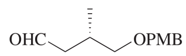
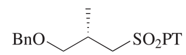
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		LiHMDS, THF, –78°, 3 h; then rt	 (78), (*E*)/(*Z*)* = 75:25	168
		LiHMDS, THF, –78°; then rt	 (see table below)	247
		KHMDS, THF, –78°; then rt	 (55), (*E*)/(*Z*)* = 95:5	248
		1. LiHMDS, THF/DMPU, –78°, 0.75 h 2. Aldehyde, –78°; then rt, 3 h	 (79), (*E*)/(*Z*)* = 83:17	249
		1. Sulfone (1 eq), LiHMDS (1.2 eq), THF/DMPU (7:1), –78°, time 1 2. Aldehyde (*x* eq), –78°, 0.33 h; then to rt, time 2		250

Ref. 247:

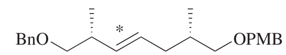
C-2	C-3		(*E*)/(*Z*)*
(*R*)	(*R*)	(78)	—
(*R*)	(*S*)	(86)	—
(*S*)	(*R*)	(69)	—
(*S*)	(*S*)	(74)	—

Ref. 250:

Aldehyde	Sulfone	*x*	Time 1 (min)	Time 2 (min)		(*E*)/(*Z*)*
(*R*)	(*R*)	1.5	40	50	(88)	67:33
(*S*)	(*S*)	1.4	45	180	(79)	83:17

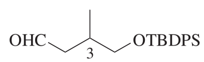
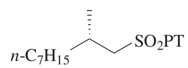
 

1. KHMDS, THF/DMPU, –78°, 0.67 h
2. Aldehyde, rt, 11.5 h

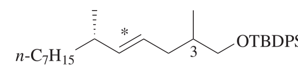


(82) $(E)/(Z)^*$ = 86:14

251

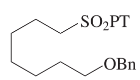
 

LiHMDS, THF, –78°; then rt

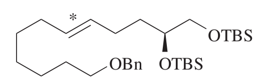


C-3		$(E)/(Z)^*$
(*S*)	(61)	70:30
(*R*)	(65)	—

247

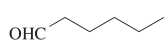
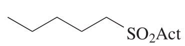
 

1. NaHMDS, DME, –78°, 5 min
2. Aldehyde, to –50°, 1 h



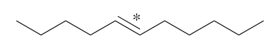
(86), $(E)/(Z)^*$ = 97:3

252

Act = BT or PT

1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h
2. Aldehyde, temp, 3 h; then to rt

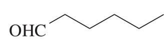
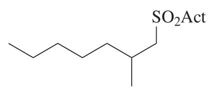
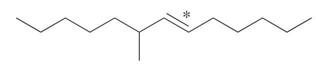


4

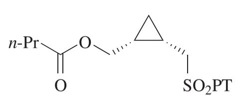
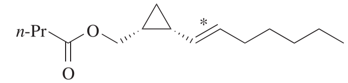
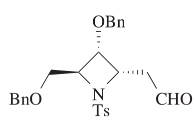
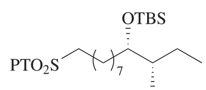
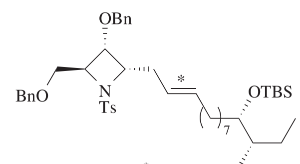
M	Solvent	Temp (°)	Act = BT	$(E)/(Z)^*$	Act = PT	$(E)/(Z)^*$
Li	toluene	–78	(5)	40:60	(55)	57:43
Li	Et_2O	–78	(7)	43:57	(76)	73:27
Li	THF	–78	(42)	60:40	(97)	75:25
Li	DME	–60	(3)	55:45	(95)	77:23
Na	toluene	–78	(29)	51:49	(80)	59:41
Na	Et_2O	–78	(17)	53:47	(90)	57:42

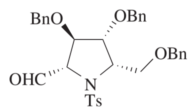
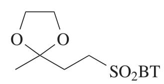
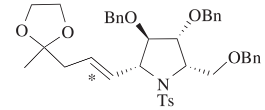
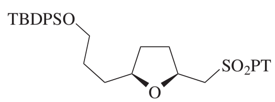
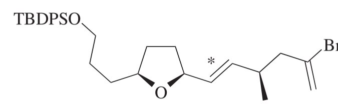
M	Solvent	Temp (°)	Act = BT	$(E)/(Z)^*$	Act = PT	$(E)/(Z)^*$
Na	THF	–78	(0)	—	(89)	76:24
Na	DME	–60	(27)	77:23	(89)	86:14
K	toluene	–78	(15)	47:53	(13)	64:36
K	Et_2O	–78	(68)	51:49	(30)	72:26
K	THF	–78	(24)	55:45	(71)	86:14
K	DME	–60	(6)	75:25	(71)	94:6

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

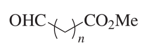
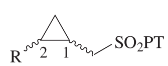
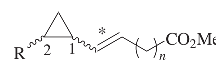
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
  Act = BT or PT	1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h 2. Aldehyde, temp, 3 h; then rt		4

M	Solvent	Temp (°)	Act = BT	(E)/(Z)*	Act = PT	(E)/(Z)*
Li	toluene	–78	(86)	54:46	(96)	43:57
Li	Et_2O	–78	(74)	60:40	(61)	48:52
Li	THF	–78	(98)	57:43	(100)	67:33
Li	DME	–60	(100)	44:56	(100)	60:40
Na	toluene	–78	(78)	57:43	(65)	38:62
Na	Et_2O	–78	(84)	58:42	(98)	32:68
Na	THF	–78	(89)	39:61	(88)	32:68
Na	DME	–60	(87)	64:36	(100)	78:22
K	toluene	–78	(31)	26:74	(25)	62:38
K	Et_2O	–78	(56)	36:64	(20)	37:63
K	THF	–78	(68)	25:75	(23)	76:24
K	DME	–60	(63)	46:54	(22)	96:4

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
	LiHMDS, THF, –20° to rt, 16 h	 (74), (E)/(Z)* = 67:33	228
 	KHMDS, THF, –78°	 (70), (E)/(Z)* = —	253

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Sulfone (1.1 eq), LiHMDS (3.2 eq), THF, –78°, 1 h 2. Aldehyde (1 eq), –78°, 1 h; then to rt; then 50°, 4 h	 (51), $(E)/(Z)^*$ = —	254
		1. KHMDS, DMF/HMPA (4:1), –78°, 10 min 2. Aldehyde, –78°, 1 h; then rt, 15 h	 (78), $(E)/(Z)^*$ >95:5	121

C_{6-9}

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Sulfone (1 eq), LiHMDS (1.2 eq), –78°, 10 min 2. Aldehyde (1.2 eq), –78°; then to rt; then rt, overnight	 $(E)/(Z)^*$ = —	255

n	C-1,C-2	R		*n*	C-1,C-2	R	
4	(*S*,*R*)	*n*-C_8H_{17}	(80)	5	(*S*,*R*)	*n*-C_8H_{17}	(78)
4	(*R*,*S*)	*n*-C_8H_{17}	(87)	5	(*R*,*S*)	*n*-C_8H_{17}	(85)
5	(*S*,*R*)	*n*-C_6H_{13}	(79)	7	(*S*,*R*)	*n*-C_6H_{13}	(82)
5	(*R*,*S*)	*n*-C_6H_{13}	(83)	7	(*R*,*S*)	*n*-C_6H_{13}	(76)

C_6

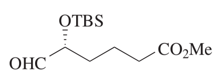
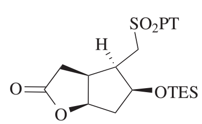
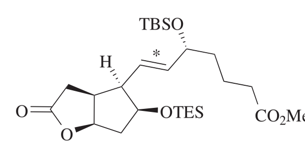
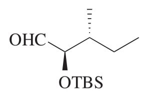
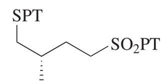
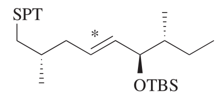
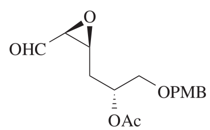
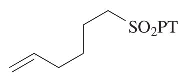
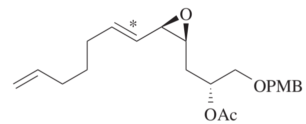
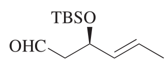
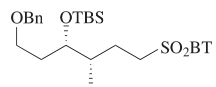
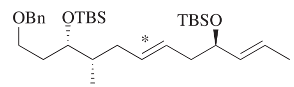
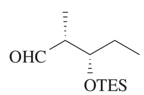
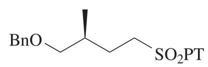
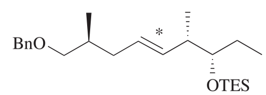
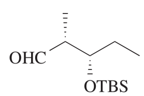
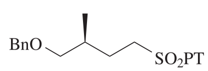
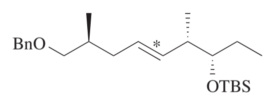
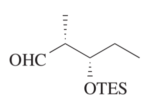
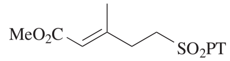
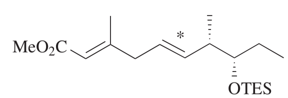
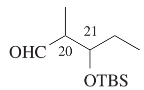
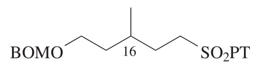
Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		KHMDS, DME, –60°; then rt, 8 h	 (52), $(E)/(Z)^*$ = 63:37	256, 257

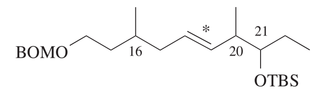
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		NaHMDS, THF, –78°; then rt, 8 h	 (96), (*E*)/(*Z*)* = 95:5	114
		NaHMDS, –78° to rt	 (74), (*E*)/(*Z*)* = 57:43	107
		LiHMDS, THF, –72 to –10°, 2 h	 (81), (*E*)/(*Z*)* = 50:50	258
		KHMDS, THF, –78°	 (68), (*E*)*-isomer only	259
		1. Sulfone (1 eq), KHMDS (1.75 eq), THF, –78°, 1 h 2. Aldehyde (2 eq), –78°, 1 h; then to rt	 (67), (*E*)*-isomer only	260
		1. KHMDS, THF/DME, –60° 2. Aldehyde	 (97), (*E*)/(*Z*)* = 94:6	259



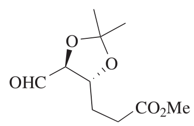


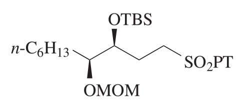
1. KHMDS, DME, –78°
2. Aldehyde, –78° to rt



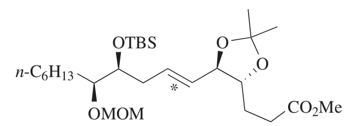
$(E)/(Z)^{*}$ = — 261

C-16	C-20	C-21	
(*R*)	(*S*)	(*S*)	(68)
(*R*)	(*R*)	(*R*)	(62)
(*S*)	(*S*)	(*S*)	(66)
(*S*)	(*R*)	(*R*)	(37)

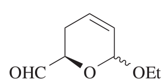


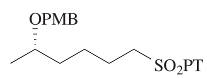


1. KHMDS, 18-crown-6, THF, –100°, 0.5 h
2. Aldehyde, –100° to rt, 2 h

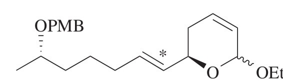


(72), $(E)/(Z)^{*}$ = 91:9 262, 263

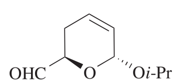


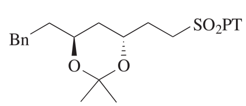


1. KHMDS, –78°, 0.33 h
2. Aldehyde, –78°, 1 h; then –10°, 12 h

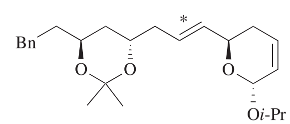


(69), $(E)/(Z)^{*}$ = 91:9 264





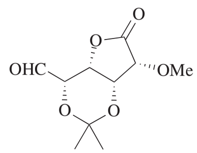
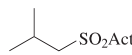
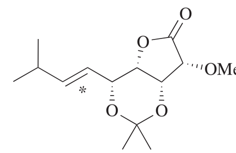
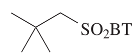
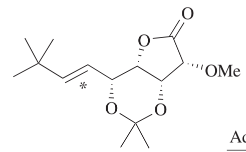
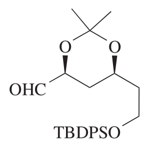
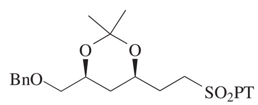
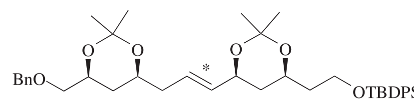
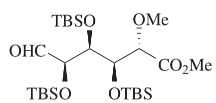
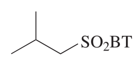
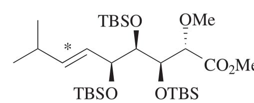
$MN(SiMe_3)_2$, DME, –55° to rt, 12 h

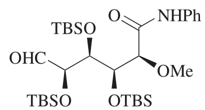
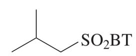
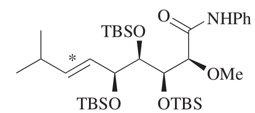
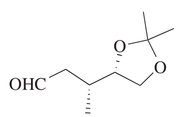
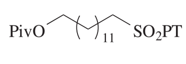
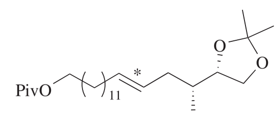
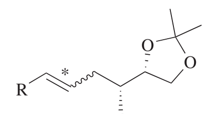


M		$(E)/(Z)^{*}$
Na	(77)	77:23
K	(61)	89:11

265

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		LiHMDS, DMF/HMPA, –35° to 35°, 12 h	 Act / / (*E*)/(*Z*)* BT (20–30) — PT (22) 95:5	169
		1. LiHMDS, THF, –55 to –75°, 1.5 h 2. Additive, –75° 3. Aldehyde, MeCN, –15 to 50°	 Additive / / (*E*)/(*Z*)* TMSCl (50) 75:25 BF_3•OEt_2 (41) 91:9	19
		LiHMDS, 18-crown-6, DME, –78°, 24 h	 (35), (*E*)/(*Z*)* = 57:43	266
		LiHMDS, DME, –78° to rt, 1.5 h	 (62), (*E*)/(*Z*)* >97:3	267

		LiHMDS, DME, –78° to rt	 (>41), $(E)/(Z)^*$ = 95:5	268
		LiHMDS, THF	 (86), $(E)/(Z)^*$ = —	269
		Aldehyde (1 eq), sulfone (1.3 eq), LiHMDS (1.7 eq), THF, temp; then to rt, 1 h		

R	Temp (°)		$(E)/(Z)^*$	Refs.
n-$C_{13}H_{27}$	–2	(67)	67:33	227
$MeO_2C(CH_2)_{13}$	–10	(61)	67:33	227, 270

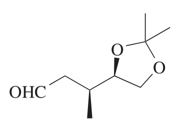
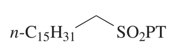
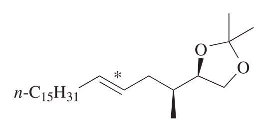
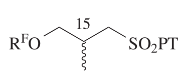
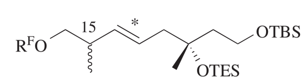
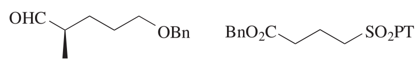
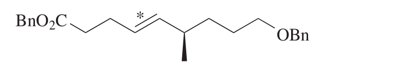
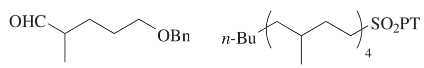
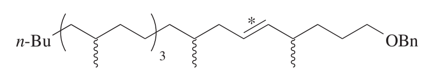
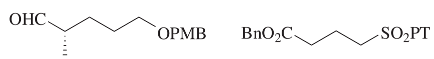
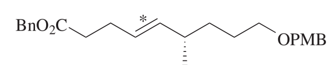
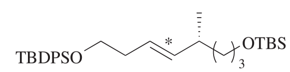
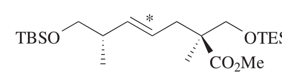
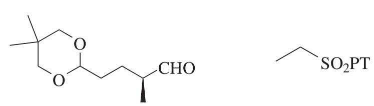
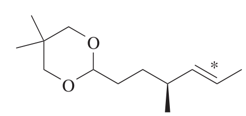
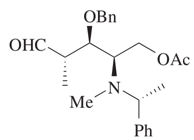
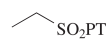
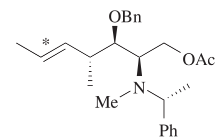
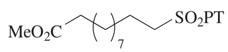
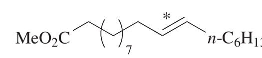
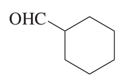
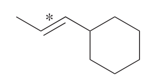
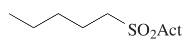
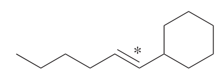
		LiHMDS, THF, –20°; then rt, 16 h	 (93), $(E)/(Z)^*$ = 71:29	228
	 (15*R*), R^F = 4-$[C_4F_9(CH_2)_3O]C_6H_4CH_2$ + (15*S*), R^F = 4-$[C_6F_{13}(CH_2)_3O]C_6H_4CH_2$	1. LDA, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h	 (83), $(E)/(Z)^*$ = 80:20	271

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

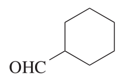
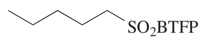
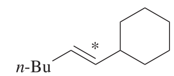
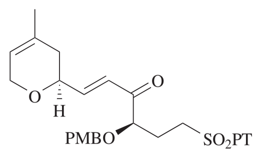
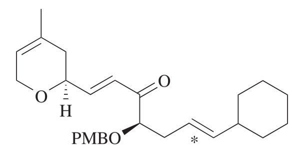
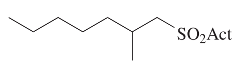
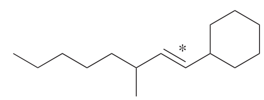
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°; then rt, 21 h	 (66), (*E*)/(*Z*)* = 77:23	272
	1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt	 (90), (*E*)/(*Z*)* —	273
	1. Sulfone (3.0 eq), NaHMDS (3.0 eq), THF, –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°, 3 h; then to 0°	 (80), (*E*)*-isomer	274
	1. Sulfone (2.8 eq), KHMDS (2.2 eq), THF, –78°, 1 h 2. Aldehyde (1.0 eq), –78°, 1 h	 (78), (*E*)*-isomer only	275
	1. LiHMDS, THF, –78, 1 h 2. Aldehyde, –78°, 1 h; then –30°, 4 h	 (96), (*E*)/(*Z*)* = 50:50	276, 277
	KHMDS, DME, –60°, 0.75 h	 (93), (*E*)/(*Z*)* = 93:7	60

		KHMDS, THF, –78°, 0.67 h		(89), $(E)^*$-isomer only	278
C_7					
n-$C_6H_{13}CHO$		1. KHMDS, THF, –55°, 0.67 h 2. Aldehyde, –55°, 1 h		(50), $(E)/(Z)^*$ = 85:15	279
		KHMDS, THF, –78°, 2 h		(54), $(E)/(Z)^*$ = 92:8	280
	 Act = BT or PT	1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h 2. Aldehyde, temp, 3 h; then rt			4

			Act = BT		Act = PT	
M	Solvent	Temp (°)		$(E)/(Z)^*$		$(E)/(Z)^*$
Li	toluene	–78	(1)	50:50	(90)	51:49
Li	Et_2O	–78	(2)	49:51	(66)	61:39
Li	THF	–78	(6)	66:34	(90)	69:31
Li	DME	–60	(2)	70:30	(94)	72:28
Na	toluene	–78	(20)	54:46	(51)	65:35
Na	Et_2O	–78	(17)	50:50	(83)	65:35

			Act = BT		Act = PT	
M	Solvent	Temp (°)		$(E)/(Z)^*$		$(E)/(Z)^*$
Na	THF	–78	(19)	62:38	(92)	73:27
Na	DME	–60	(32)	75:25	(95)	89:11
K	toluene	–78	(13)	54:46	(22)	77:23
K	Et_2O	–78	(57)	51:49	(46)	89:11
K	THF	–78	(27)	54:46	(71)	97:3
K	DME	–60	(4)	76:24	(81)	99:1

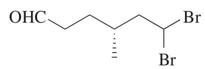
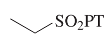
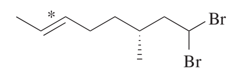
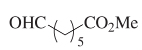
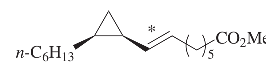
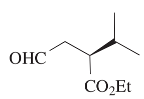
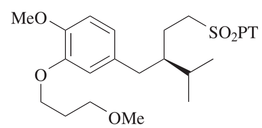
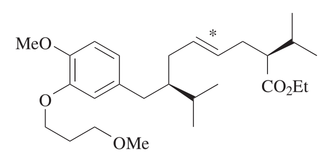
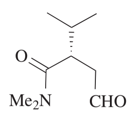
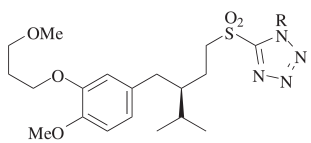
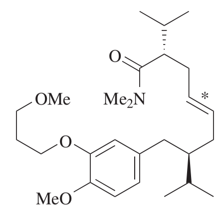
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
 	1. Base, THF, rt 2. Aldehyde, 16 h		58
	1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1.5 h	 (70), (*E*)*-isomer only	281
 Act = BT or PT	1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h 2. Aldehyde, temp, 3 h; then rt		4

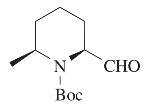
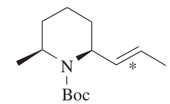
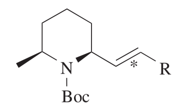
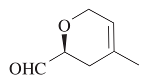
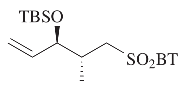
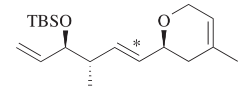
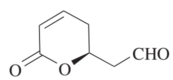
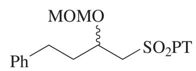
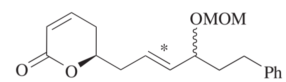
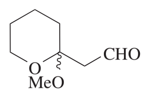
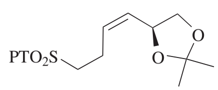
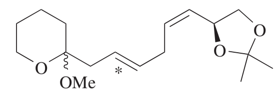
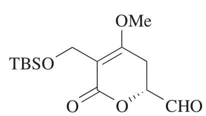
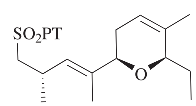
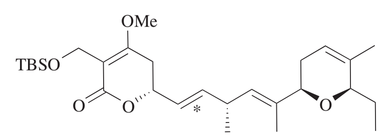
Base		(*E*)/(*Z*)*
KOH, *n*-Bu_4NBr	(50)	75:25
P4-*t*-Bu	(60)	85:15
P2-Et	(70)	90:10

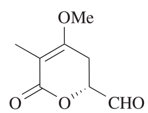
			Act = BT		Act = PT	
M	Solvent	Temp (°)		(*E*)/(*Z*)*		(*E*)/(*Z*)*
Li	toluene	–78	(88)	70:30	(85)	39:61
Li	Et_2O	–78	(70)	67:33	(74)	41:59
Li	THF	–78	(87)	72:28	(90)	53:47
Li	DME	–60	(83)	58:42	(100)	40:60
Na	toluene	–78	(66)	86:14	(83)	67:33
Na	Et_2O	–78	(75)	87:13	(98)	53:47

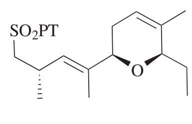
			Act = BT		Act = PT	
M	Solvent	Temp (°)		(*E*)/(*Z*)*		(*E*)/(*Z*)*
Na	THF	–78	(84)	67:33	(71)	48:52
Na	DME	–60	(96)	55:45	(100)	84:16
K	toluene	–78	(48)	76:24	(68)	98;2
K	Et_2O	–78	(68)	78:22	(28)	92:8
K	THF	–78	(85)	40:60	(58)	97:3
K	DME	–60	(100)	36:64	(59)	99:1

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		KHMDS, THF, –78°, 2 h; then rt	 (80), $(E)/(Z)^*$ = 85:15	282
		1. LiHMDS, THF, –78° 2. Aldehyde, –78°; then rt	 (73), $(E)/(Z)^*$ = 70:30	283
		1. Sulfone (1.0 eq), KHMDS (1.1 eq), DME, –78°, 0.5 h 2. Aldehyde (1.5 eq), –78 to –60°, 3 h; then to rt, overnight	 (63), $(E)/(Z)^*$ >95:5	226
		1. Sulfone (1.0 eq), base (2 eq), additive, solvent, –70°, 1 h 2. Aldehyde (4 eq), –70°, 1 h; then to rt; then rt, a few h		284

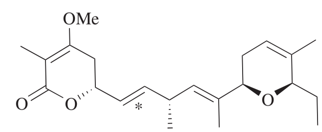
R	Base	Additive	Solvent		$(E)/(Z)^*$
Me	NaHMDS	none	DME	(92)	88:12
t-Bu	NaHMDS	none	DME	(88)	90:10
Ph	LiHMDS	none	toluene	(86)	68:32
Ph	NaHMDS	18-c-6 (2 eq)	DME	(58)	94:6
Ph	NaHMDS	18-c-6 (0.25 eq)	DME	(80)	93:7
Ph	KHMDS	none	THF	(73)	77:23

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		KHMDS, THF, –78°	 (34), (*E*)/(*Z*)* = 86:14	285
		1. KHMDS, DME, –78°, 0.33 h 2. Aldehyde, rt	 R: Me, (*E*)*-isomer (72); R: n-C_7H_{15}, (*E*)*-isomer (78)	286
		1. KHMDS, THF, –78° 2. Aldehyde, –78°; then rt	 (67), (*E*)/(*Z*)* = 88:12	156
		1. KHMDS, THF, –78° 2. Aldehyde	 (65), (*E*)*-isomer	287
		1. KHMDS, THF, –78°; then rt, 1 h 2. Aldehyde, –78°, 2 h; then rt, 1 h	 (90), (*E*)/(*Z*)* = 88:12	288
		1. LiHMDS, DMF/HMPA –60°, 0.33 h 2. Aldehyde, –60 to 0°, 2 h	 (46), (*E*)/(*Z*)* >96:4	289





1. KHMDS, THF, –78°, 10 min
2. Aldehyde, –78° to rt



(52), $(E)/(Z)^*$ >99:1

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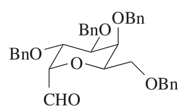
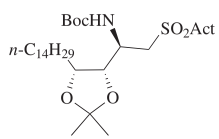
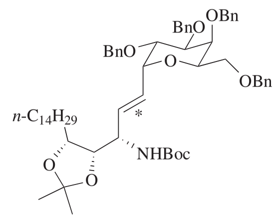




LiHMDS, solvent



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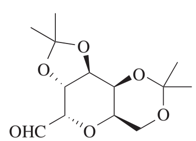
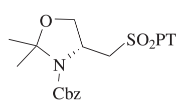
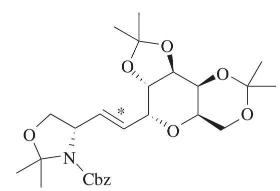
Act	Solvent	Temp (°)		$(E)/(Z)^*$
BT	THF	–78 to –10	(71)	>98:2
PYR	DME	–20 to rt	(40)	39:61





1. NaHMDS, THF, –78°, 5 min
2. Aldehyde, –78°, 1 h;
then rt, 2 h



(65), $(E)^*$-isomer

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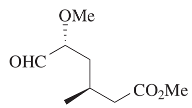
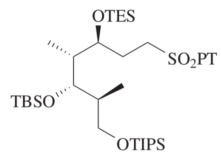
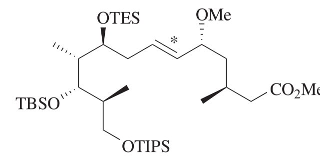
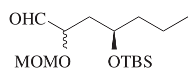
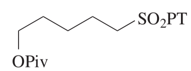
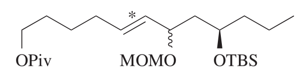
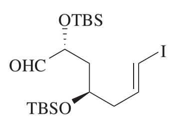
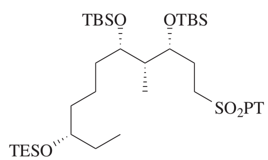
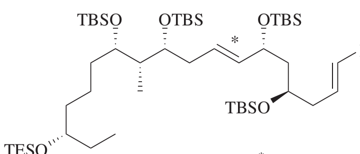
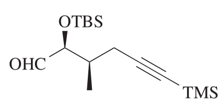
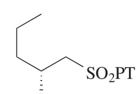
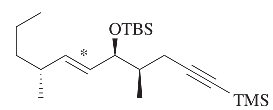
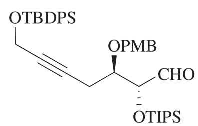
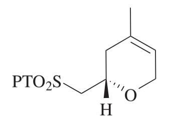
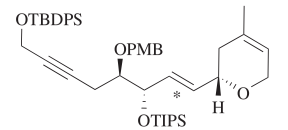
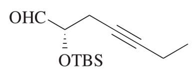
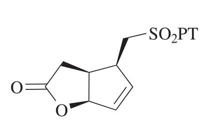
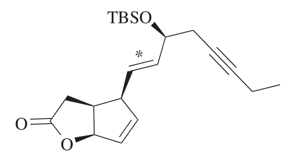
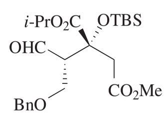
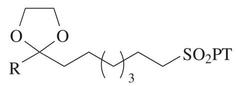
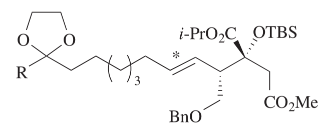
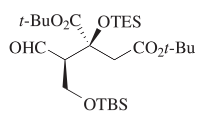
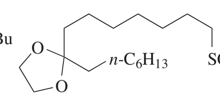
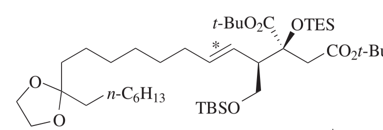
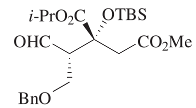
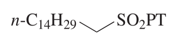
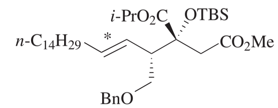
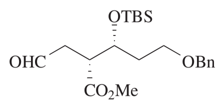
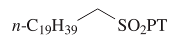
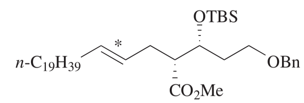
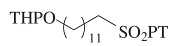
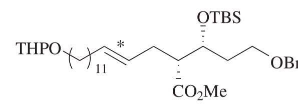
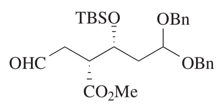
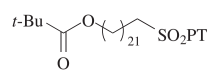
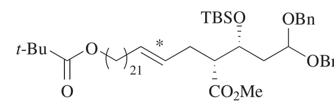
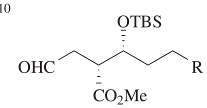
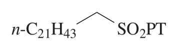
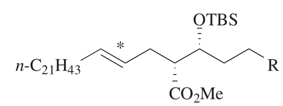
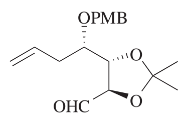
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

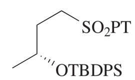
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. $MN(SiMe_3)_2$, solvent, –60°, 0.67 h 2. Aldehyde, –78°, 1 h; then to rt	 M / Solvent / / $(E)/(Z)^*$ Li / THF / (—) / 67:33 Li / DMF/HMPA / (60) / 92:8 K / THF / (—) / 50:50 K / DME / (56) / 85:15	293
		1. KHMDS, DME, –60° 2. Aldehyde, –60° to rt	 (62), $(E)^*$-isomer	294
		1. Sulfone (1 eq), KHMDS (1.2 eq), THF, –78°, 70 min 2. Aldehyde (1.1 eq), –78°, 4 h; then to rt, 1 h	 (82), $(E)/(Z)^*$ = 86:14	295, 296
		1. KHMDS, DME, –78°, 1.5 h 2. Aldehyde, to rt, 16 h	 (72), $(E)/(Z)^*$ >95:5	297, 48

		KHMDS, solvent	 Solvent / (E)/(Z)* DME (80) 57:43 DMF (81) 83:17	298
		1. Sulfone (1 eq), KHMDS (1.14 eq), DME, –78°, 50 min 2. Aldehyde (1.2 eq), –78°; then to rt, 2 h	 (52), (E)* isomer	299
		1. KHMDS, –78°, 0.5 h 2. Aldehyde, –78° to rt, 12 h	 R / (E)/(Z)* n-C_7H_{15} (84) >98:2 n-C_9H_{19} (71) >98:2	300, 301
		1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 3 h	 (>49), (E)*-isomer only	302

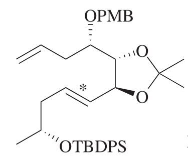
	Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			1. KHMDS, –78°, 0.5 h 2. Aldehyde, –78° to rt, 12 h	 (70), (*E*)*-isomer only	301
			LiHMDS, THF, –10° to rt	 (79), (*E*)/(*Z*)* = 67:33	303
			LiHMDS, THF, –10° to rt	 (75), (*E*)/(*Z*)* = —	304
			LiHMDS, THF, –10°; then rt	 (67), (*E*)/(*Z*)* = 67:33	304
C_{7-10}			LiHMDS, THF	 R — (*E*)/(*Z*)* BnO (83) — PivO(CH_2)$_3$ (83) —	305

C_7



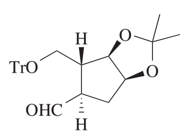


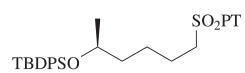
1. $MN(SiMe_3)_2$, additive THF, –98°, 0.5 h
2. Aldehyde; then rt, 2 h



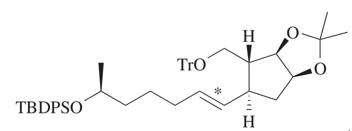
M	Additive		(*E*)/(*Z*)*
Li	—	(<5)	—
K	—	(—)	66:33
K	HMPA	(—)	80:20
K	18-c-6	(75)	95:5

306



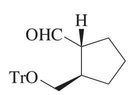


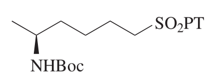
1. KHMDS, DME, –78°, 0.5 h
2. Aldehyde, –78°, 2 h; then rt, 1 h



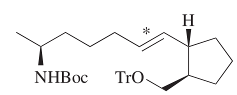
(81), (*E*)*-isomer

307



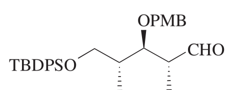


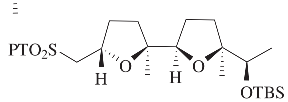
1. KHMDS, DME, –78°, 35 min
2. Aldehyde, –78°, 3 h; then rt, 1 h



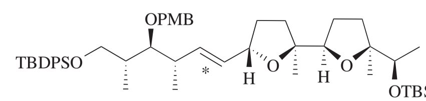
(83), (*E*)/(*Z*)* = 91:9

308



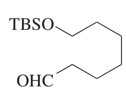


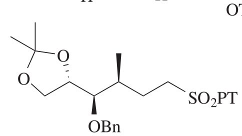
LiHMDS, THF, –78°, 1 h; then 0°



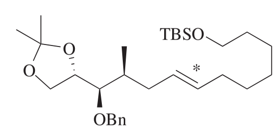
(80), (*E*)/(*Z*)* = 70:30

309





KHMDS, DME, –56°, 3 h; then rt, 2 h



(76), (*E*)*-isomer only

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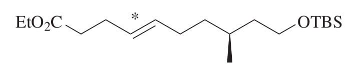
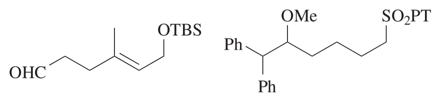
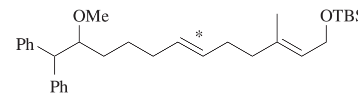
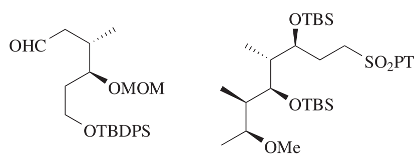
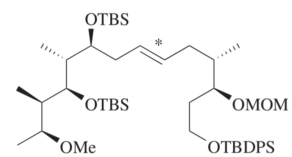
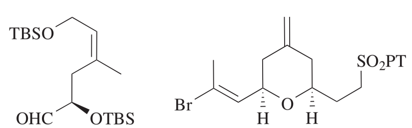
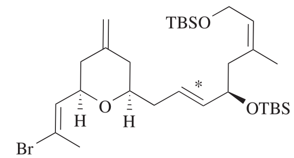
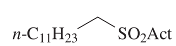
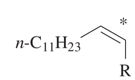
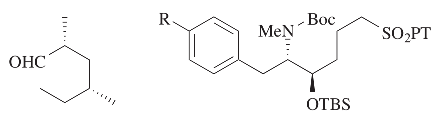
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. KHMDS, THF, –78°, 0.33 h 2. Aldehyde, –78°, 0.25 h; then –50°, 1 h	 (69), (*E*)/(*Z*)* = 96:4	311
	1. KHMDS, DME, –78° 2. Aldehyde, –78°	 (63), (*E*)/(*Z*)* = —	312
	1. NaHMDS, DME/HMPA, –78° 2. Aldehyde, –78°, 2 h	 (75), (*E*)/(*Z*)* >95:5	313
	1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt	 (88), (*E*)*-isomer only	314, 315
C_{8-12}			
RCHO 	LDA, THF, –78°, 1 h; then rt, 3 h		21

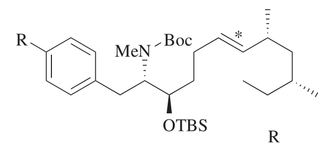
R	Act		(E)/(Z)*
n-C_5H_{11}(Me)CH	BT	(58)	43:57
n-C_5H_{11}(Me)CH	IM	(17)	2:98
n-C_5H_{11}(Me)CH	TZ	(36)	28:72
n-C_5H_{11}(Me)CH	IQ	(44)	55:45
n-$C_{11}H_{23}$	BT	(47)	46:54

R	Act		(E)/(Z)*
n-$C_{11}H_{23}$	PYR	(46)	35:65
n-$C_{11}H_{23}$	PYM	(5)	55:45
n-$C_{11}H_{23}$	IM	(12)	3:97
n-$C_{11}H_{23}$	TZ	(34)	43:57
n-$C_{11}H_{23}$	IQ	(54)	44:56

C_8

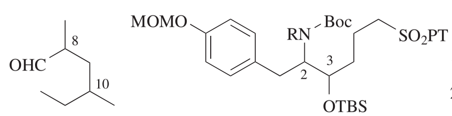


1. KHMDS, THF, –78°, 2 min
2. Aldehyde, EtOH, –78°; then rt

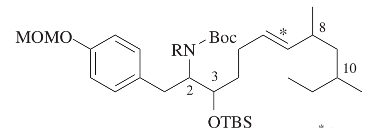


R	(E)*-isomer
H	(82)
F	(80)
MeO	(75)
Me	(83)

316



1. KHMDS, THF, –78°, 2 min
2. Aldehyde, –78°; then rt

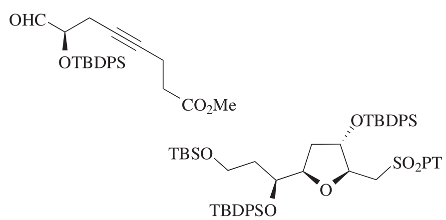
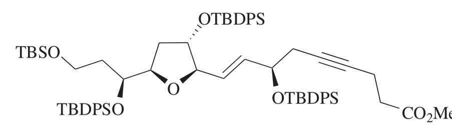
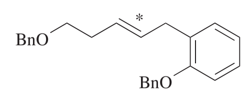
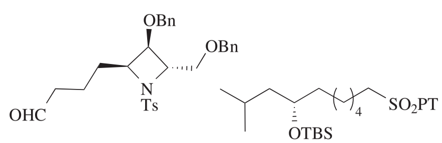
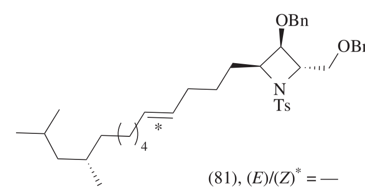
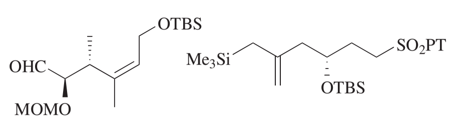
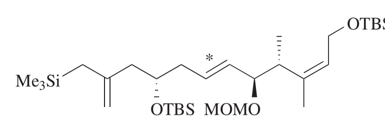


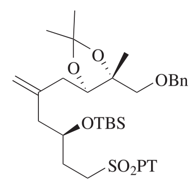
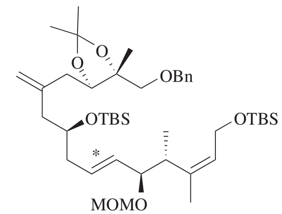
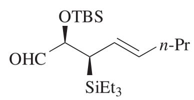
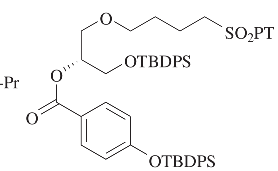
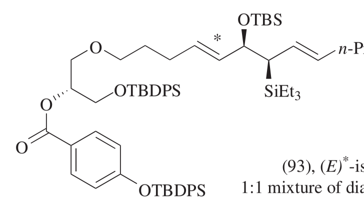
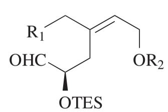
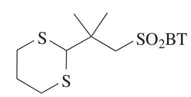
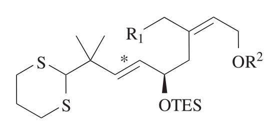
(E)*-isomer only

R	C-2	C-3	C-8	C-10	
H	(*R*)	(*R*)	(*S*)	(*S*)	(70)
Me	(*R*)	(*R*)	(*S*)	(*S*)	(67)
Me	(*S*)	(*R*)	(*S*)	(*S*)	(58)
Me	(*S*)	(*R*)	(*R*)	(*R*)	(70)
Me	(*R*)	(*S*)	(*S*)	(*S*)	(73)
Me	(*R*)	(*S*)	(*R*)	(*R*)	(56)

317, 318

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. KHMDS, DME, –65°, 0.75 h 2. Aldehyde, –65°; then rt, 1 h	 (60), (*E*)[*]-isomer only	319
	1. LiHMDS, THF, –78°; then –65°, 1 h 2. Aldehyde, –65°, 1 h; then rt, 15 h	 (77), (*E*)/(*Z*)[*] = 85:15	320
	1. Sulfone (1.5 eq), KHMDS (2.4 eq), THF, –78°, 1 h 2. Aldehyde (1 eq), –78°, 2 h	 (81), (*E*)/(*Z*)[*] = —	321
	1. KHMDS, THF 2. Aldehyde	 (71), (*E*)[*]-isomer	322

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. KHMDS, DME, –78°, 0.5 h 2. Aldehyde, –78°, 0.5 h; then rt	 (83), $(E)^*$-isomer	323
 racemic	 scalemic	1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1 h	 (93), $(E)^*$-isomer 1:1 mixture of diastereomers	116
C_{8-9}				
		1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 1–1.5 h		324

R_1	R_2		$(E)/(Z)^*$
$BOMOCH_2$	$i\text{-}Pr_3Si$	(95)	100:0
$CH{=}CH_2$	$t\text{-}BuPh_2Si$	(60)	—

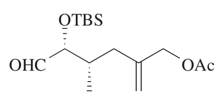
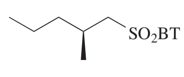
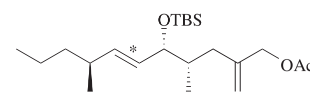
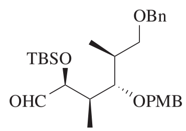
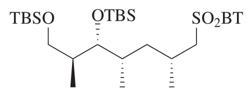
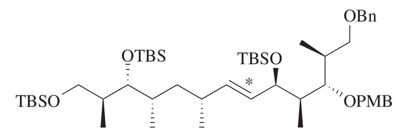
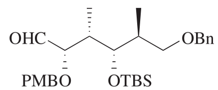
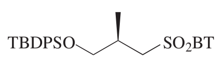
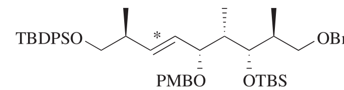
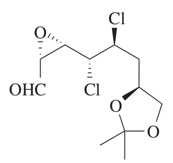
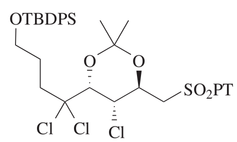
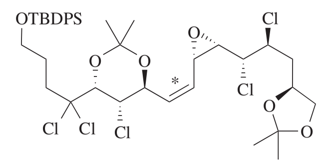
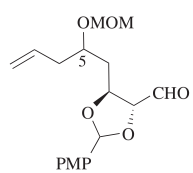
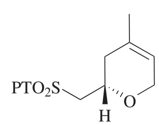
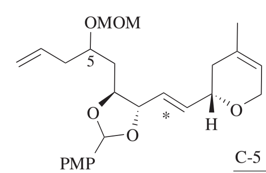
Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 4 h	 (78), $(E)/(Z)^*$ = 80:20	325

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		1. NaHMDS, DMF, –60°, 1.5 h 2. Aldehyde, –60°, 1 h; then rt, 12 h	 (80), $(E)/(Z)^*$ = —	326
		1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, THF, –78°, 12 h; then rt, 10 h	 (90), $(E)/(Z)^*$ —	327
		NaHMDS, toluene, –78° to rt, 17 h	 (47), $(E)/(Z)^*$ = 17:83	328
		LiHMDS, DMF/HMPA, –35° to rt	 C-5 — $(E)^*$-isomer (R) — (>64) (S) — (>61)	329, 330, 331

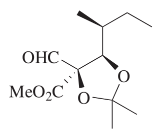
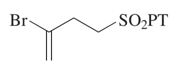
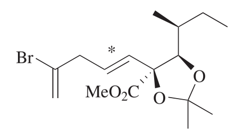
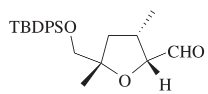
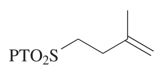
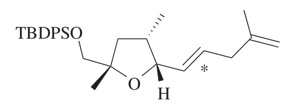
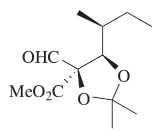
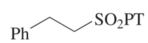
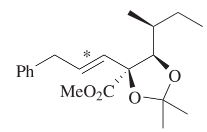
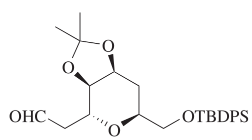
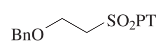
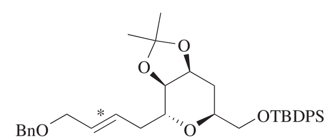
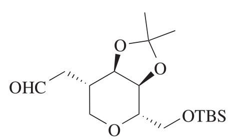
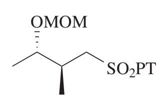
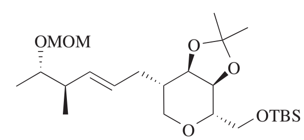
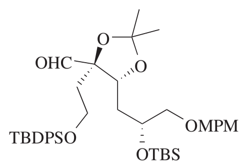
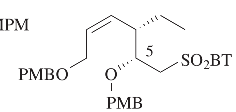
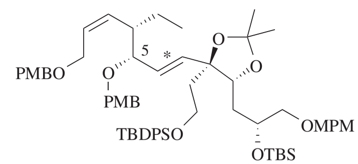
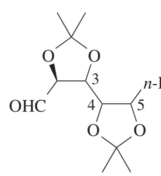
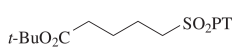
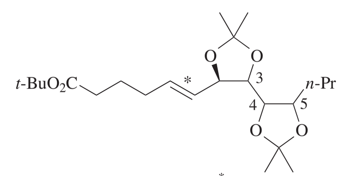
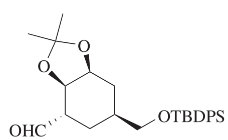
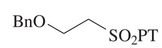
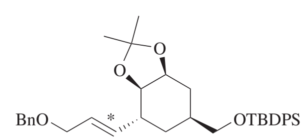
		1. KHMDS, THF, –78°, 0.25 h 2. Aldehyde, –78°; then rt, 12 h		(79), $(E)/(Z)^{*}$ = 96:4	332
		1. Sulfone (1.5 eq), KHMDS (1.46 eq), DME, –78°, 0.25 h 2. Aldehyde (1.0 eq), –78°, 0.5 h	 (59), two steps, $(E)/(Z)^{*}$ = 90:10		333
		1. KHMDS, THF, –78°, 0.25 h 2. Aldehyde, –78° to rt, 12 h		(93), $(E)/(Z)^{*}$ >96:4	332
		KHMDS	 (>63), $(E)/(Z)^{*}$ = 67:33		334
		1. Sulfone (1 eq), KHMDS (2 eq), THF, –78°, 1 h 2. Aldehyde (1 eq), –78°, 1 h; then to rt, 1 h		(72), $(E)^{*}$ isomer	335

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		$MN(SiMe_3)_2$, THF, –78°, 1 h; to 0°, 1 h		336
		1. NaHMDS, DME, –78° 2. Aldehyde, –78° to rt, 12 h		337
		KHMDS	 (63), 3 steps, (*E*)/(*Z*)* = 67:33	334

M		(*E*)/(*Z*)*	dr C-5
Li	(14)	—	100:0
Na	(49)	—	60:40
K	(5)	—	25:75

C-3	C-4	C-5		(*E*)/(*Z*)*
(*S*)	(*S*)	(*R*)	(25)	75:25
(*R*)	(*S*)	(*R*)	(46)	64:36
(*R*)	(*S*)	(*S*)	(25)	62:38

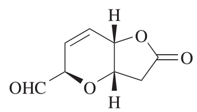
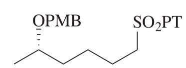
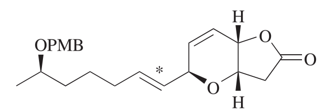
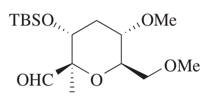
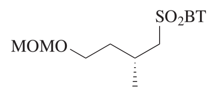
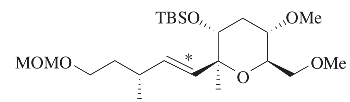
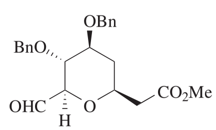
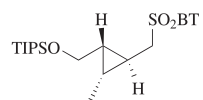
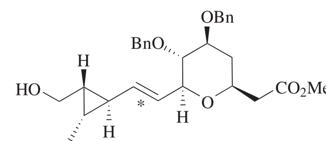
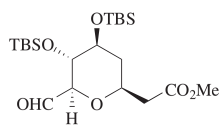
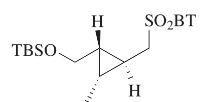
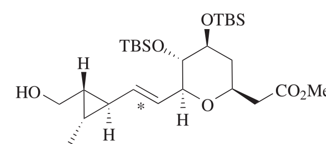
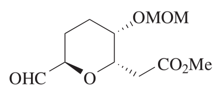
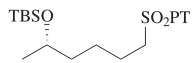
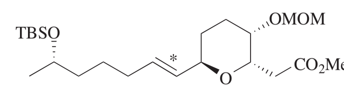
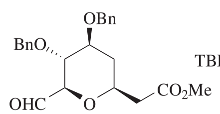
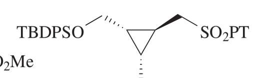
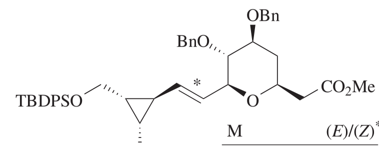
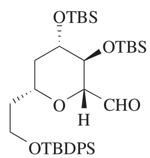
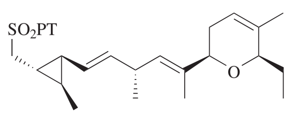
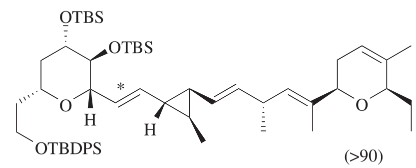
		1. $MN(SiMe_3)_2$, THF, –78°, 0.25 h 2. Aldehyde, –78°, 1.5 h; then rt	 M / / $(E)/(Z)^*$ Li (>41) 100:0 K (—) 67:33	338
		LiHMDS, THF, –78° to rt	 (79), $(E)/(Z)^*$ = —	339
		1. NaHMDS, DMF, –45° to rt 2. *p*-TsOH, MeOH	 (78), $(E)/(Z)^*$ = 58:42	340
		1. NaHMDS, DMF, –60°, 1 h; then rt, 0.5 h 2. CF_3CO_2H, THF/H_2O, rt, 3 h	 (51), $(E)/(Z)^*$ = 72:28	340, 341

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
 	1. $MN(SiMe_3)_2$, solvent, –78°, 0.25 h 2. Aldehyde, –78°, 2 h; then rt, 2 h		342
 	1. $MN(SiMe_3)_2$ (2 eq), THF/HMPA, –78°, 5 min 2. Aldehyde (2 eq), –78° to rt, 3 h		343
 	Barbier conditions. See table.	 (>90)	25

M	Solvent		(*E*)/(*Z*)*
Li	THF/HMPA	(57)	90:10
Na	THF/HMPA	(61)	88:12
K	THF/HMPA	(48)	67:33
K	THF	(54)	60:40
K	DME	(40)	50:50

M		(*E*)/(*Z*)*
Li	(63)	90:10
Na	(78)	80:20
K	(63)	50:50

Base	Solvent	Temp (°)	(*E*)/(*Z*)*
NaHMDS	THF	–78	11:89
NaHMDS	THF	–35	14:86
KHMDS	DMF	–60	50:50
KHMDS	DME/18-crown-6	–60	25:75

Base	Solvent	Temp (°)	(*E*)/(*Z*)*
LiHMDS	THF/HMPA	–60	75:25
LiHMDS	DMF/HMPA	–35	>97:3
LiHMDS	DMF/DMPU	–35	>97:3

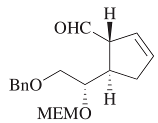
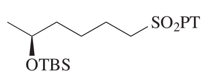
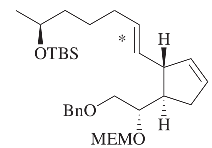
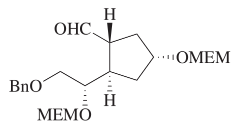
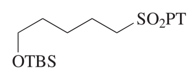
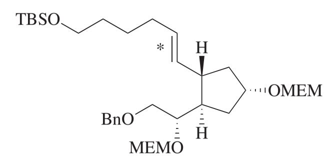
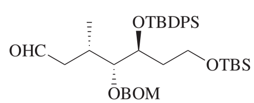
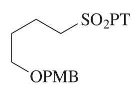
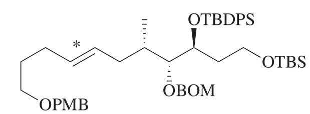
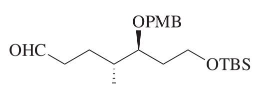
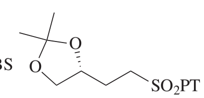
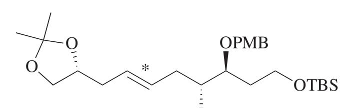
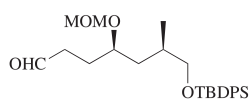
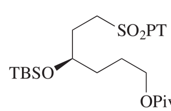
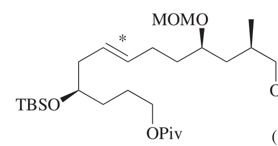
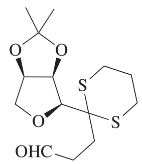
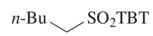
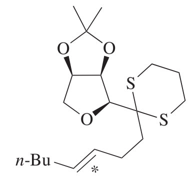
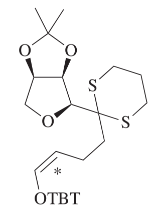
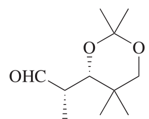
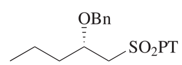
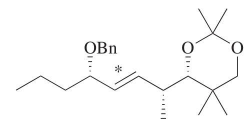
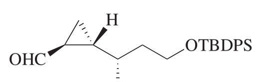
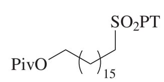
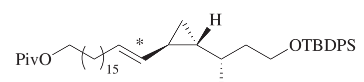
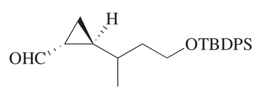
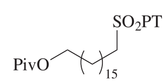
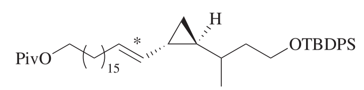
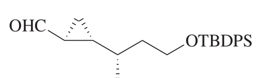
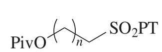
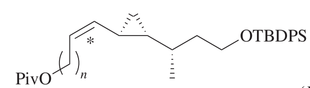
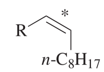
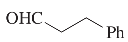
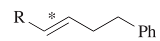
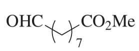
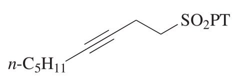
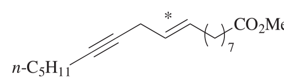
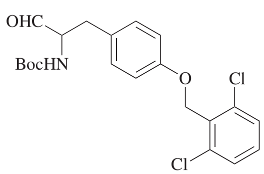
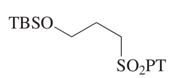
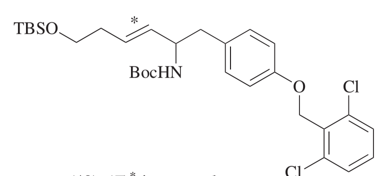
		1. KHMDS, DME, –78°, 0.5 h 2. Aldehyde, –78°; then rt		(88), (*E*)*-isomer	344
		1. KHMDS, DME, –78° 2. Aldehyde, –78°; then rt		(>27), (*E*)/(*Z*)* = —	344
		KHMDS, THF, –78°, 4 h; then rt, 12 h		(91), (*E*)*-isomer only	213
		1. Sulfone (1.5 eq), KHMDS (1.5 eq), THF, –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°, 3 h		(80), two steps, (*E*)*-isomer	176
		1. KHMDS, THF, –78°, 0.67 h 2. Aldehyde, –78°, 1 h		(60), (*E*)*-isomer	345

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		Cs_2CO_3, THF/DMF, 70°, 16 h	 (48), $(E)/(Z)^*$ = 75:25 +  (6), $(E)/(Z)^*$ = 33:67	62
		KHMDS, DME, –65° to rt, 16 h	 (63), $(E)/(Z)^*$ = —	346
		LiHMDS, THF, –20° to rt, 2 h	 (78), $(E)/(Z)^*$ = 73:27	347
		LiHMDS, THF, –15° to rt, 2 h	 (80), $(E)/(Z)^*$ = —	347
dr 1:1 		LiHMDS, THF, –12°		348

n		$(E)/(Z)^*$
6	(69)	28:72
7	(75)	—
9	(85)	22:78

C_9

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
n-$C_8H_{17}CHO$		LDA, THF, –78°, 3 h; then rt, 1h		3
		**A**: 1. KHMDS, THF, –78° 2. Aldehyde or **B**: 1. KHMDS (1.1 eq), 18-crown-6 (2.0 eq), THF, 0.5 min 2. Aldehyde, –78°, 30 min		26
		1. Sulfone (1.0 eq), KHMDS (1.1 eq), DME, –53°, 1 h 2. Aldehyde (1.5 eq), –52°; then to rt, overnight	 (47), (*E*)* isomer	349
		KHMDS, DMF, –78° to rt, 2 h	 (40), (*E*)*-isomer only	350

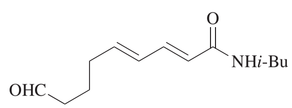
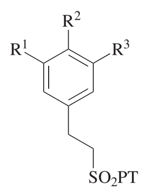
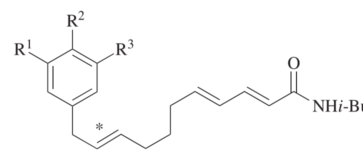
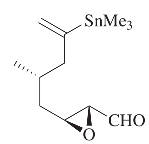
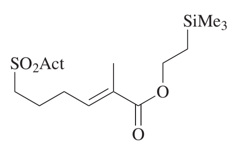
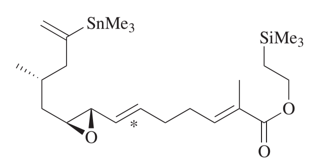
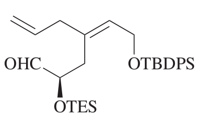
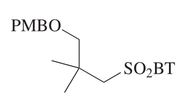
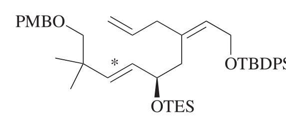
Product table for ref. 3:

R		(*E*)/(*Z*)*
Me	(26)	43:57
Et	(48)	49:51
n-Pr	(49)	50:50

Product table for ref. 26:

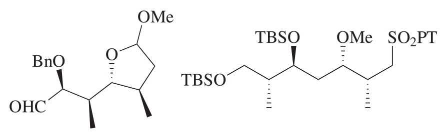
R	Conditions		(*E*)/(*Z*)*
Me	**A**	(72)	89:11
Me	**B**	(62)	>98:2
n-Pr	**A**	(74)	83:17
n-Pr	**B**	(86)	>98:2

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

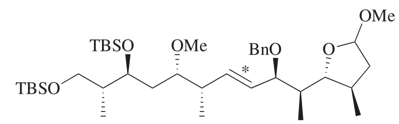
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
 	1. KHMDS, DME, –60°, 1 h 2. Aldehyde, –60°, 2 h; then rt, 0.5 h		351
 	KHMDS, DME, –78°		352
 	1. LiHMDS, THF, –78°, 033 h 2. Aldehyde, –78° to rt	 (60), (*E*)/(*Z*)* = 75:25	324

R^1	R^2	R^3		(*E*)/(*Z*)*
H	H	H	(51)	>93:7
H	F	H	(58)	—
H	Cl	H	(53)	—
H	MeO	H	(50)	—
MeO	MeO	H	(49)	—
MeO	MeO	MeO	(51)	—
–OCH_2O–		H	(58)	—
–$O(CH_2)_2O$–		H	(56)	—
–$O(CH_2)_2$–		H	(54)	—

Act		(*E*)/(*Z*)*
PT	(65)	75:25
BT	(—)	66:34

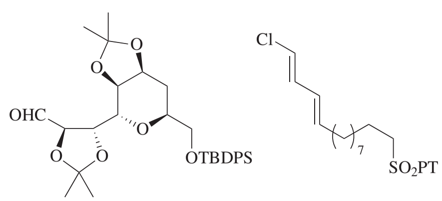


1. Sulfone (x eq), LiHMDS (x eq), solvent, temp, 0.5 h
2. Aldehyde (1.0 eq), temp, 2 h; then to rt, 8 h

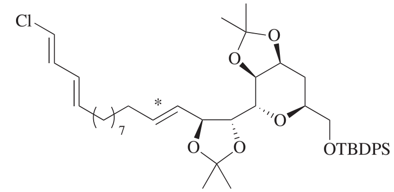


x	Solvent	Temp (°)		$(E)/(Z)^*$
2.5	DME	–55	(92)	40:60
—	THF	–78	(60)	55:45

353

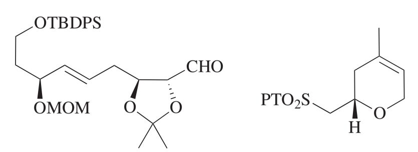


1. KHMDS, THF, –78°, 1 h
2. Aldehyde, –78°, 1 h; then rt, 2 h

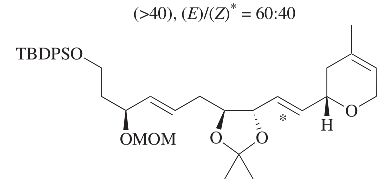


(>40), $(E)/(Z)^*$ = 60:40

334

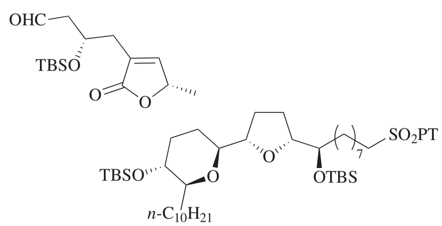


1. KHMDS, DMF/HMPA –60°, 0.25 h
2. Aldehyde, –78°; then rt, 12 h

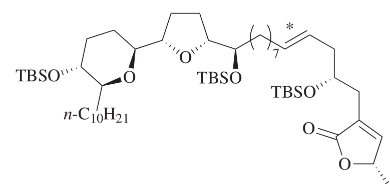


(75), $(E)^*$-isomer

354



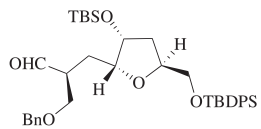
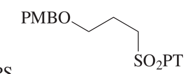
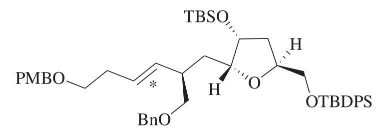
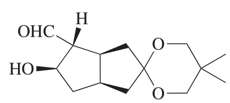
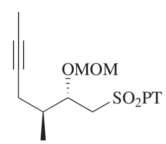
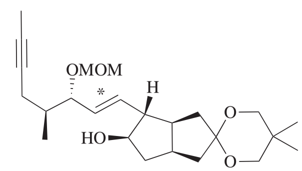
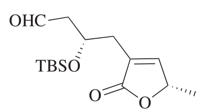
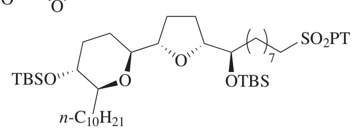
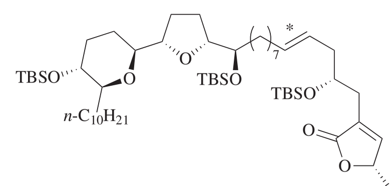
1. LiHMDS, THF, –78°, 0.67 h
2. Aldehyde, –10°, 3 h



(93), 'inseparable mixture' of $(E)/(Z)^*$-isomers

355

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
 	LiHMDS, THF, –78°	 (90), (*E*)/(*Z*)* = —	356, 357
 	1. LiHMDS, THF, HMPA, –78°, 0.33 h 2. Aldehyde, –78° to rt, 6.5 h	 (57), (*E*)/(*Z*)* = —	358
 	1. LiHMDS, THF, –78°, 0.67 h 2. Aldehyde, –10°, 3 h	 (93), 'inseparable mixture' of (*E*)/(*Z*)*-isomers	355

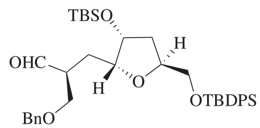
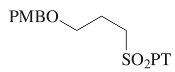
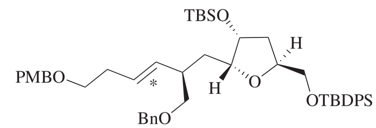
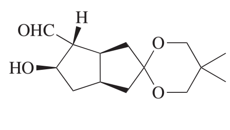
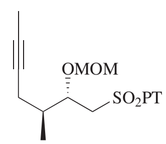
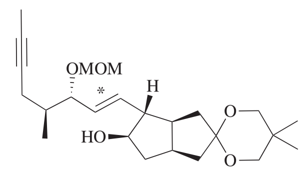
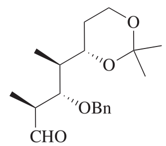
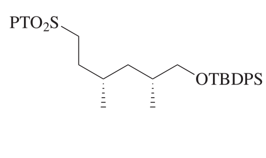
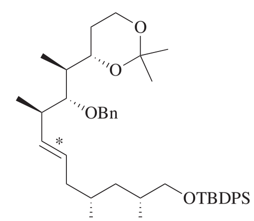
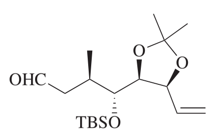
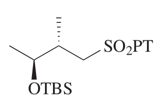
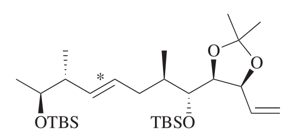
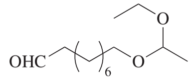
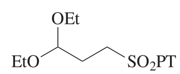
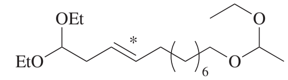
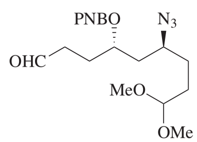
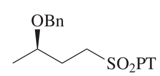
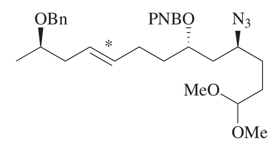
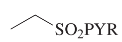
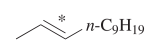
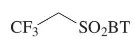
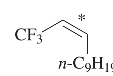
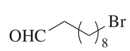
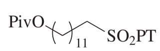
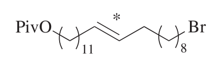
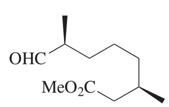
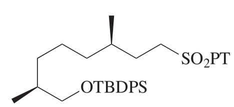
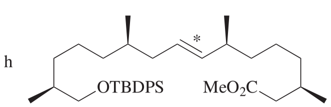
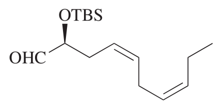
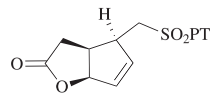
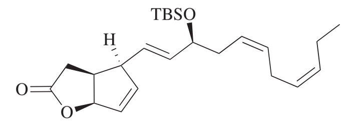
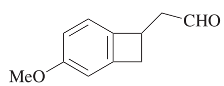
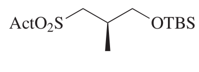
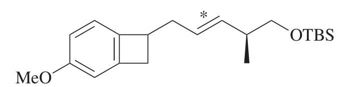
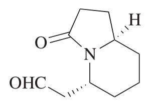
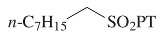
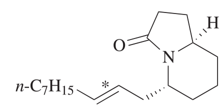
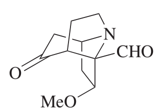
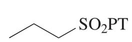
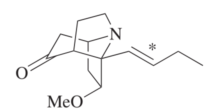
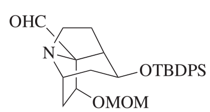
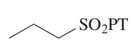
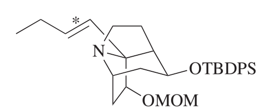
		LiHMDS, THF, –78°	 (90), $(E)/(Z)^{*}$ = —	356, 357
		1. LiHMDS, THF, HMPA, –78°, 0.33 h 2. Aldehyde, –78° to rt, 6.5 h	 (57), $(E)/(Z)^{*}$ = —	358
		1. Sulfone (1.4 eq), KHMDS (1.4 eq), THF, –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°; then to rt, 12 h	 (87), $(E)^{*}$-isomer	359
		1. Sulfone (1 eq), KHMDS (2 eq), –78°, 1 h 2. Aldehyde (1 eq), –78°, 1 h; then to rt, 1 h	 (80), $(E)^{*}$-isomer	360

