CHAPTER 1

NUCLEOPHILIC ADDITIONS OF PERFLUOROALKYL GROUPS

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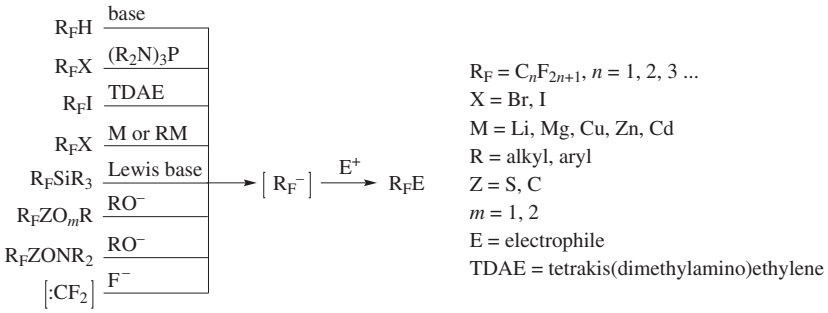
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INTRODUCTION

Trifluoromethyl- and perfluoroalkyl-containing organic compounds often possess properties that make them suitable for diverse applications in material science, agrochemistry, and the pharmaceutical industry. High electronegativity and lipophilicity together with oxidative, hydrolytic, and thermal stability make these groups unique. The trifluoromethyl group has electronegativity similar to that of oxygen[1] and a size between isopropyl and *tert*-butyl groups.[2] The higher lipophilicity enables the trifluoromethyl-containing compounds to traverse lipid membranes readily in comparison with their nonfluorinated analogues. Long-chain perfluoroalkyl groups have conformationally rigid helical structures due to repulsive 1,3-difluoro interactions.[3,4] The introduction of long perfluoroalkyl groups into an organic molecule changes its reactivity and physical properties dramatically. This strategy has been used mainly for separations by immobilization into fluorous phases[5] and also for fine-tuning solid phase properties of novel liquid crystalline materials.[6]

The trifluoromethyl or perfluoroalkyl unit can be constructed using various fluorination methods: (1) from a trichloromethyl group using anhydrous HF, (2) from a carboxylic acid group by treatment with HF/SF_4 or related reagents, (3) from dithiocarboxylic acids with XeF_2, (4) by oxidative desulfurization/fluorination with amine–HF complexes or (5) by fluorination of hydrocarbons with F_2, halogen fluorides, high oxidation state metal fluorides, or electrochemical fluorinations.[6–8] Direct introduction of perfluoroalkyl groups can be achieved by ionic (nucleophilic or electrophilic) or radical reactions. Nucleophilic perfluoroalkyl addition has been perhaps the most attractive approach during the last few decades. It is considered to

be an efficient, selective, and reliable method for introducing perfluoroalkyl groups (trifluoromethyl in particular) into organic molecules. This chapter focuses primarily on reactions between an electrophilic compound and perfluoroalkyl carbanionic species providing stable perfluoroalkylated products. The most common, synthetically useful methods to generate perfluoroalkyl carbanions are summarized in Scheme 1. Addition of fluoride ions to perfluoroalkenes also provide perfluoroalkyl carbanions (Scheme 2).



Scheme 1



$R_F = C_nF_{2n+1}$, n = 0, 1, 2, 3...

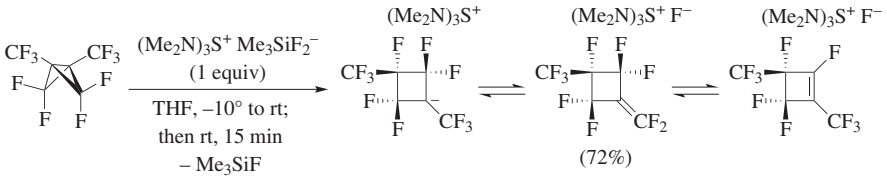
Scheme 2

This chapter is limited to the discussion of nucleophilic additions of saturated perfluoroalkyl groups to various electrophiles that have appeared in the literature up to the end of the first quarter of 2014. All electrophilic species of carbon and other group 13–18 elements as well as transition-metal electrophiles are reviewed. Reactions of only those perfluoroalkyl addition reagents or reactive species that possess nucleophilic (carbanionic) character are considered. Although reaction mechanisms for some metalloorganic species may at some point employ radicals, all reactions that have nucleophilic addition pathways are included. Reactions under typical radical conditions (UV light, radical initiator) are excluded. For example, perfluoroalkylmercury reagents generally do not display nucleophilic character and tend to undergo homolytic Hg–R_F bond dissociation.[9]

A number of reviews and book chapters about nucleophilic perfluoroalkyl transfer have appeared.[3,6,10–13] Others cover various aspects of the topic such as using organosilicon reagents,[14–27] perfluoroalkyl organometallics,[9,28–32] fluorinated carbanions,[33,34] as well as asymmetric[35–40] and enantioselective[41–46] nucleophilic perfluoroalkyl additions.

MECHANISM AND STEREOCHEMISTRY

As the title of the chapter suggests, nucleophilic perfluoroalkyl addition involves the generation of carbanionic perfluoroalkyl species from the precursors (see Schemes 1 and 2) and their reactions with electrophilic partners to form perfluoroalkyl-containing products. Perfluoroalkyl carbanions are stabilized by the negative inductive effect of their fluoro and perfluoroalkyl substituents. At the same time, α-fluoro carbanions are destabilized by electronic p–π repulsion of the fluorine lone electron pairs and at the anionic center. This property is reflected in the relatively weak acidity of CHF_3 in comparison with the other haloforms, even though fluorine has the highest electronegativity. The pK_a values of the various trihalomethanes are 30.5 (CHF_3), 22.4 ($CHCl_3$), 22.7 ($CHBr_3$), and 68–70 (CH_4).[47−48] β-Fluorocarbanions are stabilized by negative hyperconjugation in addition to negative inductive effects. Clear experimental evidence of negative hyperconjugation is obtained from X-ray structure analysis of the perfluoro-1,3-dimethylcyclobutanide anion (stable, mp 160–162°), which shows that the cyclobutane ring and the anionic center are planar (Scheme 3).[49]

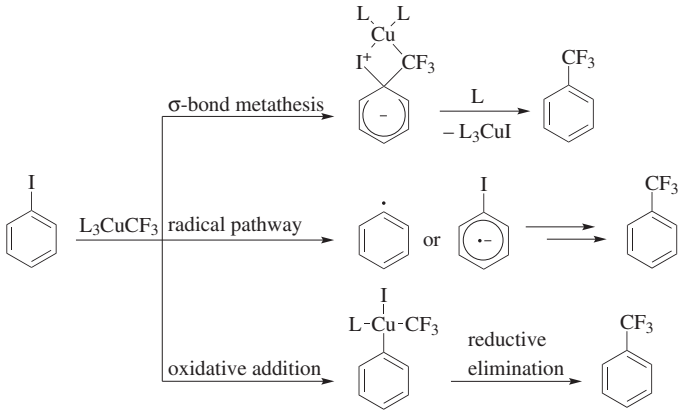


Scheme 3

Thus, in contrast to conventional alkyl organolithium and organomagnesium reagents, trifluoromethyllithium and trifluoromethylmagnesium reagents are extremely unstable and cannot be used, not even at low temperatures.[50] The rapid degradation by α-fluoride elimination to difluorocarbene and metal fluorides forces higher equivalents of the trifluoromethyl carbanion to be employed. However, long-chain perfluoroalkyl organometallics display much higher stability and can be used synthetically, with the main degradation pathway being the β-fluoride elimination to terminal perfluoroalkenes.[7]

An effective way to stabilize the trifluoromethyl carbanion is to attach the CF_3 group to an atom with more covalent character such as copper, zinc, cadmium, silicon, tin, bismuth, sulfur, or carbon. Perfluoroalkyl copper species can be obtained in a number of ways, for example by reaction of perfluoroalkyl iodides with copper powder,[51−53] by reaction of copper complexes with $TMSCF_3$,[54,55] by direct cupration of fluoroform,[56,57] or by reaction of CuI with readily available CF_3CO_2Na.[58,59] The most common use of perfluoroalkyl copper species is cross-coupling with alkyl, alkenyl, and aryl halides to afford the corresponding perfluoroalkyl alkanes, alkenes, and arenes. The mechanism of the trifluoromethylation of 4-substituted iodoaromatic compounds with the sodium trifluoroacetate/CuI system has been studied. The positive ρ value of +0.46 obtained from a Hammett plot confirms the

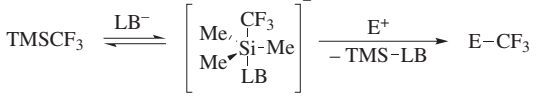
nucleophilic nature of the trifluoromethyl copper species.[59] However, using CF_3Cu obtained by direct cupration of fluoroform with CuCl and *t*-BuOK, the ρ value of +0.97 is obtained in the reaction of 3-substituted iodoaromatic compounds (using σ_m substituent constants) and +0.91 in the reaction of 4-substituted iodoaromatic compounds (using σ_p^-), clearly establishing nucleophilic attack of the aromatic ring and –M interactions in the 4-substituted iodoaromatics.[60] The efficiency of the reaction depends on the solvating power of the medium for the Cu(I) complex; DMF, NMP, pyridine, and DMSO afford the highest yields. The order of reactivity of the halogens as the aromatic leaving groups is I > Br ≫ Cl. Using AgI instead of CuI for the decarboxylation of sodium trifluoroacetate does not transfer the CF_3 group to the aryl iodide. The mechanism of copper-mediated cross-coupling of iodoarenes is unknown and several pathways for the reaction between simple phenyl iodide and CF_3Cu have been proposed (Scheme 4): (1) σ-bond metathesis (SBM);[6,30,59] (2) a radical pathway;[60] (3) oxidative addition and formation of Cu(III) species.[60–62] The trifluoromethylation reaction of a variety of aryl halides with fluoroform-derived CF_3Cu has been studied by experimental (radical clock, kinetic, Hammett correlation) and computational methods.[60] The combined data set points to a bimolecular process involving Ar–X oxidative addition to DMF-stabilized CF_3Cu as the rate determining step, followed by Ar–CF_3 reductive elimination from a Cu(III) intermediate. The computed barrier for the trifluoromethylation of iodobenzene ($\Delta G^{\ddagger}$ = 21.9 kcal/mol at 298 K) is in good agreement with the experimental value of $\Delta G^{\ddagger}$ = 24 kcal/mol at 298 K. A radical mechanism has been ruled out on the basis of both experimental and computational data. The latter have also shown prohibitively high barriers to SET (both outer and inner sphere) as well as classical S_NAr, SBM, and HAT (halogen atom transfer) processes previously proposed in the literature for some other copper-mediated coupling reactions of aryl halides.[60]



Scheme 4

(Trifluoromethyl)trimethylsilane ($TMSCF_3$), known as the Ruppert–Prakash reagent, is the most important reagent for nucleophilic addition of a trifluoromethyl group.[14,17] To exhibit nucleophilic properties, $TMSCF_3$ must be activated with a

Lewis base to generate a five-coordinate complex that serves as an equivalent of trifluoromethyl carbanion (Scheme 5).[14]

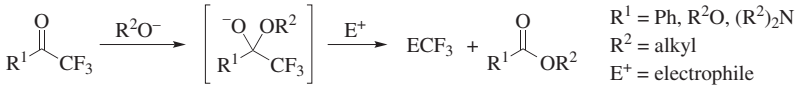


$LB^- = F^-, RO^-, RCO_2^-, Me_3N^+O^-$
E^+ = electrophile

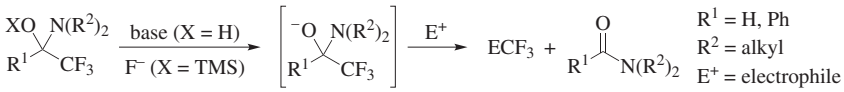
Scheme 5

Several Lewis bases (LB) can be employed to activate $TMSCF_3$, among which fluoride and oxygen nucleophiles (acetate, phenolate, carbonate) are the most effective and the most often used. The generation of five-coordinate species $[Me_3Si(CF_3)LB]^-$ is confirmed by low-temperature NMR studies (LB = F^-),[63] and one such complex (LB = CF_3^-) has been characterized by X-ray diffraction analysis.[64] The formation of five- and six-coordinate structures bearing a CF_3 group at silicon has also been studied computationally[65] and a single-crystal X-ray structure of $TMSCF_3$[66] shows a distorted tetrahedral geometry at the silicon atom and the longest known Si–C distance [Si–CF_3, 1.943(12) Å], which helps to explain the facile cleavage of the Si–CF_3 bond and CF_3 group transfer. (Trifluoromethyl)trimethylsilane in the presence of an activator behaves as a hard nucleophile and undergoes 1,2- rather than 1,4-addition to α,β-unsaturated carbonyl compounds.[14]

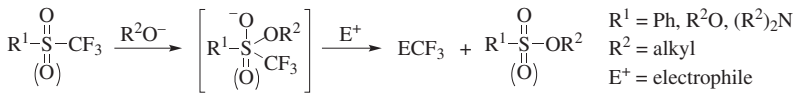
Trifluoromethyl derivatives of ketones, esters, amides, hemiaminals, hemiketals, sulfoxides, sulfones, sulfinates, and sulfinamides can be activated by alkoxides to function as sources of CF_3^- (Schemes 6–8). To avoid strong bases, derivatives containing trimethylsilyl ethers are often used to generate the alkoxides, conveniently using fluoride ions and after an intramolecular attack of the carbon or sulfur atom, the adjacent trifluoromethyl group is released as a carbanionic species.



Scheme 6

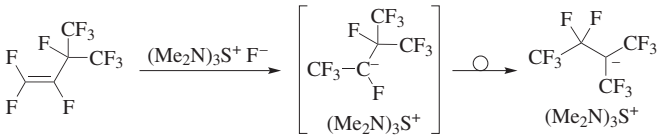


Scheme 7

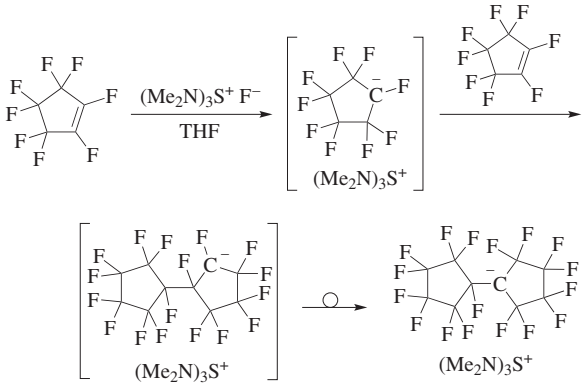


Scheme 8

Perfluoroalkyl carbanion salts can be prepared by the addition of fluoride salts to perfluorinated olefins.[49,67,68] Tertiary perfluoroalkyl carbanions are rather stable (their tris(dimethylamino)sulfonium (TAS^+) salts are stable solids) but secondary carbanions are not observed due to rearrangement to the tertiary anions (Scheme 9)[68] or dimerization by addition to another molecule of olefin and subsequent rearrangement (Scheme 10).[68]



Scheme 9



Scheme 10

Preparation of perfluoroalkyl addition reagents, generation and stability of nucleophilic species, and scope and limitations of reactivity, selectivity, and stereochemical considerations of electrophiles are covered in the next section. From the electrophile point of view, perfluoroalkyl reagents undergo nucleophilic substitution (in the case of alkyl halides, triflates, cyclic sulfates, and halogenated heteroatom electrophiles), or nucleophilic addition or addition–elimination sequences (in the case of unsaturated substrates, arenes, aryl halides, carbonyl compounds, nitrogen-containing electrophiles derived from carbonyl compounds, and transition-metal complexes).

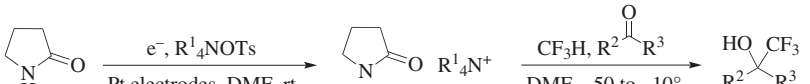
SCOPE AND LIMITATIONS

This section is divided into two parts. In the first part, different types of nucleophilic perfluoroalkyl addition reagents are introduced and their preparation is described. In the second part, the scope and limitations of perfluoroalkyl additions to various types of electrophiles is described in detail.

Overview and Preparation of Nucleophilic Perfluoroalkyl Reagents

Nucleophilic perfluoroalkyl species can be generated in various ways from chemically diverse precursors (see Scheme 1 for the most common methods). The following section provides an overview of the preparation and properties of nucleophilic perfluoroalkyl reagents and is organized by the type of precursor. The description of reactivity of those reagents with electrophilic partners is kept to a minimum. Detailed discussion of the scope and limitations for each type of electrophile is found in the next section.

Deprotonation of Trifluoromethane and Polyfluoroalkanes. Fluoroform (bp –82.1°) is a side-product of the industrial synthesis of Freon 22 (CHF_2Cl), a key intermediate in the multistep synthesis of Teflon. Deprotonation of fluoroform with Grignard reagents or alkyllithium species generates the trifluoromethyl anion, which quickly decomposes to difluorocarbene even at low temperature.[50] Despite this limitation, trifluoromethane can effectively be employed for nucleophilic trifluoromethylation by using various bases with or without solvent stabilization. Thus, trifluoromethyl anion can be formed by the deprotonation of fluoroform with various electrochemically generated bases **1** derived from 2-pyrrolidinone in DMF at –50° (Scheme 11).[69]



1

	R^1
1a	Et
1b	*n*-Bu
1c	*n*-C_8H_{17}

Scheme 11

Phenyl anion (Ph^-), produced by electroreduction of a large excess of iodobenzene in DMF, can deprotonate fluoroform or pentafluoroethane, allowing perfluoroalkylation of aldehydes or alkyl halides. Only those electrophiles that are not more easily reduced than iodobenzene can be used.[70] Other bases such as *t*-BuOK in DMF, potassium dimsylate, KHMDS in toluene or THF, and $(TMS)_3N$ together with a fluoride ion source and a catalytic amount of DMF in THF are used for the deprotonation of fluoroform and further perfluoroalkylation.[48,71–78] The solvent plays a crucial role in the stabilization of the trifluoromethyl anion. When fluoroform is added at low temperature (–50 to –10°) into a mixture of *t*-BuOK or dimsyl potassium in DMF, the trifluoromethyl anion is trapped in situ by the weak electrophile DMF to form the amino alcoholate **2** (Scheme 12).[71,72] Intermediate **2** is a masked and relatively stable form of the trifluoromethyl anion at temperatures below –10°, but a rapid degradation occurs at room temperature.[48] Intermediate **2** reacts with electrophiles

such as aldehydes, ketones, or disulfides to form the trifluoromethylated products and DMF is regenerated (Scheme 12). Alternatively, hydrolysis of intermediate **2** produces fluoral.[48,71,72] Solvents such as THF or DMF dimethyl acetal afford very low yields of the trifluoromethylated product due to carbenoid degradation. However, other dialkylformamides such as *N*-formylmorpholine can replace DMF in stabilizing the trifluoromethyl anion. DMF is also found to enhance the efficiency of trifluoromethylation of benzophenone using [^{18}F]-fluoroform for PET (positron emission tomography) applications.[79]



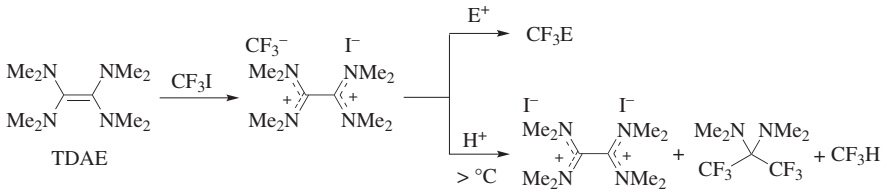
Scheme 12

In contrast to previous findings, recent reports show that fluoroform in THF or toluene solution at low temperature is deprotonated with KHMDS, allowing trifluoromethylation of TMSCl, sulfur, trialkyl borates, and carbonyl electrophiles in moderate to high yields.[77] Trifluoromethanide anion with the $[K(18\text{-crown-6})]^+$ cation is prepared from fluoroform, *t*-BuOK, and 18-crown-6 in THF and is found to be stable at –78° for a few days, allowing its characterization by NMR spectroscopy.[80] Deprotonation of fluoroform with *t*-BuOK in DMF and NMP followed by capturing trifluoromethyl anionic species with copper salts is a very important method to prepare CF_3Cu reagents.[56,57]

The sterically demanding P_4-*t*-Bu phosphazene base developed by Schwesinger and co-workers is able to deprotonate fluoroform under suitable conditions (THF, –30 to – 40°). The resulting salt or binary complex $(P_4\text{-}t\text{-Bu/H})^+CF_3^-$ is not observed by NMR spectroscopy;[81] however, the mixture is able to trifluoromethylate a variety of electrophiles such as aldehydes, ketones, carbon dioxide, acid chlorides, esters, diaryl disulfides, and even epoxides.[81,82]

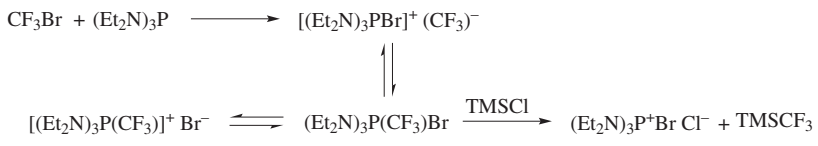
Pentafluoroethane and higher polyfluoroalkanes are converted into perfluoroalkyllithium reagents by reaction with methyllithium and are subsequently used for perfluoroalkyl additions. The perfluoro *tert*-butyl anion is generated from $(CF_3)_3CH$ and triethylamine. Subsequent reactions with electrophiles such as tropylium bromide,[83] paraformaldehyde,[84] electron-deficient alkenes,[85–87] and alkynes[88] provide the corresponding perfluoro *tert*-butyl containing products.

Reduction of Perfluoroalkyl Halides. tetrakis(Dimethylamino)ethylene (TDAE) is a strong electron donor that reacts with CF_3I (but not CF_3Br) in polar solvents such as dichloromethane or benzonitrile at low temperature to form a deep red charge-transfer complex. The complex decomposes slowly above 0°; however, in the presence of an electrophilic compound, trifluoromethylation becomes the main reaction pathway (Scheme 13).[89]



Scheme 13

An alternative method to CF_3I/TDAE is the combination of tris(dialkylamino)phosphine and CF_3Br. The reaction of CF_3Br with TMSCl mediated by $(Et_2N)_3P$ provides $TMSCF_3$ in high yields[90] and proceeds via a bromophilic attack of the phosphorus atom of $(Et_2N)_3P$ to CF_3Br. The formed phosphonium salt is in equilibrium with the pentacoordinate phosphorus intermediate which transfers the CF_3 group to TMSCl (Scheme 14).[16,17,91,92]

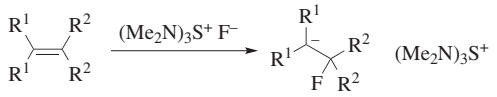


Scheme 14

Although CF_3I is more expensive than CF_3Br, one important advantage of using the TDAE rather than tris(dialkylamino)phosphine method is that trifluoromethyltris(dialkylamino)phosphonium salts are usually soluble in the reaction medium, often making the separation from the perfluoroalkylated product difficult. On the other hand, the oxidation product of TDAE is a dication, which is only slightly soluble in the above-mentioned solvents, and can be removed by filtration. Trifluoroiodomethane in combination with TDAE acts as an efficient trifluoromethylating reagent for halogenated silanes, phosphines, boranes, fluorinated alkenes, aromatic compounds, carbonyl compounds, disulfides, diselenides, carboxylic acid halides, imines, cyclic sulfates, and other electrophiles.

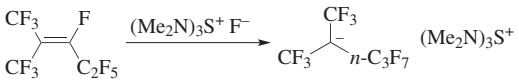
Electrochemical reduction of CF_3Br or CF_3I and the trapping of the formed trifluoromethyl anion by TMSCl or DMF has also been reported.[93−96]

Non-Metallic Perfluoroalkyl Salts from Addition of Fluoride to Perfluoroalkenes. Stable perfluoroalkyl carbanion salts are isolated by the reaction of fluorinated olefins with TASF (tris(dimethylamino)sulfonium fluoride) (Scheme 15).[67,68,49] For example, carbanion **3** (Scheme 16)[68] is stable up to 60° and is used for perfluoroalkylation of various simple electrophilic substrates such as Cl_2, Br_2, NOF, NOCl, or BnBr.[68] By contrast, the corresponding cesium salts are much less stable and in some cases cannot be detected by ^{19}F NMR spectroscopy.



$R^1 = CF_3, C_2F_5$
$R^2 = F, CF_3, C_2F_5$

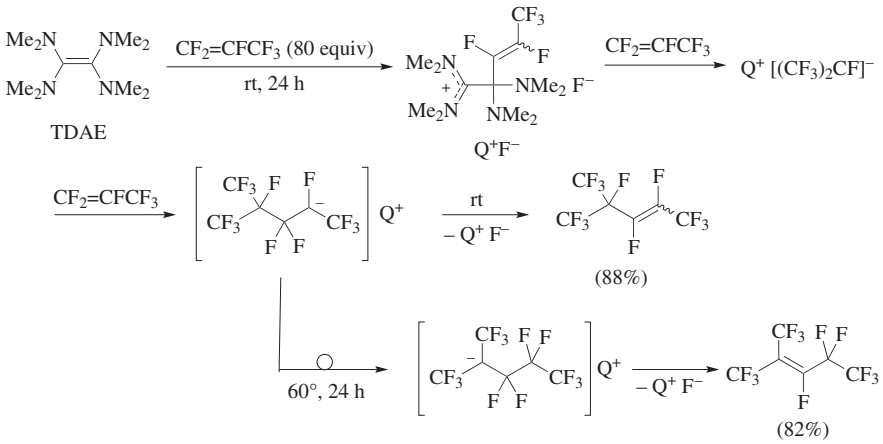
Scheme 15



3

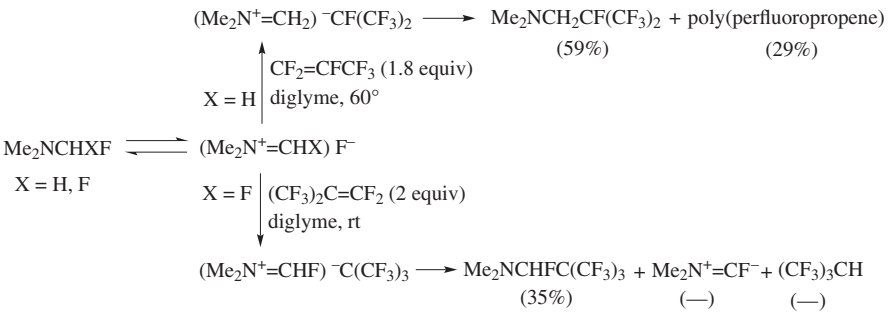
Scheme 16

Strong electron donors such as TDAE or trimethylamine react with unsaturated fluorocarbons such as hexafluoropropene or tetrafluoroethylene to produce fluoride salts that are soluble in organic solvents.[97] These fluoride salts oligomerize in the presence of excess unsaturated fluorocarbons (Scheme 17)[97] or can undergo perfluoroalkylation reactions with activated fluoroaromatic compound such as pentafluoropyridine, tetrafluoropyrimidine, trifluorotriazine, or 2,4-dinitrofluorobenzene.[97,98]



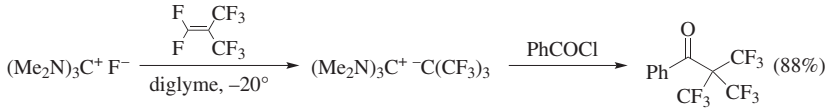
Scheme 17

Another source of metal-free anhydrous fluoride for addition to perfluoroalkenes is dimethylfluoromethylamine and dimethyldifluoromethylamine, which dissociate in polar solvents to form iminium fluorides. Reactions with unsaturated fluorocarbons afford perfluoroalkyl carbanions, which collapse to form dimethylpolyfluoroalkylamines (Scheme 18).[99,100]



Scheme 18

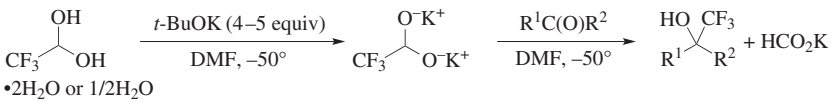
Tris(dimethylamino)fluoromethane reacts with perfluoroisobutylene to afford the stable solid perfluoro-*tert*-butyl anion quantitatively. Reaction of this anion with benzoyl chloride provides phenyl perfluro-*tert*-butyl ketone in high yield (Scheme 19).[101]



Scheme 19

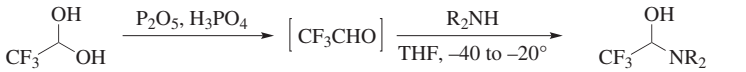
Carbon–Boron Bond Cleavage from Perfluoroalkyl Boron Reagents. Potassium trialkoxy(perfluoroalkyl)borates, prepared by the reaction of trialkoxyborates with $TMSR_F$ in the presence of KF, are stable reagents for efficient nucleophilic perfluoroalkyl additions to mainly non-enolizable aldehydes, ketones, *N*-tosylaldimines, iminium salts, and aryl iodides (under copper catalysis).[102–104]

Carbon–Carbon Bond Cleavage from Perfluoroalkyl Carbonyl Reagents and their Derivatives. Derivatives of trifluoroacetaldehyde, trifluoromethyl ketones, and perfluoroalkanoic acids have been investigated as nucleophilic perfluoroalkyl addition reagents.[48,71,72,105–107] Trifluoroacetaldehyde hydrate acts as a nucleophilic trifluoromethylating reagent for non-enolizable aldehydes and ketones in the presence of excess *t*-BuOK. Density functional theory calculations suggest that transfer of the CF_3 group takes place from the double deprotonated trifluoroacetaldehyde hydrate (Scheme 20).[106]



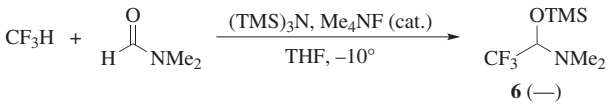
Scheme 20

Amino alcoholate **2** (Scheme 12) is too unstable to be isolated, but other more stable derivatives have been prepared. Transmetalation of compound **2** with CuI affords the copper(I) alkoxide, which upon warming to room temperature decomposes to a trifluoromethylcopper species able to form 4-trifluoromethylanisole from 4-iodoanisole in low yield.[48] This method of perfluoroalkylcopper generation is discussed later in the chapter. Hemiaminals **4** and **5** are prepared from fluoral in very good yields (Scheme 21),[105] and are used for trifluoromethylation of benzaldehyde in DMF in the presence of *t*-BuONa.[105] Although TMS-protected hemiaminal **6** forms from fluoroform, its isolation is difficult and the compound has a limited shelf life[74,75,108] (Scheme 22).[75]



	R	Yield (%)
4	Et	90
5	*n*-Bu	90

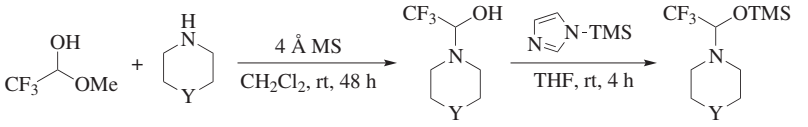
Scheme 21



6 (—)

Scheme 22

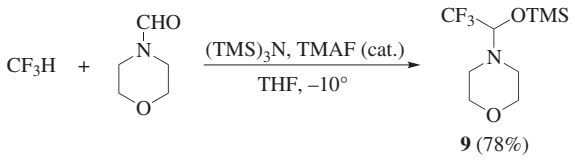
More stable hemiaminals **7** and **8** and their TMS derivatives **9** and **10** are efficiently prepared from the methyl hemiacetal of fluoral[109,110] (Scheme 23).[41] Compound **9** is also prepared from fluoroform (Scheme 24).[74] In general, reagents **7** and **8** require the use of a strong base such as *t*-BuOK, whereas trimethylsilyl derivatives **9** and **10** are activated by a fluoride salt. All reagents trifluoromethylate non-enolizable carbonyl compounds, disulfides, and diselenides. [41,74,108–112]



	Y	Yield (%)
7	O	90
8	BnN	75

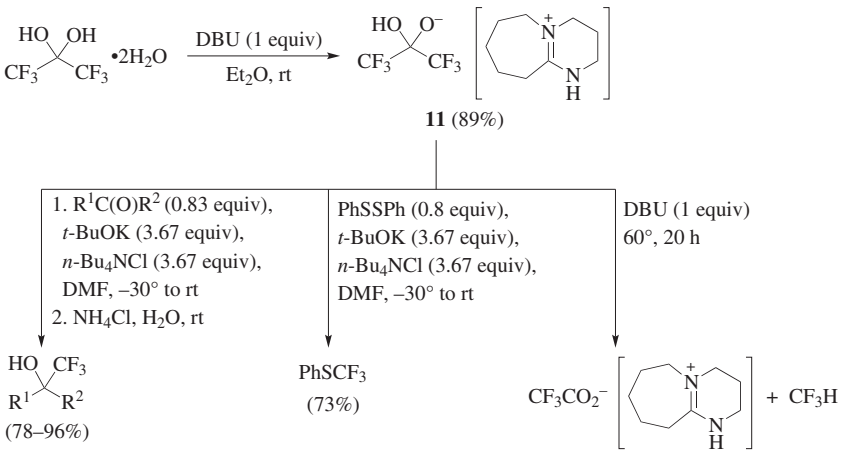
	Y	Yield (%)
9	O	100
10	BnN	100

Scheme 23



Scheme 24

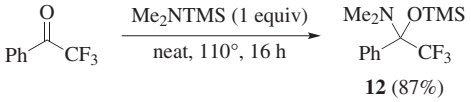
The stable and non-hygroscopic amidinate salt of hexafluoroacetone hydrate (**11**) precipitates from an ethereal solution of hexafluoroacetone hydrate upon addition of DBU. This salt effects trifluoromethylation of non-enolizable aldehydes, ketones, and diphenyl disulfide (Scheme 25).[107] It also decomposes to trifluoroacetate and fluoroform in the reaction with DBU.