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

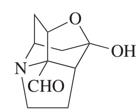
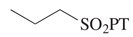
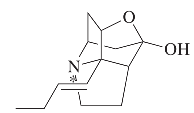
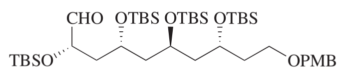
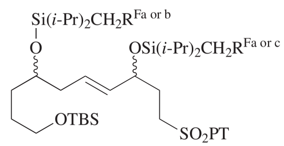
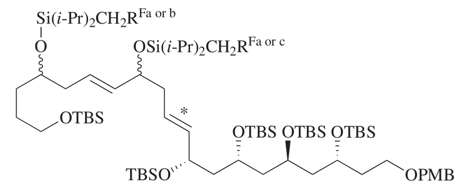
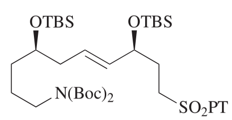
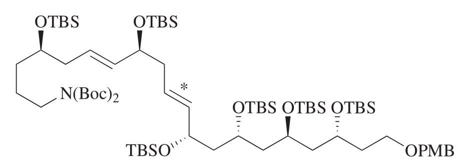
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. KHMDS, DME, –55°, 1 h 2. Aldehyde, –55° to rt, 1.5 h	 (60), (*E*)/(*Z*)* = 97:3	361
		1. LiHMDS, THF, –50°, 1 h 2. Aldehyde, –50°, 1 h; then rt, 12 h	 (75), (*E*)/(*Z*)* = 60:40	362
C_{10}				
n-C_9H_{19}CHO		1. *n*-BuLi, THF, –78°, 0.5 h 2. Aldehyde, –78°, 1.5 h; then rt	 (47), (*E*)/(*Z*)* = 52:48	3
		TBAF, THF, –78° to rt, 16 h	 (76), (*E*)/(*Z*)* = 22:78	363
		LiHMDS, THF, 0°; then rt	 (68), (*E*)/(*Z*)* = 67:33	304
		1. $MN(SiMe_3)_2$, THF, –78°, 0.5 h 2. Aldehyde, –78°; then rt	 M — (*E*)/(*Z*)* Li (84) 67:33 K (49) 100:0	364, 365

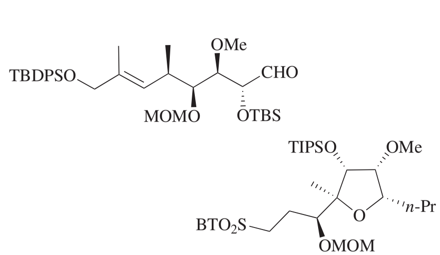
Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. KHMDS, DME, –78°, 1 h 2. Aldehyde, DME, –70°; then rt, 4 h	 (60), $(E)^{*}$-isomer only	366
		1. Sulfone (1 eq), NaHMDS (1.13 eq), toluene, –78°, 0.5 h 2. Additive (*x* eq) in toluene, –78°, 0.5 h 3. Aldehyde (1.0 eq), –78°, 3 h		367
		KHMDS, DME	 (62), $(E)/(Z)^{*}$ = 75:25	368
		KHMDS, DME, –55°	 (>70), $(E)^{*}$-isomer only	369
		KHMDS, DME, –55°, 1 h; then rt, 1 h	 (89), $(E)^{*}$-isomer	370

Entry 367:

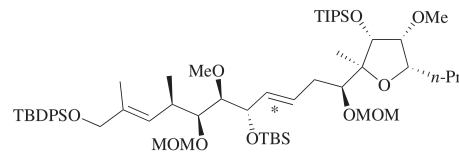
Act	Additive	*x*		$(E)/(Z)^{*}$
BT	none	—	(82)	60:40
PT	18-crown-6	1.13	(83)	>95:5

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
 	KHMDS, DME, –55°	 (94), $(E)^*$-isomer	371
  $R^{Fa} = n\text{-}C_4F_9$; $R^{Fb} = n\text{-}C_3F_7$; $R^{Fc} = n\text{-}C_6F_{13}$	1. KHMDS, DME, –78°, 0.5 h 2. Aldehyde, –78°, 1.5 h; then rt	 (77), $(E)/(Z)^* = 90{:}10$	372
	1. KHMDS 2. Aldehyde	 (94), $(E)^*$-isomer only	373

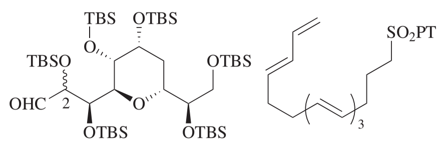


1. Sulfone (1.01 eq), LiHMDS (1.04 eq), THF, –78°, 1 h
2. Aldehyde (1.0 eq), –78°; then rt, 34 h

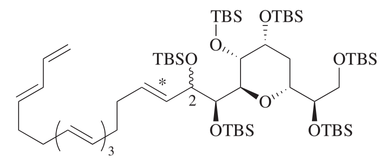


(48), (*E*)*-isomer

374

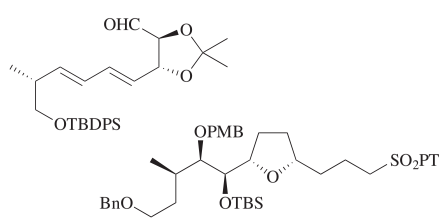


1. KHMDS, THF, –78°, 10 min
2. Aldehyde, –78°, 0.5 h; then rt, time

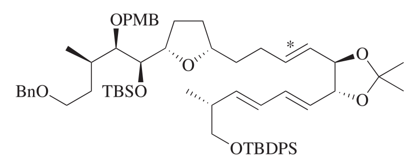


C-2	Time (h)		(*E*)/(*Z*)*
(*S*)	9	(92)	92:8
(*R*)	2	(65)	100:0

375



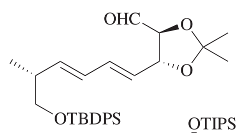
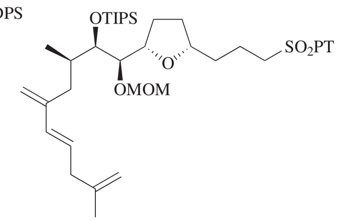
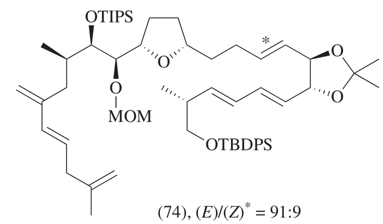
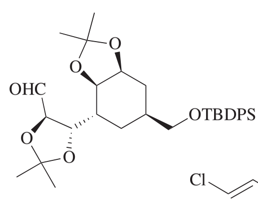
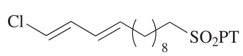
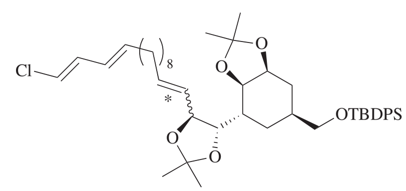
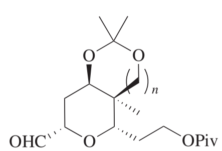
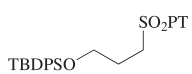
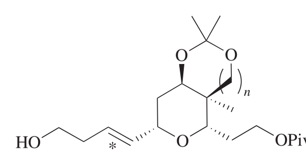
1. KHMDS, DME, –78 to –60°
2. Aldehyde, –78°; then rt



(62), (*E*)/(*Z*)* = 80:20

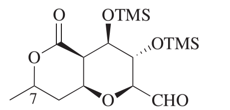
376

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

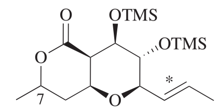
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
 	1. LiHMDS, THF, –78 to –40°, 1 h 2. Aldehyde, DMF/DMPU, –78°; then rt, 12 h	 (74), $(E)/(Z)^{*}$ = 91:9	376, 377
 	1. Sulfone (1 eq), KHMDS (1.25 eq), THF, –78°, 1 h 2. Aldehyde (2.8 eq), THF, –78°, 1 h; then to rt, 2 h	 (40), 2 steps, $(E)/(Z)^{*}$ = 60:40	334
$C_{10–11}$			
 	1. LiHMDS, DMF/HMPA, –35° 2. Aldehyde, –35° to rt 3. TBAF, THF		378, 379

C_{10}

n		(*E*)/(*Z*)*
1	(76)	95:5
2	(68)	—

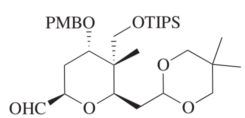


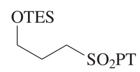
1. LiHMDS, solvent
2. Aldehyde



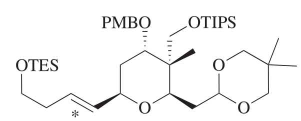
380

C-7	Solvent	Temp (°)		(*E*)/(*Z*)*
(*R*)	THF	–78	(76)	55:45
(*R*)	DMF	–60	(72)	90:10
(*R*)	DMF	–35	(73)	94:6
(*R*)	DMF/HMPA	–35	(70)	83:17
(*S*)	DMF	–35	(78)	92:8



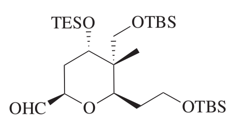


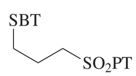
KHMDS, DME, –60° to rt



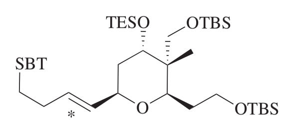
(80), (*E*)/(*Z*)* = 90:10

381





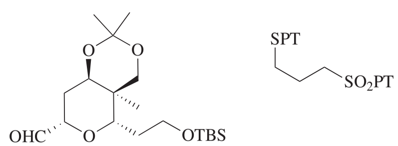
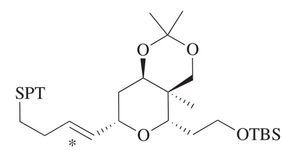
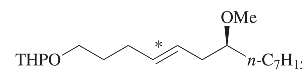
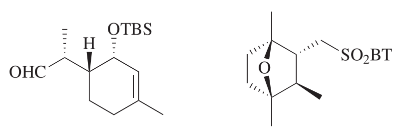
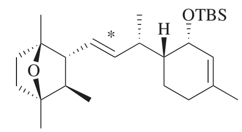
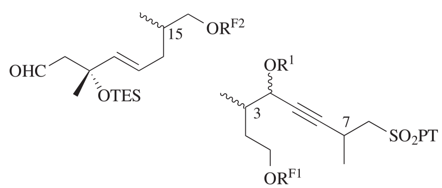
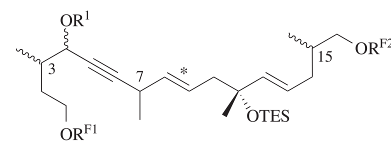
KHMDS, DME, –70° to rt

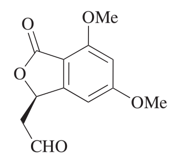
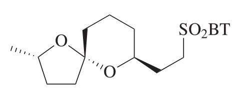
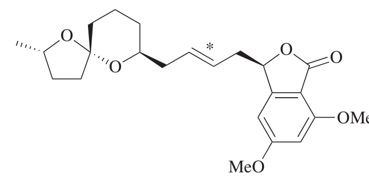
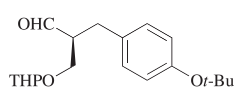
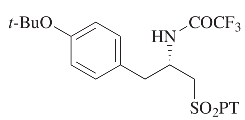
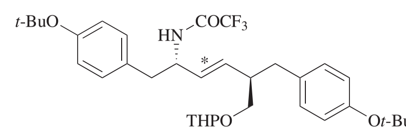
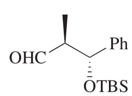
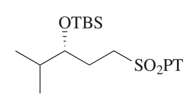
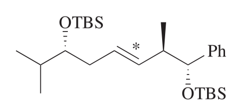


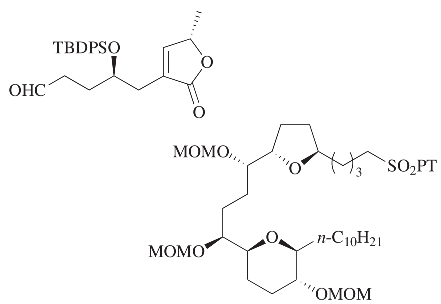
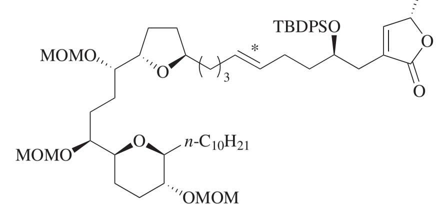
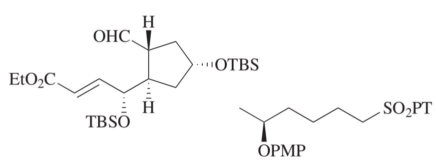
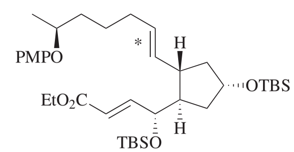
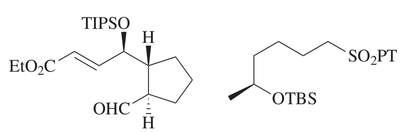
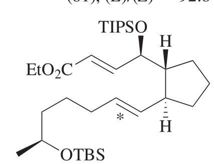
(95), (*E*)/(*Z*)* = 97:3

382

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. KHMDS, DME/HMPA, –78°, 0.5 h 2. Aldehyde, –78°, 2 h	 (90), $(E)/(Z)^*$ = —	383
	1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h; then rt	 (80), $(E)^*$-isomer	384
	LiHMDS, –78°, 2 h; then rt, 1 h	 (88), $(E)/(Z)^*$ = 50:50	385, 386
 (15*R*), R^{F2} = 4-[$C_4F_9(CH_2)_3O$]$C_6H_4CH_2$ + (15*S*), R^{F2} = 4-[$C_6F_{13}(CH_2)_3O$]$C_6H_4CH_2$ (3*S*), R^{F1} = 4-[$CF_3(CH_3)_2O$]$C_6H_4CH_2$ + (3*R*), R^{F1} = 4-[$C_4F_9(CH_2)_3O$]$C_6H_4CH_2$	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h	 C-7 / R^1 / / $(E)/(Z)^*$ (*S*) / H / (35) / — (*S*) / TES / (87) / — (*R*) / TES / (89) / —	271

		1. KHMDS, THF, –78°, 0.33 h 2. Aldehyde, –78°, 1.5 h; then rt, 1 h	 (62), $(E)/(Z)^{*}$ = —	387
		1. NaHMDS (2 eq), DME, –78°, 0.5 h 2. Aldehyde, –78° to rt, 12 h	 (53), $(E)/(Z)^{*}$ = 70:30	388, 389
		KHMDS	 (>56), $(E)/(Z)^{*}$ = —	390

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. LiHMDS, toluene, –78°, 1 h 2. Aldehyde; then rt	 (36), (*E*)/(*Z*)* = —	391
	1. KHMDS, DME, –78°, 1 h 2. Aldehyde, –78°, 1 h; then rt, 16 h	 (81), (*E*)/(*Z*)* = 92:8	392
	KHMDS, DME, –78° to rt	 (91), (*E*)*-isomer	393

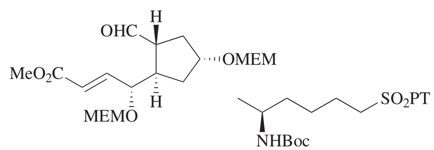
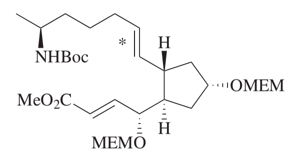
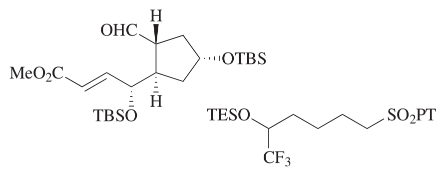
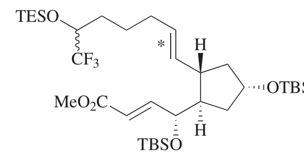
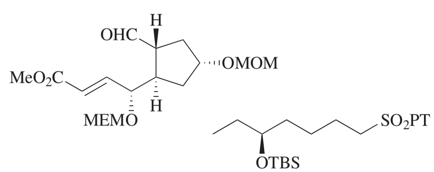
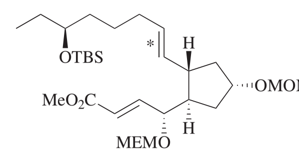
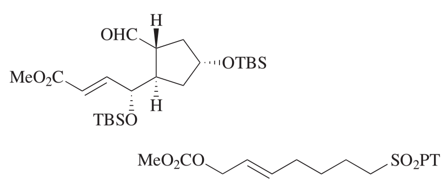
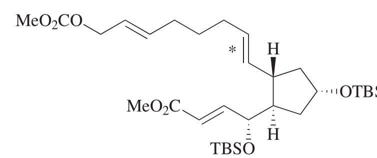
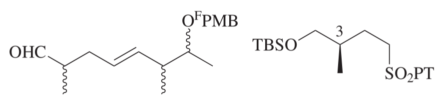
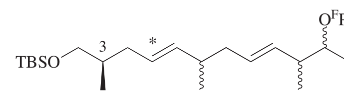
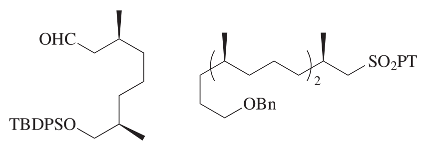
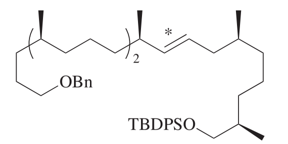
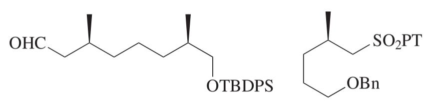
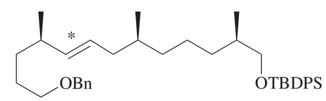
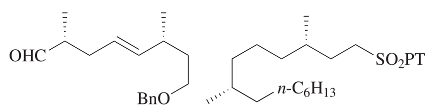
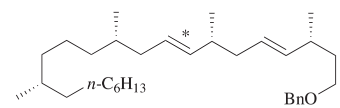
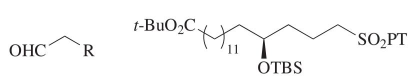
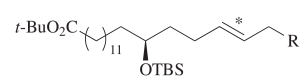
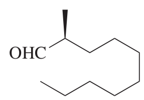
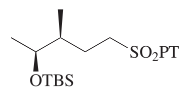
	1. KHMDS, DME, –78°, 0.5 h 2. Aldehyde, –78°, 2 h; then rt, 1 h	 (93), $(E)^*$-isomer	307
	KHMDS, DME, –78° to rt	 (90), $(E)^*$-isomer	394
	1. KHMDS, DME, –78°, 0.5 h 2. Aldehyde, –78°; then rt	 (73), $(E)^*$-isomer	394
	KHMDS, DME, –78° to rt	 (84), $(E)^*$-isomer	394

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

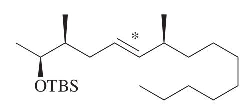
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h	 (93), (*E*)/(*Z*)* = —	119, 243
	LiHMDS, THF, –78°, 3 h; then rt	 (56), (*E*)/(*Z*)* = —	168
	LiHMDS, THF, –78°, 3 h; then rt	 (70), (*E*)/(*Z*)* = —	168
	LiHMDS, THF, –78°, 3 h; then rt	 (78), (*E*)/(*Z*)* = —	168
C_{11-12}			
	1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60°; then rt, 16 h		395

C$_{11}$



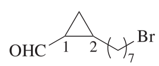


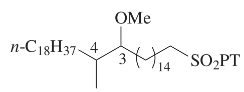
1. LiHMDS, THF, –78°, 1 h
2. Aldehyde, 1 h; then rt



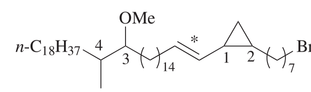
R	(E)*-isomer
n-C_9H_{19}	(67)
n-C_8H_{17} (branched, wedge)	(45)
n-C_8H_{17} (branched, hash)	(75)

(83), (E)*-isomer 396



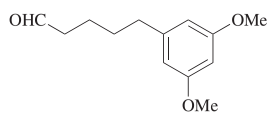


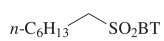
LiHMDS, THF, –15°; then rt, 16 h



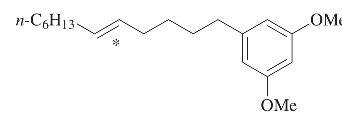
228

C-1	C-2	C-3	C-4		(E)/(Z)*
(S)	(S)	(R)	(R)	(92)	—
(S)	(S)	(S)	(S)	(87)	—

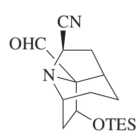


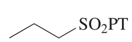


KHMDS, THF, –78°

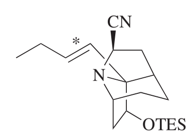


(91), (E)*-isomer 397



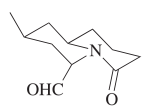
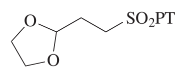
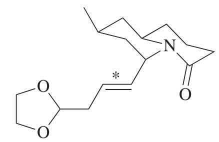
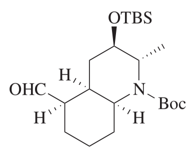
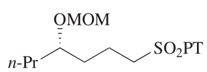
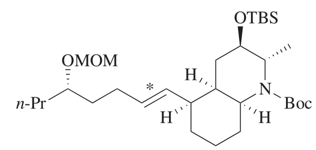
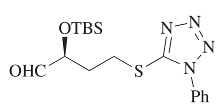
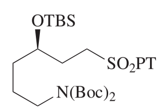
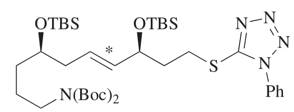
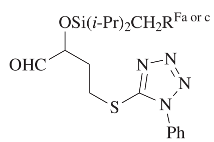
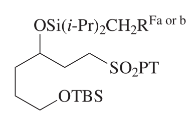
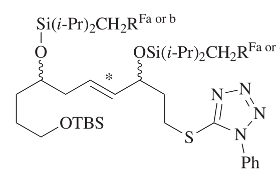


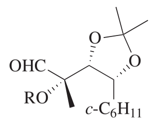
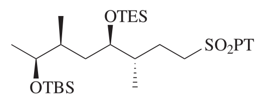
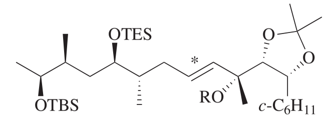
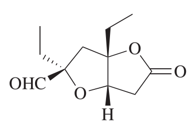
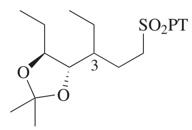
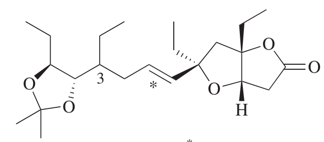
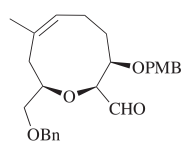
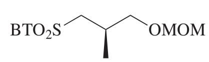
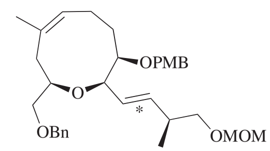
KHMDS, DME, –55°



(78), (E)*-isomer 398

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

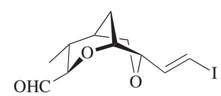
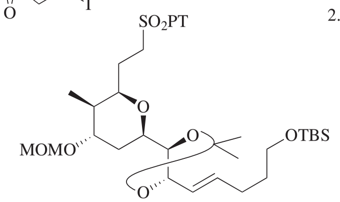
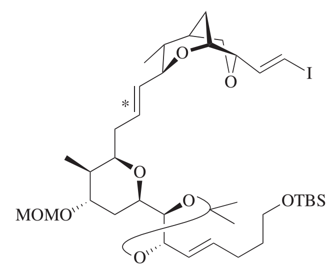
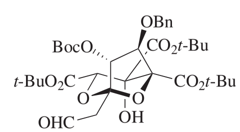
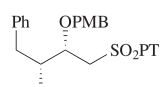
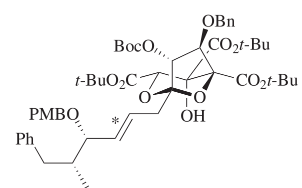
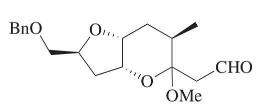
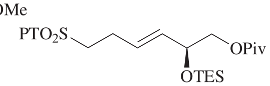
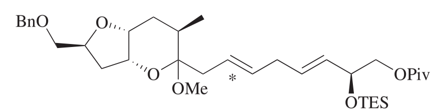
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
 	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 60 h; then rt	 (70), $(E)/(Z)^{*}$ = 93:7	399
 	1. KHMDS, THF, –78°, 0.75 h 2. Aldehyde, rt	 (66), $(E)/(Z)^{*}$ = —	400
 	1. KHMDS 2. Aldehyde	 (86), $(E)^{*}$-isomer only	373
  R^{Fa} = n-C_4F_9; R^{Fb} = n-C_3F_7; R^{Fc} = n-C_6F_{13}	1. KHMDS, DME, –78°, 0.5 h 2. Aldehyde, –78°, 1.5 h; then rt	 (80), $(E)/(Z)^{*}$ = 90:10	372

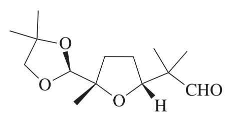
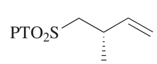
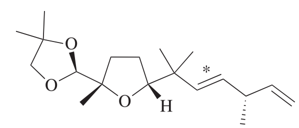
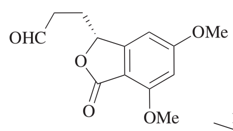
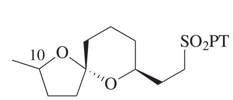
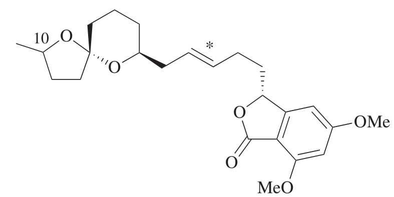
		1. KHMDS, solvent, –78°, 0.5 h 2. Aldehyde, THF, –78°, 1 h; then rt		401
		1. KHMDS, THF, –78°, 0.25 h 2. Aldehyde, –78°, 1 h; then to rt		402, 403
		KHMDS, THF, –78° to rt	 (69), $(E)^*$-isomer	404

R	Solvent		$(E)/(Z)^*$
TES	toluene	(29)	60:40
TES	THF	(27)	99:1
PMB	toluene	(tr)	—

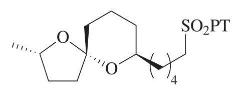
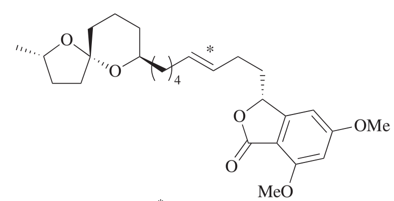
C-3	$(E)^*$-isomer
(*R*)	(54)
(*S*)	(40)

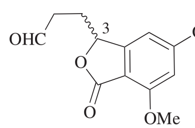
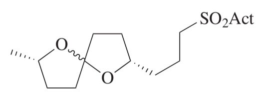
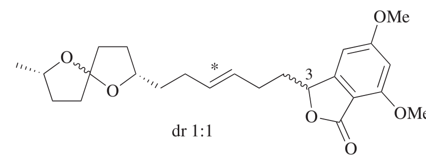
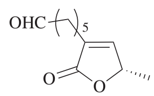
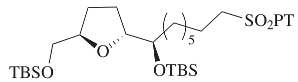
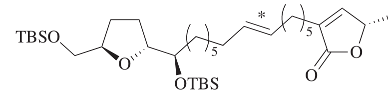
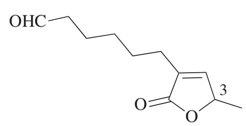
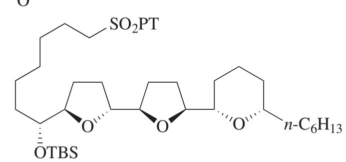
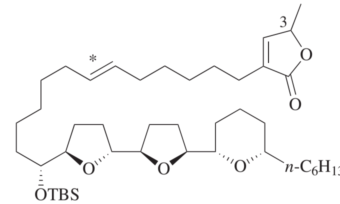
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
 	1. Base, solvent, –72° 2. Aldehyde, –72° to rt	 Base / Solvent / / $(E)/(Z)^*$ LiHMDS / DMF/HMPA / (24) / 100:0 NaHMDS / DMF/HMPA / (40) / 78:22 KHMDS / DME / (54) / 66:34 LDA / DMF/HMPA / (11) / 100:0 *t*-BuLi / DMF/HMPA / (39) / 100:0	65, 405
 	LDA, THF, –78° to rt	 (0)	406
 	1. KHMDS, DME, –60°, 0.67 h 2. Aldehyde; –50°, 1.5 h; then 0°, 1.5 h; then rt	 (88), $(E)/(Z)^*$ = 84:16	407

		1. LDA, THF, –78°, 0.33 h 2. Aldehyde, –78° to rt, 16 h; then reflux, 4 h	 (91), $(E)/(Z)^{*}$ = 90:10	408, 409
		1. Base, THF, –78°, 0.75 h 2. Aldehyde, –78°, 4 h; then rt, 0.75 h		

C-10	Base		$(E)/(Z)^{*}$	
(*R*)	KHMDS	(75)	>75:25	410
(*R*)	LDA	(40)	—	411
(*S*)	LDA	(37)	—	411

		1. KHMDS, THF, –78°, 0.33 h 2. Aldehyde, –78°, 1.5 h; then rt, 1 h	 (64), $(E)/(Z)^{*}$ = —	387

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
  dr 1:1	1. KHMDS, THF, –78°, 0.33 h 2. Aldehyde, THF, –78°, 1.5 h; then rt, 1 h	 dr 1:1	412, 413
 	1. NaHMDS, THF, –78° 2. Aldehyde, THF; then –20°	 (85), (*E*)*-isomer only	414
 	1. NaHMDS, THF, –78°, 10 min 2. Aldehyde, –78 to –20°, 4 h		252, 414

Act	C-3		(*E*)/(*Z*)*
PT	(*S*)	(84)	—
PT	(*R*)	(76)	—
BT	(*S*)	(19)	—

C-3	(*E*)*-isomer
(*S*)	(41)
(*R*)	(71)

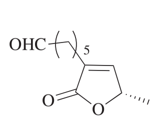
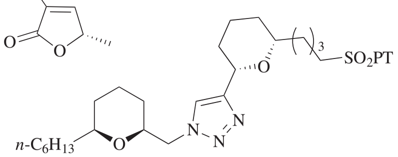
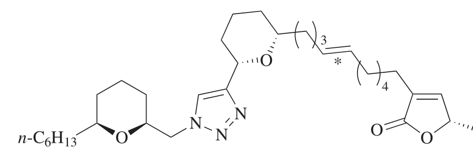
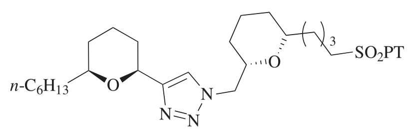
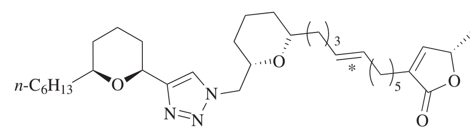
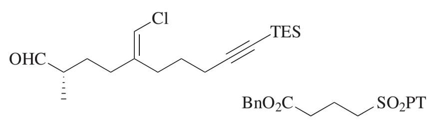
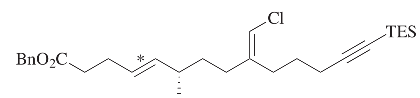
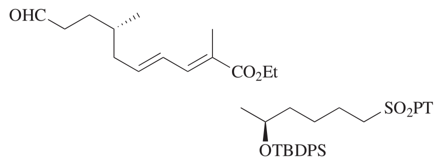
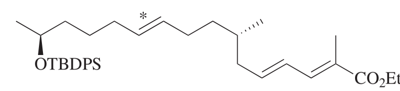
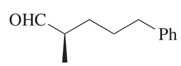
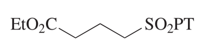
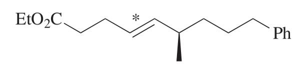
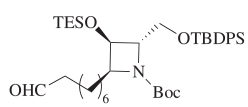
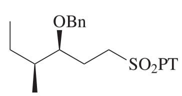
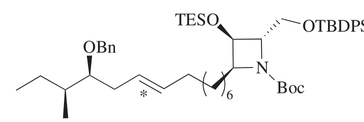
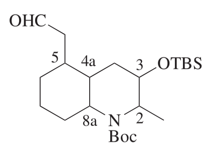
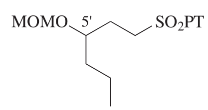
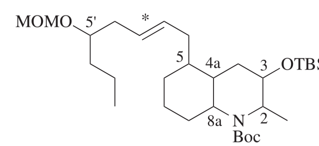
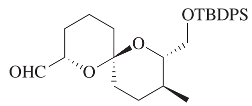
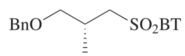
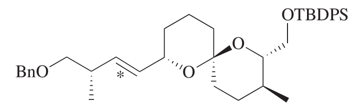
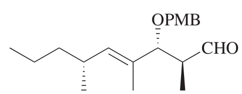
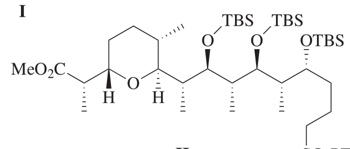
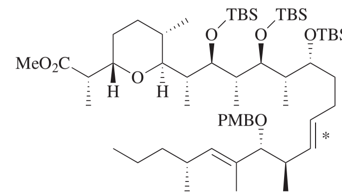
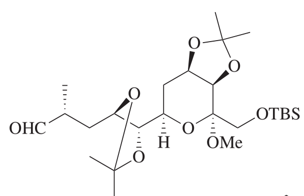
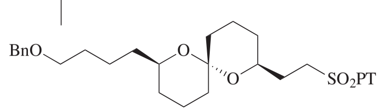
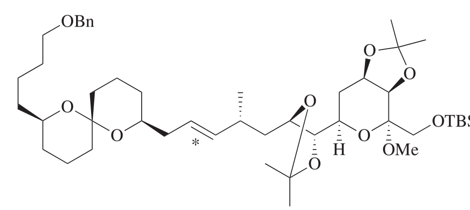
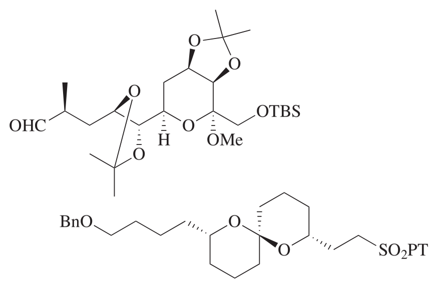
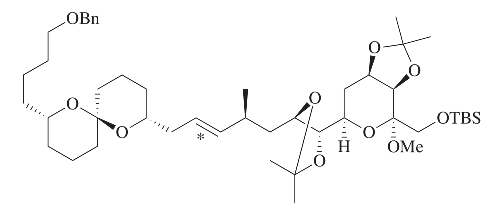
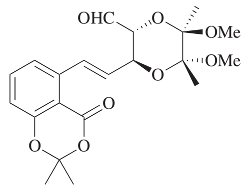
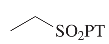
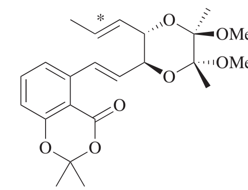
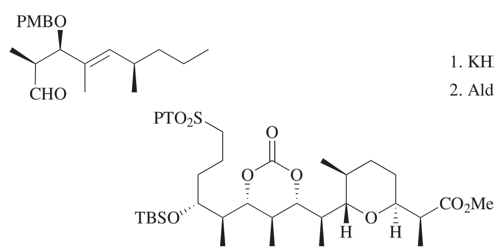
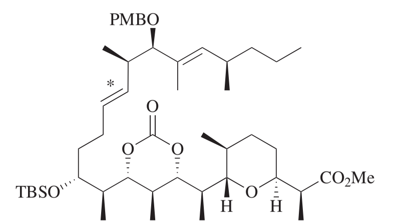
		1. Sulfone (1 eq), NaHMDS (1.55 eq), THF, –78°, 10 min 2. Aldehyde (3.6 eq), –78°, 1.25 h	 (61), $(E)^*$-isomer	415
		1. Sulfone (1 eq), NaHMDS (1.2 eq), THF, –78°, 10 min 2. Aldehyde (1.5 eq), –78°, 1.5 h	 (44), $(E)^*$-isomer	415
C_{12}		1. Sulfone (5.0 eq), NaHMDS (5.0 eq), THF, –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°, 4 h; then to 0°	 (46), $(E)^*$-isomer	274

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	1. LiHMDS, THF/HMPA –78°, 0.25 h 2. Aldehyde, –78°, 3 h	 (72), (*E*)/(*Z*)* = 93:7	165
 	1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 14 h	 (81), (*E*)/(*Z*)* = —	416
 	1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 0.25 h	 (93), "predominantly(*E*)*-isomer"	417
 	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt		

C-5'	C-5	C-4a	C-8a	C-3	C-2	(*E*)*-isomer	Refs.
(*R*)	(*R*)	(*S*)	(*R*)	(*R*)	(*S*)	(90)	418
(*S*)	(*R*)	(*S*)	(*R*)	(*R*)	(*S*)	(90)	418
(*R*)	(*S*)	(*R*)	(*S*)	(*S*)	(*S*)	(90)	419
(*R*)	(*R*)	(*S*)	(*R*)	(*S*)	(*R*)	(>60)	420
(*S*)	(*R*)	(*S*)	(*R*)	(*S*)	(*R*)	(>60)	420

 	1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78 to 60°, 1.5 h	 (85), (*E*)/(*Z*)* = 70:30	421, 422
 **I**  **II**	1. Sulfone (1.0 eq), KHMDS (1.1 eq), DMF, –55° 2. Aldehyde[b] (1.2 eq), –55°, 1 h; then –40°, 0.5 h	 + **I** (43) + **II** (24) (34), (*E*)/(*Z*)* = 9:1	423
 	1. Sulfone (4.0 eq), KHMDS (4.0 eq), THF, –100°, 10 min 2. Aldehyde (1.0 eq), –100°, 10 min	 (70), (*E*)/(*Z*)* > 95:5[c]	424

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	1. Sulfone (2.6 eq), KHMDS (2.3 eq), THF, –100°, 10 min 2. Aldehyde (1.0 eq), –100°, 20 min	 (75), (*E*)*-isomer only	425
 	KHMDS, DME, –60°	 (50), (*E*)/(*Z*)* = 80:20	426
	1. KHMDS, DME, –60° 2. Aldehyde, –60 to –20°, 1.5 h	 (69), (*E*)/(*Z*)* = 93:7	38

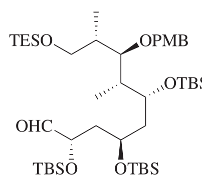
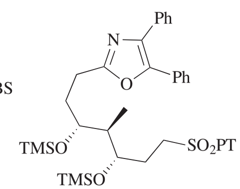
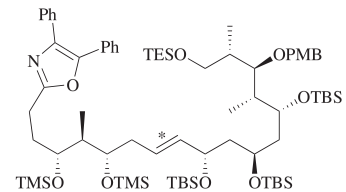
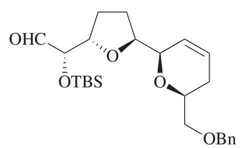
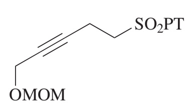
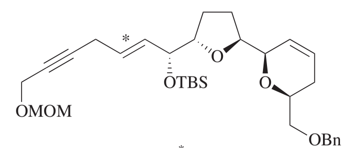
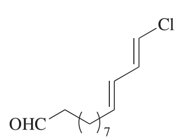
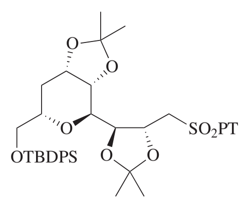
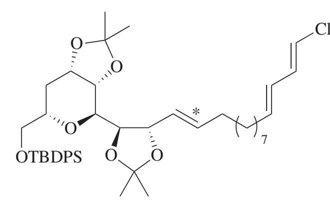
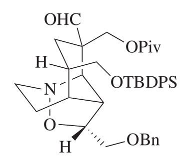
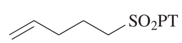
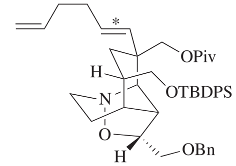
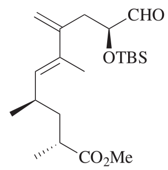
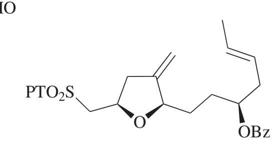
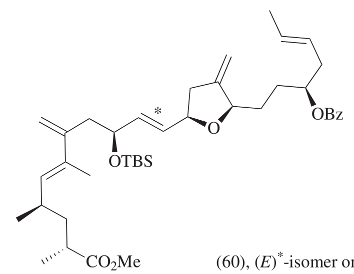
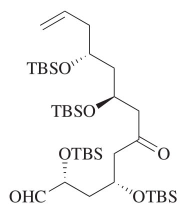
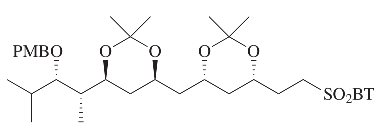
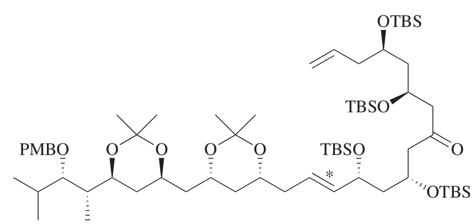
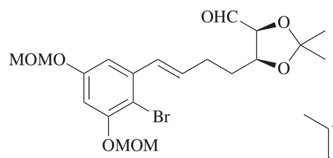
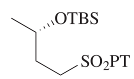
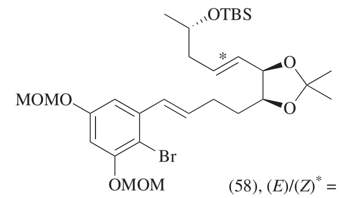
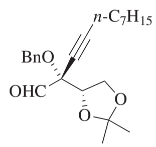
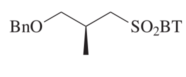
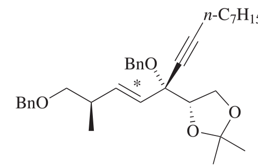
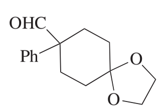
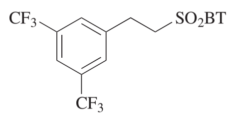
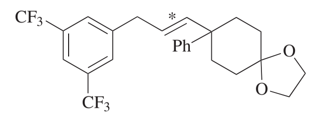
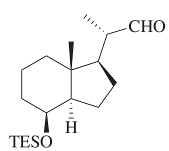
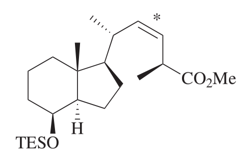
C_{13}			KHMDS, DME, –48 to 20°	 (>71), (*E*)/(*Z*)* >95:5	427
			1. KHMDS, DME, –75°, 0.5 h 2. Aldehyde, 0°, 3 h	 (90), (*E*)/(*Z*)* = 88:12	428
			1. Sulfone (1 eq), KHMDS (1.2 eq), THF, –78°, 1 h 2. Aldehyde (2 eq), THF, –78°, 1 h; then to rt, 2 h	 (25), (*E*)/(*Z*)* = 75:25	334

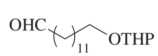
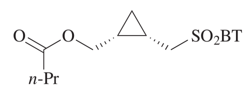
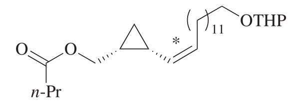
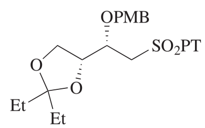
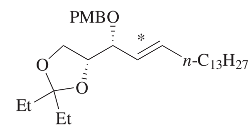
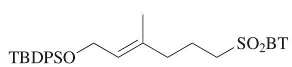
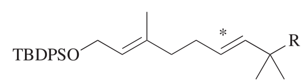
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

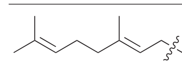
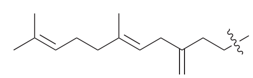
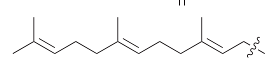
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		Aldehyde (1.0 eq), sulfone (1.5 eq), LiHMDS (1.5 eq), THF, –78°; then to –40°; then –40°, 40 min	 (95), (*E*)*-isomer	429
		KHMDS, DMF, –78°, 0.5 h; then rt, 1 h	 (60), (*E*)*-isomer only	430
		1. Sulfone (1.0 eq), KHMDS (1.1 eq), THF, –78°, 5 min 2. Aldehyde (1.1 eq), –78°, 20 min	 (74), (*E*)/(*Z*)* >95:5	431

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60°, 0.5 h; then rt, 2 h	 (58), $(E)/(Z)^*$ = 83:17	432
		LiHMDS, THF	 (90), $(E)/(Z)^*$ = 97:3	433
		LiHMDS, THF, –78° to rt	 (—), $(E)/(Z)^*$ = —	434
		1. $MN(SiMe_3)_2$ (1.1 eq), solvent, temp 2. Aldehyde (1.5 eq)		67

Act	M	Solvent	Temp (°)		$(E)/(Z)^*$
BT	Li	THF	–78	(75)	0:100
PT	Li	THF	–78	(35)	0:100
PT	Na	THF	–78	(57)	0:100
PT	Na	DME	–55	(0)	—
PT	K	THF	–55	(0)	—
PT	K	DME	–55	(4)	0:100

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		NaHMDS, THF	 (62), (*E*)/(*Z*)* = 43:57	435
C_{14}				
n-$C_{13}H_{27}CHO$		1. KHMDS, DME, –55°, 0.5 h 2. Aldehyde, –55°, 0.25 h	 (53), (*E*)/(*Z*)* = 80:20	220
$C_{14–19}$				
		NaHMDS, THF, –78°, 2 h	 (*E*)*-isomer only	436

R	
	(55)
	(58)
	(62)

C_{14}

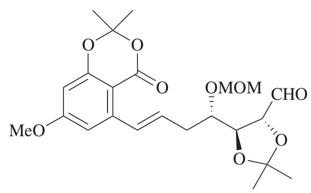
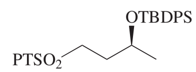
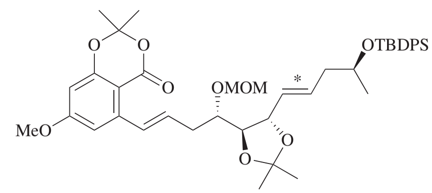
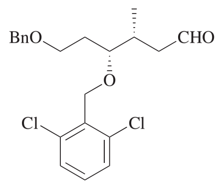
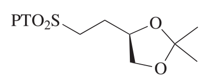
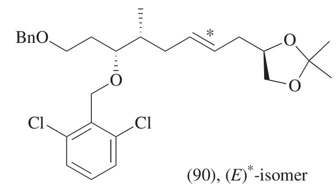
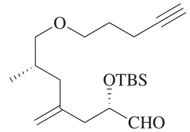
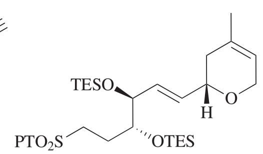
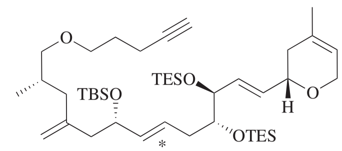
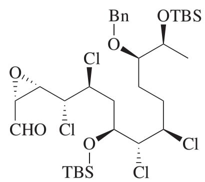
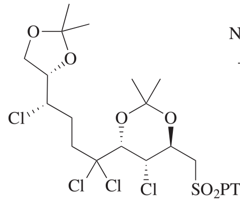
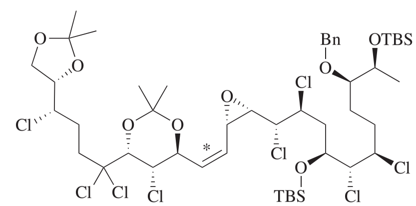
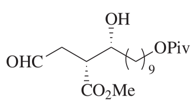
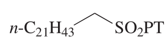
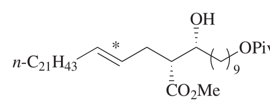
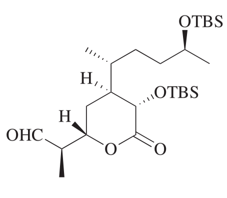
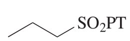
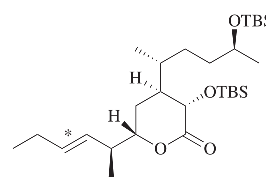
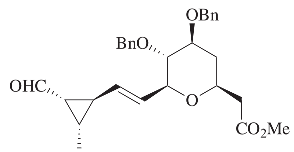
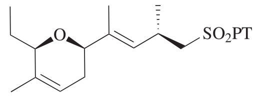
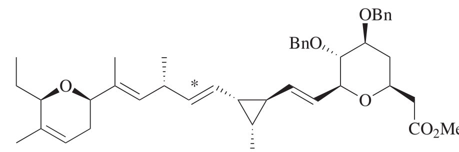
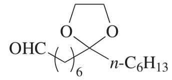
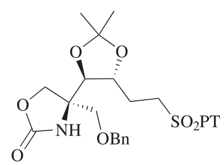
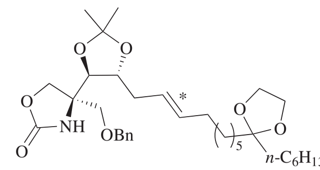
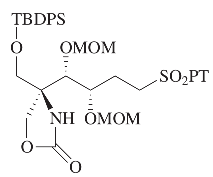
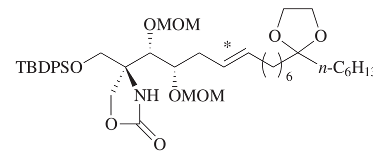
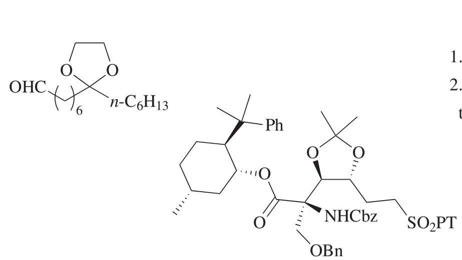
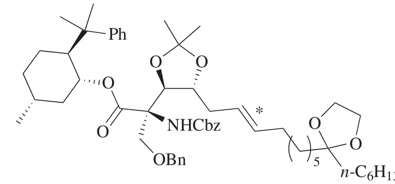
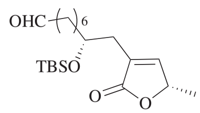
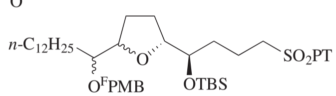
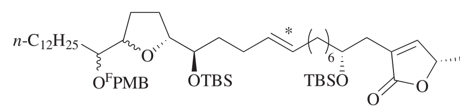
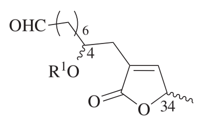
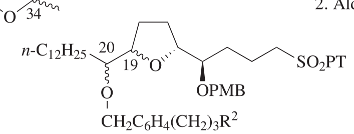
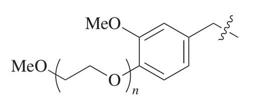
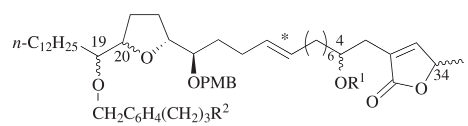
 	1. Sulfone (1.15 eq), KHMDS (1.7 eq), –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°, 3 h	 86% conv., $(E)/(Z)^{*}$ = 90:10	437
 	1. Sulfone (2.15 eq), LiHMDS (2.15 eq), DME, –78°, 0.25 h 2. Aldehyde (1.0 eq), –78°; then to rt	 (90), $(E)^{*}$-isomer	438
 	1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 90 min	 (78), $(E)^{*}$-isomer only	439

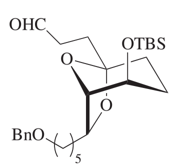
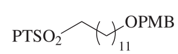
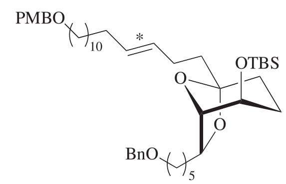
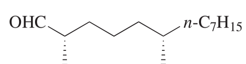
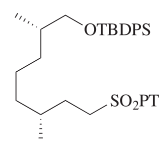
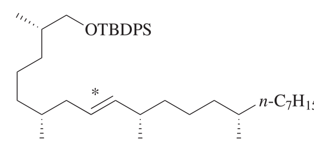
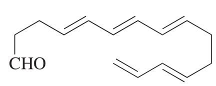
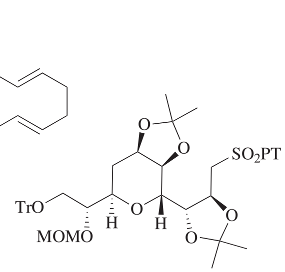
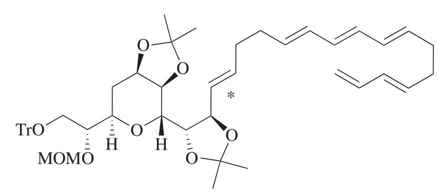
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

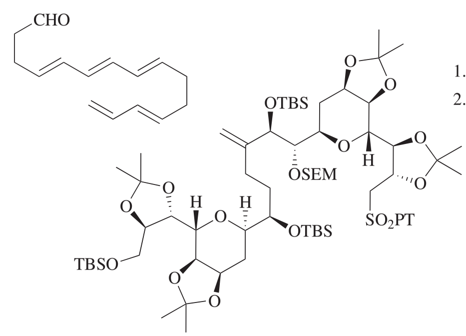
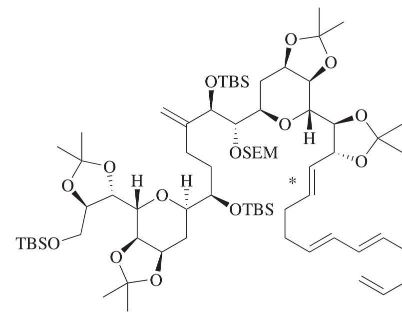
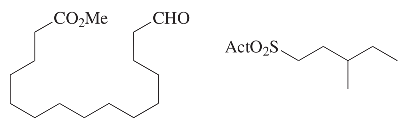
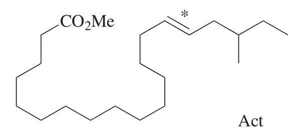
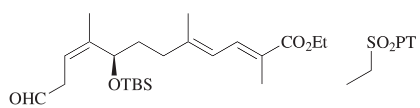
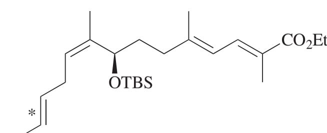
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
		NaHMDS, toluene, –78° to rt, 17 h	 (67), (*E*)/(*Z*)* = 25:75	328
		LiHMDS, THF, –10°; then rt, 3 h	 (83), (*E*)/(*Z*)* = 72:27	228
		1. Sulfone (1.3 eq), KHMDS (1.2 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –78°, 1.5 h; then to rt; then rt, 1 h	 (70), (*E*)/(*Z*)* = 95:5	440

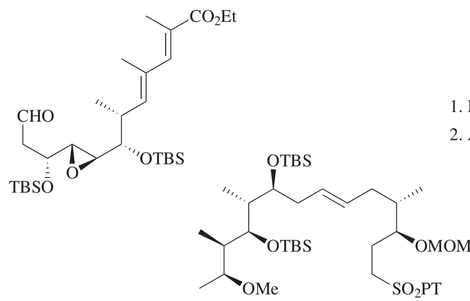
 	1. $MN(SiMe_3)_2$, THF/HMPA, –60°, 0.5 h 2. Aldehyde, –60 to 0°, 3 h	 M / / $(E)/(Z)^*$ Na (66) 68:32 K (15) 86:14	343
 	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt	 (46), $(E)/(Z)^*$ = 92:8	441
	KHMDS, DME	 (>61), "predominantly $(E)^*$-isomer"	442

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3.5 h; then rt, 1 h	 (59), $(E)^*$-isomer only	441
 	NaHMDS	 (79), $(E)/(Z)^*$ = —	443
  R^1 =  4x4 Component double mixture synthesis	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt	 x16 Compounds: (71), $(E)/(Z)^*$ = —	444

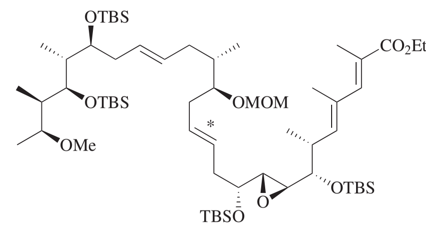
n	C-4	C-34	C-19	C-20	R^2
1	(*R*)	(*S*)	(*S*)	(*R*)	C_2F_5
2	(*R*)	(*R*)	(*S*)	(*S*)	n-C_4F_9
3	(*S*)	(*S*)	(*R*)	(*S*)	n-C_6F_{13}
4	(*S*)	(*R*)	(*R*)	(*R*)	n-C_8F_{17}

C_{15}			1. Sulfone (2 eq), LiHMDS (2.2 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –78°, 2 h	 (82), $(E)/(Z)^{*}$ = 67:33	445
			LiHMDS, THF, –78°, 3 h; then rt	 (74), "predominantly $(E)^{*}$-isomer"	446
			1. KHMDS, THF 2. Aldehyde	 (80), $(E)/(Z)^{*}$ >95:5	142

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	1. KHMDS, THF, –78°, 0.25 h 2. Aldehyde, –78° to rt, 0.5 h	 (40), (*E*)/(*Z*)* = 50:50	141
	NaHMDS, THF, –78°	 Act — (*E*)/(*Z*)* BT (30) — PT (58) —	447
	KHMDS, DME, –60°	 (26), (*E*)/(*Z*)* = —	61

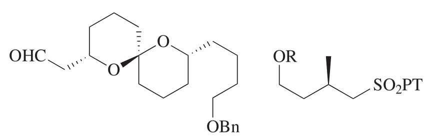


1. $MN(SiMe_3)_2$, solvent, –78°
2. Aldehyde, –78°, 3 h

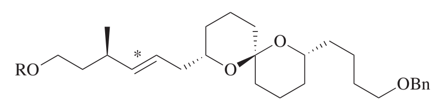


M	Solvent		(*E*)/(*Z*)*
Na	DME/HMPA	(60)	50:50
K	THF	(23)	80:20

313



1. Sulfone (1 eq), base (*x* eq), THF, temp, time
2. Aldehyde (*y* eq), THF, temp, time



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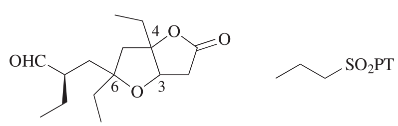
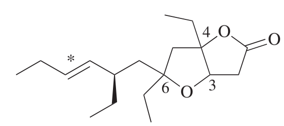
R	Base	*x*	*y*	Temp (°)	Time (h)		(*E*)/(*Z*)*
TBS	LDA	8.1	0.42	–78	0.5	(86)	83:17
TBDPS	LDA	—	—	—	—	(98)	72:28
TBDPS	NaHMDS	—	—	—	—	(77)	57:43
TBDPS	KHMDS	—	—	—	—	(27)	78:22

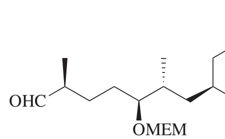
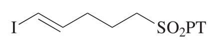
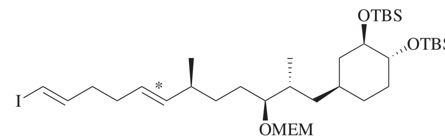
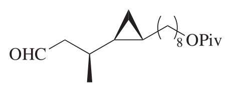
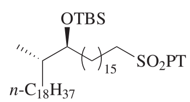
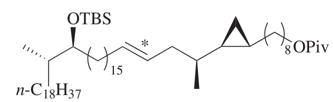
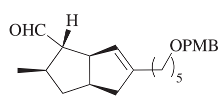
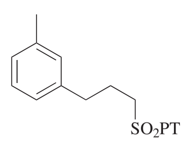
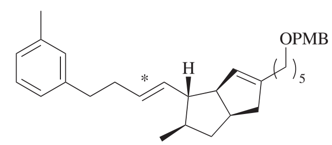
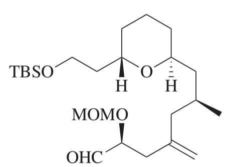
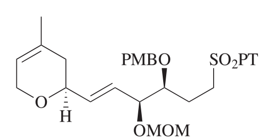
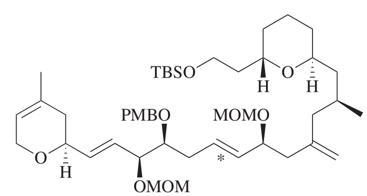


KHMDS, THF, –78°; then rt



449

C-3	C-4	C-6		(*E*)/(*Z*)*
(*R*)	(*R*)	(*R*)	(>60)	91:9
(*S*)	(*S*)	(*S*)	(>69)	—

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
 	1. Sulfone (2 eq), KHMDS (2.5 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –78°, 0.5 h	 (57), two steps, (*E*)*-isomer	450
 	LiHMDS, THF, –12°	 (70), (*E*)/(*Z*)* = 75:25	348
 	1. KHMDS, DME, –60°, 0.75 h 2. Aldehyde, –60°, 1.5 h; then rt	 (95), (*E*)*-isomer only	451
C_{16}			
 	1. KHMDS, DME, –60°, 25 min 2. Aldehyde, –60° to rt, 4 h	 (62), (*E*)/(*Z*)* = 92:8	452, 453

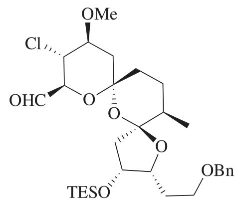
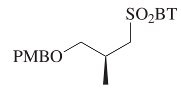
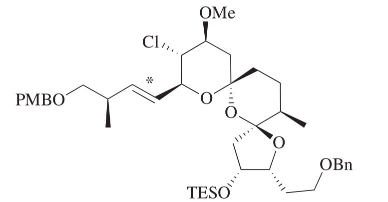
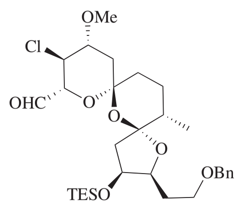
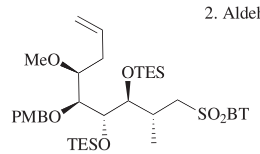
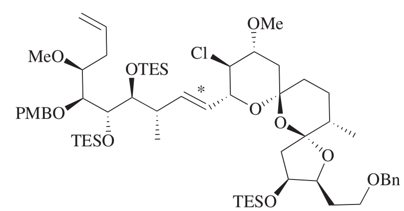
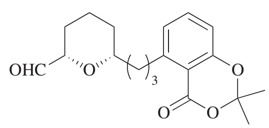
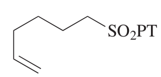
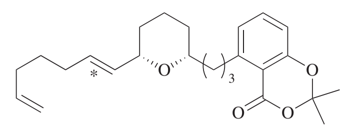
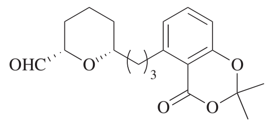
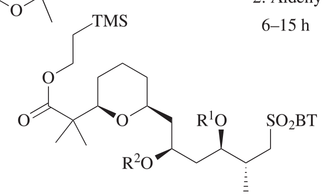
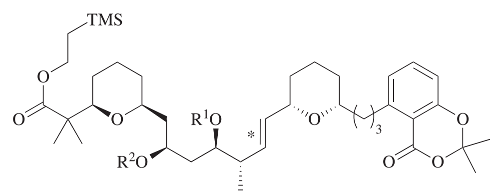
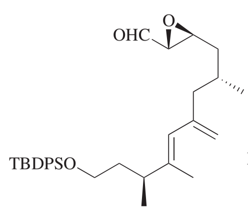
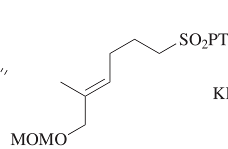
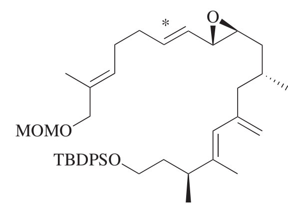
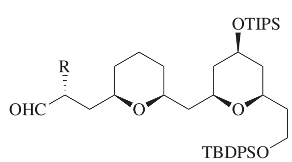
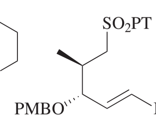
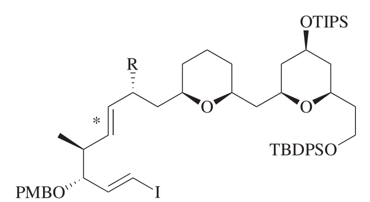
		1. LiHMDS, THF, –78° 2. Aldehyde	 (>41), $(E)/(Z)^{*}$ = —	156, 454
		1. LiHMDS, THF, –78° 2. Aldehyde, –78° to rt	 (25), $(E)^{*}$-isomer	156, 455
		1. NaHMDS, DMF/DMPU, –78°, 0.5 h 2. Aldehyde, –78° to rt, 4 h	 (61), $(E)/(Z)^{*}$ = 90:10	178

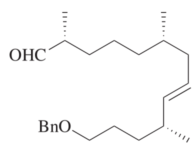
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

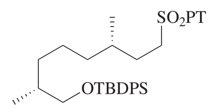
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
 	1. NaHMDS, solvent, –78°, 0.25–0.5 h 2. Aldehyde, –78° to rt, 6–15 h		
		R^1 | R^2 | Solvent | | $(E)/(Z)^*$	
		TBS | Bn | Et_2O | (83) | >95:5	456
		Bn | SEM | THF | (79) | 50:50	178
 	KHMDS, DMF, –78°, 16 h	 (75), $(E)/(Z)^*$ = 80:20	457
$C_{16–17}$			
 	1. $MN(SiMe_3)_2$, solvent 2. Aldehyde		66, 458, 459

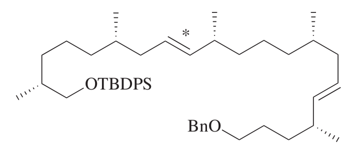
R	M	Solvent	Temp/Time (h)		(*E*)/(*Z*)*
H	Li	THF/HMPA	–78°, 0.33; rt, 3	(88)	93:7
Me	Li	THF/HMPA	–78°, 2.5; rt, 3.5	(63)	95:5
Me	Li	THF/HMPA	–78°, 0.5; rt, 2	(80)	94:6

R	M	Solvent	Temp/Time (h)		(*E*)/(*Z*)*
Me	K	DME	–55°, 1; rt, 1.5	(11)	93:7
Me	K	THF	–78°, 1; rt, 21	(14)	88:12
Me	K	THF/HMPA	–78°, 2.5; rt, 3.5	(15)	95:5

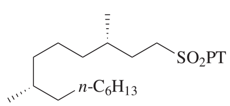
C_{16}

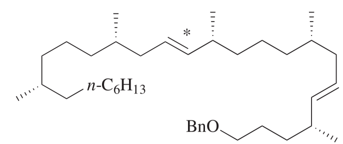




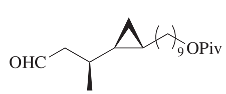
LiHMDS, THF, –78°, 3 h; then rt


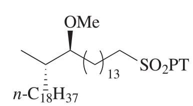
(65), (*E*)/(*Z*)* = —
168

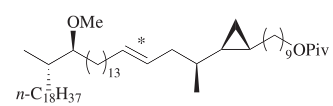


LiHMDS, THF, –78°, 3 h; then rt


(80), (*E*)/(*Z*)* = —
168

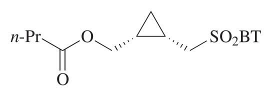
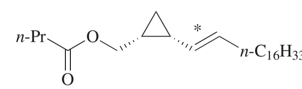
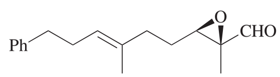
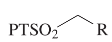
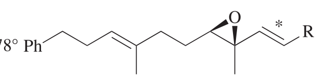
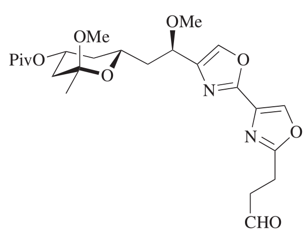
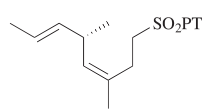
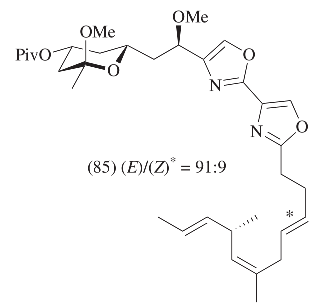




LiHMDS, THF, –20°


(54), (*E*)/(*Z*)* = —
348

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}				
n-$C_{16}H_{33}CHO$		NaHMDS, THF, –20°, 2 h; then rt, 12 h	 (68), (*E*)/(*Z*)* = 57:43	460
		1. Aldehyde (1. 0 eq), sulfone (1.6 eq), (n-$C_6H_{13})_4NBr$ (x eq), DME –78° 2. KHMDS (1.8 eq), –78°, 4 h (syringe pump); then –78°, 0.5 h; then rt, 2 h	 R / x / / (*E*)/(*Z*)*: Me 2 (88) 83:17; *i*-Pr 0 (72) 83:17; *i*-Pr 2 (88) 96:4	461
		1. KHMDS, DME, –55° 2. Aldehyde, to rt	 (85) (*E*)/(*Z*)* = 91:9	462

R	x		(*E*)/(*Z*)*
Me	2	(88)	83:17
i-Pr	0	(72)	83:17
i-Pr	2	(88)	96:4

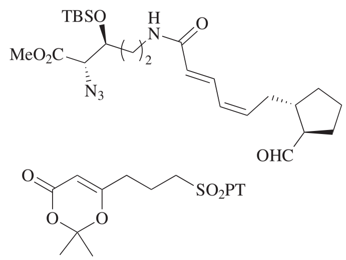
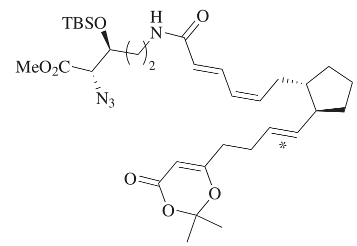
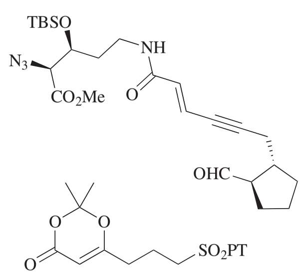
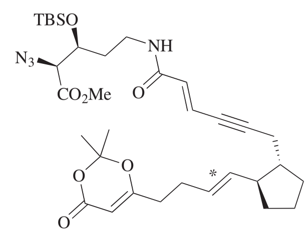
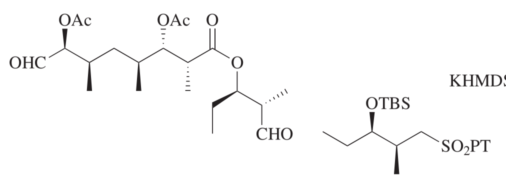
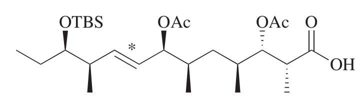
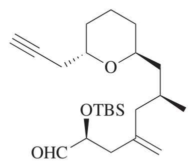
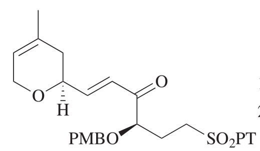
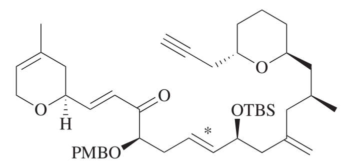
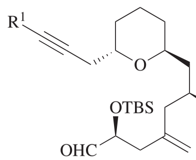
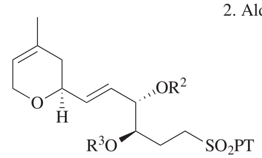
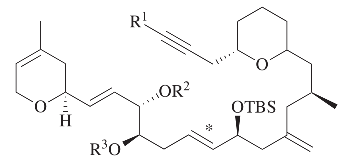
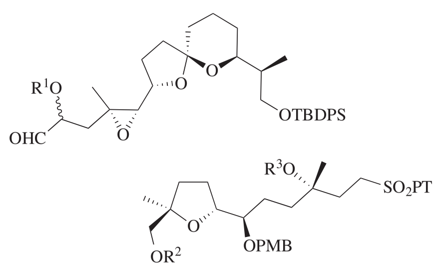
	NaHMDS, DME, –78° to rt	 (50), $(E)/(Z)^{*}$ = —	463
	NaHMDS, DME –55° to rt, 16 h	 (52), $(E)/(Z)^{*}$ = —	463
	KHMDS, THF, –78°; then rt	 (50), $(E)/(Z)^{*}$ = —	464