Scheme 25

Phenyl trihalomethyl ketones undergo haloform cleavage in sodium hydroxide. The rate constants for the reaction of trichloro- or tribromoacetophenone are many orders of magnitude higher than for trifluoroacetophenone.[113] Similarly, the hydrated form of trifluoroacetophenone undergoes cleavage with NaH in DMF to afford sodium benzoate and fluoroform.[114] These observations suggest the possibility of generating the trifluoromethyl carbanion from trifluoromethyl ketones for further trifluoromethylation reactions. Indeed, in the presence of *t*-BuOK, trifluoroacetophenone trifluoromethylates non-enolizable ketones.[115] Aromatic aldehydes do not react under these conditions.

The trimethylsilyl-protected hemiketal **12**, derived from trifluoroacetophenone, is another shelf-stable trifluoromethylating reagent for non-enolizable aldehydes and ketones[116,117] (Scheme 26).[117]

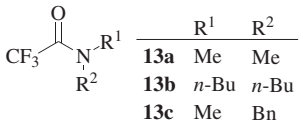


12 (87%)

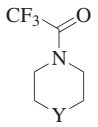
Scheme 26

Esters of perfluoroalkanoic acids undergo cleavage reactions with sodium ethoride in ethanol to provide diethyl carbonate and perfluoroalkanes in ca. 70% yields. In the case of CF_3CO_2Et, trifluoromethane is obtained in only 43% yield and a significant amount of fluoride forms in the reaction mixture, the latter arising from decomposition of the intermediate trifluoromethyl carbanion.[118] In the presence of *t*-BuOK, methyl trifluoroacetate serves as a trifluoromethylating reagent toward non-enolizable ketones in moderate yields,[119] and in the presence of CsF or CsCl and CuI under heating constitutes a valuable trifluoromethylating system for aromatic iodides and bromides.[120]

A number of trifluoroacetamides **13a–g** are capable of trifluoromethylating non-enolizable ketones in the presence of 1 equivalent of *t*-BuOK.[119] Interestingly, cyclic amine derivatives **13e–g** provide better yields than acyclic amides **13a–d**.[119]



	R^1	R^2
13a	Me	Me
13b	*n*-Bu	*n*-Bu
13c	Me	Bn
13d	*i*-Pr	*i*-Pr



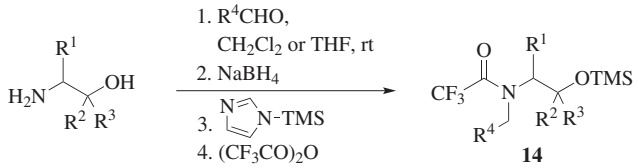
	Y
13e	O
13f	BnN
13g	CH_2

The more reactive trifluoroacetamides **14a–o** derived from *O*-silylated β-amino alcohols (Scheme 27) [41,42,121] allow slow delivery of the alcoholate by fluoride-induced desilylation followed by intramolecular attack on the amide carbonyl. Collapse of the tetrahedral intermediate to yield oxazolidinones **15** with concomitant trifluoromethylation of carbonyl compounds completes the catalytic cycle, as shown in Scheme 28.[121]

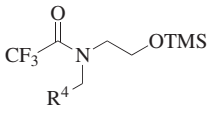
Indeed, amides **14**, with the exception of **14e**, **14f**, and **14o**, trifluoromethylate various carbonyl compounds in the presence of a catalytic amount of a fluoride source. The lack of reactivity of amide **14o** is explained by invoking an unfavorable conformer equilibrium[121] (Scheme 29).[42]

The remaining amides **14** are good trifluoromethylating agents for both enolizable and non-enolizable aldehydes and ketones using catalytic amounts of CsF in DME or TBAT (tetrabutylammonium difluorotriphenylsilicate) in THF. Amides without substitution in the α-position relative to nitrogen (**14a–c**) need thermal activation up to 80° for efficient CF_3 transfer, whereas those with substitution (**14d–n**) are more reactive and require lower temperatures (40° or rt). The exception is amide **14k**, which is able to transfer the CF_3 group only very sluggishly at rt. Many of the amides **14** are

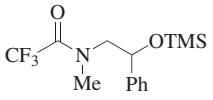
chiral; however, only low enantioselectivities are observed in reactions with prochiral substrates.[41–43]



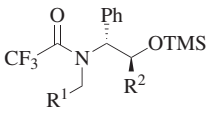
Products:



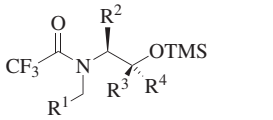
	R^4	Yield (%)
14a	H	60
14b	Ph	70



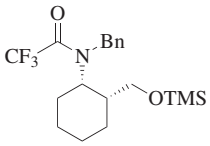
14c (71%)



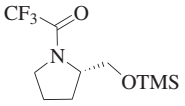
	R^1	R^2	Yield (%)
14d	Me	Ph	75
14e	*n*-Bu	H	38
14f	Ph	H	35
14g	Ph	Ph	55



	R^1	R^2	R^3	R^4	Yield (%)
14h	H	Me	H	Ph	76
14i	H	Me	Ph	H	92
14j	H	Ph	H	Ph	29
14k	*n*-Bu	Me	H	Ph	93
14l	Ph	Me	H	Ph	52
14m	Ph	Ph	H	Ph	37

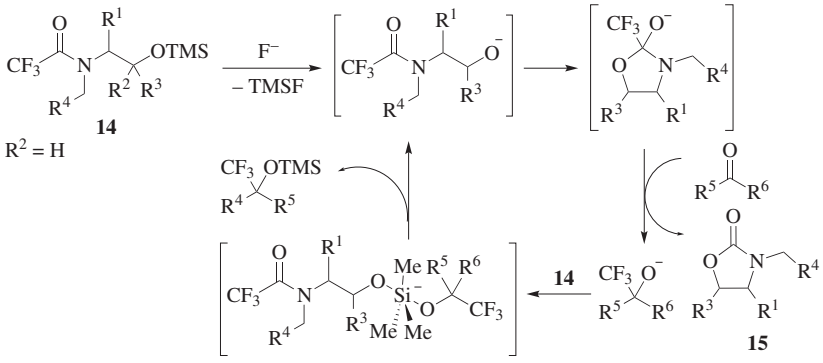


14n (70%)

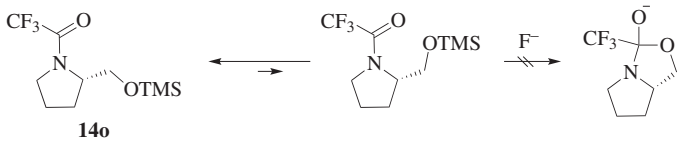


14o (56%)

Scheme 27



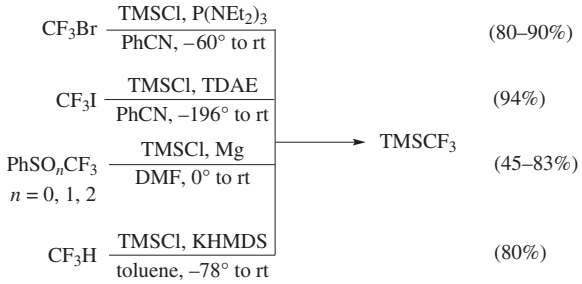
Scheme 28



14o

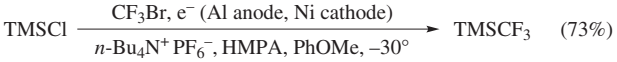
Scheme 29

Carbon–Silicon Bond Cleavage from Perfluoroalkyl Silicon Reagents. (Trifluoromethyl)trimethylsilane, also known as the Ruppert–Prakash reagent (bp 54–55°), is the most versatile nucleophilic trifluoromethylating reagent. The reagent is commercially available or it can be prepared from TMSCl in a number of ways; the most practical synthetic approaches are shown in Scheme 30.[14] The Ruppert–Prakash reagent is produced on a large scale using CF_3Br, TMSCl, and $(Et_2N)_3P$ (Scheme 30).[17] This method is also applicable to the synthesis of $TMSC_2F_5$ (50%) and $TMSC_3F_7$ (68%).[122] Trifluoroiodomethane reacts with TMSCl in the presence of tetrakis(dimethylamino)ethylene (TDAE) to afford $TMSCF_3$ in 94% yield (Scheme 30). The corresponding bromide is ineffective under similar reaction conditions.[89]



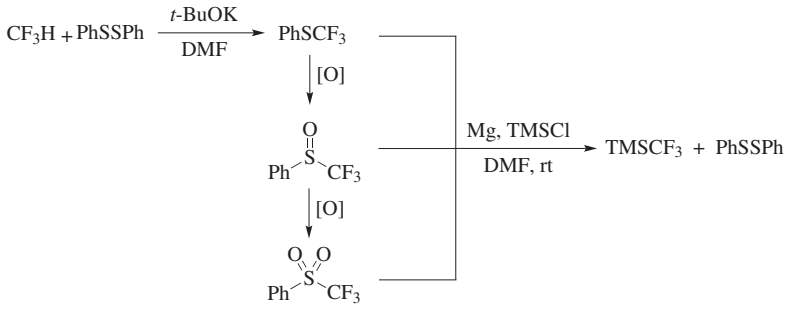
Scheme 30

The high cost of CF_3I and toxicity of $(Et_2N)_3P$ represent significant disadvantages of the methods above for the preparation of $TMSCF_3$. Consequently, several aluminum-mediated electrochemical methods have been developed. Bromotrifluoromethane undergoes efficient trimethylsilylation with TMSCl in the presence of aluminum as the sacrificial anode and $Bu_4N^+PF_6^-$ or $Bu_4N^+Br^-$ as electrolytes in an undivided cell under constant current density (Scheme 31).[94,123] (Trifluoromethyl)trimethylsilane is also prepared in 62% yield using aluminum powder and NMP without electrochemical activation.[124] Low yields of $TMSCF_3$ are obtained by the electrochemical reduction of CF_3I in the presence of TMSCl.[96]



Scheme 31

Fluoroform is the ideal starting material for the synthesis of $TMSCF_3$ and other (trifluoromethyl)silanes because of its availability on a large scale.[6] Phenyl trifluoromethyl sulfide, sulfoxide, or sulfone react with TMSCl in the presence of magnesium metal to form $TMSCF_3$ and diphenyl disulfide (Scheme 30). The latter can potentially be recovered as $PhSCF_3$ in situ by reaction with fluoroform and a base. Thus, a catalytic cycle is formed in which fluoroform is used as the source of the trifluoromethyl group in the synthesis of $TMSCF_3$ (Scheme 32).[125] However, this method has been surpassed by a more efficient sulfur-free process starting from fluoroform (see below).



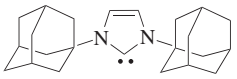
Scheme 32

Treatment of a toluene solution of fluoroform at low temperature with equimolar amounts of KHMDS and TMSCl produces the Ruppert–Prakash reagent in 80% yield (Scheme 30).[77] Good yields of various other (trifluoromethyl)silanes such as Et_3SiCF_3 (71%), *i*-Pr_3SiCF_3 (78%), *n*-$PrMe_2SiCF_3$ (58%), *t*-$BuMe_2SiCF_3$ (42%), $(TMS)_3SiCF_3$ (68%), and $Et_2Si(CF_3)_2$ (44%, from Et_2SiCl_2) are achieved using this method with diethyl ether as the solvent.[77]

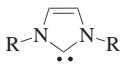
Long-chain (perfluoroalkyl)trialkylsilanes are prepared from perfluoroalkyl bromides or iodides by reaction with $(Et_2N)_3P$,[92,122,126] TDAE,[127] or by the reaction of trialkylsilyl halides with perfluoroalkyl organometallic reagents. Very good yields are reported for the reaction of perfluoroalkyllithium or perfluoroorganomagnesium reagents with trialkylsilyl chlorides.[128–130]

The Ruppert–Prakash reagent allows trifluoromethylation of a wide range of electrophiles under mild reaction conditions. This reagent effects trifluoromethylation of electron-deficient alkenes (such as arylidenemalonitriles), primary alkyl halides and triflates, aryl iodides (in the presence of CuI and KF), aldehydes, ketones, imines, azirines, nitrones, acid halides, anhydrides, esters, *N*-substituted imides, some amides, other carboxylic acid derivatives, and many heteroatom-containing electrophiles. Trifluoromethylation with $TMSCF_3$ is based on the susceptibility of its silicon center toward nucleophilic attack followed by transfer of the trifluoromethyl group to the electrophile. Many different types of activators are used, such as fluoride ions (metal fluorides, TMAF, TBAF, TBAT, TASF, or $K[Ph_3SnF_2]$),[15–17] oxygen nucleophiles (K_2CO_3,[65] metal carboxylates,[131–133] metal alkoxides,[134] phosphate,[65] DMF,[135] DMSO[136]), other ions (Et_4N^+ CN^-),[137] Lewis bases (tertiary amines,

phosphines, and arsines),[138–141] *N*-heterocyclic carbenes **16**,[142] *N*-oxides,[65,143] and electrochemically generated radical anions.[144]

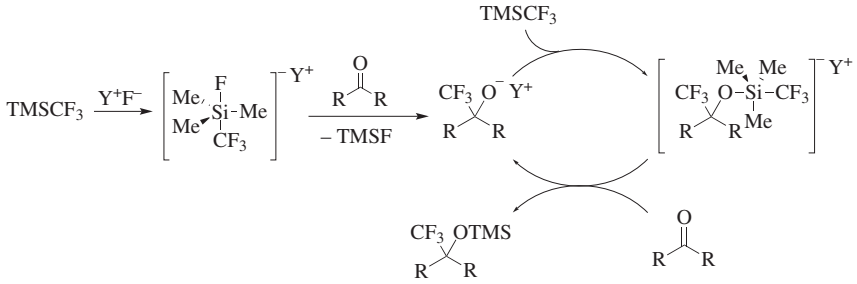


16a



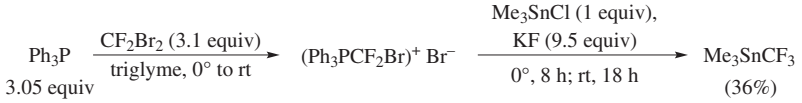
	R
16b	Mes
16c	*t*-Bu
16d	2,6-(*i*-Pr)$_2$C$_6$H$_3$

Only small amounts of activators need to be used with electrophilic substrates, which after transfer of the trifluoromethyl group provide anions or leaving groups with sufficient nucleophilicity and 'silicophilicity' for further activation of $TMSCF_3$. Scheme 33 shows an example of catalytic trifluoromethylation of carbonyl compounds initiated by fluoride ion.[17] The formation of hypercoordinate silicon species has been confirmed and is discussed in more detail in the Perfluoroalkyl Addition to Heteroatom Electrophiles – Silicon Electrophiles section.[63,64,145,146]

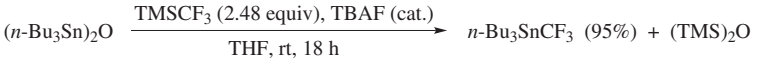


Scheme 33

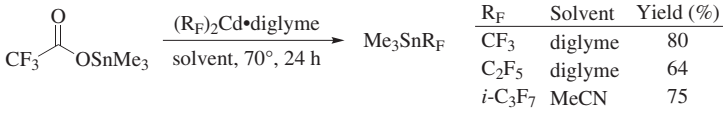
Carbon–Tin Bond Cleavage from Perfluoroalkyl Tin Reagents. Hexaorganoditin compounds are used for the preparation of perfluoroalkyltin compounds using perfluoroalkyl iodides under radical reaction conditions (heating or UV light).[147,148] (Trifluoromethyl)trimethyltin is prepared in 36% yield by the reaction of triphenylphosphine with CF_2Br_2, potassium fluoride, and trimethyltin chloride (Scheme 34).[149] Alternatively, reaction of the less toxic bis(tributyltin) oxide with $TMSCF_3$ provides (trifluoromethyl)tributyltin in 95% yield (Scheme 35).[150,151] The catalytic cycle is maintained by *n*-Bu_3SnO^- or $TMSO^-$. Perfluoroalkyltin compounds are also prepared using perfluoroalkylcadmium reagents (Scheme 36).[152,153] Other protocols for the preparation of (trifluoromethyl)trialkyltins use trifluoromethylsilver[154] or hypervalent sulfuranide dioxide salts.[155]



Scheme 34



Scheme 35

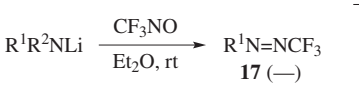


R_F	Solvent	Yield (%)
CF_3	diglyme	80
C_2F_5	diglyme	64
i-C_3F_7	MeCN	75

Scheme 36

Perfluoroalkyltins act as nucleophilic perfluoroalkyl addition reagents. Tributyl(trifluoromethyl)stannane mirrors the reactivity of $TMSCF_3$ in trifluoromethylation of aldehydes, ketones (in the presence of CsF),[156] and aryl iodides (in the presence of CuI and KF).[157] Perfluoroalkyltins are also likely to find applications in Stille coupling reactions and other transition-metal catalyzed processes.[157] Nucleophilic trifluoromethylations of boron trifluoride,[158] phosphorus pentafluoride,[159] some acyl fluorides,[160] and sulfonyl fluorides[161] with R_3SnCF_3 have been described. Trifluoromethyltrialkyltins can also be employed as a source of difluorocarbene when treated with sodium iodide at 80°.[162–164]

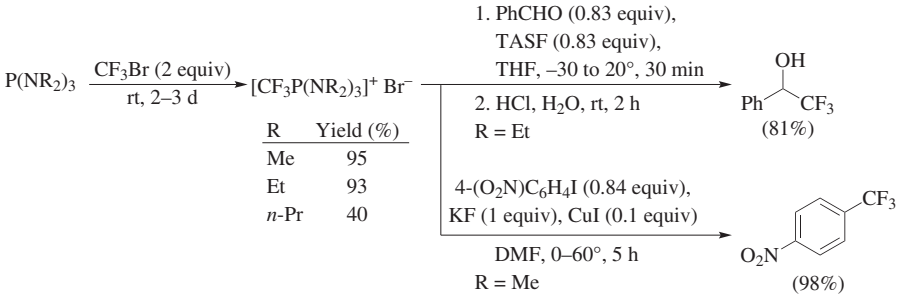
Carbon–Nitrogen Bond Cleavage from Perfluoroalkyl Nitrogen Reagents. Lithium silylamides react smoothly with CF_3NO to provide trialkylsilyl(trifluoromethyl)diazenes **17** (Scheme 37).[165] Whereas diazenes **17a** and **17b** are thermally and hydrolytically unstable, derivatives **17c** and **17d** are stable solids. Fragmentation of **17a** liberates CF_3^- under very mild conditions. For example, trifluoroacetophenone and cyclohexanone react with in situ formed diazene **17a** in THF at −100° to afford trifluoromethylated tertiary alcohols in about 30% yield.[165]



R^1	R^2	**17**
TMS	TMS	**17a**
TBS	H	**17b**
t-Bu_3Si	H	**17c**
$(TMS)_3CSi(Me_2)$	H	**17d**

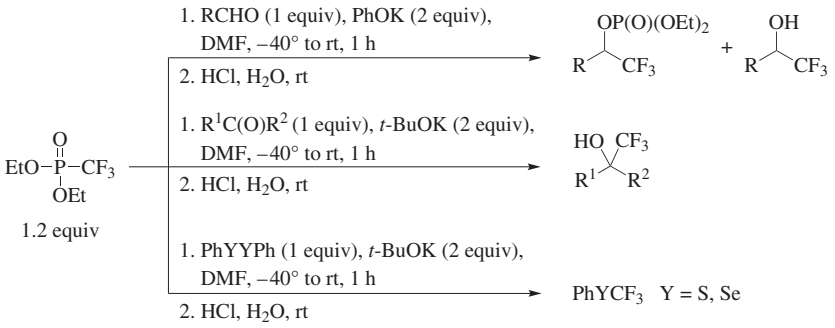
Scheme 37

Carbon–Phosphorus Bond Cleavage from Perfluoroalkyl Phosphorus Reagents. Some trifluoromethyltris(dialkylamino)phosphonium bromides are obtained as solids in the reaction of CF_3Br with $P(NR_2)_3$. In the presence of a fluoride source, these salts act as phosphorus-based nucleophilic trifluoromethylating reagents toward benzaldehyde and 4-nitroiodobenzene (Scheme 38).[166] The formation of CF_3Cu is observed with the use of KF and CuI.[166]



Scheme 38

In the presence of alkoxide ions in DMF, diethyl trifluoromethylphosphonate adds the CF_3 group to aldehydes, ketones, diphenyl disulfide, and diphenyl diselenide to provide products of nucleophilic trifluoromethylation (Scheme 39).[167] In the case of aldehydes the main products are phosphates of trifluoromethyl carbinols.[167]



Scheme 39

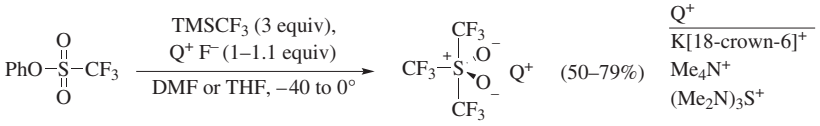
Carbon–Bismuth Bond Cleavage from Perfluoroalkyl Bismuth Reagents. Tris(trifluoromethyl)bismuth, prepared from $BiCl_3$ and $CF_3ZnBr{\bullet}2MeCN$, reacts smoothly with benzoyl chloride at room temperature using pyridine as the catalyst to afford trifluoroacetophenone in 69% yield.[168] Reaction of tris(trifluoromethyl)bismuth with $TMSCF_3$ in the presence of TMAF in diethyl ether at –70 to –50° affords tetrakis(trifluoromethyl)bismuthate $Me_4N^+[Bi(CF_3)_4]^-$ in nearly quantitative yield. At higher temperatures, the formation of $Me_4N^+[Bi(CF_3)_3F]^-$ is observed. Tetracoordinate anionic bismuth species are solids that are stable at low temperature in dry nitrogen and act as trifluoromethylating reagents toward pentafluoropyridine, Me_3SnCl, or SO_2Cl_2 even at –78° to afford 4-(trifluoromethyl)tetrafluoropyridine, Me_3SnCF_3 and CF_3SO_2Cl, respectively.[169]

Carbon–Sulfur Bond Cleavage from Perfluoroalkyl Sulfur Reagents. The germyl anion (R_3Ge^-) has a strong affinity toward the sulfur atom in $PhSCF_3$, causing

carbon–sulfur bond cleavage and generating the trifluoromethyl anionic species.[170] Temperature, solvent, steric effects, and the nature of the germyl salts are significant factors in this reaction. Under optimized reaction conditions a small excess of $PhSCF_3$ and Et_3GeNa is used in THF/HMPA at –60°. This process represents a very efficient and mild way of trifluoromethylating various aldehydes[170] and imines,[171] and chemoselectively transforming methyl esters into trifluoromethyl ketones.[172] Other functional groups such as longer alkyl esters, acetals, or epoxides are not affected.

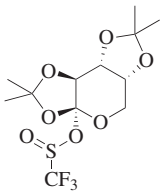
Aryl trifluoromethyl sulfones are known to undergo haloform-type reactions with metal alkoxides, Grignard, or organolithium reagents to afford sulfonates or sulfones and trifluoromethane.[173–175] Magnesium metal promotes reductive cleavage of the carbon–sulfur bond in trifluoromethyl sulfides, sulfoxides, and sulfones to generate anionic CF_3^- species, and various chlorosilanes are trifluoromethylated in this manner.[176] Phenyl trifluoromethyl sulfone upon reaction with magnesium metal activated by $HgCl_2$ causes direct trifluoromethylation of aldehydes[177] and Michael acceptors.[178] Non-enolizable aldehydes or ketones, imines, methyl benzoate, phenyl iodide (in the presence of CuI), and disulfides are trifluoromethylated by *t*-BuOK induced reaction with phenyl trifluoromethyl sulfoxide or sulfone.[179,180] Similar reactivity is observed with pentafluoroethyl phenyl sulfone in reactions with non-enolizable aldehydes, ketones, and imines.[180]

Hypercoordinate sulfuranide dioxide salts, prepared from phenyl triflate and $TMSCF_3$ (Scheme 40),[155] act as trifluoromethyl anion sources toward a variety of electrophilic compounds, such as benzaldehyde, Me_3SnCl, or SO_2Cl_2.

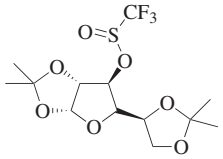


Scheme 40

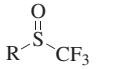
Trifluoromethanesulfinates **18–20** (derived from various protected carbohydrates) and trifluoromethanesulfinamides **21–23** (derived from secondary amines) are used as nucleophilic trifluoromethylating reagents toward non-enolizable aldehydes, ketones, and disulfides by the action of *t*-BuOK.[181]



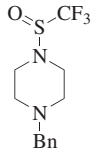
18



19

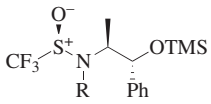


	R
20	BuO
21	Ph(Me)N
22	*n*-Bu_2N

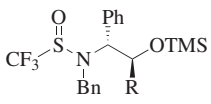


23

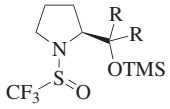
A number of trifluoromethanesulfinamides **24–30** are obtained by the reaction of chiral *O*-silylated amino alcohols with CF_3SOCl prepared from alkaline metal triflinates and $POCl_3$.[182] Mixtures of diastereoisomers with low to moderate diastereomeric ratios are typically obtained; however, enriched fractions of one diastereoisomer can be obtained by chromatographic separation.[42,182] Nonenolizable and enolizable carbonyl compounds are efficiently trifluoromethylated by the action of compounds **24–30** in the presence of fluoride initiators.[182]



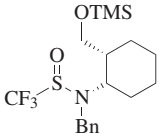
	R
24	Me
25	Bn



	R
26	H
27	Ph



	R
28	H
29	Ph

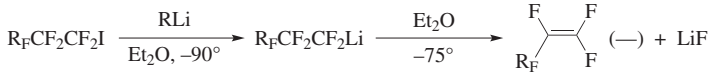


30

Carbon–Tellurium Bond Cleavage from Perfluoroalkyl Tellurium Reagents. Bis(trifluoromethyl)tellurium can be prepared from $TeBr_4$ and $Hg(CF_3)_2$ in 92% yield.[183] This compound can be fluorinated with XeF_2 and used for the preparation of $Te(CF_3)_4$, which is shown to form polymeric complex $[Te(CF_3)_3{\bullet}DMF(\mu\text{-}F)]_\infty$.[184,185] Tetrakis(trifluoromethyl)tellurium can also be prepared from $(CF_3)_2TeCl_2$ and $Cd(CF_3)_2$, and behaves as a polar as well as a radical trifluoromethylation agent.[186]

Perfluoroalkyl Organometallic Reagents.

Perfluoroalkyllithium Reagents. Perfluoroalkyllithiums are important and widely used nucleophilic perfluoroalkyl addition reagents. Direct preparation from perfluoroalkyl halides and lithium metal is not practical due to the low stability of the products.[187] Halogen–lithium exchange at low temperature is the most convenient method for the preparation of these reagents. Perfluoroethyl, perfluoropropyl, and several other long-chain perfluoroalkyllithium reagents are prepared by the reaction of the corresponding perfluoroalkyl halide with methyl, *n*-butyl, or phenyllithium in diethyl ether.[188−190] Most perfluoroalkyllithium reagents should be handled at –90° because of their low thermal stability: at –75° rapid β-fluoride elimination with the formation of perfluoroalkenes and LiF is observed (Scheme 41).[189] Cyclic perfluoroalkyllithium reagents are significantly more thermally stable. For example, perfluorobicyclo[2.2.1]hept-1-yllithium decomposes near ambient temperature.[191−194]



Scheme 41

The majority of perfluoroalkyl addition reactions are carried out either by rapid generation of the perfluoroalkyllithium reagents immediately followed by capture with an appropriate electrophile, or using Barbier-type reaction conditions, wherein perfluoroalkyl halide, alkyllithium, and electrophile are mixed simultaneously.

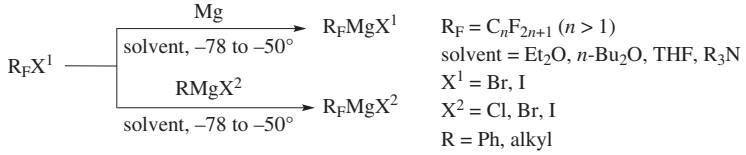
Generation of perfluoroalkyllithium reagents from hydroperfluoroalkanes by deprotonation with alkyllithium reagents does not have significant application in synthesis because of the poor availability of hydroperfluoroalkanes. However, such protocols exist and allow preparation of perfluoroalkyllithium reagents in quantities sufficient to provide good yields in reactions with various electrophiles.[128,195,196]

Additions of perfluoroalkyllithium reagents to carbonyl compounds proceed in good yields when the nucleophilic reagent is prepared using two equivalents of perflurooalkyl iodide. Using lower amounts of perfluoroalkyl iodides decreases the product yield, and with one equivalent no product is formed. These observations suggest $(R_F)_2I^-Li^+$ to be the true nucleophilic perfluoroalkyl addition reagents.[197]

A recent report demonstrates the effective generation of R_FLi species using a flow microreactor system with one equivalent of perfluorinated reagent.[198] The in situ trapping with an electrophile can be conducted at much higher temperatures than those required for batch macroreactors. However, trifluoromethyllithium cannot be prepared by either of the methods described above, due to its rapid decomposition to difluorocarbene even at low temperatures.[188]

Perfluoroalkylmagnesium Reagents. Trifluoromethylmagnesium iodide can be formed by the reaction of CF_3I and Mg.[199] However, this method has found no significant application in synthesis due to rapid decomposition and low yields of the trifluoromethyl-containing products.

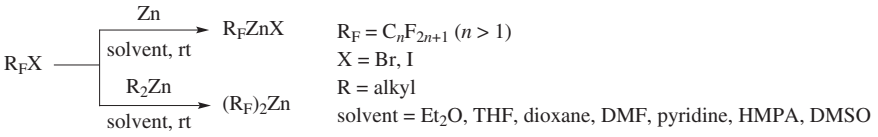
In contrast, higher perfluoroalkylmagnesium reagents are highly useful organometallic perfluoroalkyl nucleophiles. They are more thermally stable and slightly less reactive than perfluoroalkyllithium reagents. Direct preparation by the reaction of perfluoroalkyl bromides or iodides and magnesium metal provides good yields of the corresponding Grignard reagents.[200−204] The best results are obtained when magnesium free of traces of other metals is used. The most common solvents are diethyl ether, dibutyl ether, THF, and rarely, tertiary amines. Alternatively, halogen–MgX exchange is an excellent method for the preparation of perfluoroalkyl Grignard reagents.[205−207] The exchange proceeds rapidly and quantitatively at low temperatures and the choice of solvent and temperature is very important (Scheme 42). For instance, *n*-$C_8F_{17}MgBr$ in diethyl ether shows only 3% decomposition at –70° after 20 hours, but in THF, 41% decomposition is observed under the same conditions. At –40°, 39% and 89% of *n*-$C_8F_{17}MgBr$ decomposes in diethyl ether and THF, respectively.[207,208] The stability of perfluoroalkyl Grignard reagents generally increases in more dilute solutions. Some bicyclic perfluoroalkyl Grignard reagents are stable at 30°.[194]



Scheme 42

Perfluoroalkylcalcium Reagents. The preparation of perfluoroalkylcalcium reagents from perfluoroalkyl iodides and Ca/Hg has been reported several times.[209–211] Barbier-type conditions are employed using THF, dioxane, or diethyl ether as solvents at –20 to –40°. Addition of perfluoroalkylcalcium reagents to carbonyl compounds proceeds in only low to moderate yields.[210]

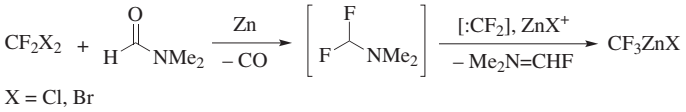
Perfluoroalkylzinc Reagents. Perfluoroalkylzinc reagents [R_FZnX and $(R_F)_2Zn$] are widely used perfluoroalkyl addition reagents that display lower reactivity and better stability than perfluoroalkyllithium or Grignard reagents. Reaction of zinc metal with perfluoroalkyl halides produces stable solutions of R_FZnX. Common solvents are THF, dioxane, DMF, pyridine, HMPA, or their combinations (Scheme 43).[212,213] Satisfactory results are obtained when trifluoromethylzinc is prepared from CF_3I and zinc metal at –20° to ambient temperature range.[214–216] Isolation of pure non-solvated perfluoroalkylzinc is possible by vacuum sublimation;[217] however, such compounds usually display low stability.[218]



Scheme 43

Bis(perfluoroalkyl)zinc can be obtained via the reaction of perfluoroalkyl iodides with dialkylzincs. This method works quantitatively for CF_3I, and can also be employed for the preparation of higher bis(perfluoroalkyl)zincs (Scheme 43).[219]

Dihalodifluoromethanes react with zinc in DMF to form CF_3ZnX.[220] Apart from being a solvent, DMF also reacts with the intermediate difluorocarbene, which forms as a result of single electron transfer mechanism, eventually producing the bis(trifluoromethyl) zinc reagent (Scheme 44).[220] Using THF as the solvent results in the formation of difluorocarbene.[221]



Scheme 44

The $Zn(CF_3)_2$•2EtCN complex is obtained in 66% yield by the transmetalation reaction between zinc and trifluoromethylsilver at 0°.[154] Transmetalation between Me_2Zn and $MeTeCF_3$ or $Te(CF_3)_2$ in DME has been observed. Depending on the reagent used and stoichiometry, $MeZnCF_3$•DME or $Zn(CF_3)_2$•DME complexes can be prepared quantitatively.[222]

Perfluoroalkylcadmium Reagents. Perfluoroalkylcadmium reagents (R_FCdX and $(R_F)_2Cd$) can be prepared in situ by the rapid exothermic reaction between

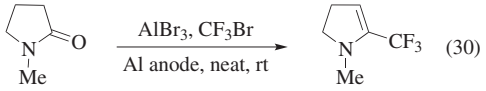
perfluoroalkyl halides and cadmium powder in DMF at room temperature.[223] This reaction provides access to a mixture of mono- and bis(perfluoroalkyl)cadmium reagents in good yields. The choice of solvent is crucial. Only the dimer of the perfluoroalkyl halide is formed if acetonitrile is used. Generally the reaction improves as the electron-donating ability of the solvent increases. This observation is consistent with a single-electron transfer mechanism where non-bonding pairs of solvent participate in stabilizing the initially formed perfluoroalkyl radicals.[224]

Perfluoroalkylcadmium reagents are also prepared in pyridine or diglyme by the metathesis reaction between dialkylcadmium and $(CF_3)_2Hg$, formed by pyrolysis of mercury trifluoroacetate in the presence of anhydrous potassium carbonate.[225] Because of an unfavorable equilibrium, an excess of $(CF_3)_2Hg$ is required to obtain good yields of $(CF_3)_2Cd$.[226] Transmetalation between Me_2Cd and $MeTeCF_3$ or $Te(CF_3)_2$ in DME is also reported.[222]

Exchange between dialkylcadmium and perfluoroalkyl iodides provides access to bis(perfluoroalkyl)cadmium reagents in excellent yields.[227,228] This reaction can be carried out in donor solvents such as glymes, pyridine, acetonitrile, and TMEDA. The stable complexes $(CF_3)_2Cd$•DME and $(CF_3)_2Cd$•MeCN are useful as trifluoromethylating reagents in reactions with various electrophiles.[229–231] bis(Perfluoroalkyl)cadmium reagents can also be obtained in good yields by transmetalation with CF_3Ag at 0° to room temperature.[154]

Electrochemical generation of CF_3MBr (M = Zn, Cd) from CF_3Br with the corresponding sacrificial electrode has been reported.[123] In the case of a Zn electrode, deposition of the metal is the preferred cathodic process and generation of the observed CF_3ZnBr occurs later.[232,233] Similarly, formation of CF_3CdBr occurs by the reaction of deposited Cd with CF_3Br,[123] which is consistent with previous reports.[227,234]

The use of an aluminum anode for electrolysis of CF_3Br in NMP does not result in the formation of trifluoromethylaluminum species, but proves to be an effective electrochemical process for direct trifluoromethylation of various chlorosilanes.[123] Electrolysis in NMP without chlorosilanes results in addition of a trifluoromethyl group to the amide carbonyl (Scheme 45).[123] Simple heating of CF_3Br in NMP, DMF, or DMA with aluminum powder also results in formation of $TMSCF_3$ in good yields.[123]

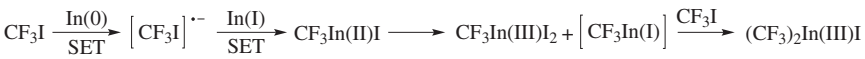


(30)

Scheme 45

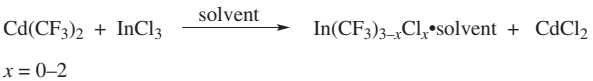
Perfluoroalkylindium Reagents. Trifluoromethylindium, which finds limited application in nucleophilic additions to carbonyl compounds, can be prepared by several methods. Trifluoromethylindium reagents are prepared directly from CF_3I by using one equivalent of indium, LiCl or NaI, and ferrocene (Scheme 46).[235] Ferrocene is the SET reagent participating in the first two steps of the reaction

sequence, and LiCl or NaI accelerates the rate-limiting oxidation of In(I) to In(II) step.