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

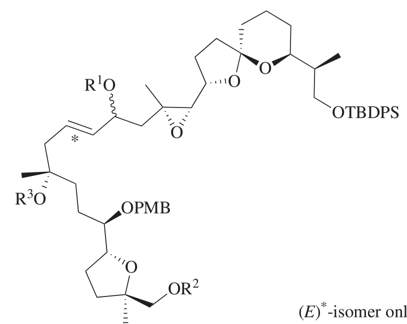
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
 	1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1.5 h	 (24), $(E)^*$-isomer only	281
$C_{17–18}$			
 	1. KHMDS, THF, –78°, 3 min 2. Aldehyde, –78°, 1.5 h		281, 465

R^1	R^2	R^3		$(E)/(Z)^*$
H	TES	PMB	(76)	100:0
H	MOM	PMB	(86)	100:0
H	TBS	PMB	(87)	100:0
H	TES	TES	(80)	100:0
Me	MOM	PMB	(74)	100:0

C_{17}

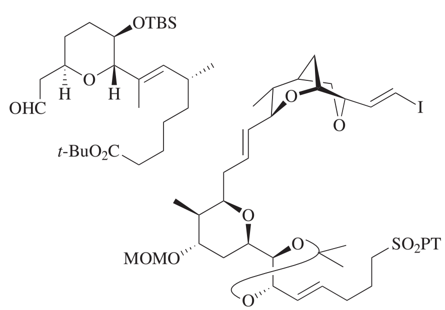


KHMDS, DME, temp, 0.5 h;
then 0°, time

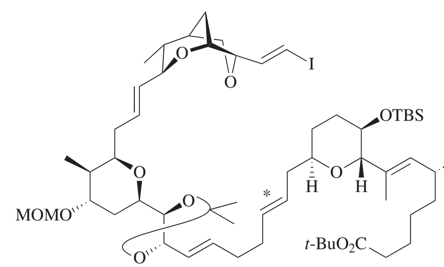


(*E*)*-isomer only

R^1	R^2	R^3	Temp (°)	Time (h)		
PMB	TBS	MOM	–75	0.25	(89)	466
TES	Bn	PMB	–70	0.5	(43)	147



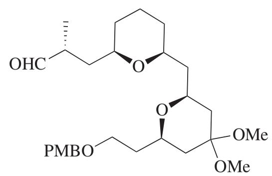
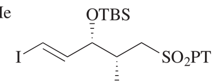
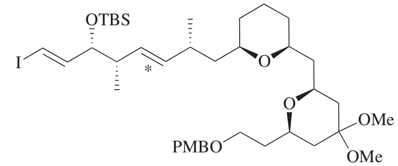
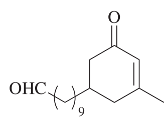
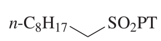
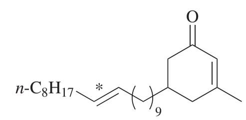
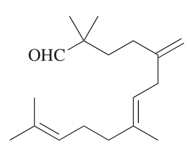
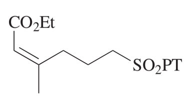
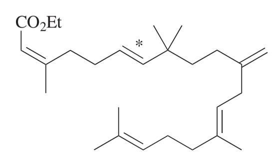
1. Base, solvent, –72°
2. Aldehyde, –72° to rt

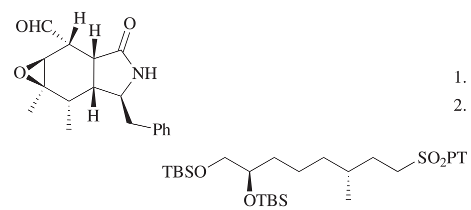


65, 405

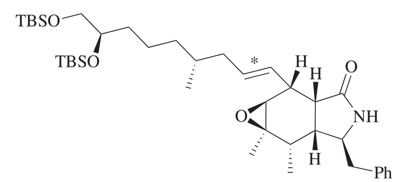
Base	Solvent		(*E*)/(*Z*)*
LiHMDS	DMF/HMPA	(30)	50:50
KHMDS	DME	(28)	100:0

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}				
		1. LiHMDS, THF/HMPA, –78°, 0.5 h 2. Aldehyde, –78°, 2 h; then rt, 15 h	 (56), (*E*)/(*Z*)* >95:5	467
		KHMDS	 (19), (*E*)/(*Z*)* = 83:17	468
		1. NaHMDS, THF/DMF, –60° 2. Bu_4NF, THF	 (92), (*E*)/(*Z*)* = 80:20	24
C_{18}				
		1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 12 h	 (80), (*E*)/(*Z*)* = 97:3	469

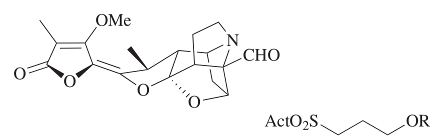


1. KHMDS, THF, –78°
2. Aldehyde, –100 to –40°

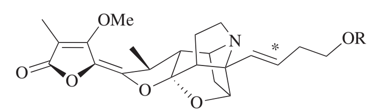


(60), $(E)^*$-isomer

470

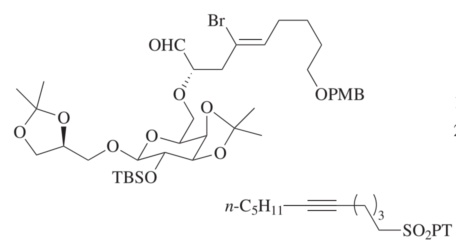


1. LiHMDS, DMF, –60°, 2 h
2. Aldehyde, –60°; then rt, 20 h

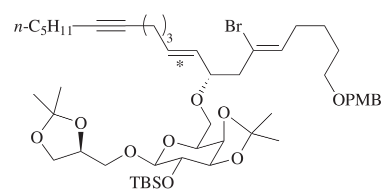


Act	R		$(E)/(Z)^*$
BT	TBS	(33)	99:1
PT	Me	(15)	99:1

471



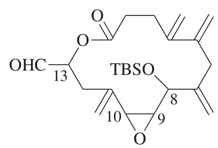
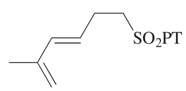
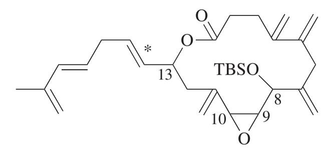
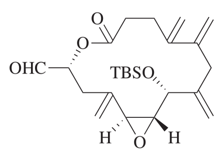
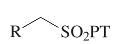
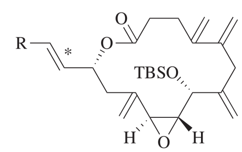
1. KHMDS, THF, –78°
2. Aldehyde



(47), $(E)/(Z)^*$ = —

472

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}			
 	1. KHMDS, solvent, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt, 0.5 h		473
 	1. KHMDS, DME/DMPU, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt, 0.5 h		473

C-8	C-9	C-10	C-13	Solvent		$(E)/(Z)^*$
(*R*)	(*S*)	(*S*)	(*R*)	THF	(—)	75:25
(*R*)	(*S*)	(*S*)	(*R*)	DME/DMPU	(70)	91:9
(*R*)	(*S*)	(*S*)	(*S*)	THF	(66)	75:25
(*S*)	(*S*)	(*S*)	(*S*)	DME/DMPU	(98)	>91:9
(*R*)	(*R*)	(*R*)	(*S*)	THF	(75)	75:25

R		$(E)/(Z)^*$
$Me_2CH(CH_2)_3$	(46)	>91:9
Bn	(28)	>91:9

C_{19}

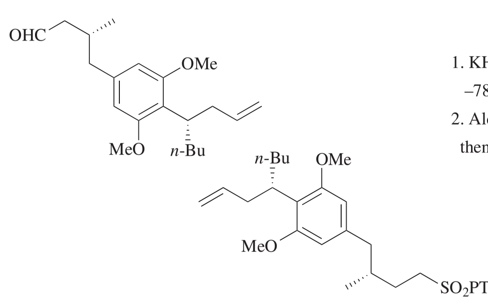
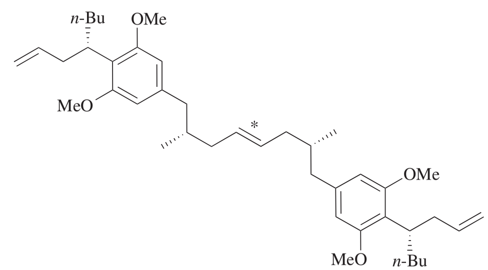
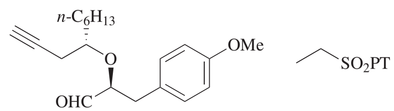
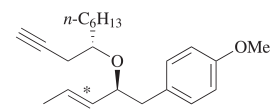
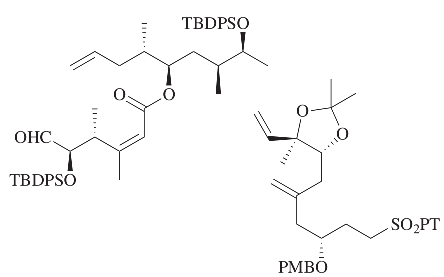
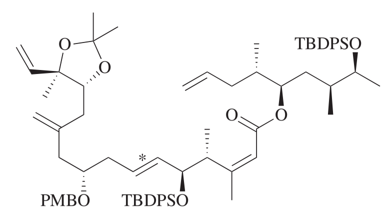
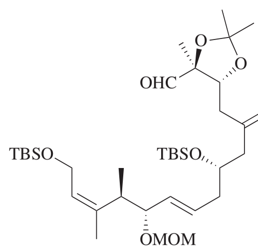
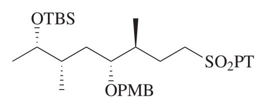
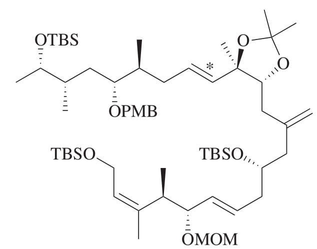
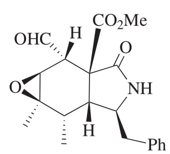
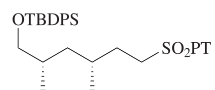
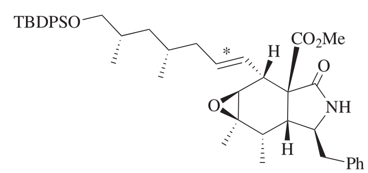
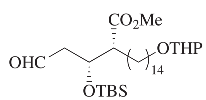
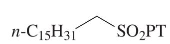
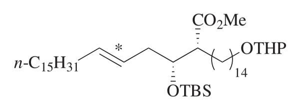
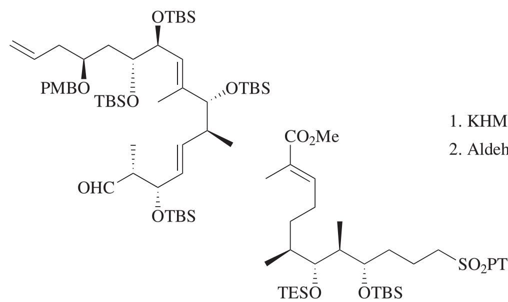
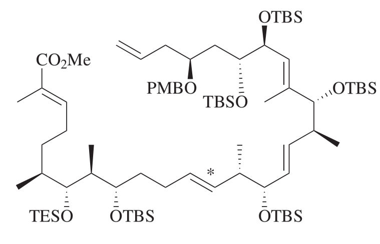
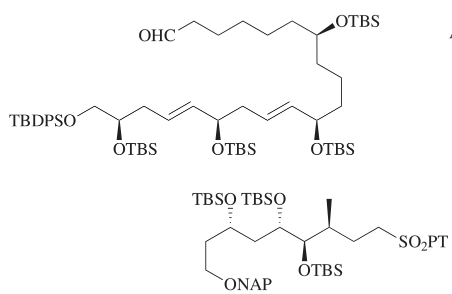
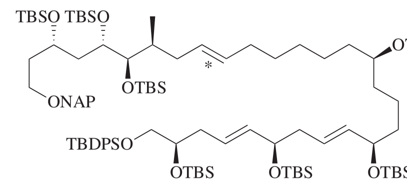
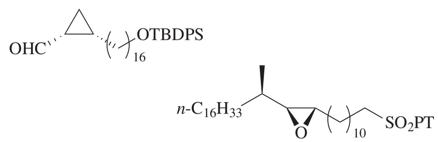
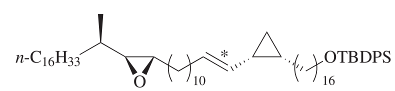
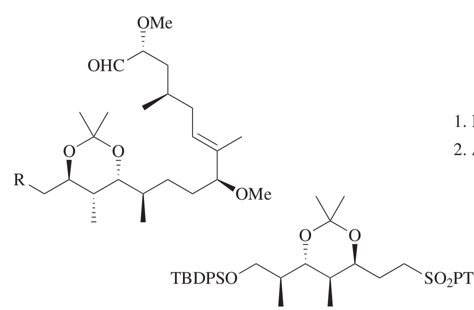
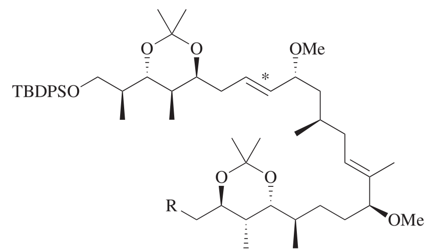
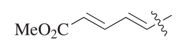
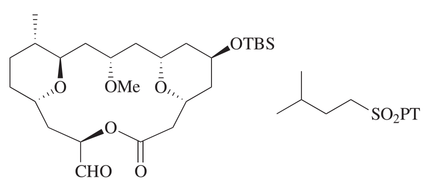
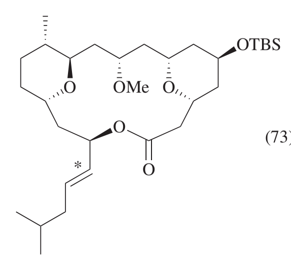
	1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h; then rt, 19 h	 (74), (*E*)/(*Z*)* >94:6	474, 475
	KHMDS, DME, –60°, 12 h	 (>20), (*E*)/(*Z*)* = —	476
	1. LiHMDS, DMF/HMPA, –50° 2. Aldehyde, –50° to rt, 16 h	 (72), (*E*)/(*Z*)* = 91:9	477

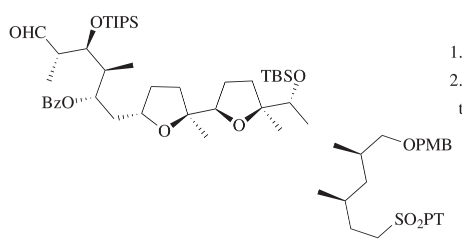
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}				
		KHMDS, DME, –78°, 1 h; then rt	 (70), $(E)^*$-isomer	323
		1. KHMDS, THF, –78° 2. Aldehyde, –100 to –40°	 (86), $(E)^*$-isomer only	470
		LiHMDS, THF, –10° to rt	 (75), $(E)/(Z)^*$ = —	304

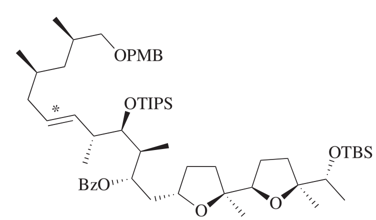
C$_{20}$

Reactants	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. KHMDS, DME, –46° 2. Aldehyde, –46° to rt	 (57), $(E)/(Z)^*$ = 88:12	124
	Aldehyde (1.0 eq), sulfone (1.6 eq), KHMDS (1.6 eq), THF, –78°, 4 h; then rt, 18 h	 (86), $(E)^*$-isomer	478
	Aldehyde (1 eq), sulfone (1.2 eq), LiHMDS (1.8 eq), THF, –10°; then to rt	 (89), dr* —	227

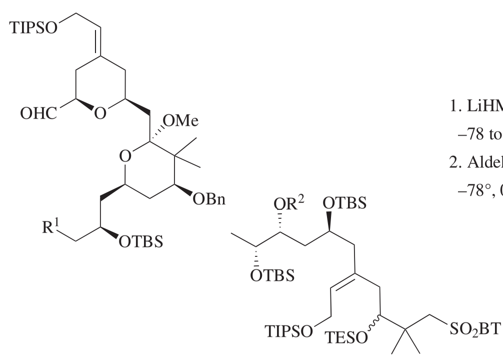
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20-24} 	1. KHMDS, DME, –78° 2. Aldehyde	 R / (E)/(Z)* $BnOCH_2$ (76) 88:12  (59) 88:12	479
C_{20} 	1. KHMDS, DME, –78° 2. Aldehyde, –78° to rt	 (73), (E)*-isomer only	480, 481



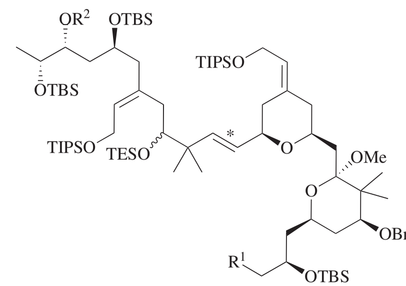
1. KHMDS, THF, −78°, 0.5 h
2. Aldehyde, −78°, 3 h; then rt, 18 h



(85), $(E)^*$-isomer only | 482

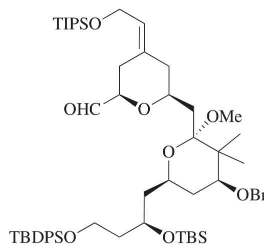
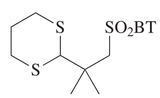
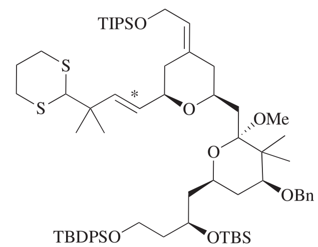
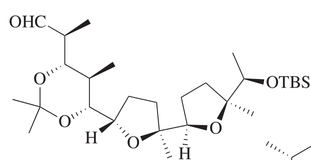
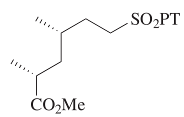
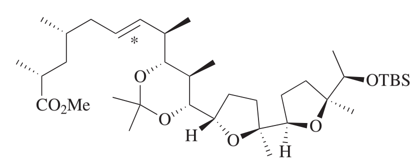


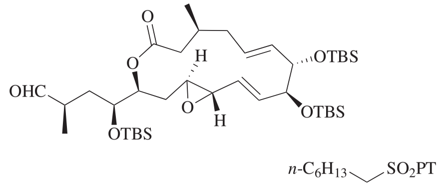
1. LiHMDS, THF, −78 to −60°, 0.5 h
2. Aldehyde, THF, −78°, 0.33 h; then rt, 0.5 h



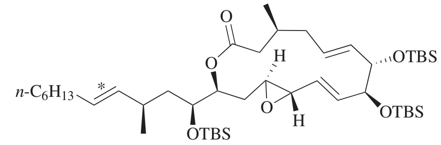
R^1	R^2	$(E)^*$-Isomer	
$TBDPSOCH_2$	SEM	(70)	324
$CH_2{=}CHCH_2O_2C$	TMS	(>60)	483

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
 	**A**: 1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 0.33 h; then rt, 2 h *or* **B**: 1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 16 h	 Conditions / (*E*)/(*Z*)* **A** (51) 100:0 **B** (78) 67:33	324
 	KHMDS, THF, –78°, 1 h; then rt	 (60), (*E*)*-isomer only	309

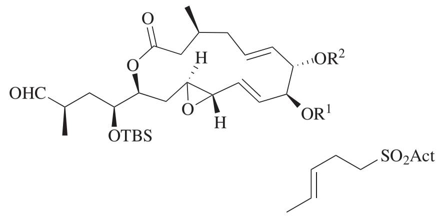


1. NaHMDS, THF/DMF, −78°, 0.67 h
2. Aldehyde, −78°, 0.75 h; then rt

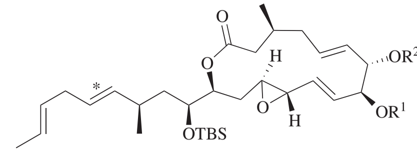


(>72), $(E)/(Z)^{*}$ = —

484

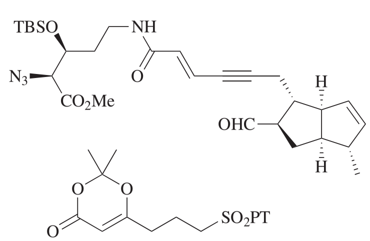


1. KHMDS, solvent, −78°, 0.67 h
2. Aldehyde, −78°, 0.75 h; then rt

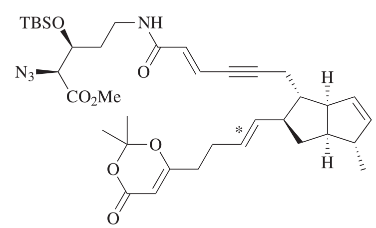


R^1	R^2	Act	Solvent		$(E)/(Z)^{*}$	
TBS	TBS	BT	THF/DMF	(>76)	93:7	484
−(Me)$_2$C−		PT	DME	(>85)	—	216

C_{21}



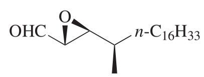
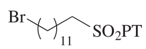
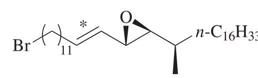
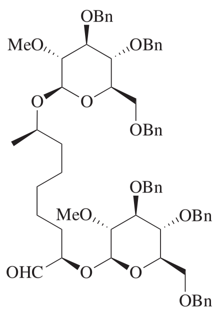
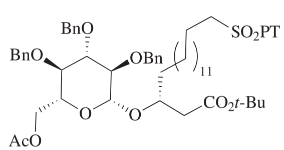
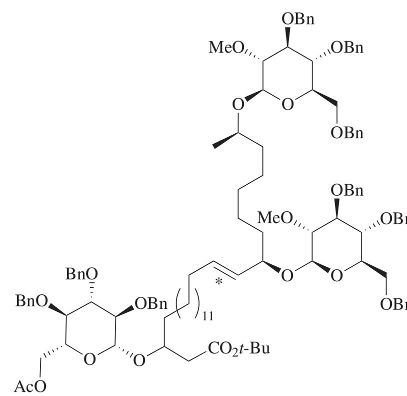
NaHMDS, DME, −55° to rt



(52), $(E)^{*}$-isomer only

485, 486

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}				
		LiHMDS, THF, –10°	 (71), (*E*)/(*Z*)* = —	270
		1. LiHMDS, DME, –78° 2. Aldehyde, –78°	 (45), (*E*)/(*Z*)* = 50:50	487

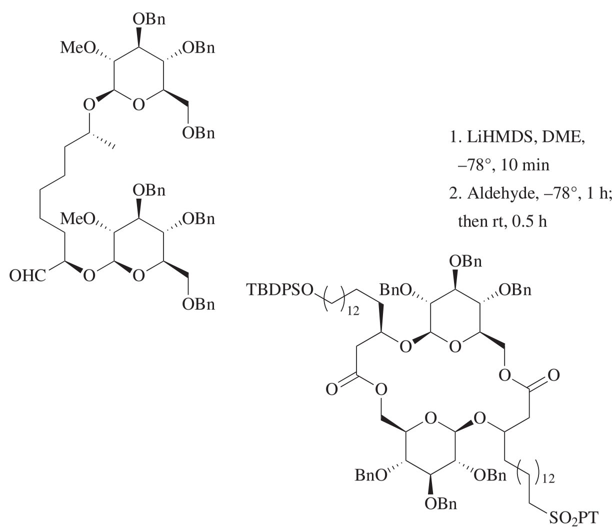
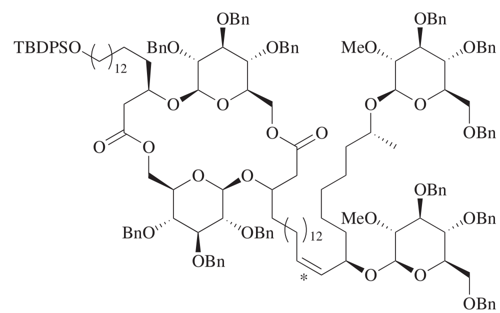
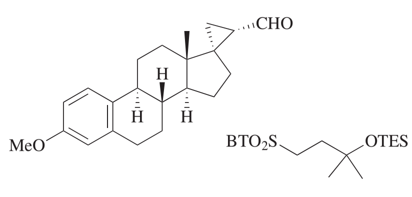
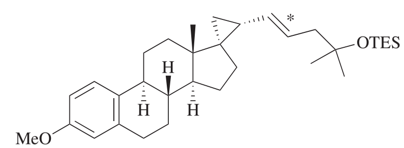
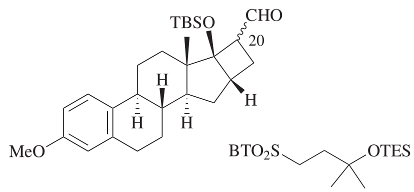
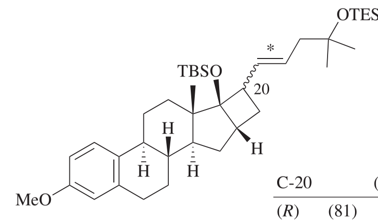
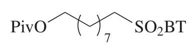
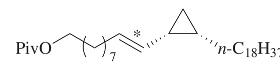
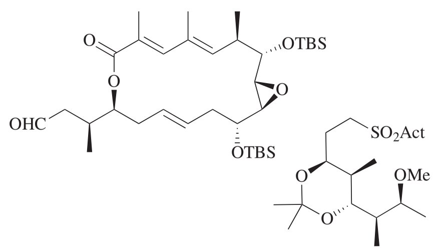
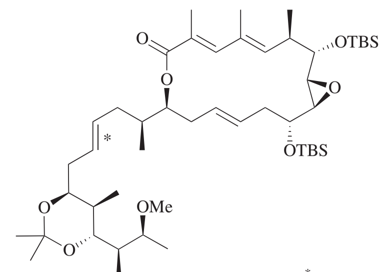
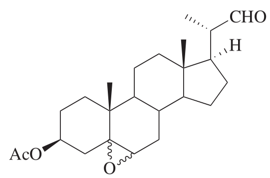
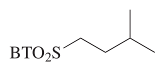
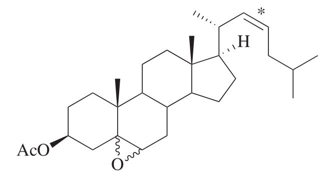
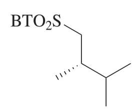
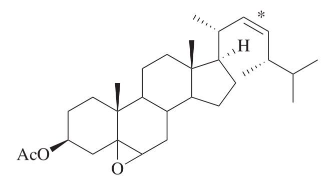
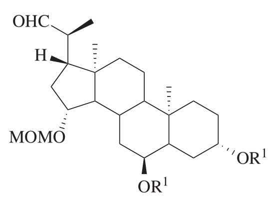
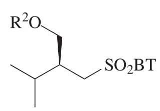
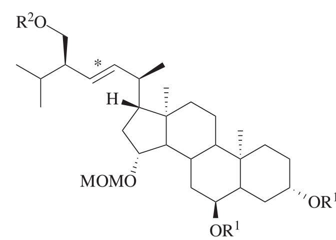
	1. LiHMDS, DME, –78°, 10 min 2. Aldehyde, –78°, 1 h; then rt, 0.5 h	 (61), $(E)/(Z)^*$ = 50:50	487, 488
	1. Sulfone (1.3 eq), LiHMDS (1.33 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –78°, 1 h	 (92), $(E)/(Z)^*$ = 80:20	489

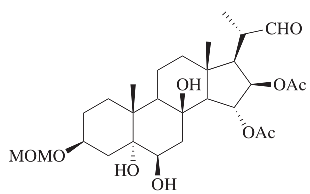
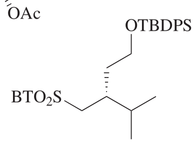
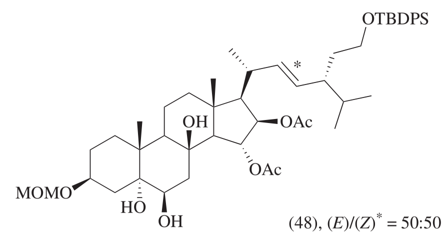
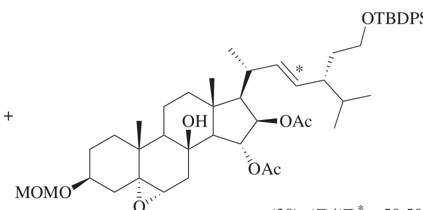
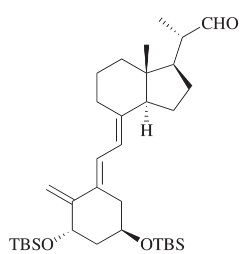
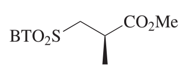
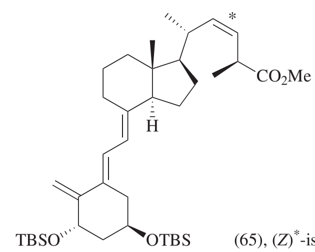
TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

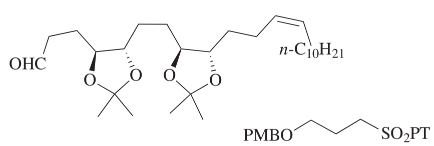
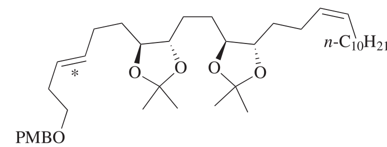
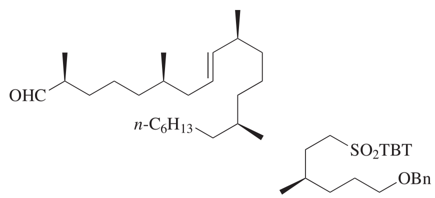
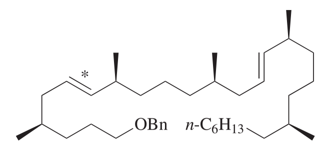
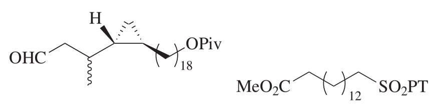
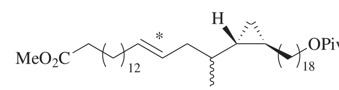
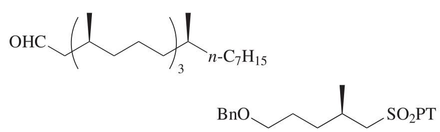
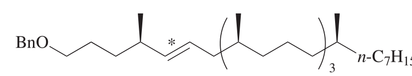
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	1. Sulfone (1.3 eq), LiHMDS (1.31 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –78°, 1 h	 C-20 / (E)/(Z)* (*R*) (81) 60:40 (*S*) (71) 50:50	489
C_{22}			
 	NaHMDS, THF, –10°, 1 h; then rt, 12 h	 (75), (*E*)/(*Z*)* = 57:43	460
	1. KHMDS, THF, –78°, 5 min 2. Aldehyde, –78°, 45 min	 Act / (E)/(Z)* BT (80) 100:0 PT (80) —	490 491

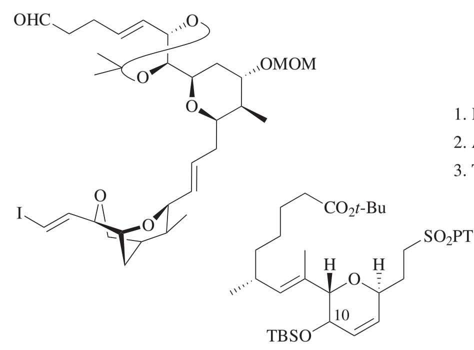
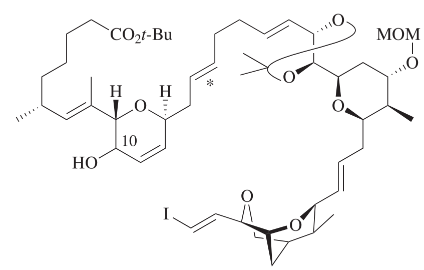
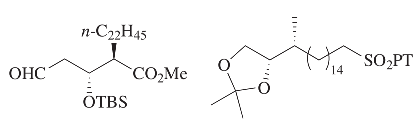
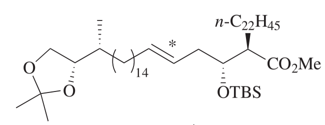
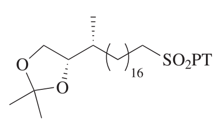
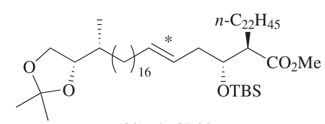
		1. LiHMDS, THF, –78°, 1 h 2. Aldehyde, THF, –78°, 1 h; then rt	 (88), $(E)/(Z)^{*}$ = 33:67	68
		1. LiHMDS, THF, –78°, 1 h 2. Aldehyde, THF, –78°, 1 h; then rt	 (90), $(Z)^{*}$-isomer only	68
		LiHMDS, THF, –78°; then rt		

R^1	R^2	$(E)^{*}$-isomer	Refs.
MOM	MOM	(57)	492
TBS	Bn	(93)	493

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
 	Aldehyde (1.0 eq), sulfone (6.2 eq), LiHMDS (9.2 eq), TMEDA (18.4 eq), THF, –78°, 1 h; then –20°, 14 h	 (48), (*E*)/(*Z*)* = 50:50 +  (30), (*E*)/(*Z*)* = 50:50	494
 	1. LiHMDS, THF, –78° 2. Aldehyde	 (65), (*Z*)*-isomer only	67, 69

C_{23}		1. KHMDS, DME, –60°, 0.33 h 2. Aldehyde, –60° to rt, 16 h	 (93), (*E*)/(*Z*)* = 93:7	495
C_{25}		1. LiHMDS, THF 2. Aldehyde, THF, –78° to rt	 (81), (*E*)/(*Z*)* = —	365, 446
		LiHMDS, THF, –15° to rt, 1 h	 Aldehyde epimer / (*E*)/(*Z*)* α (65) — β (70) —	347
C_{26}		LiHMDS, THF, –78°, 3 h; then rt	 (81), (*E*)/(*Z*)* = —	168

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}			
	1. KHMDS, DME, –72° 2. Aldehyde, –72° to rt 3. TBAF, THF	 C-10 / (*E*)/(*Z*)* (*R*) (73) 100:0 (*S*) (86) 100:0	65, 159, 405
C_{27}			
	LiHMDS, THF	 (86), (*E*)/(*Z*)* = —	269
	Aldehyde (1 eq), sulfone (1.2 eq), LiHMDS (1.6 eq), THF, –10°; then to rt, 2 h	 (89), dr 67:33	227, 270

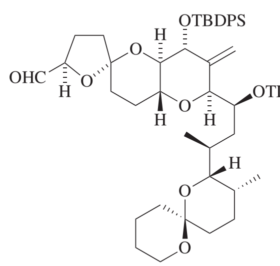
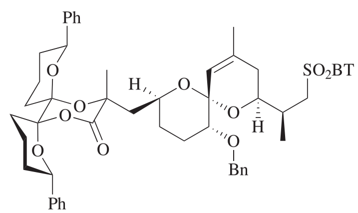
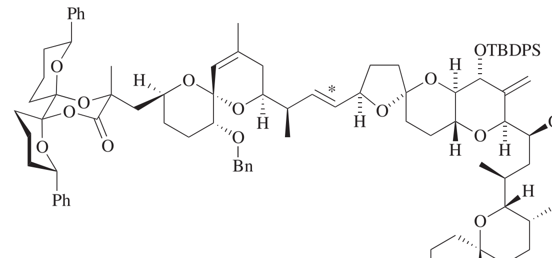
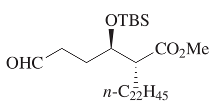
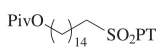
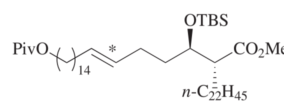
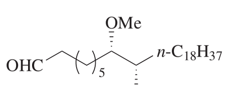
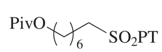
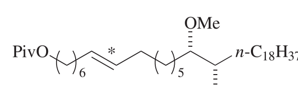
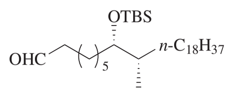
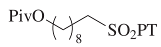
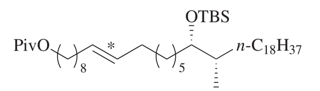
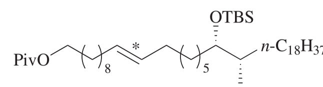
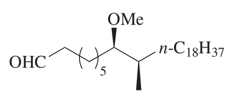
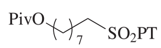
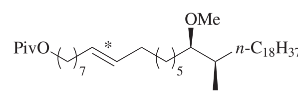
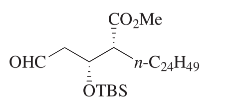
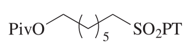
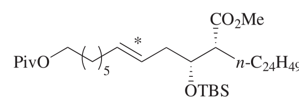
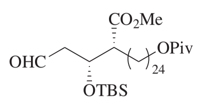
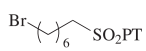
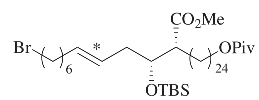
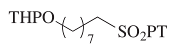
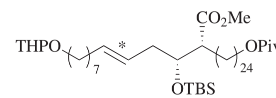
		1. NaHMDS, THF/DMF, –60° 2. Aldehyde, –60° to rt	 (66) of $(E)^*$-isomer[d]	496
C_{28}				
		LiHMDS, THF, –10° to rt	 (95), $(E)/(Z)^*$ = 67:33	303
		LiHMDS, THF, –12°	 (81), $(E)/(Z)^*$ = —	348

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}				
		LiHMDS, THF, –10°	 (91), (*E*)/(*Z*)* = 70:30	348
		LiHMDS, THF, –10° to rt, 1.5 h	 (92), isomeric ratio* = 70:30	305
		LiHMDS, THF, –2°; then rt, 16 h	 (91), (*E*)/(*Z*)* = 72:28	228
C_{29}				
		LiHMDS, THF, –15°	 (72), (*E*)/(*Z*)* = —	348
		LiHMDS, THF, –10° to rt	 (76), (*E*)/(*Z*)* = 67:33	304

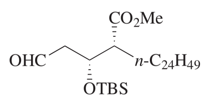


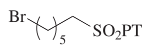
LiHMDS, THF, –10° to rt



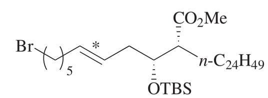
(85), $(E)/(Z)^*$ = 72:28

304



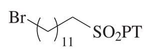


LiHMDS, THF, –12°

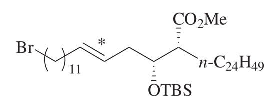


(94), $(E)/(Z)^*$ = 67:33

348



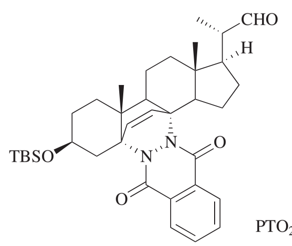
LiHMDS, THF, –12° to rt, 3 h

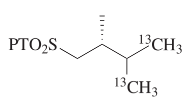


(82), $(E)/(Z)^*$ = 66:34

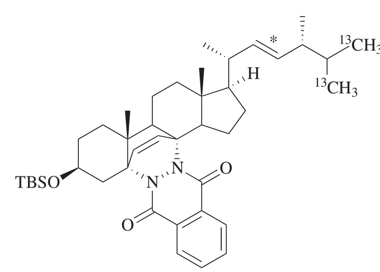
305

C_{30}





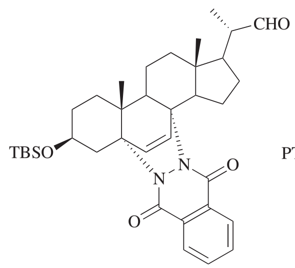
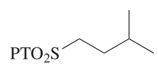
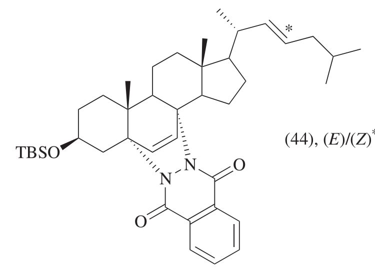
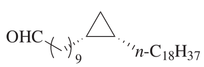
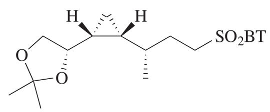
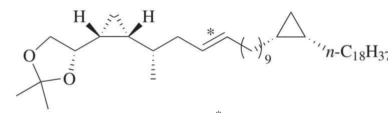
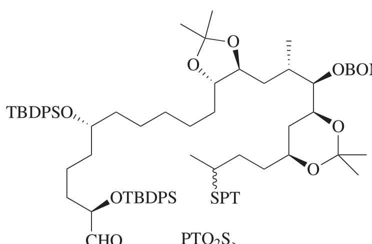
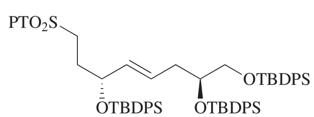
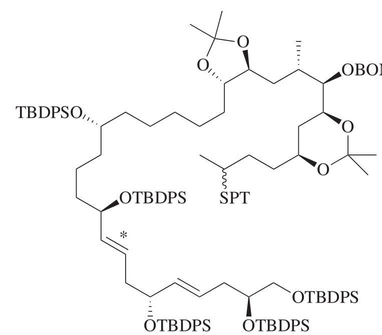
1. KHMDS, THF,
 –60 to –78°, 1 h
2. Aldehyde, –78°, 1 h;
 then rt, 20 h



(24), $(E)/(Z)^*$ = —

497

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30}  	1. Sulfone (1.1 eq), KHMDS (1.0 eq), THF, –78°, 1 h 2. Aldehyde (1.0 eq), –78°, 1 h; then rt, overnight	 (44), (*E*)/(*Z*)[*] = 86:14	498
C_{31}  	LiHMDS, THF, –5° to rt, 16 h	 (78), (*E*)/(*Z*)[*] = —	460
 	KHMDS, THF, –78°, 4 h; then rt, 12 h	 (81), (*E*)/(*Z*)[*] = 90:10	213

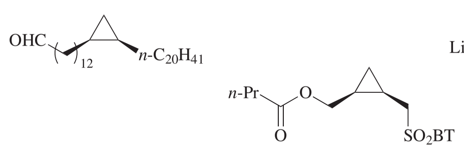
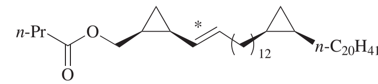
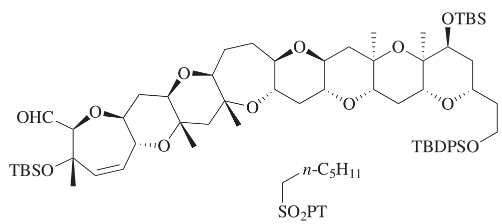
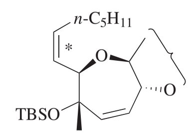
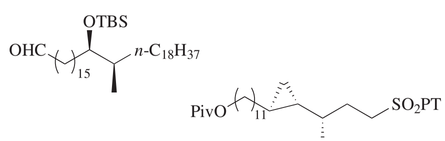
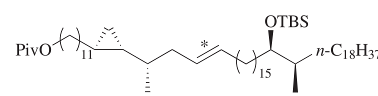
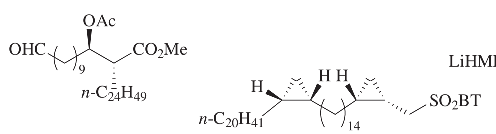
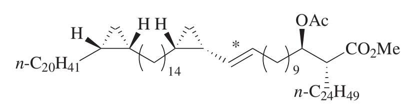
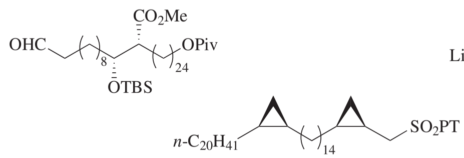
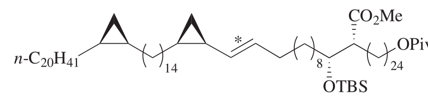
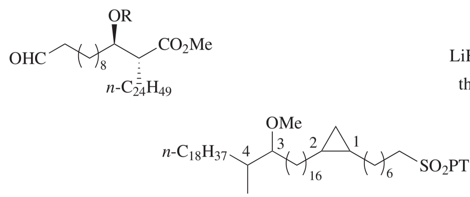
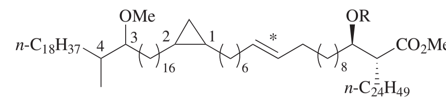
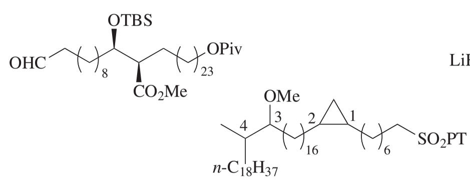
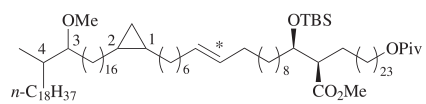
C_{36}			
	LiHMDS, THF, –15° to rt, 24 h	 (43), (*E*)/(*Z*)* = 50:50	499, 500
	1. KHMDS, THF, –78°, 0.67 h 2. Aldehyde, –78°; then rt	 (70), (*E*)/(*Z*)* = 33:67	501
C_{37}			
	LiHMDS, THF, –12°	 (80), (*E*)/(*Z*)* = 75:25	348
	LiHMDS, THF, –5° to rt, 24 h	 (37) (*E*)/(*Z*)* = 63:37	499, 500

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

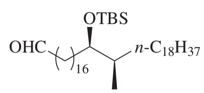
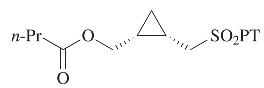
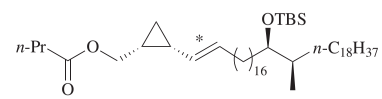
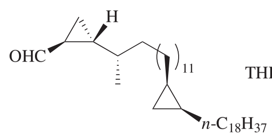
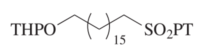
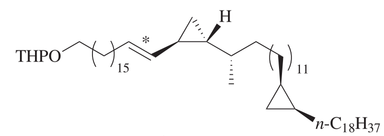
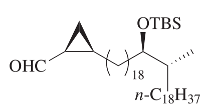
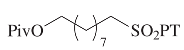
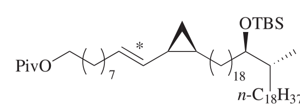
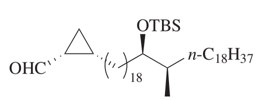
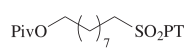
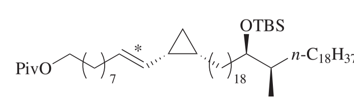
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{37}			
	LiHMDS, THF, –10° to rt	 (60), (*E*)/(*Z*)* = —	304
	LiHMDS, THF, –12°; then rt, 1–2 h		228
	LiHMDS, THF, –10° to rt		304

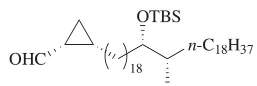
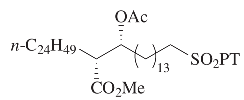
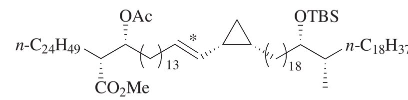
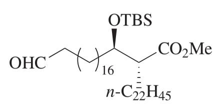
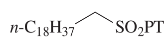
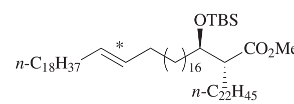
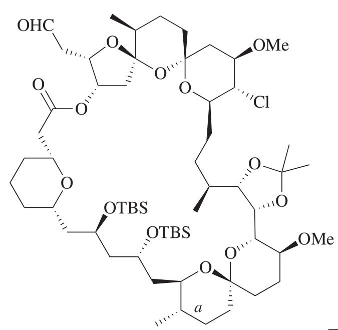
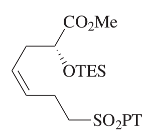
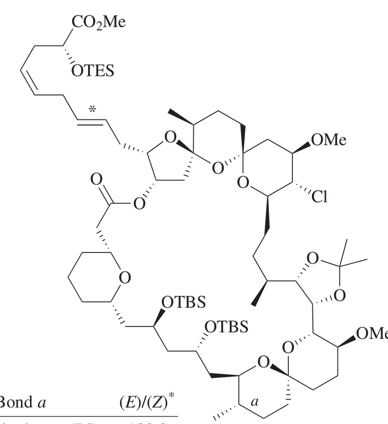
Products of the reaction with ref. 228:

R	C-1	C-2	C-3	C-4		(*E*)/(*Z*)*
Ac	(*R*)	(*R*)	(*R*)	(*R*)	(68)	71:29
Ac	(*S*)	(*S*)	(*R*)	(*R*)	(60)	70:30
TBS	(*R*)	(*R*)	(*S*)	(*S*)	(80)	—
TBS	(*R*)	(*R*)	(*R*)	(*R*)	(77)	63:37

Products of the last reaction (ref. 304):

C-1	C-2	C-3	C-4		(*E*)/(*Z*)*
(*R*)	(*S*)	(*S*)	(*S*)	(71)	67:33
(*S*)	(*R*)	(*R*)	(*R*)	(89)	67:33

C_{38}				
		LiHMDS, THF, –10° to rt, 1.5 h	 (91), (*E*)/(Z)* = 62:38	305, 502
C_{39}				
		LiHMDS, THF, –2° to rt, 2 h	 (90) (*E*)/(*Z*)*mixture	460
C_{43}				
		LiHMDS, THF	 (87) (*E*)/(*Z*)* = —	502
		LiHMDS, THF, –12° to rt, 2 h	 (87) isomeric ratio* = 86:14	305

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{43}			
 	LiHMDS, THF, –12° to rt, 2 h	 (72), isomeric ratio* = 80:20	305
 	LiHMDS, THF, –10° to rt	 (70), (*E*)/(*Z*)* = —	303
 	1. KHMDS, THF, –78°, 10 min; then to –60°, 2 h 2. Aldehyde, –78 to –65°, 1.5 h		503, 504

Bond *a*		(*E*)/(*Z*)*
single	(76)	100:0
double	(69)	100:0

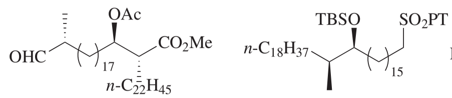
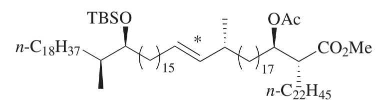
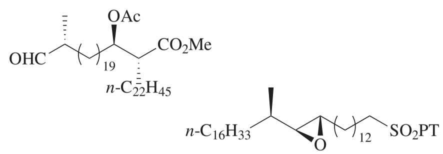
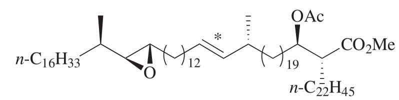
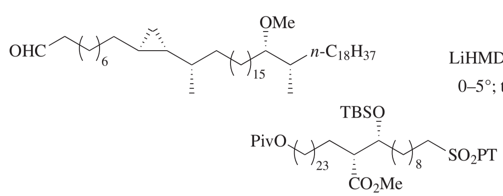
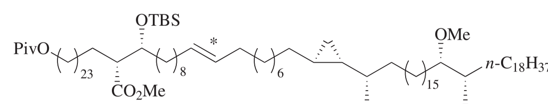
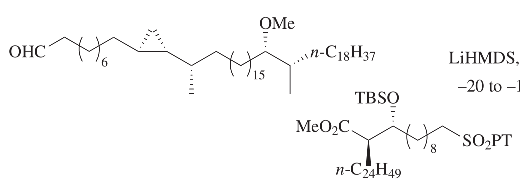
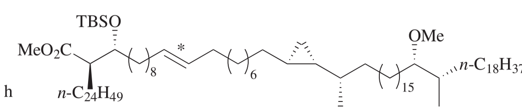
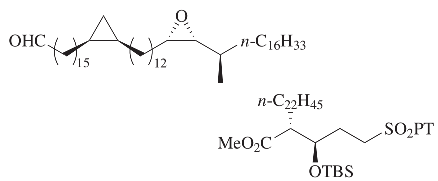
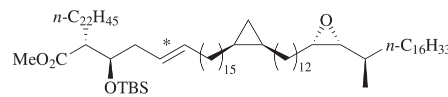
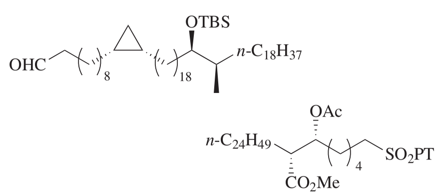
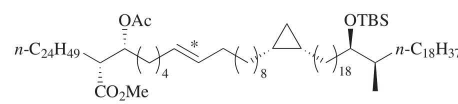
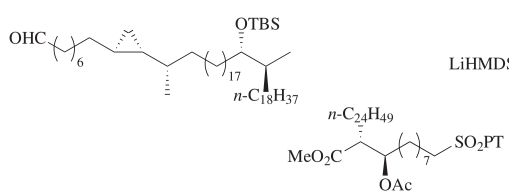
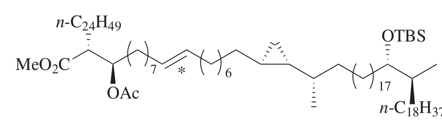
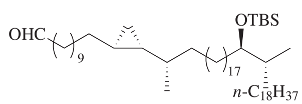
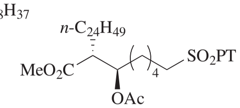
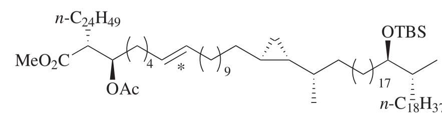
C_{45}				
		KHMDS, DME	 (44), $(E)^{*}$-isomer	269
C_{47}				
		Aldehyde (1 eq), sulfone (1.2 eq), KHMDS (1.6 eq), DME, –5°; then to 10°	 (26), $(E)/(Z)^{*}$ = —	227, 270
C_{51}				
		LiHMDS, THF, 0–5°; then rt	 (86), $(E)/(Z)^{*}$ = —	304
		LiHMDS, THF, –20 to –10°; then rt, 1 h	 (28), $(E)/(Z)^{*}$ = —	348

TABLE 3. SYNTHESIS OF NON-CONJUGATED 1,2-DISUBSTITUTED ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{51}			
	Aldehyde (1 eq), sulfone (1.2 eq), LiHMDS (1.7 eq), THF, –2°; then to rt, 1.5 h	 (68), (*E*)/(*Z*)* = —	227
C_{52}			
	LiHMDS, THF, –12° to rt, 2 h	 (56), isomeric ratio* = 66:34	305, 502
	LiHMDS, THF, –12°	 (47), (*E*)/(*Z*)* = 73:27	348

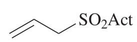
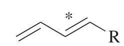
C_{55}	 	LiHMDS, THF, –5°	 (52), $(E)/(Z)^*$ = 67:33	348

[a] The corresponding Wittig reaction proceeded in 76% yield.

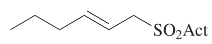
[b] The aldehyde was added immediately.

[c] With KHMDS at –78°, the yield was 80%, $(E)/(Z)^*$ = 89:11. With LDA, –78 to 0° the yield was 95%, $(E)/(Z)^*$ = 74:26.

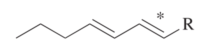
[d] A small quantity of the (Z)-isomer was detected by ^{1}H NMR spectroscopy.

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-9}			
RCHO  Act = PT or BT	**A**: KHMDS, THF, –78° *or* **B**: KHMDS, DMF, –55° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde *or* **D**: 1. KHMDS, DMF/TDA, –60°, 2 min 2. Aldehyde		32

R	Conditions	Act = PT		Act = BT	
			(*E*)/(*Z*)*		(*E*)/(*Z*)*
$BnOCH_2$	**A**	(82)	66:34	(72)	56:44
$BnOCH_2$	**B**	(67)	55:45	(66)	52:48
$BnOCH_2$	**C**	(63)	69:31	(70)	68:32
$BnOCH_2$	**D**	(72)	72:28	(71)	70:30
$BnO(CH_2)_2$	**A**	(68)	79:21	(69)	65:35
$BnO(CH_2)_2$	**B**	(47)	62:38	(65)	52:48
$BnO(CH_2)_2$	**C**	(36)	15:85	(73)	20:80
$BnO(CH_2)_2$	**D**	(48)	14:86	(74)	19:81
$Ph(CH_2)_2$	**A**	(72)	63:37	(68)	59:41
$Ph(CH_2)_2$	**B**	(65)	58:42	(53)	57:43
$Ph(CH_2)_2$	**C**	(74)	15:85	(39)	30:70
$Ph(CH_2)_2$	**D**	(78)	14:86	(42)	20:80



A:
KHMDS, THF, –78°
or **B**:
KHMDS, DMF, –55°
or **C**:
1. KHMDS, 18-crown-6, DMF, –55°, 2 min
2. Aldehyde
or **D**:
1. KHMDS, DMF/TDA, –60°, 2 min
2. Aldehyde

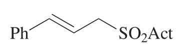
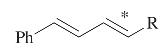


32

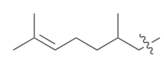
R	Conditions	Act = PT	
			(E)/(Z)*
$BnOCH_2$	**A**	(69)	55:45
$BnOCH_2$	**B**	(59)	66:34
$BnOCH_2$	**C**	(55)	75:25
$BnOCH_2$	**D**	(56)	74:26
$TBDPSOCH_2(BnO)CH$	**A**	(82)	62:38
$TBDPSOCH_2(BnO)CH$	**B**	(69)	54:46
$TBDPSOCH_2(BnO)CH$	**C**	(50)	83:17
$TBDPSOCH_2(BnO)CH$	**D**	(62)	82:18

R	Conditions	Act = PT		Act = BT	
			(E)/(Z)*		(E)/(Z)*
TBSO(Me)CH	**A**	(59)	61:39	(68)	55:45
TBSO(Me)CH	**B**	(65)	70:30	(69)	60:40
TBSO(Me)CH	**C**	(58)	94:6	(65)	90:10
TBSO(Me)CH	**D**	(63)	96:4	(70)	91:9
$c\text{-}C_6H_{11}$	**A**	(73)	65:35		
$c\text{-}C_6H_{11}$	**B**	(63)	51:49		
$c\text{-}C_6H_{11}$	**C**	(59)	77:23		
$c\text{-}C_6H_{11}$	**D**	(68)	82:18		
$Ph(CH_2)_2$	**A**	(65)	71:29	(75)	58:42
$Ph(CH_2)_2$	**B**	(58)	40:60	(72)	55:45
$Ph(CH_2)_2$	**C**	(50)	16:84	(69)	20:80
$Ph(CH_2)_2$	**D**	(40)	13:87	(73)	17:83

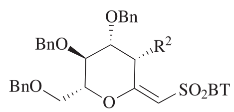
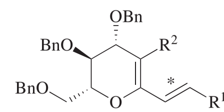
TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-10}			
RCHO  Act = PT or BT	**A**: KHMDS, THF, –78° *or* **B**: KHMDS, DMF, –55° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde *or* **D**: 1. KHMDS, DMF/TDA, –60°, 2 min 2. Aldehyde		32

R	Conditions	Act = PT	
			(*E*)/(*Z*)*
$BnOCH_2$	**A**	(81)	42:58
$BnOCH_2$	**B**	(63)	55:45
$BnOCH_2$	**C**	(55)	60:40
$BnOCH_2$	**D**	(69)	56:44
$TBDPSOCH_2(BnO)CH$	**A**	(81)	55:45
$TBDPSOCH_2(BnO)CH$	**B**	(75)	63:47 (sic)
$TBDPSOCH_2(BnO)CH$	**C**	(72)	88:12
$TBDPSOCH_2(BnO)CH$	**D**	(80)	82:18
t-Bu	**A**	(66)	58:42
t-Bu	**B**	(52)	69:21 (sic)
t-Bu	**C**	(45)	92:8
t-Bu	**D**	(49)	95:5

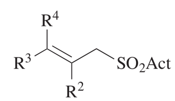
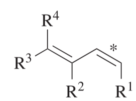
R	Conditions	Act = PT		Act = BT	
			(*E*)/(*Z*)*		(*E*)/(*Z*)*
$Ph(CH_2)_2$	**A**	(68)	56:44	(86)	57:43
$Ph(CH_2)_2$	**B**	(69)	52:48	(79)	55:45
$Ph(CH_2)_2$	**C**	(59)	16:84	(82)	18:82
$Ph(CH_2)_2$	**D**	(60)	14:86	(85)	15:85
	**A**	(57)	65:35		
	B	(53)	60:40		
	C	(36)	15:85		
	D	(48)	14:86		

C_{2-13}

Reactant	Sulfone	Conditions	Product	Yield	Refs.
R^1CHO		LiHMDS, THF, –78°, 0.5 h; then rt, 1 h		(E)*-isomer only	505

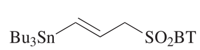
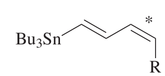
R^1	R^2	
Me	H	(24)
2-furyl	H	(70)
2- (1-methylpyrrolyl)	H	(65)
2-pyridyl	H	(85)
4-ClC_6H_4	H	(72)
4-ClC_6H_4	BnO	(0)
3-$MeOC_6H_4$	H	(64)
3,4,5-$(MeO)_3C_6H_2$	H	(66)
3-HOC_6H_4	H	(66)
2-naphthyl	H	(54)
2-(9*H*)-fluorenyl	H	(50)

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-10}				
R^1CHO		**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt *or* **B**: LDA, THF, –78°, 3 h; then rt, 1h *or* **C**: 1. *n*-BuLi, LiBr, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt		3

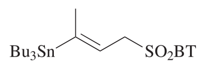
R^1	R^2	R^3	R^4	Act	Conditions		E)/(Z)*
Et	H	Ph	H	BT	**A**	(38)	33:67
Et	H	Ph	H	BT	**B**	(32)	40:60
n-Bu	H	*n*-C_8H_{17}	H	BT	**A**	(51)	52:48
n-C_6H_{13}	H	Me	Me	BT	**A**	(75)	53:47
n-C_6H_{13}	H	Me	Me	BT	**B**	(87)	45:55
n-C_6H_{13}	H	Me	Me	PYR	**C**	(73)	7:93

R^1	R^2	R^3	R^4	Act	Conditions		(E)/(Z)*
n-C_8H_{17}	H	H	H	BT	**A**	(66)	40:60
n-C_8H_{17}	H	H	H	BT	**A**[a]	(85)	55:45
n-C_8H_{17}	H	H	H	PYR	**C**	(25)	19:81
n-C_8H_{17}	Me	H	H	BT	**A**	(43)	42:58
n-C_8H_{17}	Me	H	H	BT	**B**	(46)	28:72
n-C_8H_{17}	Me	H	H	PYR	**C**[a]	(25)	>99:1
n-C_9H_{19}	H	H	H	BT	**A**	(78)	32:68

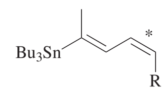
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-7}				
RCHO		1. Base, solvent, –78° 2. Aldehyde, –78° to rt		77

R	Base	Solvent		(E)/(Z)*
Et	LDA	THF	(60)	40:60
Et	KHMDS	toluene	(61)	8:92
Et	KHMDS	THF	(50)	9:91
Ph	LDA	THF	(61)	36:64
Ph	KHMDS	toluene	(62)	54:46
Ph	KHMDS	THF	(58)	16:84

C$_{3-9}$



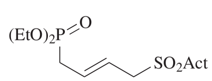
1. Base, THF, –78°
2. Aldehyde, –78° to rt



R	Base		$(E)/(Z)^*$
Et	LDA	(68)	37:63
Et	KHMDS	(54)	4:96
Ph	LDA	(60)	17:83
Ph	KHMDS	(55)	15:85

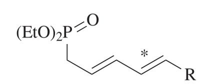
77

RCHO



Act = PT or BT

1. THF, KHMDS, –78°, 5 min
2. Aldehyde, –78°, 20 min;
then 0°, 1 h

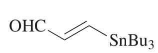


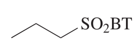
115

R	Act = PT		Act = BT	
		$(E)/(Z)^*$		$(E)/(Z)^*$
Et	(75)	91:9	(81)	75:25
i-Pr	(72)	89:11		
t-Bu	(70)	>95:5		
n-C_5H_{11}	(78)	>95:5		

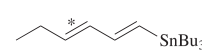
R	Act = PT		Act = BT	
		$(E)/(Z)^*$		$(E)/(Z)^*$
c-C_5H_9	(67)	95:5		
c-C_6H_{11}	(72)	91:9	(61)	86:14
$Ph(CH_2)_2$	(85)	90:10	(74)	78:22
$MeO_2C(CH_2)_7$	(70)	91:9		

C$_3$





1. Base, THF, –78°
2. Aldehyde, –78° to rt



Base		$(E)/(Z)^*$
LDA	(78)	53:47
KHMDS	(78)	61:39

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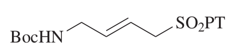
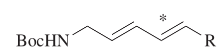
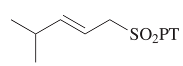
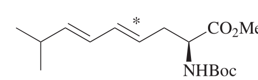
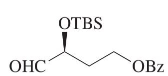
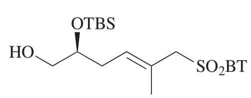
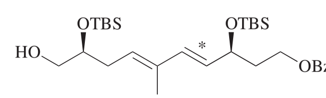
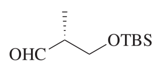
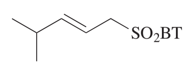
TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-7}				
RCHO		**1A**: Sulfone, LiHMDS (2.1 eq), THF, –78°, 0.5 h *or* **1B**: Sulfone, KHMDS (2.1 eq), 18-crown-6, THF, –78°, 0.5 h 2. Sulfone metallate added to aldehyde, –78°; then rt		506

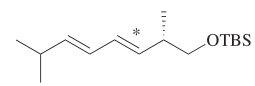
R	Condition **1A**		Condition **1B**	
		$(E)/(Z)^*$		$(E)/(Z)^*$
i-Pr	(76)	63:37	(73)	78:22
t-Bu	(88)	95:5	(23)	95:5
n-C_5H_{11}	(80)	29:71	(78)	71:29
2-furyl	(59)	34:66	(75)	84:16
Ph	(72)	13:87	(72)	72:28

R	Condition **1A**		Condition **1B**	
		$(E)/(Z)^*$		$(E)/(Z)^*$
4-ClC_6H_4	(86)	23:77	(75)	77:23
4-$O_2NC_6H_4$	(65)	65:35	(67)	80:20
4-$MeOC_6H_4$	(91)	13:87	(75)	70:30
4-$CF_3C_6H_4$	(82)	16:84	(63)	80:20
4-NCC_6H_4	(95)	25:75	(86)	75:25

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		KHMDS, DMF/HMPA	 (>70), $(E)/(Z)^*$ = 80:20	507
		1. LDA (2 eq), THF, –78°, 5 min 2. Aldehyde, –78° to rt, 3 h	 (57), $(E)^*$-isomer	508

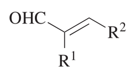
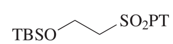
 

1. NaHMDS, THF, –78°, 0.5 h
2. Aldehyde, –78°, 3 h; then rt, 1 h

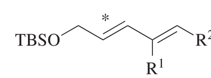


(75), $(E)/(Z)^*$ = 80:20 509

C_{4-9}

$KN(SiMe_3)_2$, solvent, –78°, 0.5 h; then rt



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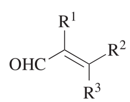
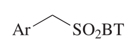
R^1	R^2	Solvent		$(E)/(Z)^*$
Me	H	THF	(91)	96:4
H	Ph	DME	(69)	99:1
H	Ph	THF	(81)	97:3

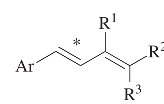
C_{4-7}

A:
1. LDA, THF, –78°, 1 h
2. Aldehyde, –78°, 3 h; then rt

or **B**:
LDA, THF, –78°, 3 h; then rt, 1 h

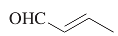
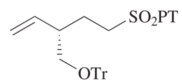
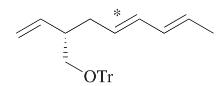
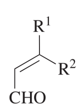
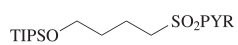
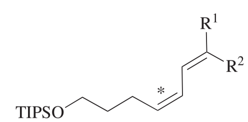
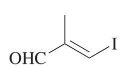
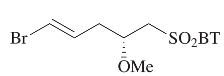
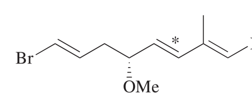
or **C**:
1. *n*-BuLi, THF, –78°, 1 h
2. Aldehyde, –78°, 3 h; then rt



3

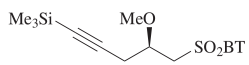
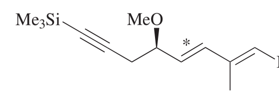
R^1	R^2	R^3	Ar	Conditions		$(E)/(Z)^*$
Me	H	H	Ph	**A**	(93)	90:10
Me	H	H	Ph	**B**	(73)	93:7
H	Me	Me	Ph	**A**	(53)	98:2
H	Me	Me	Ph	**B**	(70)	98:2
H	Me	Me	4-$MeOC_6H_4$	**A**	(61)	88:12
–$(CH_2)_4$–		H	Ph	**A**	(30)	99:1
–$(CH_2)_4$–		H	Ph	**B**	(71)	>99:1

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

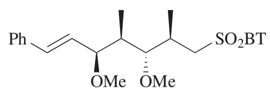
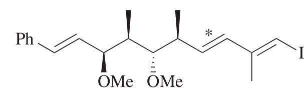
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		**A**: 1. $MN(SiMe_3)_2$, DME, –78° 2. Aldehyde; then rt *or* **B**: $MN(SiMe_3)_2$, DME, –78°; then rt		70
$C_{4–9}$				
		1. $MN(SiMe_3)_2$, toluene, temp 2. Aldehyde		34, 35
C_4				
		NaHMDS, THF, –78° to rt	 (75), (*E*)/(*Z*)* >95:5	510

M	Conditions		(*E*)/(*Z*)*
Li	**A**	(81)	80:20
K	**B**	(69)	94:6

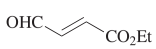
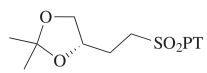
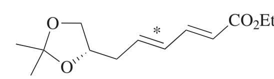
R^1	R^2	M	Temp		(*E*)/(*Z*)*
Me	H	K	–78°	(35)	16:84
Me	H	K	0°	(53)	10:90
Me	H	K	rt	(67)	9:91
Me	H	Na	rt	(54)	9:91
Pr	H	K	rt	(64)	10:90
$Me_2C{=}CH(CH_2)_2$	Me	K	rt	(64)	12:88
$Me_2C{=}CH(CH_2)_2$	Me	Na	rt	(73)	17:83
Ph	H	K	rt	(70)	8:92

 NaHMDS, DMF, –60°, 1 h  511

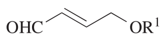
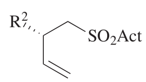
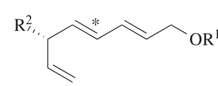
(90), $(E)/(Z)^*$ = 94:6

 NaHMDS, THF, –78°, 0.5 h; then rt, 0.5 h  512

(43), $(E)/(Z)^*$ = —

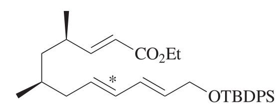
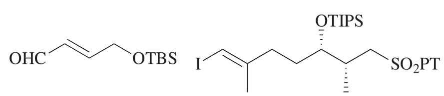
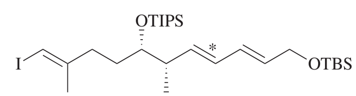
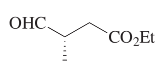
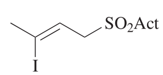
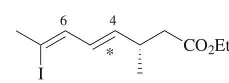
  KHMDS, THF, –78°, 3 h; then rt, 2 h  328

(77), $(E)/(Z)^*$ = 74:26

  1. $MN(SiMe_3)_2$, solvent, –78°
2. Aldehyde (x eq); then to rt  49

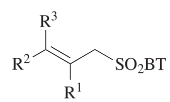
R^1	R^2	Act	M	Solvent	x		$(E)/(Z)^*$
PMB	Me	PT	Li	DME	1.0	(71)	84:16
PMB	Me	PT	Li	DME	1.5	(88)	88:12
PMB	Me	PT	K	THF	1.1	(58)	69:31
PMB	Me	PT	K	DME	1.0	(47)	88:12
PMB	Me	BT	K	DME	1.1	(80)	—
PMB	Et	PT	Li	DME	1.0	(93)	85:15
PMB	Et	BT	Li	DME	1.0	(83)	89:11

R^1	R^2	Act	M	Solvent	x		$(E)/(Z)^*$
TBDPS	Me	PT	Li	DME	1.1	(82)	88:12
TBDPS	Me	PT	K	DME	1.0	(54)	90:10
TBDPS	Me	PT	K	THF	1.0	(55)	81:19
TBDPS	Me	BT	K	DME	1.1	(80)	—
TBDPS	Et	PT	Li	DME	1.0	(97)	93:7
TBDPS	Et	PT	K	DME	1.0	(54)	84:16

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	Aldehyde (2 eq), sulfone (1 eq), KHMDS (1.3 eq), THF, –78°, 0.5 h; then rt, 12 h	 (73), (*E*)/(*Z*)* = 93:7	513
	1. Sulfone (1.0 eq), LDA (1.4 eq), THF, –78°, 0.5 h 2. Aldehyde (1.2 eq), –78°, 3 h	 (66.6), (*E*)/(*Z*)* = 87:13	514
C_5			
  Act = BT or PT	**A**: 1. MN(SiMe$_3$)$_2$, additive, THF, –78° 2. Aldehyde, –78° to temp *or* **B**: MN(SiMe$_3$)$_2$, THF, –78° to temp		122

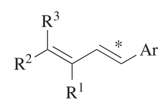
Act	Conditions	M	Additive	Temp (°)		(4*E**,6*Z*)/(4*Z**,6*Z*)/(4*E**,6*E*)/(4*Z**,6*E*)
BT	**A**	Li	none	–78	(35)	36:58:0:6
BT	**B**	Li	none	rt	(45)	35:55:3:7
BT	**A**	Li	HMPA	–78	(93)	33:54:2:11
BT	**A**	Na	none	–78	(37)	27:68:0:5
BT	**A**	K	none	–78	(60)	28:59:2:11
PT	**A**	Li	none	–78	(72)	39:52:4:5
PT	**B**	Li	none	–78	(42)	30:60:3:7
PT	**A**	K	none	–78	(15)	44:56:0:0

C_{5-8}

ArCHO 

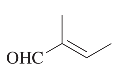
A:
1. LDA, THF, –78°, 1 h
2. Aldehyde, –78°, 3 h; then rt

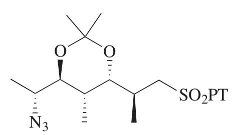
or **B**:
LDA, THF, –78°, 3 h;
then to rt, 1 h

 3

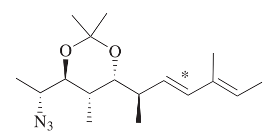
Ar	R^1	R^2	R^3	Conditions		$(E)/(Z)^*$
2-furyl	H	Me	Me	**A**	(83)	77:23
Ph	H	H	H	**A**	(50)	31:69
Ph	H	Me	Me	**A**	(80)	21:79
Ph	H	Me	Me	**B**	(76)	62:38
Ph	Me	H	H	**A**	(29)	99:1
Ph	Me	H	H	**B**	(88)	>99:1
Ph	$–(CH_2)_4–$		H	**A**	(50)	>99:1
$4\text{-}ClC_6H_4$	H	Me	Me	**B**	(79)	24:76
$4\text{-}MeOC_6H_4$	H	H	H	**A**	(58)	95:5
$4\text{-}MeOC_6H_4$	H	Me	Me	**A**	(85)	90:10
$4\text{-}MeOC_6H_4$	H	Me	Me	**B**	(93)	60:40
$3,4\text{-}(MeO)_2C_6H_3$	H	Me	Me	**A**	(64)	55:45
$4\text{-}CF_3C_6H_4$	H	Me	Me	**A**	(52)	35:65

C_5

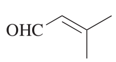


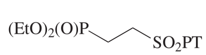


LiHMDS, DME, –65° to rt

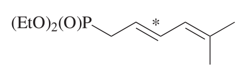


(72), $(E)/(Z)^*$ = 94:6 515



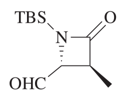
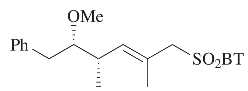
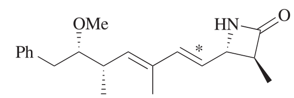
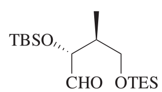
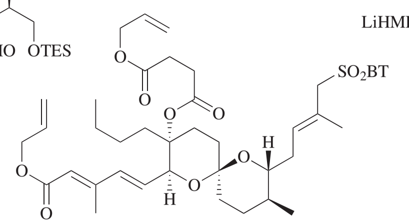
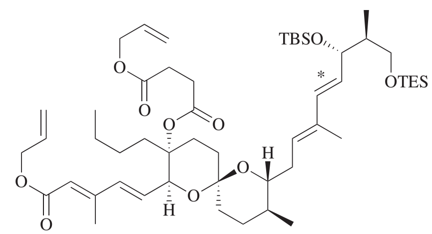


1. Sulfone (1 eq), KHMDS (1.2 eq), THF, –78°, 0.33 h
2. Aldehyde (1.5 eq), –78°, 0.33 h; then to rt, 1 h

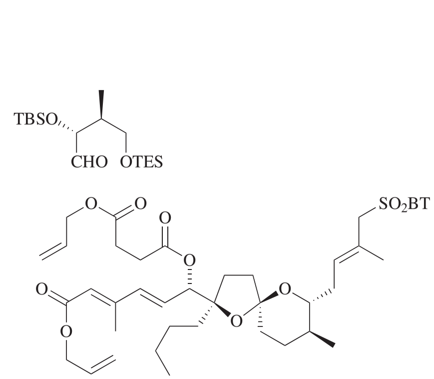


(70), $(E)/(Z)^*$ = 89:11 516

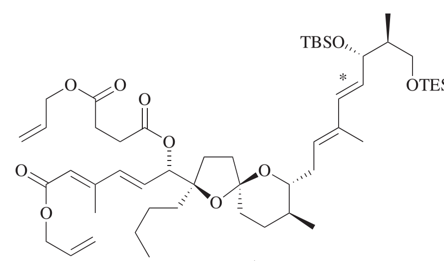
TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
 	1. $MN(SiMe_3)_2$, THF, –78° 2. KF, –78°	 M (*E*)/(*Z*)* Li (—) ~ 66:34 Na (20–25) ~ 80:20 K (40–45) ~ 75:25	517
 	LiHMDS, THF, –78° to rt	 (90), (*E*)*-isomer only	518

C$_{5-7}$



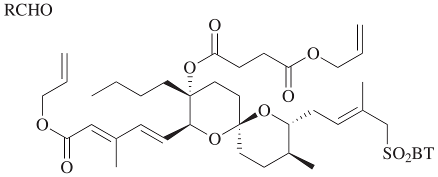
1. LiHMDS, THF, –78°
2. Aldehyde, –78 to 0°



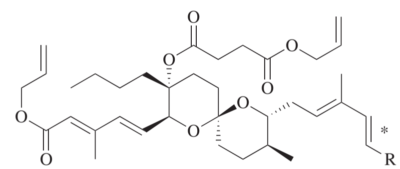
(56), $(E)^*$-isomer

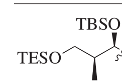
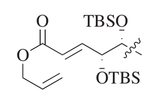
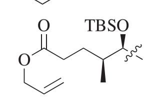
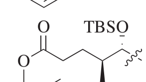
519

RCHO



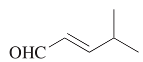
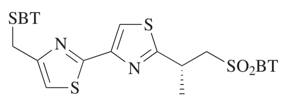
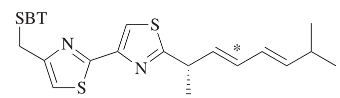
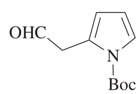
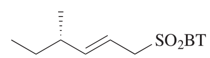
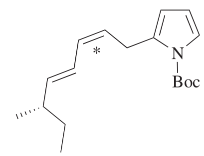
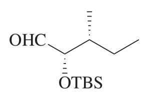
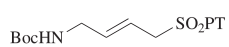
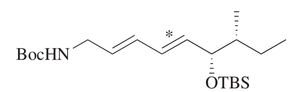
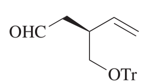
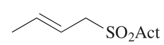
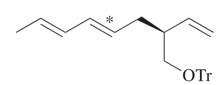
$MN(SiMe_3)_2$, THF, –78°



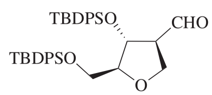
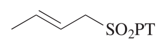
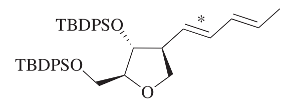
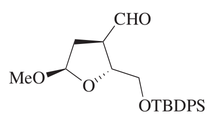
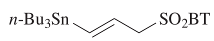
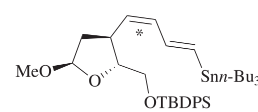
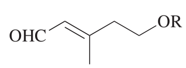
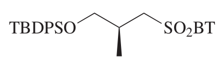
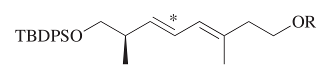
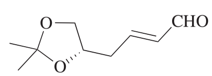
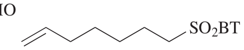
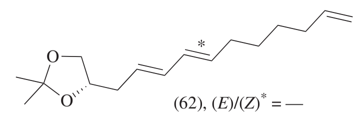
R	M		$(E)/(Z)^*$
	Li	(90)	—
	Li	(41)	—
	K	(55)	—
	Li	(72)	—

520, 521

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

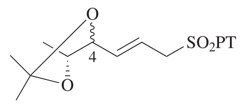
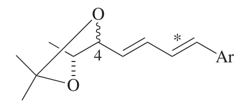
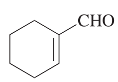
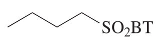
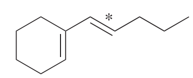
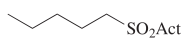
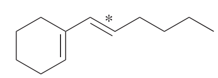
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		LiHMDS, THF, –78°, 0.25 h	 (77), (*E*)/(*Z*)* = 77:23	522
		1. LDA, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 5 h	 (—), (*E*)/(*Z*)* = 40:60	523
		1. KHMDS (2.1 eq), 18-crown-6, THF, –78°, 0.5 h 2. Aldehyde, –78°; then rt	 (93), (*E*)/(*Z*)* = 95:5	506
		**A**: 1. $MN(SiMe_3)_2$, DME, –78° 2. Aldehyde, –78° to rt *or* **B**: $MN(SiMe_3)_2$, DME, –78° to rt		70

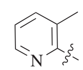
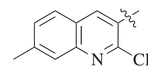
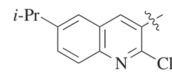
Act	M	Conditions		(*E*)/(*Z*)*
BT	Li	**A**	(100)	31:69
BT	K	**A**	(90)	50:50
PT	Li	**A**	(62)	60:40
PT	K	**B**	(81)	63:37

		1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 1 h	 (92), $(E)/(Z)^*$ = 72:28	524
		KHMDS, toluene, –78°, 8 h; then rt, 14 h	 (61), $(E)/(Z)^*$ = 10:90	79
		LiHMDS, THF, –78°		525
		KHMDS, THF	 (62), $(E)/(Z)^*$ = —	526

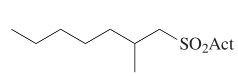
R		$(E)/(Z)^*$
$Me_2(MeO)C$	(87)	>95:5
THP	(95)	>95:5

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-13}				
ArCHO		1. Sulfone (1 eq), KHMDS (1.3 eq), THF, –78°, 0.5 h 2. Aldehyde (*x* eq), –70°, 1.5 h; then to rt		527
C_7				
		LDA, THF, –78°, 3 h; then rt, 1 h	 (33), $(E)/(Z)^*$ = 95:5	3
	 Act = BT or PT	1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h 2. Aldehyde, temp, 3 h; then rt		21

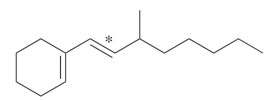
Ar	C-4	*x*		$(E)/(Z)^*$
	(*R*)	1.1	(81)	70:30
	(*S*)	1.1	(81)	60:40
	(*R*)	1.3	(71)[b]	—
	(*S*)	1.2	(70)[b]	—
	(*R*)	1.2	(70)[b]	94:6
	(*S*)	1.2	(70)[b]	—

M	Solvent	Temp (°)	Act = BT	$(E)/(Z)^*$	Act = PT	$(E)/(Z)^*$
Li	toluene	–78	(15)	95:5	(74)	88:12
Li	Et_2O	–78	(24)	99:1	(95)	89:11
Li	THF	–78	(35)	96:4	(91)	67:33
Li	DME	–60	(2)	—	(84)	84:16
Na	toluene	–78	(43)	97:3	(81)	80:20
Na	Et_2O	–78	(48)	97:3	(82)	75:25
Na	THF	–78	(13)	86:14	(99)	75:25
Na	DME	–60	(26)	77:23	(100)	88:12
K	toluene	–78	(17)	>95:5	(41)	61:39
K	Et_2O	–78	(60)	94:6	(69)	58:42
K	THF	–78	(39)	79:21	(93)	66:34
K	DME	–60	(35)	55:45	(64)	85:15



Act = BT or PT

1. $MN(SiMe_3)_2$, solvent, temp, 0.5 h
2. Aldehyde, temp, 3 h; then rt



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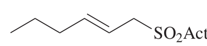
M	Solvent	Temp (°)	Act = BT		Act = PT	
				(*E*)/(*Z*)*		(*E*)/(*Z*)*
Li	toluene	–78	(69)	98:2	(71)	94:6
Li	Et_2O	–78	(16)	97:3	(79)	95:5
Li	THF	–78	(96)	>99:1	(100)	98:2
Li	DME	–60	(93)	>99:1	(83)	99:1
Na	toluene	–78	(98)	97:3	(90)	82:18
Na	Et_2O	–78	(89)	97:3	(85)	79:21

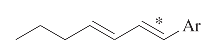
M	Solvent	Temp (°)	Act = BT		Act = PT	
				(*E*)/(*Z*)*		(*E*)/(*Z*)*
Na	THF	–78	(96)	94:6	(78)	85:15
Na	DME	–60	(100)	91:9	(48)	92:8
K	toluene	–78	(70)	97:3	(27)	55:45
K	Et_2O	–78	(88)	96:4	(31)	50:50
K	THF	–78	(76)	86:14	(44)	58:42
K	DME	–60	(94)	72:28	(38)	81:19

ArCHO



Act = PT or BT

A:
KHMDS, THF, –78°
or **B**:
KHMDS, DMF, –55°
or **C**:
1. KHMDS, 18-crown-6, DMF, –55°, 2 min
2. Aldehyde
or **D**:
1. KHMDS, DMF/TDA, –60°, 2 min
2. Aldehyde



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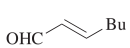
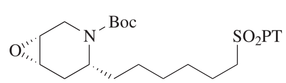
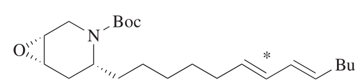
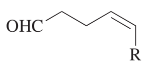
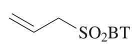
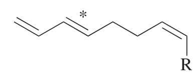
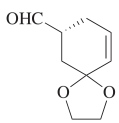
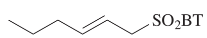
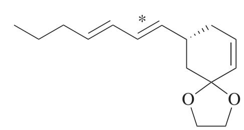
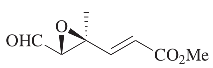
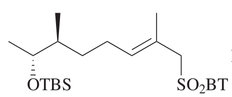
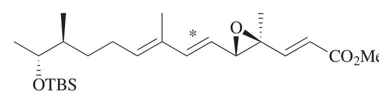
Ar	Conditions	Act = PT		Act = BT	
			(*E*)/(*Z*)*		(*E*)/(*Z*)*
4-ClC_6H_4	**A**	(64)	55:45	(56)	49:51
4-ClC_6H_4	**B**	(55)	51:49	(49)	45:55
4-ClC_6H_4	**C**	(51)	76:24	(53)	72:28
4-ClC_6H_4	**D**	(58)	74:26	(55)	78:22
4-$O_2NC_6H_4$	**A**	(70)	56:44		
4-$O_2NC_6H_4$	**B**	(60)	48:52		
4-$O_2NC_6H_4$	**C**	(65)	86:14		
4-$O_2NC_6H_4$	**D**	(63)	89:11		

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		KHMDS, THF, –78°, 0.5 h	 (82), (*E*)/(*Z*)* = 90:10	528
C_{7-18}				
		Aldehyde (1.1 eq), sulfone (1.0 eq), NaHMDS (1.1 eq) –78°, 1 h; then rt, 1 h	 R / (*E*)/(*Z*)* Et (72) 56:44 *n*-C_5H_{11} (91) 59:41 2,3-$(MeO)_2C_6H_3(CH_2)_7$ (90) 63:37	529
C_7				
		1. LiHMDS, –78°, 1 h 2. Aldehyde, 2 h	 (70), (*E*)/(*Z*)* = —	530
		LiHMDS, additive, THF	 Additive / Temp (°) / (*E*)/(*Z*)* none –78 (≥14) 50:50 none –98 (≥62) 38:62 HMPA, 4 Å MS –98 (≥52) 70:30	531

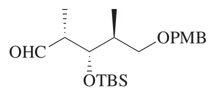
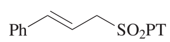
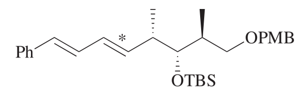
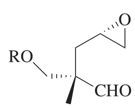
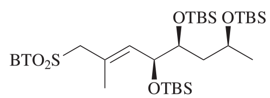
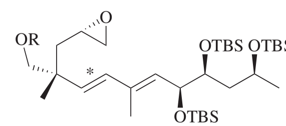
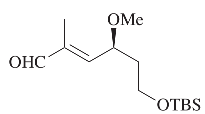
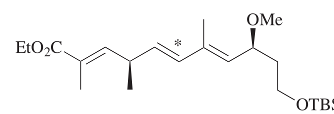
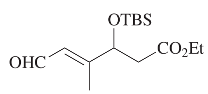
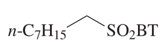
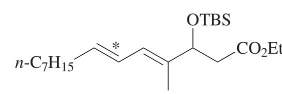
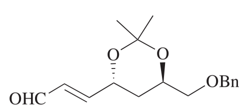
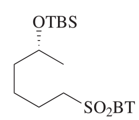
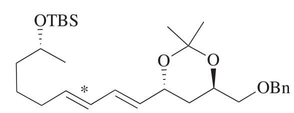
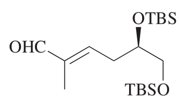
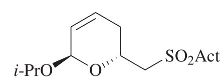
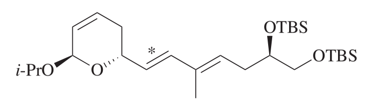
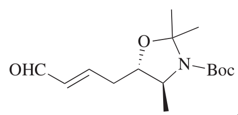
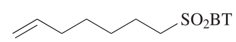
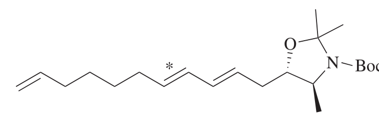
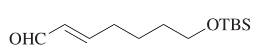
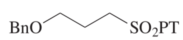
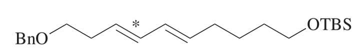
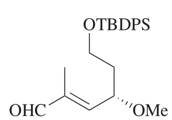
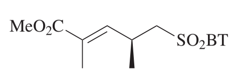
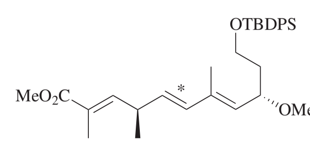
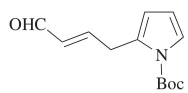
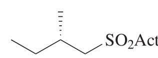
		1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60°, 0.5 h; then rt	 (68), $(E)/(Z)^*$ = 50:50	532
		Aldehyde (1.2 eq), sulfone (1.0 eq), LiHMDS (2 eq), THF, –78°, 70 min	 R / $(E)^*$-isomer MEM (84) MPM (86)	533
		NaHMDS, THF, –78° to rt	 (89), $(E)/(Z)^*$ = 80:20	534
		KHMDS, THF, –78°; then rt, 2 h	 (72), $(E)/(Z)^*$ = 94:6	36
		NaHMDS, THF, –78°; then rt, 0.5 h	 (78), $(E)/(Z)^*$ = 90:10	535

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

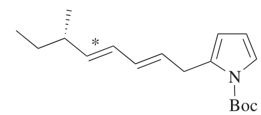
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
 	KHMDS, solvent, –78°, 4 h; then rt	 Act / Solvent / / $(E)/(Z)^*$ BT / THF / (82) / 94:6 PT / DME / (76) / 88:12	536
 	KHMDS, THF	 (65), $(E)/(Z)^* = 83:17$	232
 	1. LiHMDS, THF, –78°; then –65°, 1 h 2. Aldehyde, –65°, 1 h; then rt, 18 h	 (90), $(E)/(Z)^* = 85:15$	537, 538
 	LiHMDS, THF, –78°, 0.5 h; then rt, 2 h	 (97), $(E)/(Z)^* = 96:4$	539

C$_8$



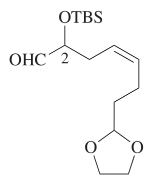


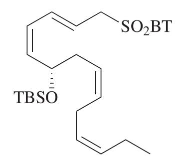
1. LDA, THF, –78°, 0.5 h
2. Aldehyde, –78° to rt, 5 h



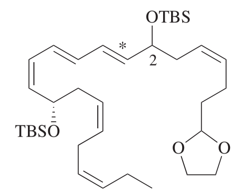
Act		$(E)/(Z)^*$
BT	(—)	87:13
PT	(58)	90:10

523





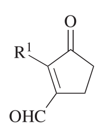
P4-*t*-Bu, MeCN, –40° to rt, 2 h

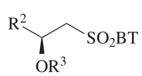


C-2		$(E)/(Z)^*$
(*R*)	(56)	61:39
(*S*)	(63)	56:44

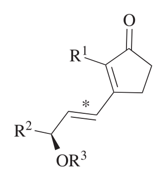
540

C$_{8-14}$





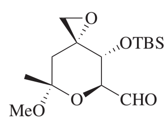
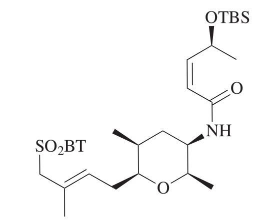
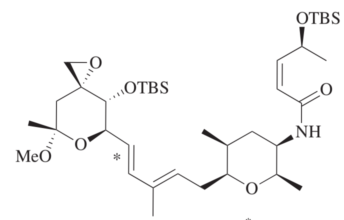
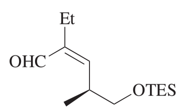
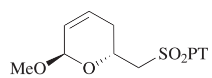
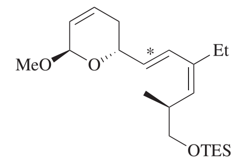
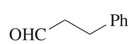
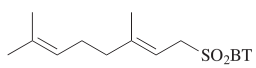
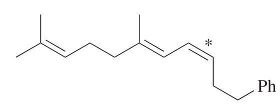
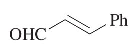
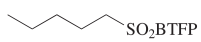
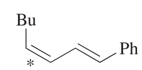
A:
KHMDS, THF, –78°, 10 min;
then rt, 2 h
or **B**:
1. KHMDS, THF, –78°, 0.5 h
2. Aldehyde, –78°; then rt



541

R^1	R^2	R^3	Conditions		$(E)/(Z)^*$
Et	$MeO_2C(CH_2)_7$	TBS	**A**	(0)	—
Et	$MeO_2C(CH_2)_7$	*t*-Bu	**B**	(65)	100:0
$MeO_2C(CH_2)_6$	*n*-C_5H_{11}	TBS	**A**	(28)	86:14
$MeO_2C(CH_2)_6$	*n*-C_5H_{11}	*t*-Bu	**B**	(52)	100:0
$MeO_2C(CH_2)_7$	Et	TBS	**A**	(42)	86:14
$MeO_2C(CH_2)_7$	Et	*t*-Bu	**B**	(61)	100:0

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
 	1. LiHMDS, THF, –78°, 10 min 2. Aldehyde, –78°, 1 h; then rt, 2 h	 (68), (*E*)* -isomer only	542
 	NaHMDS, DME/HMPA, –78°	 (35), (*E*)* -isomer only	543
C_9			
 	LiHMDS (2 eq), CH_2Cl_2, rt	 (75), (*E*)/(*Z*)* = 13:87	34, 35
 	1. Base, THF, temp 2. Aldehyde, 16 h		58

Base	Temp		(*E*)/(*Z*)*
KOH, *n*-Bu_4NBr	rt	(30)	12:88
P4-*t*-Bu	–78°	(28)	50:50

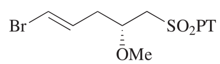
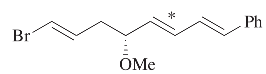
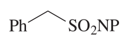
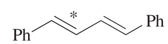
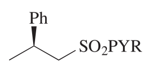
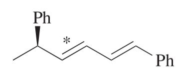
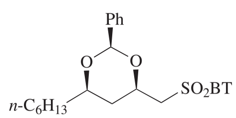
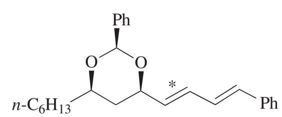
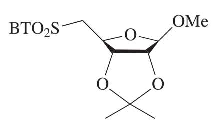
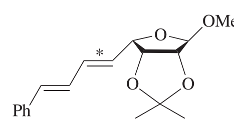
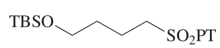
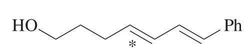
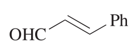
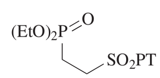
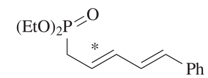
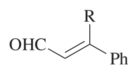
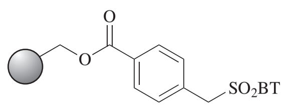
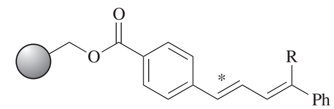
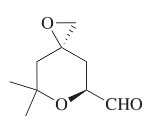
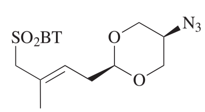
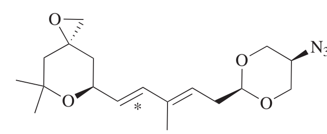
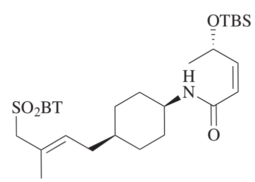
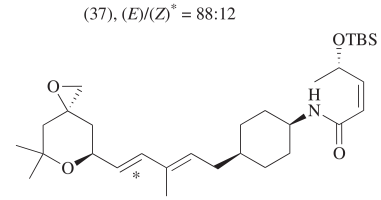
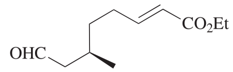
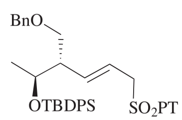
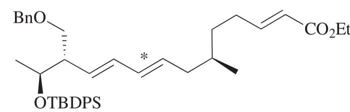
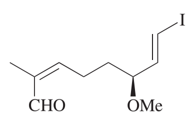
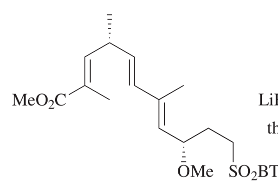
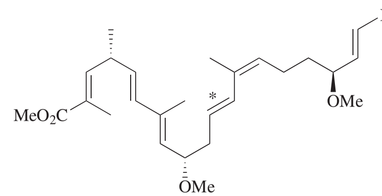
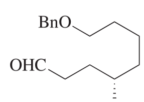
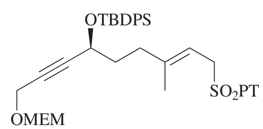
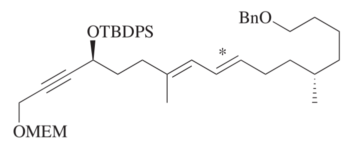
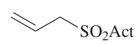
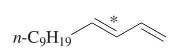
	1. KHMDS, DME, –78° 2. Aldehyde	 (81), (*E*)/(*Z*)* = 89:11	544
	NaH, DMF, rt, 1 h	 (77), (*E*)/(*Z*)* = —	545
	1. KHMDS, DME, –78°, 3 min 2. Aldehyde, –78°, 2 h	 (89), (*E*)/(*Z*)* = 87:13	201
	NaH, THF, 20°	 (93), (*E*)/(*Z*)* = 64:36	51
	1. Sulfone (1.2 eq), KHMDS (2.9 eq), THF, –78° 2. Aldehyde (1 eq), –78°; then to rt, 0.33 h	 (90), (*E,E*)*/(*Z,E*)* = 97:3[c]	546
	1. Sulfone (1.0 eq), LiHMDS (1.17 eq), THF, –78°, 0.67 h 2. Aldehyde (1.5 eq), –78°; then to rt, 3 h 3. HCl, MeOH	 (99), (*E*)/(*Z*)* = 89:11	547

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. THF, KHMDS, –78°, 5 min 2. Aldehyde, –78°, 0.33 h; then 0°, 1 h	 (75), (*E*)/(*Z*)* = 86:14	115
C_{9-15}				
	  = Wang resin	1. DBU, CH_2Cl_2, rt, 0.25 h 2. Aldehyde, rt, 24 h	 R — (*E*)/(*Z*)* H (70) 57:43 Ph (58) 50:50	548
C_9				
		1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 1.5 h; then rt, 12 h	 (37), (*E*)/(*Z*)* = 88:12	549
		1. LiHMDS, THF, –78°, 10 min 2. Aldehyde, –78°, 1 h; then rt, 2 h	 (>95), (*E*)/(*Z*)* = —	550

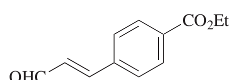
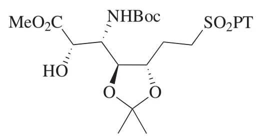
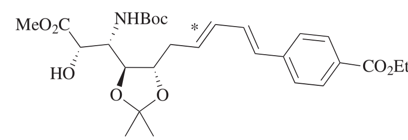
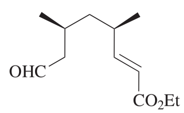
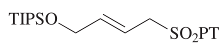
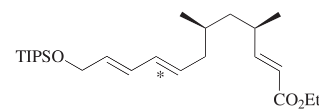
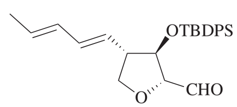
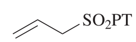
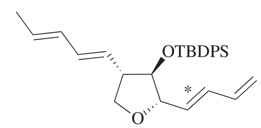
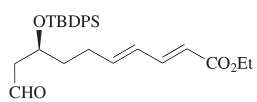
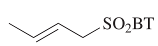
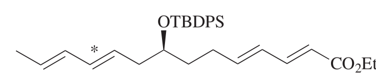
		1. Sulfone (1.0 eq), KHMDS (1.2 eq), THF, –78°, 0.5 h 2. Aldehyde (1.1 eq), –78°, 0.5 h; then to 0°, 1 h	 (84), $(E)/(Z)^*$ = 93:7	551
		LiHMDS, THF, –78°, 2 h; then rt, 0.5 h	 (57), $(E)/(Z)^*$ = 88:12	552, 539
		KHMDS, THF, –78°	 (>55), "predominantly $(E)^*$-isomer"	553

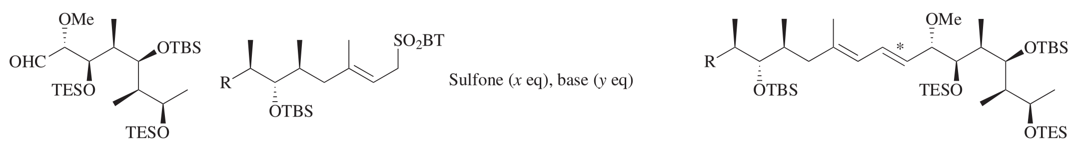
C_{10}

n-$C_9H_{19}CHO$		1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60° to rt		5

Act		$(E)/(Z)^*$
PT	(39)	67:33
TBT	(60)	4:96

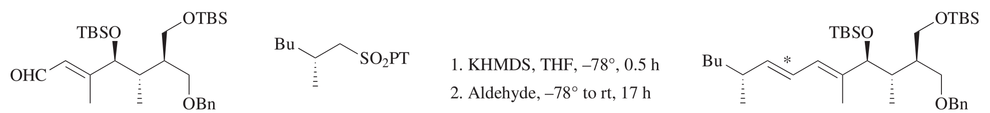
TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
 	KHMDS, THF, –78°, 0.5 h	 (23), (*E*)/(*Z*)* = >99:1	554
 	KHMDS, DME, –60°, 2 h	 (82), (*E*)/(*Z*)* = 75:25	513
 	1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 1 h	 (85), (*E*)/(*Z*)* = 67:33	524
 	Aldehyde (1 eq), sulfone (1 eq), KHMDS (1 eq), THF, –78°; then to 0°; then 0°, 2 h	 (63), two steps, (*E*)/(*Z*)* = 75:25	555



556

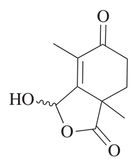
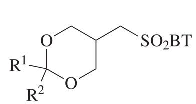
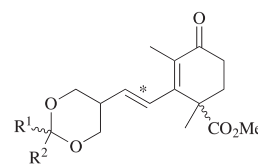
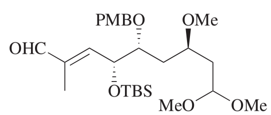
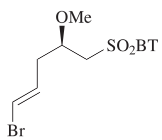
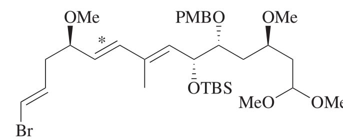
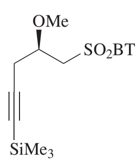
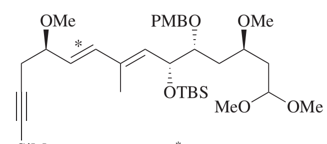
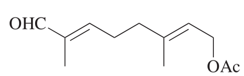
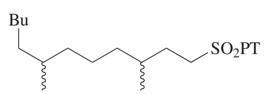
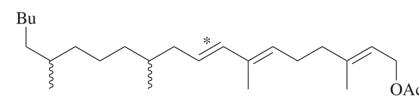
R	x	Base	y	Temp/Time		$(E)/(Z)^*$
$TESOCH_2$	1.2	NaHMDS	1.2	–78°, 1 h; 0°	(81)	71:29
$TESOCH_2$	1.2	NaHMDS	2.0	–78°, 2 h; rt	(68)	81:19
$TESOCH_2$	1.2	LiHMDS	2.0	–78°, 2 h; rt	(85)	76:24
$TESOCH_2$	1.2	KHMDS	2.0	–78°, 2 h; rt	(90)	58:42
(*E*)-$EtO_2CC(Me)$=CH	0.8	NaHMDS	1.2	–78°, 0.5 h; –40°, 10 min; 0°	(86)	66:34
(*E*)-$EtO_2CC(Me)$=CH	1.1	NaHMDS	1.1	–78°, 0.5 h; –40°, 0.33 h; 0°	(40)	80:20
(*E*)-$EtO_2CC(Me)$=CH	1.1	NaHMDS	2.2	–78°, 2 h; –40°, 10 min; 0°	(56)	80:20
(*E*)-$EtO_2CC(Me)$=CH	1.1	LiHMDS	2.3	–78°, 0.33 h; –40°, 0.67 h; 0°	(75)	50:50
(*E*)-$EtO_2CC(Me)$=CH	1.1	KHMDS	2.2	–78°, 70 min; –40°, 0.33 h; 0°	(39)	75:25
(*E*)-$HOCH_2C(Me)$=CH	0.8	NaHMDS	1.7	–78°, 1 h; –40°, 10 min; 0°	(65)	78:22



(73), $(E)/(Z)^*$ >95:5

557

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
 	1. LDA, THF, –78° 2. Add sodium alkoxide of lactol (NaH + lactol) 3. CH_2N_2, ether	 R^1 / R^2 / / $(E)/(Z)^*$ Me / Me / (78) / — *n*-Pr / H / (78) / —	558, 559
 	NaHMDS, THF, –78° to rt	 (93), $(E)^*$-isomer only	560, 561
	NaHMDS, THF, –78°	 (74), $(E)^*$-isomer only	561, 562
 	1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt	 (90), $(E)/(Z)^*$ = —	273

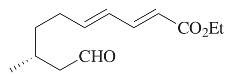
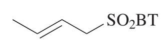
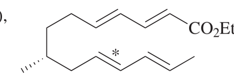
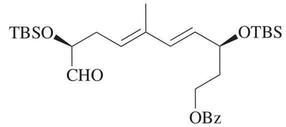
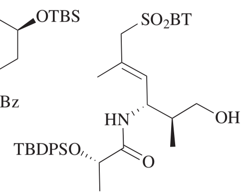
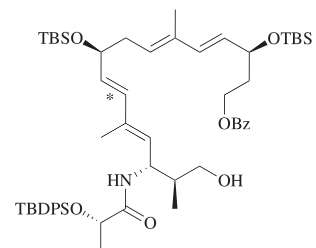
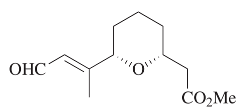
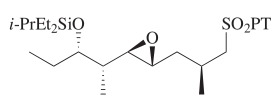
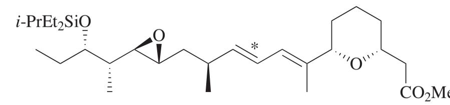
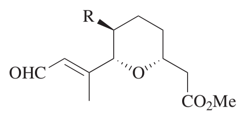
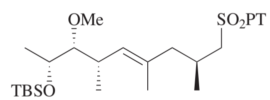
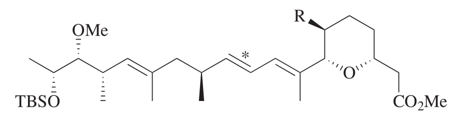
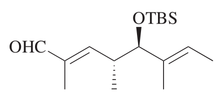
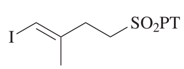
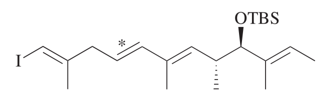
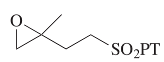
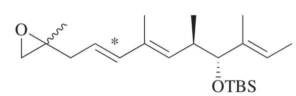
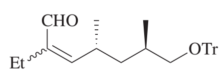
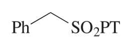
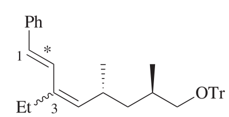
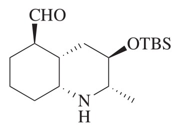
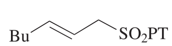
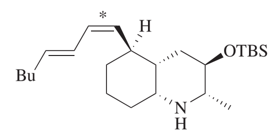
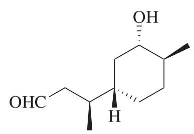
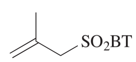
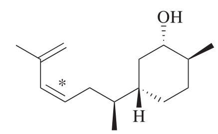
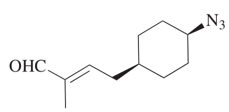
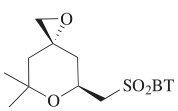
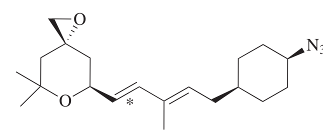
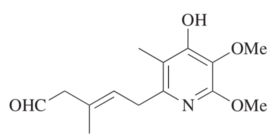
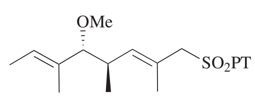
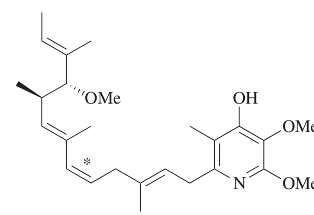
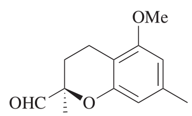
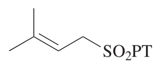
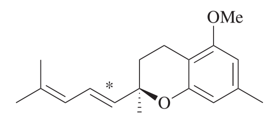
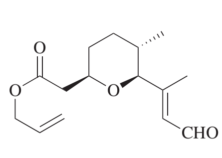
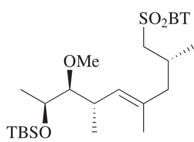
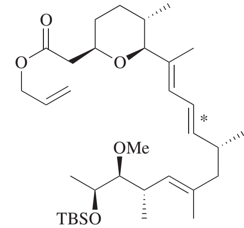
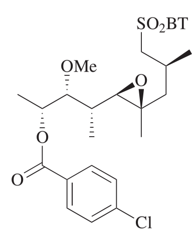
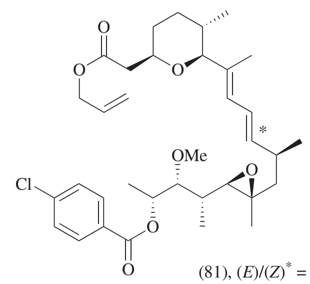
C_{11}				
		Aldehyde (1 eq), sulfone (1.2 eq), LiHMDS (1.2 eq), THF, –78°; then to rt, 2 h	 (63), two steps, $(E)/(Z)^{*}$ = 75:25	563
		1. LDA (2 eq), THF, –78°, 5 min 2. Aldehyde, –78° to rt	 (72), $(E)^{*}$-isomer	508
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1 h	 (46), $(E)/(Z)^{*}$ = 93:7	564

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12}			
 	1. Sulfone (*x* eq), KHMDS (*y* eq), THF, –78°, 1 h 2. Aldehyde (1 eq), –78°, time		564
C_{11}			
 	1. KHMDS, DME, –60°, 0.33 h 2. Aldehyde, –60°, 7 h; then rt	 (60), $(E)^*$-isomer only	565, 566
	1. NaHMDS, DME, –78°; then –60°, 0.5 h 2. Aldehyde, 0°, 18 h	 (83), $(E)/(Z)^*$ = 93:7	567, 568
 (*E*)/(*Z*) = 17:83 	1. LiHMDS, THF, 0°, 0.33 h 2. Aldehyde, –78° to rt, 12 h	 (78), $(1E^*,3Z)/(1E^*,3E)/(1Z^*,3Z)/(1Z^*,3E)$ = 72:15:10:3	569

R	*x*	*y*	Time (h)		$(E)/(Z)^*$
H	1.2	0.78	2	(45)	78:22
Me	1.3	1.2	1.5	(53)	78:22

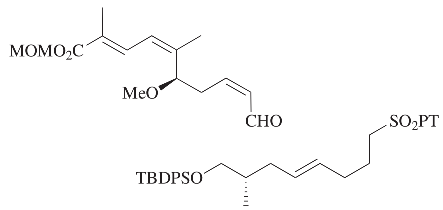
		KHMDS	 (90), (*Z*)*-isomer only	418
		NaHMDS (2 eq), DME, –60° to rt, 2 h	 (79), (*E*)/(*Z*)* = 25:75	74
		Aldehyde (1.0 eq), sulfone (1.1 eq), NaHMDS (1.2 eq), THF, –78°, 70 min; then to 0°, 15 min; then rt, 30 min	 (81), (*E*)/(*Z*)* = 95:5	570
C_{12}				
		KHMDS, THF, –78°, 12 h	 (43), predominantly (*Z*)*-isomer	571

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
		1. $MN(SiMe_3)_2$, solvent, temp 2. Aldehyde, –78°; then rt		572
		1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 1.5 h; then rt	 (71), (*E*)/(*Z*)* = 92:8	23
		1. LDA, THF, –78°, 0.25 h 2. Aldehyde, –78 to –20°, 1.5 h	 (81), (*E*)/(*Z*)* = 91:9	60

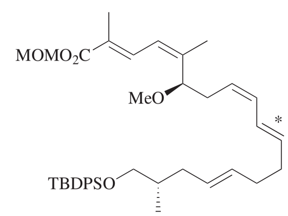
Product table for the first entry (ref. 572):

M	Solvent	Temp (°)		(*E*)/(*Z*)*
Li	DMF/HMPA	–35	(88)	83:17
Li	DMF/HMPA	–78	(98)	95:5
K	THF	–78	(88)	50:50

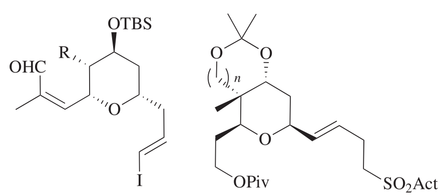
C_{12-13}



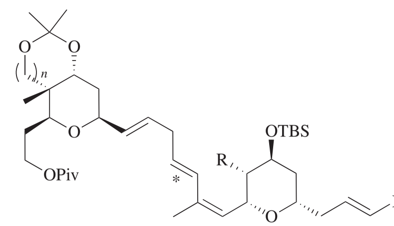
KHMDS, THF, –78°



(88), two steps, "excellent $(E)^*$ selectivity" 573

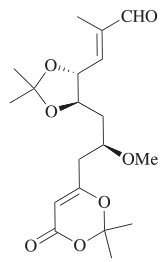
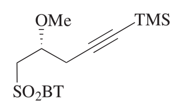
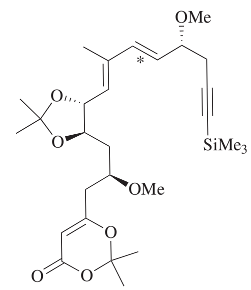
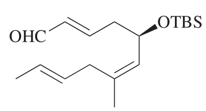
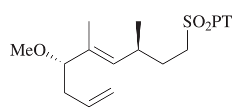
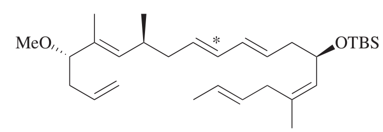
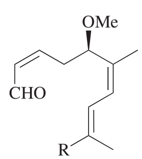
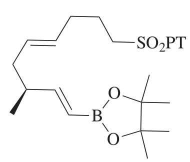
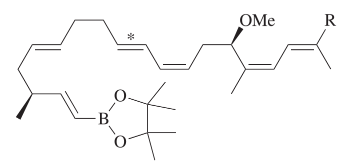


1. LiHMDS, THF, –78°
2. Aldehyde, –78° to rt



R	*n*	Act		$(E)/(Z)^*$	
H	1	PT	(—)	(—)	574
Me	1	BT	(70)	95:5	378
Me	1	PT	(86)	95:5	379
Me	2	PT	(—)	(—)	379

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}					
		1. NaHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 0.5 h; then rt, 2 h		(79), (*E*)*-isomer	511
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1 h; then rt	 (88), (*E*)/(*Z*)* = 95:5		575
		1. Sulfone (1.16 eq), KHMDS (2.0 eq), THF, –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°, 3.5 h			
			R	(*E*)/(*Z*)*	
			$BzOCH_2$ (75)[d]	100:0	573
			$MOMO_2C$ (92)[d]	100:0	573, 576

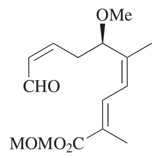
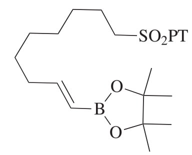
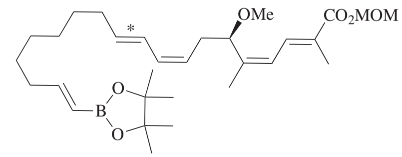
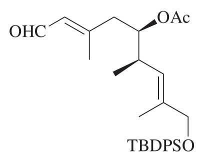
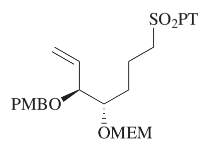
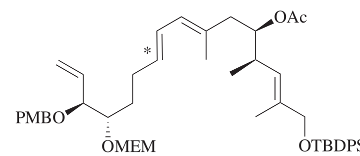
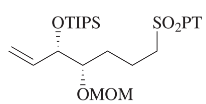
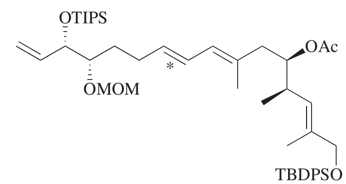
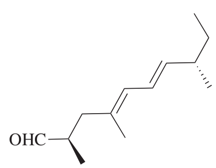
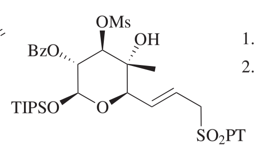
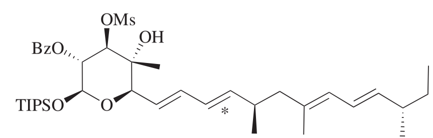
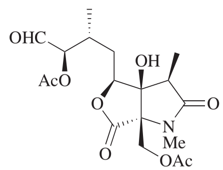
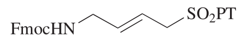
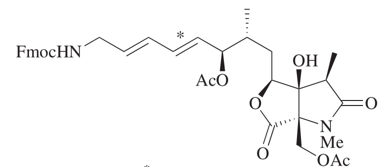
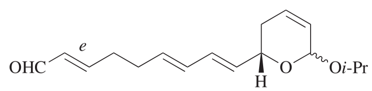
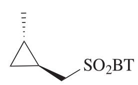
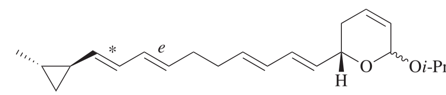
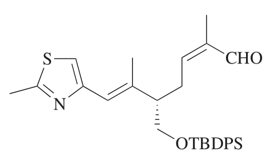
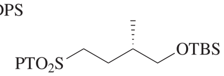
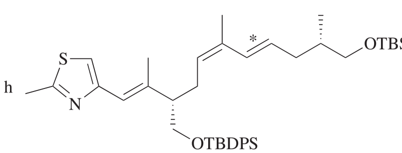
	 	1. Sulfone (1.3 eq), KHMDS (2.5 eq), THF, –78°, 1 h 2. Aldehyde (1.0 eq), –78°, 2 h	 (80), $(E)^*$-isomer	573
	 	LiHMDS, THF, –78°, 1 h	 (60), $(E)/(Z)^*$ = 92:8	72
		LiHMDS, THF, –78°, 0.75 h	 (80), $(E)/(Z)^*$ = 95:5	72, 577
C_{13}	 	1. KHMDS (2 eq), THF, –78° 2. Aldehyde, –78°, 3 h; then rt	 (79), $(E)^*$-isomer only	578

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
 	1. NaHMDS, THF, –78°, 0.25 h 2. Aldehyde, –78°, 1 h	 (77), (*E*)/(*Z*)* = 82:18	75
C_{14}			
 (*E*)/(*Z*)^e = 86:14  (racemic)	Aldehyde (1 eq), sulfone (1.5 eq), base (2 eq), DME, –78°	 Base / Time (min) / (%) / (*E*)/(*Z*)*: LiHMDS, 10, (54), 9:91 NaHMDS, 20, (95), 73:27 KHMDS, 10, (95), 71:29	579
 	1. Sulfone, KHMDS, –78°, 0.33 h 2. Aldehyde, –78°, 0.5 h	 (86), (*E*)*-isomer	580

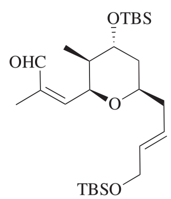
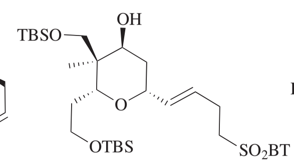
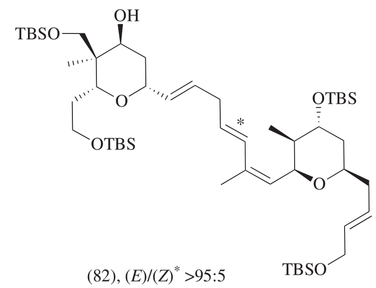
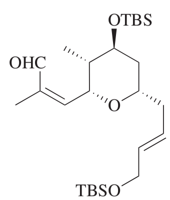
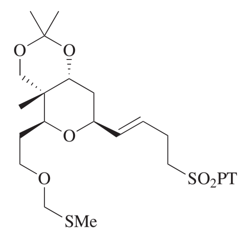
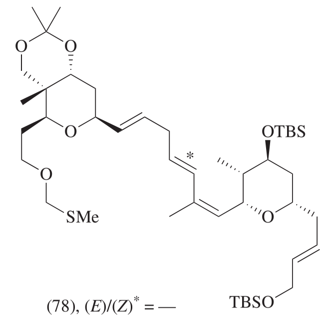
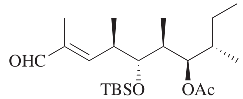
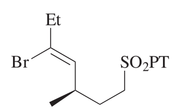
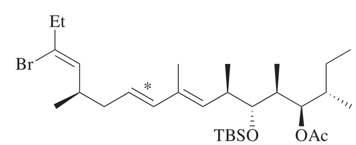
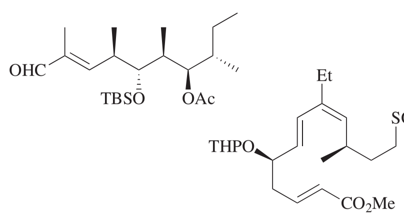
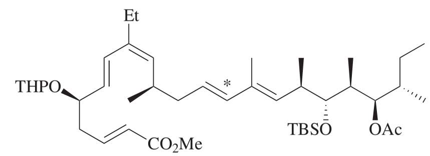
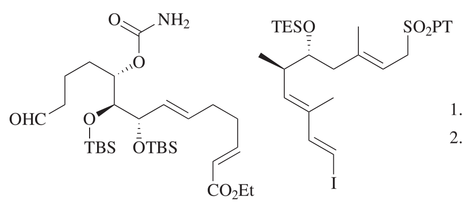
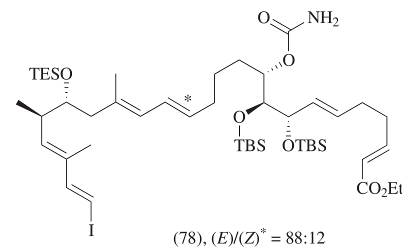
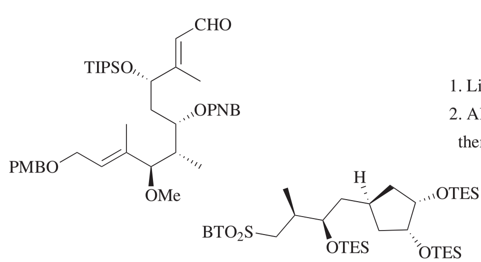
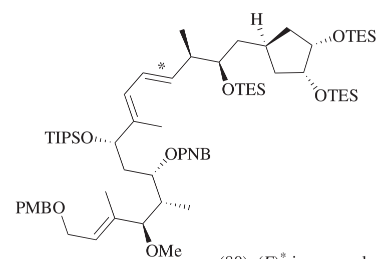
		LiHMDS, DME, –70° to rt	 (82), $(E)/(Z)^*$ >95:5	117, 382
		KHMDS, THF, –78°, 1 h; then rt	 (78), $(E)/(Z)^*$ = —	54, 581
		KHMDS, DME, –60°	 (54), $(E)/(Z)^*$ = 88:12	582

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	KHMDS, DME, –60°	 (38), (*E*)/(*Z*)* >95:5	582
	1. NaHMDS, THF, –78°, 5 min 2. Aldehyde, –78 to –50°, 1 h	 (78), (*E*)/(*Z*)* = 88:12	583
	1. LiHMDS, THF, –78°, 0.67 h 2. Aldehyde, –78°, 1 h; then rt, 0.5 h	 (80), (*E*)*-isomer only	584

C_{15}

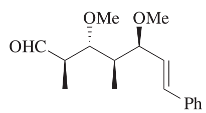
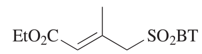
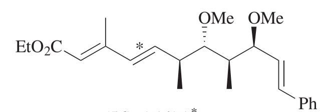
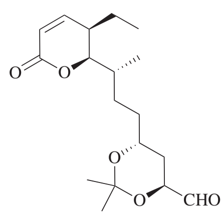
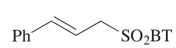
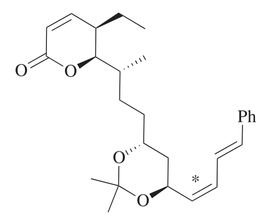
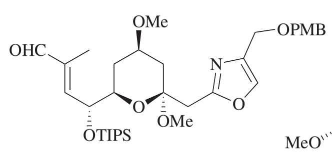
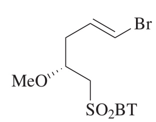
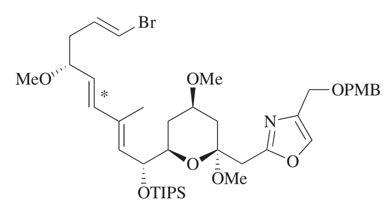
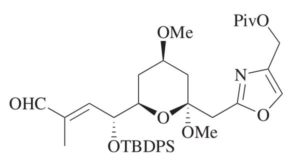
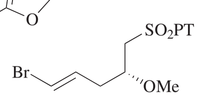
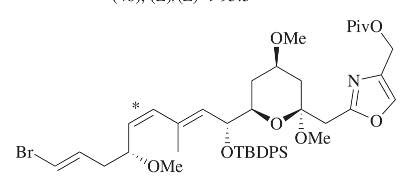
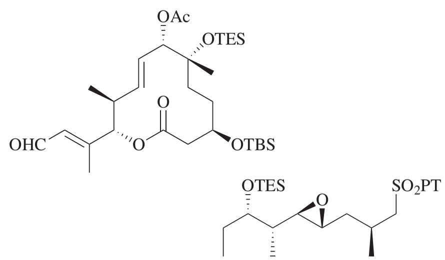
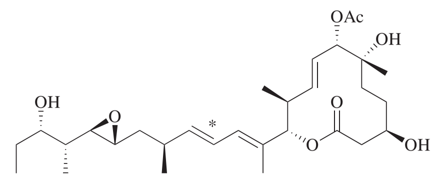
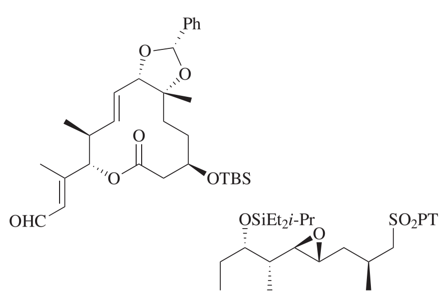
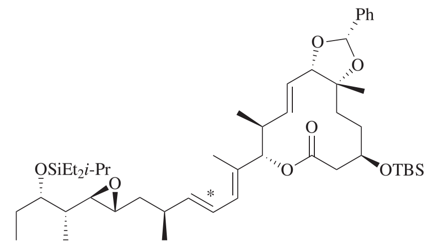
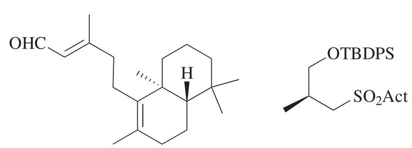
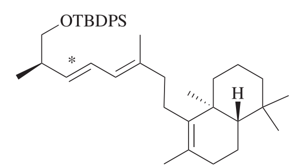
		1. LiHMDS, THF, –78° 2. Aldehyde, –78°	 (56), (*E*)/(*Z*)* = —	585
		1. MN(SiMe$_3$)$_2$, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt, 1 h	 M | | (*E*)/(*Z*)* Li | (>56) | 66:33 Na | (—) | 29:71 K | (—) | 17:83	586
		1. NaHMDS, THF, –78° 2. Aldehyde	 (46), (*E*)/(*Z*)* >95:5	587
		1. KHMDS, DME, –78° 2. Aldehyde	 (60), (*E*)/(*Z*)* <11:89	588

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	1. KHMDS, THF, –78°, 025 h 2. Aldehyde, –78°, 1 h 3. TBAF, THF, rt, overnight	 (67), $(E)^*$-isomer	589
	KHMDS, THF, –78°	 (64), $(E)^*$-isomer only	259
C_{20}			
	LiHMDS, THF, –78°	 Act / Time (h) / / $(E)/(Z)^*$ BT / 1 / (73) / 86:14 PT / 3 / (83) / 92:8	590

C_{21}

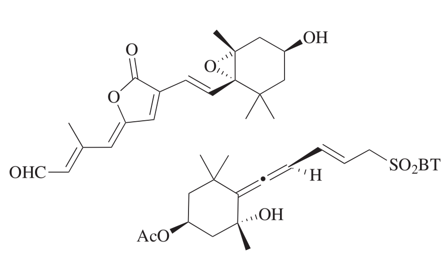
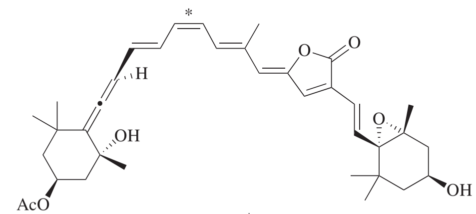
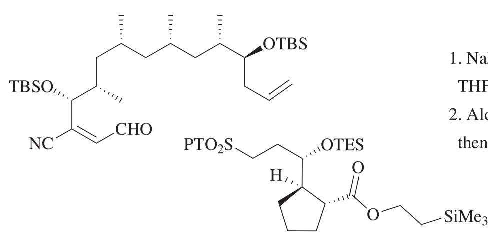
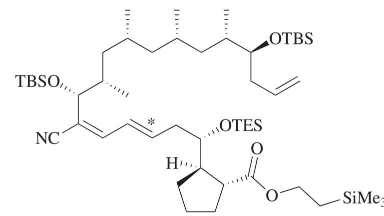
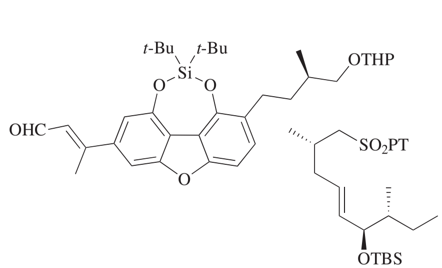
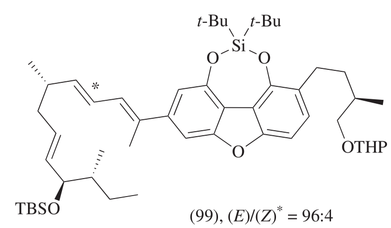
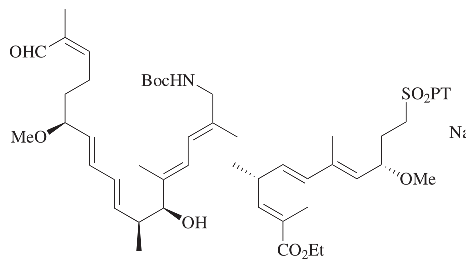
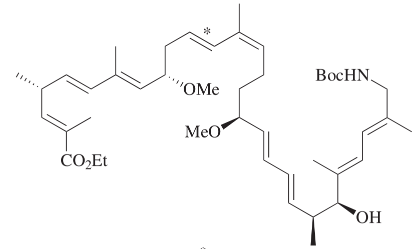
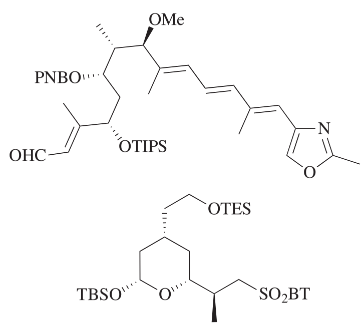
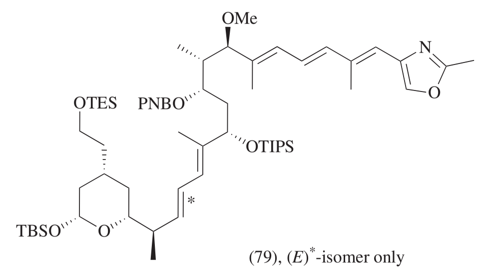
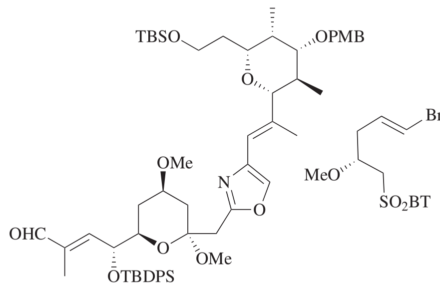
Reactants	Conditions	Product(s)	Refs.
	NaHMDS (3 eq), THF, –78°, 5 min, dark	 (39), (*E*)/(*Z*)* = 15:85	591
	1. NaHMDS, 15-crown-5, THF, –78°, 0.25 h 2. Aldehyde, –78°, 0.5 h; then rt, 1.5 h	 (66), (*E*)/(*Z*)* = 83:17	592
	1. LiHMDS, THF, –78°, 10 min 2. Aldehyde, –78°, 20 min	 (99), (*E*)/(*Z*)* = 96:4	114

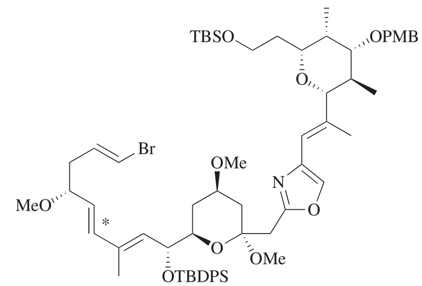
TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	NaHMDS, THF, –78° to rt	 (57), (*E*)/(*Z*)* >91:9	534
C_{22}			
	LiHMDS, THF, –78°, 2 h; then rt	 (79), (*E*)*-isomer only	593, 594

C_{26}

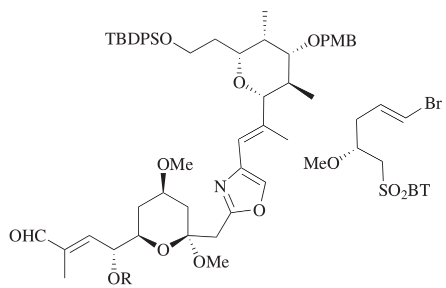


NaHMDS, THF, –78°, 0.5 h; then 0°, 0.25 h; then rt, 0.5 h

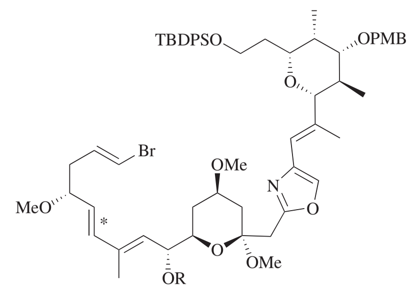


(99), $(E)^*$-isomer

595, 596

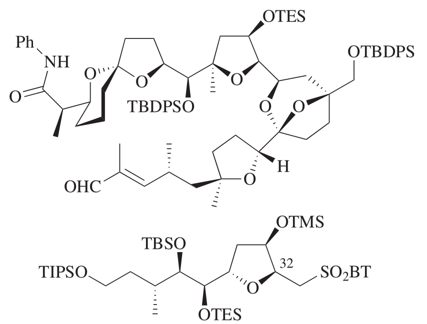
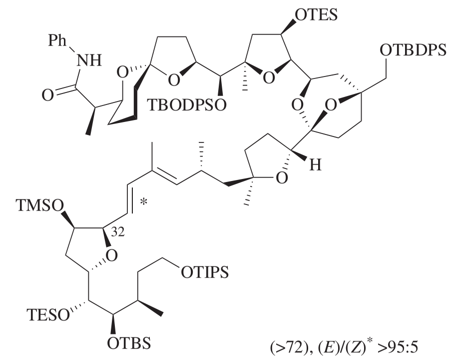
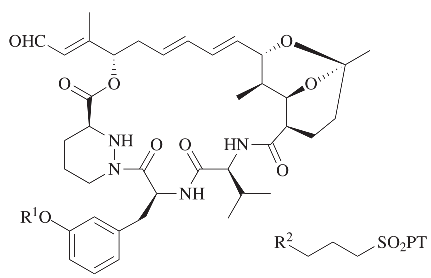
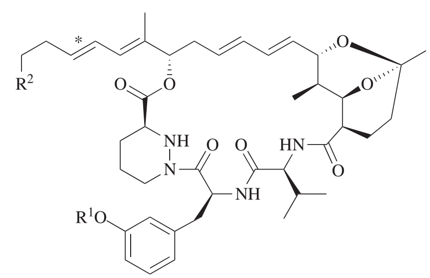


NaHMDS, THF, –78°, 0.67 h

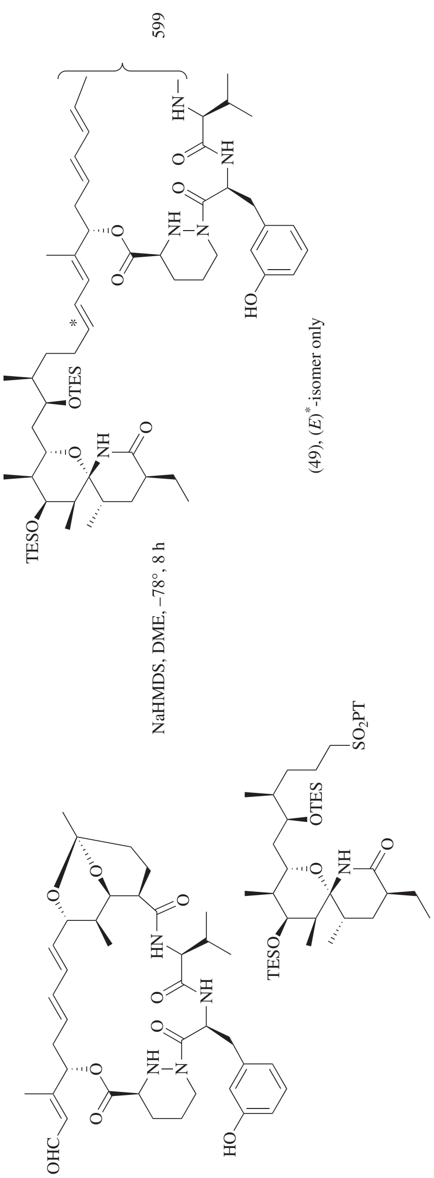


R		$(E)/(Z)^*$	
TIPS	(78)	>95:5	597
TBDPS	(86)	92:8	71

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

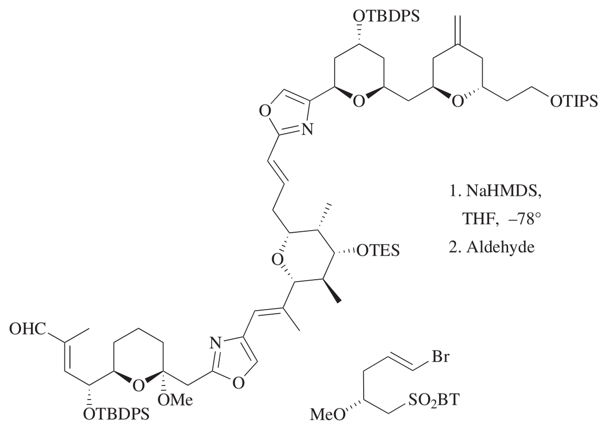
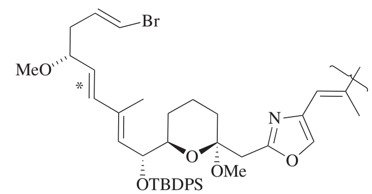
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{36}			
	LiHMDS, THF, –78° to rt	 (>72), (*E*)/(*Z*)* >95:5 dr (C-32) 88:12	120
C_{39}			
	NaHMDS, DME, –78° to rt		

R^1	R^2		(*E*)/(*Z*)*	Refs.
TBS	H	(49)	>91:9	598
Me	H	(74)	>91:9	598
$Ph(CH_2)_3$	TBSO	(64)	>91:9	599



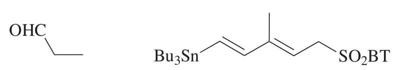
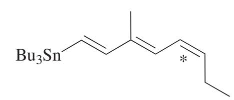
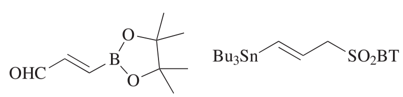
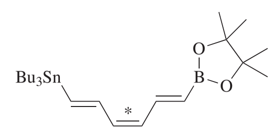
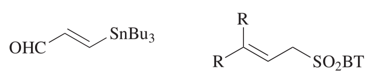
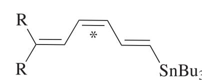
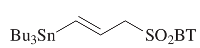
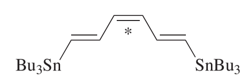
(49), (*E*)*-isomer only

TABLE 4. SYNTHESIS OF 1,3- DIENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{44} 	1. NaHMDS, THF, −78° 2. Aldehyde	 (98), (*E*)/(*Z*)* >95:5	588, 600

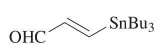
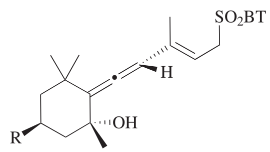
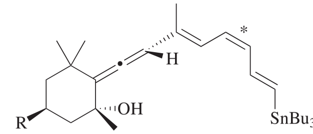
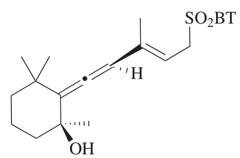
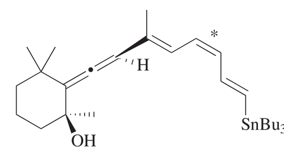
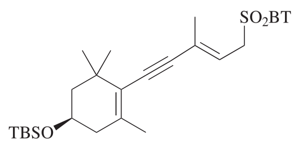
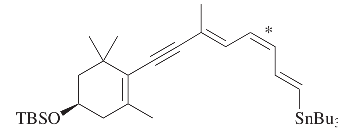
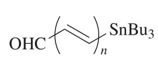
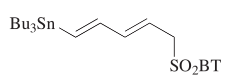
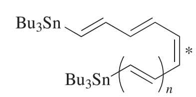
[a] LiBr (3 eq) was added prior to sulfone lithiation.
[b] The yield includes the removal of the acetonide.
[c] Citral was unreactive in this reaction.
[d] The yield is for the two steps of alcohol oxidation and Julia-Kocienski olefination.

TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES

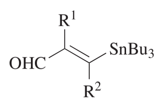
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
	1. KHMDS, THF, –78°, 8 min 2. Aldehyde, –78° to rt, 4 h	 (58), (*E*)/(*Z*)* = 14:86	77
	KHMDS, THF, –78°, 16 h	 (41), (*E*)/(*Z*)* = 4:96	601
	1. Base, THF, –78° 2. Aldehyde, –78° to rt		77
	KHMDS, THF, –78° to rt	 (69), (*E*)/(*Z*)* = 4:96	77, 602, 603

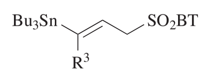
R	Base		(*E*)/(*Z*)*
H	LDA	(59)	9:91
H	KHMDS	(60)	10:90
Me	LDA	(41)	29:71
Me	KHMDS	(43)	61:39

TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES (*Continued*)

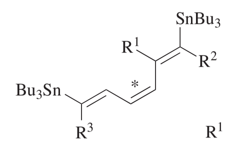
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		1. NaHMDS (3 eq), THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h	 R / (E)/(Z)* H (79) 17:83 AcO (70) 25:75	81, 604
		1. NaHMDS, THF, –78° 2. Aldehyde, –78° to rt	 (82), (*E*)/(*Z*)* = 14:86	605
		1. NaHMDS (3 eq), THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h	 (78), (*Z*)*-isomer only	606
C_{3-5}				
		KHMDS, THF, –78° to rt	 *n* / (E)/(Z)* 1 (73) 5:95 2 (49) 5:95	78

C_{3-4}





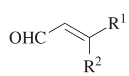
KHMDS, THF, –78° to rt

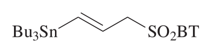


R^1	R^2	R^3		$(E)/(Z)^*$
H	H	H	(66)	4:96
H	H	Me	(56)	5:95
Me	H	H	(53)	18:82
H	Me	Me	(64)	5:95

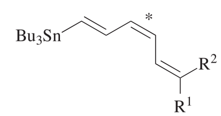
78

C_{4-9}





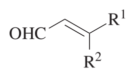
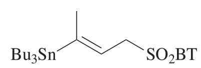
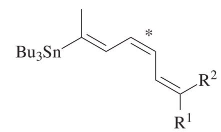
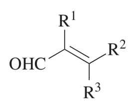
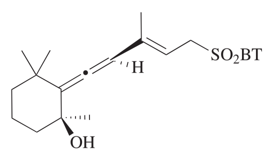
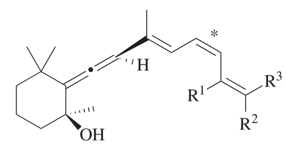
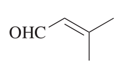
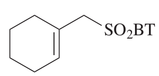
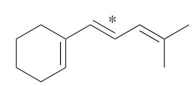
1. Base, solvent, –78°
2. Aldehyde, –78° to rt



77

R^1	R^2	Base	Solvent		$(E)/(Z)^*$
Me	H	LDA	THF	(58)	22:78
Me	H	KHMDS	toluene	(55)	17:83
Me	H	KHMDS	THF	(55)	7:93
Me	Me	LDA	THF	(62)	62:38
Me	Me	LiHMDS	THF	(43)	60:40
Me	Me	KHMDS	toluene	(59)	19:81
Me	Me	KHMDS	THF	(56)	3:97
Ph	H	LDA	THF	(62)	60:40
Ph	H	KHMDS	toluene	(60)	21:79
Ph	H	KHMDS	THF	(50)	6:94

TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-9}			
 	1. Base, THF, –78° 2. Aldehyde, –78° to rt		77
 	1. NaHMDS, THF, –78° 2. Aldehyde, –78° to rt		605
C_5			
 	**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt *or* **B**: LDA, THF, –78°, 3 h; then rt, 1h		3

Product data for the first entry (ref. 77):

R^1	R^2	Base		$(E)/(Z)^*$
Me	H	LDA	(58)	23:77
Me	H	KHMDS	(58)	5:95
Me	Me	LDA	(61)	32:68
Me	Me	KHMDS	(56)	5:95
Ph	H	LDA	(57)	28:72
Ph	H	KHMDS	(52)	8:92

Product data for the second entry (ref. 605):

R^1	R^2	R^3		$(E)/(Z)^*$
H	Me	H	(0)	—
H	Me	Me	(86)	8:92
Me	$TBSO(CH_2)_2$	H	(78)	29:71
H	Ph	H	(83)	22:78

Product data for the C_5 entry (ref. 3):

Conditions		$(E)/(Z)^*$
A	(15)	78:22
B	(22)	93:7

C$_6$

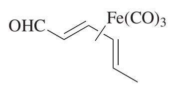
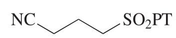
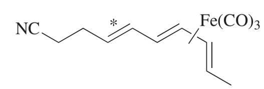
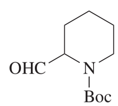
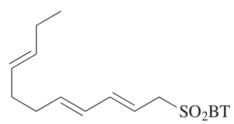
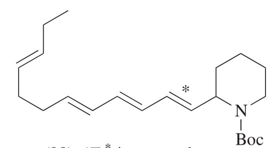
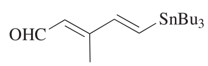
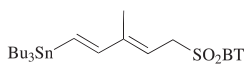
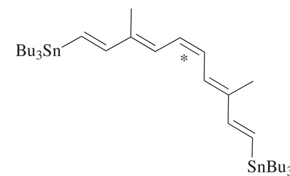
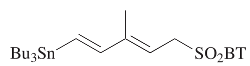
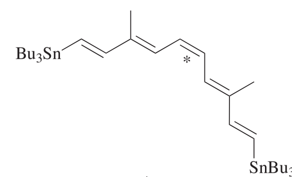
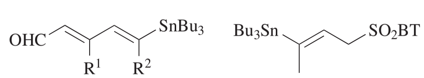
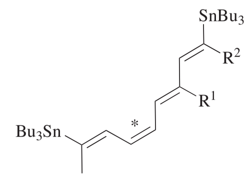
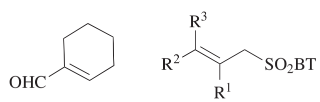
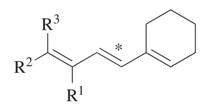
		KHMDS, THF, –78°, 2 h; then rt, 20 h	 (74), $(E)/(Z)^*$ = 96:4	607
		1. KHMDS, 18-crown-6, THF, –80°, 1 h 2. Aldehyde, THF, –80°, 2.5 h; then rt	 (98), $(E)^*$-isomer only	608
		1. NaHMDS, THF, –78° 2. Aldehyde, –78° to rt, 12 h	 (83), $(Z)^*$-isomer only	77, 605, 609
		KHMDS, THF, –78° to rt	 (63), $(E)/(Z)^*$ = 6:94	78

TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES (*Continued*)

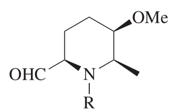
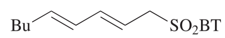
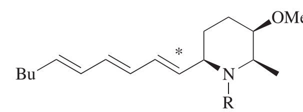
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	KHMDS, THF, –78° to rt		78
C_7			
	**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt *or* **B**: LDA, THF, –78°, 3 h; then to rt, 1 h		3

C6 product:

R^1	R^2		(*E*)/(*Z*)*
H	Me	(64)	5:95
Me	H	(73)	5:95

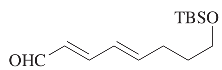
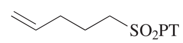
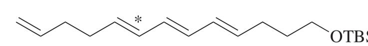
C7 product:

R^1	R^2	R^3	Conditions		(*E*)/(*Z*)*
H	Me	Me	**A**	(16)	67:33
H	Me	Me	**B**	(72)	80:20
Me	H	H	**A**	(29)	99:1
Me	H	H	**B**	(71)	>99:1
–$(CH_2)_4$–		H	**A**	(26)	>99:1
–$(CH_2)_4$–		H	**B**	(20)	>99:1

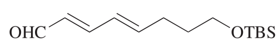
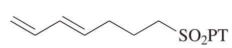
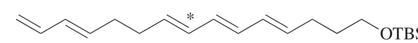
  1. $MN(SiMe_3)_2$, additive, THF, 0.5 h 2. Aldehyde, 2 h  610

R	M	Additive	Temp (°)		(E)/(Z)*
Me	Li	none	–78	(25)	50:50
Me	K	none	–78	(32)	50:50
Boc	Li	none	–78	(83)	50:50
Boc	Li	12-crown-4	–78	(80)	50:50
Boc	K	none	–78	(71)	50:50
Boc	K	HMPA	–78	(83)	67:33
Boc	K	18-crown-6	–78	(78)	75:25
Boc	K	18-crown-6	–100	(53)	75:25

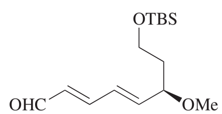
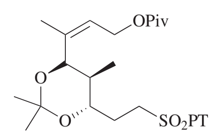
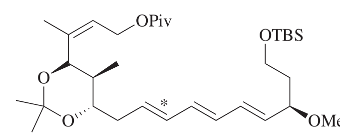
C_8

  KHMDS, THF, –78°  611

(62), (E)/(Z)* = 90:10

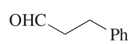
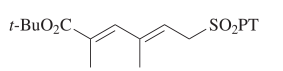
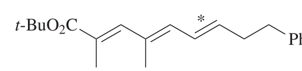
  KHMDS, THF, –78°  611

(65), (E)/(Z)* = 90:10

  1. KHMDS, THF, –78°, 20 min 2. Aldehyde, –78°, 1 h; then rt, 1 h  612, 613

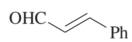
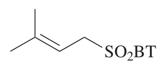
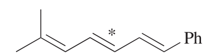
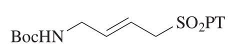
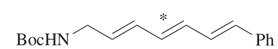
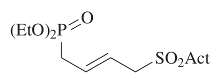
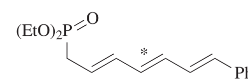
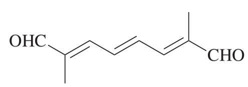
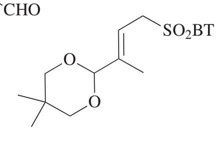
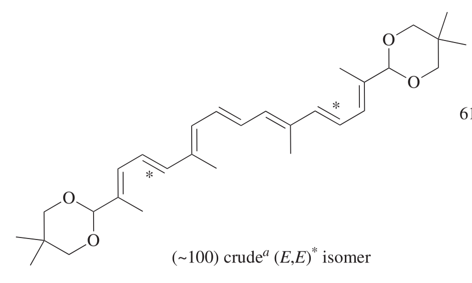
(85), (E)/(Z)* = 91:9

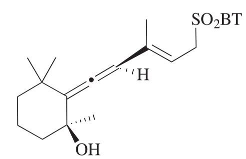
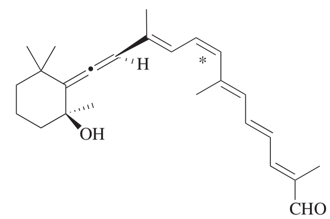
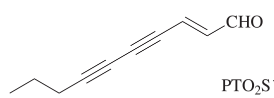
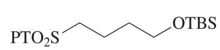
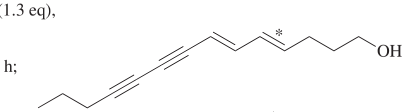
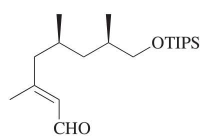
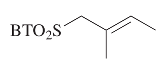
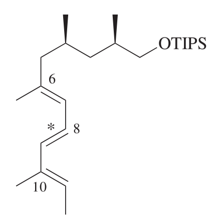
C_9

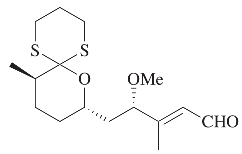
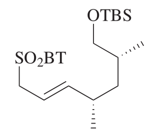
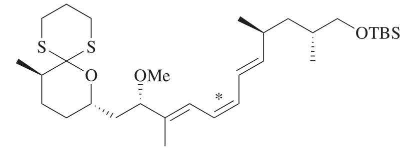
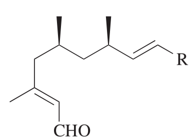
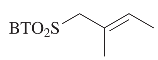
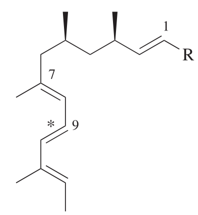
  n-BuLi, THF, –78°  614

(<10), (E)/(Z)* = —

TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES (*Continued*)

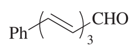
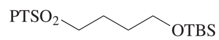
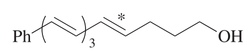
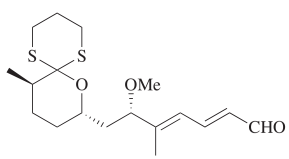
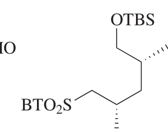
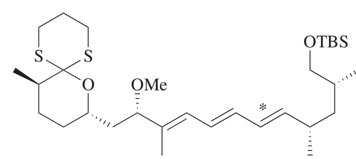
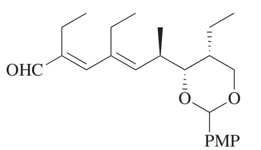
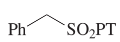
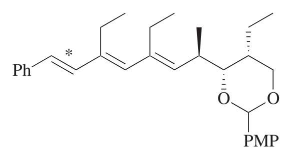
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt *or* **B**: LDA, THF, –78°, 3 h; then to rt, 1 h	 Conditions — (*E*)/(*Z*)* **A** (77) 66:34 **B** (81) 65:35	3
		1. Base (2.1 eq), additive, THF, –78°, 0.5 h 2. Sulfone metallate added to aldehyde, –78°; then rt	 Base — Additive — (*E*)/(*Z*)* LiHMDS none (88) 23:77 KHMDS 18-crown-6 (59) 95:5	506
		1. THF, KHMDS, –78°, 5 min 2. Aldehyde, –78°, 20 min; then 0°, 1 h	 Act — (*E*)/(*Z*)* PT (39) 62:38 BT (57) 68:32	115
C_{10}				
		1. Sulfone (2.20 eq), NaHMDS (2.21 eq), THF, –78°, 10 min 2. Dialdehyde (1.0 eq), –78°, 3 h	 (~100) crude[a] (*E*,*E*)* isomer	615

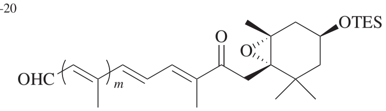
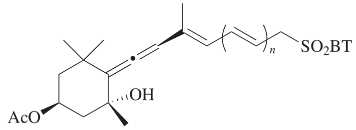
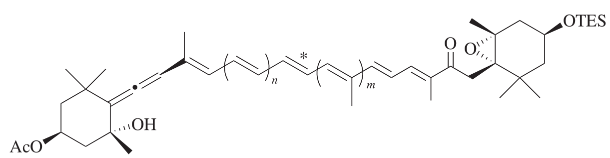
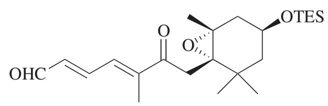
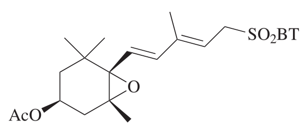
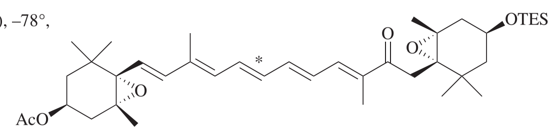
			1. NaHMDS, THF, –78° 2. Dialdehyde, –78° to rt	 (65), (*E*)/(*Z*)* = 0:100[b]	605
			1. Sulfone (1.3 eq), LiHMDS (1.3 eq), THF, –78°, 0.5 h 2. Aldehyde (1 eq), –78°, 0.25 h; then to 0°, 2 h 3. MeOH/HCl (10:1), rt, 0.5 h	 (79), (*E*)/(*Z*)* = 68:32	616
C_{11}			Aldehyde (1 eq), sulfone (1.5 eq), LiHMDS (1.5 eq), –78°, 1 h; then rt, 2 h	 (74), (6*E*,8*E**,10*E*)/(6*E*,8*Z**,10*E*)/(6*E*,8*E**,10*Z*) = 91:5:4	617

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
 	$MN(SiMe_3)_2$, THF, –80°		22
C_{12-15}			
 	Aldehyde (1 eq), sulfone (1.5 eq), LiHMDS (1.5 eq), –78°, 1 h; then rt, time		617

M		(*E*)/(*Z*)*
Li	(—)	29:71
Na	(79)	43:57
K	(—)	18:82

R	Time (h)		
n-Bu_3Sn	2	(75)	(1*E*,7*E*,9*E**,11*E*)/(1*E*,7*E*,9*Z**,11*E*)/(1*E*,7*E*,9*E**,11*Z*) = 88:7:5
EtO_2C	2	(73)	(1*E*,7*E*,9*E**,11*E*)/(1*E*,7*E*,9*Z**,11*E*)/(7*E*,9*E**,11*Z*) = 87:6:7
$EtO_2C(CH_2)_2$	1	(74)	(1*E*,7*E*,9*E**,11*E*)/(1*E*,7*E*,9*Z**,11*E*)/(1*E*,7*E*,9*E**,11*Z*) = 91:4:5

C_{13}				
 (*E*)/(*Z*) >95:5		1. Sulfone (1.0 eq), LiHMDS (1.17 eq), THF, –78°, 40 min 2. Aldehyde (1.5 eq), –78°; then to rt, 3 h 3. HCl, MeOH	 (89), (*E*)/(*Z*)* = 89:11	547
C_{14}				
		LiHMDS, THF, –80°, 3 h; then rt, 1 h	 (68), (*E*)/(*Z*)* = 95:5	22
C_{16}				
		LiHMDS, THF	 (82), (*E*)*-isomer	618

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17-20}  	1. Aldehyde (1.0 eq), sulfone (*x* eq), additive (10 eq), THF 2. NaHMDS (*y* eq), –78°, dark, time 3. H_2O		619
C_{17}  	1. Aldehyde (1.04 eq), sulfone (1.0 eq), THF 2. NaHMDS (2 eq), –78°, dark, 3 min 3. H_2O	 (53), $(E)^*$-isomer	619

m	*n*	*x*	Additive	*y*	Time (min)	$(E)^*$-isomer
0	0	1.05	none	2.0	3	(45)
1	0	1.0	none	2.4	5	(57)
1	1	1.14	Bu_4NI	2.9	5	(63)

C_{20}

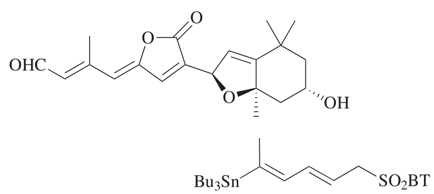
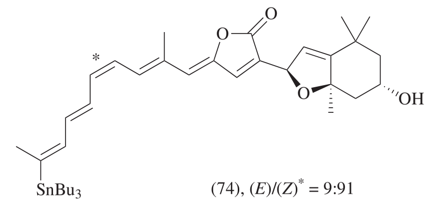
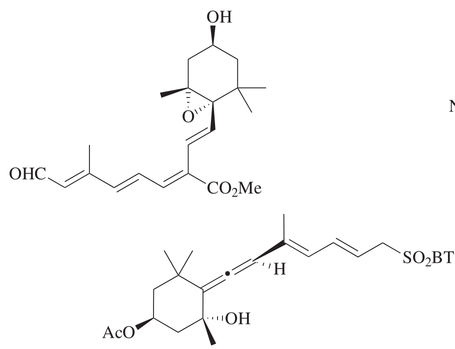
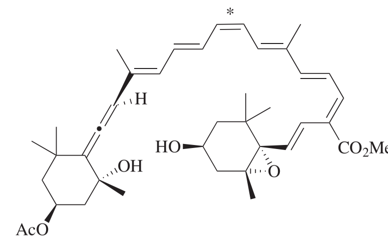
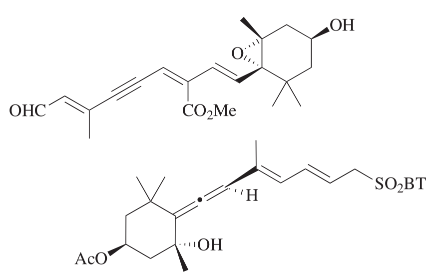
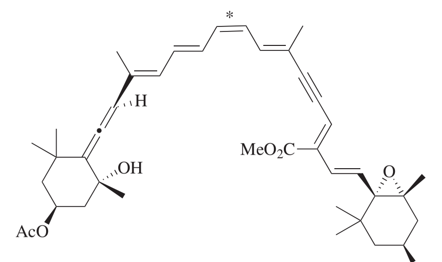
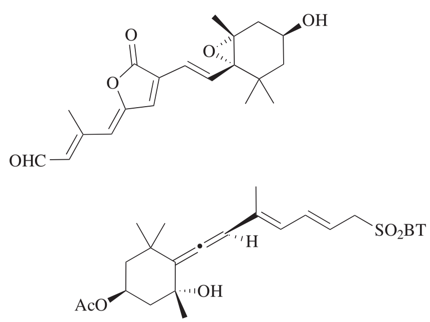
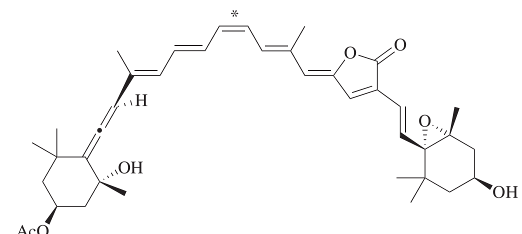
	NaHMDS, THF, –78°, 2 h	 (74), (*E*)/(*Z*)* = 9:91	83
	NaHMDS (3 eq), THF, –78°, 5 min, dark	 (48), "mixture of isomers"	620

TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	NaHMDS (3 eq), THF, –78°, 5 min, dark	 (63), (*E*)/(*Z*)* = 22:78	620
	NaHMDS (2 eq), THF, –78°, 5 min, dark	 (50), (*E*)/(*Z*)* = 25:75	80, 621

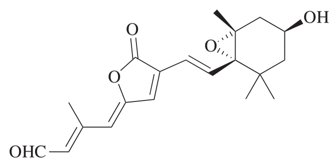
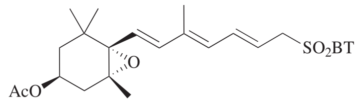
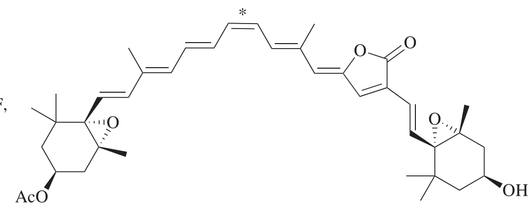
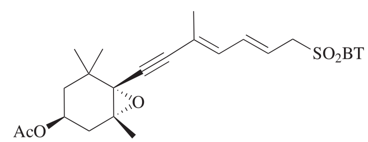
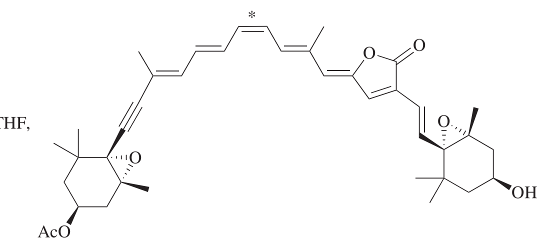
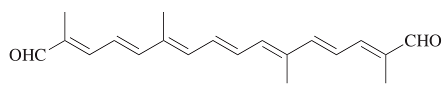
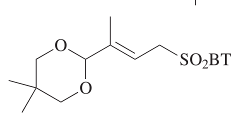
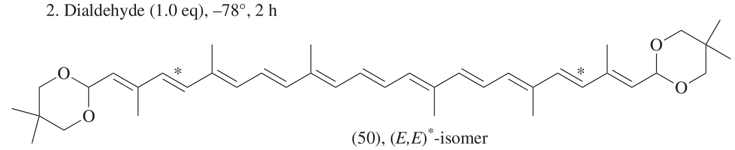
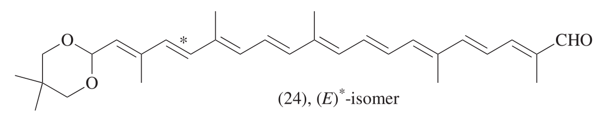
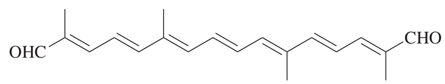
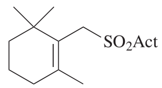
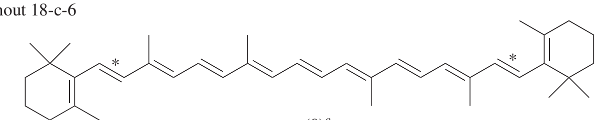
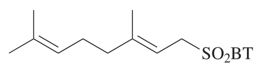
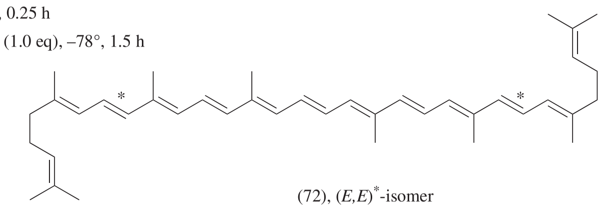
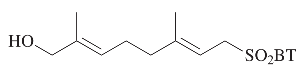
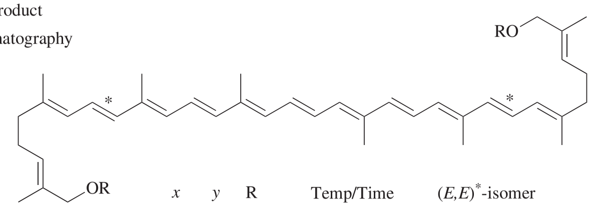
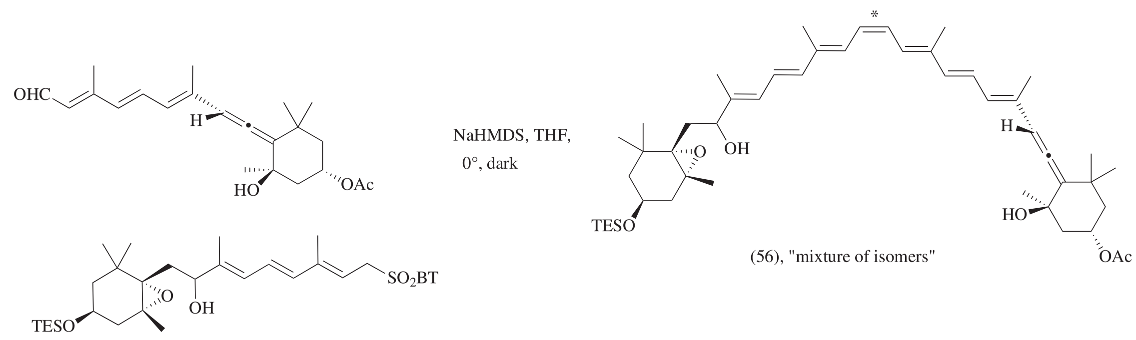
 	NaHMDS (3 eq), THF, –78°, 5 min, dark	 (48), "mixture of isomers"	82
	NaHMDS (2.7 eq), THF, –78°, 5 min, dark	 (42), "mixture of isomers"	82
 	1. Sulfone (2.10 eq), NaHMDS (2.5 eq), THF, –78°, 0.25 h 2. Dialdehyde (1.0 eq), –78°, 2 h	 (50), $(E,E)^*$-isomer +  (24), $(E)^*$-isomer	615

TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
  Act = BT or PT	NaHMDS, KHMDS, or *t*-BuOK, with or without 18-c-6	 (0)[c]	615
	1. Sulfone (2.08 eq), NaHMDS (2.31 eq), THF, –78°, 0.25 h 2. Aldehyde (1.0 eq), –78°, 1.5 h	 (72), $(E,E)^*$-isomer	615
	1. Sulfone (*x* eq), NaHMDS (*y* eq), THF, –78°, 0.25 h 2. Aldehyde (1.0 eq), temp, time; then crude product 3. SiO_2 chromatography		615

x	*y*	R	Temp/Time	$(E,E)^*$-isomer
2.0	2.3	H	–78°, 1.5 h	(33)
2.2	5.0	BT	–78°; to rt; rt, 14 h	(25)

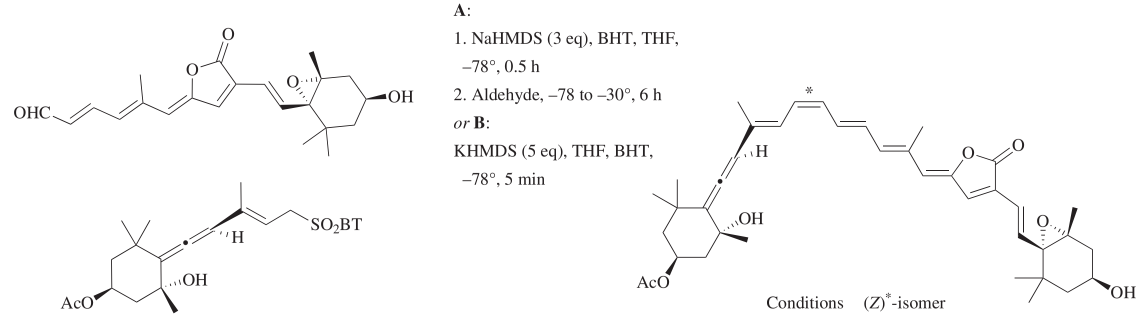
C$_{22}$



NaHMDS, THF,
0°, dark

(56), "mixture of isomers"

622



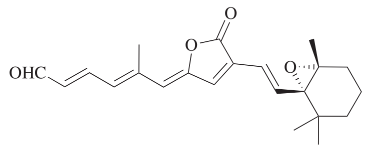
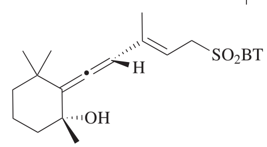
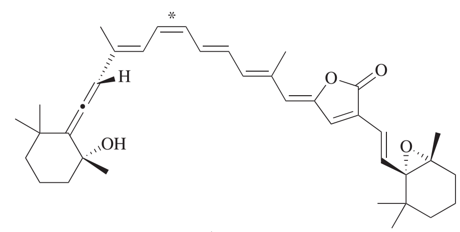
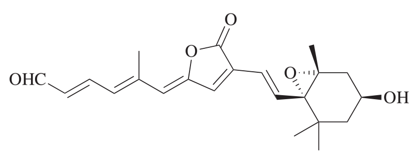
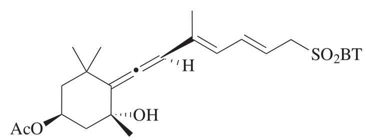
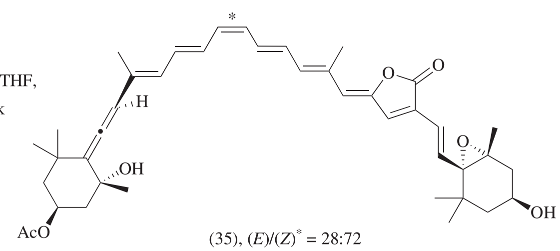
A:
1. NaHMDS (3 eq), BHT, THF, −78°, 0.5 h
2. Aldehyde, −78 to −30°, 6 h

or **B**:
KHMDS (5 eq), THF, BHT, −78°, 5 min

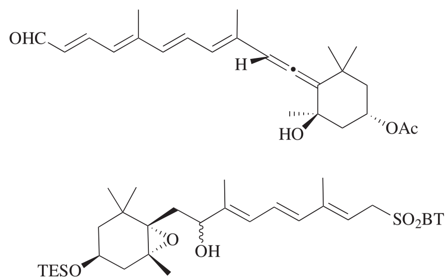
Conditions	(*Z*)*-isomer
A	(53)
B	(54)

81, 44

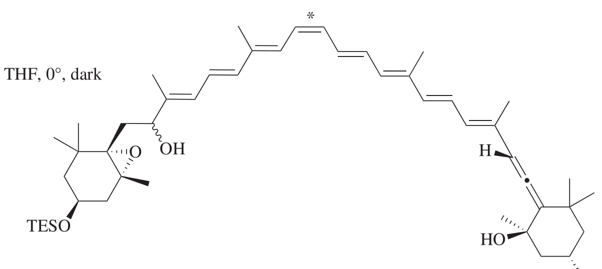
TABLE 5. SYNTHESIS OF 1,3,5-TRIENES AND HIGHER CONJUGATED POLYENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}			
 	1. NaHMDS (2.5 eq), THF, –78°, 0.5 h 2. Aldehyde, –78 to 0°, 2 h	 (63), (*Z*)*-isomer only	81, 605
 	NaHMDS (3 eq), THF, –78°, 5 min, dark	 (35), (*E*)/(*Z*)* = 28:72	591

C$_{30}$

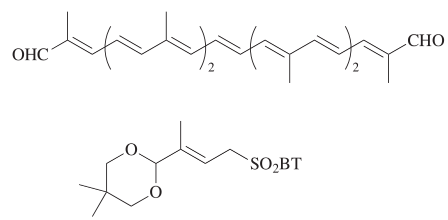


NaHMDS, THF, 0°, dark

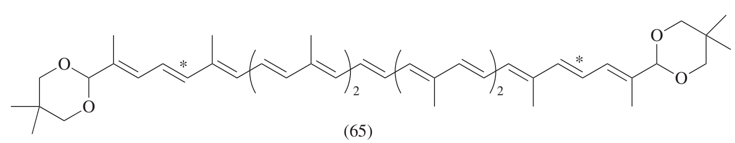


(45), "mixture of isomers"

622

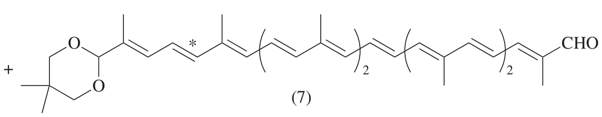


1. Sulfone (2.04 eq), NaHMDS
(3.1 eq), THF, –78°, 15 min
2. Dialdehyde (1.0 eq), –78°, 2 h



(65)

+



(7)

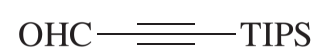
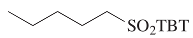
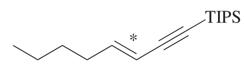
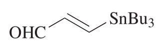
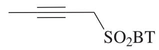
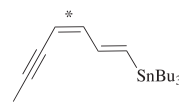
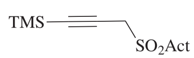
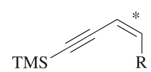
615

[a] On chromatography with SiO_2, partial and complete deacetalization occurred to give the monoacetal (48%) and the dialdehyde (38%) in addition to the diacetal (12%).

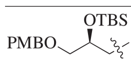
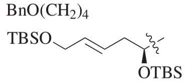
[b] Ten percent of the bis-olefination product was also isolated.

[c] The sulfone was destroyed and the aldehyde was recovered.

TABLE 6. SYNTHESIS OF 1,3- ENYNES

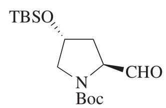
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		Cs_2CO_3, THF/DMF, 70°, 16 h	 (72), (*E*)/(*Z*)* = 80:20	62
		1. Base, THF, –78° 2. Aldehyde, –78° to rt		77
C_{4-9}				
RCHO		**A**: 1. KHMDS, solvent, –65°, –.5 h 2. Aldehyde, –65°, 3 h; then 0°, 1 h *or* **B**: KHMDS, solvent, –65 to 0°		623, 624

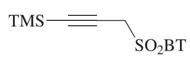
Base		(*E*)/(*Z*)*
LDA	(33)	5:95
KHMDS	(38)	5:95

R	Act	Conditions	Solvent		*E*)/(*Z*)*
	BT	**A**	THF	(56)	<2:98
$BnO(CH_2)_4$	BT	**A**	THF	(44)	21:79
$BnO(CH_2)_4$	BT	**B**	THF	(23)	7:93
	BT	**A**	THF	(76)	14:86
3-furyl	BT	**A**	THF	(50)	5:95
3-furyl	BT	**B**	THF	(41)	<2:98

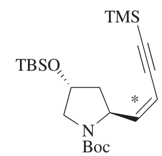
R	Act	Conditions	Solvent		(*E*)/(*Z*)*
Ph	BT	**A**	THF	(50)	13:87
Ph	BT	**B**	THF	(80)	4:96
Ph	BT	**A**	DME	(31)	2:98
Ph	PT	**B**	THF	(38)	2:98
4-$MeOC_6H_4$	BT	**A**	THF	(51)	22:78
4-$MeOC_6H_4$	BT	**B**	THF	(43)	3:97
(*E*)-PhCH=CH	BT	**A**	THF	(42)	43:66 (sic)
(*E*)-PhCH=CH	BT	**B**	THF	(46)	6:94

C_5





Aldehyde (1.6 eq),
sulfone (1 eq),
NaHMDS (1.2 eq),
THF, –55°; then –55°, 4 h;
then to rt, 1 h

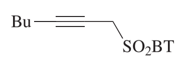


(61), $(E)/(Z)^*$ = 5:95

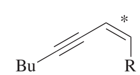
625

C_{5-7}

RCHO



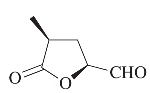
A:
1. LDA, THF, –78°, 1 h
2. Aldehyde, –78°, 3 h; then rt
or **B**:
LDA, THF, –78°, 3 h; then rt, 1 h

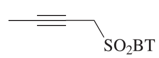


3

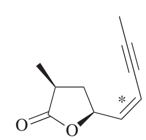
R	Conditions		$(E)/(Z)^*$
Bu	**A**	(27)	3:97
Bu	**B**	(37)	5:95
2-furyl	**A**	(32)	<1:99
4-$MeOC_6H_4$	**A**	(70)	16:84
4-$MeOC_6H_4$	**B**	(59)	12:88
n-C_7H_{15}	**A**	(26)	<1:99
n-C_7H_{15}	**B**	(22)	<1:99

C_6



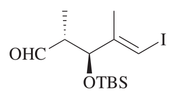
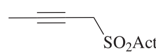
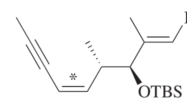
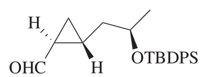
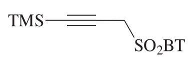
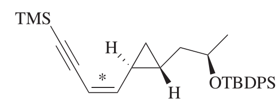
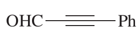
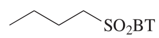
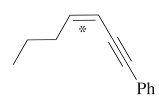
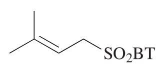
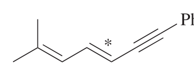
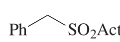
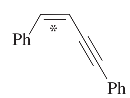


1. Sulfone (1.2 eq),
KHMDS (1.3 eq),
THF, –55°, 1 h
2. Aldehyde (1 eq), –55°, 3 h



(68), 2 steps, $(Z)^*$-isomer

626

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. Sulfone (2.5 eq), KHMDS (2.3 eq), THF, –55°, 0.5 h 2. Aldehyde (1.0 eq), –55°, 13 h		
			Act / (*E*)/(*Z*)*	
			BT (56) 4:95	76, 627
			PT (42) —	627
		KHMDS, –78°, 1 h; then –50°, 6 h	 (60), (*E*)/(*Z*)* = 5:95	628
C_9				
		LDA, THF, –78°, 3 h; then rt, 1 h	 (21), (*E*)/(*Z*)* = 47:53	3
		1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt	 (86), (*E*)/(*Z*)* = 58:42	3
		1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt	 (82), (*E*)/(*Z*)* = 46:56 (*sic*)	3

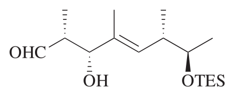
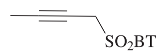
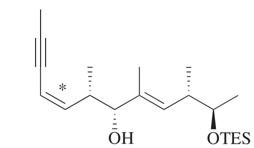
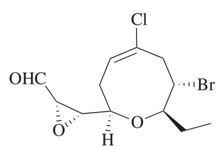
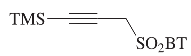
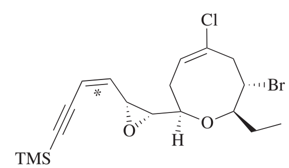
C_{11}						
			KHMDS, THF, –55°		(59), (*Z*)*-isomer only	629, 630
C_{12}						
			Aldehyde (1 eq), sulfone (10.4 eq), KHMDS (8.4 eq), THF, –78°, 0.5 h	 (53), (*E*)/(*Z*)* = 6:94		631

TABLE 7. SYNTHESIS OF ALLENES

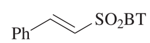
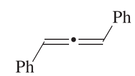
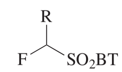
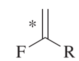
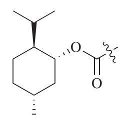
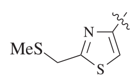
	Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7						
	PhCHO		1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 2 h; then rt		(26)	3

TABLE 8. SYNTHESIS OF VINYL HALIDES

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1			
$[CH_2O]_n$ 	Base (*x* eq), solvent, rt, 15 h		100

R	Base	*x*	Solvent	
$PhSO_2$	Cs_2CO_3	2	CH_2Cl_2	(75)
$PhSO_2$	Cs_2CO_3	2	THF	(39)
EtO_2C	Cs_2CO_3	2	CH_2Cl_2	(64)
$PhCH_2O_2C$	DBU	3	CH_2Cl_2	(54)
$PhCH_2O_2C$	Cs_2CO_3	2	CH_2Cl_2	(66)
(MeO)MeNOC	Cs_2CO_3	2	CH_2Cl_2	(89)
	Cs_2CO_3	2	CH_2Cl_2	(68)
	DBU	10	CH_2Cl_2	(99)
	Cs_2CO_3	2	CH_2Cl_2	(92)
	Cs_2CO_3	2	THF	(83)
Ph	DBU	10	CH_2Cl_2	(71)[a]
Ph	Cs_2CO_3	2	CH_2Cl_2	(86)

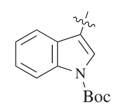
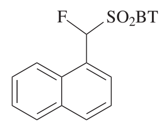
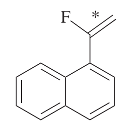
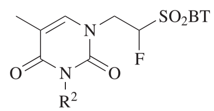
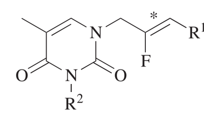
R	Base	*x*	Solvent	
$2-BrC_6H_4$	DBU	10	CH_2Cl_2	(57)
$2-BrC_6H_4$	DBU	3	CH_2Cl_2	(51)
$2-BrC_6H_4$	Cs_2CO_3	2	CH_2Cl_2	(61)
$2-BrC_6H_4$	Cs_2CO_3	2	THF	(54)
$3,4,5-(MeO)_3C_6H_2$	DBU	3	CH_2Cl_2	(95)
$3,4,5-(MeO)_3C_6H_2$	DBU	10	CH_2Cl_2	(92)
$3,4,5-(MeO)_3C_6H_2$	Cs_2CO_3	2	CH_2Cl_2	(81)
$3,4,5-(MeO)_3C_6H_2$	Cs_2CO_3	2	THF	(90)
$4-O_2NC_6H_4$	DBU	3	CH_2Cl_2	(76)
$4-O_2N_2C_6H_4$	Cs_2CO_3	2	CH_2Cl_2	(78)
$4-O_2NC_6H_4$	Cs_2CO_3	2	THF	(71)
	Cs_2CO_3	2	CH_2Cl_2	(53)
	Cs_2CO_3	2	THF	(63)
2-naphthyl	DBU	3	CH_2Cl_2	(92)
2-naphthyl	DBU	10	CH_2Cl_2	(69)
2-naphthyl	Cs_2CO_3	2	CH_2Cl_2	(74)
2-naphthyl	Cs_2CO_3	2	THF	(91)

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1			
$[CH_2O]_n$ or CH_2O (aq) 	**A**: Paraformaldehyde, base (*x* eq), solvent, rt *or* **B**: CH_2O (37% aq), base (*x* eq), solvent, rt		100

Base	Conditions	*x*	Solvent	
Et_3N	**A**	10	CH_2Cl_2	(0)
K_2CO_3	**A**	10	acetone	(0)
K_2CO_3	**A**	10	THF/H_2O	(23)
Cs_2CO_3	**A**	10	CH_2Cl_2	(57)
Cs_2CO_3	**A**	2	CH_2Cl_2	(49)
Cs_2CO_3	**A**	10	THF	(67)
Cs_2CO_3	**A**	2	THF	(71)
Cs_2CO_3	**B**	2	THF	(0)
TMG	**A**	10	CH_2Cl_2	(25)
DBU	**A**	10	CH_2Cl_2	(67)
DBU	**A**	3	CH_2Cl_2	(62)
DBU	**A**	10	THF	(68)
DBU	**B**	10	THF	(8)

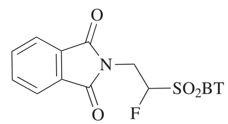
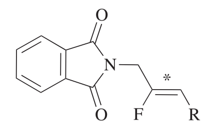
C_{2-20}

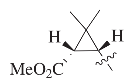
R^1CHO  NaHMDS, THF, –78° to temp  52

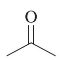
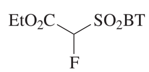
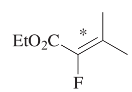
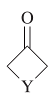
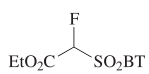
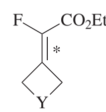
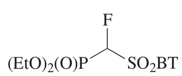
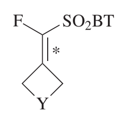
R^1	R^2	Temp (°)		(E)/(Z)*
Me	H	20	(82)	39:61
Me	Bz	–20	(88)	41:59
$BnO(CH_2)_3$	H	20	(59)	30:70
$BnO(CH_2)_3$	Bz	–20	(66)	32:68
$BnO(CH_2)_4$	H	20	(57)	27:73
$BnO(CH_2)_4$	Bz	–20	(52)	29:71
$BnO(CH_2)_5$	H	20	(63)	27:73
$BnO(CH_2)_5$	Bz	–20	(61)	30:70
3-pyridyl	H	20	(66)	12:88
3-pyridyl	Bz	–20	(61)	16:84
c-C_6H_{11}	H	20	(57)	21:79
c-C_6H_{11}	Bz	–20	(83)	28:72

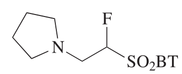
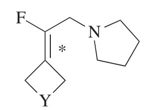
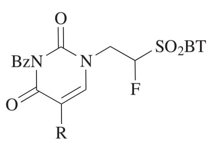
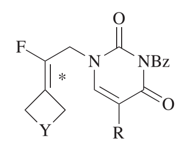
R^1	R^2	Temp (°)		(E)/(Z)*
n-C_6H_{13}	H	20	(67)	30:70
n-C_6H_{13}	Bz	–20	(61)	29:71
4-BrC_6H_4	H	20	(55)	17:83
4-BrC_6H_4	Bz	–20	(86)	8:92
4-$O_2NC_6H_4$	Bz	–20	(63)	32:68
4-$MeOC_6H_4$	H	20	(76)	7:93
4-$MeOC_6H_4$	Bz	–20	(79)	4:96
n-C_8H_{17}	H	20	(78)	28:72
n-C_8H_{17}	Bz	–20	(52)	30:70
Ph_3C	H	20	(65)	15:85
Ph_3C	Bz	–20	(82)	17:83

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-15}				
RCHO		**A**: *t*-BuOK, –17°, THF, 1 h *or* **B**: NaHMDS, THF, –78 to 0°, 3 h		632

R	Conditions		$(E)/(Z)^*$
TBDPSO$(CH_2)_2$	**A**	(—)	—
BnO$(CH_2)_2$	**A**	(77)	46:54
	**B**	(50)	52:48
4-BrC_6H_4	**B**	(56)	10:90
CH_2=CH$(CH_2)_8$	**B**	(66)	38:62
9-anthracenyl	**B**	(70)	15:85

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		DBU, THF, rt, 6 h	 (10)	633
C_{3-4}				
		Ketone (1.2 eq), sulfone (1.0 eq), DBU (1.7 eq), THF, 0°; then 20°, overnight	 Y: BocN (89); O (94); CH_2 (96)	634
		Ketone (1.3 eq), sulfone (1 eq), Et_3N (1.1 eq), LiCl (1.2 eq), THF, 0°; then 20°, overnight	 Y: BocN (96); O (84); CH_2 (71)	634

Ketone	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ketone (1.2 eq), sulfone (1 eq), NaHMDS (1.5 eq), THF, –78°, 1 h; then 20°, 3 h	 Y: BocN (67); O $(87)^{b,c}$; CH_2 (53)	634
		Ketone (x eq), sulfone (1 eq), NaHMDS (1.5 eq), THF		634

Y	R	x	Temp/Time	
BocN	H	1.2	–78°, 1 h; to 20°, 3 h	(57)
BocN	Me	1.05	–78°, 1 h; to 20°, 3 h	(20)
O	H	1.2	–78°, 1 h; to 20°, 3 h	(87)
O	Me	1.05	–78°; to 20°, overnight	(50)
CH_2	H	1.2	–78°, 1 h; to 20°, 3 h	$(10)^{b}$
CH_2	Me	1.05	–78°; to 20°, overnight	(50)

C_3

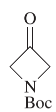
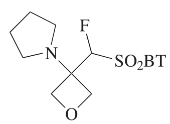
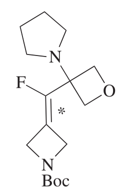
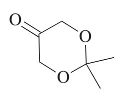
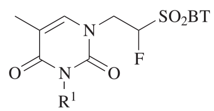
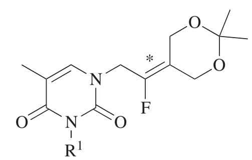
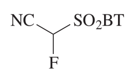
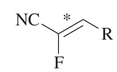
Ketone	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ketone (1.2 eq), sulfone (1 eq), NaHMDS (1.5 eq), THF, –78°, 1 h; then 20°, 3 h	 (64)	634

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		NaHMDS, THF, –78 to –20°	 (60)	52
C_{4-11}				
RCHO		1. Aldehyde (1 eq), DBU (4 eq), CH_2Cl_2, temp 2. Sulfone (2 eq), temp, 1 h; then rt		104

R	Temp		(*E*)/(*Z*)*
3-Boc-5-imidazolyl	rt	(59)	18:82
2-thienyl	rt	(96)	17:83
Et_2CH	rt	(76)	15:85
Et_2CH	–78°	(77)	8:92
Ph	rt	(93)	19:81
$2\text{-}FC_6H_4$	rt	(91)	16:84
$2\text{-}O_2NC_6H_4$	rt	(60)	15:85
$4\text{-}O_2NC_6H_4$	rt	(72)	17:83
$2\text{-}MeOC_6H_4$	rt	(91)	37:63
$2\text{-}MeOC_6H_4$	–78°	(91)	27:73
$4\text{-}MeOC_6H_4$	rt	(95)	16:84

R	Temp		(*E*)/(*Z*)*
n-C_7H_{15}	rt	(97)	23:77
n-C_7H_{15}	–78°	(90)	16:84
$2\text{-}MeC_6H_4$	rt	(94)	17:83
$Ph(CH_2)_2$	rt	(80)	23:77
$Ph(CH_2)_2$	–78°	(81)	12:88
(*E*)-PhCH=CH	rt	(81)	17:83
2-naphthyl	rt	(98)	15:85
2-naphthyl	–78°	(97)	8:92
N-Boc-3-indolyl	rt	(86)	20:80
ferrocenyl	rt	(92)	17:83

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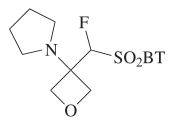
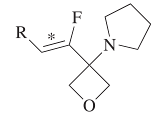
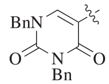
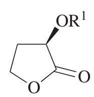
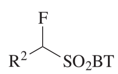
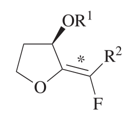
R^1	R^2	Temp		(*E*)/(*Z*)*
N-Ts-4-imidazolyl	*t*-Bu	rt	(99)	74:26
2-thienyl	Et	rt	(94)	87:13
2-thienyl	*t*-Bu	rt	(88)	85:15
2-thienyl	8-Ph-menthyl	rt	(70)	86:14
Et_2CH	*t*-Bu	rt	(77)	64:36
Et_2CH	8-Ph-menthyl	rt	(65)	61:39
Ph	*t*-Bu	rt	(78)	75:25
4-$O_2NC_6H_4$	*t*-Bu	rt	(84)	72:28
4-$MeOC_6H_4$	*t*-Bu	rt	(87)	83:17
n-C_7H_{15}	*t*-Bu	rt	(82)	71:29
n-C_7H_{15}	*t*-Bu	–78°	(75)	83:17

R^1	R^2	Temp		(*E*)/(*Z*)*
(*E*)-PhCH=CH	*t*-Bu	rt	(93)	76:24
(*E*)-PhCH=CH	8-Ph-menthyl	rt	(80)	75:25
N-Ts-3-indolyl	*t*-Bu	rt	(90)	83:17
2-benzofuranyl	*t*-Bu	rt	(93)	82:18
2-benzofuranyl	8-Ph-menthyl	rt	(79)	85:15
5-benzofuranyl	*t*-Bu	rt	(99)	80:20
2-naphthyl	Et	rt	(78)	78:22
2-naphthyl	*t*-Bu	rt	(93)	77:23
2-naphthyl	*t*-Bu	–78°	(70)	88:12
2-naphthyl	8-Ph-menthyl	rt	(92)	73:27
ferrocenyl	Et	rt	(71)	54:46
ferrocenyl	*t*-Bu	rt	(83)	57:43

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

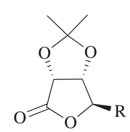
Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-8}			
RCHO 	Aldehyde (*x* eq), sulfone (1 eq), NaHMDS (1.5 eq), THF		634

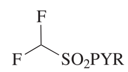
R	*x*	Temp/Time		(*E*)/(*Z*)*
$BnO(CH_2)_3$	1.2	–78°, 1 h; 20°, 3 h	(55)	22:78
	1.05	–78°; to 20°, overnight	(47)	39:61
2-furyl	1.2	–78°, 1 h; 20°, 3 h	(92)	21:79
n-C_6H_{13}	1.2	–78°, 1 h; 20°, 3 h	(87)	16:84
Ph	1.2	–78°, 1 h; 20°, 3 h	(81)	39:61
4-BrC_6H_4	1.2	–78°, 1 h; 20°, 3 h	(57)	22:78
Bn	1.2	–78°, 1 h; 20°, 3 h	(90)	9:91

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
 	1. LiHMDS, additive, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h		635

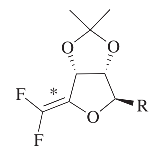
R^1	R^2	Additive		(*E*)/(*Z*)*
TES	H	none	(20)	40:60
TES	H	BF_3•OEt_2	(68)	50:50
TES	Me	none	(29)	20:80
TES	Me	BF_3•OEt_2	(68)	30:70
Bn	H	none	(60)	60:40
Bn	Me	none	(60)	30:70

C_{4-5}





1. Lactone (2 eq), sulfone (1 eq), BF_3•Et_2O (2 eq), THF, –78°
2. LiHMDS (2 eq), –78°, 0.67 h
3. H_2O
4. Toluene, microwave heating, 140°, 1 h



R	
H	(19)
$TBDPSOCH_2$	(7)

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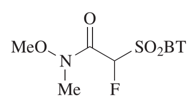
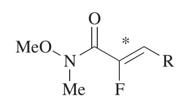
C_{5-11}

RCHO



A:
NaH, THF, rt, 1–1.5 h
or **B**:
DBU, THF, –78°, 2.5–4 h
or **C**:
DBU, DMPU, rt, 16–17 h



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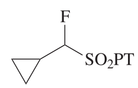
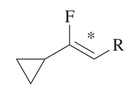
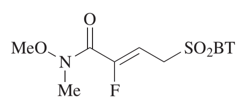
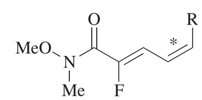
	Conditions **A**		Conditions **B**		Conditions **C**	
R		(*E*)/(*Z*)*		(*E*)/(*Z*)*		(*E*)/(*Z*)*
2-thienyl	(99)	2:98	(78)	74:26	(81)	86:14
Et_2CH	(71)	0:100				
4-$O_2NC_6H_4$	(85)	<1:99	(92)	3:97	(83)	67:33
4-$MeOC_6H_4$	(89)	1:99				
2-MeC_6H_4	(80)	<1:99				
n-C_8H_{17}	(83)	<1:99	(74)	54:46	(69)	67:33
2-naphthyl	(90)	0:100	(86)	6:94	(93)	78:22
ferrocenyl	(100)	0:100				

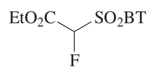
TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-11}			
RCHO 	**A**: LiHMDS, $MgBr_2$•OEt_2, THF, rt, 3 h *or* **B**: KHMDS, THF, –78 to –60°, 2 h		98
	Aldehyde (1 eq), sulfone (1.5 eq), DBU (4 eq), CH_2Cl_2, 0°, overnight		637

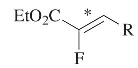
R	Conditions		(*E*)/(*Z*)*
2-thienyl	**A**	(60)	9:91
4-$O_2NC_6H_4$	**A**	(45)	73:27
4-$O_2NC_6H_4$	**B**	(71)	67:33
4-$MeOC_6H_4$	**A**	(57)	5:95
2-MeC_6H_4	**A**	(72)	50:50
n-C_7H_{15}	**A**	(63)	42:58
n-C_7H_{15}	**B**	(72)	36:64
(*E*)-PhCH=CH	**A**	(53)	49:51
2-naphthyl	**A**	(70)	38:62
2-naphthyl	**B**	(83)	50:50

R		(*E*)/(*Z*)*
2-thienyl	(63)	10:90
4-$O_2NC_6H_4$	(74)	40:60
4-$MeOC_6H_4$	(50)	23:77
$Ph(CH_2)_2$	(51)	15:85
2-naphthyl	(66)	35:65

C_{5-9}

RCHO 

A:
NaHMDS, THF, 20°, 2 h
or **B**:
DBU, THF, –78°, 0.5 h;
then 20°, 1.5 h
or **C**:
DBU, $MgBr_2$, THF, 20°, 2 h



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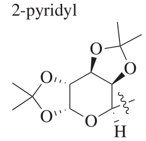
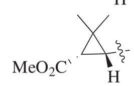
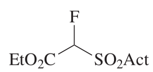
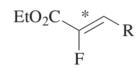
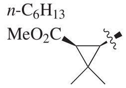
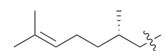
R	Conditions **A**		Conditions **B**		Conditions **C**	
		(*E*)/(*Z*)*		(*E*)/(*Z*)*		(*E*)/(*Z*)*
2-furyl	(71)	29:71	(77)	98:2	(37)	49:51
2-thienyl	(75)	23:77	(83)	98:2	(45)	24:76
2-pyridyl	(78)	24:76	(90)	61:39	(27)	22:78
	(81)	25:75	(82)	49:51	(72)	6:94
	(87)	55:45	(83)	65:35	(90)	20:80
c-C_6H_{11}	(56)	35:65	(86)	72:28	(77)	10:90
Ph	(69)	15:85	(70)	76:24	(71)	8:92
4-$O_2NC_6H_4$	(85)	16:84	(72)	88:12	(66)	6:94
3-$MeOC_6H_4$	(75)	15:85	(74)	85:15	(49)	13:87
n-C_8H_{17}	(76)	48:52	(66)	76:24	(87)	12:88

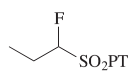
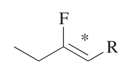
TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-11} RCHO 	Aldehyde (1.05 eq), sulfone (1 eq), NaHMDS (1.5 eq), –78°, 0.5 h; then to rt, 2 h		638

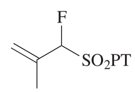
R	Act		(*E*)/(*Z*)*
2-furyl	BT	(75)	12:88
2-furyl	PYM	(87)	1:99
2-thienyl	BT	(80)	17:83
2-thienyl	5-O_2NBT	(82)	17:83
2-thienyl	PYM	(69)	0:100
n-C_6H_{13}	BT	(50)	47:53
n-C_6H_{13}	5-O_2NBT	(60)	26:74
n-C_6H_{13}	PYM	(84)	0:100
	BT	(57)	67:33
	PYM	(72)	5:95

R	Act		(*E*)/(*Z*)*
c-C_6H_{11}	BT	(62)	29:71
c-C_6H_{11}	5-O_2NBT	(60)	12:88
c-C_6H_{11}	PYM	(60)	1:99
4-BrC_6H_4	BT	(72)	15:85
4-BrC_6H_4	5-O_2NBT	(74)	8:92
4-BrC_6H_4	PYM	(72)	0:100
3,6-$Br_2C_6H_3$	BT	(52)	2:98
3,6-$Br_2C_6H_3$	5-O_2NBT	(78)	4:96
3,6-$Br_2C_6H_3$	PYM	(83)	1:99

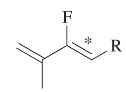
R	Act		(*E*)/(*Z*)*
n-C_8H_{17}	BT	(81)	54:46
n-C_8H_{17}	5-O_2NBT	(92)	16:84
n-C_8H_{17}	PYM	(73)	1:99
Ph$(CH_2)_2$	BT	(40)	31:69
Ph$(CH_2)_2$	PYM	(52)	3:97
	BT	(49)	45:55
	PYM	(81)	3:97
CH_2=CH$(CH_2)_8$	BT	(66)	57:43
CH_2=CH$(CH_2)_8$	5-O_2NBT	(82)	15:85
CH_2=CH$(CH_2)_8$	PYM	(79)	4:96

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
	**A**: LiHMDS, $MgBr_2$•OEt_2, THF, rt, 3 h *or* **B**: KHMDS, THF, –78 to –60°, 2 h		98

R	Conditions		(*E*)/(*Z*)*
2-thienyl	**A**	(75)	1:99
4-$O_2NC_6H_4$	**A**	(66)	50:50
4-$O_2NC_6H_4$	**B**	(90)	67:33
4-$MeOC_6H_4$	**A**	(87)	3:97
n-C_7H_{15}	**A**	(71)	44:56
n-C_7H_{15}	**B**	(74)	27:73
2-MeC_6H_4	**A**	(77)	18:82
(*E*)-PhCH=CH	**A**	(72)	19:81
2-naphthyl	**A**	(94)	14:86
2-naphthyl	**B**	(64)	73:27



A:
LiHMDS, $MgBr_2{\bullet}OEt_2$,
THF, rt, 3 h
or **B**:
KHMDS, THF, –78 to –60°, 2 h



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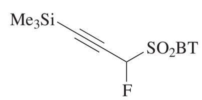
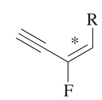
R	Conditions		$(E)/(Z)^*$
2-thienyl	**A**	(78)	0:100
$4\text{-}O_2NC_6H_4$	**A**	(61)	73:27
$4\text{-}MeOC_6H_4$	**A**	(60)	<1:99
$n\text{-}C_7H_{15}$	**A**	(63)	80:20
$n\text{-}C_7H_{15}$	**B**	(83)	50:50
$2\text{-}MeC_6H_4$	**A**	(77)	28:72
(*E*)-PhCH=CH	**A**	(—)	38:62
2-naphthyl	**A**	(78)	16:84
2-naphthyl	**B**	(73)	46:54



A:
1. DBU, CH_2Cl_2, –55°
2. $n\text{-}Bu_4N^+ F^-$
or **B:**
1. LiHMDS, THF, –78°
2. $n\text{-}Bu_4N^+ F^-$



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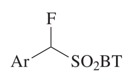
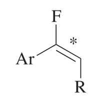
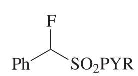
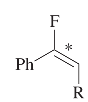
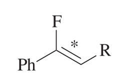
	Conditions **A**		Conditions **B**	
R		$(E)/(Z)^*$		$(E)/(Z)^*$
2-thienyl	(78)	75:25	(78)	91:9
Ph	(90)	76:24	(59)	94:6
$4\text{-}ClC_6H_4$	(81)	70:30	(95)	94:6
$4\text{-}O_2NC_6H_4$	(59)	51:49	(81)	72:28
$2\text{-}MeOC_6H_4$	(92)	78:22	(87)	90:10
$4\text{-}MeOC_6H_4$	(92)	81:19	(97)	95:5

	Conditions **A**		Conditions **B**	
R		$(E)/(Z)^*$		$(E)/(Z)^*$
$n\text{-}C_7H_{15}$	(79)	85:15	(—)	—
$Ph(CH_2)_2$	(54)	80:20	(63)	70:30
(*E*)-PhCH=CH	(95)	72:28	(96)	80:20
3-indolinyl	(95)	75:25	(92)	91:9
2-naphthyl	(95)	74:26	(97)	88:12
ferrocenyl	(95)	83:17	(98)	90:10

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-11}				
RCHO		LiHMDS, THF, 0°, 1.5–2 h		639

R	Ar		(*E*)/(*Z*)*
2-thienyl	2-thienyl	(91)	82:18
2-thienyl	Ph	(98)	68:32
2-thienyl	2-naphthyl	(100)	72:28
n-C_7H_{15}	2-thienyl	(95)	62:38
n-C_7H_{15}	Ph	(100)	66:34
n-C_7H_{15}	2-naphthyl	(100)	66:34

R	Ar		(*E*)/(*Z*)*
(*E*)-PhCH=CH	2-thienyl	(86)	42:58
(*E*)-PhCH=CH	Ph	(90)	50:50
(*E*)-PhCH=CH	2-naphthyl	(90)	36:64
2-naphthyl	2-thienyl	(100)	73:27
2-naphthyl	2-naphthyl	(98)	78:22
ferrocenyl	2-thienyl	(100)	6:94
ferrocenyl	Ph	(100)	0:100
ferrocenyl	2-naphthyl	(98)	0:100

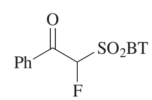
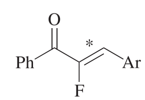
Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Aldehyde (1.2 eq), sulfone (1.0 eq), LiHMDS (*x* eq), DMF/HMPA (10:1), –55°; then to rt, 3 h; then rt, 1.5 h 2. H_2O, Et_2O 3. Et_2O contains the (*Z*)* isomer 4. To aqueous phase + DMF, added TsOH•H_2O at –50°; then to rt; then extraction with Et_2O gives the (*E*)* isomer	 (*E*) +  (*Z*)	640

R	*x*	(*E*)*	(*E*)/(*Z*)	(*Z*)*	(*E*)/(*Z*)
t-Bu	1.8	(32)	61:39	(46)	1:>99
2-thienyl	1.8	(48)	95:5	(34)	1:>99
3-pyridyl	1.8	(56)	97:3	(26)	1:99
c-C_6H_{11}	1.8	(25)	99:1	(53)	1:>99

R	*x*	(*E*)*	(*E*)/(*Z*)	(*Z*)*	(*E*)/(*Z*)
4-$CF_3C_6H_4$	1.8	(42)	>99:1	(26)	1:99
4-NCC_6H_4	1.8	(45)	>99:1	(26)	1:99
(*E*)-PhCH=CH	1.8	(45)	97:3	(17)	7:93
Ph(Me)CH	2.2	(25)	96:4	(45)	1:99

2-ClC_6H_4	1.8	(37)	99:1	(33)	1:99	4-*t*-BuC_6H_4	1.8	(32)	99:1	(46)	1:>99
4-BrC_6H_4	1.8	(51)	99:1	(29)	1:>99	1-naphthyl	1.8	(27)	>99:1	(60)	1:>99
3-$O_2NC_6H_4$	1.8	(41)	>99:1	(25)	1:99	2-naphthyl	1.8	(37)	99:1	(46)	1:>99
2-$MeOC_6H_4$	2.2	(27)	97:3	(47)	1:99						

C_{5-7}

ArCHO  DBU, THF, reflux, 0.5 h 

(*Z*)*-isomer only

Ar	
2-thienyl	(71)
4-$O_2NC_6H_4$	(81)
2-$MeOC_6H_4$	(64)
4-$MeOC_6H_4$	(61)

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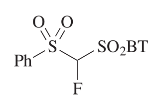
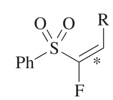
C_{5-11}

RCHO  DBU (1.5 eq), additive, solvent, rt 

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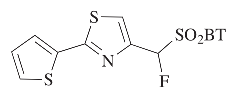
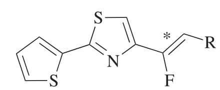
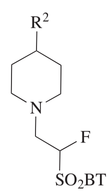
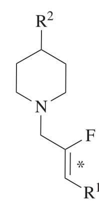
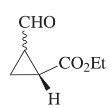
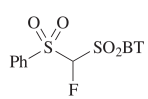
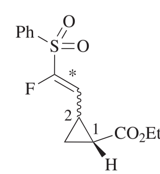
R	Additive	Solvent	Time (min)		(*E*)/(*Z*)*
2-thienyl	none	CH_2Cl_2	90	(82)	11:89
2-thienyl	$MgBr_2$	THF	90	(96)	9:91
Et_2CH	none	CH_2Cl_2	90	(59)	23:77
Ph	none	CH_2Cl_2	80	(90)	16:84
4-ClC_6H_4	none	CH_2Cl_2	70	(89)	17:83
4-$O_2NC_6H_4$	none	CH_2Cl_2	90	(85)	22:78
4-$O_2NC_6H_4$	$MgBr_2$	THF	90	(84)	29:71
2-$MeOC_6H_4$	none	CH_2Cl_2	120	(75)	48:52