Scheme 46

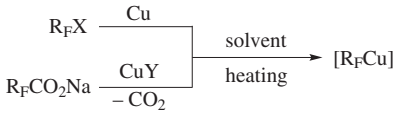
In polar solvents such as acetonitrile, DMSO, DMF, THF, and pyridine, indium trichloride undergoes exchange with $(CF_3)_2Cd$ to produce trifluoromethylindium species (Scheme 47).[236] In acetonitrile and DMF/CH_2Cl_2 mixtures, $In(CF_3)_3$•2MeCN and $In(CF_3)I$•DMF can be obtained selectively by varying the stoichiometry of the reagents. Interestingly, when carried out in DMSO, a trifluoromethylated sulfoxide is formed as a side product by methyl–trifluoromethyl exchange between the trifluoromethylindium species and DMSO.[236]



x = 0–2
solvent = DMSO, THF, MeCN, DMF, pyridine

Scheme 47

Perfluoroalkylcopper Reagents. Perfluoroalkylcopper reagents are perhaps the most popular perfluoroalkyl organometallic nucleophiles. These reagents are prepared by a direct reaction between perfluoroalkyl halides and excess copper metal at elevated temperatures in solvents such as DMSO, pyridine, DMF, DMA, HMPA, and less often, PhCN, MeCN, NMP, or dimethylurea (Scheme 48).[51] The electron-donating ability of the solvent is important for perfluoroalkylcopper species to display nucleophilic character.[237] Nucleophilic trifluoromethylation with CF_3Cu generated from CF_3I and copper metal is also described.[52,53]

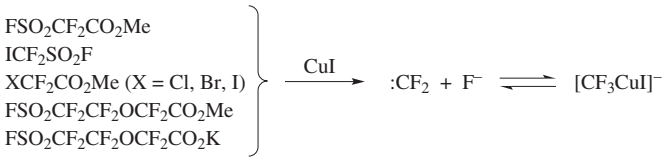


X = Br, I
Y = Cl, Br, I
solvent = DMSO, DMF, DMA, pyridine, HMPA, NMP

Scheme 48

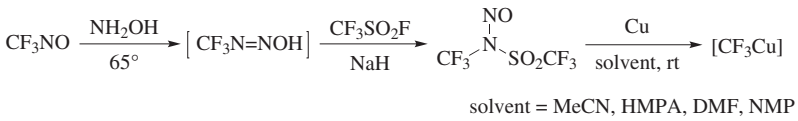
Another approach to the preparation of perfluoroalkylcopper reagents is the decarboxylation of perfluorocarboxylates in the presence of Cu(I) salts (Scheme 48).[58,59,238–241] Usually, the perfluoroalkyl carboxylate, Cu(I) halide, and substrate are mixed together and heated in a solvent mentioned above. This method works for the generation of CF_3Cu; however, a minimum 2-fold excess of the trifluoroacetate/Cu(I) reagent is needed to achieve reasonable yields.

Several other methods for the generation of CF_3Cu species have been reported and used in organic synthesis. These methods usually include in situ generation of trifluoromethylcopper from such precursors as XCF_2CO_2Me (X = Cl, Br, I),[242–248] $FSO_2CF_2CF_2OCF_2CO_2K$,[247] $FSO_2CF_2CF_2OCF_2CO_2Me$,[247,249] $FSO_2CF_2CO_2Me$,[247,248,250–258] FSO_2CF_2I,[259] and CF_3SO_2Cl.[260] Most of these precursors generate difluorocarbene and fluoride anion, which establish an equilibrium with CF_3^-. In the presence of CuI, the equilibrium is readily shifted to $[CF_3CuI]^-$, which then reacts with organic halides to afford products of trifluoromethylation (Scheme 49). Example applications of these reagents can be found in the sections describing perfluoroalkyl addition to alkenyl, aryl, and heteroaryl halides and pseudohalides.



Scheme 49

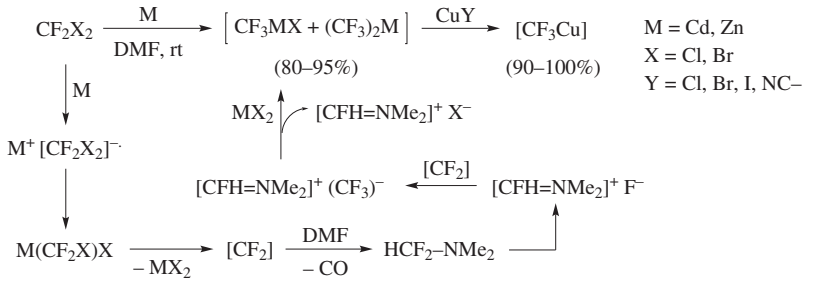
Heating of $(CF_3)_2Hg$ and copper metal in NMP or DMA at 140° provides CF_3Cu,[261] but because of the toxicity of $(CF_3)_2Hg$ this approach is not used extensively. The thermally unstable *N*-trifluoromethyl-*N*-nitrosotrifluoromethanesulfonamide reacts with activated copper in MeCN, HMPA, DMF, or NMP at room temperature to yield CF_3Cu species (Scheme 50).[262]



Scheme 50

Perfluoroalkylcopper species can also be accessed by metathesis of other perfluoroalkylorganometallics with copper metal or copper(I) salts. For instance, successful preparation of R_FCu has been reported from R_FZnX[263–266] and R_FCdX.[266–272] The limited use of R_FLi and R_FMgX in these reactions is due to their low thermal stability.

The reaction of dihalomethanes with Cd or Zn in DMF at ambient temperature generates CF_3MX, which undergoes a metathesis reaction with Cu(I) halides. Trifluoromethylzinc halide reagents participate in this metathesis reaction at room temperature; CF_3CdX reacts more readily and gives access to CF_3Cu species at –40° (Scheme 51).[273] This reaction proceeds by formation of difluorocarbene, which is trapped by DMF, releasing fluoride ion and carbon monoxide. The fluoride anion then reacts with difluorocarbene and CuX to form $[CF_3Cu]$.



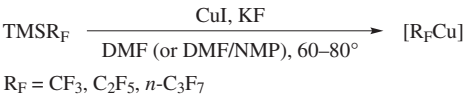
Scheme 51

Solutions of CF_3Cu in DMF tend to slowly decompose to C_2F_5Cu at room temperature, but solutions in DMF/HMPA (1:1) do not decompose.[264,273] At higher temperatures, trifluoromethylcopper in DMF is transformed into higher perfluoroalkylcopper species (Scheme 52), but addition of potassium fluoride or charcoal to the reaction mixture suppresses this oligomerization.[9,274] Addition of $Et_3N{\bullet}(HF)_3$ or $Py{\bullet}(HF)_n$ is currently widely used to stabilize perfluoroalkylcopper species.[56,57]



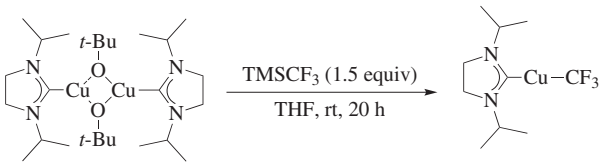
Scheme 52

Trifluoromethyl-, pentafluoroethyl-, and heptafluoropropylcopper species can also be generated in situ by reaction between (perfluoroalkyl)trimethylsilanes and CuI in the presence of a fluoride anion source (Scheme 53).[275]



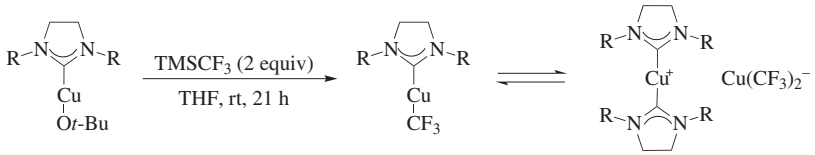
Scheme 53

More detailed investigations on the nature of trifluoromethylcopper reveal that reaction of $TMSCF_3$ with spray-dried KF and CuBr in DMF or DMI (1,3-dimethyl-2-imidazolidinone) at 0° generates a stable solution of the species: $CF_3Cu{\bullet}KBr$, $[(CF_3)_2Cu]^-K^+$, and $[(CF_3)_4Cu]^-K^+$, identified by NMR spectroscopy.[276] The well-defined Cu(I)–CF_3 complex **32** is prepared in situ from *tert*-butoxy copper complex **31** and $TMSCF_3$ (Scheme 54), and is used for the trifluoromethylation of benzyl bromide or aryl iodides at room temperature.[277] In the case of analog **33**, an equilibrium with cuprate salt **34** is observed (Scheme 55).[278]



31 **32** (91%)

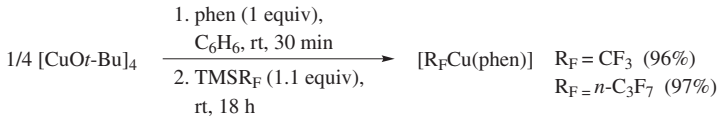
Scheme 54



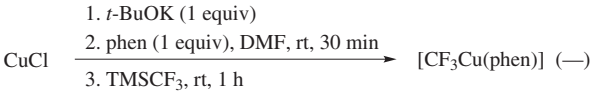
R = 2,4,6-$Me_3C_6H_2$ **33** **34** (67%)

Scheme 55

Hartwig reports the preparation of trifluoromethyl- and perfluoropropylcopper complexes stabilized by 1,10-phenanthroline, [R_FCu(phen)], which react with both electron poor and electron rich aryl iodides (Scheme 56 and Scheme 57).[54] Use of the trifluoromethyl version of this reagent has become a convenient method for the trifluoromethylation of aromatic and heteroaromatic systems.[54] The complex can be prepared in situ from CuCl or from [CuO*t*-Bu]$_4$ and stored under an inert gas without losing activity.

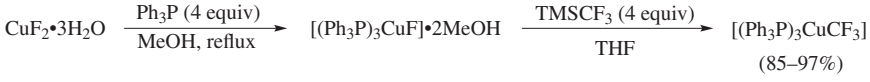


Scheme 56



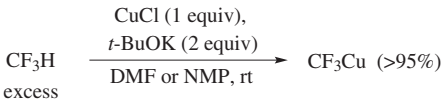
Scheme 57

Simple preparations of well-defined [$(Ph_3P)_3CuCF_3$] and [(phen)$(PPh_3)CuCF_3$] complexes are reported by Grushin.[55] These triphenylphosphine complexes are easily prepared from CuF_2•$3H_2O$ and $TMSCF_3$ (Scheme 58),[55] and readily transfer a trifluoromethyl group to iodoarenes under mild conditions.

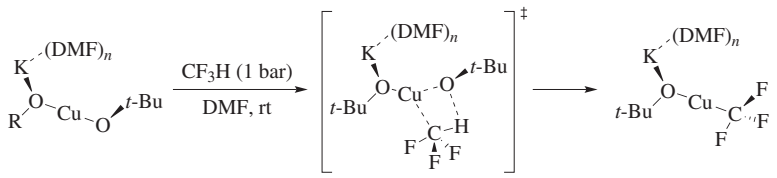


Scheme 58

Direct formation of CF_3Cu species from fluoroform can be achieved under mild conditions using CuCl and *t*-BuOK in DMF or NMP.[56] This cupration of fluoroform proceeds via alkoxycuprates, which readily react with fluoroform at room temperature and atmospheric pressure to provide CF_3Cu species rapidly and in high yield (Scheme 59).[56] Importantly, the reaction does not generate observable quantities of $[CF_3CH(O)NMe_2]^-$, which is well known to form when CF_3^- is generated in DMF. Performing the cupration in the presence of styrene does not afford products of carbene addition across the double bond, indicating that the reaction is not mediated by difluorocarbene. A pronounced concentration effect on the stability of CF_3Cu is observed: CF_3Cu decays more rapidly at higher concentrations, suggesting that the decomposition is unlikely to be a unimolecular process. The true reactive complex seems to be $[K(DMF)][(t\text{-}BuO)_2Cu]$, wherein the role of the counterion is crucial. Rather, both experimental and computational studies indicate that the cupration process is governed by a unique mechanism that involves synchronous carbon–hydrogen bond cleavage and Cu–CF_3 bond formation with electrophilic assistance from the alkali-metal counterion (Scheme 60).[57]

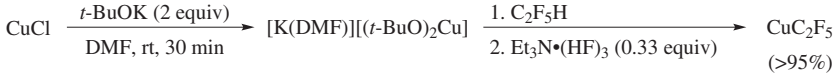


Scheme 59



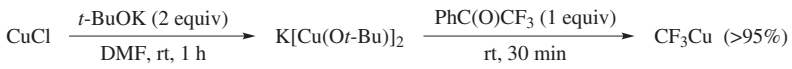
Scheme 60

Similar to fluoroform, pentafluoroethane reacts directly with the CuCl/*t*-BuOK system or with pregenerated $[K(DMF)][(t\text{-}BuO)_2Cu]$ to afford $[K(DMF)_2][(t\text{-}BuO)Cu(C_2F_5)]$ in nearly quantitative yield.[279] Interestingly, higher perfluoroalkyls cannot be transfered onto copper in the same fashion. Perfluoroethyl copper species are more stable than CF_3Cu, allowing isolation of the complex and determination of its X-ray crystal structure (Scheme 61).[279]



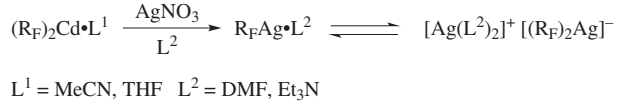
Scheme 61

One of the recent protocols to prepare CF_3Cu employs trifluoromethyl phenyl ketone and $K[Cu(Ot\text{-}Bu)_2]$ in DMF at room temperature (Scheme 62).[280] Trifluoromethylcopper prepared via this method should be stabilized with $Et_3N{\bullet}(HF)_3$.[280]



Scheme 62

Perfluoroalkylsilver Reagents. Reaction of silver fluoride with perfluoropropene in acetonitrile at room temperature affords perfluoro-*iso*-propylsilver, isolated as a stable complex with acetonitrile.[281] Trifluoromethylsilver is quantitatively formed in the reaction of silver fluoride with $TMSCF_3$.[154,282] Perfluoroalkylsilver reagents ($R_F = CF_3$, C_2F_5, *n*-C_3F_7, *i*-C_3F_7, *n*-C_4F_9) can also be prepared by the reaction of bis(perfluoroalkyl)cadmium with silver nitrate in DMF or Et_3N. The product exists in an equilibrium shifted to the dissociated form in DMF and to the associated form in Et_3N at –30°,[283,284] (Scheme 63).[283] The trifluoromethylsilver complex $[Ag(CF_3)_4]^-$ is formed in the reaction of $(CF_3)_2Cd$ with silver nitrate in acetonitrile.[285] Perfluoroalkylsilver reagents are rarely used in organic synthesis.[154,282]



Scheme 63

Table A summarizes the preparation of the most comon and synthetically useful organometallic perfluoroalkyl addition reagents.

Perfluoroalkyl Addition to Carbon Electrophiles

Alkenes. Simple olefins are unreactive toward nucleophilic perfluoroalkyl additions. Even reactive Michael acceptors such as arylidenemalonates do not react with $TMSCF_3$. However, more electron-deficient arylidenemalonitriles or arylidene or alkylidene Meldrum's acids undergo efficient conjugate additions of $TMSCF_3$ or $TMSC_2F_5$ in the presence of excess sodium acetate in DMF (Schemes 64 and 65, respectively).[133,286] In the case of Meldrum's acid derivatives, the trifluoromethylation with $TMSCF_3$ has to be performed at elevated temperature. Heating the addition product with an acid causes hydrolysis of the 1,3-dioxane moiety and concomitant decarboxylation to acid **35** which for isolation purposes is esterified to **36** or reduced to alcohol **37** (Scheme 65).[286] Similarly, 2-nitrocinnamates undergo perfluoroalkylation with $TMSCF_3$ or $TMSC_2F_5$ (Scheme 66).[287] The product diastereomeric ratio is generally low and does not depend on the configuration of the starting 2-nitrocinnamates. Nucleophilic trifluoromethylation of arylidenemalononitriles (Scheme 67)[178] and arylidene Meldrum's acids (Scheme 68)[178] with phenyl trifluoromethyl sulfone and magnesium metal with small amounts of $HgCl_2$ affords products of 1,4-addition in moderate to good yields. Acrylonitrile also undergoes

Table A. Summary of the Preparation of Common Perfluoroalkyl Organometallics

Entry	R_FM	Preparation	Solvent(s)	Temp.
1	R_FLi	$R_FX + RLi$ $R_F = C_nF_{2n+1}$ ($n > 1$), R = Me, Bn, Ph, X = Br, I	Et_2O	$\leq -78°$
2	R_FLi	$R_FH + RLi$ $R_F = C_2F_5$, *n*-C_3F_7, *i*-C_3F_7, R = Me, *n*-Bu	Et_2O	$\leq -78°$
3	R_FMgX	$R_FX + Mg$ $R_F = C_nF_{2n+1}$ ($n \geq 1$), X = Br, I	ethers	$<0°$
4	R_FMgX	$R_FY + RMgX$ $R_F = C_nF_{2n+1}$ ($n \geq 1$), Y = Br, I R = Ph, alkyl, X = Cl, Br, I	ethers	$<0°$
5	$R_FZnX/(R_F)_2Zn$	$R_FX + Zn$ $R_F = C_nF_{2n+1}$ ($n \geq 1$), X = Br, I	ethers, py, DMF, HMPA, DMSO	various
6	$R_FZnI/(R_F)_2Zn$	$R_FI + R_2Zn$ $R_F = C_nF_{2n+1}$ ($n \geq 1$)	ethers, py, DMF, HMPA, DMSO	various
7	CF_3Zn	$CF_2XY + Zn$ X, Y = Cl, Br	DMF	rt

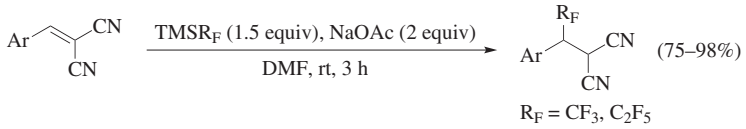
8	$R_FCdX/(R_F)_2Cd$	$R_FX + Cd$ $R_F = C_nF_{2n+1}$ ($n \geq 1$), X = Br, I	DMF, DMSO	rt
9	$R_FCdI/(R_F)_2Cd$	$R_FI + R_2Cd$ $R_F = C_nF_{2n+1}$ ($n \geq 1$), R = alkyl	glymes, MeCN, py, TMEDA	−10° to rt
10	$(CF_3)_2Cd$	$(CF_3)_2Hg + R_2Cd$, R = alkyl	diglyme, py	34°
11	R_FCu	$R_FX + Cu$ $R_F = C_nF_{2n+1}$ ($n \geq 1$), X = Br, I	DMSO, DMF, DMA, py, HMPA	heating
12	R_FCu	$R_FCO_2M + CuX$ $R_F = C_nF_{2n+1}$ ($n \geq 1$), X = Cl, Br, I	DMSO, DMF, HMPA, NMP	heating
13	CF_3Cu	$XCF_2CO_2Me + CuI + KF$ X = Cl, Br, I	DMF, HMPA	heating
14	CF_3Cu	$FSO_2CF_2CF_2OCF_2CO_2K + CuI$	DMF, HMPA, NMP	heating
15	CF_3Cu	$FSO_2CF_2CF_2OCF_2CO_2Me + CuI$	DMF	heating
16	CF_3Cu	$FSO_2CF_2CO_2Me + CuI$	DMF, DMSO	heating
17	CF_3Cu	$FSO_2CF_2I + Cu$	DMF	heating

(*continued*)

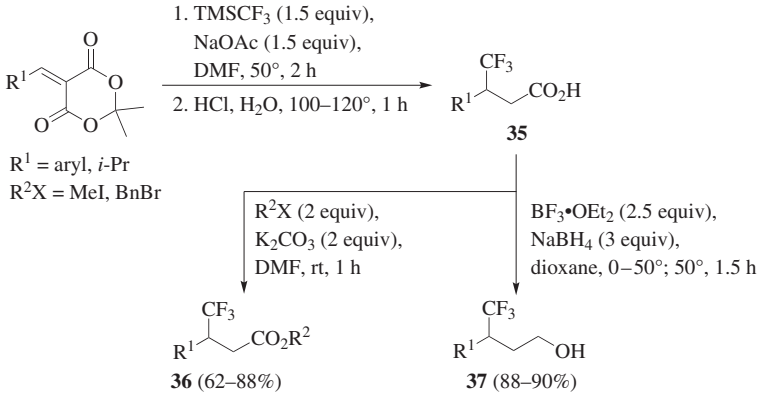
Table A. (*Continued*)

Entry	R_FM	Preparation	Solvent(s)	Temp.
18	R_FCu	$R_FTMS + CuI + KF$ $R_F = C_nF_{2n+1}$ ($n \geq 1$)	DMF, NMP	60–80°
19	$(Ph_3P)_3CuCF_3$	$TMSCF_3 + CuF_2 \cdot 3H_2O + PPh_3$	THF	rt
20	$(phen)CuR_F$	$R_FTMS + (CuOt\text{-}Bu)_4 + phen$ $R_F = CF_3$, $n\text{-}C_3F_7$	benzene	rt
21	$(phen)CuCF_3$	$TMSCF_3 + CuCl + phen + K^+ t\text{-}BuO^-$	DMF	rt
22	CF_3Cu	$PhC(O)CF_3 + K[Cu(Ot\text{-}Bu)]_2$	DMF	rt
23	CF_3Ag	$TMSCF_3 + AgF$	DMF, RCN	rt
24	R_FAg	$(R_F)_2Cd + AgNO_3$ $R_F = CF_3$, C_2F_5, $n\text{-}C_3F_7$, $i\text{-}C_3F_7$, $n\text{-}C_4F_9$	DMF, Et_3N	–30°

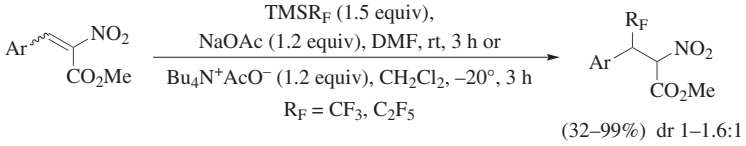
perfluoro *tert*-butyl group addition using $(CF_3)_3CH$ in the presence of small amounts of Et_3N (100°, 77 h) in 66% yield.[85,86]



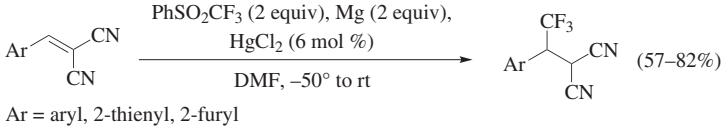
Scheme 64



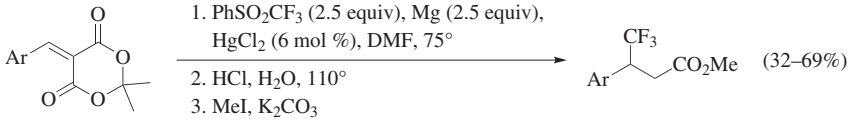
Scheme 65



Scheme 66



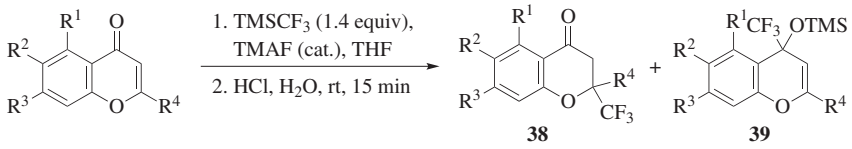
Scheme 67



Scheme 68

Trifluoromethylations of α,β-unsaturated aldehydes, ketones, and esters, such as acrolein, 3-methyl-2-butenal, 2-butenal, 4-methyl-3-penten-2-one, PhCH=CHC(O)R (R = H, Me, OMe, CF_3, Ph), 2-cyclohexenone, 1-(1-cyclohexen-1-yl)-1-ethanone, and 1,4-benzoquinone, with $TMSCF_3$ and a fluoride source are reported to proceed exclusively with 1,2-addition.[15–17] However, in other reports, 1,4-addition products are also observed in ≤10% yield for 2-cyclohexenone and 3-methyl-2-cyclohexenone.[288,289] Highly site-selective 1,4-trifluoromethylation of 2-cyclohexenone is achieved by blocking the carbonyl moiety with a bulky aluminum-centered Lewis acid such as aluminum tris(2,6-diphenylphenoxide).[290]

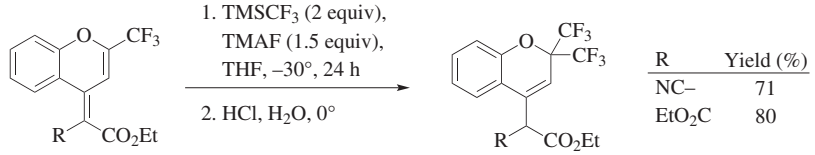
Reactions of 2-perfluoroalkylchromones[291–293] (Scheme 69),[292] 3-arylchromones,[258] quinolones,[291,292] and coumarins[290] with (perfluoroalkyl)trimethylsilanes proceed as 1,4-perfluoroalkylations (product **38**). Thiochromones, on the other hand, afford predominantly 1,2-addition products (analogous to product **39**, Scheme 69).[292]



						Yield (%)	
R^1	R^2	R^3	R^4	Temp (°)	Time (h)	**38**	**39**
H	H	H	CF_3	–10	4	86	11–12
H	Me	H	CF_3	–10	4	61	11–12
H	MeO	H	CF_3	–30	24	76	—
H	H	MeO	CF_3	–30	24	67	—
H	MeO	H	CF_2H	–30	24	50	—
MeO	H	MeO	CF_3	–30	24	64	—

Scheme 69

The condensation products of 2-trifluoromethylchromone with ethyl cyanoacetate or diethyl malonate undergo nucleophilic 1,6-addition with $TMSCF_3$ (Scheme 70).[294]

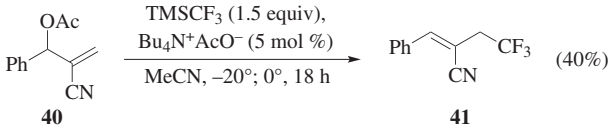


R	Yield (%)
NC–	71
EtO_2C	80

Scheme 70

Morita–Baylis–Hillman adducts react inefficiently with $TMSCF_3$ in simple S_N2' allylic substitution.[295] Nitrile **40** affords allylic substitution product **41** in moderate yield (Scheme 71)[295] and when ester or keto substituents are used instead of the cyano

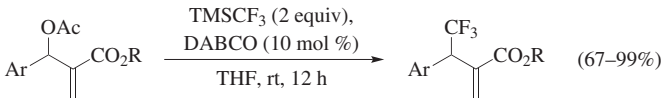
group, attack of $TMSCF_3$ is observed preferentially on the carbonyl group over the carbon–carbon double bond.



40 **41**

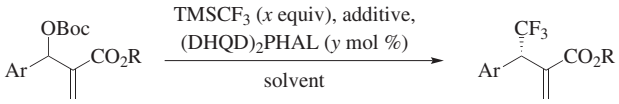
Scheme 71

On the other hand, in the presence of substoichiometric amounts of tertiary amines such as DABCO, the Morita–Baylis–Hillman adducts undergo trifluoromethylation with $TMSCF_3$ via sequential S_N2'/S_N2'substitutions in high yields (Scheme 72).[296] The reaction can be extended to enantioselective allylic trifluoromethylations with high er's by the use of a bis-cinchona alkaloid catalyst (Scheme 73).[296,297]



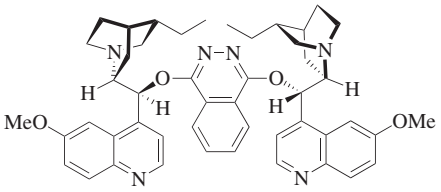
R = Me, *t*-Bu

Scheme 72



R = Me, *t*-Bu

x	Additive	*y*	Solvent	Temp (°)	Time (h)	Yield (%)	er
2.5	KF (10 mol %)	0.15	DME/MeCN	rt	48–120	32–86	74.0:26.0 to 97.0:3.0
5	—	0.1	THF	60	120	37–60	94.0:6.0 to 97.0:3.0

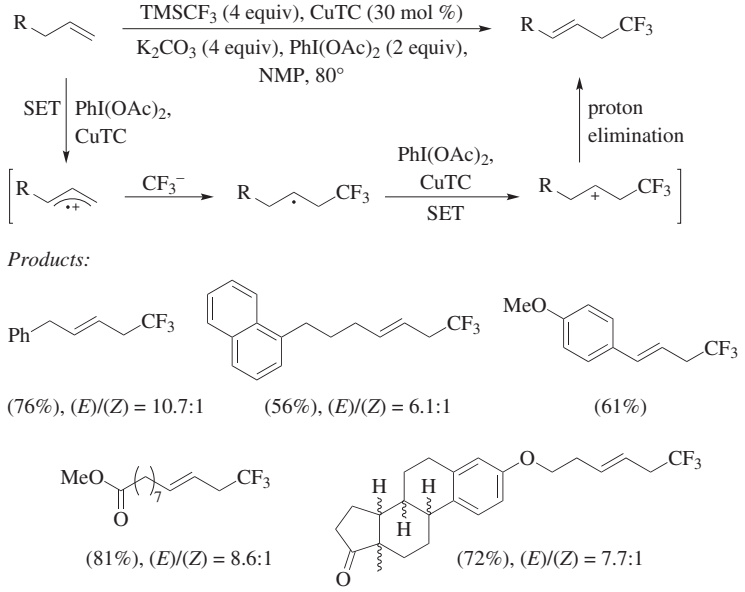


$(DHQD)_2PHAL$

Scheme 73

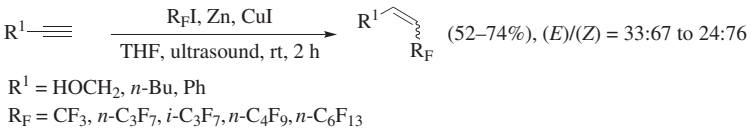
An interesting variation of formal nucleophilic allylic trifluoromethylation is reported using a $CuI/TMSCF_3$ system with $PhI(OAc)_2$ as oxidant for terminal alkenes. In this process $PhI(OAc)_2$ oxidizes the alkene double bond to the radical cation, which undergoes nucleophilic addition of trifluoromethyl anion and produces

a radical species. A second oxidation by $PhI(OAc)_2$ produces the cation, which is deprotonated to give rise to the formal product of allylic nucleophilic displacement with CF_3 (Scheme 74).[298]



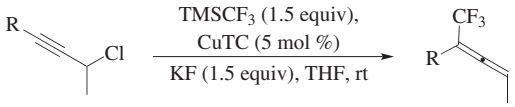
Scheme 74

Alkynes. Ultrasound-promoted perfluoroalkyl additions of perfluoroalkylcopper species, formed in situ from perfluoroalkyl iodides and zinc in the presence of CuI in THF, to terminal alkynes proceeds smoothly and in good yields. These reactions show moderate selectivity in favor of (*Z*)-products[299,263] (Scheme 75).[263]



Scheme 75

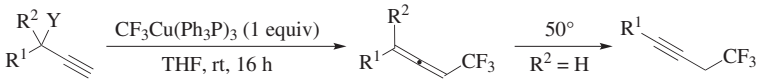
Propargylic halides and tosylates undergo addition–elimination reactions with perfluoroalkylcopper reagents to provide perfluoroalkyl allenes in good yields.[267,300,301] Secondary propargylic chlorides afford trifluoromethylated allenes from $TMSCF_3$ under catalysis by copper(I) thiophene-2-carboxylate (CuTC) (Scheme 76).[302] An enantiomerically enriched secondary propargylic chloride affords a racemic trifluoromethyl allene. Primary propargylic chlorides, on the other hand, afford the corresponding propargylic trifluoromethylated products.[302]



R	Temp (°)	Time (h)	Yield (%)
Ph	60	20	89
4-ClC_6H_4	60	20	81
4-$MeOC_6H_4$	40	48	77
4-MeC_6H_4	60	20	79
$Ph(CH_2)_2$	60	20	71

Scheme 76

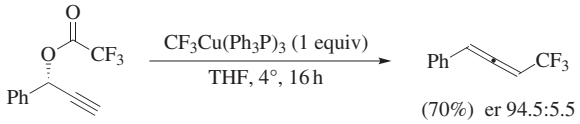
Secondary propargylic halides and trifluoroacetates react efficiently with the $CF_3Cu(Ph_3P)_3$ complex to provide trifluoromethylated allenes. Under mild heating these compounds rearrange to propargylic CF_3 derivatives (Scheme 77).[303] Furthermore, enantiopure trifluoromethyl allenes can be obtained from trifluoroacetates of chiral propargylic alcohols (Scheme 78).[303]



R^1 = aryl, alkyl
R^2 = H, alkyl
Y = Cl, Br, CF_3CO_2

(52–92%)

Scheme 77



er 95:5

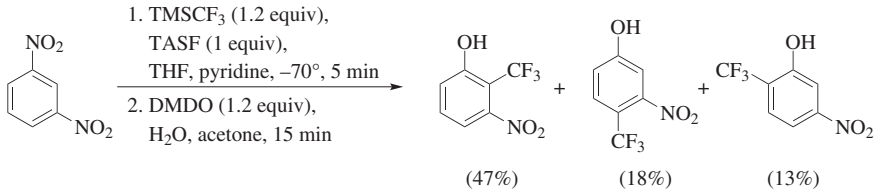
(70%) er 94.5:5.5

Scheme 78

Perfluoro *tert*-butyl addition, from $(CF_3)_3CH$ and catalytic amounts of Et_3N, to dimethyl 2-butynedioate and 1-phenylpropynone have been described.[88]

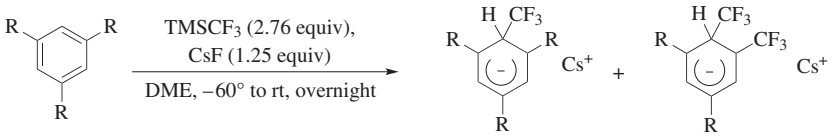
Arenes. Nucleophilic addition of perfluoroalkyl groups to aromatic rings is not common; however, electron-deficient arenes can be attacked by nucleophilic perfluoroalkyl species. Aromatic nitro and cyano groups are readily exchanged for trifluoromethyl using $TMSCF_3$ under different conditions. Pentafluoronitrobenzene reacts with $TMSCF_3$ and one equivalent of TBAF in THF at 0° to afford octafluorotoluene and bis(trifluoromethyl)tetrafluorobenzene in a ratio of 9:1.[17,304] Trifluoromethylation of 1,2-dinitrobenzene with $TMSCF_3$/KF in

DMA provides 2-nitrotrifluorotoluene (16%).[305,306] Under the same conditions, 1,3-dinitrobenzene yields a mixture of products arising from trifluoromethyldenitration, protodenitration, and direct trifluoromethylation. Similar reactions occur with 3,5-dinitrobenzonitrile. 2-Nitrobenzonitrile affords 2-trifluoromethylbenzonitrile (10%) and 2-nitrotrifluorotoluene (5%). 4-Nitrobenzonitrile yields 4-trifluoromethylbenzonitrile (7%) and traces of the trifluoromethyldecyanation product. 2-Chloro-6-nitrobenzonitrile affords the trifluoromethyldenitration product (51%) and the trifluoromethyldecyanation product (20%).[305,306] Electron-deficient nitroarenes can be trifluoromethylated with $TMSCF_3$ in the presence of TASF to produce σ^H adducts, which are subsequently oxidized with dimethyldioxirane (DMDO) to form substituted trifluoromethyl phenols (Scheme 79).[307] A σ^H adduct is the product formed by the attachment of an electrophilic or nucleophilic entering group or of a radical to a ring carbon of an aromatic species so that a new σ-bond is formed and the original conjugation is disrupted.

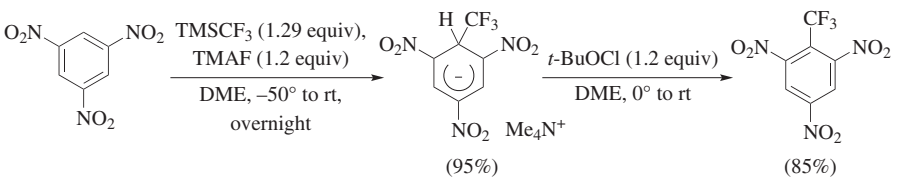


Scheme 79

Good yields of products of nucleophilic addition of CF_3 to 1,3,5-electron-acceptor-substituted benzenes are obtained using $TMSCF_3$ and CsF or TMAF. In some cases, side-products of *ipso*-substitution are observed, such as products **42** and **43** in Scheme 80.[308] With 1,3,5-trinitrobenzene the stable σ-adduct is formed in high yield and can be oxidized to 1,3,5-trinitrobenzotrifluoride (Scheme 81).[308]

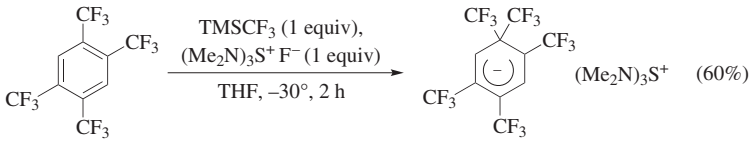


Scheme 80



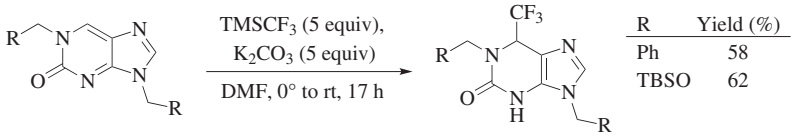
Scheme 81

The reaction of 1,2,4,5-tetrakis(trifluoromethyl)benzene with $TMSCF_3$ and TASF affords a stable delocalized carbanion salt (mp 19°) in 60% yield (Scheme 82).[309]



Scheme 82

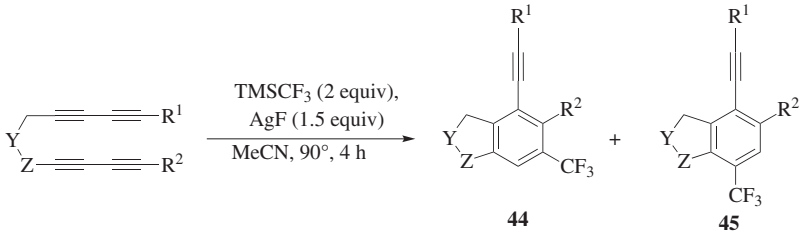
Tropylium bromide reacts with $(CF_3)_3CH$ in the presence of triethylamine to afford 7-(perfluoro-*tert*-butyl)cycloheptа-1,3,5-triene in a 53% yield.[83] Certain *N*-substituted 2-oxopurines are susceptible to trifluoromethylation with $TMSCF_3$ in DMF in the presence of potassium carbonate (Scheme 83).[310]



R	Yield (%)
Ph	58
TBSO	62

Scheme 83

A non-traditional synthesis of trifluoromethylated aromatic compounds involves a hexadehydro Diels–Alder reaction of triynes in the presence of Ag(I) salts. The formed silver-stabilized aryne or aryl cation reacts with $TMSCF_3$ to provide trifluoromethylated aromatic products **44** and **45** (Scheme 84).[311]

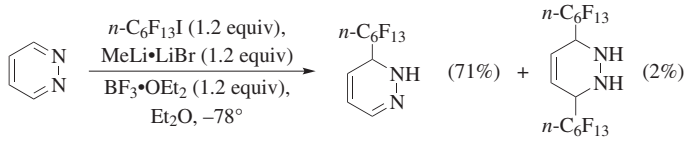


44 **45**

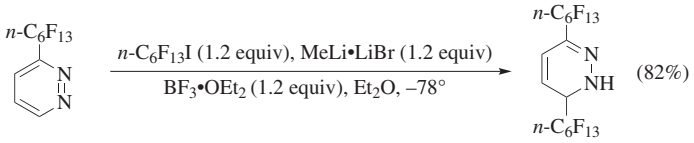
R^1	R^2	Y	Z	**44** + **45**, Yield (%)	**44**/**45**
n-Bu	*n*-Bu	*p*-TsN	CH_2	76	60:40
n-Bu	*n*-Bu	CH_2	*p*-TsN	75	100:0
n-C_6H_{13}	*n*-C_6H_{13}	O	CH_2	76	50:50
Ph	$Cl(CH_2)_3$	CH_2	*p*-TsN	75	100:0
4-$(CF_3)C_6H_4$	*n*-Pr	CH_2	*p*-TsN	78	100:0

Scheme 84

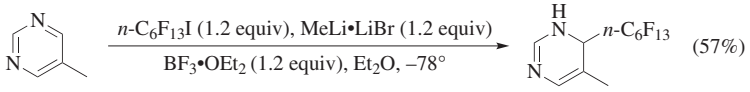
Heteroarenes. Electron-deficient nitrogen heterocycles, such as pyridine, pyridinium salts, quinoline, isoquinoline, quinoxaline, phthalazine, pyridazine, pyrazine, pyrimidine, phenanthroline, and similar structures undergo nucleophilic addition of perfluoroalkyllithiums at the 2-position relative to nitrogen. Reactions are carried out in the presence of BF_3•OEt_2. These reactions can also be viewed as nucleophilic additions to imines or iminium salts. Product yields depend on the substrate and some examples with good yields are shown in Schemes 85–88.[312,313]



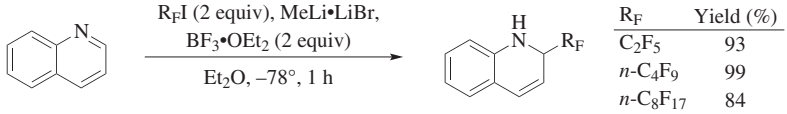
Scheme 85



Scheme 86



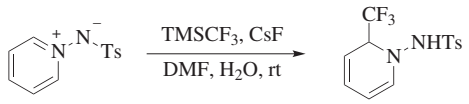
Scheme 87



R_F	Yield (%)
C_2F_5	93
n-C_4F_9	99
n-C_8F_{17}	84

Scheme 88

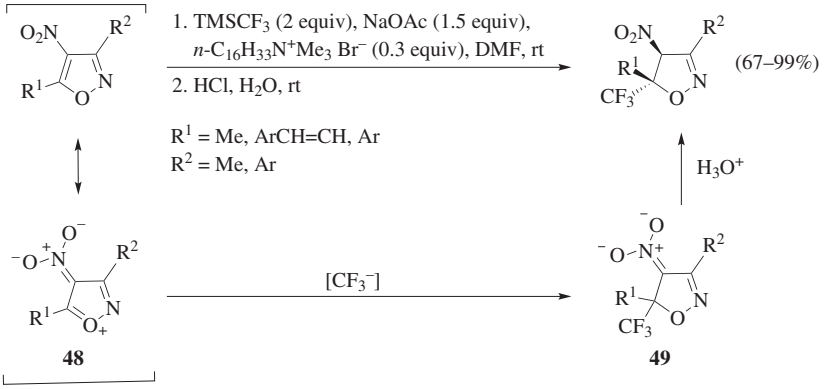
Treatment of crystalline pyridinium salt **46** with $TMSCF_3$ leads to the formation of dihydropyridine **47** with exclusive site selectivity (Scheme 89).[314] Pyridine *N*-oxide undergoes addition of perfluorohexyllithium in the presence of BF_3•OEt_2 at –78° to form 2-perfluorohexylpyridine in only 10% yield.[312]



46 **47** (79%)

Scheme 89

Trifluoromethylation of 4-nitroisoxazoles proceeds efficiently by nucleophilic addition at the 5-position using $TMSCF_3$ (Scheme 90).[315] The reaction is diastereoselective and tolerates a broad range of aromatic, heteroaromatic, and aliphatic substitutions at the 3- and 5-positions. The nitro group at the 4-position is essential for a successful transformation because it activates the double bond for nucleophilic addition of $TMSCF_3$ in 1,2-addition fashion to furnish intermediate **49**. Kinetically controlled protonation of intermediate **49** results in the complete diastereoselectivity observed in the product.[315]



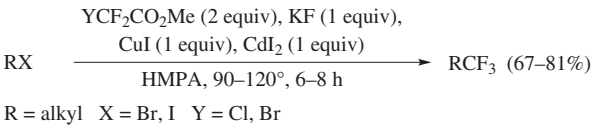
Scheme 90

Alkyl, Alkenyl, and Aryl Halides and Pseudohalides. The most widely used perfluoroalkyl addition reagents for substitution of halogen in alkyl, alkenyl, and aryl halides and pseudohalides for perfluoroalkyl groups are the perfluoroalkylcopper organometallics. These are generated in a number of ways (see sections Overview and Preparation of Nucleophilic Perfluoroalkyl Reagents – Perfluoroalkyl Organometallic Reagents – Perfluoroalkylcopper Reagents).

Alkyl Halides and Pseudohalides. 1,1,1-Trifluoro-*n*-heptane is obtained in 60% yield by trifluoromethylation of 1-bromohexane with fluoroform and electrochemically generated phenyl anion.[70] Pentyl iodide reacts with $C_2F_5CO_2Na$/CuI in NMP at 170°, affording the pentafluoroethyl adduct in only 20% yield.[59] Ethyl iodide undergoes perfluoroalkylation with the *n*-$C_8F_{17}I$/AgBr/Li system in THF under ultrasound activation.[316] Selective perfluoroalkylation of alkyl iodides and bromides is possible with $TMSCF_3$ or $TMSC_2F_5$ in DME or diethyl ether using CsF/15-crown-5, and TMAF (tetramethylammonium fluoride) or TASF (tris(dimethylamino)sulfonium difluorotrimethylsilicate) as fluoride sources. Reactions with secondary or tertiary alkyl iodides suffer from HI eliminations, whereas alkyl chlorides are unreactive under these conditions.[317] The conversion of 15-iodopentadec-1-yne to 16,16,16-trifluorohexadec-1-yne in 88% yield using equimolar amounts of $TMSCF_3$, CsF, and 15-crown-5 in DME has recently been reported.[318] Hexamethylguanidinium fluoride [$(Me_2N)_3C^+F^-$] undergoes trifluoromethylation with an excess of $TMSCF_3$ in diethyl

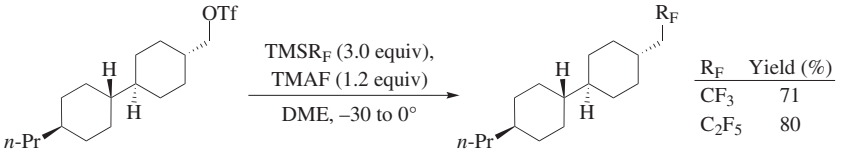
ether to afford 1,1,1-trifluoro-2,2,2-tris(dimethylamino)ethane [$(Me_2N)_3C–CF_3$] in 96% yield.[64,319]

Another method for trifluoromethylation of alkyl iodides and bromides consists of using the $XCF_2CO_2Me/KF/CuI/CdI_2$ system (X = Cl, Br) in HMPA at elevated temperatures (Scheme 91).[242]



Scheme 91

Treatment of primary alkyl triflates with a three-fold excess of $TMSCF_3$ or $TMSC_2F_5$ and one equivalent of TMAF affords the corresponding perfluoroalkyl derivatives in high yields (Scheme 92).[320] The nature of the fluoride ion source used significantly influences the reaction. With TASF instead of TMAF, significant amounts of alkyl fluorides, alkenes, and alcohols are formed.[320]



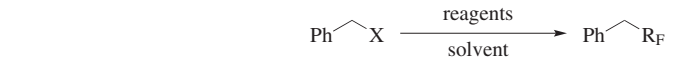
Scheme 92

The conditions used for transformation of benzyl halides into the corresponding benzylated perfluoroalkanes are shown in Scheme 93. The methods can be divided into two categories. In the first category, perfluoroalkylcopper species are generated, usually employing a copper source, elevated temperature, a and polar aprotic solvent. In the second category, CsF is added into a perfluoroalkene at room temperature. *N*-Heterocyclic carbene-Cu(I)–CF_3 complex **32** is prepared in situ from the *tert*-butoxy copper complex **31** (Scheme 54) and $TMSCF_3$ and is used for the trifluoromethylation of benzyl bromide to $PhCH_2CF_3$ at room temperature in 58% yield (NMR analysis).[277] Benzyl bromide is also trifluoromethylated in 10% yield (^{19}F NMR analysis) using fluoroform and KHDMS in THF.[77]

Benzylic methanesulfonates undergo smooth reaction with $TMSCF_3$ in the presence of stoichiometric amounts of copper and fluoride sources (Scheme 94).[323]

Copper-catalyzed trifluoromethylation of primary propargylic chlorides with $TMSCF_3$ affords the corresponding trifluoromethylated products **50** in high yields (Scheme 95).[302] Under these conditions the formation of trifluoromethylated allenes

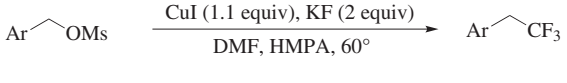
arising from attack of the fluorinated nucleophile on the alkyne is suppressed. Similar reactions take place with $(Ph_3P)_3CuCF_3$.[303]



X	Reagents	R_F	Solvent (s)	Temp (°)	Yield (%)	Refs
Cl	$FSO_2CF_2CO_2Me$, CuI (12 mol %)	CF_3	DMF	80	53	250
Br	$ClCF_2CO_2Me$, KF, CuI	CF_3	DMF	110–120	84	243, 244
Br	$FSO_2CF_2CF_2OCF_2CO_2K$, CuI	CF_3	DMF	45	68	247
Br	CF_3Cu•bpy[a]	CF_3	DMF	80–120	90	234
Br	$FSO_2CF_2CO_2Me$, CuI (12 mol %)	CF_3	DMF	80	72	250
Br	FSO_2CF_2I, Cu	CF_3	DMF	90	72	259
Br	$FSO_2CF_2CO_2Me$, Cu	CF_3	DMF	80	70	252
Br	$FSO_2CF_2CF_2OCF_2CO_2K$, CuI, DMF	CF_3	DMF, HMPA	40	74	247
Br	$(CF_3)_2C{=}CF_2$, CsF	$(CF_3)_3C$	DME	20	88	321
Br	$(CF_3)_2C{=}CFC_2F_5$, CsF	$(CF_3)_2(C_3F_7)C$	DME	20	87	321
Br	Et_3SiCF_3, CuI, KF	CF_3	DMF, NMP	80	73	275
Br	$TMSC_2F_5$, CuI, KF	C_2F_5	DMF, NMP	80	90	275
I	$FSO_2CF_2CO_2Me$, CuI (12 mol %)	CF_3	DMF	70	81	250
I	FSO_2CF_2I, Cu	CF_3	DMF	90	79	259
I	$FSO_2CF_2CO_2Me$, Cu	CF_3	DMF	80	80	252

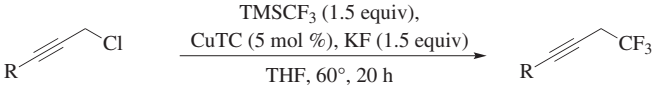
[a] CF_3Cu was generated electrochemically from CF_3Br and au anode.

Scheme 93



Ar	Yield (%)
Ph	76
4-FC_6H_4	75
4-BrC_6H_4	78
4-$O_2NC_6H_4$	40
2-naphthyl	78

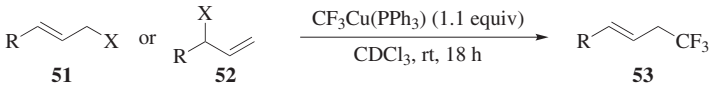
Scheme 94



R = aryl, Bn, $Ph(CH_2)_2$ **50** (62–93%)

Scheme 95

Allylic chlorides and trifluoroacetates react with $(Ph_3P)_3CuCF_3$ site selectively with both linear (**51**) and branched (**52**) substrates to provide access to terminally trifluoromethyl-substituted products **53** (Scheme 96).[322] The mechanism of this transformation is likely nucleophilic, however, radical processes cannot be excluded.

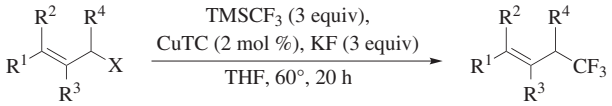


51 **52** **53**

Substrate	R	X	**53** Yield (%)
51	Ph	Cl	68
51	Ph	CF_3CO_2	53
52	Ph	CF_3CO_2	61
51	4-$O_2NC_6H_4$	Cl	51
51	*c*-C_6H_{11}	Cl	59

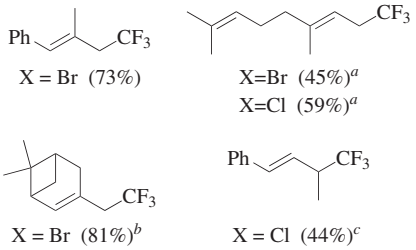
Scheme 96

Efficient allylic and propargylic trifluoromethylations from reaction of the corresponding halides with catalytic amounts of CuTC and $TMSCF_3$ have been reported.[61,302] This process is site-selective for primary and secondary allylic (Scheme 97)[61] and primary propargylic systems and provides good to excellent yields of the corresponding trifluoromethylation products. However, secondary propargylic chlorides demonstrate different site selectivity, providing access to the corresponding trifluoromethylated allenes.[302]



Products:

X	R	Yield (%)
Br	4-ClC_6H_4	74
Br	4-$MeOC_6H_4$	46
Cl	4-$MeOC_6H_4$	58
Br	4-MeC_6H_4	82
Br	4-$MeO_2CC_6H_4$	68
Br	1-naphthyl	68



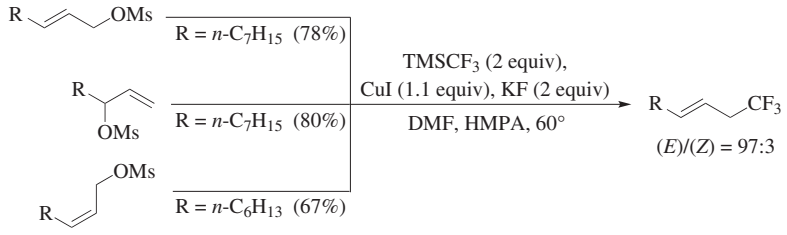
[a] The reaction was run at rt for 48 h.
[b] The reaction was run at 60° for 48 h.
[c] The reaction required 10 mol % of CuTC and 40°.

Scheme 97

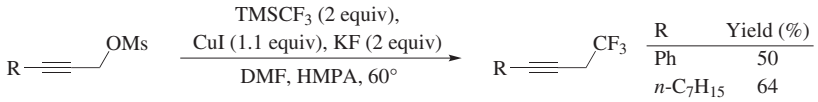
3-Phenyl-1-bromopropane does not react under these conditions, which indicates that an allylic or propargylic system is necessary for the reaction to occur. Furthermore, in the reaction of (*Z*)-cinnamyl bromide, the (*E*)-configured product is obtained in 66% yield without the formation of (*Z*)-product. Additional experiments confirm that the presence of CuTC mediates this isomerization and points to the possible involvement of [(allyl)Cu(CF_3)Br] species. Interestingly, DMF is an ineffective solvent for this process, likely because of the coordination of DMF to the Cu(III) complex and inhibition of the regeneration of Cu(I).[61]

Enantiomerically enriched secondary propargylic (*R*)-1-phenyl-2-chloro-3-butyne reacts with $TMSCF_3$ in the presence of a catalytic amount of CuTC to afford the racemic allene, indicating possible involvement of propargyl/allenyl-copper complexes as reactive intermediates.[302]

Similar copper-mediated processes with allylic, propargylic, and benzylic methanesulfonates are reported for CuI using DMF and HMPA solvent mixtures.[323] Lower yields of the trifluoromethylated products are obtained in the presence of the 1,10-phenanthroline ligand with this protocol. Allylic substrates produce (*E*)-isomers of trifluoromethylated products, regardless of the initial alkene geometry. In addition, isomeric allylic methanesulfonates display the same site selectivity, which suggests formation of a π-allyl-Cu(III) complex (Scheme 98).[323] Under the same conditions, primary propargylic methanesulfonates form propargylic trifluoromethylated products (Scheme 99)[323] whereas secondary propargylic methanesulfonates produce allenes[323] in accord with other reports.[302]



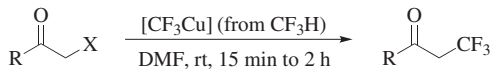
Scheme 98



R	Yield (%)
Ph	50
n-C_7H_{15}	64

Scheme 99

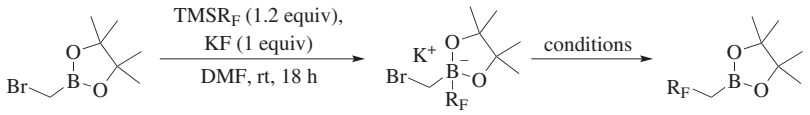
α-Halo ketones can be trifluoromethylated with CF_3Cu under mild conditions to provide access to α-trifluoromethylated ketones in excellent yields (Scheme 100).[324] The trifluoromethylating reagent should be stabilized to avoid undesired decomposition to higher perfluoroalkyl copper species. No addition to the carbonyl group is observed using these conditions.



R	X	Yield (%)
2-thienyl	Br	96
2-pyridyl	Br	52
Ph	Br	93
4-FC_6H_4	Cl	89
4-$MeOC_6H_4$	Br	96
4-MeC_6H_4	Br	94
2-naphthyl	Br	94–96
4-PhC_6H_4	Br	95

Scheme 100

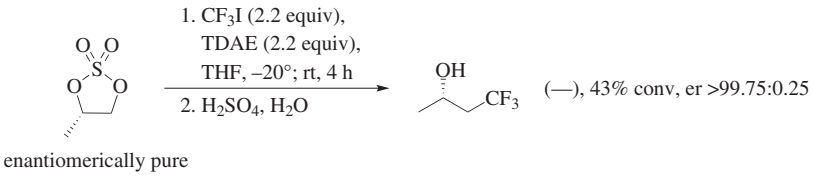
An interesting nucleophilic perfluoroalkylation of the bromomethyl moiety of aliphatic pinacolboranes occurs via formation of the borate salts followed by intramolecular nucleophilic substitution of the bromine atom (Scheme 101).[104]



R_F	Temp (°)	Time (h)	Yield (%)
CF_3	70	1.5	45
C_2F_5	50	1	80

Scheme 101

Cyclic sulfates of vicinal diols do not react with $TMSCF_3$ but undergo highly site-selective ring opening with CF_3I and TDAE in THF (Scheme 102).[325] Iodide is present in the process, and competes with the trifluoromethyl anion as the nucleophile. Stereogenic centers are not epimerized in the ring-opening reaction.



Scheme 102

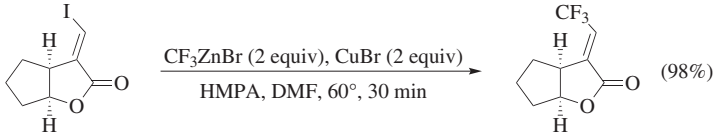
Alkenyl Halides and Pseudohalides. Substitution of a fluorine atom in perfluoroalkenes such as hexafluoropropene, perfluorocyclobutene, or perfluorocyclopentene for a perfluoroalkyl group takes place with *n*-$C_6F_{13}TMS$ and *n*-$C_8F_{17}TMS$ in the presence of CsF in DME or THF.[326] Alkenyl halides (mainly iodides and bromides) are excellent substrates for nucleophilic perfluoroalkylation reactions with perfluoroalkylcopper reagents (Scheme 103). In these reactions perfluoroalkylation normally proceeds with retention of configuration on the double bond (Scheme 104);[327] however, partial isomerization is also often observed[255,256,328,329] (Scheme 105).[256] Interestingly, selective reaction with one isomer is observed for certain substrates and reaction conditions (Scheme 106).[328]

In situ generated CF_3Cu in DMPU can be used for efficient trifluoromethylation of vinyl bromides and iodides, with retention of double bond configuration (Scheme 107).[331] In this process DMPU acts as a ligand for copper.

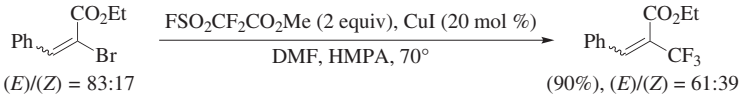


X	R^1	R^2	R^3	R^4	Conditions	Yield (%)	Refs
Cl	H	Ph	H	CF_3	$FSO_2CF_2CF_2OCF_2CO_2K$, CuI, DMF, 120°	67	249
Br	H	Ph	H	CF_3	$ClCF_2CO_2Me$, KF, CuI, DMF, 110–120°	81	243, 244
Br	H	Ph	H	CF_3	CF_3Cu•bipy, DMF, 80–120°	98	234
Br	H	Ph	H	CF_3	FSO_2CF_2I, Cu, DMF, 80°	74	259
Br	H	H	Ph	CF_3	CF_3Br, e^-, Cu anode, DMF, TMEDA, 80°	84	234
Br	H	Ph	H	n-C_7F_{15}	n-$C_7F_{15}I$, Cu, pyridine, 100°	95	330
Br	H	Ph	EtO_2C	CF_3	FSO_2CO_2Me, CuI, DMF, HMPA, 70°	92	255
Br	Ph	H	Ac	CF_3	$(CF_3)_2Hg$, Cu, DMA, 140°	87	329
I	n-Bu	I	H	CF_3	$FSO_2CF_2CO_2Me$, CuI (10 mol %), DMF, 75–80°, 9 h	80	251
I	n-C_8H_{17}	H	H	CF_3	Et_3SiCF_3, CuI, KF, DMF, NMP, 80°	90	275
I	n-C_8H_{17}	H	H	C_2F_5	$TMSC_2F_5$, CuI, KF, DMF, NMP, 80°	77	275

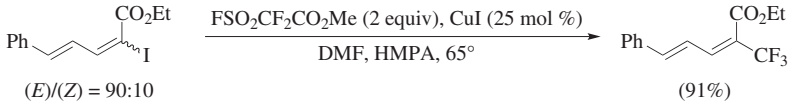
Scheme 103



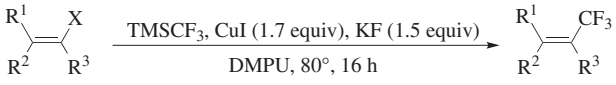
Scheme 104



Scheme 105



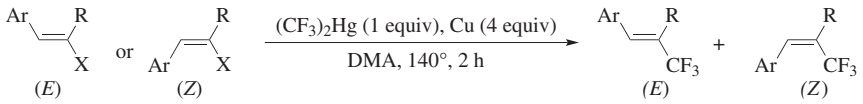
Scheme 106



R^1	R^2	R^3	X	(*E*)/(*Z*)	Yield (%)	(*E*)/(*Z*)
MeO_2C	H	Et	I	0:100	86	0:100
H	Ph	H	Br	85:15	99	85:15
H	Ph	H	I	100:0	99	100:0
n-Pr	H	*n*-Pr	I	0:100	99	0:100
H	2-BrC_6H_4	H	I	100:0	99	100:0
Me	Ph	H	Br	100:0	78	100:0

Scheme 107

Bromo- and iodoalkenes (including protected 5-iodouracil derivatives) also undergo efficient trifluoromethylation with trifluoromethylcopper generated from $(CF_3)_2Hg$ and Cu in DMA (Scheme 108).[329] These reactions probably involve formation of copper allenoates. Variable stereoselectivity is observed with substrates bearing an α-carbonyl group, while substrates bearing α-hydrogen or α-alkyl groups afford products with retention of configuration.