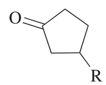
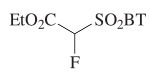
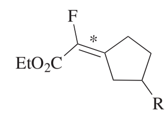
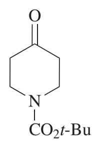
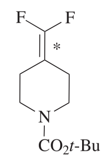
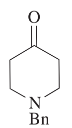
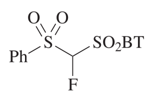
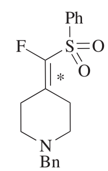
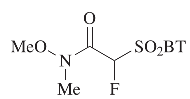
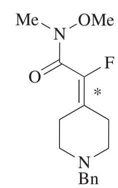
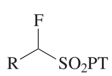
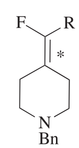
R	Additive	Solvent	Time (min)		(*E*)/(*Z*)*
2-$MeOC_6H_4$	$MgBr_2$	THF	120	(91)	36:64
4-$MeOC_6H_4$	none	CH_2Cl_2	90	(90)	12:88
n-C_7H_{15}	none	CH_2Cl_2	90	(85)	22:78
n-C_7H_{15}	$MgBr_2$	THF	90	(95)	4:96
$Ph(CH_2)_2$	none	CH_2Cl_2	35	(66)	23:77
(*E*)-PhCH=CH	none	CH_2Cl_2	40	(87)	13:87
2-naphthyl	none	CH_2Cl_2	120	(94)	16:84
ferrocenyl	none	CH_2Cl_2	80	(72)	44:56

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-11}				
RCHO		LiHMDS, THF, 0°, 1.5–2 h		639
C_{5-7}				
R^1CHO		Aldehyde (1.05 eq), sulfone (1.0 eq), NaHMDS (1.5 eq), THF, –78°, 0.5 h; then "stirred at rt"		642
C_5				
 *trans*:*cis* = 90:10		DBU, CH_2Cl_2, rt	 (80), 1,2-*cis* (*E*)/(*Z*)* = 25:75; 1,2-*trans* (*E*)/(*Z*)* = 22:78	641

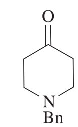
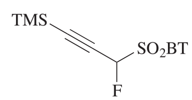
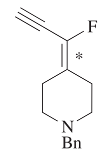
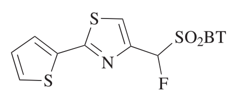
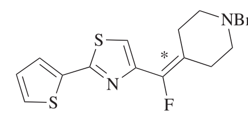
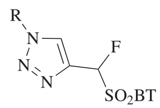
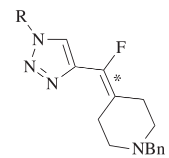
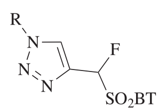
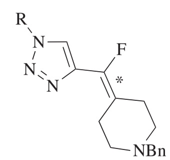
R		(*E*)/(*Z*)*
2-thienyl	(93)	40:60
n-C_7H_{15}	(100)	42:58
(*E*)-PhCH=CH	(87)	21:79
2-naphthyl	(97)	40:60
ferrocenyl	(96)	4:96

R^1	R^2		(*E*)/(*Z*)*
t-Bu	OBn	(65)	19:81
t-Bu	OTBS	(100)	27:73
n-C_6H_{13}	OBn	(75)	36:64
n-C_6H_{13}	OTBS	(59)	36:64
4-BrC_6H_4	H	(91)	45:55
4-BrC_6H_4	OBn	(80)	48:52
4-BrC_6H_4	OTBS	(94)	48:52

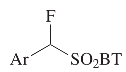
C_{5-6}				
		DBU, THF, rt, 6 h	 R / (E)/(Z)* H (40) — Me (70) —	633
C_5				
	CHF_2SO_2PYR	*t*-BuOK, DMF, –50°; then –20°, 3 h	 (84)	97
		Base, solvent, rt		641
		1. Cs_2CO_3, DMF, rt, 0.5 h 2. Ketone, rt, 30 h	 (59)	103
		LiHMDS, THF, 0°, 2 h	 R Et (77) *c*-C_3H_5 (71)	98

Base	Solvent	Time (h)	
DBU	CH_2Cl_2	24	(47)
DBU	THF	6	(65)
LiHMDS	THF	—	(70)

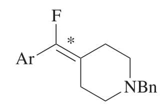
TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. LiHMDS, THF, –78° 2. n-$Bu_4N^+F^-$	 (77)	99
		LiHMDS, THF, 0°, 1.5–2 h	 (100)	639
	 R = 4-$MeOC_6H_4$	LiHMDS, DMF, DMPU, –78°	 (87)	643
		Ketone (1 eq), sulfone (x eq), LiHMDS (2.4 eq), THF, 0°		644

R	x	Time (min)	
4-$MeOC_6H_4$	1.3	5	(87)
$Ph(CH_2)_3$	1.2	120	(58)

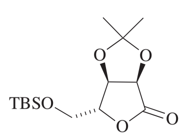


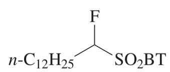
LiHMDS, THF, 0°, 1.5–2 h



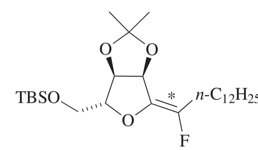
Ar	
2-thienyl	(100)
Ph	(100)
2-naphthyl	(100)

639



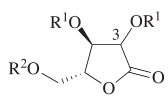


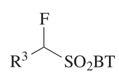
1. LiHMDS, THF, –78°, 0.75 h
2. DBU, THF, rt, 1 h



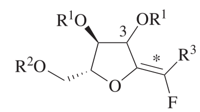
(83), $(E)/(Z)^{*}$ = 20:80

635





1. LiHMDS, additive, THF, –78°, 0.75 h
2. DBU, THF, rt, 1 h



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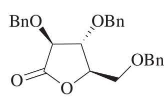
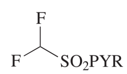
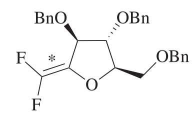
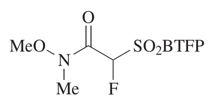
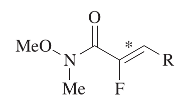
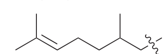
R^1	R^2	R^3	C-3	Additive		$E)/(Z)^{*}$
i-Pr	TBS	H	(*R*)	none	(70)	60:40
TBS	TBS	H	(*R*)	none	(46)	70:30
TBS	TBS	H	(*R*)	BF_3•OEt_2	(43)	70:30
Bn	Bn	H	(*S*)	none	(77)	70:30

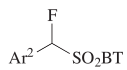
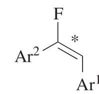
R^1	R^2	R^3	C-3	Additive		$E)/(Z)^{*}$
i-Pr	TBS	Me	(*R*)	none	(83)	30:70
i-Pr	TBS	Me	(*R*)	BF_3•OEt_2	(40)	30:70
TBS	TBS	Me	(*R*)	none	(37)	30:70
TBS	TBS	Me	(*R*)	BF_3•OEt_2	(27)	20:80
Bn	Bn	Me	(*S*)	none	(70)	30:70

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

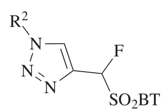
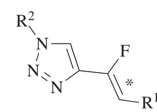
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_5					
		1. Lactone (2 eq), sulfone (1 eq), BF_3•Et_2O (2 eq), THF, –78° 2. LiHMDS (2 eq), –78°, 0.67 h 3. H_2O 4. Toluene, MW, 140°, 1 h		(59)	636
C_{6-11}					
RCHO		1. K_2CO_3, Bu_4NBr, DMF, rt, 0.25 h 2. Aldehyde, rt, 18 h		(*Z*)*-isomer only	105

R		R	
c-C_5H_9	(51)	Ph(CH_2)$_2$	(57)
c-C_6H_{11}	(65)	Ph(Me)CH	(46)
Ph	(83)	*n*-C_9H_{19}	(56)
2-ClC_6H_4	(99)		(63)
4-ClC_6H_4	(62)		
4-$MeOC_6H_4$	(45)	2-naphthyl	(81)
4-$CF_3C_6H_4$	(63)	6-MeO-2-naphthyl	(55)

C_{6-8}

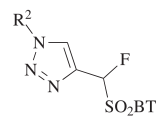
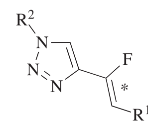
Ar^1CHO  LiHMDS, THF, 0°, 1.5 h  645

Ar^1	Ar^2		$(E)/(Z)^*$
4-pyridyl	2-BrC_6H_4	(51)	82:18
2-F-3-pyridyl	4-$CF_3C_6H_4$	(85)	86:14
2-Cl-3-pyridyl	2-BrC_6H_4	(57)	100:0
2-BrC_6H_4	2-Cl-3-pyridyl	(60)	71:29
2-BrC_6H_4	2-$CF_3C_6H_4$	(20)	0:100
2-$CF_3C_6H_4$	4-ClC_6H_4	(65)	29:71
2-$CF_3C_6H_4$	2-BrC_6H_4	(61)	77:23

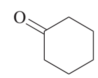
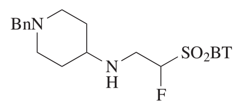
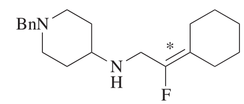
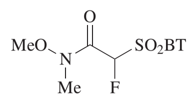
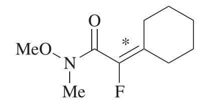
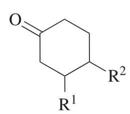
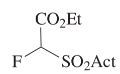
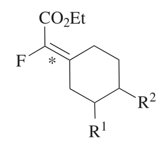
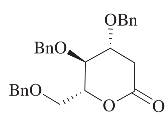
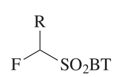
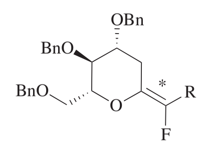
R^1CHO  LiHMDS, DMF, DMPU, –78°  643

R^1	R^2		$(E)/(Z)^*$
Et_2CH	4-$MeOC_6H_4$	(60)	15:85
Et_2CH	$Ph(CH_2)_3$	(57)	19:81
4-$O_2NC_6H_4$	$Ph(CH_2)_3$	(76)	38:62
4-$MeOC_6H_4$	4-$MeOC_6H_4$	(72)	14:86
4-$MeOC_6H_4$	$Ph(CH_2)_3$	(90)	7:93
n-C_7H_{15}	4-$MeOC_6H_4$	(68)	34:66
n-C_7H_{15}	$Ph(CH_2)_3$	(63)	36:64
2,4,6-$Me_3C_6H_2$	$Ph(CH_2)_3$	(47)	26:74

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-11}			
R^1CHO 	**A**: Aldehyde (1 eq), sulfone (x eq)^d, DBU (4 eq), THF, reflux, time *or* **B**: Aldehyde (1 eq), sulfone (1.2 eq), LiHMDS (2.4 eq), THF/DMF/DMPU, –78°, 5 min		644

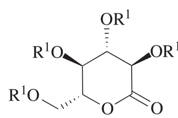
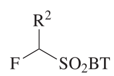
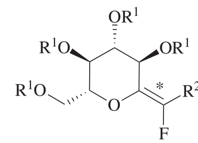
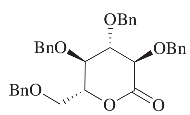
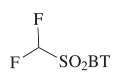
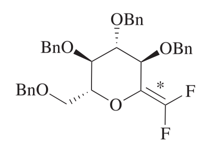
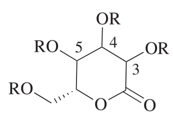
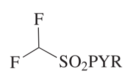
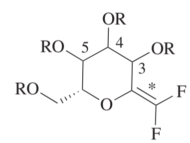
R^1	R^2	Conditions	x	Time (h)		$(E)/(Z)^*$
Et_2CH	4-$O_2NC_6H_4$	**A**	1.2–1.7	—	(3)	54:46
Et_2CH	4-$O_2NC_6H_4$	**B**	—	—	(68)	12:88
Et_2CH	4-$MeOC_6H_4$	**A**	1.2–1.7	—	(47)	54:46
Et_2CH	4-$MeOC_6H_4$	**B**	—	—	(59)	15:85
Et_2CH	$Ph(CH_2)_3$	**A**	1.2–1.7	—	(5)	61:39
Et_2CH	$Ph(CH_2)_3$	**B**	—	—	(57)	19:81
4-$O_2NC_6H_4$	$Ph(CH_2)_3$	**A**	1.2–1.7	—	(85)	57:43
4-$O_2NC_6H_4$	$Ph(CH_2)_3$	**B**	—	—	(76)	38:62
4-$MeOC_6H_4$	4-$O_2NC_6H_4$	**A**	1.2	3	(82)	87:13
4-$MeOC_6H_4$	4-$O_2NC_6H_4$	**B**	—	—	(62)	19:81
4-$MeOC_6H_4$	4-$MeOC_6H_4$	**A**	1.4	6.5	(80)	81:19
4-$MeOC_6H_4$	4-$MeOC_6H_4$	**B**	—	—	(72)	14:86
4-$MeOC_6H_4$	$Ph(CH_2)_3$	**A**	1.7	20	(75)	76:24
4-$MeOC_6H_4$	$Ph(CH_2)_3$	**B**	—	—	(90)	7:93
4-$CF_3C_6H_4$	4-$O_2NC_6H_4$	**A**	1.2	4	(87)	60:40
4-$CF_3C_6H_4$	4-$O_2NC_6H_4$	**B**	—	—	(73)	15:85
4-$CF_3C_6H_4$	4-$MeOC_6H_4$	**A**	1.2	4	(52)	64:36
4-$CF_3C_6H_4$	4-$MeOC_6H_4$	**B**	—	—	(77)	30:70
4-$CF_3C_6H_4$	$Ph(CH_2)_3$	**A**	1.2	4	(80)	63:37
4-$CF_3C_6H_4$	$Ph(CH_2)_3$	**B**	—	—	(72)	20:80
n-C_7H_{15}	4-$O_2NC_6H_4$	**A**	1.2–1.7	—	(33)	58:42
n-C_7H_{15}	4-$O_2NC_6H_4$	**B**	—	—	(61)	32:68
n-C_7H_{15}	4-$MeOC_6H_4$	**A**	1.2–1.7	—	(61)	57:43
n-C_7H_{15}	4-$MeOC_6H_4$	**B**	—	—	(68)	34:66
n-C_7H_{15}	$Ph(CH_2)_3$	**A**	1.2–1.7	—	(56)	61:39
n-C_7H_{15}	$Ph(CH_2)_3$	**B**	—	—	(63)	36:64
2,4,6-$Me_3C_6H_2$	$Ph(CH_2)_3$	**B**	—	—	(47)	26:74
2-Np	4-$MeOC_6H_4$	**A**	1.4	20	(75)	76:24
2-Np	4-$MeOC_6H_4$	**B**	—	—	(76)	7:93

C_6				
		NaHMDS, THF, –78°; then rt	 (80)	52
		1. Cs_2CO_3, DMF, rt, 0.5 h 2. Ketone, rt, 30 h	 (42)	103
$C_{6–10}$				
		DBU, THF, rt, 6 h	 $(E)/(Z)^*$ = —	633
C_6				
		1. LiHMDS, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h		635

R^1	R^2	Act	
H	H	BT	(57)
Me	H	BT	(60)
H	*t*-Bu	BT	(82)
H	*t*-Bu	PT	(47)
H	*t*-Bu	PYM	(46)

R		$(E)/(Z)^*$
H	(82)	30:70
Me	(58)	70:30

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
 	1. LiHMDS, additive, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h		635
 	1. Lactone (1.2 eq), sulfone (1 eq), LiHMDS (2 eq), BF_3•Et_2O (1.5 eq), THF, –78° 2. DBU, rt	 (32)	636
 	1. Lactone (2 eq), sulfone (1 eq), BF_3•Et_2O (2 eq), THF, –78° 2. LiHMDS (2 eq), –78°, 0.67 h 3. H_2O 4. Toluene, MW, 140°, 1 h		636

R^1	R^2	Additive		$(E)/(Z)^*$
TES	H	BF_3•OEt_2	(94)	80:20
TES	Me	BF_3•OEt_2	(93)	40:60
Bn	H	none	(85)	60:40
Bn	Me	none	(85)	40:60
Bn	n-$C_{12}H_{25}$	none	(53)	30:70

R	C-3	C-4	C-5	
TES	(*R*)	(*S*)	(*R*)	(0)
Bn	(*R*)	(*S*)	(*R*)	(64)
Bn	(*R*)	(*S*)	(*S*)	(69)
Bn	(*S*)	(*R*)	(*R*)	(63)

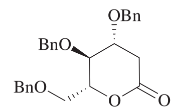
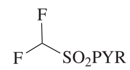
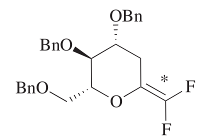
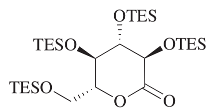
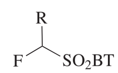
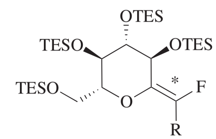
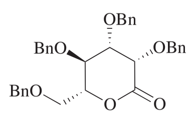
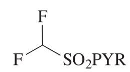
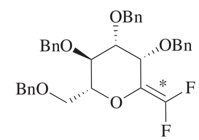
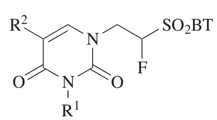
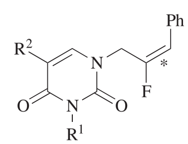
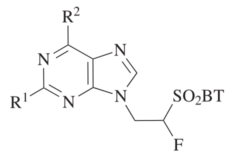
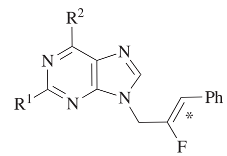
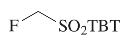
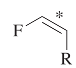
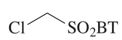
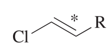
			1. Lactone (2 eq), sulfone (1 eq), BF_3•Et_2O (2 eq), THF, –78° 2. LiHMDS (2 eq), –78°, 0.67 h 3. H_2O 4. Toluene, MW, 140°, 1 h		(58)	636
			1. Lactone (1.5 eq), sulfone (1 eq), LiHMDS (2 eq), THF, –78°, 55 min 2. H_2O 3. DBU (2 eq), THF, rt, 1 h		R / (E/Z)* Me (77) 40:60 *n*-Bu (70) 60:40 *n*-C_8H_{17} (56) 60:40	646
			1. Lactone (1 eq), sulfone (1.5 eq), LiHMDS (2 eq), THF/HMPA (1:1), –98°; then –78°, 0.5 h 2. H_2O 3. *t*-BuOMe, $NaHCO_3$ (satd aq), reflux, overnight		(62)	647
C_7	PhCHO		NaHMDS, THF, –78 to –20°		R^1 R^2 / (E)/(Z)* H F (69) 53:47 Bz H (69) 94:6 Bz F (39) 95:5 Bz Me (87) 95:5	52

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
PhCHO		*t*-BuOK, THF, –17° to rt		52
C_{7-13}				
RCHO		LiHMDS, THF/HMPA, 0°		96
C_{7-9}				
RCHO		LDA, THF, –78°, 3 h; then rt, 1h		3

Product table for PhCHO entry (ref. 52):

R^1	R^2		$(E)/(Z)^*$
H	Cl	(61)	45:55
i-Pr(O)CHN	HO	(55)	60:40

Product table for C_{7-13} entry (ref. 96):

R		$(E)/(Z)^*$
2,4-$Cl_2C_6H_3$	(78)	50:50
4-BrC_6H_4	(73)	47:53
4-$BnOC_6H_4$	(87)	34:66
3,4-$(OCH_2O)C_6H_3$	(78)	34:66
2,5-$(MeO)_2C_6H_3$	(90)	47:53
3-BnO-4-$MeOC_6H_3$	(81)	35:65
$Ph(CH_2)_2$	(51)	48:52
4-PhC_6H_4	(86)	42:58

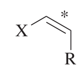
Product table for C_{7-9} entry (ref. 3):

R		$(E)/(Z)^*$
4-$MeOC_6H_4$	(95)	83:17
n-C_8H_{17}	(92)	48:52

C_{7-11}

RCHO

A:
LiHMDS, $MgBr_2$•OEt_2, THF, rt, 2 h
or **B**:
LiHMDS, HMPA, THF, rt, 0.5 h



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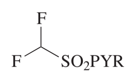
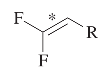
R	X	Conditions **A**		Conditions **B**	
			(*E*)/(*Z*)*		(*E*)/(*Z*)*
4-IC_6H_4	Cl	(38)	27:73	(79)	18:82
4-IC_6H_4	Br			(63)	7:93
4-$MeOC_6H_4$	Cl	(69)	94:6	(95)	10:90
4-$MeOC_6H_4$	Br			(70)	5:95
2-MeC_6H_4	Cl	(43)	12:88	(99)	10:90
2-MeC_6H_4	Br			(69)	5:95
2-naphthyl	Cl	(47)	71:29	(86)	9:91
2-naphthyl	Br			(79)	5:95

R	X	Conditions **B**	
			(*E*)/(*Z*)*
2-Cl-5-$(NO_2)C_6H_3$	Cl	(48)	62:38
2-Cl-5-$(NO_2)C_6H_3$	Br	(73)	55:45
3,4-$(OCH_2O)C_6H_3$	Cl	(80)	9:91
3,4-$(OCH_2O)C_6H_3$	Br	(75)	6:94
$Ph(CH_2)_2$	Cl	(64)	35:65
$Ph(CH_2)_2$	Br	(73)	23:77
(*E*)-PhCH=CH	Cl	(75)	14:86
(*E*)-PhCH=CH	Br	(69)	8:92
2-Cl-quinolin-3-yl	Cl	(62)	52:48
2-Cl-quinolin-3-yl	Br	(50)	50:50



Base, DMF, –50 to –20°, 3 h



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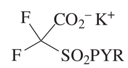
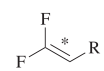
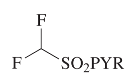
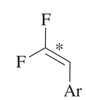
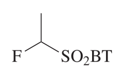
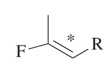
R	Base	
2,4-$Cl_2C_6H_3$	*t*-BuOK	(72)
4-BrC_6H_4	*t*-BuOK	(72)
4-$Me_2NC_6H_4$	*t*-BuOK	(91)
3-$O_2NC_6H_4$	*t*-BuOK	(72)
4-$MeOC_6H_4$	*t*-BuOK	(86)
3,4-$(OCH_2O)C_6H_3$	*t*-BuOK	(93)
$Ph(CH_2)_2$	LiHMDS	(40)
(*E*)-PhCH=CH	*t*-BuOK	(62)
4-*t*-BuC_6H_4	*t*-BuOK	(74)

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-13}				
RCHO		1. Aldehyde (1 eq), sulfone (1.5 eq), DMF, 40°, 2 h 2. 3 N HCl, 40°, 2 h		648
C_{7-11}				
ArCHO		Aldehyde (1.2 eq), sulfone (1 eq), KO*t*-Bu (1.8 eq), DMF, –40°, 0.25 h		649
C_{7-9}				
RCHO		**A**: *t*-BuOK, THF, –17°, 0.5 h *or* **B**: NaHMDS, THF, –78°		650

Products for ref. 648:

R		R	
4-ClC_6H_4	(94)	$PhCH_2CH_2$	(48)
4-BrC_6H_4	(90)	(*E*)-PhCH=CH	(51)
3,5-$Br_2C_6H_3$	(84)	2-benzofuryl	(89)
3-$O_2NC_6H_4$	(99)	2-benzothienyl	(91)
4-$MeOC_6H_4$	(65)	2,4,6-$Me_3C_6H_2$	(64)
4-$BnOC_6H_4$	(74)	2-naphthyl	(87)
4-$CF_3C_6H_4$	(80)	4-PhC_6H_4	(84)

Products for ref. 649:

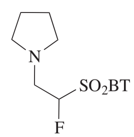
Ar	
2,4-$Cl_2C_6H_3$	(78)
2,5-$Cl_2C_6H_3$	(36)
3-$O_2NC_6H_4$	(25)
4-$MeOC_6H_4$	(86)
4-MeC_6H_4	(48)
4-*t*-BuC_6H_4	(61)

Products for ref. 650:

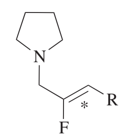
R	Conditions		(*E*)/(*Z*)*
2-$O_2NC_6H_4$	**A**	(86)	63:37
4-$O_2NC_6H_4$	**A**	(88)	61:39
4-HO-3-$MeOC_6H_3$	**A**	(48)	49:51

C_{7-15}

RCHO



A:
t-BuOK, THF, –17°, 1 h
or **B**:
NaHMDS, THF, –78 to 0°, 3 h



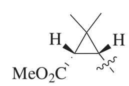
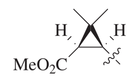
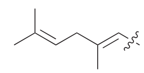
R	Conditions		(*E*)/(*Z*)*
4-BrC_6H_4	**A**	(53)	55:45
4-BrC_6H_4	**B**	(70)	60:40
	**B**	(73)	40:60
CH_2=CH$(CH_2)_8$	**A**	(31)	—
CH_2=CH$(CH_2)_8$	**B**	(74)	45:55
9-anthracenyl	**A**	(60)	—
9-anthracenyl	**B**	(83)	—
	**A**	(80)	45:55
(*E*)-PhCH=CH	**A**	(55)	62:38
	**A**	(71)	52:48
	B	(74)	—

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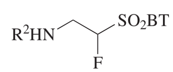
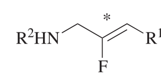
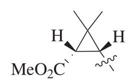
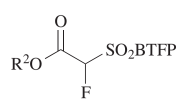
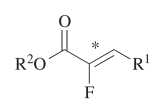
TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-15}				
R^1CHO		**A**: t-BuOK, THF, –17°, 1 h *or* **B**: NaHMDS, THF, –78 to 0°, 3 h		632

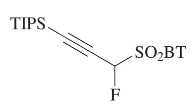
R^1	R^2	Conditions		$(E)/(Z)^*$
4-BrC_6H_4	t-$BuO_2CCH_2(t$-$BuO_2C)CH$	**B**	(72)	40:60
4-BrC_6H_4	c-C_6H_{11}	**A**	(88)	70:30
4-BrC_6H_4	$EtO_2C(Bn)CH$	**B**	(58)	48:52
	t-$BuO_2CCH_2(t$-$BuO_2C)CH$	**B**	(77)	41:59
	c-C_6H_{11}	**A**	(62)	40:60
	$EtO_2C(Bn)CH$	**B**	(20)	30:70
CH_2=$CH(CH_2)_8$	t-$BuO_2CCH_2(t$-$BuO_2C)CH$	**B**	(75)	25:75
CH_2=$CH(CH_2)_8$	c-C_6H_{11}	**A**	(79)	45:55
CH_2=$CH(CH_2)_8$	$EtO_2C(Bn)CH$	**B**	(21)	40:60
9-anthracenyl	t-$BuO_2CCH_2(t$-$BuO_2C)CH$	**B**	(74)	30:70
9-anthracenyl	c-C_6H_{11}	**A**	(68)	15:85
9-anthracenyl	$EtO_2C(Bn)CH$	**B**	(60)	80:20

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-11}				
R^1CHO		1. K_2CO_3, Bu_4NBr, DMF, rt, 0.25 h 2. Aldehyde, rt, 18 h		105

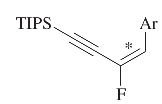
R^1	R^2		$(E)/(Z)^*$
c-C_6H_{11}	Me	(71)	7:93
c-C_6H_{11}	t-Bu	(91)	15:85
Ph	Me	(>95)	7:93
Ph	t-Bu	(75)	18:82
2-ClC_6H_4	Me	(68)	10:90
4-ClC_6H_4	Me	(60)	8:92
4-ClC_6H_4	t-Bu	(68)	17:83
4-$MeOC_6H_4$	t-Bu	(94)	39:61

R^1	R^2		$(E)/(Z)^*$
4-$CF_3C_6H_4$	Me	(50)	6:94
4-$CF_3C_6H_4$	t-Bu	(42)	12:88
$Ph(CH_2)_2$	Me	(66)	52:48
$Ph(CH_2)_2$	t-Bu	(92)	77:23
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	Me	(61)	57:43
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	t-Bu	(75	81:19
2-naphthyl	Me	(47)	9:91
2-naphthyl	t-Bu	(72))	21:79

ArCHO



A:
DBU, CH_2Cl_2, –55°
or **B:**
LiHMDS, THF, –78°

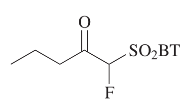


Ar	Conditions		$(E)/(Z)^*$
4-$O_2NC_6H_4$	**A**	(64)	67:33
4-$O_2NC_6H_4$	**B**	(87)	76:24
2-naphthyl	**A**	(87)	71:29

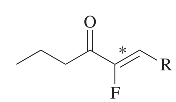
99

C_{7-9}

RCHO



DBU, THF, reflux, 0.5 h



$(Z)^*$-isomer only

R	
4-$O_2NC_6H_4$	(86)
4-$MeOC_6H_4$	(89)
$Ph(CH_2)_2$	(73)
5-benzofuranyl	(90)

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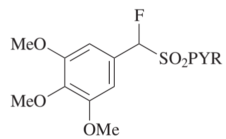
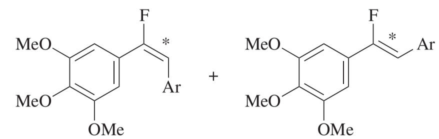
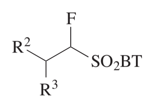
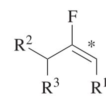
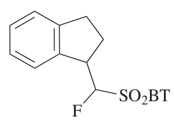
TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
ArCHO		1. Aldehyde (1.2 eq), sulfone (1.0 eq), LiHMDS (*x* eq), DMF/HMPA (10:1), –55°; then to rt, 3 h; then rt, 1.5 h 2. H_2O, Et_2O 3. Et_2O contains the (*Z*)*-isomer 4. To aqueous phase + DMF, added $TsOH•H_2O$, –50°; then to rt; then extraction with Et_2O gives the (*E*)* isomer	 (*E*)* + (*Z*)*	640
$C_{7–9}$				
R^1CHO		NaHMDS, THF, –78°; then rt, 3 h		47

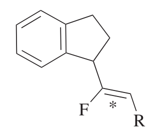
Ar	*x*	(*E*)*	(*E*)/(*Z*)*	(*Z*)*	(*E*)/(*Z*)*
$4-MeOC_6H_4$	1.8	(20)	98:2	(46)	1:>99
$3-HO-4-MeOC_6H_3$	2.5	(37)	90:10	(51)	1:>99

R^1	R^2	R^3		(*E*)/(*Z*)*
Ph	Ph	Me	(72)	60:40
$4-BrC_6H_4$	Et	Me	(63)	71:29
$4-BrC_6H_4$	$CH_2=CH$	Me	(68)	75:25
$4-BrC_6H_4$	$–(CH_2)_4–$		(87)	74:26
$4-BrC_6H_4$	$2-BrC_6H_4$	Me	(49)	76:24
$4-BrC_6H_4$	$Ph(CH_2)_2$	Me	(66)	69:31
$4-MeOC_6H_4$	Ph	Me	(57)	51:49
$n-C_8H_{17}$	Ph	Me	(58)	17:83

RCHO



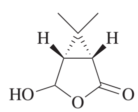
NaHMDS, THF, –78°; then rt, 3 h

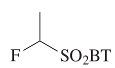


R		$(E)/(Z)^*$
4-BrC_6H_4	(51)	71:29
n-C_8H_{17}	(51)	38:62

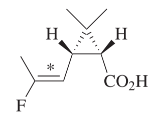
47

C_7





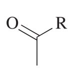
t-BuOK, THF, –17°, 0.5 h

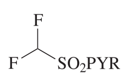


(82), $(E)/(Z)^*$ = 55:45

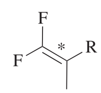
650

C_{8-14}





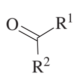
Base, DMF, –50°; then –20°, 3 h

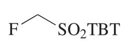


R	Base	
4-BrC_6H_4	t-BuOK	(77)
$Ph(CH_2)_2$	LiHMDS	(72)
(E)-PhCH=CH	t-BuOK	(80)
4-PhC_6H_4	t-BuOK	(81)

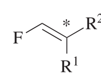
97

C_{8-10}





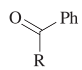
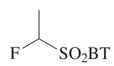
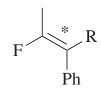
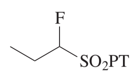
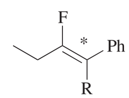
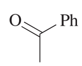
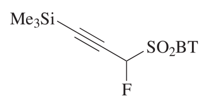
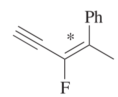
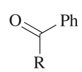
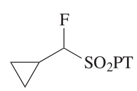
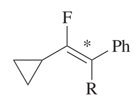
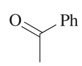
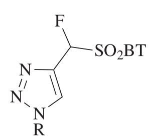
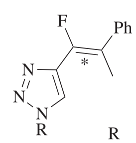
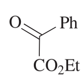
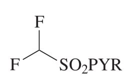
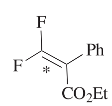
LiHMDS, THF/HMPA, 0°



R^1	R^2		$(E)/(Z)^*$
Ph	Me	(75)	30:70
Ph	Ph	(89)	—
4-ClC_6H_4	Me	(86)	25:75
4-BrC_6H_4	Me	(84)	28:72
4-$MeOC_6H_4$	Me	(69)	30:70
4-MeC_6H_4	Me	(60)	33:67
$Ph(CH_2)_2$	Me	(52)	49:51

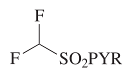
96

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

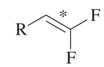
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-13}				
		NaHMDS, THF, –78°, 2 h; then rt	 R / (E)/(Z)* CF_3 (45) — Ph (49) —	650
		LiHMDS, THF, 0°, 2 h	 R / (E)/(Z)* Me (88) 26:74 Ph (99) —	98
C_8				
		1. LiHMDS, THF, –78° 2. *n*-$Bu_4N^+F^-$	 (88), (E)/(Z)* = 100:0	99
C_{8-13}				
		LiHMDS, THF, 0°, 2 h	 R / (E)/(Z)* Me (96) 25:75 Ph (91) —	98
C_8				
		Ketone (1 eq), sulfone (1.2 eq), LiHMDS (2.4 eq), THF, 0°	 R / Time (h) / / (E)/(Z)* 4-$MeOC_6H_4$ 0.25 (64) 28:72 $Ph(CH_2)_3$ 0.5 (77) 20:80	644
		1. Ketone (2 eq), sulfone (1 eq), LiHMDS (2 eq), DMF, –60°, 35 min 2. HCl (conc), –50° to rt	 (74)	651

C_{9-18}

RCHO



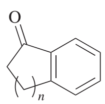
Aldehyde (1.5 eq), sulfone (1 eq), $N(TMS)_3$ (x eq), CsF (x eq), DMF, rt, 8 h

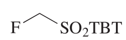


R	x	
$PhCH_2CH_2$	2	(60)
$PhCH_2CH_2$	2.5	(74)
$4\text{-}BrC_6H_4CH_2CH_2$	2	(85)
$4\text{-}MeOC_6H_4CH_2CH_2$	2	(71)
$n\text{-}C_{11}H_{23}$	2	(80)
$PhCO(CH_2)_4$	2.5	(72)
$n\text{-}C_{15}H_{31}$	2	(66)
$n\text{-}C_{17}H_{35}$	2	(64)

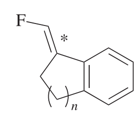
651

C_{9-10}





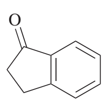
LiHMDS, THF/HMPA, 0°

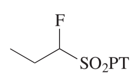


n		$(E)/(Z)^*$
1	(67)	76:24
2	(66)	59:41

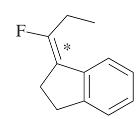
96

C_9



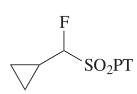


LiHMDS, THF, 0°, 2 h

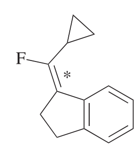


(77), $(E)/(Z)^* = 78:22$

98



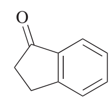
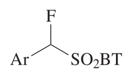
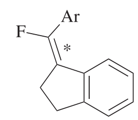
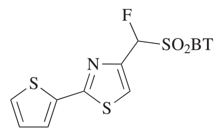
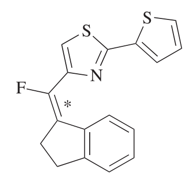
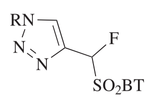
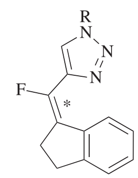
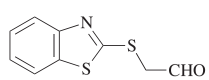
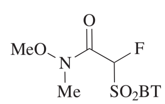
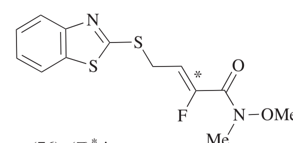
LiHMDS, THF, 0°, 2 h



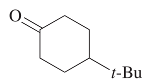
(88), $(E)/(Z)^* = 78:22$

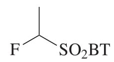
98

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

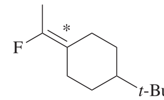
Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
 	LiHMDS, THF, 0°, 1.5–2 h	 Ar / (%) / $(E)/(Z)^*$: 2-thienyl (85) 92:8; Ph (91) 94:6; 2-naphthyl (87) 95:5	639
	LiHMDS, THF, 0°, 1.5–2 h	 (62), $(E)/(Z)^*$ = 78:22	639
 R = ferrocenyl	Ketone (1 eq), sulfone (1.2 eq), LiHMDS (2.4 eq), THF, 0°, 2 h; then LiHMDS (1.6 eq), 0°, 2 h	 (58)[e]	644
 	Aldehyde (1 eq), sulfone (2 eq), LiHMDS (3 eq), THF, –78°, 3.5 h	 (76), $(Z)^*$-isomer	637

C_{10}

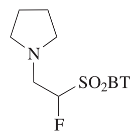




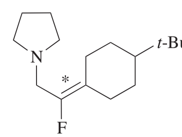
NaHMDS, THF, –78°, 2 h; then rt



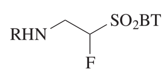
(69) 650



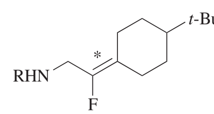
A:
t-BuOK, THF, –17°, 1 h
or **B**:
NaHMDS, THF, –78 to 0°, 3 h



Conditions		
A	(34)	632
B	(95)	

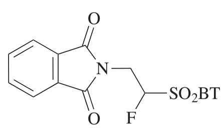


A:
t-BuOK, THF, –17°, 1 h
or **B**:
NaHMDS, THF, –78 to 0°, 3 h

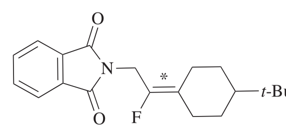


632

R	Conditions	
t-BuO_2CCH_2(*t*-BuO_2C)CH	**B**	(27)
c-C_6H_{11}	**A**	(24)
c-C_6H_{11}	**B**	(78)

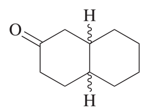
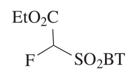
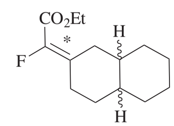
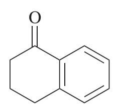
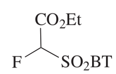
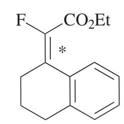
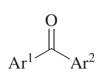
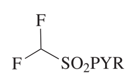
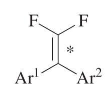


NaHMDS, THF, –78 to 0°, 3 h



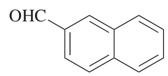
(63) 632

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

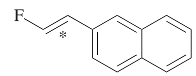
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{10}					
		DBU, THF, rt, 6 h		(60), $(E)/(Z)^{*}$ = —	633
		DBU, THF, rt, 6 h		(0)	633
C_{11-19}					
		1. Sulfone (1 eq), ketone (2 eq), LiHMDS (2 eq), –60°, 1 h 2. 2 M HCl, to rt; then reflux, 4–10 h			651

Ar[1]	Ar[2]		Ar[1]	Ar[2]	
Ph	2-thienyl	(63)	Ph	4-$MeOC_6H_4$	(69)
Ph	2-pyridyl	(0)	4-FC_6H_4	4-FC_6H_4	(79)
Ph	Ph	(75)	4-ClC_6H_4	4-ClC_6H_4	(77)
Ph	4-FC_6H_4	(67)	4-BrC_6H_4	4-BrC_6H_4	(77)
Ph	4-ClC_6H_4	(83)	Ph	4-$CF_3C_6H_4$	(67)
Ph	4-BrC_6H_4	(75)	4-$MeOC_6H_4$	4-$CF_3C_6H_4$	(64)
Ph	2-$MeOC_6H_4$	(72)	Ph	4-PhC_6H_4	(70)
Ph	3-$MeOC_6H_4$	(80)			

C_{11}



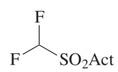
$MN(SiMe_3)_2$ (x eq), solvent



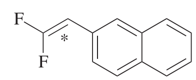
96

Act	M	x	Solvent	Temp (°)		$(E)/(Z)^*$
BT	Li	2.4	THF	0	(0)	—
BT	Li	2.4	THF/HMPA	0	(68)	50:50
PT	Li	2.4	THF	0	(39)	36:64
PT	Li	2.4	THF/HMPA	0	(66)	54:46
TBT	Li	2.4	THF	0	(31)	22:78
TBT	Li	2.4	THF/HMPA	0	(75)	45:55

Act	M	x	Solvent	Temp (°)		$(E)/(Z)^*$
TBT	Li	1.5	THF/HMPA	0	(88)	42:58
TBT	Na	1.5	THF/HMPA	0	(63)	57:43
TBT	K	1.5	THF/HMPA	0	(47)	74:26
TBT	Li	1.5	DMF/HMPA	–78	(>80)	75:25
TBT	Li	1.5	Et_2O/toluene	0	(>80)	25:75

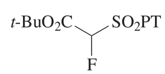


t-BuOK, DMF, –50 to –20°, 3 h

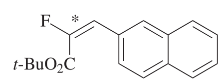


Act	
PYR	(92)
BT	(42)
PT	(0)
TBT	(0)

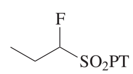
97



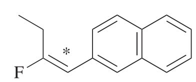
DBU, CH_2Cl_2, rt



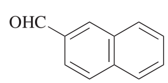
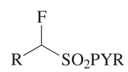
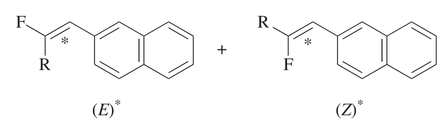
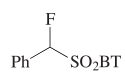
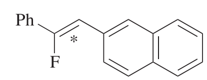
(95), $(E)/(Z)^*$ = 75:25 101



LiHMDS, THF, 0°, 2 h



(92), $(E)/(Z)^*$ = 57:43 639

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
 	1. Aldehyde (1.2 eq), sulfone (1.0 eq), LiHMDS (1.8 eq), DMF/HMPA (10:1), –55°; then to rt, 3 h; then rt, 1.5 h 2. H_2O, Et_2O 3. Et_2O contains the $(Z)^*$ isomer 4. To aqueous phase + DMF added $TsOH{\bullet}H_2O$ at –50°; then to rt; then extraction with Et_2O gives the $(E)^*$ isomer		640
	$MN(SiMe_3)_2$, solvent		639

R	$(E)^*$	$(E)/(Z)^*$	$(Z)^*$	$(E)/(Z)^*$
i-Pr	(24)	96:4	(48)	3:97
i-Bu	(27)	84:16	(44)	11:89
c-C_6H_{11}	(18)	97:3	(45)	3:97
4-BrC_6H_4	(33)	>99:1	(34)	1:>99
4-MeC_6H_4	(32)	99:1	(53)	1:>99

M	Solvent	Temp/Time		$(E)/(Z)^*$
Li	DMF/DMPU	–78°, 40 min; –45°, 35 min; rt, 2 h	(—)	8:92
Li	DMF/DMPU	0°, 1.5 h	(—)	22:78
Li	DMF/DMPU	rt, 2 h	(—)	42:58
Li	THF	–78°, 40 min; –45°, 35 min; rt, 2 h	(—)	69:31
Li	THF	0°, 2 h	(100)	69:31
Na	THF	–78°, 40 min; –45°, 35 min; rt, 2 h	(—)	67:33

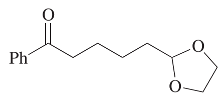
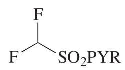
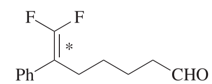
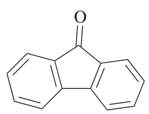
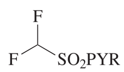
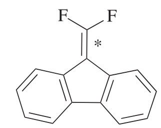
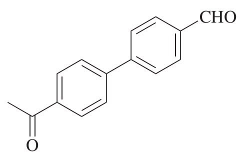
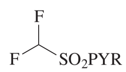
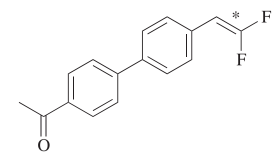
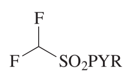
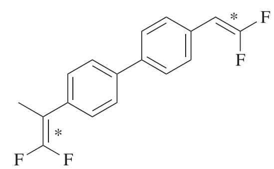
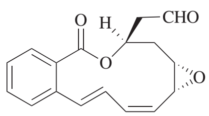
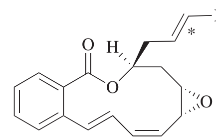
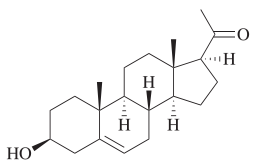
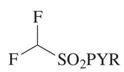
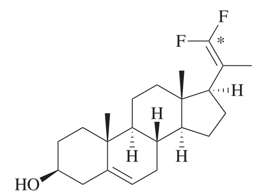
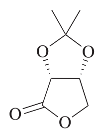
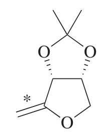
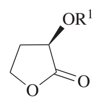
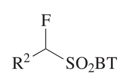
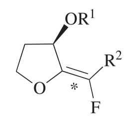
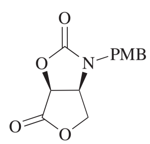
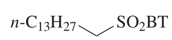
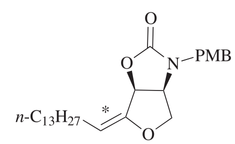
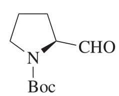
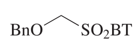
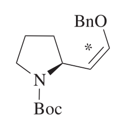
C_{12}					
		1. Sulfone (1 eq), ketone (2 eq), LiHMDS (2 eq), DMF, –50°, 35 min; then to rt 2. 2 M HCl, 50°, 12 h		(54)	651
C_{13}					
		*t*-BuOK, DMF, –50°; then –20°, 3 h		(87)	97
C_{15}					
		Aldehyde (1.5 eq), sulfone (1 eq), $N(TMS)_3$ (2.5 eq), CsF (2.5 eq), DMF, rt, 8 h		(70)	651
		Aldehyde (1.0 eq), sulfone (2.5 eq), LiHMDS (3 eq), THF/HMPA (10:1), –78°, 1 h		(38)	651

TABLE 8. SYNTHESIS OF VINYL HALIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{17}					
		1. NaHMDS, THF, –78°, 5 min 2. Aldehyde, –78° to rt, 12 h		(62), (*E*)/(*Z*)* = 50:50	107
C_{21}					
		LiHMDS, THF, HMPA, –78° to rt		(57)	97

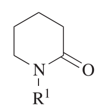
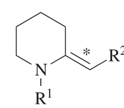
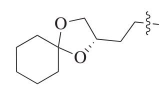
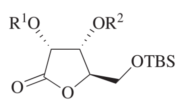
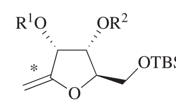
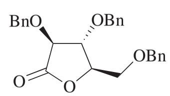
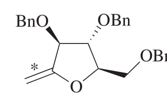
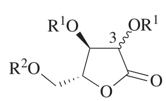
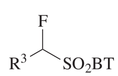
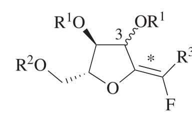
[a] With PT as the activating group, "the reaction proceeded to completion and [the product] was formed in the reaction." No yield was given.
[b] This is the conversion as determined by ^{19}F NMR spectroscopy.
[c] The product was unstable.
[d] In some cases, the sulfone was added in portions during the reaction.
[e] The product was a single isomer of undetermined configuration.

TABLE 9. SYNTHESIS OF VINYL ETHERS, VINYL ESTERS, AND VINYL AMIDES

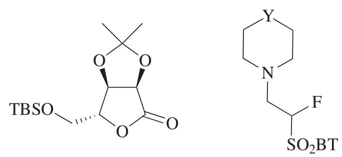
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_4					
	$MeSO_2BT$	1. LiHMDS, THF, –78°, 0.5 h 2. AcOH 3. DBU, THF, rt, 1 h		(51)	110
		1. LiHMDS, additive, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h		see below	635
		LiHMDS, THF, –78°, 0.5 h		(55), $(E)/(Z)^*$ = 67:33	652
C_5					
		LiHMDS, THF, 0°, 5 min; then rt, 0.5 h		(61), $(E)/(Z)^*$ = 33:67	653

R^1	R^2	Additive		$(E)/(Z)^*$
TES	H	none	(20)	40:60
TES	H	BF_3•OEt_2	(68)	50:50
Bn	H	none	(60)	60:40
TES	Me	none	(29)	20:80
TES	Me	BF_3•OEt_2	(68)	30:70
Bn	Me	none	(60)	30:70

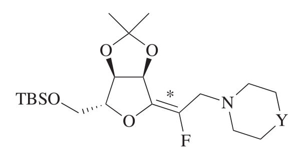
TABLE 9. SYNTHESIS OF VINYL ETHERS, VINYL ESTERS, AND VINYL AMIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		1. Lactam (2.5 eq), sulfone (1 eq), LiHMDS (4 eq), THF, –78° 2. BF_3•OEt_2 (2.5 eq), –78° 3. DBU (2 eq), THF, rt, 1 h	 R¹ | R² | Act | | (E)/(Z)* Boc | *n*-Pr | BT | (30) | 100:0 Boc |  | BT | (23) | 29:71[b] Ts | | BT | (0) | — Ts | | PYR | (68)[a] | —	654
	$MeSO_2BT$	1. LiHMDS, THF, –78°, 0.5 h 2. AcOH, –78° 3. DBU, THF, rt, 1 h	 R¹ | R² | TES | TES | (46) —Me_2C— | | (58)	110
	$MeSO_2BT$	1. LiHMDS, THF, –78°, 0.5 h 2. AcOH, –78° 3. DBU, THF, rt, 1 h	 (66)	110
		1. LiHMDS, additive, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h		635

R^1	R^2	C-3	R^3	Additive		(E)/(Z)*
TBS	TBS	(R)	H	none	(46)	70:30
TBS	TBS	(R)	H	BF_3•OEt_2	(43)	70:30
TBS	TBS	(R)	Me	none	(37)	30:70
TBS	TBS	(R)	Me	BF_3•OEt_2	(27)	20:80
i-Pr	TBS	(R)	H	none	(70)	60:40
i-Pr	TBS	(S)	Me	none	(83)	30:70
i-Pr	TBS	(R)	Me	BF_3•OEt_2	(40)	30:70
Bn	Bn	(R)	H	none	(77)	70:30
Bn	Bn	(S)	Me	none	(70)	30:70

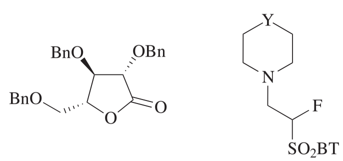


1. LiHMDS, THF, –78°, 0.75 h
2. DBU, THF, rt, 1 h

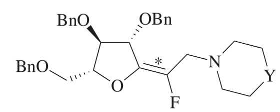


Y		(E)/(Z)*
O	(91)	20:80
CH_2	(39)	5:95

635



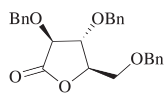
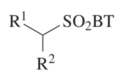
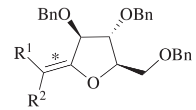
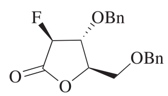
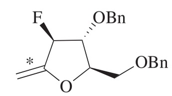
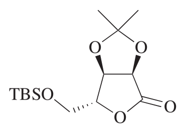
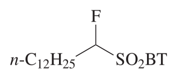
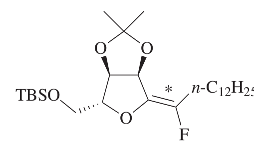
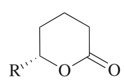
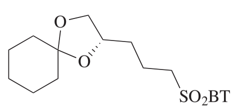
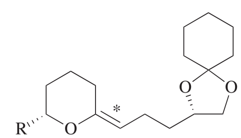
1. LiHMDS, THF, –78°, 0.75 h
2. DBU, THF, rt, 1 h



Y		(E)/(Z)*
O	(61)	20:80
CH_2	(41)	0:100

635

TABLE 9. SYNTHESIS OF VINYL ETHERS, VINYL ESTERS, AND VINYL AMIDES (*Continued*)

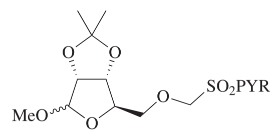
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. LiHMDS, THF, –78°, 0.5 h 2. AcOH 3. DBU, THF, rt, 1 h		111
	$MeSO_2BT$	1. Lactone (1.0 eq), sulfone (1.2 eq), LiHMDS (2.4 eq), THF, –78°, 55 min 2. DBU, THF, rt, 1 h	 (78)	655
		1. LiHMDS, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h	 (83), (*E*)/(*Z*)* = 20:80	635
C_{5-6}				
		**A:** LiHMDS, BF_3•Et_2O THF, –78°; then DBU, THF, rt *or* **B:** LiHMDS, BF_3•Et_2O, THF, –78°		656

R^1	R^2		(*E*)/(*Z*)*
Me	H	(77)	80:20
Me	Me	(60)	—
CH_2=$CHCH_2$	H	(64)	>90:10
$THPO(CH_2)_3$	H	(63)	90:10
—$(CH_2)_4$—		(61)	—
n-C_6H_{13}	H	(63)	90:10

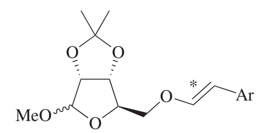
R	Conditions	$(E)^*$-isomer
H	**B**	(60)
$BnOCH_2$	**A**	(55)
$TBDPSOCH_2$	**A**	(31)

C_{5-11}

ArCHO



KOH, Bu_4NBr, THF, rt, 24 h

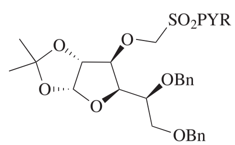


Ar		$(E)/(Z)^*$
2-furyl	(92)	67:33
Ph	(72)	94:6
2-ClC_6H_4	(45)	78:22
4-ClC_6H_4	(48)	92:8
$4\text{-Me}_2NC_6H_4$	(81)	86:14
2-MeOC_6H_4	(83)	71:29
4-MeOC_6H_4	(88)	78:22
4-MeO-2-naphthyl	(70)	81:19

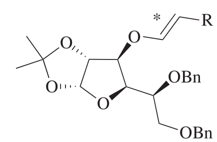
109

C_{5-7}

RCHO



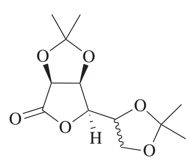
KOH, Bu_4NBr, THF, rt, 24 h



R		$(E)/(Z)^*$
t-Bu	(31)	<1:99
Ph	(78)	71:29
4-FC_6H_4	(58)	69:31

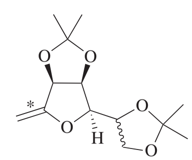
109

C_6



$MeSO_2BT$

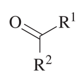
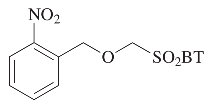
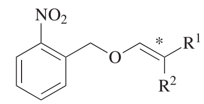
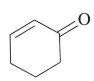
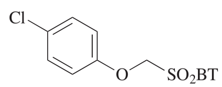
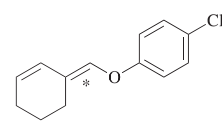
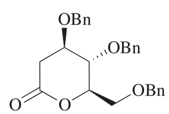
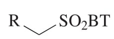
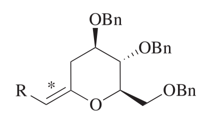
1. LiHMDS, THF, –78°, 0.5 h
2. AcOH
3. DBU, THF, rt, 1 h



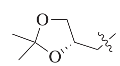
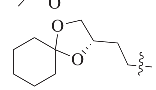
(66)

110

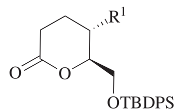
TABLE 9. SYNTHESIS OF VINYL ETHERS, VINYL ESTERS, AND VINYL AMIDES (*Continued*)

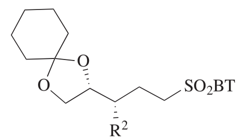
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-13}				
		LiHMDS, THF, 0°, 5 h		657
C_6				
		LiHMDS, THF, 0°, 1.5 h	 (71), (*E*)/(*Z*)* = 57:43	108
		1. LiHMDS, THF, –78°, 0.5 h 2. AcOH, –78° 3. DBU, THF, rt, 1 h		658

R^1	R^2		(*E*)/(*Z*)*
—$(CH_2)_5$—		(82)	—
Me	Ph	(97)	33:67
Me	2-$MeOC_6H_4$	(51)	14:86
Me	4-$MeOC_6H_4$	(27)	50:50
Ph	Ph	(62)	—

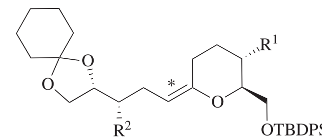
R		(*E*)/(*Z*)*
$THPO(CH_2)_3$	(67)	60:40
	(54)	40:60
	(59)	60:40

C_{6-7}





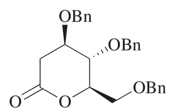
1. LiHMDS, LiCl, THF, –78°
2. AcOH, –78°; then rt, 0.25 h
3. DBU, THF, rt, 1 h

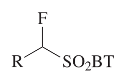


R^1	R^2		$(E)/(Z)^*$
H	Me	(23)	—
Me	H	(23)	—

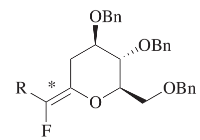
421, 422

C_6



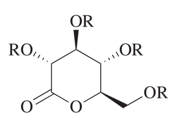


1. LiHMDS, THF, –78°, 0.75 h
2. DBU, THF, rt, 1 h



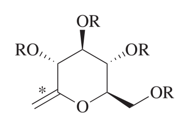
R		$(E)/(Z)^*$
H	(82)	30:70
Me	(58)	70:30

635



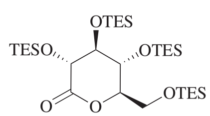
$MeSO_2BT$

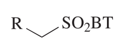
1. LiHMDS, THF, –78°, 0.5 h
2. AcOH, –78°; then rt, 0.25 h
3. DBU, THF, rt, 1 h



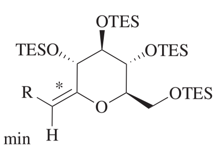
R	
TES	(74)
Bn	(53)

110





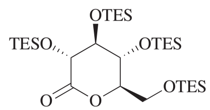
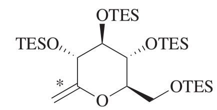
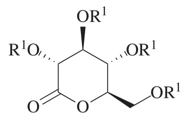
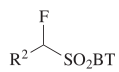
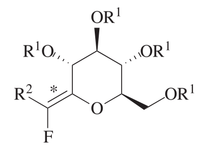
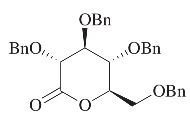
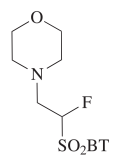
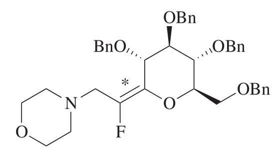
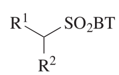
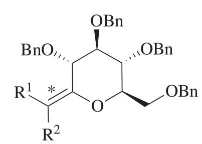
1. Lactone (eq),
sulfone (1.2 eq),
LiHMDS (2 eq),
THF, –78°, 55 min
2. Hydrolyzed at –78°; then rt, 20 min
3. DBU (2 eq), THF, rt, 1 h



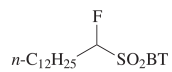
R		$(E/Z)^*$
Me	(56)	60:40
Bu	(41)	60:40
n-C_8H_{17}	$(17)^c$	53:47

646

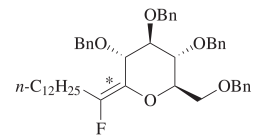
TABLE 9. SYNTHESIS OF VINYL ETHERS, VINYL ESTERS, AND VINYL AMIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$MeSO_2BT$	1. LiHMDS, THF, –78°, 0.5 h 2. DBU, THF, rt, 1 h	 (74)	659
		1. LiHMDS, additive, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h		635
		1. LiHMDS, THF, –78°, 0.75 h 2. DBU, THF, rt, 1 h	 (54), (*E*)/(*Z*)* = 20:80	635
		1. LiHMDS, THF, –78°, 0.5 h 2. AcOH, –78° 3. DBU, THF, rt, 1 h		111

R^1	R^2	Additive		(*E*)/(*Z*)*
TES	H	BF_3•OEt_2	(94)	80:20
TES	Me	BF_3•OEt_2	(93)	40:60
Bn	H	none	(85)	60:40
Bn	Me	none	(85)	40:60

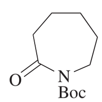


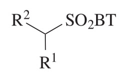
1. LiHMDS, THF, –78°, 0.75 h
2. DBU, THF, rt, 1 h



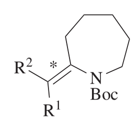
(53), $(E)/(Z)^{*}$ = 30:70 — 635

R^1	R^2		$(E)/(Z)^{*}$
Me	H	(62)	60:40
Me	Me	(35)	—
CH_2=$CHCH_2$	H	(33)	80:20
THPO(CH_2)$_3$	H	(49)	50:50
—(CH_2)$_4$—		(28)	—
n-C_6H_{13}	H	(33)	50:50





1. Lactam (2.5 eq), sulfone (1 eq), LiHMDS (4 eq), THF, –78°
2. BF_3•OEt_2 (2.5 eq), –78°
3. DBU (2 eq), THF, rt, 1 h



654

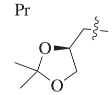
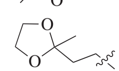
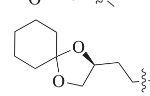
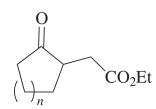
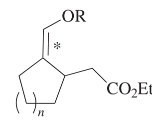
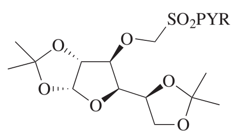
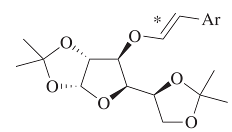
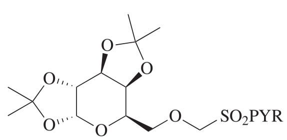
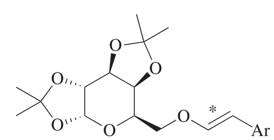
R^1	R^2		$(E)/(Z)^{*}$
H	H	(12)	—
Me	Me	(0)	—
H	Pr	(53)	100:0
H		(54)	100:0
H		(42)	100:0
H		(43)	100:0[d]

TABLE 9. SYNTHESIS OF VINYL ETHERS, VINYL ESTERS, AND VINYL AMIDES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 		LiHMDS, THF, 0°, 1.5 h		108
C_7 ArCHO		KOH, Bu_4NBr, THF, rt, 24 h	 $(E)/(Z)^*$ = 75:25	109
		KOH, Bu_4NBr, THF, rt, 24 h		109

Product table for ref. 108:

n	R		$(E)/(Z)^*$
1	4-ClC_6H_4	(75)	50:50
1	Bn	(70)	50:50
2	4-ClC_6H_4	(76)	67:33
2	Bn	(71)	67:33

Product table for the first ref. 109 entry:

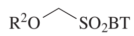
Ar	
Ph	(63)
4-FC_6H_4	(54)

Product table for the second ref. 109 entry:

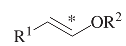
Ar		$(E)/(Z)^*$
Ph	(71)	96:4
4-FC_6H_4	(40)	93:7
2-$MeOC_6H_4$	(78)	89:11
4-$MeOC_6H_4$	(91)	89:11

C_{8-9}

R[1]CHO

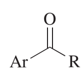


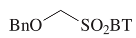
LiHMDS, THF, 0°, 1.5 h



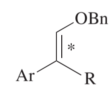
R^1	R^2		$(E)/(Z)^*$
4-MeC_6H_4	4-ClC_6H_4	(83)	55:45
4-MeC_6H_4	Bn	(73)	50:50
$Ph(CH_2)_2$	Bn	(46)	52:48
benzothien-2-yl	Bn	(71)	67:33

108





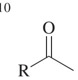
LiHMDS, THF, 0°, 1.5 h

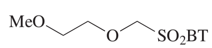


Ar	R		$(E)/(Z)^*$
Ph	CF_3	(82)	64:36
4-FC_6H_4	Me	(90)	52:48
4-IC_6H_4	Me	(75)	50:50
4-$MeOC_6H_4$	Me	(87)	50:50
3,4-$(OCH_2O)C_6H_3$	Me	(86)	50:50
2-MeC_6H_4	Me	(79)	68:32

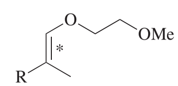
108

C_{8-10}





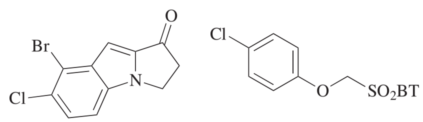
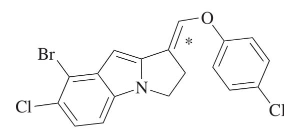
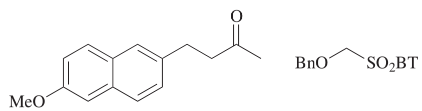
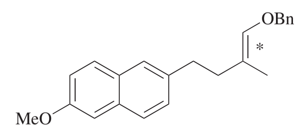
LiHMDS, THF, 0°, 1.5 h



R		$(E)/(Z)^*$
Ph	(86)	57:43
4-ClC_6H_4	(87)	62:38
3,4-$(OCH_2O)C_6H_3$	(76)	57:43
$Ph(CH_2)_2$	(83)	57:43

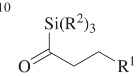
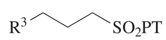
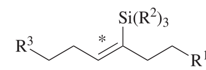
108

TABLE 9. SYNTHESIS OF VINYL ETHERS, VINYL ESTERS, AND VINYL AMIDES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	LiHMDS, THF, 0°, 1.5 h	 (65), (*E*)/(*Z*)* = 74:26	108
C_{14}			
	LiHMDS, THF, 0°, 1.5 h	 (86), (*E*)/(*Z*)* = 60:40	108

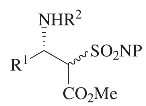
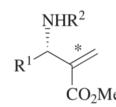
[a] The product still containing the $SO_{2pyridyl}$ group was obtained.
[b] The configurations of the two products were not determined.
[c] The yield is for the mixture of (*E*) and (*Z*) isomers of the tetraacetyl derivative obtained on desilylation and acetylation.
[d] A single isomer of unknown configuration was formed.