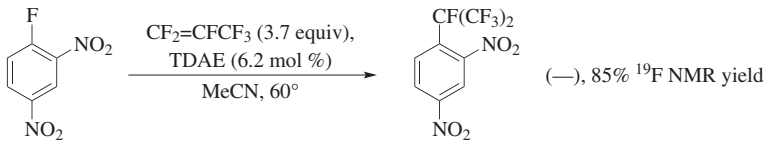


Ar	R	X	Config	(*E*) + (*Z*), Yield (%)	(*E*)/(*Z*)
Ph	CHO	Br	(*Z*)	90	75:25
Ph	MeCO	Br	(*E*)	90	74:26
Ph	MeO_2C	Br	(*Z*)	92	5:95
1-naphthyl	H	I	(*Z*)	93	0:100

Scheme 108

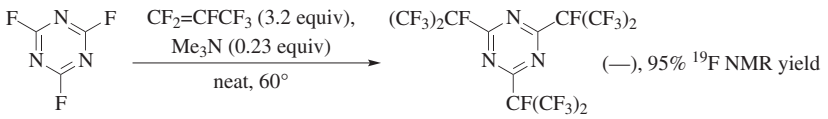
Aryl and Heteroaryl Halides and Pseudohalides. Typically, perfluoroalkyl additions to aryl halides are performed in the presence of transition metals, especially copper; however, aryl and heteroaryl fluorides are somewhat of an exception because nucleophilic aromatic substitution of fluorine atom(s) is facile. Therefore aryl and heteroaryl fluorides are discussed first in this section followed by other aryl halides.

Activated fluoroarenes and heteroarenes undergo perfluoroalkylation with $CF_3Br/(Et_2N)_3P$ at low temperature in low to moderate yields.[332] Salts prepared by reaction of perfluoroalkenes with strong electron donors such as TDAE or trimethylamine are also reported to react with aryl and heteroaryl fluorides (Schemes 109 and 110).[97] Additionally, polyfluoroaromatic compounds such as pentafluoropyridine,[326,333] perfluorotoluene,[326,333] pentafluorobenzonitrile,[326] perfluorobiphenyl,[333] tetrafluorophthalonitrile,[334] tetrafluoroisophthalonitrile,[334] and pentafluoronitrobenzene[289,304] undergo perfluoroalkylation with (perfluoroalkyl)trimethylsilanes in the presence of CuI/KF, TASF, or TBAF to generally provide a mixture of products. Reaction of cyanuric fluoride with *n*-$C_8F_{17}TMS$ in the presence of CsF affords 2,4,6-tris(perfluorooctyl)-1,3,5-triazine in 57% yield.[335]



(—), 85% ^{19}F NMR yield

Scheme 109



(—), 95% ^{19}F NMR yield

Scheme 110

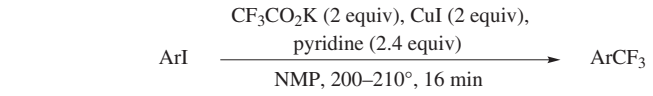
For other aryl halides the general trend in reactivity with perfluoroalkylcopper reagents is ArI > ArBr ≫ ArCl.[59] Important synthetic protocols for nucleophilic perfluoroalkylations of phenyl halides are summarized in Scheme 111. The majority of these methods are also applicable to substituted aryl and heteroaryl bromides and iodides.

PhX $\xrightarrow[\text{solvent}]{\text{reagents}}$ Ph–R_F

X	Conditions	Solvent	Temp (°)	R_F	Yield (%)	Refs
I	$ClCF_2CO_2Me$, KF, CuI	DMF	120	CF_3	88	243, 244
Br	$ClCF_2CO_2Me$, KF, CuI	DMF	110–120	CF_3	60	243
I	$FSO_2CF_2CF_2OCF_2CO_2K$, CuI	DMF	45	CF_3	72	247
Br	$FSO_2CF_2CF_2OCF_2CO_2K$, CuI	DMF	45	CF_3	61	247
Cl	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI	DMF	110–120	CF_3	52	249
Br	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI	DMF	110	CF_3	73	249
I	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI	DMF	100	CF_3	80	249
I	$FSO_2CF_2CO_2Me$, CuI (12 mol %)	DMF	60	CF_3	84	252
Br	$FSO_2CF_2CO_2Me$, CuI (12 mol %)	DMF	80	CF_3	61	252
I	FSO_2CF_2I, Cu	DMF	80	CF_3	80	259
I	$(CF_3)_2Hg$, Cu	NMP	130–150	CF_3	65	261
I	CF_3CO_2Na, CuI	NMP	160	CF_3	87	58
I	CF_3I, Cu	pyridine	140	CF_3	100	336
I	*n*-$C_7F_{15}I$, Cu	DMSO	110	*n*-C_7F_{15}	70	337
I	$[CF_3Cu(phen)]$	DMF	rt	CF_3	88	54
I	$[(PPh_3)_3CuCF_3]$, (*t*-Bu)$_2$ bipy	toluene	80	CF_3	65	55
I	$[(phen)(PPh_3)CuCF_3]$	DMF	80	CF_3	65	55
I	$[(MeO)_3BCF_3]^- K^+$, CuI (20 mol %), 1,10-phenanthroline (20 mol %)	DMSO	60	CF_3	91	103
I	C_2F_5H (CF_3H), [K(DMF)][Cu(*t*-BuO)$_2$]	DMF	rt	C_2F_5 (CF_3)	95	279

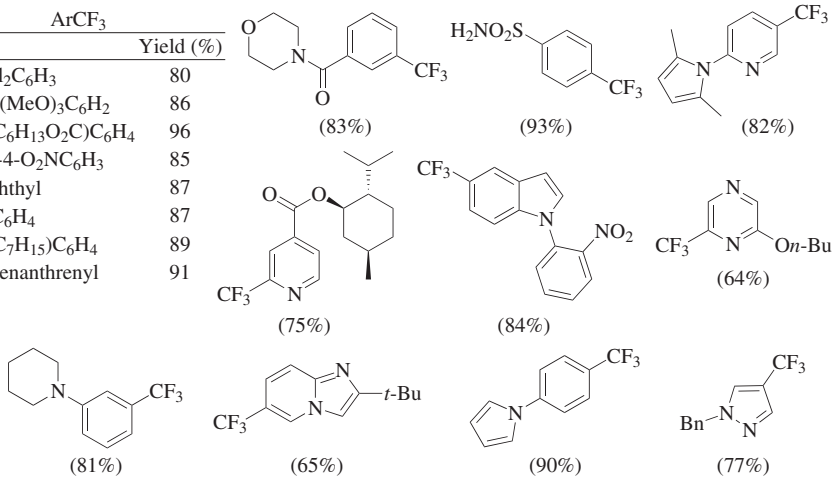
Scheme 111

Whereas high temperature and the increased pressure that occurs in decarboxylation protocols cause certain problems under batch conditions, a flow process developed by Buchwald readily allows access to trifluoromethylarenes in excellent yields within minutes (Scheme 112).[338] A solution of potassium trifluoroacetate, CuI, and pyridine in NMP is mixed with a solution of iodoarene in NMP and introduced into a stainless steel tube reactor submerged in a preheated 200° bath using an optimized 16 minutes residence time. At this point, the mixture is diluted with a stream of ethyl acetate (controlled with backpressure regulators). Finally, the resulting mixture is collected and subsequently purified by column chromatography.[338] These flow conditions prove to be particularly effective for heteroaromatic systems. The positive ρ value for this reaction is consistent with the presence of a nucleophilic CF_3Cu species that undergoes reaction with aryl iodides, and slightly favors substrates with electron-withdrawing groups.



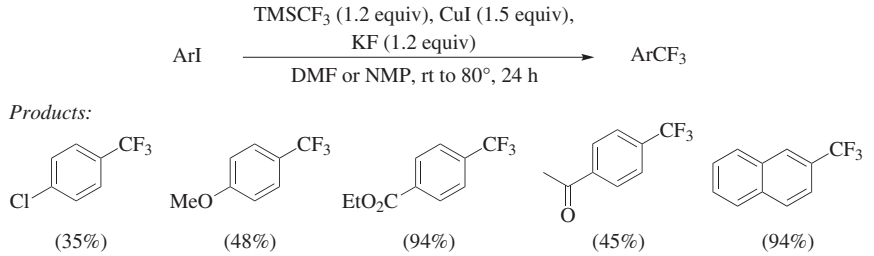
Products:

$ArCF_3$	
Ar	Yield (%)
3,5-$Cl_2C_6H_3$	80
3,4,5-$(MeO)_3C_6H_2$	86
4-(*n*-$C_6H_{13}O_2C)C_6H_4$	96
2-Me-4-$O_2NC_6H_3$	85
1-naphthyl	87
4-PhC_6H_4	87
4-(*n*-$C_7H_{15})C_6H_4$	89
10-phenanthrenyl	91

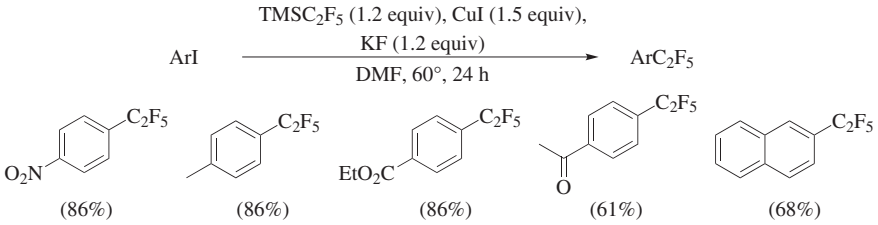


Scheme 112

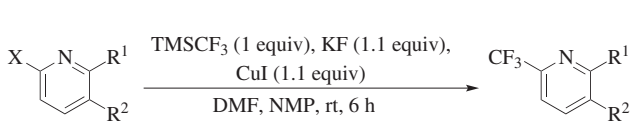
Aryl iodides also undergo cross-coupling reactions with perfluoroalkylcopper species generated in situ from (perfluoroalkyl)trialkylsilanes in the presence of copper(I) iodide and potassium fluoride.[275] The reaction is usually carried out at elevated temperatures (60–80°) in a mixture of DMF and NMP[275] or morpholinium ionic liquids.[339] Successful perfluoroalkylation of aryl iodides[275,340–345] (Schemes 113[275] and 114[275]), bromo- and iodopyridines[346–350] (Scheme 115[349] and 116[349]), and iodoquinolines (Scheme 117)[350] has been reported. In one variant, aryl iodides are prepared in situ by heating 1-aryl-3,3-diisopropyltriazenes with iodomethane followed by trifluoromethylation with $TMSCF_3$/CuI/KF in NMP.[351]



Scheme 113

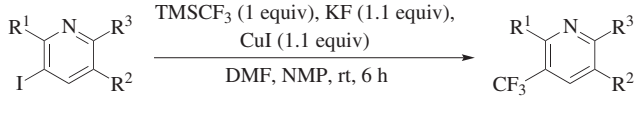


Scheme 114



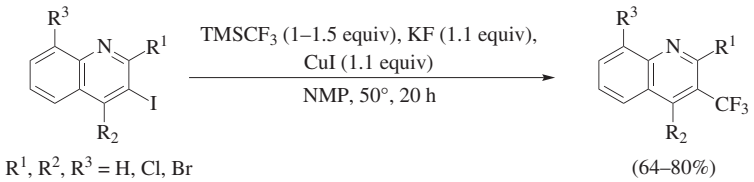
X	R^1	R^2	Yield (%)
Br	Cl	H	32
Br	Br	H	28
I	H	H	68
I	Cl	H	59
I	Br	H	79
I	H	Br	69

Scheme 115



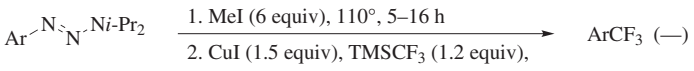
R^1	R^2	R^3	Yield (%)
H	H	H	23
Cl	H	H	67
H	H	Br	29
H	Br	H	48

Scheme 116



Scheme 117

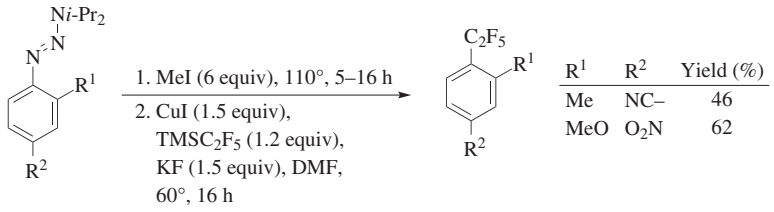
An interesting example of trifluoromethylation of arenes is reported for 3,3-diisopropyltriazenes via a one-pot, two-step procedure. These substrates are converted into the aryl iodide upon reaction with iodomethane, then undergo trifluoromethylation with CuI, 1,10-phenanthroline, and $TESCF_3$. Excess CuI without ligand is required if $TMSCF_3$ is employed as the source of the trifluoromethyl group (Scheme 118).[351] Similar conditions can be used for perfluoroethylation of 3,3-diisopropyltriazenes (Scheme 119).[351]



Ar	Conv (%)[a]	Ar	Conv (%)[a]
4-ClC_6H_4	33	4-$EtO_2CC_6H_4$	90
2-$MeOC_6H_4$	54	2-Me-4-NCC_6H_3	99
6-Me-2-$O_2NC_6H_3$	40	1-(4-Br-naphthyl)	87
4-Me-3-ClC_6H_3	66	2-Bz-4-MeC_6H_3	81

[a] Conversion determined by ^{19}F NMR.

Scheme 118



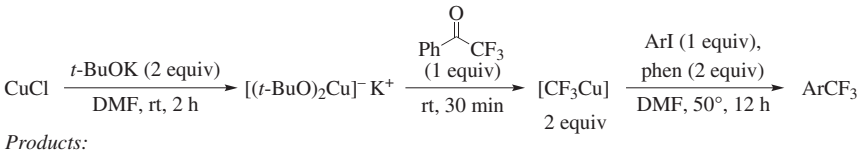
R^1	R^2	Yield (%)
Me	NC–	46
MeO	O_2N	62

Scheme 119

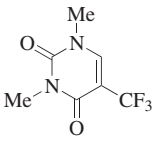
Apart from trifluoromethylated products, pentafluoroethylated compounds are also obtained in significant yields in some reactions of Et_3SiCF_3 and aryl iodides.[275] This outcome can be explained by conversion of the CF_3Cu species into C_2F_5Cu in DMF via difluorocarbene.[220,275]

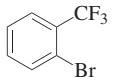
The reactive trifluoromethylcopper species prepared from $TMSCF_3$ and spray-dried KF/CuBr stabilized by DMI or NMP reacts with polyiodoaromatic compounds at 0° to room temperature to afford polytrifluoromethylated products. For example, C_6I_5Cl provides $C_6(CF_3)_5Cl$ in 81% yield and C_6I_5Me provides $C_6(CF_3)_5Me$ in 41% yield. Hexaiodobenzene under similar conditions provides $C_6(CF_3)_6$ (45%), $C_6(CF_3)_5OK$ (20%, due to the side reaction with DMI) and $C_6H(CF_3)_5$ (14%).[276] Cu(I)–CF_3 complex **32** (Scheme 54) mediates trifluoromethylation of aryl iodides at room temperature.[277] This reagent is more efficient than the CuI/KF protocol.

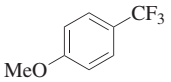
Trifluoromethylcopper, prepared from trifluoromethyl phenyl ketone, is reactive in trifluoromethylation of iodoarenes (Scheme 120),[280] and oxidative trifluoromethylation of boronic acids and terminal alkynes. The last two protocols are similar to other oxidative methods of trifluoromethylation of boronic acids and alkynes discussed in the Comparison with Other Methods section.[352–363]

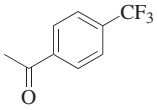


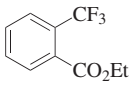
Products:

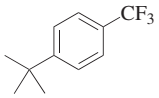

(78%)

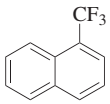

(93%)


(65%)


(80%)[a]


(87%)[a]

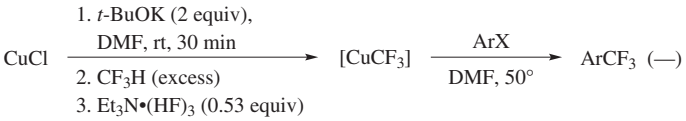

(71%)


(91%)

[a] The reaction was run at rt.

Scheme 120

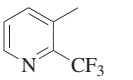
Direct cupration of fluoroform with *t*-BuOK leads to the formation of CF_3Cu species, which are reactive toward iodoarenes and produce trifluoromethylarenes in good yields. The trifluoromethylcopper reagent prepared by this protocol should be stabilized with $Et_3N{\bullet}(HF)_3$ prior to trifluoromethylation to suppress formation of the undesirable aryl *tert*-butyl ether (Scheme 121).[56,78]

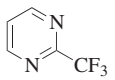


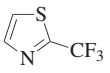
Products:

X	$ArCF_3$ Ar	Conv (%)[a]
I	2-pyridyl	95–99
Br	2-pyridyl	30
I	Ph	80–85
I	4-ClC_6H_4	90–95
I	4-$MeOC_6H_4$	70–75

[a] Determined by ^{19}F NMR spectroscopy.
[b] Slow addition of $[CF_3Cu]$.


X = Br (88%)[a,b]

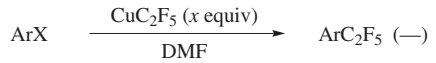

X = Br (95%)[a,b]


X = Br (35%)[a,b]

Scheme 121

The perfluoroethylcopper complex should also be stabilized with $Et_3N{\bullet}(HF)_3$ or $py{\bullet}(HF)_n$ prior to use in pentafluoroethylation reactions. The reagent works not only for aryl iodides, but also for aryl bromides (Scheme 122).[279] Aryl and heteroaryl bromides with electron-withdrawing groups generally provide higher yields of

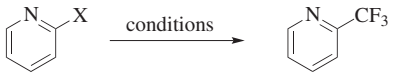
trifluoromethylated products, which points to the true nucleophilic nature of CF_3Cu species.



X	*x*	Temp (°)	Time (h)	Conv (%)
Br	1.5–2.5	50–90	18–96	80–99
I	1.2	23–50	0.5–40	90–99

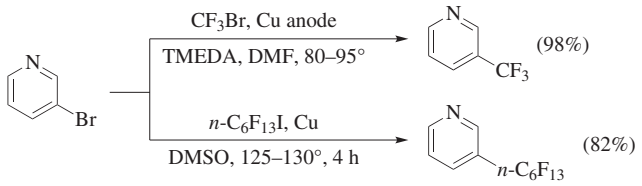
Scheme 122

Iodopyridines provide perfluoroalkylpyridines in higher yield than bromopyridines[349] and chemoselective trifluoromethylation of an iodo versus a bromo substituent is observed.[344,346,349,350] Other methods for conversion of 2-halopyridines into 2-trifluoromethylpyridines are summarized in Scheme 123.[247,249,261] In addition, 3- and 4-perfluoroalkyl-substituted pyridines are also accessible via nucleophilic perfluoroalkylation[234,364,365] (Scheme 124).[364,365]



X	Reagents	Solvent	Temp (°)	Yield (%)	Refs
Cl	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI	DMF	120	64	249
Br	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI	DMF	120	70	249
Br	$FSO_2CF_2CF_2OCF_2CO_2K$, CuI	DMF	45	52	247
Br	$CF_3Cu{\bullet}PBu_3$	DMF	80–120	90	234
Br	CF_3Cu, TMEDA	DMF	90	98	364
Br	CF_3Br, e^-, Cu anode, TMEDA	DMF	80–95	95	364
Br	CF_3CO_2Na, CuI	NMP	140–160	41	58
I	$(CF_3)_2Hg$, Cu	NMP	140–150	74	261

Scheme 123

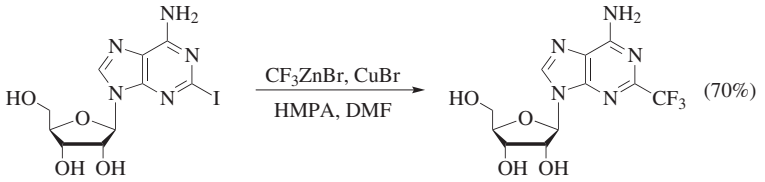


Scheme 124

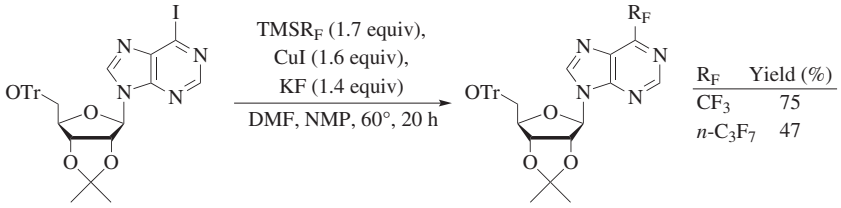
Quinolinyl and isoquinolinyl halides are reactive toward perfluorocopper reagents. It is worth mentioning that, in some cases, iodides afford lower yields of trifluoromethylated heterocycles than chlorides. Reaction with the CF_3I/Cu system in DMF gives access to trifluoromethylquinolines and isoquinolines in moderate

yields.[366] Trifluoromethylation of 3-bromoquinoline is possible under mild conditions using electrochemically generated CF_3Cu. The advantage of this method is the use of CF_3Br instead of CF_3I, and generally, higher yields of the trifluoromethylated aryl and heteroaryl aromatics.[364] Perfluoroalkyl pyrimidines,[51,59,367,368] imidazoles,[268,269,369] furans,[336,365] thiophenes,[234,365,370] and other heterocycles are also prepared in variable yields from their halogenated precursors.

Various iodo-substituted purine bases,[371,372] nucleosides[265,368,371,373,374] (Scheme 125[265] and Scheme 126[371]), and acyclic nucleotide analogues[371,375] undergo perfluoroalkylation with perfluoroalkylcopper reagents. All of the above-mentioned methods employ at least equimolar amounts of copper.

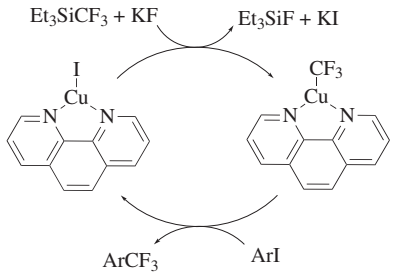


Scheme 125



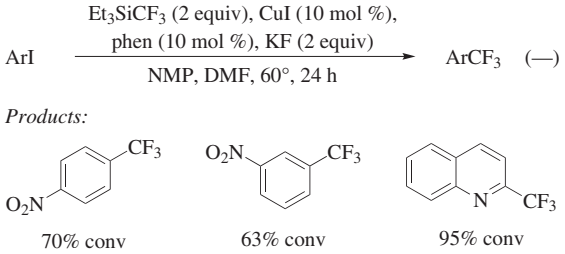
Scheme 126

Trifluoromethylation of iodoarenes employing catalytic amounts of copper is reported by Amii.[376] The key reactive intermediate is proposed to be a 1,10-phenanthroline complex of CF_3Cu that upon reaction with an iodoarene produces 1,10-phenanthroline-bound CuI, which in turn traps a nucleophilic trifluoromethyl group generated from Et_3SiCF_3 (Scheme 127).[376]



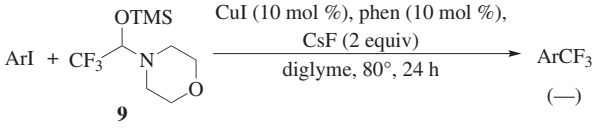
Scheme 127

Compared to other reports claiming the use of substochiometric amounts of copper in trifluoromethylation of aryl iodides,[275] the phenanhthroline ligand allows for significantly reduced loadings of copper, presumably due to the fast regeneration of the CuI complex. The Amii catalytic process works efficiently for electron-deficient substrates at 60° in an NMP/DMF mixture (Scheme 128).[376] Decreasing the loadings of copper to less than 10 mol % leads to decreased yields of trifluoromethylarenes.



Scheme 128

Another reported method for catalytic trifluoromethylation of iodoarenes uses a morpholine aminal derivative of fluoral (**9**). This method provides good yields for electron-poor substrates as well as satisfactory yields for electron-rich substrates (Scheme 129).[377]



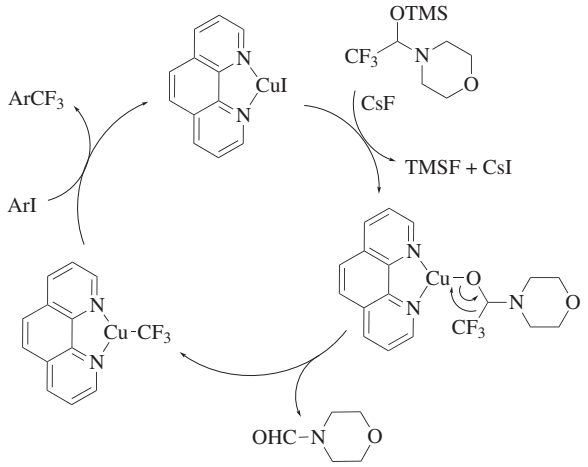
Ar	Yield (%)[a]
4-BrC_6H_4	53
4-$EtOC_6H_4$	57
2-$O_2NC_6H_4$	47
4-$O_2NC_6H_4$	77
4-NCC_6H_4	93
3-$EtO_2CC_6H_4$	60
1-naphthyl	97

[a] ^{19}F NMR yields.

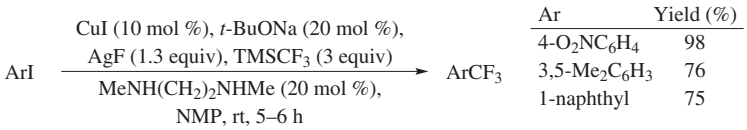
Scheme 129

The key difference in the catalytic cycle (compared to the use of Et_3SiCF_3) is in the ability of the aminal to coordinate to copper and transfer the CF_3 group without formation of a free trifluoromethyl anion (Scheme 130).[377]

A cooperative effect of silver in the copper-catalyzed trifluoromethylation of aryl iodides is observed.[378] 1-Iodonaphthalene couples with $TMSCF_3$ at 90° in NMP to produce 1-(trifluoromethyl)naphthalene in 71% yield in the presence of AgF and 10 mol % of CuI. Efficient reaction takes place with a variety of aryl iodides (Scheme 131).[378] In the absence of copper, none of the desired product is observed. The proposed mechanism is shown in Scheme 132.[378]

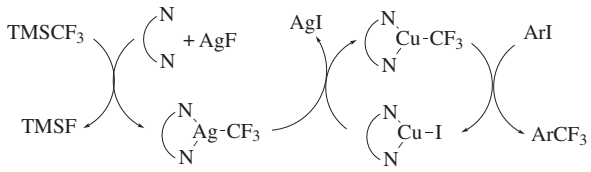


Scheme 130



Ar	Yield (%)
4-$O_2NC_6H_4$	98
3,5-$Me_2C_6H_3$	76
1-naphthyl	75

Scheme 131

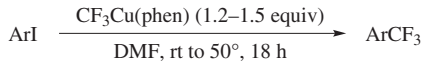


Scheme 132

In a variation of this process, Cu(0) is used in stochiometric quantities. In this case a redox reaction between $AgCF_3$ and Cu(0) leads to the formation of a trifluoromethylcopper species, which is reactive toward activated aryl iodides and bromides.[379] The Ag/Cu-mediated process for trifluoromethylation of 5-iodosubstituted triazoles is also reported.[380] The use of silver carbonate in this process is important to obtain higher yields of trifluoromethylated triazoles and avoid the formation of protodehalogenation side products.

An important improvement on the trifluoromethylation reported by Amii is Hartwig's copper-mediated trifluoromethylation of iodoarenes. Although Hartwig's process employs stoichiometric amounts of copper, it is applicable not only to

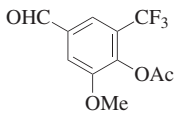
electron-poor substrates but also to electron-rich iodoarenes, and tolerates a wide variety of functional groups (Scheme 133).[54] Interestingly, substrates containing alcohol, ketone, and aldehyde functional groups that are reported to not undergo palladium- or copper-catalyzed trifluoromethylation reactions readily react with the [(phen)$CuCF_3$] complex to form trifluoromethylarenes in high yields. The presence of free nucleophilic trifluoromethyl anionic species not bound to copper in catalytic trifluoromethylation reactions seems to be the main reason for lower yields and functional group incompatibility in these processes.



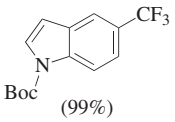
Products:

$ArCF_3$		
Ar	Yield (%)	Conv (%)[a]
4-$MeOC_6H_4$	—	96
4-$BnOC_6H_4$	89	—
4-$AcNHC_6H_4$	85	—
4-$O_2NC_6H_4$	—	100
4-$OHCC_6H_4$	—	89
4-$EtO_2CC_6H_4$	—	94

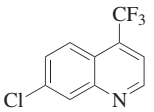
[a] Determined by ^{19}F NMR spectroscopy.
[b] Using 3 equiv of CF_3Cu(phen).



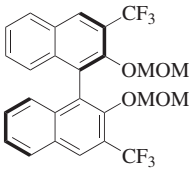
(68%)



(99%)



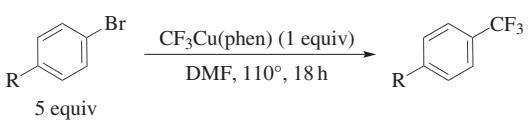
(89%)



(97%)[b]

Scheme 133

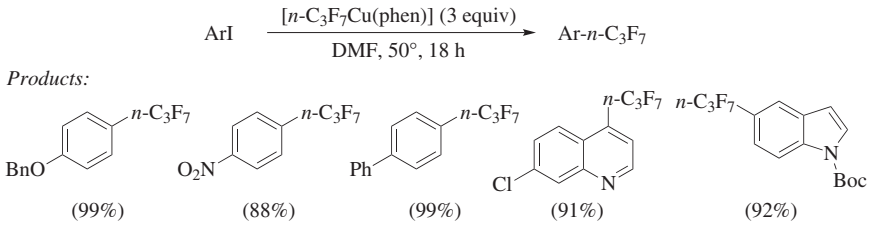
Electron-deficient bromides are significantly less reactive and require heating in DMF to react with [(phen)$CuCF_3$]. However, esters, aldehydes, and nitriles are well tolerated under these conditions (Scheme 134).[54] Hartwig also reported a similar difluoromethylation process employing $TMSCF_2H$.[381]



R	Yield (%)
EtO_2C	61
CHO	66
NC–	60

Scheme 134

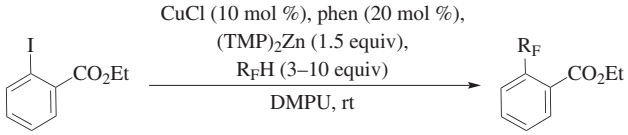
The [(phen)$CuCF_3$] complex can also be formed in situ from CuCl and used for trifluoromethylation to provide comparable yields of the trifluoromethyl arenes. Phenanthroline-stabilized perfluoropropylcopper [(phen)$CuCF_2CF_2CF_3$] reacts readily with aryl iodides at 50° to produce perfluoropropyl arenes in excellent yields (Scheme 135).[54]



Scheme 135

Notably, if $[(PPh_3)_3CuCF_3]$ is used together with an equimolar amount of a chelating nitrogen ligand (phen, bipy, $(t\text{-Bu})_2$-bipy), better results in terms of suppression of the undesired pentafluoromethylation are obtained compared to the ligand-free protocol.[55]

Trifluoromethylzinc can be used for successful trifluoromethylation of aryl iodides in the presence of catalytic amounts of Cu(I). Although this process is shown to work only on electron-poor substrates, the conditions are mild and do not require the use of a fluoride source, which may be beneficial in some cases.[62] Taking into account the relative stability of perfluoroalkylzinc reagents and the relative acidity of the carbon–hydrogen bond in perfluoroalkanes, copper-catalyzed perfluoroalkylation of aryl iodides with 1*H*-perfluoroalkanes ($H(CF_2)_nCF_3$) can be achieved by deprotonation with $(TMP)_2Zn$. This method works for trifluoromethane, longer chain 1*H*-perfluoroalkanes, and substituted 1*H*-perfluoroalkanes (Scheme 136).[382] First, deprotonation of the perfluoroalkane with $(TMP)_2Zn$ leads to the formation of $(R_F)_2Zn$ species, which undergo metal exchange, producing $[R_FCuX]^-$ species that are reactive toward aryl iodides.



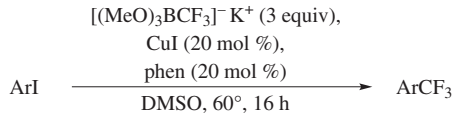
R_F	Yield (%)
CF_3	51[a]
C_2F_5	96
$n\text{-}C_3F_7$	83
$n\text{-}C_6H_{13}$	87
$n\text{-}C_{10}H_{21}$	81

[a] Using 2 equiv of phen.