TABLE 10. SYNTHESIS OF VINYL SILANES

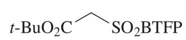
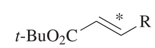
Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{9-10}  	LiHMDS, solvent, –78°, 0.5 h		113

R^1	R^2	R^3	Solvent		$(E)/(Z)^*$
Ph	Me	Ph	THF	(93)	64:36
Ph	Me	Ph	toluene	(74)	33:67
Ph	Et	Ph	THF	(24)	50:50
Ph	Me	n-C_9H_{19}	THF	(79)	65:35
Ph	Me	n-C_9H_{19}	toluene	(69)	39:71
Bn	Me	Ph	THF	(78)	62:38
Bn	Me	Ph	toluene	(76)	32:68
Bn	Me	n-C_9H_{19}	THF	(84)	68:32
Bn	Me	n-C_9H_{19}	toluene	(61)	42:58

TABLE 11. SYNTHESIS OF α,β-UNSATURATED ESTERS

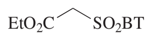
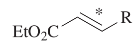
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
HCHO (aq)		Cs_2CO_3, DMF, 0° to rt		64

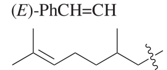
R^1	R^2		er
Me	Boc	(88)	95.0:5.0
i-Pr	Boc	(74)	93.5:6.5
t-Bu	Cbz	(76)	92.0:8.0
n-C_5H_{11}	Cbz	(79)	94.0:6.0
n-C_6H_{13}	Boc	(91)	98.0:2.0
c-C_6H_{11}	Boc	(84)	96.0:4.0
Ph	Boc	(85)	95.5:4.5
4-ClC_6H_4	Boc	(70)	90.0:10.0
2-BrC_6H_4	Cbz	(75)	97.0:3.0
4-$MeOC_6H_4$	Boc	(63)	94.5:5.5
$Ph(CH_2)_2$	Boc	(85)	95.5:4.5
$Ph(CH_2)_2$	Cbz	(74)	89.0:11.0
2-naphthyl	Boc	(84)	92.0:8.0

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-11}				
RCHO		K_2CO_3, Bu_4NBr, DMF, 120°, 18 h		16

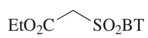
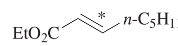
R		$(E)/(Z)^*$
2-thienyl	(46)	85:15
4-pyridyl	(96)	96:4
c-C_6H_{11}	(15)	75:25
Ph	(95)	96:4
2-ClC_6H_4	(52)	>99:1
4-ClC_6H_4	(56)	>99:1
4-BrC_6H_4	(62)	>99:1
4-$MeOC_6H_4$	(45)	>99:1
4-$CF_3C_6H_4$	(74)	>99:1
n-C_9H_{19}	(14)	68:32
2-naphthyl	(48)	95:5
6-MeO-2-naphthyl	(31)	95:5

C_{5-10}

Aldehyde	Sulfone	Conditions	Product	Refs.
RCHO		DBU, CH_2Cl_2, rt, 16 h		20

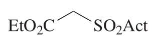
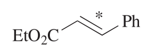
R		$(E)/(Z)^*$
t-Bu	(21)	>98:2
n-C_5H_{11}	(41)	19:81
Et_2CH	(88)	>98:2
c-C_6H_{11}	(80)	80:20
Bn	(80)	>98:2
(*E*)-PhCH=CH	(0)	—
	(64)	30:70

C_6

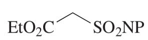
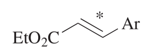
Aldehyde	Sulfone	Conditions	Product	Refs.
n-C_5H_{11}CHO		**A**: DBU, CH_2Cl_2, –78°, 16 h *or* **B**: NaHMDS, THF, 0 to 65°, 2 h		20

Conditions		$(E)/(Z)^*$
A	(47)	8:92
B	(31)	95:5

C_7

Aldehyde	Sulfone	Conditions	Product	Refs.
PhCHO		NaHMDS, THF, 65°, 2 h		20

Act		$(E)/(Z)^*$
BT	(63)	>95:5
PT	(5)	>95:5
TBT	(0)	>95:5

Aldehyde	Sulfone	Conditions	Product	Refs.
ArCHO		1. Cs_2CO_3, DMF, temp 2. Aldehyde, time		545

Ar	Temp	Time (d)		$(E)/(Z)^*$
4-ClC_6H_4	60°	2	(50)	>99:1
4-BrC_6H_4	rt	4	(49)	>99:1
4-$O_2NC_6H_4$	rt	0.75	(41)	>99:1
4-$MeOC_6H_4$	60°	6	(40)	>99:1

TABLE 11. SYNTHESIS OF α,β-UNSATURATED ESTERS (*Continued*)

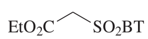
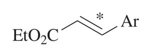
	Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)				Refs.
C_{7-11}								
	ArCHO		DBU, CH_2Cl_2, rt, 16 h		Ar		$(E)/(Z)^*$	
					Ph	(78)	>95:5	20
					2-ClC_6H_4	(72)	95:5	
					4-ClC_6H_4	(77)	95:5	
					2,6-$Cl_2C_6H_3$	(83)	>98:2	
					4-$O_2NC_6H_4$	(89)	>98:2	
					4-$MeOC_6H_4$	(93)	92:8	
					4-$HO_2CC_6H_4$	(57)	96:4	
					2,4,6-$Me_3C_6H_2$	(70)	>98:2	
					1-naphthyl	(86)	96:4	
					2-naphthyl	(65)	93:7	
					ferrocenyl	(82)	96:4	

TABLE 12. SYNTHESIS OF α,β-UNSATURATED AMIDES

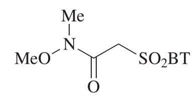
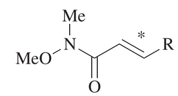
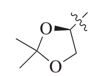
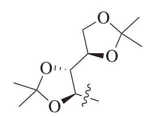
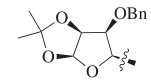
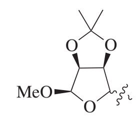
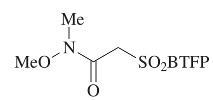
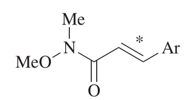
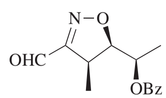
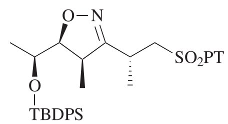
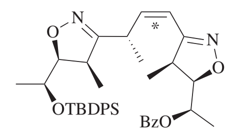
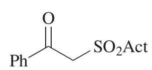
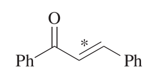
	Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{3-7}				
RCHO		1. NaH, THF, rt, 2 min 2. Aldehyde, rt, 24 h	 $(E)^*$-isomers only	84
			R / (yield)	
			 (50)	
			Pr (48)	
			2-furyl (52)	
			2-thienyl (63)	
			CH_2=CH$(CH_2)_2$ (57)	
			 (72)	
			 (55)	
			 (53)	
			5-(TBSOCH_2)-2-furyl (59)	
			Ph (67)	
			4-MeOC_6H_4 (44)	
C_{5-11}				
ArCHO		K_2CO_3, Bu_4NBr, DMF, 120°, 18 h	 $(E)/(Z)^*$ >99:1	16
			Ar / (yield)	
			2-furyl (50)	
			2-thienyl (49)	
			Ph (66)	
			2-ClC_6H_4 (84)	
			4-ClC_6H_4 (47)	
			4-BrC_6H_4 (51)	
			4-MeOC_6H_4 (20)	
			4-$CF_3C_6H_4$ (82)	
			2-naphthyl (30)	
			6-MeO-2-naphthyl (25)	

TABLE 13. SYNTHESIS OF α,β-UNSATURATED KETONES AND THEIR DERIVATIVES

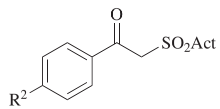
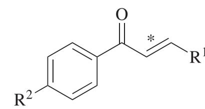
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		1. Base, solvent, –78°, 40 min 2. Aldehyde, –78°, 1 h; then rt		660
PhCHO		1. Base, solvent, temp 2. Aldehyde, time		85

Base	Solvent		(*E*)/(*Z*)*
LDA	toluene	(55–95)	28:72
LDA	THF	(55–95)	39:61
LDA	DME	(55–95)	42:58
KHMDS	toluene	(55–95)	27:73
KHMDS	THF	(96)	32:68
KHMDS	DME	(55–95)	41:59
KHMDS	DMF	(55–95)	49:51

Act	Base	Solvent	Temp (°)	Time (h)		(*E*)/(*Z*)*
BT	LiHMDS	THF	0	14	(36)	98:2
BT	P4-*t*-Bu	THF	0	16	(37)	95:5
BT	DBU	THF	0	16	(81)	99:1
BT	DBU	CH_2Cl_2	0	—	(45)	—
BT	DBU	$CHCl_3$	0	—	(38)	—
BT	DBU	CH_3CN	0	—	(33)	—
BT	DBU	MeOH	0	—	(0)	—
BT	DBU	THF	–78	—	(46)	—
BT	*t*-BuOK	THF	0	—	(0)	—
BT	DABCO	THF	0	—	(0)	—

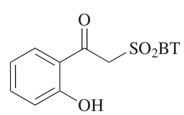
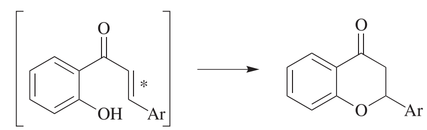
Act	Base	Solvent	Temp	Time (h)		(*E*)/(*Z*)*
PT	LiHMDS	THF	0	18	(23)	—
PT	P4-*t*-Bu	THF	0	19	(26)	—
PT	DBU	THF	0	16	(79)	99:1
PYR	LiHMDS	THF	0	18	(<5)	—
PYR	P4-*t*-Bu	THF	0	19	(12)	—
PYR	DBU	THF	0	24	(37)	—
BTFP	LiHMDS	THF	0	—	—	—
BTFP	P4-*t*-Bu	THF	0	—	—	—
BTFP	DBU	THF	0	24	(<10)	—

C_{7-11}

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
R^1CHO	 Act = BT or PT	1. DBU, THF 2. Aldehyde, 13-21 h	 (*E*)/(*Z*)* >99:1	85

R^1	R^2	Act = BT	Act = PT
Ph	H	(81)	(74)
Ph	MeO	(79)	(69)
4-FC_6H_4	H	(77)	(59)
4-ClC_6H_4	H	(74)	(63)
4-$AcHNC_6H_4$	H	(66)	—
3-$MeOC_6H_4$	MeO	(81)	(80)
4-$MeOC_6H_4$	H	(84)	(69)
4-$MeOC_6H_4$	MeO	(76)	(64)
4-$AcOC_6H_4$	H	(74)	—
4-$[Cl(CH_2)_2O]C_6H_4$	H	(86)	(75)
4-MeC_6H_4	H	(73)	(46)
(*E*)-PhCH=CH	H	(88)	(82)
3-indolyl	H	(67)	(24)
3-indolyl	MeO	(69)	(43)
1-naphthyl	H	(63)	(71)
ferrocenyl	H	(78)	(64)

C_7

Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
ArCHO		DBU, THF, heat		85

Ar	Time (h)	
Ph	13	(62)
4-BrC_6H_4	16	(65)
4-HOC_6H_4	18	(40)
4-$MeOC_6H_4$	11	(68)

C_8

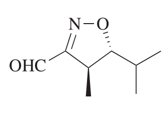
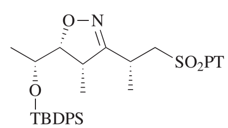
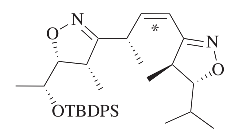
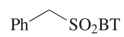
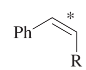
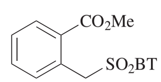
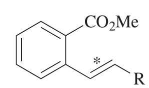
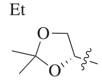
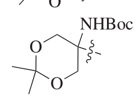
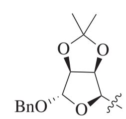
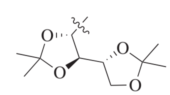
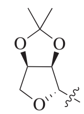
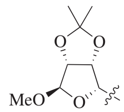
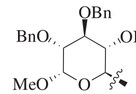
Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. KHMDS, THF, –78°, 1 h 2. Aldehyde, –78°, 1.5 h; then rt, 0.5 h	 (75), (*E*)/(*Z*)* = 45:55	660

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES

	Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-9}	RCHO		**A**: KHMDS, THF, –78° *or* **B**: KHMDS, DMF, –55° *or* **C**: 1. KHMDS, 18-crown-6, DMF, –55°, 2 min 2. Aldehyde *or* **D**: 1. KHMDS, DMF/TDA, –60°, 2 min 2. Aldehyde		32
C_{3-6}	RCHO		**A**: K_2CO_3, DMF, 70°, 12 h *or* **B**: 1. NaH, DMF, 0°, 10 min 2. Aldehyde; then rt, 1 h		661

R	Conditions		$(E)/(Z)^*$
$BnOCH_2$	**A**	(85)	42:58
$BnOCH_2$	**B**	(70)	32:68
$BnOCH_2$	**C**	(91)	81:19
$BnOCH_2$	**D**	(92)	83:17
$Ph(CH_2)_2$	**A**	(95)	48:52
$Ph(CH_2)_2$	**B**	(92)	42:58
$Ph(CH_2)_2$	**C**	(74)	15:85
$Ph(CH_2)_2$	**D**	(73)	14:86

R	Conditions		$(E)/(Z)^*$
Et	**A**	(84)	50:50
	**B**	(65)	83:17
	**A**	(80)	100:0
	**B**	(65)	85:15
	**B**	(64)	94:6

	**B**	(75)	100:0		
	**B**	(56)	100:0		
	**B**	(50)	100:0		

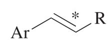
C_{3-9}

RCHO 

A:
1. LDA, THF, –78°, 1 h
2. Aldehyde, –78°, 3 h; then rt

or **B**:
LDA, THF, –78°, 3 h; then rt, 1 h

or **C**:
1. *n*-BuLi, THF, –78°, 1 h
2. Aldehyde, –78°, 3 h; then rt

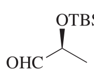
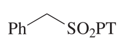


3

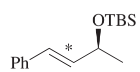
R	Ar	Act	Conditions		(*E*)/(*Z*)*
Et	4-$MeOC_6H_4$	BT	**A**	(73)	30:70
Et	4-$MeOC_6H_4$	PYR	**C**	(12)	12:82 (sic)
Et	4-$MeOC_6H_4$	PYR	**C**[a]	(18)	8:92
i-Pr	Ph	BT	**A**	(51)	90:10
i-Pr	Ph	BT	**B**	(69)	45:55
t-Bu	Ph	BT	**B**	(63)	>99:1

R	Ar	Act	Conditions		(*E*)/(*Z*)*
c-C_6H_{11}	Ph	BT	**A**	(78)	50:50
c-C_6H_{11}	Ph	BT	**B**	(67)	60:40
n-C_8H_{17}	Ph	BT	**A**	(81)	37:63
n-C_8H_{17}	Ph	BT	**B**	(80)	23:77
n-C_8H_{17}	Ph	PYR	**C**	(42)	10:90
n-C_8H_{17}	Ph	PYR	**C**[a]	(51)	10:90
n-C_8H_{17}	Ph	PYM	**C**	(74)	74:26

C_3

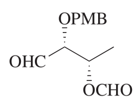
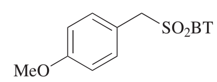
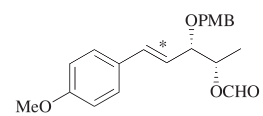
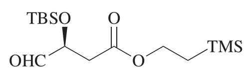
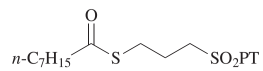
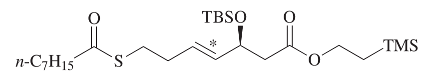
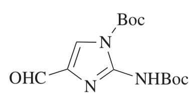
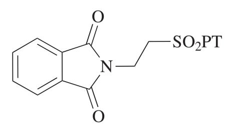
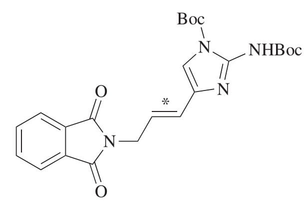
1. KHMDS, DME, –78°, 0.5 h
2. Aldehyde; then rt



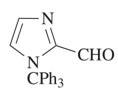
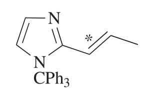
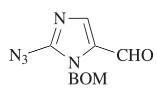
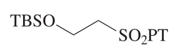
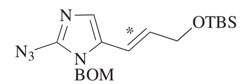
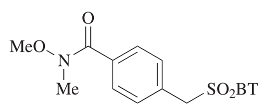
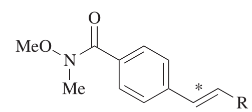
(73), (*E*)/(*Z*)* = 91:9

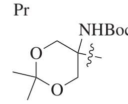
662

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

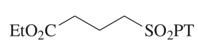
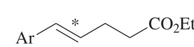
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
 	1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt, 3 h	 (>72), $(E)/(Z)^*$ = —	663, 664
 	Aldehyde (1.0 eq), sulfone (1.0 eq), NaHMDS (2.0 eq), DMF, –65°, 4 h; then to rt	 (80), $(E)/(Z)^*$ = 95:5	665
 	Barbier conditions with aldehyde (x eq) and $MN(SiMe_3)_2$ (y eq) as base, solvent		666, 667

x	M	y	Solvent	Temp (°)		$(E)/(Z)^*$
1.0	Li	2.0	DME	–55	(65)	75:25
1.0	K	2.0	DME	–55	(<43)	81:19
1.0	Na	1.0	DME	–55	(—)	~50:50
1.0	Na	2.0	DME	–55	(60)	80:20
1.0	Na	2.0	THF	–55	(61)	87:13
1.0	Na	2.0	THF	–55	(63)	90:10
1.0	Na	3.0	DME	–78	(31)	84:16
1.5	Na	2.5	THF	–78	(79)	87:13

		Aldehyde (1.0 eq), sulfone (1.2 eq), KHMDS, (1.1 eq), THF, –78°; then 0°, 4 h	 (51), $(E)^*$-isomer	668
		Aldehyde (1.0 eq), sulfone (1.05 eq), KHMDS (1.4 eq) THF, –78°; then to rt, 2.5 h	 (64)[b], $(E)/(Z)^*$ = —	669
RCHO		K_2CO_3, 70°, 17 h		670

R	Solvent		$(E)/(Z)^*$
Pr	THF/DMF	(78)	67:33
	DMF	(70)	100:0
	THF/DMF	(55)	—

C_5

ArCHO		1. Sulfone (1.0 eq), NaHMDS (1.1 eq), DME, –78°, 0.5 h 2. Aldehyde (x eq), –78°; then to rt		671

Ar	x	$(E)^*$-isomer
2-furyl	1.5	(67)
2-thienyl	1.1	(79)

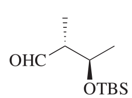
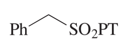
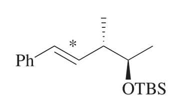
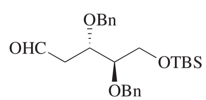
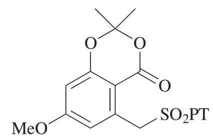
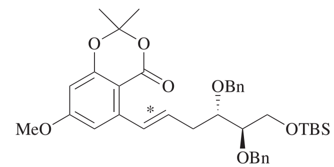
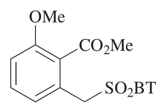
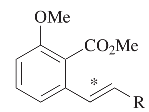
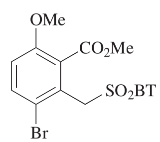
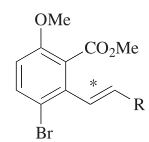
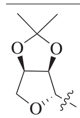
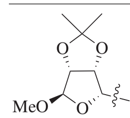
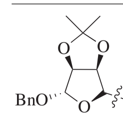
		1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde; then rt	 (69), $(E)/(Z)^*$ = 54:46	210

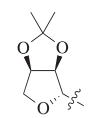
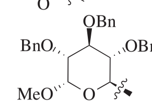
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. Sulfone (1.5 eq), 18-crown-6 (2.2 eq), KHMDS (1.5 eq), DME, –78°, 0.33 h 2. Aldehyde (1.0 eq), –78°, 1 h; then to –10°	 (84), (*E*)*-isomer	672
RCHO		1. NaH, DMF, 0°, 10 min 2. Aldehyde; then rt, 1 h		661
$C_{5–6}$				
RCHO		1. NaH, DMF, 0°, 10 min 2. Aldehyde; then rt, 1 h		661

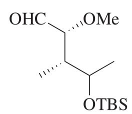
R substituents for ref. 661 (C_5):

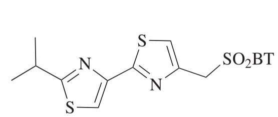
R	Yield (%)	(*E*)/(*Z*)*
	(67)	100:0
	(77)	90:10
	(70)	80:20

R substituents for ref. 661 ($C_{5–6}$):

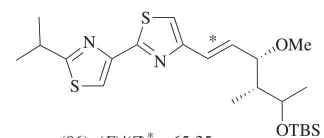
R	Yield (%)	(*E*)/(*Z*)*
	(54)	100:0
	(77)	100:0

C$_6$





1. LiHMDS, THF, 0°, 15 min
2. Aldehyde, 0°, 10 min

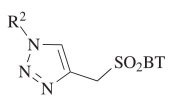


(96), $(E)/(Z)^*$ = 65:35

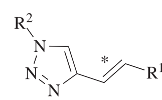
673

C$_{6-8}$

R^{1}CHO



LiHMDS, DMF/DMPU, –78°

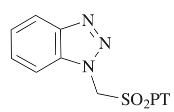


R^1	R^2		$(E)/(Z)^*$
Et_2CH	4-MeOC$_6$H$_4$	(67)	86:14
Et_2CH	Ph(CH$_2$)$_3$	(41)	77:23
n-C$_7$H$_{15}$	4-MeOC$_6$H$_4$	(71)	72:28
n-C$_7$H$_{15}$	Ph(CH$_2$)$_3$	(31)	7:93

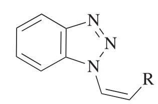
643

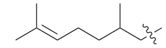
C$_{6-10}$

RCHO



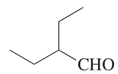
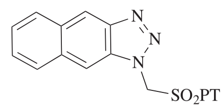
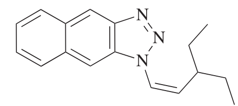
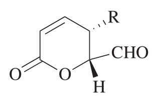
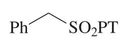
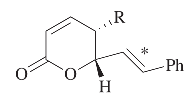
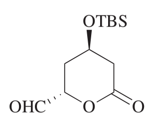
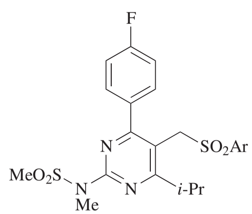
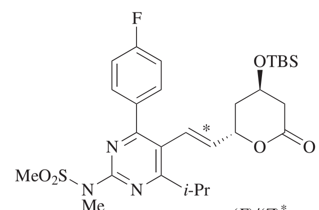
A:
LiHMDS, THF, 0°
or **B:**
DBU, THF, reflux



R	Conditions	Time (h)		$(E)/(Z)^*$
Et_2CH	**A**	0.5	(73)	22:78
Et_2CH	**B**	16	(50)	3:97
c-C$_6$H$_{11}$	**A**	2	(53)	20:80
n-C$_7$H$_{15}$	**A**	0.5	(67)	4:96
	**A**	1	(80)	16:84

112

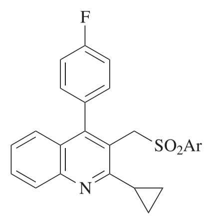
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		LiHMDS, solvent, 0°		112
		1. KHMDS, THF, 0° to rt, 0.33 h 2. Aldehyde, –78°, 3 h; then rt, 8 h		674-676
		1. Sulfone (1.0 eq), NaHMDS (1.1 eq), THF, –60°, 5 min 2. Aldehyde (1.2 eq), –60°, few seconds	 (*E*)/(*Z*)* = —	677

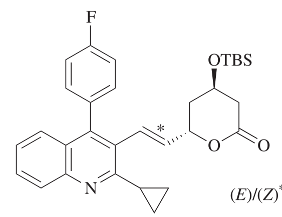
Solvent	Time (min)		(*E*)/(*Z*)*
THF	25	(54)	22:78
DMF	40	(74)	33:67

R		(*E*)/(*Z*)*
H	(20)	—
TBSO	(40)	>93:7

Ar	Conv. (%)	
1-methyl-2-1*H*-imidazolyl	(27)	(—)
2-thiazolyl	(36)	(9)
2-pyridyl	(51)	(5)
4-$O_2NC_6H_4$	(72)	(—)
3,5-$(CF_3)_2C_6H_3$	(28)	(—)
1-methyl-1*H*-benzo[*d*]imidazolyl	(56)	(19)
2-benzo[*d*]oxazolyl	(90)	(41)
2-benzo[*d*]thiazolyl	(81)	(64)



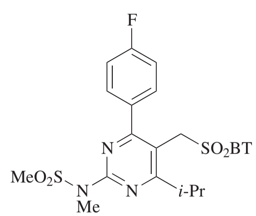
1. Sulfone (1.0 eq),
NaHMDS (1.1 eq),
THF, –60°, 5 min
2. Aldehyde (1.2 eq), –60°,
few seconds



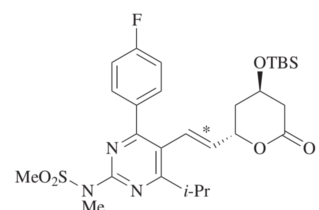
(*E*)/(*Z*)* = —

Ar	Conv. (%)	
1-methyl-2-1*H*-imidazolyl	(60)	(—)
2-thiazolyl	(65)	(11)
2-pyridyl	(37)	(—)
4-$O_2NC_6H_4$	(54)	(—)
3,5-$(CF_3)_2C_6H_3$	(62)	(—)
1-methyl-1*H*-benzo[*d*]imidazolyl	(53)	(33)
2-benzo[*d*]oxazolyl	(86)	(45)
2-benzo[*d*]thiazolyl	(83)	(63)

677



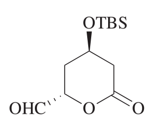
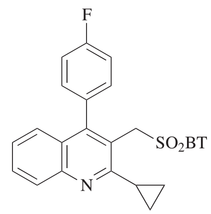
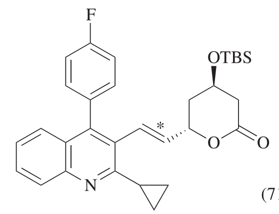
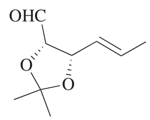
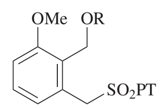
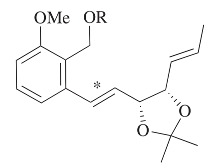
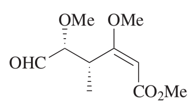
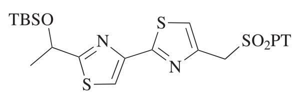
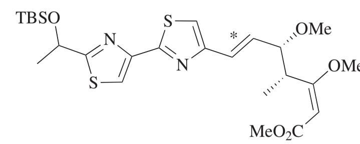
1. Sulfone (1 eq),
NaHMDS (1.3 eq),
THF, –60°, 5 min
2. Aldehyde (1.5 eq), –60°,
few seconds

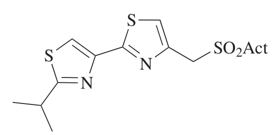


(66), (*E*)/(*Z*)* = 99.2:0.8

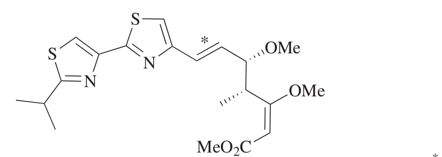
677

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
 	1. Sulfone (1 eq), NaHMDS (1.3 eq), THF, –60°, 5 min 2. Aldehyde (1.2 eq), –60°, few seconds	 (71), (*E*)/(*Z*)* = 99.7:0.3	677
 	Aldehyde (*x* eq), sulfone (1 eq), KHMDS (1 eq), DME, –60°, 1 h; then to rt, 1.5 h	 R / *x* / / (*E*)/(*Z*)* Ac / 1 / (75) / 100:0 TBS / 3 / (90) / 85:15	678
C_7			
 	1. LiHMDS, THF, 0°, 0.25 h 2. Aldehyde, 0°	 (73), (*E*)/(*Z*)* = 91:9	679

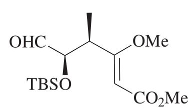


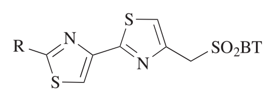
1. LiHMDS, THF, 0°, 15 min
2. Aldehyde, 0°, 10 min



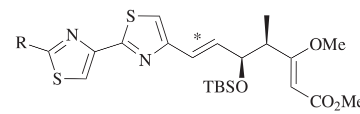
Act		$(E)/(Z)^*$
BT	(64)	94:6
PT	(66)	80:20

680

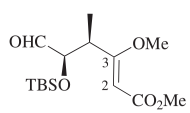


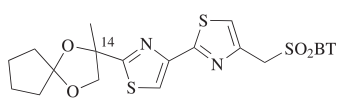


1. LiHMDS, THF, temp, 0.25 h
2. Aldehyde, temp, 0.5 h

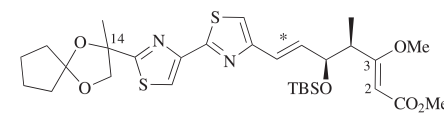


R	Temp (°)		$(E)/(Z)^*$	
i-Pr	–50	(84)	95:5	681
$Me_2C(OH)$	–78	(55)	94:6	682
CH_2=C(Me)	–60	(53)	96:4	682





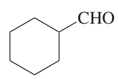
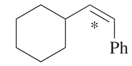
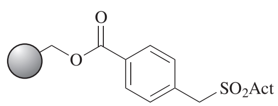
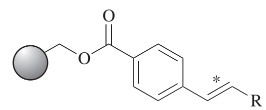
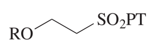
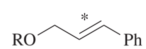
1. LiHMDS, THF, –78 to –30°, 0.25 h
2. Aldehyde, –78 to 0°, 0.5 h



681

C-2/C-3	C-14		$(E)/(Z)^*$
(*E*)	(*R*)	(76)	100:0
(*Z*)	(*R*)	(80)	95:5
(*Z*)	(*S*)	(75)	90:10

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
 	1. Base, THF, rt 2. Aldehyde, 16 h		58
C_{7-8}			
RCHO   = Wang resin	1. DBU, CH_2Cl_2, rt, 0.25 h 2. Aldehyde, rt, 24 h		548
C_7			
PhCHO 	$MN(SiMe_3)$, solvent, –78°, 0.5 h; then rt		188

Base		(*E*)/(*Z*)*
KOH, Bu_4NBr	(14)	34:66
P4-*t*-Bu	(86)	50:50
P2-Et	(75)	25:75

R	Act		(*E*)/(*Z*)*
c-C_6H_{11}	BT	(60)	—
c-C_6H_{11}	PT	(70)	—
Bn	BT	(40)	50:50
Bn	PT	(50)	100:0

R	M	Solvent		(*E*)/(*Z*)*
TMS	Li	THF	(45)	62:38
TMS	Na	THF	(35)	72:28
TMS	K	THF	(28)	81:19
TBS	Li	THF	(81)	67:23
TBS	Na	THF	(79)	89:11
TBS	K	THF	(83)	98:2
TBS	K	DME	(80)	>99:1

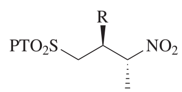
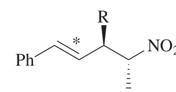
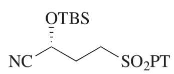
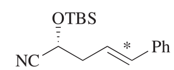
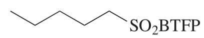
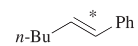
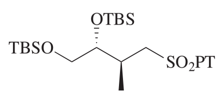
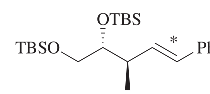
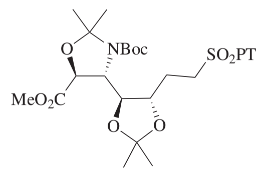
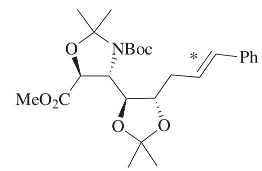
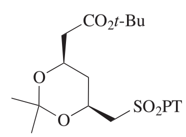
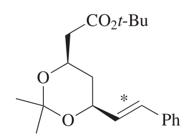
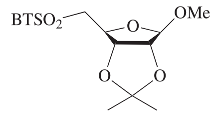
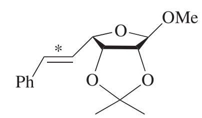
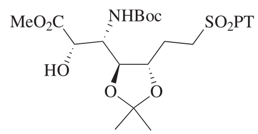
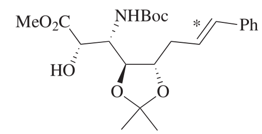
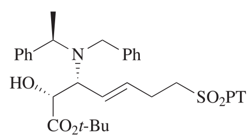
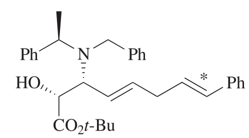
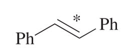
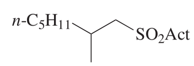
 dr >20:1	Aldehyde (5 eq), sulfone (1 eq), MesLi (2 eq), Et_2O (1 eq), benzene/toluene, 20°, 20 h	 dr >20:1, (*E*)*-isomer; R / Sulfone er / er: Me, 97.5:2.5, (72), 97.5:2.5; Ph, 94.0:6.0, (82), 93.5:6.5	683
	1. KHMDS, THF, –78°, 0.75 h 2. Aldehyde, –78° to rt, 3 h	 (99), (*E*)/(*Z*)* = 98:2	200
	1. Base, THF, rt 2. Aldehyde, 16 h	 Base / (*E*)/(*Z*)*: KOH, Bu_4NBr, (70), 67:33; P4-*t*-Bu, (45), 75:25	58
	1. KHMDS, DME, –55°, 0.67 h 2. Aldehyde, –55°, 1 h; then rt, 1 h	 (70), (*E*)*-isomer only	684
	KHMDS, THF, –78°, 0.5 h	 (28), (*E*)/(*Z*)* >99:1	554
	Aldehyde (1.2 eq), sulfone (1 eq), LiHMDS (1.2 eq), THF, –78°, 1 h; then –78°, 1 h; then rt, 0.5 h	 (85), (*E*)*-isomer	685

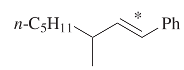
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

	Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
PhCHO		1. Sulfone (1 eq), KHMDS (2.4 eq), THF, –78° 2. Aldehyde (4 eq), –78°; then to rt, 20 min	 (100), (*E*)/(*Z*)* = 95:5	546
		KHMDS, THF, –78°, 0.5 h	 (79), (*E*)/(*Z*)* = —	554
		KHMDS, THF, –78°, 0.5 h	 (66), (*E*)*-isomer	554
	Ph⌒SO_2Act	1. Base, solvent, temp 2. Aldehyde, 16 h		58

			Act = BTFP		Act = BT		Act = PT		Act = TBT	
Base	Solvent	Temp (°)		(*E*)/(*Z*)*		(*E*)/(*Z*)*		(*E*)/(*Z*)*		(*E*)/(*Z*)*
KOH, Bu_4NBr	THF	rt	(78)	84:16	(45)	75:25	(50)	66:34	(53)	60:40
P4-*t*-Bu	THF	–78	(65)	98:2	(55)	85:15	(30)	95:5	(35)	95:5
P4-*t*-Bu	THF/HMPA	–78	(78)	95:5						
P2-Et	THF	–78	(67)	97:3						
LDA	THF	–78	(<5)	—						
KHMDS	DME	–60 to rt	(20)	99:1						
t-BuOK	THF	rt	(<5)	—						
DBU	CH_2Cl_2	rt	(<5)	—						

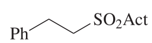


LDA, THF, –78°, 1 h;
then rt, 3 h

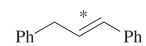


Act		$(E)/(Z)^*$
BT	(39)	>99:1
TZ	(39)	62:38
IQ	(39)	96:4
PT	(90)	>99:1

21

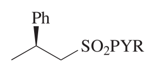


Barbier conditions.

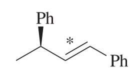


686

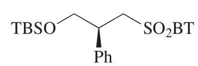
			Act = *p*-NPT		Act = *m*-NPT	
Base	Solvent	Temp (°)		$(E)/(Z)^*$		$(E)/(Z)^*$
LiHMDS	THF	–78	(46)	95:5	(76)	96:4
Cs_2CO_3	MeCN	rt	(37)	91:9	(41)	90:10
DBU	MeCN	0	(<5)	83:17	(50)	91:9
DBU, LiCl	MeCN	0	(28)	90:10	(86)	88:12
DBU, NaI	MeCN	0	(—)	—	(77)	96:4



1. KHMDS, DME, –78°, 3 min
2. Aldehyde, –78°, 2 h

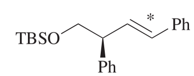


(87), "predominantly $(E)^*$" 687



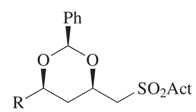
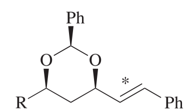
er 96:4

1. Sulfone (1 eq),
KHMDS (1.1 eq),
THF, –55°, 0.5 h
2. Aldehyde (1.1 eq), –55°, 1 h;
then to rt, 3 h



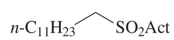
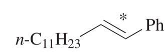
(90), er 96:4 688

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

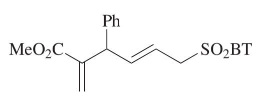
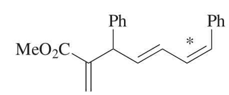
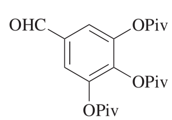
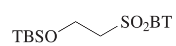
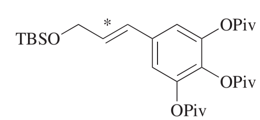
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
PhCHO 	Base, solvent		51

R	Act	Base	Solvent	Temp (°)		$(E)/(Z)^*$
n-C_6H_{13}	BT	LiHMDS	THF	–78 to 20	(41)	83:17
n-C_6H_{13}	BT	NaHMDS	THF	–78 to 20	(75)	83:17
n-C_6H_{13}	BT	KHMDS	THF	–78	(81)	75:25
n-C_6H_{13}	BT	KHMDS	DMF	–60	(78)	88:12
n-C_6H_{13}	BT	NaH	THF	20	(71)	97:3

R	Act	Base	Solvent	Temp (°)		$(E)/(Z)^*$
$Ph(CH_2)_2$	PYR	NaH	THF	20	(<5)	—
$Ph(CH_2)_2$	PYR	NaH	DMF	20	(50)	89:11
$Ph(CH_2)_2$	PYR	KHMDS	THF	–78 to 20	(40)	83:17
$Ph(CH_2)_2$	PYR	KHMDS	PhMe	–78 to 20	(44)	90:10
$Ph(CH_2)_2$	PYR	KHMDS	CH_2Cl_2	–78 to 20	(47)	94:6

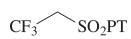
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
	LDA, THF, –78°, 1 h; then rt, 3 h		21

Act		$(E)/(Z)^*$
BT	(30)	79:21
IM	(<1)	54:46
TZ	(44)	38:62
IQ	(40)	74:26

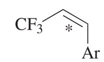
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
	LDA, DME, –50°, 8 h	 (70), $(E)/(Z)^*$ = 11:89	689
 	KHMDS, THF, –78°, 2 h; then rt, 2 h	 (75), $(E)/(Z)^*$ = 75:25	690

C_{7-17}

ArCHO



CsF, DMSO, rt



Ar		(E)/(Z)*
4-$O_2NC_6H_4$	(52)	37:63
3-$MeOC_6H_4$	(37)	39:61
4-NCC_6H_4	(42)	39:61
4-$MeO_2CC_6H_4$	(50)	38:62
1-naphthyl	(65)	52:48
2-naphthyl	(86)	41:59
6-MeO-2-naphthyl	(51)	44:56
4-PhC_6H_4	(23)	40:60
9-anthracenyl	(50)	92:8
9-phenanthrenyl	(42)	56:44
1-pyrenyl	(62)	61:39

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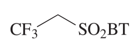
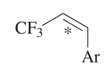
C_{7-13}

ArCHO



TBAF, THF, –78° to rt, 16 h



Ar		(E)/(Z)*
2,4-$Cl_2C_6H_3$	(74)	100:0
2-BrC_6H_4	(61)	76:24
4-BrC_6H_4	(61)	46:54
3-$O_2NC_6H_4$	(78)	23:77
4-$O_2NC_6H_4$	(92)	100:0
4-$MeOC_6H_4$	(45)	44:56
3-$PhOC_6H_4$	(73)	30:70
2-(4-ClC_6H_4)SC_6H_4	(83)	65:35
4-$MeO_2CC_6H_4$	(56)	27:73
4-*t*-BuC_6H_4	(75)	46:54
1-naphthyl	(73)	58:42
2-naphthyl	(80)	38:62
4-PhC_6H_4	(83)	36:64

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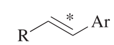
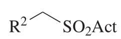
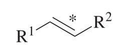
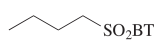
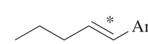
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

	Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7					
	ArCHO		LDA, THF, –78°, 3 h; then rt, 1 h		3

Ar	R		$(E)/(Z)^*$
Ph	t-BuO$(CH_2)_2$	(15)	97:3
4-$MeOC_6H_4$	Me	(54)	98:2
3,4-$(MeO)_2C_6H_3$	Me	(39)	98:2
4-$MeOC_6H_4$	Et	(54)	98:2

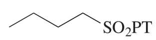
	Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-10}					
	R^1CHO		1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60° to rt		5

		Act = PT		Act = TBT	
R^1	R^2		$(E)/(Z)^*$		$(E)/(Z)^*$
Ph	n-Bu	(48)	>99:1	(80)	79:21
n-C_9H_{19}	Ph	(70)	29:71	(95)	<1:99

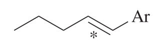
	Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8}					
	ArCHO		LDA, THF, –78°, 3 h; then rt, 1h		3

Ar		$(E)/(Z)^*$
Ph	(68)	94:6
4-ClC_6H_4	(51)	77:23
4-BrC_6H_4	(52)	93:7
4-$MeOC_6H_4$	(95)	99:1
4-NCC_6H_4	(44)	86:14

C$_7$

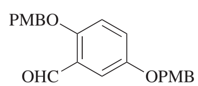
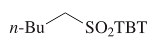
ArCHO 

A:
1. KHMDS, THF, –78°
2. Aldehyde
or **B**:
1. KHMDS (1.1 eq), 18-crown-6 (2.0 eq), THF, 0.5 min
2. Aldehyde, –78°, 30 min

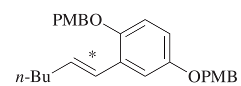


Ar	Conditions **A**		Conditions **B**	
		(*E*)/(*Z*)*		(*E*)/(*Z*)*
4-ClC$_6$H$_4$	(47)	98:2	(65)	96:4
3-O$_2$NC$_6$H$_4$	(61)	95:5	(74)	91:9
4-O$_2$NC$_6$H$_4$	(54)	97:3	(54)	95:5
2-MeOC$_6$H$_4$	(59)	>98:2	(64)	>98:2

26

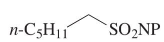
 

Cs$_2$CO$_3$, THF/DMF, 70°, 16 h

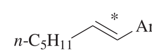


(98), (*E*)/(*Z*)* = 80:20

62

ArCHO 

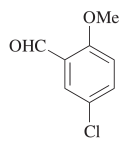
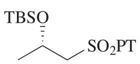
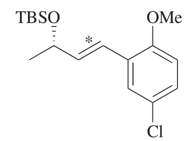
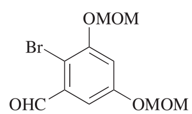
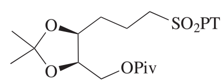
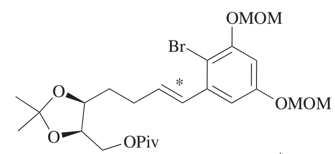
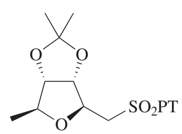
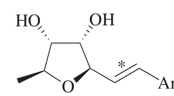
NaH, DMF, rt, 1 h



Ar		(*E*)/(*Z*)*
Ph	(43)	94:6
4-ClC$_6$H$_4$	(68)	80:20
4-BrC$_6$H$_4$	(81)	82:18
2-O$_2$NC$_6$H$_4$	(64)	72:28
3-O$_2$NC$_6$H$_4$	(53)	77:23
4-O$_2$NC$_6$H$_4$	(64)	75:25
4-MeOC$_6$H$_4$	(78)	81:19
3,4-(MeO)$_2$C$_6$H$_3$	(82)	84:16
3,5-(MeO)$_2$C$_6$H$_3$	(89)	88:12
2,4,6-(MeO)$_3$C$_6$H$_2$	(54)	>99:1
3,4,5-(MeO)$_3$C$_6$H$_2$	(84)	85:15

545

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
 	1. Sulfone (1.2 eq), KHMDS (1.5 eq), THF, –78°, 0.75 h 2. Aldehyde (1.0 eq), –78°, 3 h	 (70), (*E*)/(Z)* >98:2, er 99.5:0.5	692
 	1. KHMDS, DME, –60°, 0.5 h 2. Aldehyde, –60°, 1 h; then rt, 3 h	 (68), (*E*)/(Z)* = 96:4	432
C_{7-8}			
ArCHO 	1. KHMDS, DME, –30° to rt, 12 h 2. aq. HCl, THF, rt		693

Ar		(*E*)/(Z)*	Ar		(*E*)/(Z)*
Ph	(88)	60:40	4-$MeOC_6H_4$	(59)	69:31
2-FC_6H_4	(43)	81:19	2,4-$(MeO)_2C_6H_3$	(61)	>99:1
4-FC_6H_4	(42)	71:29	2,5-$(MeO)_2C_6H_3$	(59)	90:10
4-BrC_6H_4	(98)	57:43	2-$CF_3C_6H_4$	(41)	>99:1
2-$MeOC_6H_4$	(49)	61:39	3-$CF_3C_6H_4$	(77)	48:52

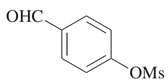
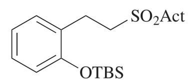
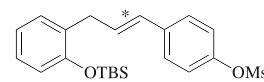
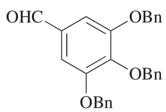
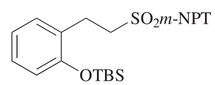
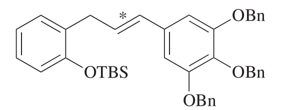
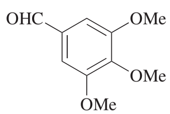
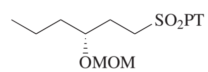
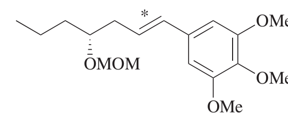
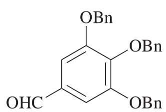
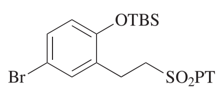
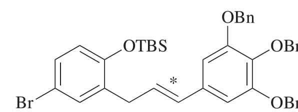
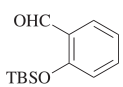
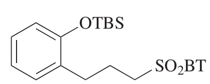
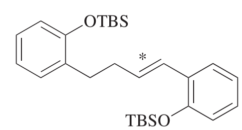
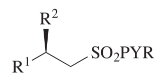
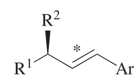
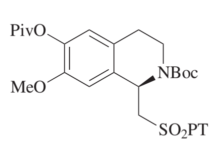
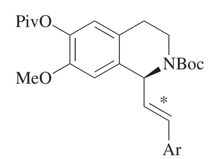
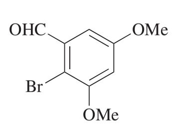
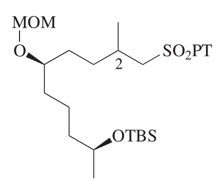
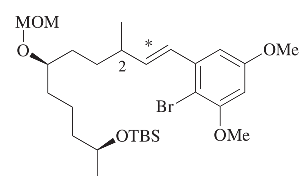
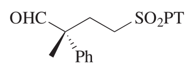
C_7			**A**: LiHMDS, THF, –78° *or* **B**: DBU, LiCl, MeCN, 0°	 Act / Conditions / (*E*)/(*Z*)* PT / **A** / (46) / — *m*-NPT / **B** / (79) / —	686
			DBU, LiCl, MeCN, 0°	 (81), (*E*)/(*Z*)* = 96:4	686
			Aldehyde (1 eq), sulfone (1 eq), NaHMDS (1.8 eq), THF, 0°; then rt, 3 h	 (88), (*E*)*-isomer	694
			1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, 2 h	 (96), (*E*)*-isomer only	695
			1. LDA, THF, –80°, 1 h 2. Aldehyde, rt, 1.5 h	 (79), (*E*)*-isomer	696

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

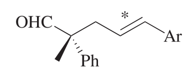
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
ArCHO 	1. KHMDS, DME, –78°, 3 min 2. Aldehyde, –78°, 2 h	 Ar / R^1 / R^2 / / $(E)/(Z)^*$ Ph / Me / Ph / (94) / 99:1 Ph / Me / 4-FC_6H_4 / (93) / 99:1 Ph / n-C_5H_{11} / Ph / (92) / 99:1 4-FC_6H_4 / Me / Ph / (90) / 90:10	201
	LiHMDS, THF, –35°, 1 h	 $(E)^*$-isomer only Ar 4-$MeOC_6H_4$ (86) 4-$PivOC_6H_4$ (79) 3,4-$(OCH_2O)C_6H_3$ (85)	697
 	1. KHMDS, THF, –80°, 0.75 h 2. Aldehyde, 30 min; then rt, 1 h	 $(E)^*$-isomer C-2 (*R*) (70) (*S*) (81)	698

C$_8$

ArCHO

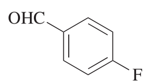


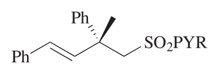
A:
NaHMDS, DME, –78°
or **B**:
1. Sulfone, ethylene glycol, 4-TsOH, benzene
2. Aldehyde, KHMDS, DME, –78°
3. HCl, THF, 50°



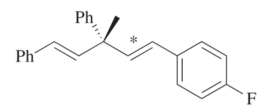
Ar	Conditions		$(E)/(Z)^*$
Ph	**A**	(48)	91:9
Ph	**B**	(72)	91:9
4-$O_2NC_6H_4$	**B**	(77)	90:10
4-$MeOC_6H_4$	**B**	(60)	91:9

53

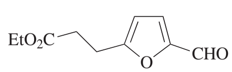


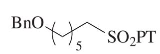


1. KHMDS, DME, –78°, 3 min
2. Aldehyde, –78°, 2 h

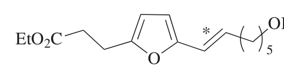


(89), $(E)^*$-isomer only 699

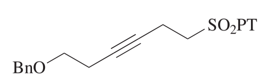




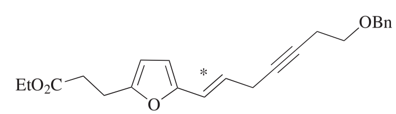
1. Sulfone (1 eq), KHMDS (1.4 eq), THF, –78°, 0.5 h
2. Aldehyde (1.5 eq), –78°, 2 h



(90), $(E)/(Z)^* = 90:10$ 445

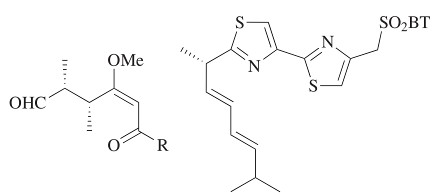
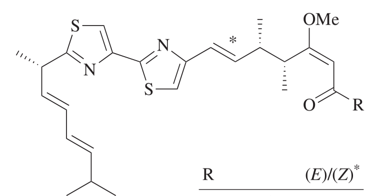
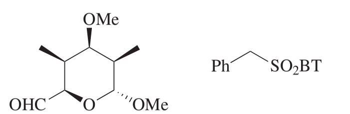
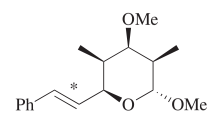
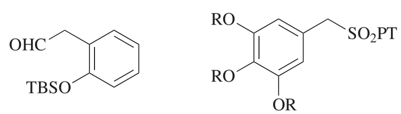
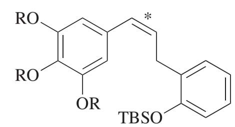
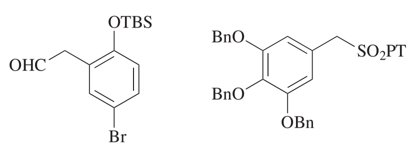
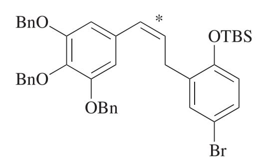


1. Sulfone (1.0 eq), KHMDS (1.2 eq), THF, –78°, 0.5 h
2. Aldehyde (1.6 eq), –78°, 2 h



(87), $(E)/(Z)^* = 91:9$ 700

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. LiHMDS, THF, –78 to –30°, 0.5 h 2. Aldehyde, –78 to –60°	 R / (E)/(Z)* H_2N (61) — MeO (73) 90:10	522
	1. LiHMDS, THF, –78° 2. Aldehyde	 (>50), (*E*)/(*Z*)* = —	585
	LiHMDS, THF, 0°	 R / (E)/(Z)* TBS (75) 9:91 Ms (12) 50:50 Bn (95) 0:100	701
	1. LiHMDS, THF, 0°, 0.5 h 2. Aldehyde, 2 h	 (87), (*Z*)*-isomer only	695

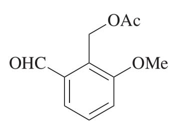
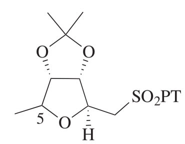
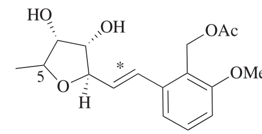
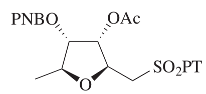
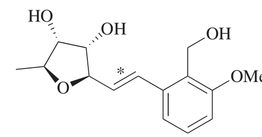
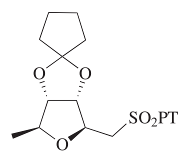
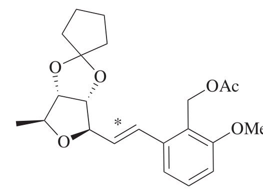
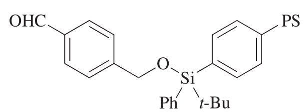
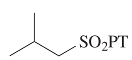
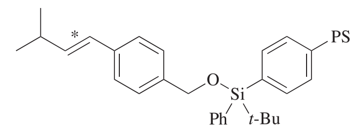
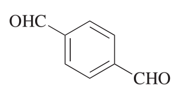
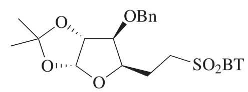
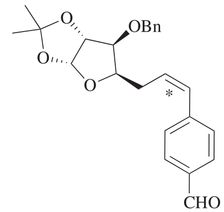
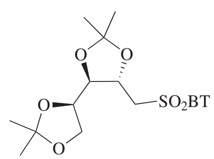
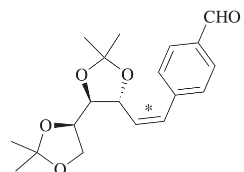
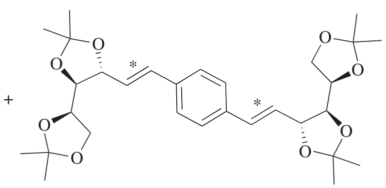
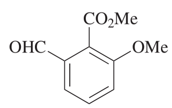
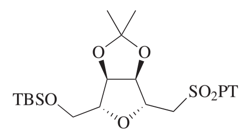
Aldehyde	Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. KHMDS, DME, –30° to rt, 12 h 2. NaOMe, MeOH, rt, 4 h 3. aq. HCl, THF, rt, 5 h	 C-5 / (*E*)/(*Z*)*: (*R*) (78) 56:44 (*S*) (76) 74:26	702, 693
		1. KHMDS, DME, –55° to rt, 10 h 2. NaOMe, MeOH, rt, 4 h	 (63), (*E*)/(*Z*)* = —	703
		1. KHMDS, DMF/HMPA, –78°, 10 min 2. Aldehyde; then rt, 12 h	 (94), (*E*)*-isomer only	704
		1. KHMDS, THF, –78°, 0.67 h 2. Aldehyde, –35° to rt, 16 h	 (69), (*E*)/(*Z*)* >89:11	705

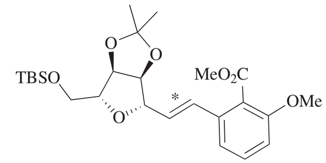
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
 	1. NaH, DMF, 0° 2. Aldehyde, 0°; then rt, 24 h	 (60), (*E*)/(*Z*)* = 25:75	706
	1. NaH, DMF, 0° 2. Aldehyde, 0°; then rt, 24 h	 **I** (30), (*E*)/(*Z*)* = 38:62 +  **II** (60), (*EE*)/(*EZ*)/(*ZZ*)* = —	706



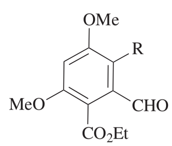


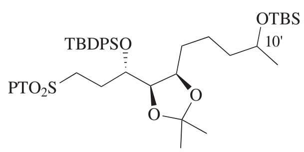
LiHMDS, DME, –78° to rt, 1 h



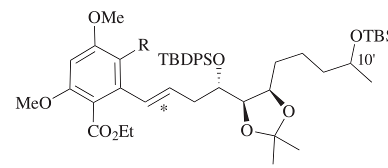
(76), $(E)/(Z)^{*}$ = 65:35

707



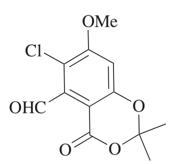


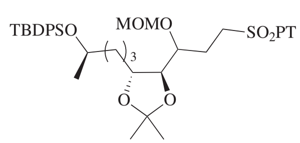
1. Sulfone (1.0 eq), KHMDS (1.1 eq), THF, –78°, 0.67 h
2. Aldehyde (1.2 eq), –78°; then to rt



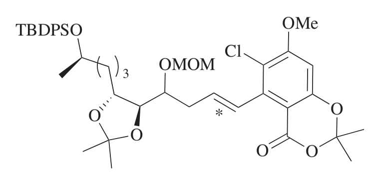
R	C-10'	$(E)^{*}$-isomer
H	(*S*)	(80)
H	(*R*)	(82)
Cl	(*R*)	(78)

202





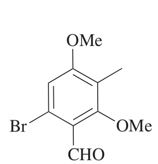
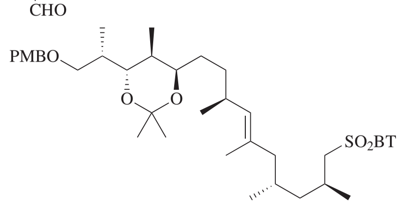
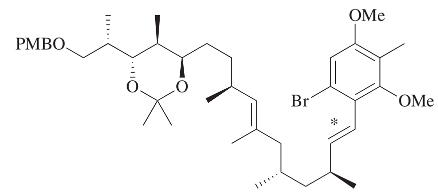
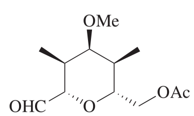
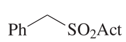
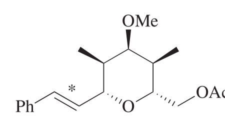
1. KHMDS, 18-crown-6, THF, –78°, 0.5 h
2. Aldehyde, –78° to rt, 2 h



(72), $(E)/(Z)^{*}$ = 92:8

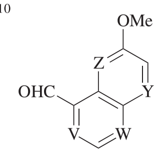
708

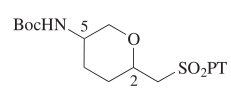
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
 	1. LDA, THF, –78°, 25 min 2. Aldehyde, THF; then rt, 1 h	 (80), $(E)^*$-isomer only	709
C_9			
  Act = BT or PT	$MN(SiMe_3)_2$, solvent, temp, 0.5 h; then to 0°, 0.5 h		710

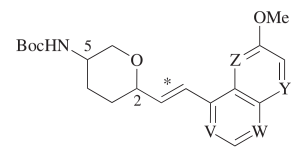
			Act = BT		Act = PT	
M	Solvent	Temp (°)		$(E)/(Z)^*$		$(E)/(Z)^*$
Na	THF	–78	(85)	85:15	(76)	81:19
Na	DME	–60	(75)	81:19	(87)	79:21
K	THF	–78	(85)	86:14	(72)	63:37
K	DME	–60	(87)	87:13	(72)	89:11

C_{9-10}





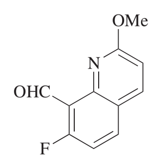
$MN(SiMe_3)_2$, DME, –60°, 0.5 h; then rt, 0.75 h

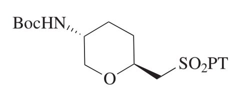


711

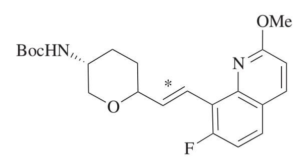
V	W	Y	Z	C-2	C-5	M	(*E*)*-isomer
CH	CH	N	N	(*S*)	(*R*)	Li	(57)
CH	N	CH	N	(*S*)	(*R*)	K	(68)
CH	N	CH	N	(*R*)	(*S*)	K	(75)
CF	CH	N	N	(*S*)	(*R*)	Li	(52)
CF	N	CH	N	(*S*)	(*R*)	Li	(68)
CH	CH	CH	N	(*S*)	(*R*)	K	(30)
CH	CH	N	CH	(*S*)	(*R*)	Li	(42)
CH	N	CH	CH	(*S*)	(*R*)	K	(41)
CH	N	CF	CH	(*S*)	(*R*)	—	(74)
CF	N	CH	CH	(*S*)	(*R*)	Li	(39)

C_{10}

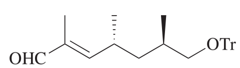


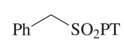


1. Sulfone (1.0 eq), LiHMDS (1.7 eq), DME, –78°, 0.33 h
2. Aldehyde (1.0 eq), –78°, 1 h; then to rt

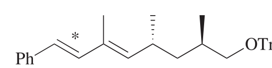


(83), (*E*)*-isomer 712





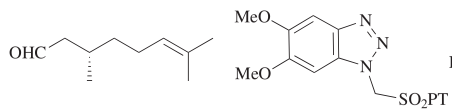
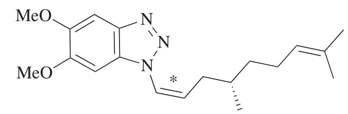
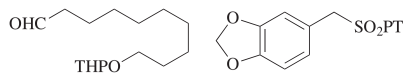
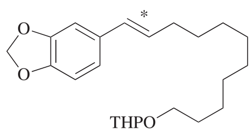
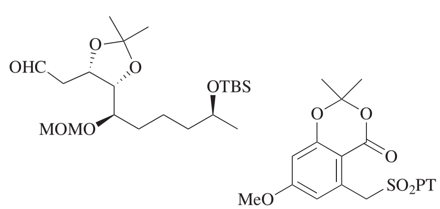
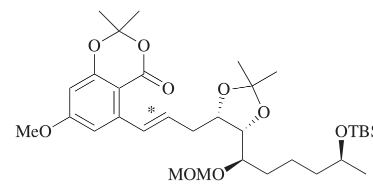
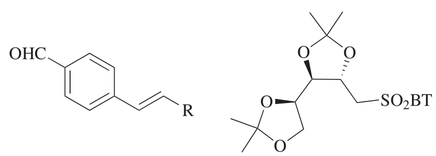
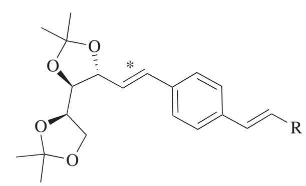
1. LiHMDS, THF, 0°, 0.33 h
2. Aldehyde, –78° to rt, 12 h

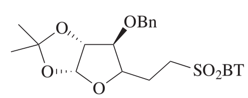


(80), (*E*)/(*Z*)* = 91:9

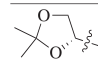
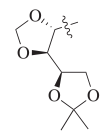
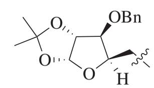
713, 569

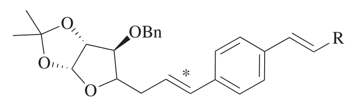
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

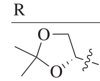
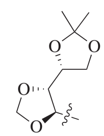
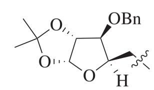
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	LiHMDS, THF, 0°, 25 min	 (69), (*E*)/(*Z*)* = 41:59	112
	LiHMDS, THF, –78° to rt, 12 h	 (70), (*E*)/(*Z*)* = —	714
	1. Sulfone (1.5 eq), KHMDS (1.5 eq), 18-crown-6 (1.5 eq), DME, –78°, 0.33 h 2. Aldehyde (1.0 eq), –78°, 1 h; then to –10°; then –10°, overnight	 (85), (*E*)/(*Z*)* = 90:10	715
$C_{11–14}$			
	1. NaH, DMF, 0°, 10 min 2. Aldehyde, 0°, 0.5 h; then rt, 2 h		706



1. NaH, DMF, 0°, 10 min
2. Aldehyde, 0°, 0.5 h; then rt, 2 h

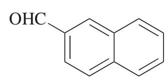
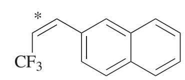
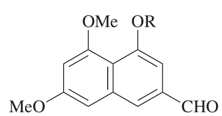
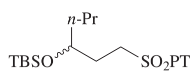
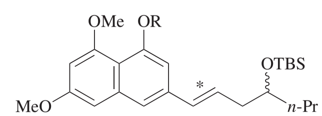
R		$(E)/(Z)^{*}$
	(62)	—
	(65)	—
	(82)	—



R		$(E)/(Z)^{*}$
	(62)	—
	(65)	—
	(80)	—

706

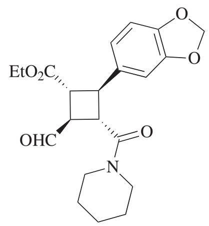
TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

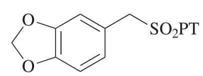
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}  	Base, solvent		691
 	1. Sulfone (*x* eq), KHMDS (*y* eq), THF, –78°, time 1 2. Aldehyde (1.0 eq), LiCl (*z* eq), –78°; then temp, time 2		716

Act	Base	Solvent	Temp		(*E*)/(*Z*)*
BT	TBAF	THF	rt	(27)	27:73
BT	TBAF	THF	0°	(29)	20:80
BT	TASF	CH_2Cl_2	rt	(23)	35:65
BT	CsF	DMSO	rt	(58)	44:56
PT	DBU	CH_2Cl_2	rt	(7)	28:72
PT	TBAF	MeCN	rt	(34)	37:63
PT	TBAF	THF	rt	(47)	31:69
PT	CsF	DMSO	rt	(86)	41:59
PT	TBAF	DMSO	rt	(85)	40:60
TBT	CsF	DMSO	rt	(40)	30:70

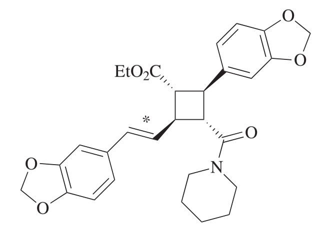
R	Config.	*x*	*y*	*z*	Time 1 (h)	Mode of Addition	Temp	Time 2 (h)		(*E*)/(*Z*)*
Ac	(*R*/*S*)	—		—	0.5	aldehyde to sulfone anion	to rt	16	(75)	98:2
TBS	(*R*/*S*)	1.3	1.4	1.5	0.5	aldehyde to sulfone anion	to rt	16	(94/89)[c]	98:2
TBS	(*S*)	1.7	1.7	1.2	1	sulfone anion to aldehyde	–15°	1	(98)	98:2

C_{13}





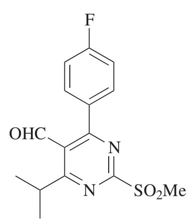
KHMDS, DMF/HMPA, –35° to rt, 6 h

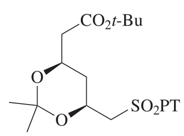


(>50), (*E*)/(*Z*)* = 100:0

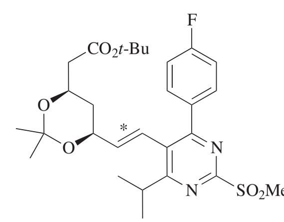
717

C_{14}





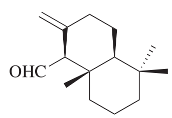
LiHMDS, THF, –60°, 0.25 h; then rt

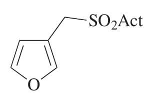


(99), (*E*)/(*Z*)* = —

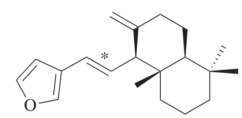
718

C_{15}





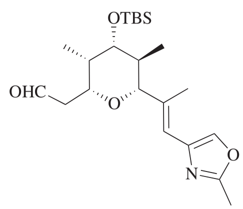
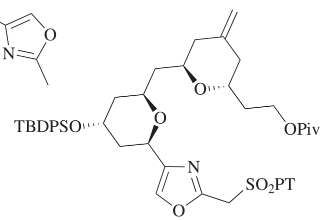
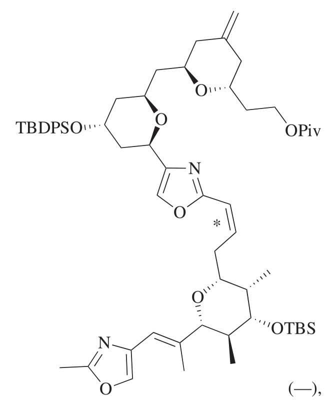
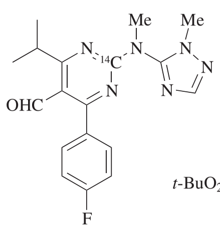
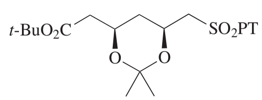
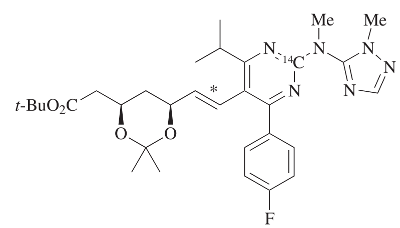
1. $MN(Si(CH_3)_3)_2$, solvent, –78°, 0.33 h
2. Aldehyde, –78°, 0.5 h



Act	M	Solvent		(*E*)/(*Z*)*
BT	Li	THF	(88)	87:13
BT	Na	THF	(74)	88:12
BT	K	THF	(75)	91:9
BT	K	DME	(86)	97:3
PT	K	DME	(73)	98:2

719

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
 	KHMDS, DME, –65 to 0°	 (—), (*E*)/(*Z*)* = 9:91	588
 	Aldehyde (*x* eq), sulfone (*y* eq), LiHMDS (*z* eq), THF		

x	*y*	*z*	Temp/Time		(*E*)/(*Z*)*	Refs.
1.0 (27.5 kg)	1.1 (38.4 kg)	1.2	–80°, 1.3 h; –10°, 1 h	(74)	99:1	73
—	—	—	78°, 0.5 h	(84)	95:5	720

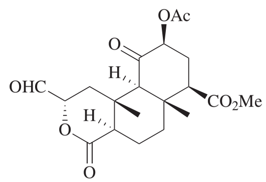
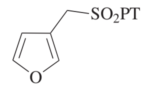
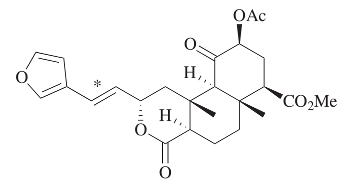
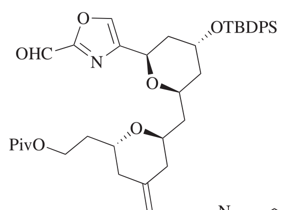
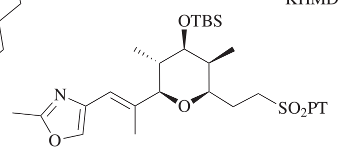
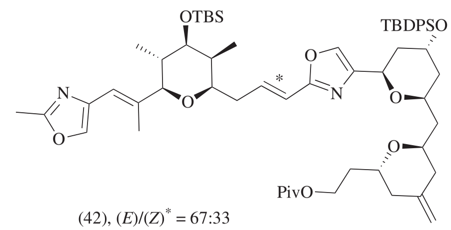
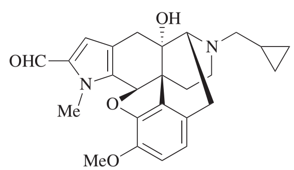
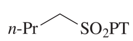
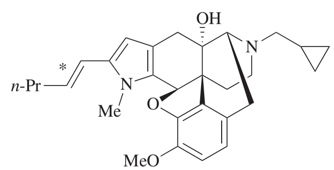
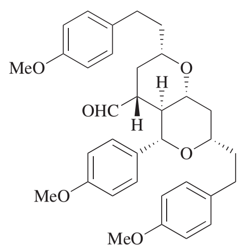
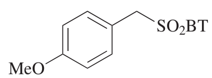
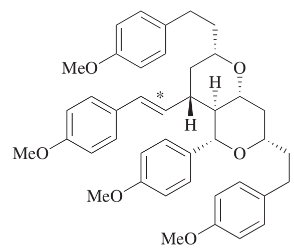
C_{17}			1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h	 (12), (*E*)/(*Z*)[*] = 67:33	721
C_{18}			KHMDS, DME, –65 to 0°	 (42), (*E*)/(*Z*)[*] = 67:33	722
C_{19}			KHMDS, THF, –78° to rt	 (86–91), (*E*)/(*Z*)[*] = —	723

TABLE 14. SYNTHESIS OF VINYL ARENES AND VINYL HETEROARENES (*Continued*)

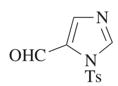
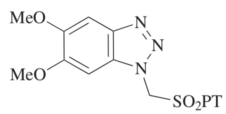
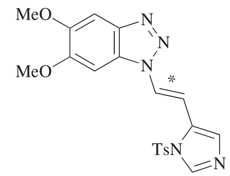
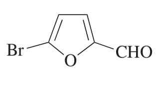
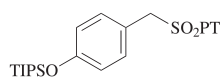
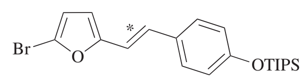
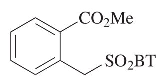
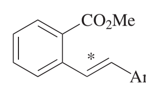
Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{31}			
 	1. LiHMDS, THF, –78°, 0.33 h 2. Aldehyde, –78°, 3 h; then rt, 3 h	 (77), (*E*)/(*Z*)* = 98:2	724, 725

[a] LiBr (3 eq) was added prior to sulfone lithiation.

[b] The yield includes that of an additional step.

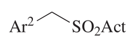
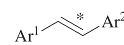
[c] The yields are those reported in the text/supporting information.

TABLE 15. SYNTHESIS OF 1,2-DIARYL/HETEROARYL ALKENES

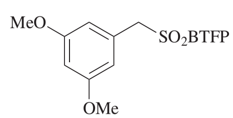
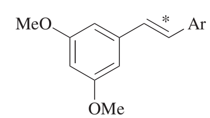
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		LiHMDS, THF, 0°, 25 min	 (80), (*E*)/(*Z*)* = 60:40	112
C_5				
		1. Sulfone (1.3 eq), KHMDS (1.4 eq), THF, –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°, 2 h	 (88), (*E*)/(*Z*)* >95:5	726
$C_{5–9}$				
ArCHO		K_2CO_3, DMF, 70°, 12 h		661

Ar		(*E*)/(*Z*)*
2-furyl	(79)	80:20
2-pyridyl	(87)	100:0
2-ClC_6H_4	(86)	96:4
2-$O_2NC_6H_4$	(80)	100:0
2,4,6-$(MeO)_3C_6H_2$	(75)	80:20
1-Boc-3-indolyl	(75)	80:20

TABLE 15. SYNTHESIS OF 1,2-DIARYL/HETEROARYL ALKENES (*Continued*)

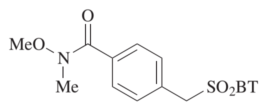
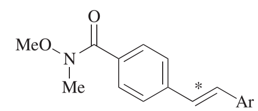
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-8}				
Ar^1CHO		**A**: 1. LDA, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt *or* **B**: 1. BuLi, THF, –78°, 1 h 2. Aldehyde, –78°, 3 h; then rt		3

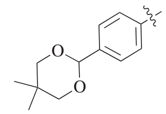
Ar^1	Ar^2	Act	Conditions		$(E)/(Z)^*$
2-furyl	Ph	BT	**A**	(64)	>99:1
Ph	Ph	PYR	**B**	(76)	98:2
Ph	Ph	PYM	**A**	(75)	98:2
Ph	4-$MeOC_6H_4$	BT	**A**	(84)	97:3
4-ClC_6H_4	Ph	BT	**A**	(69)	98:2
4-$MeOC_6H_4$	Ph	BT	**A**	(57)	98:2
4-MeC_6H_4	Ph	BT	**A**	(74)	98:2

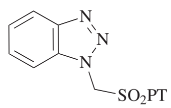
Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-7}				
ArCHO		**A**: KOH, *n*-Bu_4NBr, THF, rt, 16 h *or* **B**: P4-*t*-Bu, THF/HMPA, –78°, 16 h		58

Ar	Conditions		$(E)/(Z)^*$	Ar	Conditions		$(E)/(Z)^*$
3-furyl	**A**	(40)	71:29	4-$MeOC_6H_4$	**B**	(74)	98:2
2-thienyl	**A**	(55)	87:13	2,4-$(MeO)_2C_6H_3$	**A**	(35)	86:14
2-thienyl	**B**	(73)	90:10	3,4-$(MeO)_2C_6H_3$	**A**	(40)	86:14
4-pyridyl	**A**	(60)	75:25	3,5-$(MeO)_2C_6H_3$	**A**	(32)	85:15
4-$MeOC_6H_5$	**A**	(81)	75:25	3,4,5-$(MeO)_3C_6H_2$	**A**	(25)	96:4

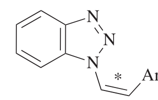
C_{5-9}

ArCHO  K_2CO_3, THF/DMF, 70°, 17 h  670

Ar		(E)/(Z)*
2-furyl	(75)	55:45
Ph	(72)	67:33
2-$O_2NC_6H_4$	(70)	90:10
3,4-$(MeO)_2C_6H_3$	(66)	75:25
4-$OHCC_6H_4$	(57)	90:10
	(64)	75:25
N-Boc-3-indolyl	(56)	60:40

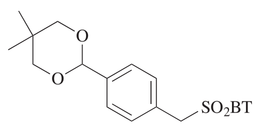
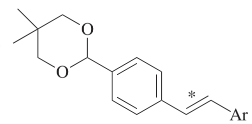


A:
LiHMDS, THF, 0°
or **B:**
DBU, THF, reflux

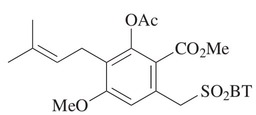
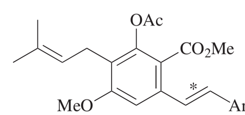
 112

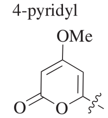
Ar	Conditions	Time (h)		(E)/(Z)*
2-thienyl	**A**	0.5	(90)	40:60
2-thienyl	**B**	5	(47)	25:75
2-FC_6H_4	**A**	0.5	(83)	41:59
2-FC_6H_4	**B**	5	(57)	11:89
2-$MeOC_6H_4$	**A**	0.5	(86)	93:7
2-$MeOC_6H_4$	**B**	5	(57)	15:85
4-$CF_3C_6H_4$	**A**	2	(62)	29:71
5-benzofuranyl	**A**	1	(65)	64:36
5-benzofuranyl	**B**	14	(60)	20:80
3-(1-tosyl-1*H*-indolyl)	**A**	3	(72)	71:29
5-(1-tosyl-1*H*-imidazolyl)	**A**	2	(71)	29:71

TABLE 15. SYNTHESIS OF 1,2-DIARYL/HETEROARYL ALKENES (*Continued*)

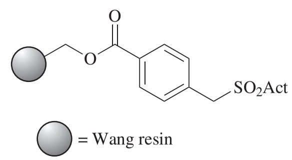
	Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-8}				
ArCHO		1. NaH (1.5 eq), DMF, 0°, 10 min 2. Aldehyde (1.3 eq), 0°; then rt, 4–5 h 3. I_2 (cat.), toluene, reflux, 12 h		727

Ar	$(E)^*$-isomer[a]
2-pyridyl	(66)
C_6F_5	(62)
2-ClC_6H_5	(73)
4-$O_2NC_6H_5$	(72)
2,3,4-$(MeO)_3C_6H_2$	(82)
2-MeC_6H_4	(77)
4-NCC_6H_4	(68)

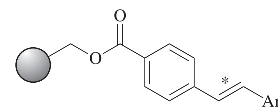
	Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-7}				
ArCHO		1. Sulfone (1 eq), NaH (1.5 eq), DMF, 0°, 10 min 2. Aldehyde (1.2 eq), to rt; then rt, 4–5 h	 $(E)^*$-isomer only	728

Ar		Ar		Ar	
2-pyridyl	(77)	Ph	(83)	3,4-$(OCH_2O)C_6H_3$	(65)
3-pyridyl	(65)	4-FC_6H_4	(62)	3,5-$(MeO)_2C_6H_3$	(77)
4-pyridyl	(80)	2,4-$F_2C_6H_3$	(76)	2,3,4-$(MeO)_3C_6H_2$	(83)
	(74)	3,4-$Cl_2C_6H_3$	(76)	3,4,5-$(MeO)_3C_6H_2$	(80)
		4-$MeOC_6H_4$	(74)		

C_{7-8}

ArCHO 

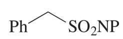
1. DBU, CH_2Cl_2, rt, 0.25 h
2. Aldehyde, rt, 24 h



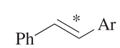
548

Ar	Act		$(E)/(Z)^*$
Ph	BT	(64)	100:0
4-ClC_6H_4	BT	(66)	—
2-BrC_6H_4	BT	(0)	—
4-BrC_6H_4	BT	(77)	—
4-BrC_6H_4	PT	(50)	—
4-$Me_2NC_6H_4$	BT	(40)	—
4-$O_2NC_6H_4$	BT	(50)	67:33
4-$MeOC_6H_4$	BT	(10)	—
4-$MeOC_6H_4$	PT	(15)	—
4-MeC_6H_4	BT	(32)	80:20

C_7

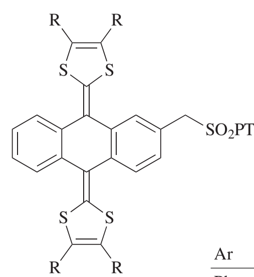
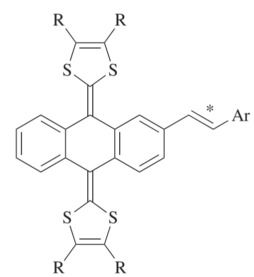
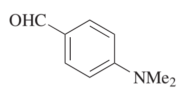
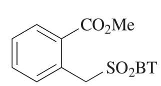
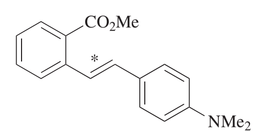
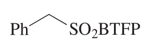
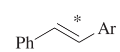
ArCHO 

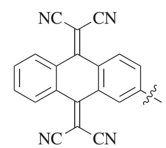
NaH, DMF, rt, 1 h



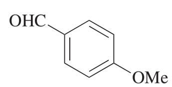
545

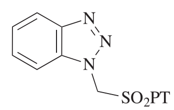
Ar		$(E)/(Z)^*$
Ph	(73)	63:37
2-ClC_6H_4	(78)	54:46
2-Cl-5-$O_2NC_6H_3$	(87)	81:19
4-BrC_6H_4	(47)	56:44
2-$O_2NC_6H_4$	(85)	50:50
3-$O_2NC_6H_4$	(94)	51:49
4-$O_2NC_6H_4$	(97)	70:30
4-$MeOC_6H_4$	(78)	53:47
3,4-$(MeO)_2C_6H_3$	(92)	61:39
3,5-$(MeO)_2C_6H_3$	(92)	65:35
2,4,6-$(MeO)_3C_6H_2$	(97)	>99:1
3,4,5-$(MeO)_3C_6H_2$	(92)	74:26

Aldehyde and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-21}				
ArCHO		1. NaHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h		729
C_7				
		K_2CO_3, DMF, 70°, 12 h	 (90), (*E*)*-isomer only	730
ArCHO		1. Base, THF, temp 2. Aldehyde, 16 h		58

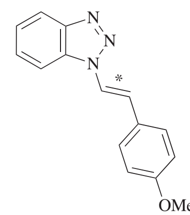
Ar	R	(*E*)*-isomer
Ph	H	(71)
	MeS	(94)

Ar	Base	Temp		(*E*)/(*Z*)*
4-$O_2NC_6H_4$	KOH, *n*-Bu_4NBr	rt	(12)	66:34
4-$O_2NC_6H_4$	P4-*t*-Bu	–78°	(67)	40:60
4-$MeOC_6H_4$	KOH, *n*-Bu_4NBr	rt	(52)	86:14
4-$MeOC_6H_4$	P4-*t*-Bu	0°	(81)	94:6



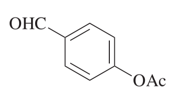


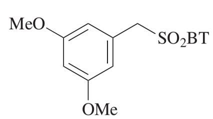
Base (x eq), additive, solvent



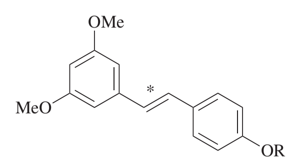
112

Base	x	Additive	Solvent	Temp (°)	Time (h)		$(E)/(Z)^*$
DBU	2.0	none	THF	66	2	(47)	26:74
KHMDS	2.4	none	THF	0	0.5	(66)	60:40
NaHMDS	2.4	none	THF	0	0.5	(45)	60:40
LiHMDS	2.4	none	THF	0	4	(76)	79:21
LiHMDS	2.4	none	THF	66	2	(81)	70:30
LiHMDS	2.4	none	DMF/DMPU	–50	20	(—)	57:43
LiHMDS	3.0	$MgBr_2{\bullet}Et_2O$	THF	rt	5	(30)	77:23
LiHMDS	4.0	none	THF	–78	32	(—)	28:72





1. Sulfone (1 eq),
LiHMDS (1.2 eq),
THF, –78°, 0.5 h
2. Aldehyde (1.25 eq), –78°, 3 h

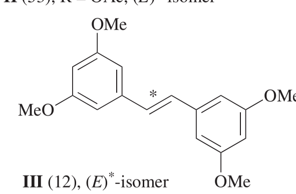


I (19), R = H
$(E)^*$-isomer

731

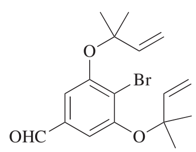
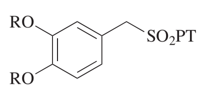
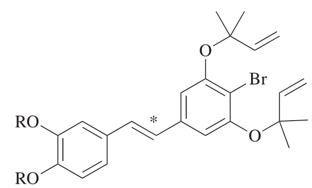
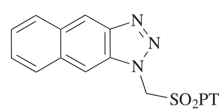
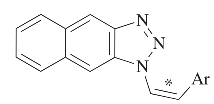
\+ **II** (53), R = OAc, $(E)^*$-isomer

\+



III (12), $(E)^*$-isomer

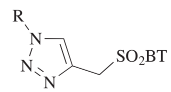
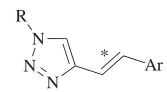
TABLE 15. SYNTHESIS OF 1,2-DIARYL/HETEROARYL ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
 	1. KHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78° to rt, 3 h		732
C_{7-8}			
ArCHO 	**A:** LiHMDS, solvent, 0° *or* **B:** DBU, THF, reflux		112

R		$(E)/(Z)^*$
Boc	(80)	100:0
TBS	(95)	67:33

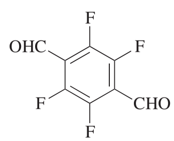
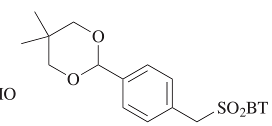
Ar	Conditions	Solvent	Time (h)		$(E)/(Z)^*$
3,4,5-$(MeO)_3C_6H_2$	**A**	THF	0.33	(80)	65:35
3,4,5-$(MeO)_3C_6H_2$	**A**	DMF	0.67	(93)	37:63
3,4,5-$(MeO)_3C_6H_2$	**B**	THF	4	(52)	25:75
4-$CF_3C_6H_4$	**A**	THF	0.33	(56)	44:56
4-$CF_3C_6H_4$	**A**	DMF	0.67	(62)	41:59

C_{7-10}

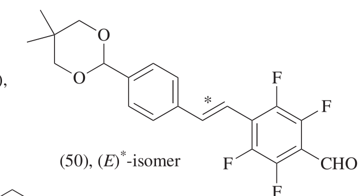
ArCHO  LiHMDS, DMF/DMPU, –78°  643

Ar	R		$(E)/(Z)^*$
4-$O_2NC_6H_4$	Ph$(CH_2)_3$	(44)	83:17
4-$MeOC_6H_4$	Ph$(CH_2)_3$	(65)	72:28
2,4,6-$Me_3C_6H_2$	4-$MeOC_6H_4$	(73)	33:67
2,4,6-$Me_3C_6H_2$	Ph$(CH_2)_3$	(85)	15:85

C_8

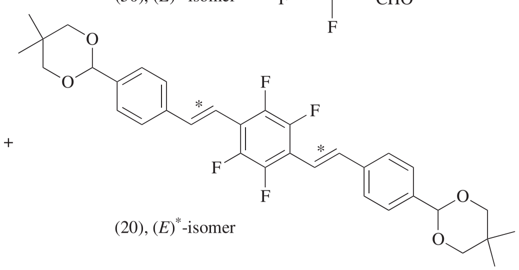
1. Sulfone (1 eq), NaH (1.37 eq), DMF, 0°, 10 min
2. Aldehyde (0.91 eq), 0°; then rt, 1 h



(50), $(E)^*$-isomer

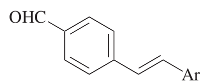
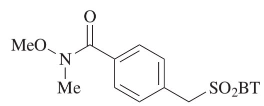
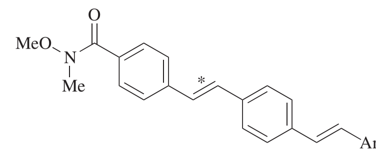
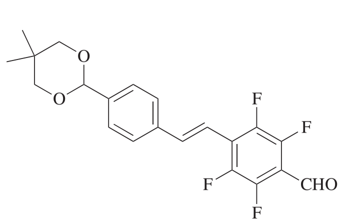
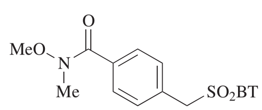
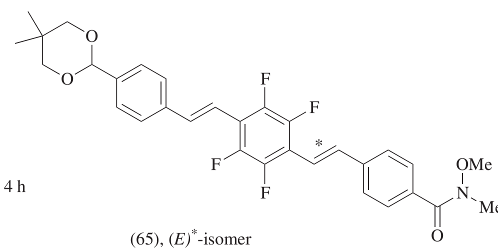
727

+



(20), $(E)^*$-isomer

TABLE 15. SYNTHESIS OF 1,2-DIARYL/HETEROARYL ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14-16}			
 	1. NaH (1.5 eq), sulfone (1 eq), DMF, 0°, 10 min 2. Aldehyde (1.5 eq), 0°; then rt, 4–5 h 3. I_2 (cat.), toluene, reflux, 12 h	 Ar / $(E)^*$-isomer[a] 2-pyridyl (60) C_6F_5 (82) $2\text{-}ClC_6H_4$ (70) $4\text{-}O_2NC_6H_4$ (65) $2,3,4\text{-}(MeO)_3C_6H_2$ (76) $2\text{-}MeC_6H_4$ (74) $4\text{-}NCC_6H_4$ (80)	727
C_{16}			
 	1. Sulfone (1 eq), NaH (1.37 eq), DMF, 10 min 2. Aldehyde (0.91 eq), rt, 4 h	 (65), $(E)^*$-isomer	727

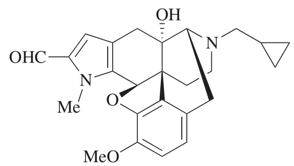
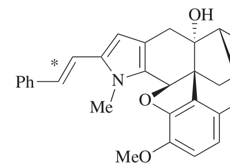
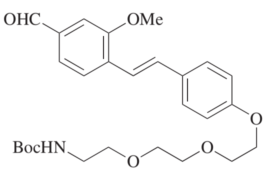
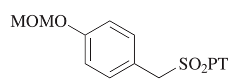
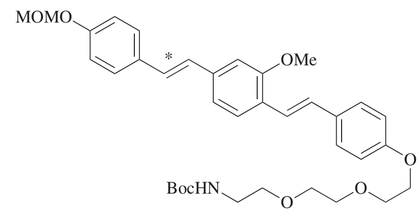
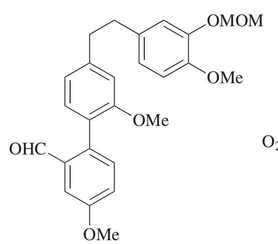
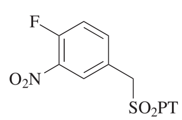
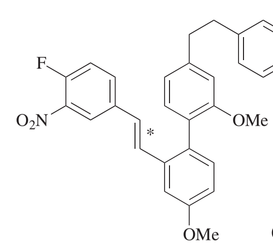
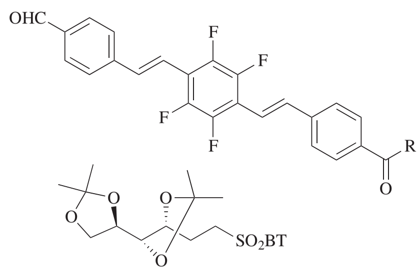
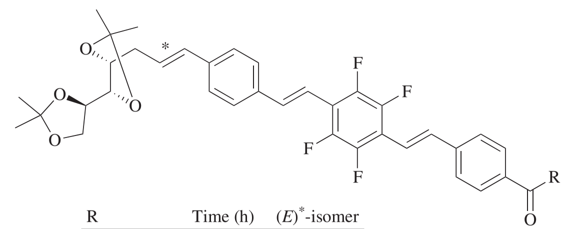
C_{19}				
		KHMDS, THF, –78° to rt	 (86–91), (*E*)/(*Z*)* = —	723
C_{21}				
		KHMDS, DMF/DMPU, –65° to rt, 12 h	 (69), (*E*)*-isomer	733
		1. LiHMDS, THF, –78 to 0°, 0.5 h 2. Aldehyde, THF, –78 to 0°, 3 h	 (89), (*E*)/(*Z*)* = 94:6	734

TABLE 15. SYNTHESIS OF 1,2-DIARYL/HETEROARYL ALKENES (*Continued*)

Aldehyde and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24-28}			
	1. Sulfone (1 eq), NaH (1.5 eq), DMF, 0°, 10 min 2. Aldehyde (0.92 eq), rt, time		727

R	Time (h)	$(E)^*$-isomer
(MeO)MeN	4	(93)
Bu	2	(64)

[a] The (*E*)/(*Z*) ratios in the originally formed mixtures were not reported.

TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES

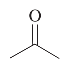
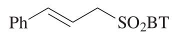
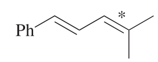
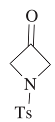
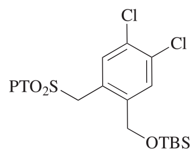
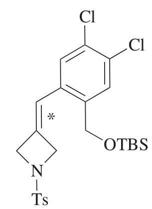
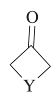
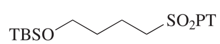
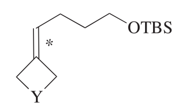
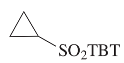
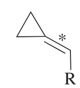
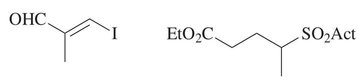
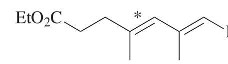
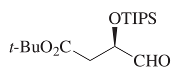
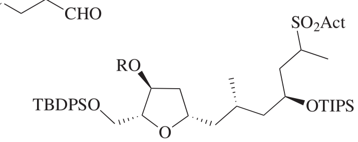
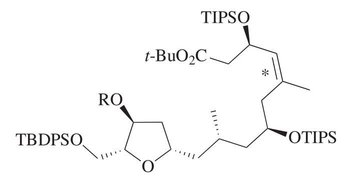
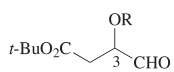
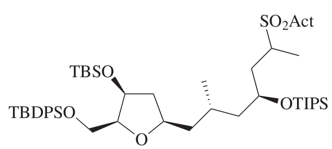
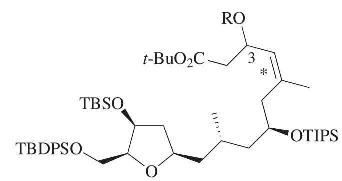
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		1. LDA, THF, –78°, 1 h 2. Ketone, –78°, 3 h; then rt	 (51)	3
		NaHMDS, THF, –78° to rt	 (62)	735
C_{3-16}				
		NaHMDS, THF, –78°; then rt	 Y t-BuO_2CN (74) BzN (45) TsN (>52) Ph_2C (51)	735
C_{4-13}				
RCHO		Cs_2CO_3, THF/DMF, 70°, 40 h	 R $TBSO(CH_2)_3$ (43) 2-Br-4,5-$(MeO)_2C_6H_2$ (59) 3-$BnOC_6H_4$ (66) 4-$BnOC_6H_4$ (56) 2,5-$(MeO)_2C_6H_3$ (64) 3,4-$(MeO)_2C_6H_3$ (62) 2-(CH_2=$CHCH_2O$)-3-$MeOC_6H_3$ (80) 4-$MeO_2CC_6H_4$ (60) 4-PhC_6H_4 (76)	87

TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	KHMDS, DME, –60°, 3 h		736
 	1. Sulfone (1 eq), LDA (2 eq), HMPA (2 eq), THF, 4 Å MS, rt, 1 min 2. Aldehyde (2 eq), rt, 2 h		737
 	1. Sulfone (1 eq), LDA (2 eq), additive (2 eq), 4 Å MS, THF, rt, 1 min 2. Aldehyde (2 eq), rt, 2 h		738

Ref. 736:

Act		$(E)/(Z)^*$
PT	(48)	73:27
TBT	(60)	63:37

Ref. 737:

Act	R		$(E)/(Z)^*$
TBT	TMS	(42)	3:97
PT	TBS	(38)	30:70

Ref. 738:

R	C-3	Act	Additive		$(E)/(Z)^*$
MOM	(*R*)	TBT	HMPA	(59)	12:88
Ac	(*S*)	TBT	HMPA	(20)	13:87
t-Bu	(*R*)	PT	none	(30)	50:50
t-Bu	(*R*)	PT	HMPA	(42)	33:67
t-Bu	(*R*)	TBT	HMPA	(47)	3:97
TIPS	(*R*)	PT	none	(42)	35:65
TIPS	(*R*)	PT	HMPA	(45)	31:69
TIPS	(*R*)	TBT	HMPA	(61)	3:97

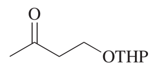
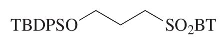
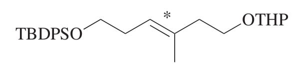
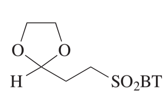
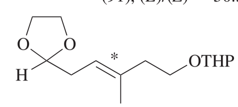
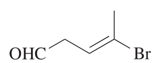
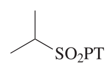
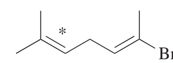
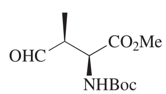
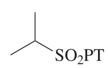
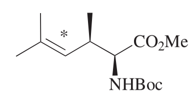
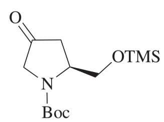
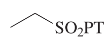
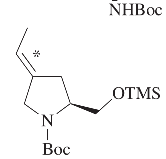
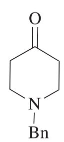
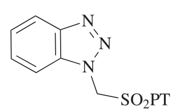
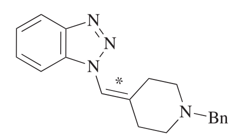
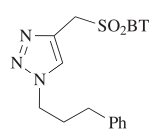
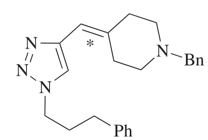
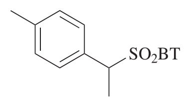
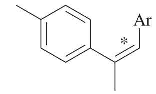
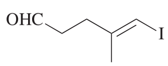
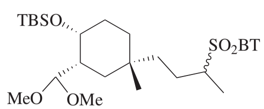
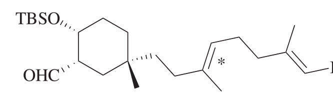
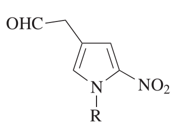
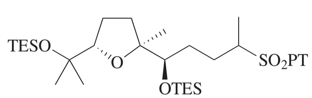
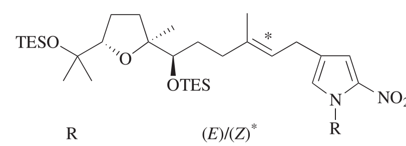
			LiHMDS, THF, –78°, 1.5 h		(91), $(E)/(Z)^{*}$ = 50:50	739
			LiHMDS, THF, –78°, 2 h		(100), $(E)/(Z)^{*}$ = 67:33	739
C_5			1. LiHMDS, THF, –78°, 35 min 2. Aldehyde, –78° to rt, 16 h		(70)	740
			Sulfone (2.5 eq), LiHMDS (2.3 eq), THF, –78°, 0.5 h		(59)	741
			1. LDA, THF, –78°, 10 min 2. Ketone, –78°, 30 min		(50), $(E)/(Z)^{*}$ = 67:33	742
			LiHMDS, THF, 0°, 3 h		(77)	112
			LiHMDS, DMF/DMPU, –78°		(59)	643

TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

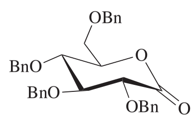
Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-8}			
ArCHO 	LDA, THF, –78°; then rt, 15 h		93
C_6			
 	1. NaHMDS, solvent, –78° 2. Aldehyde, –78°, 1 h; then rt 3. AcOH/THF/H_2O, 45°, 8 h		743
 	1. Sulfone (1 eq), NaHMDS (1.15 eq), THF, –78°, 0.25 h 2. Aldehyde (1 eq), –78° to rt; then rt, overnight		90

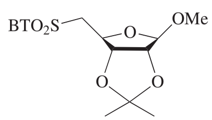
Ar		E)/(Z)*
3-furyl	(97)	5:95
2-thienyl	(81)	5:95
3-thienyl	(68)	5:95
Ph	(75)	5:95
4-ClC_6H_4	(82)	5:95
4-$Me_2NC_6H_4$	(85)	10:90

Ar		E)/(Z)*
4-$O_2NC_6H_4$	(50)	7:93
4-$MeOC_6H_4$	(90)	5:95
4-$CF_3C_6H_4$	(64)	5:95
4-NCC_6H_4	(38)	8:92
4-$MeO_2CC_6H_4$	(67)	*5:95*

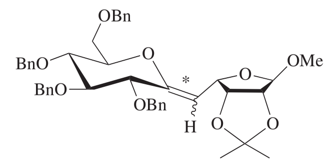
Solvent		(E)/(Z)*
DME	(72)	57:43
DMF	(—)	33:67

R		(E)/(Z)*
$BnOCH_2$	(42)	53:47
$BzOCH_2$	(30)	53:47



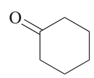


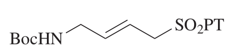
Lactone (2.1 eq), sulfone (1 eq), LiHMDS (20 eq), THF, –75°, 10 min; then –75°, overnight



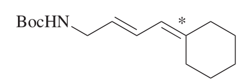
(34), isomeric ratio* = 74:26[a]

546



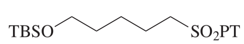


1. KHMDS (2.1 eq), 18-crown-6, THF, –78°, 0.5 h
2. Sulfone metallate added to ketone, –78°; then rt

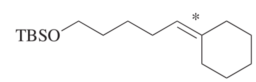


(76)

506



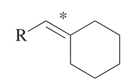
NaHMDS, THF, –78°, 0.5 h



(74)

744

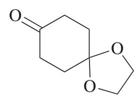
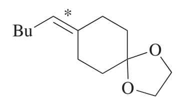
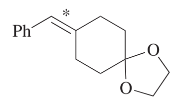
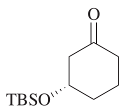
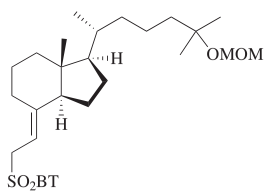
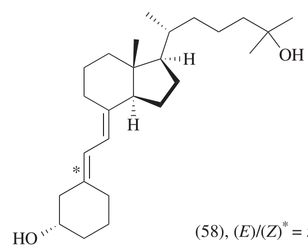
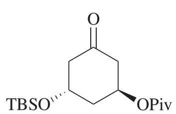
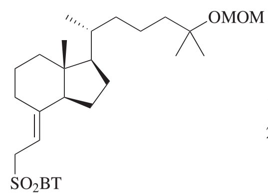
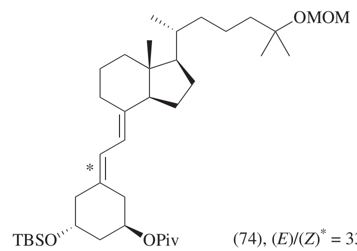
A:
1. LDA, THF, –78°, 1 h
2. Ketone, –78°, 3 h; then rt
or **B**:
LDA, THF, –78°, 3 h; then rt, 1 h

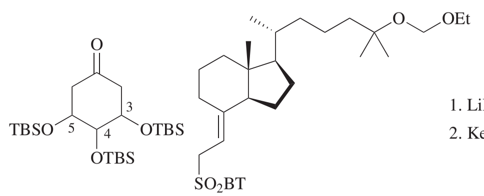


3

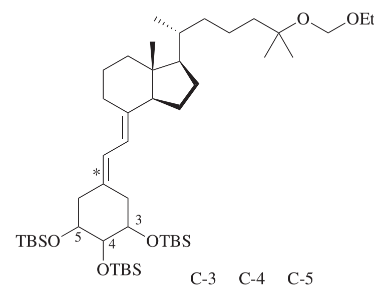
R	Act	Conditions	
Me_2C=CH	BT	**A**	(56)
Me_2C=CH	BT	**B**	(68)
Me_2C=CH	PYR	**A**[b]	(43)
Ph	BT	**A**	(61)
Ph	PYM	**A**	(81)
(*E*)-PhCH=CH	BT	**A**	(40)
(*E*)-PhCH=CH	PYM	**A**	(50)

TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		Sulfone (*x* eq), P4-*t*-Bu (*y* eq), THF, 0° to rt, 12 h	 *x* / *y*: 1.0 / 1.2 (26); 2.0 / 2.4 (90)	95
		Sulfone (2 eq), ketone (1 eq), P4-*t*-Bu (2.4 eq), THF, 0° to rt, 12 h	 (90)	95
		1. LiHMDS, THF, –78°, 65 min 2. Ketone, –78°, 3 h 3. CSA, MeOH, rt, 20 h	 (58), (*E*)/(*Z*)* = 50:50	745
		1. LiHMDS, THF, –78, 0.5 h 2. Ketone, –78 to 0°, 1 h	 (74), (*E*)/(*Z*)* = 33:67	746

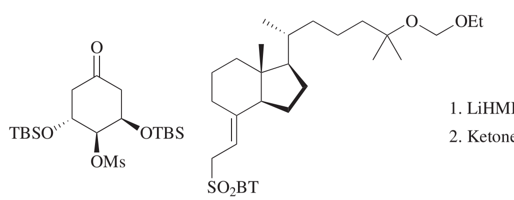


1. LiHMDS, THF, –50, 2 h
2. Ketone, –50°, 5 h

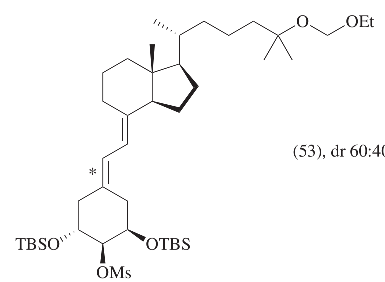


C-3	C-4	C-5		dr
(*R*)	—	(*R*)	(68)	76:24
(*S*)	(*R*)	(*R*)	(49)	50:50
(*R*)	(*S*)	(*S*)	(—)	70:30

747



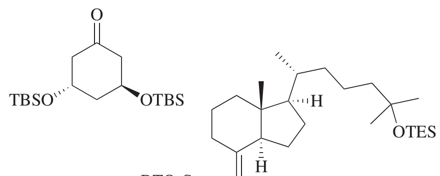
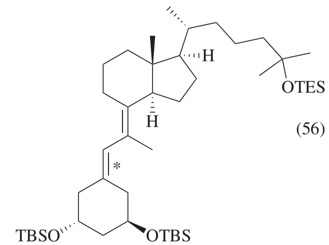
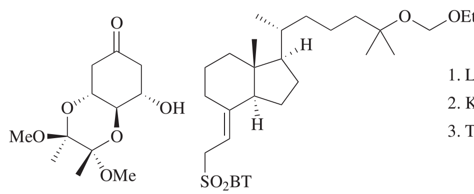
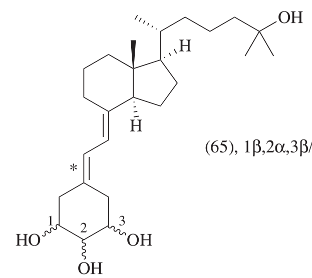
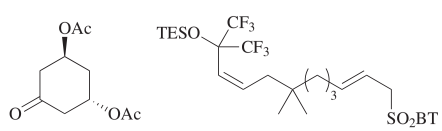
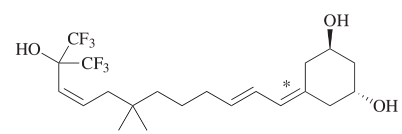
1. LiHMDS, THF, –50, 2 h
2. Ketone, –50°, 5 h



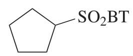
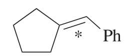
(53), dr 60:40

747

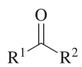
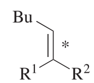
TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
 **I**	1. Sulfone (1.1 eq), LiHMDS (1.1 eq), THF, –78°, 1 h 2. Ketone (1 eq), –78°, 2 h; then to –30°; then –30°, 0.5 h	 (56) + **I** (43)	748
	1. LiHMDS, THF, –50°, 2 h 2. Ketone, –50°, 5 h 3. TFA, H_2O, 30 min	 (65), 1β,2α,3β/1α,2β,3α = 30:70	747
	1. LiHMDS, THF, –78°, 1.3 h 2. Ketone, –78°, 4 h; then rt, 18 h 3. K_2CO_3, MeOH/H_2O, 22 h	 (85)	749

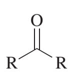
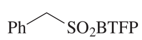
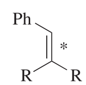
C_7

PhCHO  LDA, THF, –78°, 3 h; then rt, 1h  (38) 3

C_{7-13}

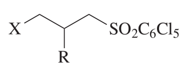
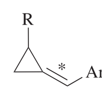
  Sulfone (*x* eq), P4-*t*-Bu (*y* eq), THF, 12 h  95

R^1	R^2	*x*	*y*	Temp		(*E*)/(*Z*)*
c-C_3H_5	*c*-C_3H_5	2.0	2.4	0° to rt	(35)	—
Ph	Ph	2.0	2.4	0° to rt	(40)	—
Ph	Ph	3.0	3.6	0° to rt	(84)	—
4-ClC_6H_4	Ph	2.0	2.4	0° to rt	(75)	55:45
4-ClC_6H_4	Ph	2.0	2.4	rt to reflux	(77)	40:60
4-ClC_6H_4	4-ClC_6H_4	1.0	2.4	0° to rt	(97)	—
4-ClC_6H_4	4-ClC_6H_4	2.0	1.2	0° to rt	(40)	—

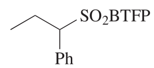
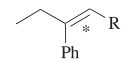
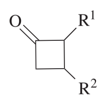
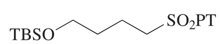
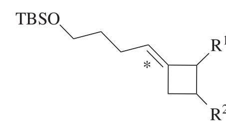
  Sulfone (2 eq), ketone (1 eq), P4-*t*-Bu (2.4 eq), THF, 0° to rt, 12 h  95

R	
c-C_3H_5	(50)
4-ClC_6H_4	(<5)

C_{7-8}

ArCHO  1. *t*-BuOK, DMF, –30° 2. Aldehyde, *t*-BuOK, –35 to 60°  88

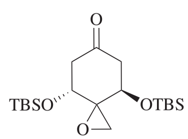
Ar	R	X		(*E*)/(*Z*)*
Ph	H	Br	(54)	—
4-ClC_6H_4	H	Br	(55)	—
4-$Me_2NC_6H_4$	H	Br	(52)	—
4-$MeOC_6H_4$	H	Br	(57)	—
4-$MeOC_6H_4$	Me	Cl	(57)	23:77
4-MeC_6H_4	H	Br	(63)	—
4-MeC_6H_4	Me	Cl	(47)	23:77

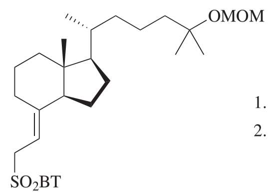
Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-11}			
RCHO 	Aldehyde (1 eq), sulfone (2 eq), P4-*t*-Bu (2.4 eq), THF, 12 h		95
C_{7-16}			
 	**A**: NaHMDS, THF, –78° to rt *or* **B**: LiHMDS, toluene, –78° to rt		750

R	Temp		(*E*)/(*Z*)*
Ph	–78° to rt	(77)	30:70
Ph	–78°	(50)	15:85
(*E*)-PhCH=CH	–78° to rt	(63)	7:93
6-MeO-2-naphthyl	–78° to rt	(50)	35:65

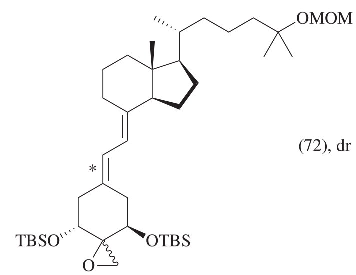
R^1	R^2	Conditions		(*E*)/(*Z*)*
Pr(Ts)N$(CH_2)_3$	H	**A**	(50)	60:40
Ph	H	**B**	(66)	50:50
2,4-$Cl_2C_6H_3$	H	**B**	(75)	50:50
2-$BnOC_6H_4$	H	**A**	(39)	70:30
4-$BnOC_6H_4$	H	**A**	(32)	56:44
n-C_7H_{15}	H	**A**	(51)	70:30
4-$MeO_2CC_6H_4$	H	**B**	(37)	50:50
(*R*)-Ph	(*R*)-Ph	**B**	(49)	45:55

C_7



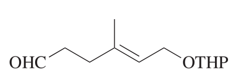


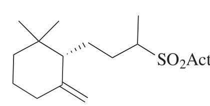
1. LiHMDS, THF, –78, 0.5 h
2. Ketone, –78 to 0°, 1 h



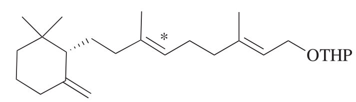
(72), dr 3:2

746





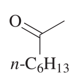
1. Sulfone (1.0 eq), KHMDS (1.04 eq), THF, –30°, 1 h
2. Aldehyde (1.12 eq), temp, 3 h; then to rt

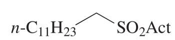


Act	Temp (°)		$(E)/(Z)^*$
PT	–90	(46)	83:17
BT	–78	(23)	48:52

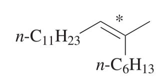
751

C_8





LDA, THF, –78°, 1 h; then rt, 3 h



Act		$(E)/(Z)^*$
BT	(60)	33:67
IM	(4)	31:69
TZ	(15)	22:78
IQ	(56)	47:53

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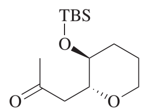
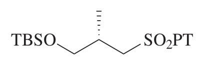
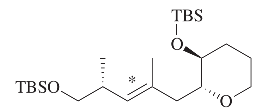
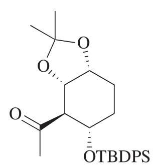
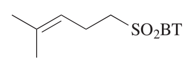
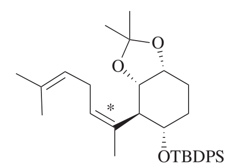
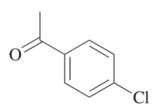
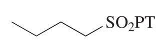
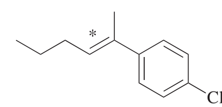
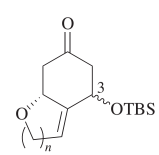
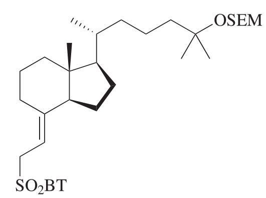
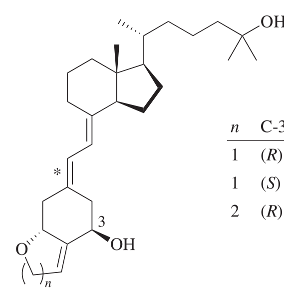
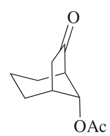
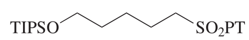
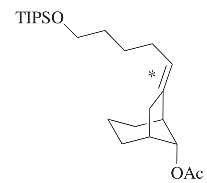
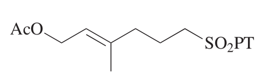
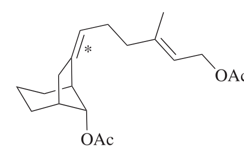
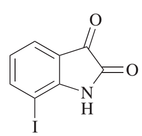
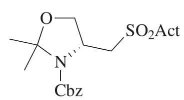
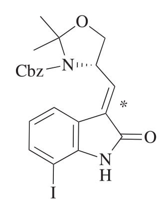
TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

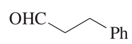
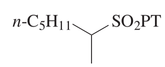
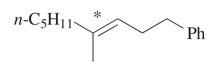
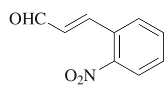
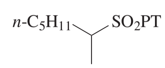
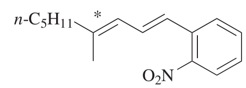
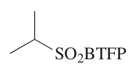
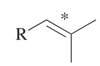
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		1. LDA, THF, –78° 2. Ketone, additive, THF, –78 to 0°, 70 min	 Additive / (E)/(Z)* none (38) 50:50 $CeCl_3$ (80) 62:38	89
		LiHMDS, THF, –78°, 1.5 h; then rt, 10 min	 (87), (*E*)/(*Z*)* = 14:86	752
		1. LiHMDS, 12-crown-4 (2 eq), THF, 0.5 min 2. Ketone, –78°, 0.5 h	 (87), (*E*)/(*Z*)* = 72:28	26
C_{8-9}				
		1. LiHMDS, THF, –78°, 0.33 h 2. Ketone, –78°, 1.5 h; then –10°, 1.5 h 3. CSA, MeOH	 *n* C-3 (*E*)/(*Z*)* 1 (*R*) (23) 74:26 1 (*S*) (>26) — 2 (*R*) (44) —	753 754 755

C_8

		LiHMDS, THF, –10°		(87), $(E)/(Z)^* = 50:50$	756
		Ketone (1.0 eq), sulfone (2.0 eq), LiHMDS (2.0 eq), Et_2O, –10°, 0.5 h; then to rt		(64), $(E)/(Z)^* = 42:58$	757
		Barbier conditions. See table.		(79)	758, 759

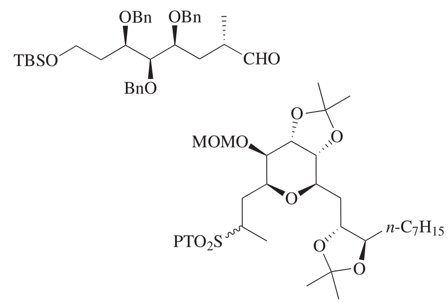
Act	Base	Solvent(s)	Temp (°)	$(E)/(Z)^*$
PT	NaHMDS	THF	–78	50:50
PT	LiHMDS	DMF/DMPU	–45	66:34
BT	NaHMDS	THF	–78	50:50
BT	LiHMDS	DMF/DMPU	–78	71:29
BT	LiHMDS	DMF/DMPU	–45	75:25
BT	LiHMDS	DMF/DMPU	0	83:17

TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

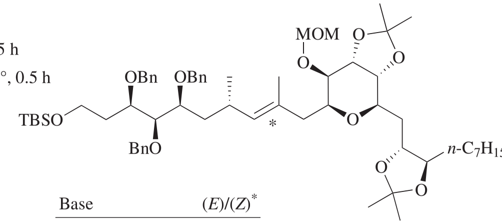
Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_9					
		1. LiHMDS, 12-crown-4 (2 eq), THF, 0.5 min 2. Aldehyde, –78°, 0.5 h		(97), (*E*)/(*Z*)* = 55:45	26
		1. LiHMDS, 12-crown-4 (2 eq), THF, 0.5 min 2. Aldehyde, –78°, 0.5 h		(75), (*E*)/(*Z*)* = 55:45	26
C_{9-11}					
RCHO		Aldehyde (1 eq), sulfone (2 eq), base (2 eq), THF, rt, 12 h			95

R	Base	
$Ph(CH_2)_2$	P4-*t*-Bu	(52)
(*E*)-PhCH=CH	P4-*t*-Bu	(89)
n-C_9H_{19}	P4-*t*-Bu	(67)
6-MeO-2-naphthyl	KOH, Bu_4NBr	(71)
6-MeO-2-naphthyl	KHMDS	(<5)
6-MeO-2-naphthyl	BEMP	(<5)
6-MeO-2-naphthyl	P4-*t*-Bu	(95)

C_9

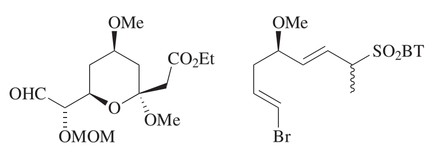


1. Base, THF, –78°, 0.25 h
2. Aldehyde, –78 to –40°, 0.5 h

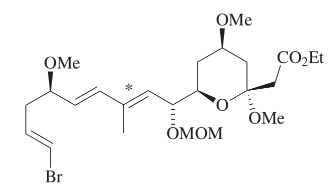


Base		$(E)/(Z)^*$
LDA	(61)	60:40
LiHMDS	(43)	50:50
NaHMDS	(<5)	—
KHMDS	(<5)	—

760



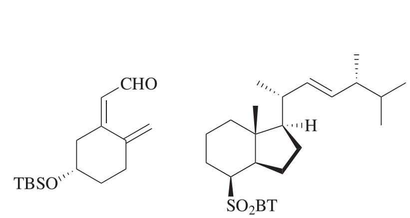
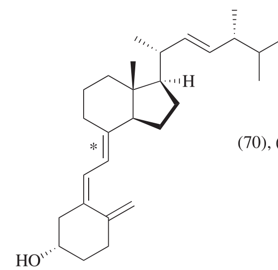
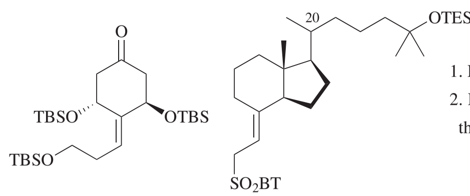
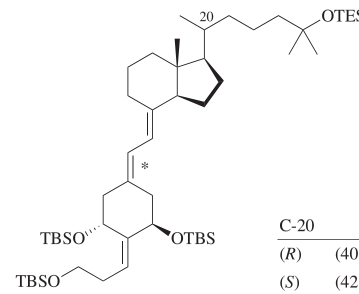
NaHMDS, THF, –78°

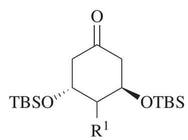


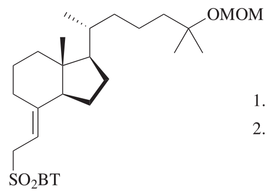
(70), $(E)/(Z)^*$ = 50:50

92

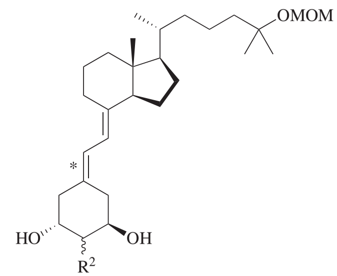
TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	1. NaHMDS, Et_2O, –78°, 1 h 2. Aldehyde, –100° to rt, 12 h 3. Bu_4NF, THF, rt, 12 h	 (70), (*E*)/(*Z*)* = 72:28	39
	1. LiHMDS, THF, –78, 1 h 2. Ketone, –78°, 2 h; then –50°, 50 min	 C-20 / (*E*)/(*Z*)* (*R*) (40) 57:43 (*S*) (42) 57:43	761





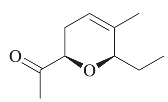
1. LiHMDS, THF, –78 to 0°
2. CSA, MeOH, 0°; rt, 19 h

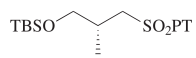


R^1	R^2		dr
CH_2=CHCH$_2$	CH_2=CHCH$_2$	(47)	1:1
Pr	Pr	(51)	1:1
TBSO(CH_2)$_3$	HO(CH_2)$_3$	(62)	1:1

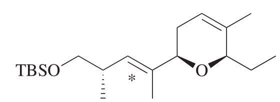
762, 763

C_{10}



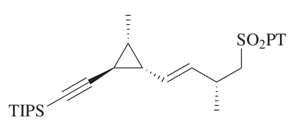


LiHMDS, CH_2Cl_2

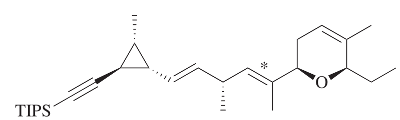


(—), (*E*)/(*Z*)* = 75:25

289

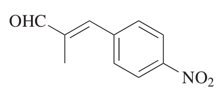


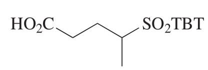
LiHMDS



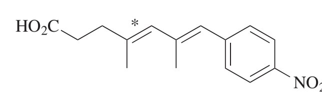
(—), (*E*)/(*Z*)* = 75:25

764





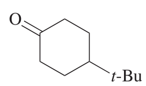
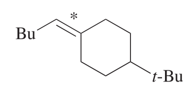
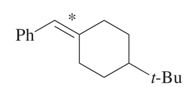
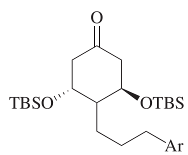
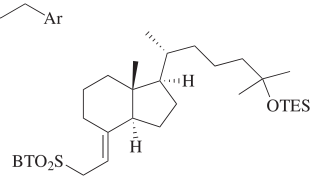
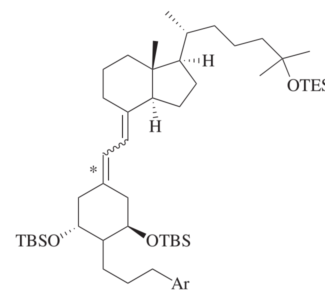
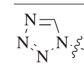
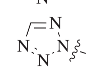
KHMDS, DME, –60°



(25), (*E*)/(*Z*)* = 62:38

765

TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{10}					
		Sulfone (*x* eq), P4-*t*-Bu (*y* eq), THF, 0° to rt, 12 h		*x* *y* 1.0 1.2 (16) 2.0 2.4 (60)	95
		Ketone (1 eq), sulfone (2 eq), P4-*t*-Bu (2.4 eq), THF, 0° to rt, 12 h		(25)	95
		1. Sulfone (2.0 eq), LiHMDS (1.0 eq), THF, –78°, 0.5 h 2. Ketone (1.0 eq), –78°, 1 h; then to rt, 2 h	 Ar / dr  (98) crude 58:42  (51)[c] 60:40		766

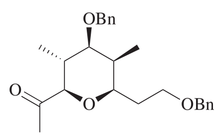
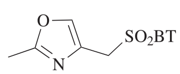
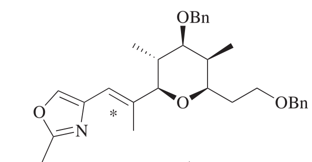
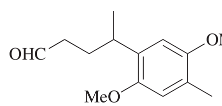
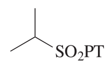
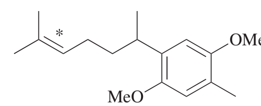
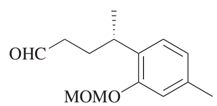
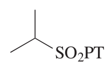
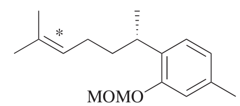
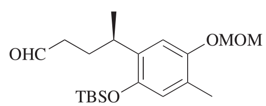
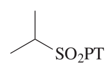
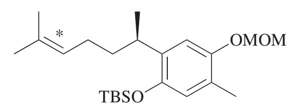
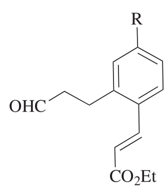
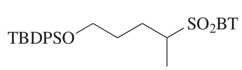
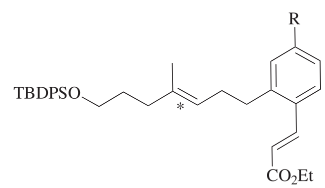
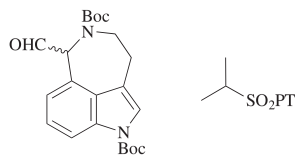
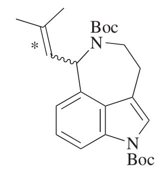
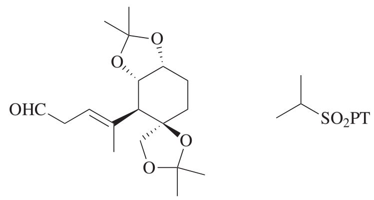
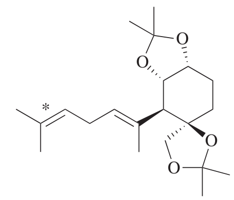
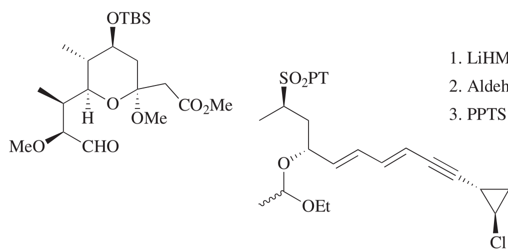
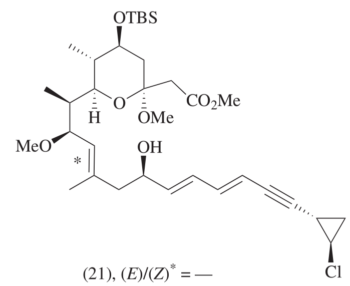
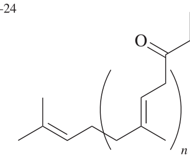
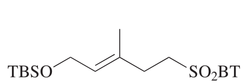
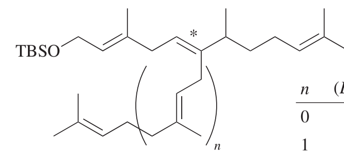
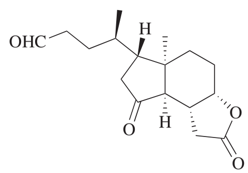
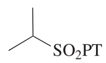
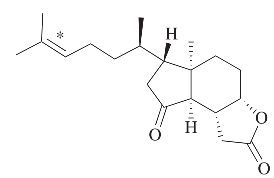
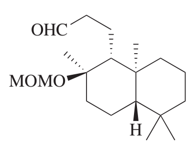
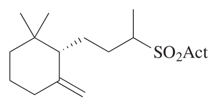
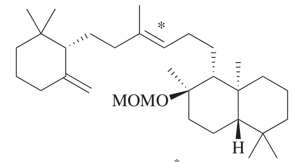
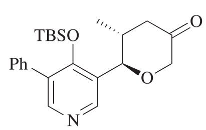
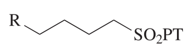
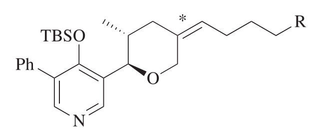
C_{11}					
		NaHMDS, THF, –78° to rt, 4 h	 (70), $(E)/(Z)^{*}$ = 90:10		767
C_{12}					
		1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, THF, –78°, 3 h; then rt		(88)	166
		1. LiHMDS, THF, –78° 2. Aldehyde; then rt		(88)	768
		1. Sulfone (2.5 eq), LiHMDS (2.5 eq), THF, –78°, 0.5 h 2. Aldehyde (1.0 eq), –78°, 10 min; then to rt, 40 min		(99), 2 steps	769, 770
		NaHMDS, THF, –78° to rt, 12 h	 R = H, OMe (38–55), $(E)/(Z)^{*}$ = 60:40		771

TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	1. Sulfone (2.4 eq), LiHMDS (2.4 eq), THF, –78°, 0.25 h 2. Aldehyde (1.0 eq), –78°, 4 h	 Config. / er (*R*) (75) 95.5:4.4 (*S*) (80) 95.0:5.0	772
	1. LiHMDS, THF, –78°, 0.5 h 2. Aldehyde, –78°, 2 h; then rt, 3 h	 (>42)	773
	1. LiHMDS, THF, –78° 2. Aldehyde, –78° to rt 3. PPTS, MeOH	 (21), (*E*)/(*Z*)* = —	774

Reactant		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14-24} 		LiHMDS, THF, –65°, 3 h; then rt, 16 h		775
C_{17} 		1. LiHMDS, THF, –78°, 1 h 2. Aldehyde, 50 min	 (68)	776
		1. LiHMDS, THF, –78° 0.33–0.5 h 2. Aldehyde, 0°, 0.5–1 h		777
		1. LiHMDS, DME, –78°, 0.25 h 2. Ketone, –78°, 0.5 h		778, 779

Product table for ref. 775:

n	$(E)^*$-isomer
0	(32)
1	(24)
2	(27)

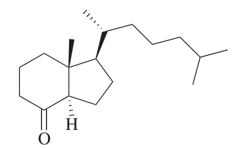
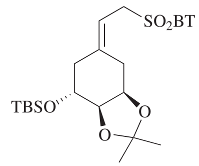
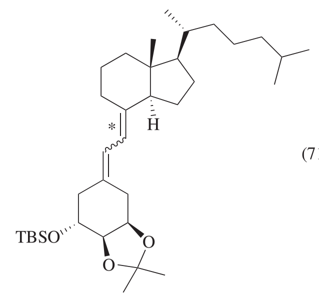
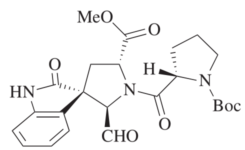
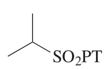
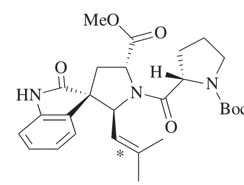
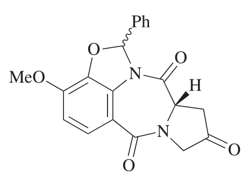
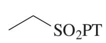
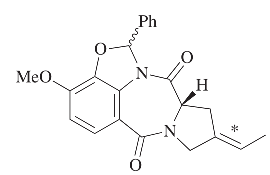
Product table for ref. 777:

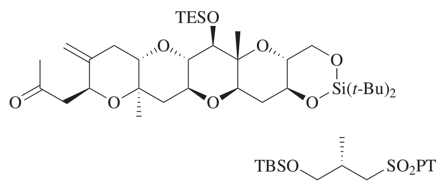
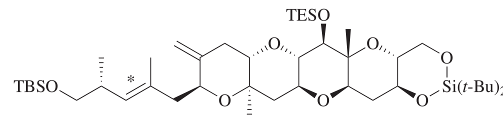
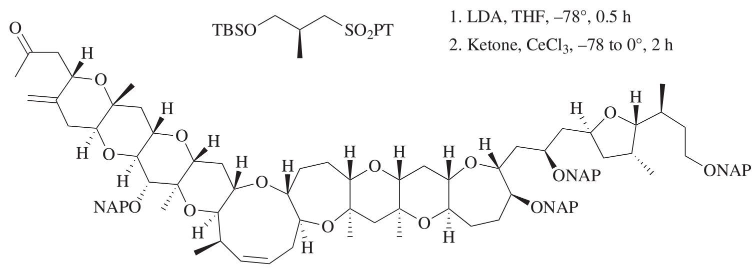
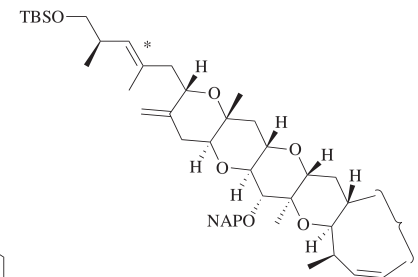
Act		$(E)/(Z)^*$
BT	(52)	50:50
PT	(89)	50:50

Product table for refs. 778, 779:

R		$(E)/(Z)^*$
Me	(—)	—
(*R*)-EtMeCHCH_2	(69)	50:50
(*S*)-EtMeCHCH_2	(69)	50:50
n-$C_{10}H_{21}$	(—)	—

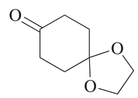
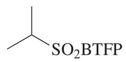
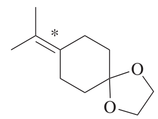
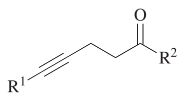
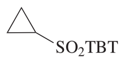
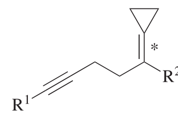
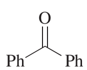
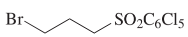
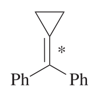
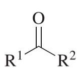
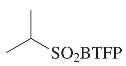
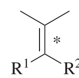
TABLE 16. SYNTHESIS OF TRISUBSTITUTED ALKENES (*Continued*)

Carbonyl Compound and Sulfone		Conditions	Product(s) and Yield(s) (%)		Refs.
C_{18}					
		"Basic conditions"		(71), (*E*)/(*Z*)* = —	780
		1. LiHMDS (2.3 eq), THF, –78°, 0.5 h 2. Aldehyde, –78°, 3 h; then rt, 8 h		(78)	86
C_{19}					
		1. Sulfone (2 eq), NaHMDS (2 eq), THF, –78°, 0.25 h 2. Ketone, 78°, 35 min		(67), (*E*)/(*Z*)* = 83:17	781

C_{21}		1. LDA, THF, –78° 2. Ketone, $CeCl_3$, THF, –78 to 0°, 2 h	 (76), (*E*)/(*Z*)* = 76:24	89
C_{55}		1. LDA, THF, –78°, 0.5 h 2. Ketone, $CeCl_3$, –78 to 0°, 2 h	 (74), (*E*)/(*Z*)* = 72:28	91

[a] This is the ratio reported in the Experimental Section. The absolute configurations were not determined. Acetone was unreactive in this reaction.
[b] The lithiation was conducted with *n*-BuLi
[c] The yield is for a second-step product.

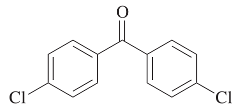
TABLE 17. SYNTHESIS OF TETRASUBSTITUTED ALKENES

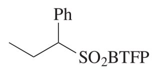
Ketone and Sulfone		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		Sulfone (2 eq), ketone (1 eq), P4-*t*-Bu (2 eq), THF, rt to reflux, 12 h	 (35)	95
C_{11-17}				
		Ketone (1 eq), sulfone (1.2 eq), KHMDS (1.3 eq), THF, –78°; then to rt; then rt, overnight		782
C_{13}				
		1. *t*-BuOK, DMF, –30° 2. Ketone, *t*-BuOK, –35 to 60°	 (60)	88
		Sulfone (2 eq), ketone (1 eq), base (≥2 eq), THF, 12 h		95

R^1	R^2	
H	Ph	(30)
Ph	Me	(65)
Ph	CH_2=CH	(71)
Ph	*c*-C_3H_5	(70)
Ph	allyl	(77)
Ph	Ph	(96)
Ph	4-FC_6H_4	(80)
Ph	4-ClC_6H_4	(83)
Ph	4-$MeOC_6H_4$	(68)

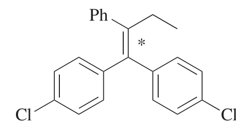
R^1	R^2	Base	Temp	
Ph	Ph	P4-*t*-Bu	rt to reflux	(40)
4-ClC_6H_4	Ph	P4-*t*-Bu	rt to reflux	(70)
4-ClC_6H_4	4-ClC_6H_4	KOH	rt	(<5)
4-ClC_6H_4	4-ClC_6H_4	P4-*t*-Bu	0° to rt	(30)
4-ClC_6H_4	4-ClC_6H_4	P4-*t*-Bu	rt to reflux	(71)
4-$MeOC_6H_4$	4-$MeOC_6H_4$	P4-*t*-Bu	rt to reflux	(10)

C_{14-19}

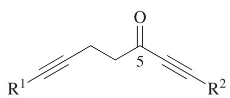


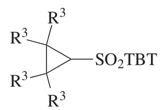


Sulfone (2 eq), ketone (1 eq), P4-*t*-Bu (2.4 eq), THF, rt to reflux, 12 h

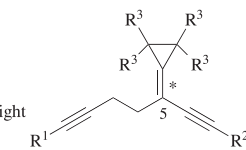


(<5) 95





Ketone (1 eq), sulfone (1.2 eq), KHMDS (1.3 eq), THF, –78°; then to rt; then rt, overnight

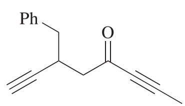


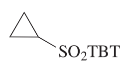
783

R^1	R^2	R^3	C-5	
Ph	Me	H	^{12}C	(77)
Ph	Me	H	^{13}C	(65)
Ph	Me	D	^{12}C	(72)
$4\text{-}FC_6H_4$	Me	H	^{12}C	(54)
$4\text{-}ClC_6H_4$	Me	H	^{12}C	(71)
$4\text{-}MeOC_6H_4$	Me	H	^{12}C	(56)

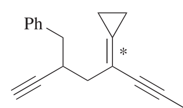
R^1	R^2	R^3	C-5	
Ph	*i*-Pr	H	^{12}C	(81)
$4\text{-}NCC_6H_4$	Me	H	^{12}C	(64)
$n\text{-}C_{10}H_{21}$	Me	H	^{12}C	(72)
1-naphthyl	Me	H	^{12}C	(63)
Ph	$c\text{-}C_6H_{11}$	H	^{12}C	(63)

C_{15}



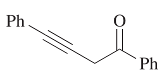


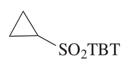
Ketone (1 eq), sulfone (1.2 eq), KHMDS (1.3 eq), THF, –78°; then to rt; then rt, overnight



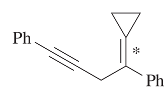
(62) 783

C_{16}



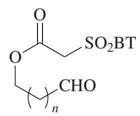
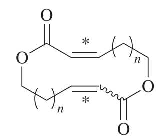


Ketone (1 eq), sulfone (1.2 eq), KHMDS (1.3 eq), THF, –78°; then to rt; then rt, overnight

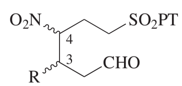
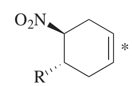


(40) 782

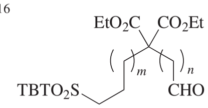
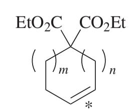
TABLE 18. INTRAMOLECULAR REACTIONS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-9} 	Syringe pump addition to DBU, CH_2Cl_2, 14–18 h		149

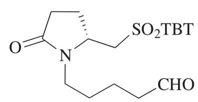
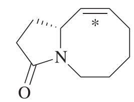
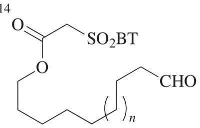
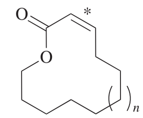
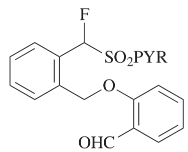
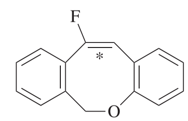
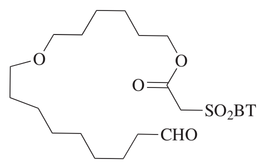
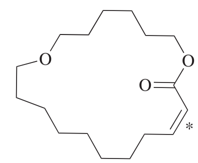
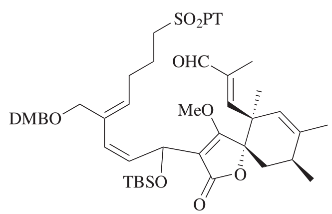
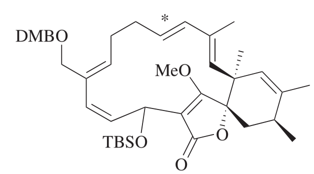
n	Temp		(*EZ*)/(*ZZ*)*
2	–78° to rt	(31)	15:85
2	rt	(27)	11:89
3	rt	(70)	33:67
4	rt	(13)	37:63
5	–78° to rt	(44)	35:65

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-12} 	**A**: 1. Cs_2CO_3, THF/DMF, 70°, 2 h 2. DBU, CH_3CN, –40°, 15 min *or* **B**: DBU, CH_3CN, 0 to –40°, 0.5 h		784

R	Config.	dr			dr	er[a]
Me	(3*S*,4*S*)/(3*S*,4*R*)	63:37	**B**	(45)	79:21	93.0:7.0
Et	(3*S*,4*S*)/(3*S*,4*R*)	64:36	**A**	(51)	92:8	95.0:5.0
$(MeO)_2CHCH_2$	(3*S*,4*S*)/(3*S*,4*R*)	64:36	**A**	(60)	90:10	97.0:3.0
n-Pr	(3*S*,4*S*)/(3*S*,4*R*)	62:38	**A**	(57)	91:9	95.0:5.0
n-Bu	(3*S*,4*S*)/(3*S*,4*R*)	64:36	**B**	(60)	85:15	95.5:4.5
(*Z*)-EtCH=CH$(CH_2)_2$	—	—	**A**	(63)	75:25	95.0:5.0
Ph	(3*R*,4*S*)/(3*R*,4*R*)	54:46	**B**	(52)	94:6	96.0:4.0
4-ClC_6H_4	(3*R*,4*S*)/(3*R*,4*R*)	55:45	**B**	(50)	91:9	93.0:7.0
4-$O_2NC_6H_4$	(3*R*,4*S*)/(3*R*,4*R*)	55:45	**B**	(49)	91:9	87.5:12.5
4-$MeOC_6H_4$	(3*R*,4*S*)/(3*R*,4*R*)	54:46	**B**	(52)	85:15	94.5:5.5
n-C_9H_{19}	(3*S*,4*S*)/(3*S*,4*R*)	61:39	**A**	(61)	76:24	97.5:2.5

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-16} 	Cs_2CO_3, THF/DMF, 70°, 16 h		62

m	*n*		(*E*)/(*Z*)*
1	1	(91)	0:100
2	2	(32)	50:50
8	2	(56)	66:34

C_{10}		$CsCO_3$, DMF/THF, H_2O, 70°, 10 h	 (56), $(Z)^*$-isomer only	785
C_{11-14}		Syringe pump addition to DBU, CH_2Cl_2, rt, 14 h	 *n* (E)/(Z)* 1 (44) 13:87 2 (24) 22:78 4 (25) 20:80	149
C_{15}		*t*-BuOK, DMF, –50° to rt	 (80), $(E)^*$-isomer only	786
C_{17}		Syringe pump addition to DBU, CH_2Cl_2, –78° to rt, 14 h	 (43), $(E)/(Z)^* = 15:85$	149
C_{25}		KHMDS, THF, –78°, 0.5 h; then rt, 1.5 h	 (15), $(E)/(Z)^* = 100:0$	787

[a] The er is for the major diastereomer.

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