TMP = 2,2,6,6-tetramethylpiperidinyl

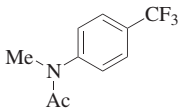
Scheme 136

Potassium trimethoxy(trifluoromethyl)borate is a novel, shelf-stable reagent capable of transferring a trifluoromethyl group to metals, such as copper. This reagent is prepared by the reaction of $TMSCF_3$ and $B(OMe)_3$ in the presence of KF in THF[103] and is used in copper-catalyzed trifluoromethylation of aryl iodides. The optimized reaction conditions employ catalytic amounts of CuI and 1,10-phenanthroline, which allows smooth conversion of aryl iodides into trifluoromethylarenes in DMSO at 60°. The reaction is applicable to both electron-rich and -deficient substrates, as well as to some heterocycles (Scheme 137).[103]

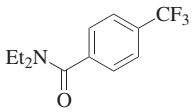


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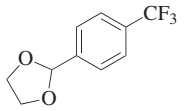
ArCF$_3$	
Ar	Yield (%)
2-thienyl	85
Ph	91
4-ClC$_6$H$_4$	75
4-O$_2$NC$_6$H$_4$	81
4-Me$_2$NC$_6$H$_4$	52
4-MeOC$_6$H$_4$	77
3-MeC$_6$H$_4$	92
4-NCC$_6$H$_4$	95
1-naphthyl	97



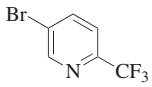
(96%)



(95%)



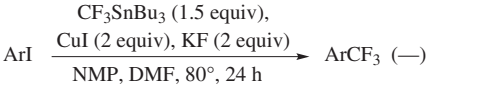
(84%)



(81%)

Scheme 137

Tributyl(trifluoromethyl)tin is also efficient in Cu-mediated trifluoromethylation reactions. Using CuI, tributyl(trifluoromethyl)stannane and KF along with a coordinating solvent, such as DMF/NMP (1:1), allows the conversion of a variety of aryl iodides to trifluoromethylarenes under relatively mild conditions (Scheme 138).[157] Although trifluoromethylations with Bu_3SnCF_3 mirror the reactivity and overall efficiency of the CuI-mediated trifluoromethylations of aryl iodides involving R_3SiCF_3 (R = Me, Et), the CF_3Cu complex formation of the former is somewhat slower than that of the latter.[157]



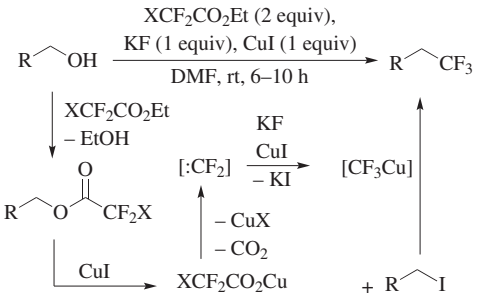
Ar	Conv (%)[a]	Ar	Conv (%)[a]
3-pyridyl	96	4-(BnO$_2$C)C$_6$H$_4$	91
4-O$_2$NC$_6$H$_4$	87	4-MeC$_6$H$_4$	99
4-ClC$_6$H$_4$	95	1-naphthyl	98
4-MeOC$_6$H$_4$	96	4-*t*-BuC$_6$H$_4$	82
4-[Ph(CH$_2$)$_3$O]C$_6$H$_4$	87		

[a] Conversion determined by ^{19}F NMR.

Scheme 138

Alcohols. Alcohols are generally considered nucleophilic rather than electrophilic substrates, unless the hydroxyl group is activated to behave as a leaving group. One of the ways to achieve such activation in nucleophilic trifluoromethyl addition

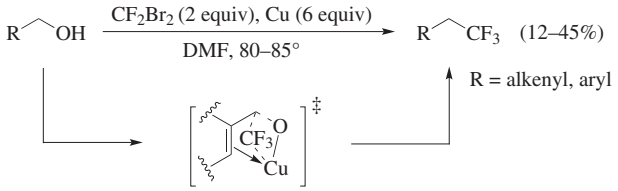
chemistry is the formation of halodifluoroacetate esters via transesterification of primary alcohols with simple alkyl halodifluoroacetates. In situ formation of such esters in the presence of KF and CuI in DMF at elevated temperatures is usually followed by rearrangement and decarboxylation, which leads to the product of formal hydroxyl substitution by a trifluoromethyl group (Scheme 139).[245]



R	X	Temp (°)	Yield (%)
CH_2=CH	Cl	100	71
Ph	Cl	100	43
Ph	Br	90	39
Ph	FSO_2	70	47
4-BrC_6H_4	Cl	100	40
(*E*)-PhCH=CH	Cl	100	64
(*E*)-PhCH=CH	Br	90	72
(*E*)-PhCH=CH	FSO_2	65	63

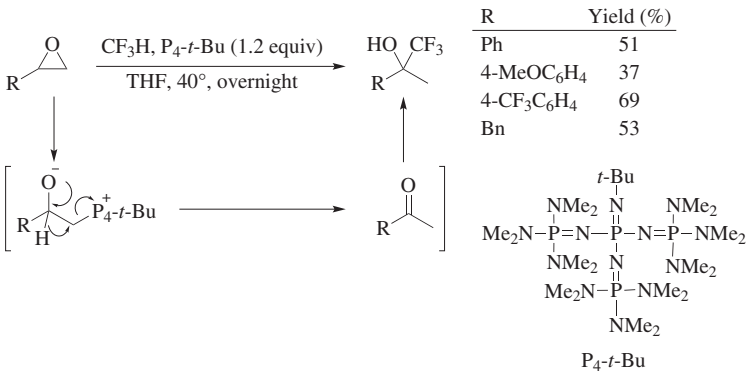
Scheme 139

Another interesting case of alcohol trifluoromethylation involves Cu-coordinated species. Trifluoromethylation of allylic or benzylic alcohols with CF_2Br_2/Cu proceeds in moderate yields. However, the structure of the proposed intermediate does not explain the lack of reactivity of α-substituted alcohols and is also not in line with the site of nucleophile approach in traditional nucleophilic processes (Scheme 140).[383]



Scheme 140

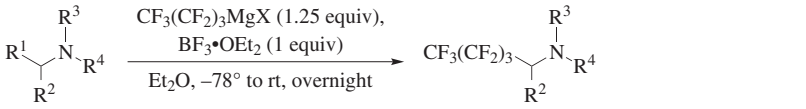
Epoxides. Although epoxide opening with perfluoroalkyl organometallic reagents has been reported,[199,321] epoxides are generally unreactive toward various nucleophilic perfluoroalkyl addition reagents. Recently, a combination of fluoroform and organo-superbase P_4-*t*-Bu has been reported to react with styrene oxides to form tertiary alcohols. The reaction is probably initiated by nucleophilic attack of P_4-*t*-Bu base at the terminal carbon of styrene oxide, then 1,2-hydride shift to a ketone followed by nucleophilic addition of the CF_3 group (Scheme 141).[81]



R	Yield (%)
Ph	51
4-$MeOC_6H_4$	37
4-$CF_3C_6H_4$	69
Bn	53

Scheme 141

Amines. *N*-(α-Aminoalkyl)benzotriazoles react with perfluoroalkyl Grignard reagents in the presence of BF_3•OEt_2 to form the corresponding perfluoroalkylated amines in moderate to good yields (Scheme 142).[384] In these reactions the benzotriazole moiety acts as a leaving group.



R^2	R^3	R^4	Yield (%)
H	Ph	Me	73
i-Pr	Ph	Me	60
i-Pr	Bn	Bn	56
Ph	Ph	Me	45
4-$O_2NC_6H_4$	$–(CH_2)_2O(CH_2)_2–$		61
$Ph(CH_2)_2$	Bn	Bn	64

Scheme 142

Aldehydes. Aldehydes are typical electrophilic substrates for nucleophilic perfluoroalkyl additions, and together with ketones make up more than half of all reported nucleophilic perfluoroalkyl addition reactions. Aldehydes are transformed into perfluoroalkyl-containing secondary alcohols using a wide range of perfluoroalkylating reagents described in the section Overview and Preparation of Nucleophilic Perfluoroalkyl Reagents. Aldehydes are typically the most reactive electrophilic carbonyl-containing compounds and therefore can be perfluoroalkylated with more stable and less reactive reagents such as perfluoroalkylzincs.

The most widely used nucleophilic reagents for perfluoroalkylation of aldehydes, including reaction conditions and approximate yields for various types of aldehydes are summarized in Table B.

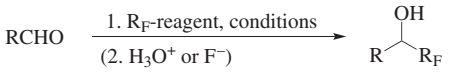


Table B. Summary of Reagents and Conditions for Nucleophilic Perfluoroalkyl Additions to Aldehydes

Entry	R_F-Reagent	Conditions	Yields (%)	Refs
	Aryl aldehydes			
1	CF_3H	electrogenerated **1b** or **1c**, DMF, –50° to –10°	34–92	69
2	CF_3H	PhI, electroreduction, DMF	12–76	70
3	CF_3H	*t*-BuOK, DMF, –40°	67	71
4	CF_3H	*t*-BuOK, toluene	34–51	77
5	CF_3H	$MeS(O)CH_2^-K^+$, DMF, –40° to rt	20–72	48,72
6	CF_3H	P_4-*t*-Bu, THF, –40 to –30°	52–88	81,82
7	CF_3CF_2H	*t*-BuOK, DMF, –40°	71	71
8	CF_3CF_2H	PhI, electroreduction, DMF	40	70
9	CF_3I	TDAE, DMF, (sun lamp irradiation), –20° to rt	68–90	127,385
10	R_FI ($R_F = CF_3$, C_2F_5, *n*-C_4F_9)	TDAE, DMF, –20° to rt	35–quant	127,386
11	$CF_3B(OMe)_3^-$ K^+	DMF, 50°	78–96	102
12	$CF_3CH(OH)_2$	*t*-BuOK, DMF, –50°	0–94	106
13	**11**	*t*-BuOK, *n*-BuN^+Cl^-, DMF, –30°	80–96	107
14	**7**, **8**	*t*-BuONa, THF, rt	65–98	110,111
15	**9**	CsF (cat.), DME, 60–80°	70–95	74,109
16	**12**	CsF (cat.), THF, reflux	69–89	116,117

(*continued*)

Table B. (*Continued*)

Entry	R_F-Reagent	Conditions	Yields (%)	Refs
17	**14c**	CsF (cat.), DME, rt	89–93	121
18	CF_3TMS	cat. TBAF, TMAF, TBAT, or TASF, THF or DME, rt	"high"	14–17
19	CF_3TMS	cat. KOH or $CsOH•H_2O$, $CF_3CH_2CF_2CH_3$, rt	"high"	387
20	CF_3TMS	cat. TBD, DMF, rt	"high"	388
21	CF_3TMS	cat. CsF, K_2CO_3, $Me_3N^+O^-$, DMF, rt	"high"	65,389
22	CF_3TMS	4 Å MS, DMF or DMSO, rt	"high"	136
23	CF_3Sn*n*-Bu_3	CsF, THF, rt	49–83	156
24	$CF_3P(O)(OEt)_2$	PhOK, DMF, –40° to rt	50–80	167
25	CF_3SPh	$Et_3Ge^-Na^+$, THF, –60°	91–92	170
26	CF_3SOPh	*t*-BuOK, DMF, –50° to rt	62–83	125
27	**18–20**, **21–23**	*t*-BuOK, THF, 0° to rt	30–91	181
28	R_FSO_2Ph ($R_F = CF_3$, C_2F_5)	*t*-BuOK, DMF or THF, –75° to rt	62–91	179,180
29	CF_3SO_2Ph	Mg, $HgCl_2$ (cat.), DMF –15° to rt	28–88	177
30	R_FI ($R_F = CF_3$, C_2F_5, *n*-C_4F_9, *n*-C_8F_{17})	Zn, paraquat (cat.), MeCN, rt	42–65	390
31	R_FLi ($R_F = C_2F_5$, *n*-C_3F_7)	Et_2O, –95 to –40°, Barbier conditions	54–91	188–190,391,392
32	R_FInX ($R_F = CF_3$, *n*-C_6F_{13})	DMF, ferrocene, LiCl, rt	41–54	235

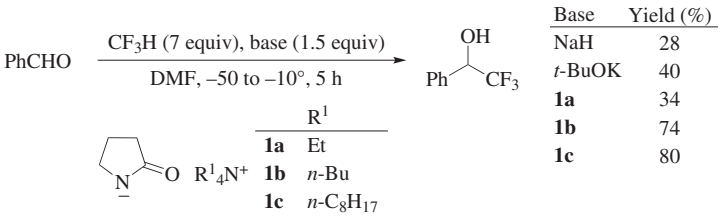
	Non-enolizable alkyl or alkenyl aldehydes			
33	CF_3H	PhI, electroreduction, DMF	46	70
34	CF_3H	P_4-*t*-Bu, THF, –40 to –30°	81	81,82
35	R_FI ($R_F = CF_3$, C_2F_5, *n*-C_4F_9)	TDAE, DMF, –20° to rt	80	127,386
36	$CF_3B(OMe)_3^-\ K^+$	DMF, 50°	97	102
37	CF_3SiMe_3	cat. TBAF, TMAF, TBAT, or TASF, THF or DME, rt	"high"	14–17
38	CF_3SiMe_3	cat. KOH or $CsOH{\bullet}H_2O$, $CF_3CH_2CF_2CH_3$, rt	"high"	387
39	CF_3SiMe_3	cat. TBD, DMF, rt	"high"	388
40	CF_3SiMe_3	cat. CsF, K_2CO_3, $Me_3N^+O^-$, DMF, rt	"high"	65,389
41	CF_3SiMe_3	4 Å MS, DMF or DMSO, rt	"high"	136
42	CF_3SPh	$Et_3Ge^-Na^+$, THF, –60°	92–96	170
43	R_FSO_2Ph ($R_F = CF_3$, C_2F_5)	*t*-BuOK, DMF or THF, –75° to rt	79–89	179,180
44	R_FMgX ($R_F = C_2F_5$, *n*-C_3F_7, *n*-C_4F_9, *n*-C_6F_{13}, *n*-C_8F_{17})	Et_2O or THF, –70 to –40°	60–70	393–395,202,204

(*continued*)

Table B. (*Continued*)

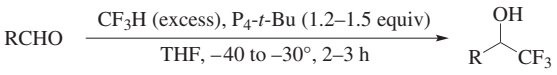
Entry	R_F-Reagent	Conditions	Yields (%)	Refs
	Enolizable alkyl aldehydes			
45	CF_3H	$MeS(O)CH_2^-K^+$, DMF, –40° to rt	45	48,72
46	CF_3H	P_4-*t*-Bu, THF, –40 to –30°	48–53	81,82
47	CF_3I	TDAE, DMF, (sun lamp irradiation), –20° to rt	0–62	127,385
48	R_FI ($R_F = CF_3$, C_2F_5, *n*-C_4F_9)	TDAE, DMF, –20° to rt	5–35	127,386
49	$CF_3B(OMe)_3^-$ K^+	DMF, 50°	48–53	102
50	CF_3TMS	cat. TBAF, TMAF, TBAT, or TASF, THF or DME, rt	"high"	14–17
51	CF_3TMS	cat. KOH or $CsOH•H_2O$, $CF_3CH_2CF_2CH_3$, rt	"high"	387
52	CF_3TMS	cat. TBD, DMF, rt	"high"	388
53	CF_3TMS	4 Å MS, DMF or DMSO, rt	"high"	136
54	$CF_3P(O)(OEt)_2$	PhOK, DMF, –40° to rt	50–80	167
55	CF_3SPh	$Et_3Ge^-Na^+$, THF, –60°	86	170
56	CF_3SO_2Ph	Mg, $HgCl_2$ (cat.), DMF –15° to rt	45	177
57	R_FX (X = Br, I, R_F = CF_3, C_2F_5, *n*-C_4F_9, *n*-C_8F_{17})	Zn, ultrasound, DMF	47–71	396
58	R_FI ($R_F = CF_3$, C_2F_5, *n*-C_4F_9, *n*-C_8F_{17})	Zn, paraquat (cat.), MeCN, rt	48–68	390
59	R_FLi ($R_F = C_2F_5$, *n*-C_3F_7)	Et_2O, –95 to –40°, Barbier conditions	up to 98	188–190,391,392
60	R_FMgX (R_F = C_2F_5, *n*-C_3F_7, *n*-C_4F_9, *n*-C_6F_{13}, *n*-C_8F_{17})	Et_2O or THF, –70 to –40°	low	393–395,202,204
61	R_FInX	DMF, ferrocene, LiCl, rt	43	235

Trifluoromethylation of benzaldehyde by the trifluoromethyl anion formed by the deprotonation of fluoroform with an electrochemically generated base (from 2-pyrrolidinone in DMF at –50°) yields the corresponding carbinol (Schemes 143 and 11).[69] This process is more efficient than using common strong bases such as NaH or *t*-BuOK, in which benzyl alcohol and benzoic acid are the main products of the competing Cannizzaro reaction. A range of aromatic aldehydes are trifluoromethylated using base **1b** and fluoroform.[69]



Scheme 143

Phenyl anion, produced by electroreduction of a large excess of iodobenzene in DMF, is able to deprotonate fluoroform or pentafluoroethane in the presence of a series of aldehydes to afford the corresponding perfluoroalkylated carbinols. Good yields are obtained for aldehydes less easily reduced than iodobenzene.[70] Under appropriate experimental conditions, trifluoromethylation of aromatic aldehydes can be performed by an excess of fluoroform in the presence of *t*-BuOK in toluene[77] or DMF at low temperature.[71,75,76] The corresponding pentafluoroethylation with C_2F_5H proceeds with comparable efficiency.[71,75,76] Dimsyl potassium as the base affords a 65% yield for the trifluoromethylation of benzaldehyde, whereas dimsyl sodium or KH alone are much less effective.[48] Other aromatic, non-enolizable aldehydes are trifluoromethylated using fluoroform and dimsyl potassium in moderate to good yields, whereas the enolizable cyclohexanecarbaldehyde offers the trifluoromethylated product in 45% yield.[48,72] The very sterically demanding Schwesinger organo-superbase P_4-*t*-Bu is sufficiently strong to deprotonate fluoroform to effect trifluoromethylation of a variety of aldehydes, including enolizable ones, in good yields (Scheme 144).[81,82]



R	Yield (%)	R	Yield (%)
t-Bu	81	4-$O_2NC_6H_4$	52
2-thienyl	65	4-MeC_6H_4	76
n-C_6H_{13}	48	1-naphthyl	65
Ph	75	2-naphthyl	88
4-ClC_6H_4	86	1-Br-2-naphthyl	65
4-BrC_6H_4	80	2-anthryl	74

Scheme 144

Non-enolizable aldehydes are efficiently trifluoromethylated using the CF_3I/TDAE system with irradiation by a sun lamp.[385,386]

Potassium trialkoxy(trifluoromethyl)borates, prepared from trialkoxyborates and $TMSCF_3$, act as nucleophilic trifluoromethylating reagents toward non-enolizable aldehydes. Enolizable aldehydes provide lower yields because of competing self-condensation reactions.[102]

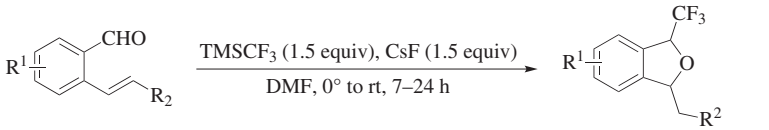
Trifluoroacetaldehyde hydrate in the presence of *t*-BuOK trifluoromethylates aromatic aldehydes.[106] Similar trifluoromethylation of aromatic aldehydes is observed with the non-hygroscopic amidinate salt of hexafluoroacetone hydrate, compound **11**.[107] Trifluoromethylation of benzaldehyde and other non-enolizable aldehydes using trifluoroacetaldehyde-derived hemiaminals **4**, **5**, and **8** (Schemes 21 and 23) in the presence of *tert*-butoxide proceeds in good to excellent yields.[105,110,111] Application of trimethylsilyl-containing hemiaminals **9** and **10** (Scheme 23) avoids the use of strong base. Thus, in the presence of CsF, non-enolizable aldehydes are transformed into trifluoromethyl-containing trimethylsilyl ethers in high yields.[109,74] Trimethylsilyl-protected hemiketal **12** (Scheme 26) derived from trifluoroacetophenone is another shelf-stable trifluoromethylating reagent for non-enolizable aldehydes.[116,117] In contrast to ketones, aromatic aldehydes are not trifluoromethylated by trifluoroacetophenone in the presence of *t*-BuOK.[115] A similar lack of reactivity is observed for methyl trifluoroacetate/*t*-BuOK.[119] Amide **14c** (Scheme 27) is able to trifluoromethylate aldehydes using catalytic amounts of CsF in DME or TBAT in THF.[42,121]

(Perfluoroalkyl)trialkylsilanes in the presence of fluoride or other Lewis base initiators transform a wide range of structurally diverse aldehydes into perfluoroalkyl-containing secondary alcohols. Polar solvents such as DMSO or DMF in the presence of 4 Å molecular sieves also promote the addition of $TMSCF_3$ to aldehydes;[136] however, it should be noted that $TMSCF_3$ adds to both DMSO and DMF in the presence of TBAF or Et_4NCN.[75,137,397] A variety of functional groups are compatible in the perfluoroalkyl addition of $TMSCF_3$ to aldehydes (or ketones), including halogens, *O*, *N*, *S*-heterocycles,[398,399] nitro,[65] cyano,[400,401] azido,[402] dialkylamino,[446,403–405] hydroxy,[134,398,406] alkoxy,[407–409] silyloxy,[410–413,446] arylsulfonyl,[400,414,415] ester,[410,416–418] *N*,*N*-dialkylamide,[419–422] phosphonate,[423] and phosphate[424] groups. Several porphyrins, chlorins, and bacteriochlorins (nickel or zinc complexes or free bases) containing an aldehyde group are trifluoromethylated to the corresponding trifluoromethyl carbinols using the $TMSCF_3$/TBAF (cat.) system.[425–431] Trifluoromethylation of various aldehydes with $TMSCF_3$ in flow using a monolithic fluoride column provides products in high yields.[432]

α,β-Unsaturated aldehydes, such as acrolein, prenal, phenylpropynal, or cinnamaldehyde, undergo exclusively 1,2-addition to the carbonyl group using $TMSCF_3$.[289,65,398,433–437] α-Keto aldehydes react with two moles of $TMSCF_3$ and catalytic amounts of CsF to generate a mixture of trifluoromethylated products; trifluoromethylated hydroxy ketones (major) and 1,2-bis(trifluoromethyl)-1,2-diols (minor), resulting from addition to the formyl, and both keto and formyl functions, respectively.[438] 4-Acetylbenzaldehyde also yields a product mixture with one

equivalent of $TMSCF_3$ in the presence of TBAF in various solvents.[142] Interestingly, chemoselective trifluoromethylation of aldehydes over ketones is achieved using carbene **16a** (0.5 mol %) and an excess of $TMSCF_3$ (5 equiv) in DMF.[142]

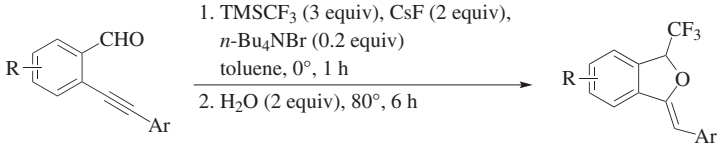
Tandem nucleophilic addition and intramolecular cyclization of 2-formyl cinnamic acid derivatives (Scheme 145)[439] and 2-alkynyl aryl aldehydes (Scheme 146)[440] requires the use of an excess of a fluoride initiator to ensure the presence of a sufficient concentration of alkoxide anion for 5-*exo-trig* or 5-*exo-dig* cyclizations.



R^1 = H, 4-O_2N, 3,4-OCH_2O
R^2 = R^3CO, R^3O_2C, NC–

(57–91%) dr 60:40 to 80:20

Scheme 145

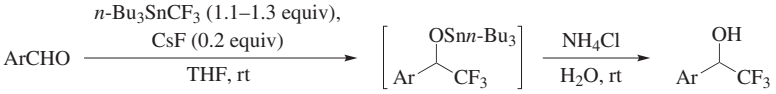


R = H, 3-Cl, 3-MeO, 3,4-OCH_2O, 3-CF_3, 3-SCH=CH-4-

(53–93%)

Scheme 146

Tributyl(trifluoromethyl)stannane reacts with aromatic aldehydes under CsF activation to afford the corresponding trifluoromethylated stannane ether intermediate, which under mildly acidic workup provides trifluoromethylated secondary alcohols (Scheme 147).[156]

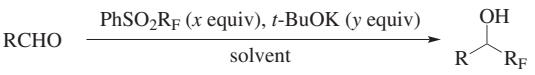


Ar	Time (h)	Yield (%)
4-BrC_6H_4	9	70
4-$O_2NC_6H_4$	9	49
4-$Me_2NC_6H_4$	22	70
4-$MOMOC_6H_4$	8	67
4-$THPOC_6H_4$	8	64
5-$TrOC_6H_4$	8	68[a]
9-anthryl	8	83

[a] Decomposes upon standing.

Scheme 147

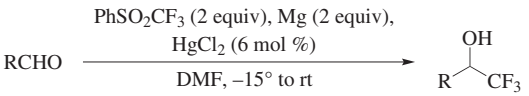
A variety of sulfur-based nucleophilic perfluoroalkylating reagents show reactivity toward aldehydes. Trialkylgermyl anion (R_3Ge^-) in combination with $PhSCF_3$ is used for efficient and mild trifluoromethylation of aldehydes.[170] Phenyl trifluoromethyl sulfoxide,[179] trifluoromethanesulfinates **18–20**, and trifluoromethanesulfinamides **21–23** (derived from secondary amines in the presence of *t*-BuOK[181]) are used as nucleophilic trifluoromethylating reagents for non-enolizable aldehydes. Non-enolizable aldehydes undergo alkoxide-induced nucleophilic trifluoromethylation and pentafluoroethylation using perfluoroalkyl sulfones (Scheme 148).[179,180] In a conceptually different process, phenyl trifluoromethyl sulfone participates in nucleophilic trifluoromethylation of aldehydes (including enolizable ones) in the presence of magnesium activated with a catalytic amount of mercury(II) chloride (Scheme 149).[177]



R	R_F	*x*	*y*	Solvent	Temp (°)	Yield (%)
t-Bu	CF_3	2	2.5	DMF	–50 to rt	— (79)[a]
Ph	CF_3	2	2.5	DMF	–50 to rt	77
Ph	C_2F_5	1.5	4.5	THF	–78 to –70	91
4-BrC_6H_4	C_2F_5	1.5	4.5	THF	–78 to –70	85
4-MeC_6H_4	C_2F_5	1.5	4.5	THF	–78 to –70	84
4-EtC_6H_4	CF_3	2	2.5	DMF	–50 to rt	83
(*E*)-PhCH=CH	C_2F_5	1.5	4.5	THF	–78 to –70	89
2-naphthyl	CF_3	2	2.5	DMF	–50 to rt	62
4-PhC_6H_4	CF_3	2	2.5	DMF	–50 to rt	76

[a] Conversion determined by ^{19}F NMR spectroscopy.

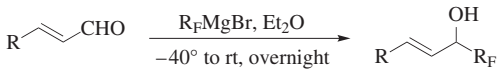
Scheme 148



R	Yield (%)
Ph	88
2-ClC_6H_4	60
4-$O_2NC_6H_4$	28
4-$MeOC_6H_4$	88
$Ph(CH_2)_2$	45
1-naphthyl	60

Scheme 149

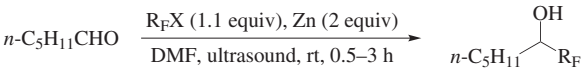
Simple aldehydes including formaldehyde, acetaldehyde, benzaldehyde, and α,β-unsaturated aldehydes (Scheme 150)[202,393,395] undergo nucleophilic perfluoroalkylation with perfluoroalkyl Grignard reagents to afford the corresponding perfluoroalkyl secondary alcohols in moderate to good yields. The reactions are performed in ether solvent at low temperature.[202,393,395] Formation of bis(perfluoroalkyl) ketones and bis(perfluoroalkyl) alcohols is observed in the reaction of perfluoroalkyl aldehydes with *n*-C_3F_7MgI.[204]



R	R_F	Yield (%)
Me	C_2F_5	60
Ph	C_2F_5	70
Ph	n-C_6F_{13}	60
Ph	n-C_8F_{17}	60

Scheme 150

Both enolizable and non-enolizable aldehydes react readily with perfluoroalkyllithium reagents in dilute ethereal solution at low temperature (–78° or lower).[188,190,391] Aliphatic and aromatic aldehydes are readily perfluoroalkylated by ultrasound-promoted reactions of perfluoroalkyl halides and zinc in DMF in moderate to good yields (Scheme 151).[396] Perfluoroalkyl bromides usually react slower and give lower yields of products than perfluoroalkyl iodides.[396]

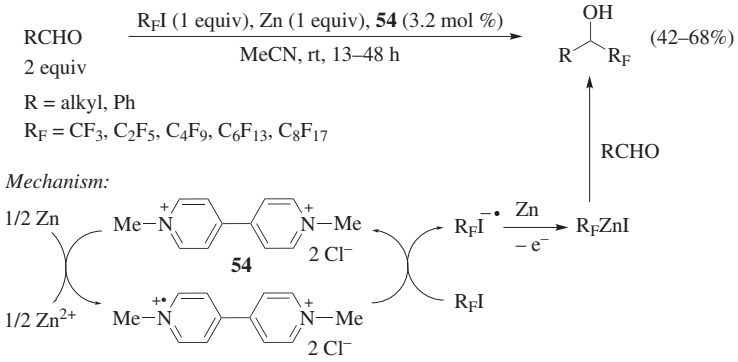


$R_F = CF_3, C_2F_5, C_4F_9, C_8F_{17}$
X = Br, I

(47–71%)

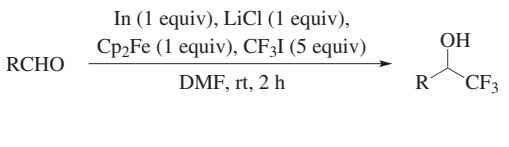
Scheme 151

The use of paraquat (**54**) as an electron-transfer catalyst allows efficient aldehyde perfluoroalkylation using perfluoroalkyl iodides and zinc in acetonitrile (Scheme 152).[390] The reaction does not take place without paraquat.



Scheme 152

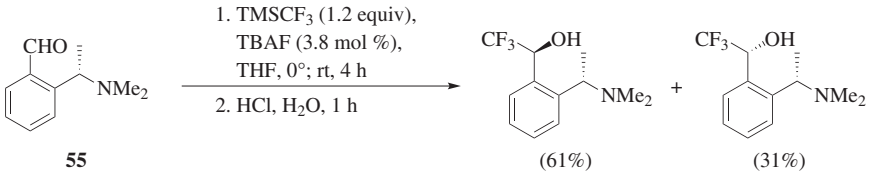
Addition of trifluoromethylindium to aldehydes provides moderate yields of trifluoromethyl alcohols. This process allows direct nucleophilic trifluoromethylation with CF_3I in the presence of ferrocene as a single-electron transfer mediator (Scheme 153).[235]



R	Yield (%)
Ph	54
n-C_7H_{15}	43
β-styryl	50
1-naphthyl	54
2-naphthyl	41

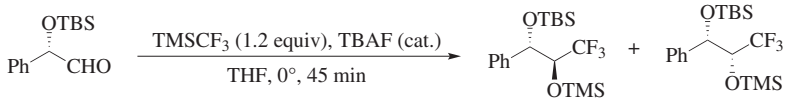
Scheme 153

Diastereoselective Perfluoroalkyl Addition to Aldehydes. Simple addition of $TMSCF_3$ to substituted carbonyl compounds generally does not provide high diastereomeric selectivities. 2-Phenylpropanal undergoes trifluoromethylation with $TMSCF_3$ in the presence of triethylamine to afford the corresponding trifluoromethylated secondary carbinol in an 85:15 diastereomeric ratio.[138] Several artemisinin analogues possessing an aldehyde group are trifluoromethylated in good yields and moderate diatereoselectivities.[441,442] Aromatic amino aldehyde **55** undergoes trifluoromethylation in good yield and a 67:33 dr (Scheme 154).[443] Aldehyde **56** derived from L-mandelic acid undergoes trifluoromethylation to provide a separable diastereomeric mixture of protected 1,2-diols **57** and **58** with low dr (Scheme 155).[444] Amino aldehydes **59** (Scheme 156)[445] and **60** (Scheme 157)[411] provide mixtures of diastereomers in good yields and better ratios of 82:18 and 86:14, respectively.



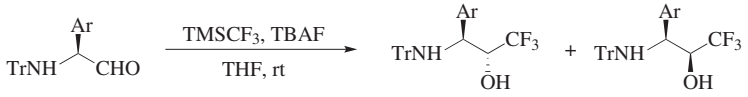
55 (61%) (31%)

Scheme 154



56 **57** (36%) **58** (40%)

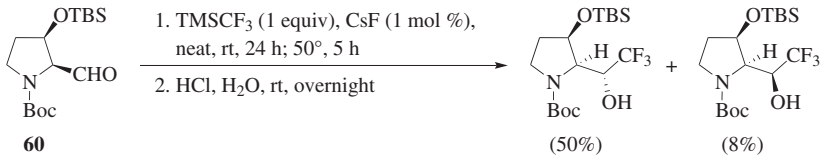
Scheme 155



59
Ar = 4-$O_2NC_6H_4$

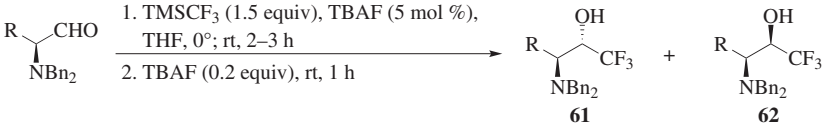
(72%) (16%)

Scheme 156



Scheme 157

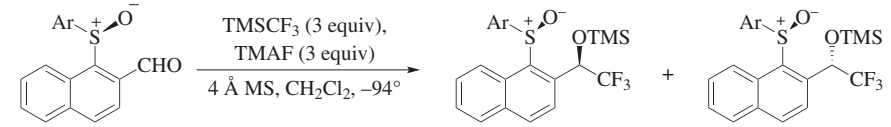
Enantiopure α-dibenzylamino aldehydes, prepared from the corresponding α-amino acids, react with $TMSCF_3$ in the presence of TBAF to afford moderate to good yields of β-amino-α-(trifluoromethyl) alcohols **61** and **62** with low to moderate diastereoselectivity (Scheme 158).[446] A number of chiral amino alcohols are accessed by trifluoromethylation of *N*-protected α-amino aldehydes (derived from α-amino acids) with low to good diastereoselectivity.[447,448]



R	**61** + **62**, Yield (%)	**61/62**
Me	74	80:20
i-Pr	63	84:16
i-Bu	81	72:28
Ph	40	46:54
Bn	72	76:24

Scheme 158

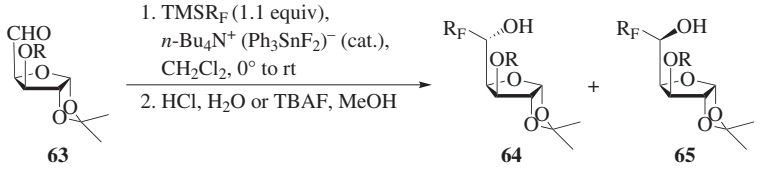
Diastereoselective trifluoromethylation of 1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthaldehyde with $TMSCF_3$ in the presence of TMAF and molecular sieves affords the trifluoromethylated product in high yield and diastereoselectivity (Scheme 159).[449] Subsequent desilylation, recrystallization, and cleavage of the sulfinyl group affords the enantiomerically pure 1-(2-naphthyl)-2,2,2-trifluoroethanol.



Scheme 159

A number of trifluoromethyl derivatives of carbohydrates have been synthesized by nucleophilic perfluoroalkyl addition.[450] Open-chain carbohydrate aldehydes generally react with low diastereoselectivity compared to cyclic sugars. Thus,

trifluoromethylation of a protected aldehyde derivative of D-lyxose with $TMSCF_3$ and TBAF proceeds in 79% yield but without diastereoselectivity.[408] Similarly, trifluoromethylation of a protected aldehyde derived from L-arabinose gives a 50:50 mixture of diastereomers of the trifluoromethylated products in 85% yield.[409] Benzyl or allyl derivatives **63** undergo perfluoroalkyl addition in the presence of n-$Bu_4N^+(Ph_3SnF_2)^-$ to form a mixture of alcohols **64** and **65** in good yields and moderate diastereoselectivities (Scheme 160).[216] Interestingly, yields drop but diastereoselectivity improves to 95:5 when perfluoroalkyl Grignard reagents are used.[216]

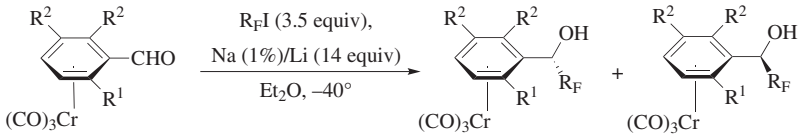


63 **64** **65**

R	R_F	**64** + **65**, Yield (%)	**64/65**
CH_2=$CHCH_2$	CF_3	98	88:12
Bn	CF_3	95	80:20
Bn	n-C_4F_9	65	85:15

Scheme 160

The addition of perfluoroalkyllithium reagents to substituted benzaldehyde–chromium(0) complexes is highly diastereoselective affording products **66** and **67**[451,452] (Scheme 161).[452]



66 **67**

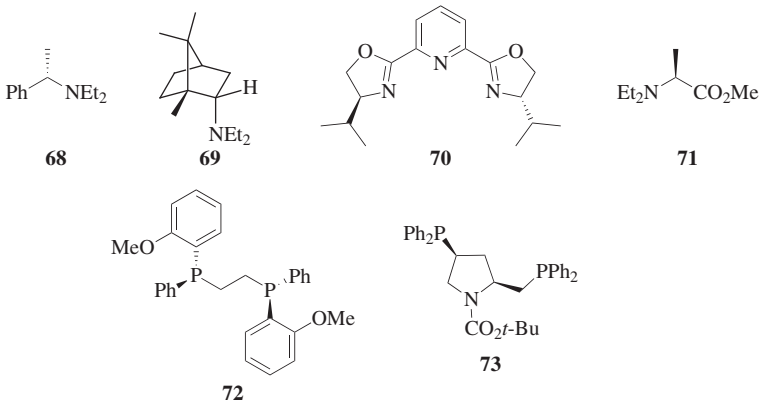
R^1	R^2	R_F	Time (h)	**66** + **67**, Yield (%)	**66/67**
H	MeO	C_2F_5	2	72	>99:1
H	MeO	i-C_3F_7	12	51	>99:1
MeO	H	C_2F_5	1	72	>99:1
Me	H	C_2F_5	1	87	94:6
Me	H	i-C_3F_7	12	40	88:12

Scheme 161

Enantioselective Perfluoroalkyl Addition to Aldehydes. Two different approaches are employed in the design of enantioselective trifluoromethylations of aldehydes and ketones using $TMSCF_3$. The first approach employs the chiral Lewis basic site of the initiator, essentially generating chiral, hypercoordinate silicon trifluoromethylating species. Although only a small amount of the initiator is needed, many enantioselective trifluoromethylations use substoichiometric amounts of chiral

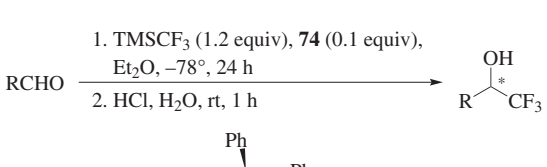
inducers to suppress the undesirable background reaction leading to the racemic product. However, the autocatalytic reaction with the generated alkoxide adducts can still compromise product enantioselectivity. The second approach employs an initiator containing a chiral cation. This approach derives from the mechanism of trifluoromethylation using tetraalkylammonium fluoride as the initiator where the cation is closely associated with the alkoxy adduct during the reaction (Scheme 33).

Enantioselective trifluoromethylation of benzaldehyde using $TMSCF_3$ employs chiral Lewis bases such as amines (epinephrine, **68–70**), the amino acid derivative **71**, alkaloids (nicotine, quinine, quinidine), and phosphines (**72**, **73**) as effective catalysts, but the enantioselectivities are low. With quinine, the enantioselectivity of trifluoromethylation can be somewhat improved by using bulky groups in the trialkyl(trifluoromethyl)silanes (up to 60:40 er with Et_3SiCF_3).[139,138] 4-Bromobenzaldehyde is trifluoromethylated in quantitative yield but with only 53:47 er using $TMSCF_3$ and 10 mol % of sodium L-mentholate as Lewis basic initiator.[134]

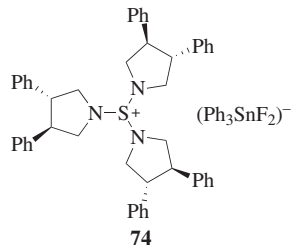


68 **69** **70** **71** **72** **73**

The (*S,S*)-3,4-diphenylpyrrolidine-derived chiral triaminosulfonium salt **74** catalyzes the trifluoromethylation of aldehydes in very good yields and low to moderate enantioselectivities (Scheme 162),[453] as does the C_2-symmetric chiral crown ether catalyst **75** (Scheme 163).[454]

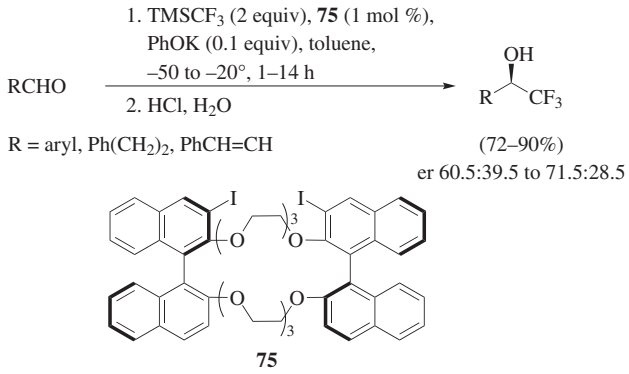


R	Yield (%)	er
c-C_6H_{11}	88	55:45
Ph	96	76:24
4-ClC_6H_4	93	65:35
4-$MeOC_6H_4$	97	68.5:31.5
2-MeC_6H_4	98	66.5:33.5
4-$CF_3C_6H_4$	90	62:38
(*E*)-PhCH=CH	99	59:41
1-naphthyl	71	56:44



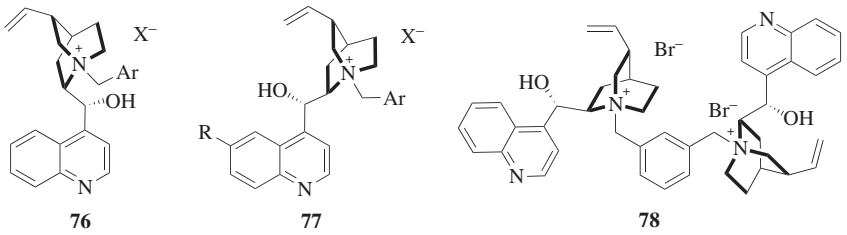
74

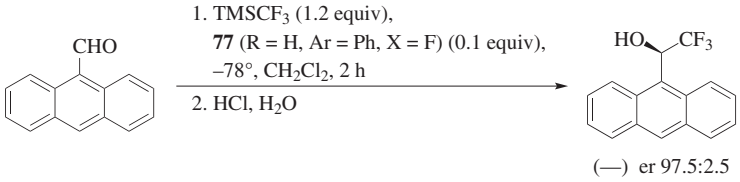
Scheme 162



Scheme 163

Chiral quaternary ammonium salts **76–78** derived from cinchona alkaloids have been investigated in detail in enantioselective trifluoromethylations of aldehydes. The use of *N*-benzylquinidinium fluoride in dichloromethane at −78° allows trifluoromethylation of 9-anthryl aldehyde in 97.5:2.5 er (no yield or conversion reported) (Scheme 164).[455] *N*-[(Trifluoromethyl)benzyl]cinchonium fluorides are effective catalysts for the enantioselective trifluoromethylation of aldehydes and ketones and provide the corresponding alcohols with low to moderate enantiomeric ratios.[456]

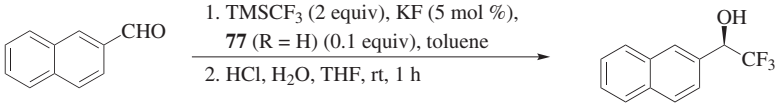




Scheme 164

Potassium fluoride – an inexpensive fluoride source – in combination with the chiral ammonium chloride or bromide **77** (R = H) catalyses the enantioselective trifluoromethylation of 2-naphthaldehyde. Enantiomeric ratios of up to 70:30 are obtained

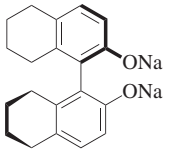
(Scheme 165).[457] A similar enantioselectivity (er 70.5:29.5) is achieved with catalyst **78** and TMAF.[458]



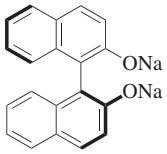
77 Ar	**77** X	Temp (°)	Time (h)	Yield (%)	er
Ph	Br	rt	10	67	95:5
2-$CF_3C_6H_4$	Br	rt	24	44	59.5:40.5
3-$CF_3C_6H_4$	Br	rt	24	67	59.5:40.5
4-$CF_3C_6H_4$	Br	0	2	81	63:37
2,4-$(CF_3)_2C_6H_3$	Br	rt	16	58	65.5:34.5
2,5-$(CF_3)_2C_6H_3$	Br	rt	48	34	64:36
3,5-$(CF_3)_2C_6H_3$	Cl	0	3.5	90	68:32
3,5-$(CF_3)_2C_6H_3$	Br	rt	18	54	70:30

Scheme 165

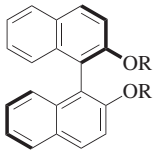
Improved enantioselectivities in the trifluoromethylation of 2-naphthaldehyde are observed when a combination of chiral quaternary ammonium salt **77** with chiral Lewis bases such as disodium binaphtholates **79–81a** or chiral Schiff bases **82** are used. Disodium binaphtholate **81a** is prepared in situ from sodium hydroxide and (*R*)-binaphthol (**81b**), and in the presence of molecular sieves the product, 1,1,1-trifluoro-2-naphthalen-2-yl-propan-2-ol, is obtained in 85% yield and with 85.5:14.5 er (Scheme 166).[459] Importantly, the reaction does not proceed with a monosodium binaphtholate. The authors suggest a mechanism involving activation of $TMSCF_3$ to form a hexacoordinate silicon intermediate that includes both oxygens of the binaphtholate, and activation of the carbonyl group of the substrate by the positively charged nitrogen atom of **77**. Under optimized conditions a range of aryl aldehydes are trifluoromethylated in very good yields and with moderate enantioselectivities (Scheme 167).[459]



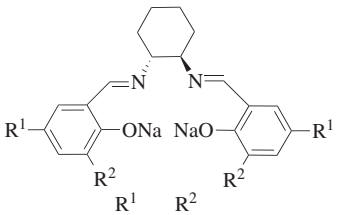
79



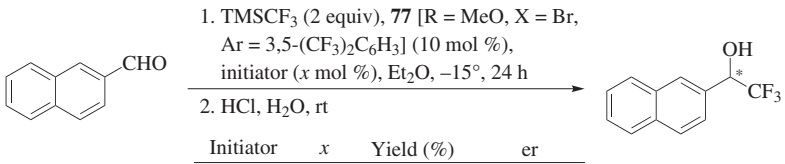
80



	R
81a	Na
81b	H



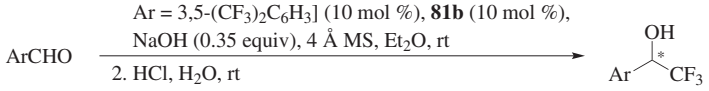
	R^1	R^2
82a	H	Ph
82b	*t*-Bu	*t*-Bu
82c	*t*-Bu	1-adamantyl



Initiator	x	Yield (%)	er
79	10	27	69:31
80	20	80	69:31
81a	10	86	76.5:23.5
81a	20	87	75:25
81b[a]	10	85	85.5:14.5
82a	10	33	71:29
82b	20	80	70:30
82c	10	69	72:28

[a] NaOH (0.25 equiv) and 4 Å MS were added and the reaction was carried out for 2 h.

Scheme 166



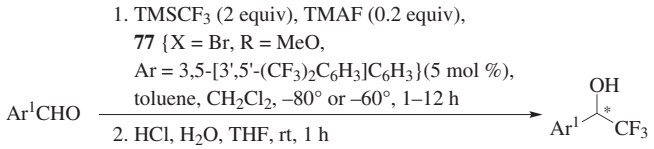
Ar	Yield (%)	er
2-thienyl	68[a]	72.5:27.5
Ph	72	78:22
4-FC_6H_4	86[a]	78.5:21.5
3-ClC_6H_4	95[a]	78:22
4-ClC_6H_4	72	75:25
4-$MeOC_6H_4$	87	70.5:29.5
3-MeC_6H_4	88[a]	79:21
4-MeC_6H_4	87	80:20
4-PhC_6H_4	73	78:22

[a] The product was isolated as the trimethylsilyl ether.

Scheme 167

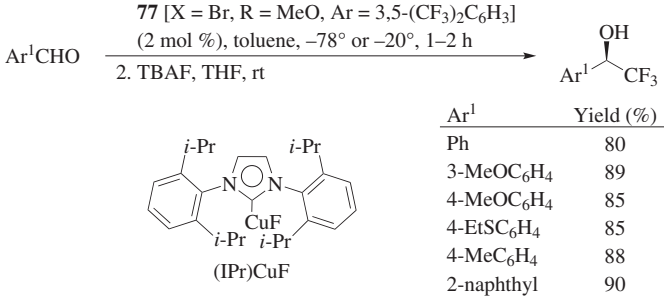
The best enantioinduction in nucleophilic trifluoromethylation of aromatic aldehydes is observed using sterically demanding cinchona alkaloid derived phase-transfer catalyst **77** {X = Br, R = MeO, Ar = 3,5-[3′,5′-$(CF_3)_2C_6H_3$]C_6H_3} in combination with substoichiometric amounts of TMAF (Scheme 168)[460] or with cooperative catalysts **77** [X = Br, R = MeO, Ar = 3,5-$(CF_3)_2C_6H_3$] and (IPr)CuF (Scheme 169).[461,462] In the first case, some background reaction (generating racemic product) initiated by TMAF in the absence of catalyst **77** is observed; in the second case, (IPr)$CuCF_3$ is believed to be formed. In both cases the hydroxyl group of catalyst **77** presumably contributes to stabilization of the transition structure in enantioselective trifluoromethylation by hydrogen bonding with the carbonyl group of the aldehyde substrate. Additional stabilizing interactions are possible from π-π stacking of the aromatic ring of the aldehyde and the quinolone moiety of the catalyst, supported by the increased enantioselectivity observed with aldehydes bearing electron-donating

substituents, compared to those with electron-withdrawing groups. An electrostatic interaction of the nitrogen cation of the chiral catalyst **77** with the trifluoromethyl carbanion or formed alkoxide intermediate is also considered to be significant.[460,461,462]



Ar^1	Yield (%)	er
3-ClC_6H_4	70	77.5:22.5
3-$MeOC_6H_4$	82	85:15
4-MeC_6H_4	76	80:20
2-naphthyl	92	83:17
9-anthryl	96	75:25

Scheme 168

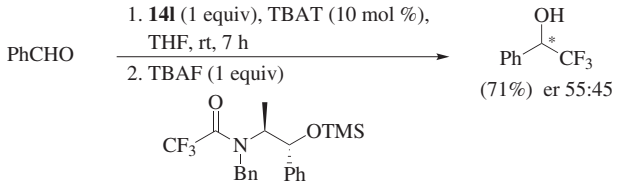


(IPr)CuF

Ar^1	Yield (%)	er
Ph	80	80:20
3-$MeOC_6H_4$	89	87:13
4-$MeOC_6H_4$	85	83.5:16.5
4-$EtSC_6H_4$	85	87:13
4-MeC_6H_4	88	84:16
2-naphthyl	90	87.5:12.5

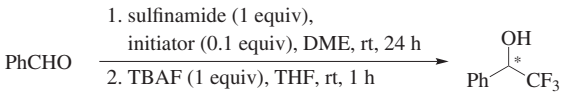
Scheme 169

Enantioselective trifluoromethylations of aldehydes using chiral trifluoroacetamides **14d–n** provide disappointing results; racemic mixtures of 1-phenyl-2,2,2-trifluoroethanol are obtained from benzaldehyde and amides **14d**, **14g**, **14j**, **14m**, or **14n** (Scheme 27), and low er is observed using amide **14h**. Amide **14l** is the only reagent that produces a significant enantioinduction and the product is obtained in about 55:45 er (Scheme 170).[42] Rather low enantioselectivities are also observed in trifluoromethylations of benzaldehyde with chiral sulfinamides **26** or **30** in the presence of CsF or chiral fluoride salt **77**[41–43] (Scheme 171).[42]



14l

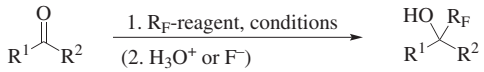
Scheme 170



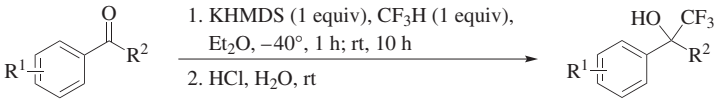
Sulfinamide	Initiator	Yield (%)	er
26	CsF	65	60:40
26	**77** (R = H, Ar = Ph, X = F)	31	65:35
30	CsF	33	58.5:41.5

Scheme 171

Ketones. Ketones, like aldehydes, are very common substrates in nucleophilic perfluoroalkyl additions. Their reactivity is somewhat lower than that of aldehydes (especially for sterically hindered ketones), but still much higher than the reactivity of esters or amides. The most widely used nucleophilic reagents for perfluoroalkylation of ketones are summarized in Table C. The perfluoroalkyl addition reagents and conditions can be broadly divided into two categories. The methods in the first category provide good yields only with aromatic and other non-enolizable ketones; the methods in the second category avoid the use of strongly basic conditions and reagents and are applicable to all ketones.



Several methods for trifluoromethylating ketones using fluoroform are available. Base **1b**, generated by electroreduction of 2-pyrrolidone, deprotonates, fluoroform, and the resulting trifluoromethyl carbanion trifluoromethylates ketones, including enolizable ones, in good yields.[69] The system consisting of $(TMS)_3N$/TBAF in DMF also provides good results.[73] The yields for non-enolizable ketones such as benzophenone are high; however, for enolizable ketones such as acetophenone the yields reach only 26–50%. α,β-Unsaturated ketones exclusively generate 1,2-addition products. A stoichiometric amount of fluoroform with KHMDS is used for efficient trifluoromethylation of aromatic ketones and chalcones (Scheme 172).[77] Organo-superbase P_4-*t*-Bu deprotonates fluoroform and stabilizes the trifluoromethyl anion for nucleophilic addition to ketones, including (enolizable) acetophenone (Scheme 173).[81,82]



R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
H	Ph	71	H	(*E*)-PhCH=CH	67
4-F	Ph	81	4-F	(*E*)-4-FC_6H_4CH=CH	38
3-O_2N	Ph	78	4-Cl	(*E*)-PhCH=CH	60
4-MeO	Ph	54	4-O_2N	(*E*)-PhCH=CH	0
4-Me	Ph	53	4-MeO	(*E*)-PhCH=CH	63

Scheme 172

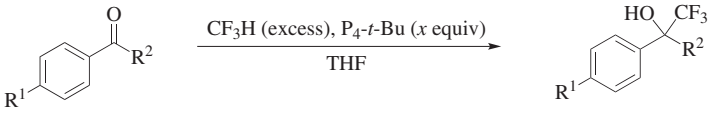
Table C. Summary of Reagents and Conditions for Nucleophilic Perfluoroalkyl Additions to Ketones

Entry	R_F-Reagent	Conditions	Yields (%)	Ref.
	Non-enolizable ketones			
1	CF_3H	electrogenerated **1b**, HMDS, DMF, –50° to –10°	65–84	69
2	CF_3H	$(TMS)_3N$, TBAT, DMF, –10°	33–91	73
3	CF_3H	*t*-BuOK, DMF, –10°	56–75	73
4	CF_3H	KHMDS, Et_2O	0–67	77
5	CF_3H	P_4-*t*-Bu, THF, –40° to –30°	72–99	81,82
6	CF_3I, C_2F_5I	TDAE, DMF, (sun lamp irradiation), –20° to rt	53–95	385,386
7	$CF_3B(OME)_3^-$ K^+	DMF, 50°	90	102
8	$CF_3CH(OH)_2$	*t*-BuOK, DMF, –50°	45–96	106
9	**11**	*t*-BuOK, *n*-BuN^+Cl^-, DMF, –30°	78–94	107
10	**8**	*t*-BuOK, THF, rt	47–80	110
11	**9**, **10**	CsF (cat.), DME, 60° or 80°	70–90	74,109
12	$PhC(O)CF_3$	*t*-BuOK, THF, DMF, rt	50–98	115
13	**12**	CsF (cat.), THF, heating	41–92	117,116
14	**13**	*t*-BuOK, THF, DMF, rt	10–95	119
15	**14c**	CsF (cat.), DME or TBAT (cat.), THF, rt	36–76	121
16	CF_3TMS	cat. TBAF, CsF, THF or DME, rt	"high"	14–17
17	CF_3TMS	cat. CsF, K_2CO_3, TBD, *n*-Bu_4N^+ $^-OP(O)(OEt)_2$, DMF, rt	"high"	65,388

(*continued*)

Table C. (*Continued*)

Entry	R_F-Reagent	Conditions	Yields (%)	Ref.
18	CF_3TMS	PhOLi (18-crown-6) (cat.), THF, rt	"high"	463
19	CF_3Sn*n*-Bu_3	CsF, THF, rt	41–78	156
20	$CF_3PO_3Et_2$	*t*-BuOK, DMF, –40° to rt	83	167
21	CF_3SOPh, CF_3SO_2Ph	*t*-BuOK, DMF, –50° to rt	73–86	179
22	$C_2F_5SO_2Ph$	*t*-BuOK, THF, –75° to –70°	67–99	180
23	**24**	CsF (cat.), DME or TBAT (cat.), THF	61–83	182
24	R_FLi or R_FMgBr (R_F = C_2F_5, C_3F_7, *n*-C_8F_{17})	Et_2O, –78° to rt	51–86	206,391,392
	Enolizable ketones			
25	CF_3H	electrogenerated **1b**, HMDS, DMF, –50° to –10°	60–83	69
26	CF_3H	$(TMS)_3N$, TBAT, DMF, –10°	26–50	73
27	CF_3I, C_2F_5I	TDAE, DMF, (sun lamp irradiation), –20° to rt	20–50	385,386
28	$CF_3B(OMe)_3^-$ K^+	DMF, 50°	43	102
29	**14c**	CsF (cat.), DME or TBAT (cat.), THF, rt	30–90	121
30	CF_3SiMe_3	cat. TBAF, CsF, THF or DME, rt	high	14–17
31	CF_3TMS	cat. CsF, K_2CO_3, TBD, *n*-Bu_4N^+ $^-OP(O)(OEt)_2$, DMF, rt	high	65,388
32	CF_3TMS	PhOLi (18-crown-6) (cat.), THF, rt	high	463
33	CF_3Sn*n*-Bu_3	CsF, THF, rt	51	156
34	**24**	CsF (cat.), DME or TBAT (cat.), THF	45–76	182

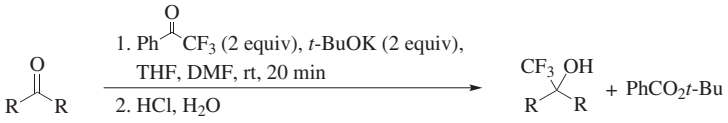


R^1	R^2	*x*	Temp (°)	Time (h)	Yield (%)
H	Me	1.2	–40	3	95
H	Ph	1.2	–40	3	99
H	Ph	0.5	–40	24	80[a]
H	Ph	0.3	–40	48	56[a]
H	Ph	1.5	–30	2	92
Cl	4-ClC_6H_4	1.5	–30	2	82
H	(*E*)-PhCH=CH	1.2	–40	3	74
H	(*E*)-PhCH=CH	0.3	–40	48	35[a]
H	(*E*)-PhCH=CH	1.5	–30	2	72
H	PhC≡C	1.5	–30	2	92

[a] Trimethylsilylpropyne (2.5 equiv) was added.

Scheme 173

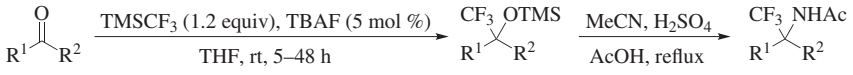
Good to moderate yields are achieved in the trifluoromethylation of non-enolizable ketones using the CF_3I/TDAE system under sun lamp irradiation;[385,386] however, poor results are observed with enolizable compounds. Heating potassium trimethoxy(trifluoromethyl)borate with benzophenone in DMF provides the trifluoromethylated alcohol in 90% yield; however, the method is not suitable for enolizable ketones.[102] Non-enolizable ketones, such as benzophenone or fluorenone, can be trifluoromethylated in good yields using trifluoroacetaldehyde hydrate,[106] an amidinate salt of hexafluoroacetone **11** (Scheme 25),[107] or hemiaminal **8** (Scheme 23),[110] derived from trifluoroacetaldehyde in the presence of strong bases such as potassium *tert*-butoxide. Trimethylsilyl-containing hemiaminals **9** and **10** (Scheme 23), on the other hand, require the presence of CsF for activation.[109,74] Trifluoroacetophenone in the presence of *t*-BuOK in THF/DMF acts as a nucleophilic trifluoromethylating reagent toward non-enolizable ketones (Scheme 174).[115] Similarly, trimethylsilyl-containing hemiaminal **12** (Scheme 26) in the presence of catalytic amounts of CsF in THF under reflux effects trifluoromethylation of non-enolizable ketones in high yields.[116,117]



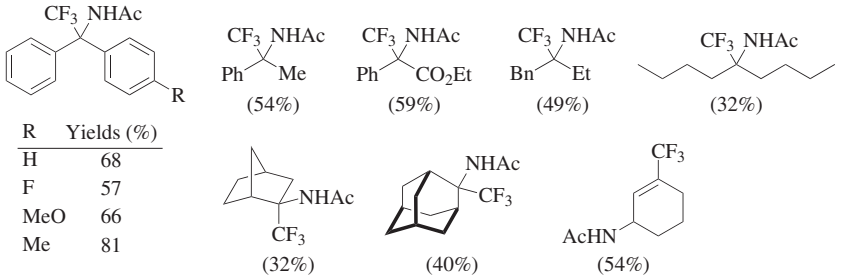
Scheme 174

Methyl trifluoroacetate trifluoromethylates non-enolizable ketones in the presence of *t*-BuOK in moderate yields.[119] Amides **13** behave similarly, and amides **14** (Scheme 27) are able to trifluoromethylate enolizable ketones in the presence of CsF in DME or TBAT in THF.[121,42]

As seen with aldehydes, ketones are readily perfluoroalkylated with (perfluoroalkyl)trialkylsilanes in the presence of various initiators. The employment of initiators such as TBAF, CsF, K_2CO_3, and TBD (1,5,7-triazabicyclo[4,4,0]dec-5-ene) affords products of trifluoromethylation of non-enolizable and enolizable ketones in high yields.[14−17,65,388] bis(Perfluoroalkyl) ketones or bis(perfluoroaryl) ketones provide perfluoroalkoxides in the reaction with (perfluoroalkyl)trimethylsilanes. These alkoxides $(R_F)_3CO^-$ are not nucleophilic enough for efficient activation of the silane reagent and therefore addition of at least one equivalent of KF or CsF is required.[129,397,464−466,587] Alkoxides readily react with $C_6F_5CH_2Br$ or $R_FC(O)X$ (X = halogen) to afford highly fluorinated aromatic ethers or esters, which are important high-temperature lubricants and solvent elastomers.[466,587] Trifluoromethyl-containing acetamides are conveniently prepared in moderate to good yields via the Ritter reaction of the corresponding trifluoromethylated silyl ethers derived from $TMSCF_3$ and ketones (Scheme 175).[467] 2-Cyclohexenone undergoes amidation at the double bond, whereas no amidation occurs with the silyl ether derivative of benzaldehyde.



Products:

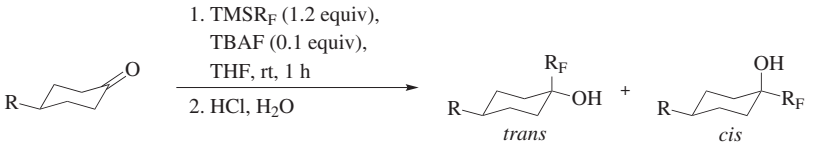


R	Yields (%)
H	68
F	57
MeO	66
Me	81

(54%) (59%) (49%) (32%) (32%) (40%) (54%)

Scheme 175

Addition of $TMSCF_3$ or $TMSC_2F_5$ to 4-substituted cyclohexanones preferentially affords the *trans* alcohols with the perfluoroalkyl group in the axial position[468,469] (Scheme 176).[468] Similarly, addition of perfluorohexyllithium to 4-(*tert*-butyl)cyclohexanone provides a mixture of *trans* and *cis* products in 85:15 ratio.[197]

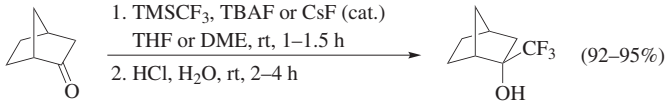


R = alkyl, Ph
$R_F = CF_3, C_2F_5$

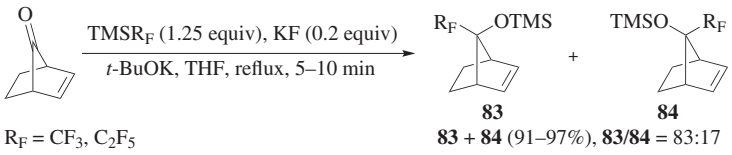
trans + *cis* (68–89%)
trans/*cis* = 69:31 to 78:22

Scheme 176

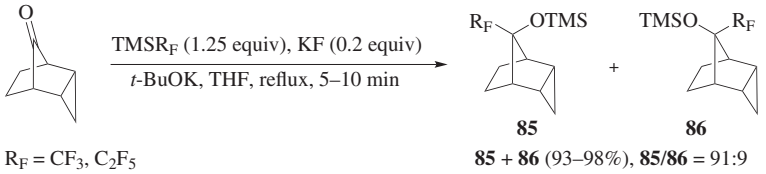
Stereoselective additions of (perfluoroalkyl)trimethylsilanes to polycyclic ketones are known. The perfluoroalkyl group preferably adds from the *exo* face (Schemes 177,[288,470] 178,[92] 179,[92] and 180[471]). Perfluoroalkylation of other polycyclic ketones has been studied.[92,339,469,470]



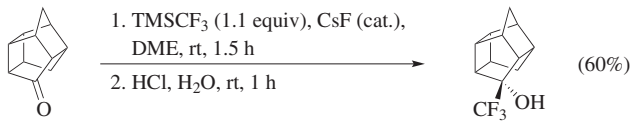
Scheme 177



Scheme 178

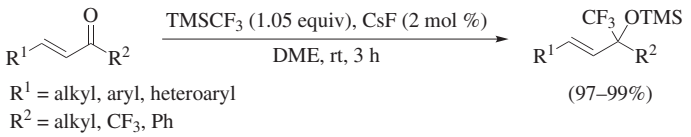


Scheme 179



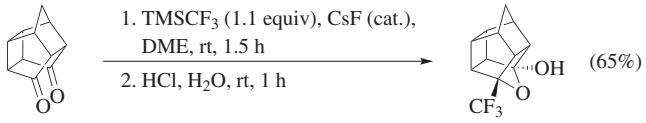
Scheme 180

α,β-Unsaturated ketones undergo preferential 1,2-addition using $TMSCF_3$; however, 1,4-addition is possible under certain conditions. Exclusive 1,2-addition is observed for 4-phenyl-3-butyn-2-one, 3-hexyn-2-one,[289,437] 4-methyl-3-penten-2-one,[289] ethyl 1-cyclohexenyl oxoacetate,[472] and some polyunsaturated ketones[289,398,473,474] (Scheme181).[475] For a discussion of the 1,4-addition of (perfluoroalkyl)trimethylsilanes to α,β-unsaturated ketones see the section on Perfluoroalkyl Additions to Carbon Electrophiles – Alkenes.



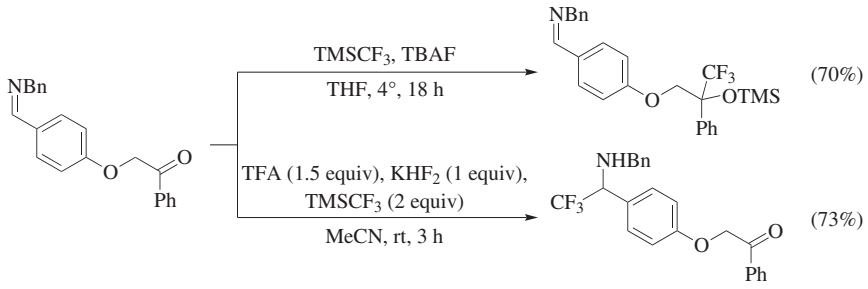
Scheme 181

Diketones undergo mono- or bisperfluoroalkyl addition depending on the stoichiometry.[289,438,476–484] If the two keto groups are in close proximity, transannular cyclization takes place even with an excess of $TMSCF_3$, and after the first trifluoromethylation, the hemiacetal rather than the expected double-addition product is formed[471,479,485] (Scheme 182).[471] Both 1,4- and 1,2-quinones can undergo double addition with an excess of $TMSCF_3$ to provide *trans* products.[482,483,486–488] The corresponding monoadducts have also been prepared and studied.[486,489,490*a*]



Scheme 182

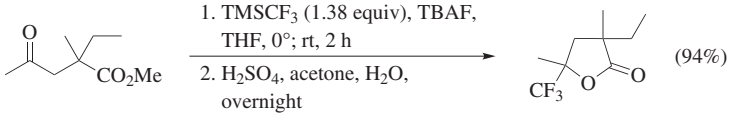
Keto imines are chemoselectively trifluoromethylated on the keto group if the reaction is initiated by TBAF or CsF.[471,478,485] However, in the presence of trifluoroacetic acid and KHF_2 in acetonitrile, chemoselective trifluoromethylation of the imine of 2-[4-(benzyliminomethyl)phenoxy]-1-phenylethanone takes place due to the formation of the reactive iminium salt (Scheme 183).[490]



Scheme 183

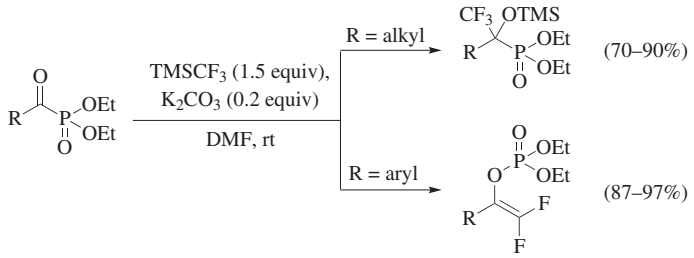
Keto esters undergo perfluoroalkylation of the keto group.[131,418,491–493], In γ- and δ-keto esters, lactone formation is observed under acidic catalysis.[416,494]

(Scheme 184).[494] Similarly, keto amides are trifluoromethylated on the ketone carbonyl function.[421,495–498]



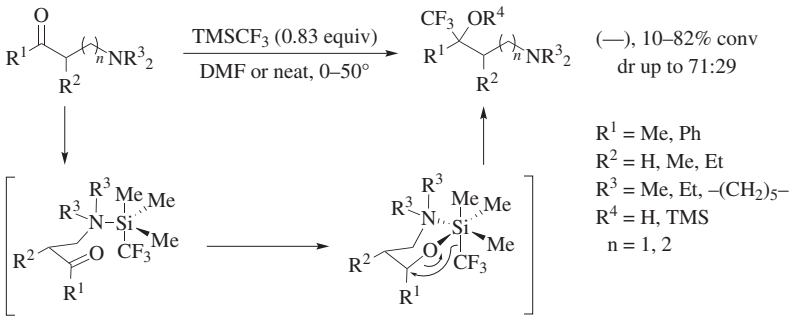
Scheme 184

Acylphosphonates readily react with $TMSCF_3$ in the presence of potassium carbonate in DMF to produce diethyl 1-alkyl-2,2,2-trifluoro-1-(trimethylsilyloxy)phosphonates in high yields. When benzoyl phosphonates are used the intermediate alcoholates undergo a phosphonate–phosphate rearrangement to form the 1-phosphonoxy-2,2,2-trifluoroethyl carbanions followed by elimination of fluoride ion to provide 1-aryl-2,2-difluoroethenyl phosphates in excellent yields (Scheme 185).[423]



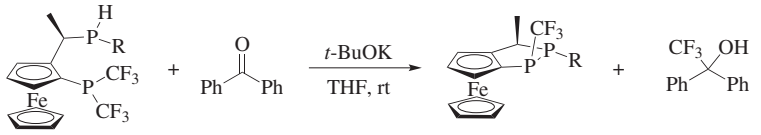
Scheme 185

Dialkylamino ketones display unique reactivity toward $TMSCF_3$. In DMF in the absence of initiators, efficient trifluoromethylation of β- and γ-dialkylamino ketones is observed. The reaction mechanism probably involves a cyclic transition structure in which the amino and the carbonyl groups coordinate to the silicon atom. Low to moderate diastereoselectivities are observed for branched amino ketones (Scheme 186).[404]



Scheme 186

Tributyl(trifluoromethyl)stannane behaves similarly to $TMSCF_3$ and trifluoromethylation of ketones with CsF catalysis proceeds in good yields.[156] Diethyl trifluoromethyphosphonate is comparable in its trifluoromethylation power toward trifluoroacetophenone; with *t*-BuOK in DMF trifluoromethylation of aromatic ketones takes place.[167] Ferrocenyl diphosphine **87** (dr = 86:14) upon deprotonation with a strong base forms the ferrocenodiphosphole **88** (dr not reported), releasing one of the diastereotopic trifluoromethyl groups that is efficiently trapped with benzophenone (Scheme 187).[499]



87 dr 86:14
R = adamantyl

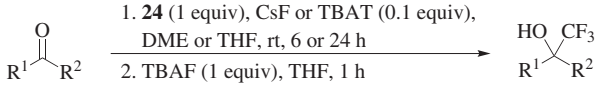
88

(75%)

Scheme 187

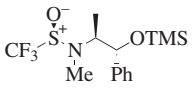
Excess amounts of both phenyl trifluoromethyl sulfoxide or sulfone and *t*-BuOK in DMF at −50° to room temperature transform non-enolizable ketones into trifluoromethyl carbinols in good yields.[179] Similarly, transfer of the pentafluoroethyl group to non-enolizable ketones is observed with pentafluoroethyl phenyl sulfone.[180]

Various ketones are efficiently trifluoromethylated by the action of trifluoromethyl sulfur reagent **24** in the presence of fluoride initiators (Scheme 188).[182]



R^1, R^2 = alkyl, alkenyl, aryl, heteroaryl

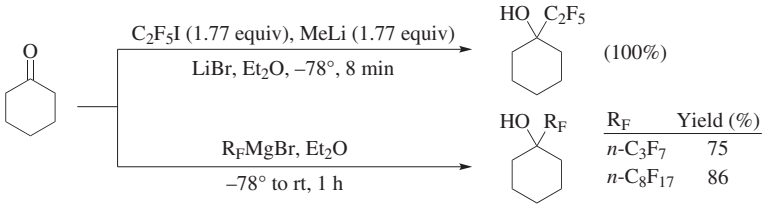
(45–83%)



24 dr 60:40

Scheme 188

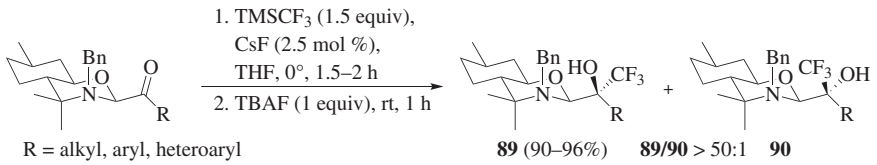
Both enolizable and non-enolizable ketones are suitable substrates in the addition of perfluoroalkyllithium reagents and perfluoralkyl Grignard reagents (Scheme 189).[206,391,392]



R_F	Yield (%)
n-C_3F_7	75
n-C_8F_{17}	86

Scheme 189

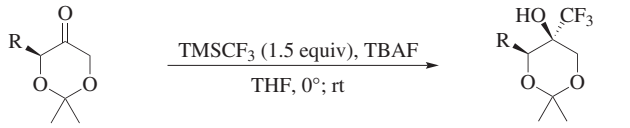
Diastereoselective Perfluoroalkyl Addition to Ketones. Diastereoselective nucleophilic trifluoromethylation and perfluoroalkylation of chiral ketones is an important method for the synthesis of enantiopure tertiary trifluoromethyl (and perfluoroalkyl) carbinols. The topic was reviewed in 2009[40] and the vast majority of reported reactions involve addition of $TMSCF_3$. 2-Methylcyclohexanone reacts with $TMSCF_3$ and TBAT at 0° or –78° to afford a mixture of diastereomeric products (60:40 dr).[122] 3-Ethyl-5-methyl-2-hexanone affords the product of trifluoromethylation with 63:37 dr.[404] $TMSCF_3$ adds to chiral 2-acyl-1,3-perhydrobenzoxazines with high diastereoselectivity, leading to tertiary trifluoromethyl alcohols **89** and **90** in excellent yields (Scheme 190).[500] Further transformation of the major diastereomer **89** yields enantiomerically enriched trifluoromethyl 1,2-diols and 1,2-amino alcohols.[500]



R = alkyl, aryl, heteroaryl **89** (90–96%) **89/90** > 50:1 **90**

Scheme 190

α-Substituted dioxanones are trifluoromethylated in good yields and high diastereoselectivities (Scheme 191).[501] Deprotection of the adducts provides essentially enantiomerically pure 2-trifluoromethylated 1,2,3-triols.



enantiomerically pure
R = Me, Et, *i*-Pr, *n*-Bu, *n*-C_6H_{13}

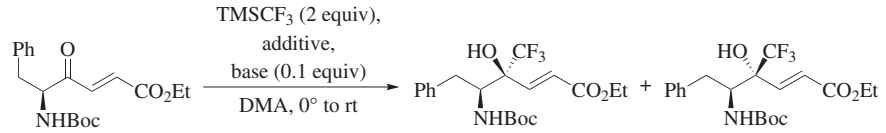
(64–94%) dr >98:2

Scheme 191

α,β-Unsaturated γ-keto ester **91** reacts with $TMSCF_3$ in the presence of potassium carbonate to afford allylic alcohols **92** and **93** in good yields and diastereoselectivities. Addition of chiral alcohols such as BINOL (1,1′-bi(2-naphthol)) has little effect on the diastereoselectivity of the addition but speeds up the reaction (Scheme 192).[502]

Monotrifluoromethylation of the tartaric acid derived diketone **94** with $TMSCF_3$ proceeds with high diastereoselectivity (Scheme 193).[484,503]

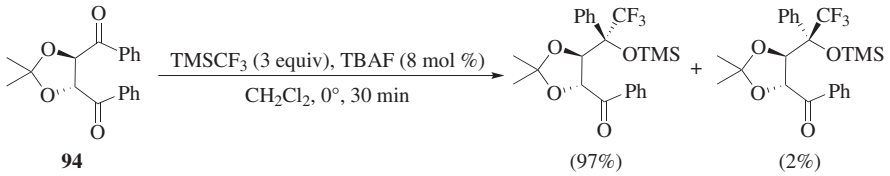
Several chiral keto esters are diastereoselectively trifluoromethylated. For example, keto ester **95** provides a single diastereoisomer of the corresponding adduct in 81% yield (Scheme 194).[504] The high diastereoselectivity of the trifluoromethylation of keto esters **96** can be explained by the addition of $TMSCF_3$ from the sterically less congested convex face (Scheme 195).[410,505]



91 **92** **93**

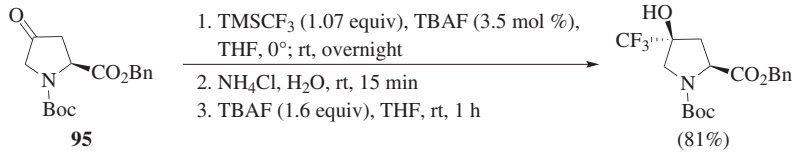
Additive	Base	Time (h)	**92** + **93**, Yield (%)	**92/93**
—	K_2CO_3	12	59	88.5:11.5
MeOH (0.2 equiv)	Cs_2CO_3	0.83	67	88.5:11.5
(*S*)-BINOL (0.1 equiv)	K_2CO_3	2	68	91.5:8.5
(*R*)-BINOL (0.1 equiv)	K_2CO_3	2.5	61	88.5:11.5

Scheme 192



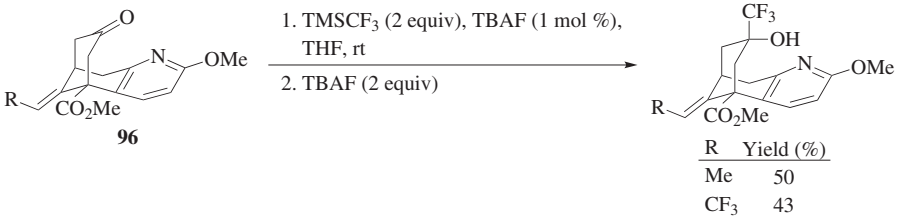
94 (97%) (2%)

Scheme 193



95 (81%)

Scheme 194



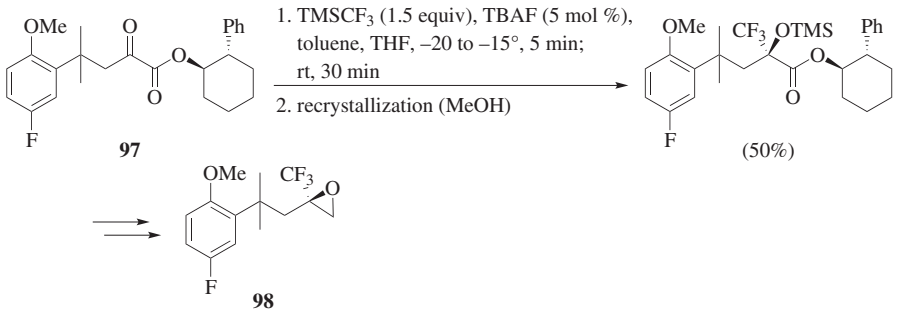
96

R	Yield (%)
Me	50
CF_3	43

Scheme 195

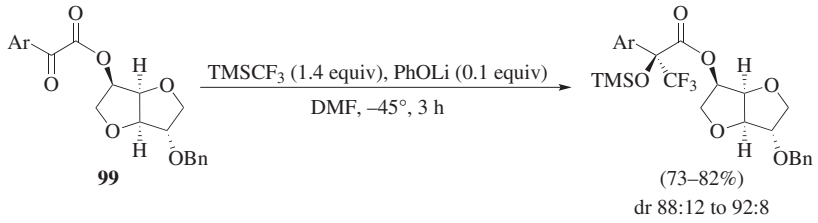
A practical process for the synthesis of the pharmaceutically active α-trifluoromethyl-α-alkyl epoxide **98** involves TBAF-initiated trifluoromethyl addition to keto ester **97**, which proceeds with an 86:14 diastereoselectivity. The

pure, major diastereomer is obtained by crystallization and transformed into epoxide **98**.[506,507] (Scheme 196).[506]



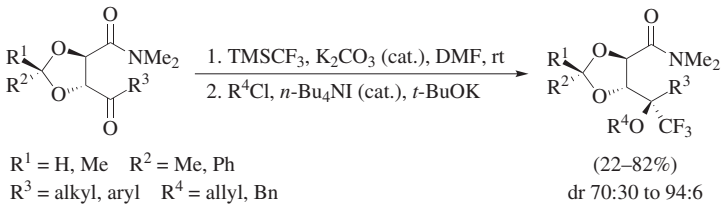
Scheme 196

Trifluoromethylation of isosorbide-derived chiral α-keto esters **99** with $TMSCF_3$ in the presence of a Lewis base initiator provides the corresponding trifluoromethylated α-hydroxy esters in good yields with moderate to good diastereoselectivities (Scheme 197).[417] Hydrolysis of the product (Ar = Ph) with lithium hydroxide affords the OTMS analogue of (*S*)-Mosher's acid, while the chiral auxiliary is recovered quantitatively.[417]



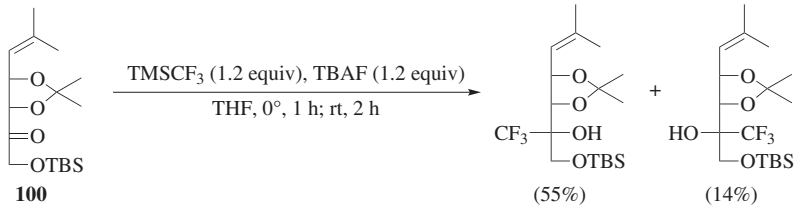
Scheme 197

Keto amides derived from L-tartaric acid undergo trifluoromethylation with $TMSCF_3$ in the presence of potassium carbonate in DMF to provide the corresponding adducts, which may be alkylated in situ. The products are obtained with good diastereoselectivities and moderate to good yields (Scheme 198).[422,508] Further transformation leads to enantiomerically enriched α-trifluoromethylated α-alkoxy aldehydes.



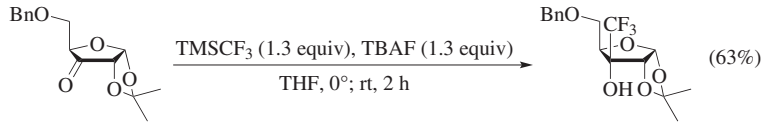
Scheme 198

Ribulose derivative **100** reacts with $TMSCF_3$ in the presence of TBAF to afford a mixture of trifluoromethylated alcohols in 69% yield and 80:20 dr (Scheme 199).[509] 3′-Trifluoromethyl ribonucleosides can be accessed via diastereoselective trifluoromethylation of keto sugar **101**[510,511] (Scheme 200).[510] (Perfluoroalkyl)trimethylsilanes also add in highly diastereoselective fashion to the structurally similar 3-oxoglucose derivative **102** (Scheme 201).[512,216] In contrast, addition of perfluoroalkyl Grignard reagents to keto sugar **102** proceeds only with moderate diastereoselectivity. This outcome may be explained by the higher steric demand of the nucleophile delivered in the form of a hypercoordinate silicon intermediate.



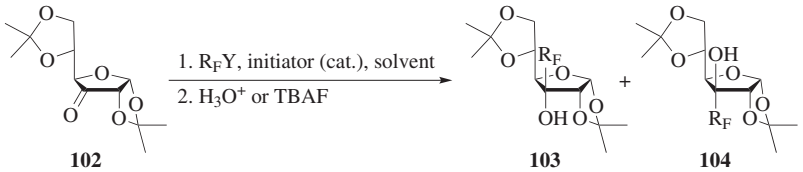
100

Scheme 199



101

Scheme 200

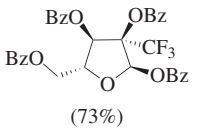


102 **103** **104**

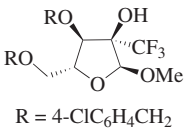
R_F	Y	Initiator	Solvent	Temp (°)	**103** + **104**, Yield (%)	**103/104**
CF_3	TMS	$Bu_4N^+ [Ph_2SnF_2]^-$	CH_2Cl_2	rt	88	100:0
n-C_4F_9	TMS	$Bu_4N^+ [Ph_2SnF_2]^-$	CH_2Cl_2	rt	70	100:0
n-C_4F_9	MgBr	—	Et_2O	−45	68	78:22
n-C_6F_{13}	MgBr	—	Et_2O	−45	59	73:27

Scheme 201

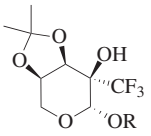
Very high diastereoselectivities are achieved in the trifluoromethylation of various 2-oxosugars. Attack of the CF_3 group takes place from the less hindered face of the ring.[407,513–516]



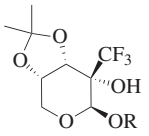
(73%)



R = 4-$ClC_6H_4CH_2$
(67%)

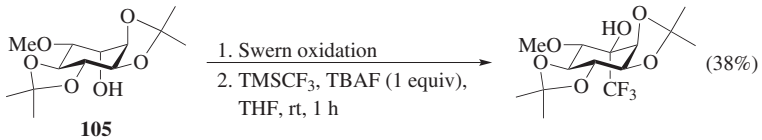


R	Yield (%)
Me	64
Bn	65



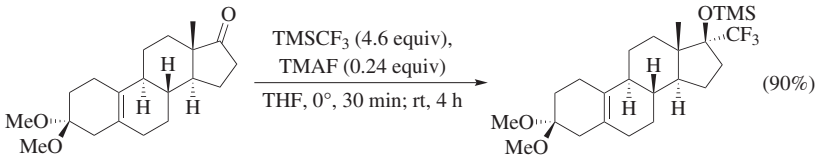
R	Yield (%)
Me	70
Bn	41

Swern oxidation of inositol derivative **105** to the unstable ketone followed by trifluoromethylation with $TMSCF_3$ provides a single diastereomer of the product, albeit in modest yield (Scheme 202).[517]



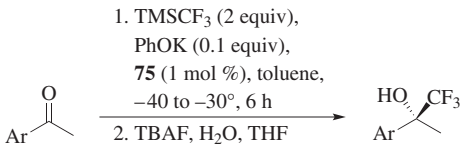
Scheme 202

Trifluoromethyl-containing steroids can be prepared by trifluoromethylation of ketone derivatives with $TMSCF_3$. Usually an excess of $TMSCF_3$ is used together with varying amounts of initiators (TBAF or TMAF for hindered ketones). The intermediate silylated compounds are typically hydrolysed to alcohols by means of aqueous hydrochloric or hydrofluoric acid. Depending on the structure of the steroid ketone, low[518–522] or good diastereoselectivities are observed (Scheme 203).[122,288,469,520,523–526]



Scheme 203

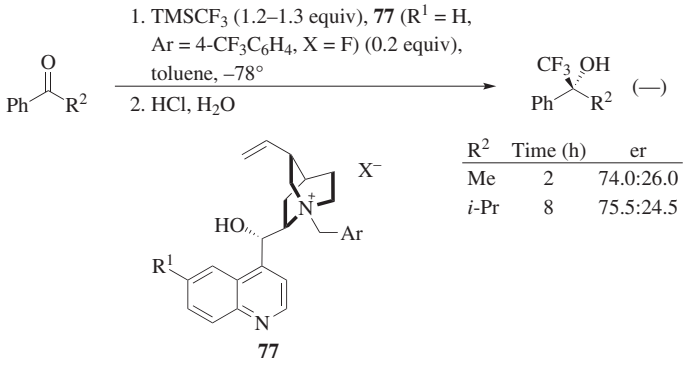
Enantioselective Perfluoroalkyl Addition to Ketones. As with aldehydes, several strategies for enantioselective perfluoroalkyl additions to ketones have been developed. The chiral cation approach using C_2-symmetric chiral crown ether catalyst **75** (Scheme 163) with potassium phenolate as the initiator in the trifluoromethylation of aryl methyl ketones (using $TMSCF_3$) provides products with moderate enantioselectivities (Scheme 204).[454]



Ar	Yield (%)	er
Ph	66	69:31
4-BrC_6H_4	80	65.5:34.5
2-naphthyl	91	67:33

Scheme 204

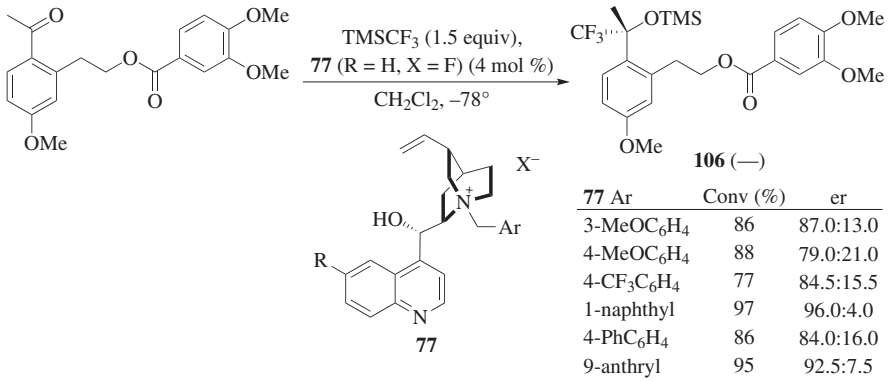
The best enantioinduction is achieved using cinchona alkaloid derived quaternary ammonium salts **76–78** as chiral ion-pairing catalysts. *N*-[(4-Trifluoromethyl)benzyl]cinchonium fluorides **77** (R^1 = H, X = F) are effective catalysts for the asymmetric trifluoromethylation of some ketones with $TMSCF_3$ to provide the corresponding alcohols with moderate enantioselectivities (Scheme 205).[456]



R^2	Time (h)	er
Me	2	74.0:26.0
i-Pr	8	75.5:24.5

Scheme 205

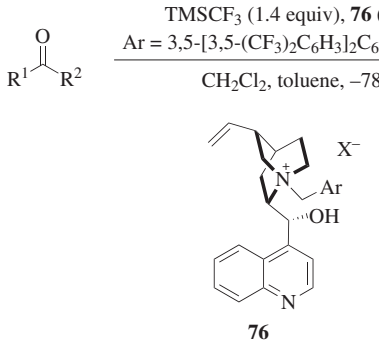
The enantiomerically enriched alcohol **106** is prepared by trifluoromethylation of an acetophenone derivative (Scheme 206).[527] The introduction of bulky aryl groups on the quaternary nitrogen of the cinchona alkaloid leads to enhanced enantioselectivity. Alkaloids that have the benzylic hydroxy group etherified do not promote the reaction. The use of as low as 4 mol % of catalyst **77** (R = H, X = F) allows the preparation of compound **106** with er up to 96.0:4.0 (Scheme 206). However, the best catalyst does not prove to be generally applicable and affords products with only low to moderate enantioselectivities for simple aromatic aldehydes and ketones.[527,416]



77 Ar	Conv (%)	er
3-$MeOC_6H_4$	86	87.0:13.0
4-$MeOC_6H_4$	88	79.0:21.0
4-$CF_3C_6H_4$	77	84.5:15.5
1-naphthyl	97	96.0:4.0
4-PhC_6H_4	86	84.0:16.0
9-anthryl	95	92.5:7.5

Scheme 206

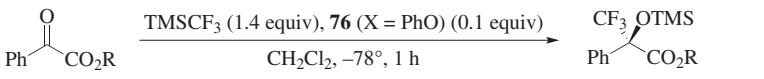
Cinchonidine-derived quaternary ammonium phenoxides **76** (X = PhO) catalyze the enantioselective trifluoromethylation of ketones (Scheme 207)[528,529] and α-keto esters (Scheme 208)[528] with $TMSCF_3$. The effects of the aryl group in catalyst **76** and of the solvent have been investigated. Under optimized conditions, products of trifluoromethylation are isolated in excellent yields and with low to good enantioselectivities.[529,528]

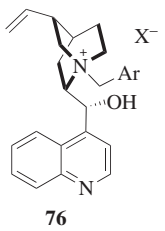


76

R^1	R^2	Yield (%)	er
2-furyl	Me	72	66.5:33.5
3-pyridyl	Me	90	73.0:27.0
4-pyridyl	Me	93	80.0:20.0
$3\text{-}BrC_6H_4$	Me	97	80.5:19.5
$4\text{-}BrC_6H_4$	Me	97	72.0:28.0
$2\text{-}O_2NC_6H_4$	Me	93	85.5:14.5
$3\text{-}O_2NC_6H_4$	Me	98	93.5:6.5
$3\text{-}O_2NC_6H_4$	Et	99	82.0:18.0
$4\text{-}O_2NC_6H_4$	Me	97	86.5:13.5
$3\text{-}MeOC_6H_4$	Me	90	79.5:20.5
$3\text{-}NCC_6H_4$	Me	96	85.5:14.5
1-naphthyl	Me	91	75.5:24.5
2-naphthyl	Me	95	88.5:11.5

Scheme 207





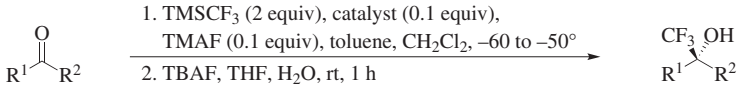
76

R	**76** Ar	Yield (%)	er
Me	$3,5\text{-}[3,5\text{-}(CF_3)_2C_6H_3]_2C_6H_3$	90	65.5:34.5
Et	$3,5\text{-}[3,5\text{-}(CF_3)_2C_6H_3]_2C_6H_3$	86	69.0:31.0
t-Bu	Ph	86	55.0:45.0
t-Bu	1-naphthyl	92	57.5:42.5
t-Bu	2-naphthyl	95	60.0:40.0
t-Bu	$3,5\text{-}(MeO)_2C_6H_3$	77	65.5:34.5
t-Bu	$3,5\text{-}(CF_3)_2C_6H_3$	89	65.5:34.5
t-Bu	$3,5\text{-}Ph_2C_6H_3$	84	68.5:31.5
t-Bu	$3,5\text{-}[3,5\text{-}(CF_3)_2C_6H_3]_2C_6H_3$	99	80.0:20.0
$Ph(CH_2)_2Me_2C$	$3,5\text{-}[3,5\text{-}(CF_3)_2C_6H_3]_2C_6H_3$	91	66.5:33.5
1-adamantyl	$3,5\text{-}[3,5\text{-}(CF_3)_2C_6H_3]_2C_6H_3$	93	57.0:43.0

Scheme 208

A combination of a chiral ammonium chloride or bromide salt derived from a cinchona alkaloid and TMAF is used for catalytic, enantioselective trifluoromethylation of ketones. The reactions are carried out in a mixture of toluene and dichloromethane solvents at low temperature. Enantiomeric ratios of up to 97.0:3.0 are observed for

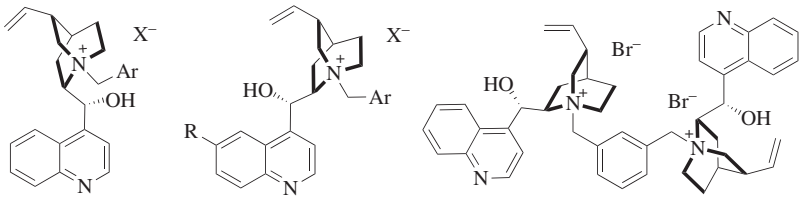
aryl ketones (particularly with catalyst **78**); aliphatic ketones, however, afford only low to moderate enantioselectivities (Scheme 209).[458]



R^1	R^2	Catalyst	Time (h)	Yield (%)	er
4-BrC_6H_4	Me	**78**	3	81	93.0:7.0
4-$O_2NC_6H_4$	Me	**77** (R= H, X= Br, Ar= 3,5-$(CF_3)_2C_6H_3$)[a]	3	97	76.0:24.0
Ph	Et	**78**	14	65	91.0:9.0
4-BrC_6H_4	Et	**78**[b]	12	84	96.5:3.5
1-indanone		**78**	12	34	87.0:13.0
Ph	Pr	**78**	7	83	88.0:12.0
PhCH=CH	Me	**78**	3	85	85.0:15.0
$Ph(CH_2)_2$	Me	**78**	6	37	55.0:45.0
1-tetralone		**78**	3	75	97.0:3.0
1-benzosuberone		**78**	2	53	86.5:13.5
2-naphthyl	Me	**76** (X= Br, Ar= 3,5-$(CF_3)_2C_6H_3$)	3	70	11.5:88.5
2-naphthyl	Me	**77** (R= H, X= Br, Ar= 3,5-$(CF_3)_2C_6H_3$)	2	65	90.5:9.5
2-naphthyl	Me	**78**	6	87	92.5:7.5

[a] TMAF (0.2 equiv) was used.

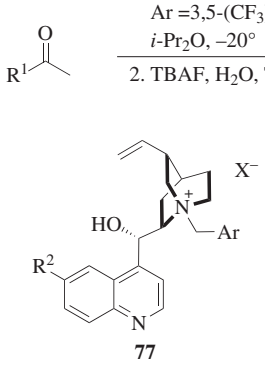
[b] The reaction was carried out at –80 to –70°.



76 **77** **78**

Scheme 209

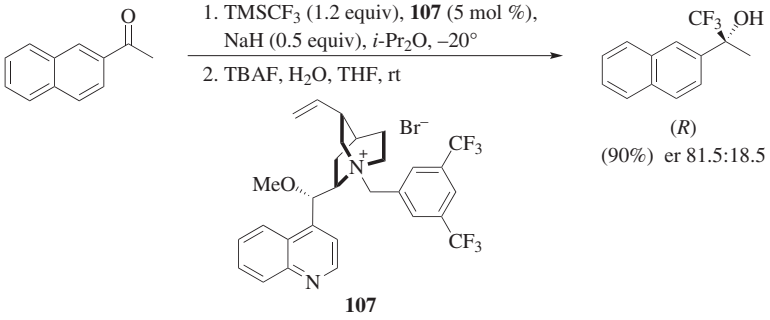
Optimization of the reaction of ammonium bromides **76** and **77** (X = Br) with various aryl methyl ketones reveals that a combination of cinchonine-derived catalyst **77** (R = H, X = Br) and sodium hydride in diisopropyl ether represents an effective enantioselective trifluoromethylation system with good substrate scope (Scheme 210).[530] Interestingly, only slightly lower enantioselectivity is observed in the trifluoromethylation of methyl 2-naphthyl ketone using catalyst **107** (a derivative of catalyst **77** with a methylated hydroxyl group) in the presence of sodium hydride (Scheme 211).[530] A control experiment revealed that trifluoromethylation does not take place in the absence of sodium hydride. On the basis of these observations the authors suggest that the hydride anion serves as a Lewis base in the activation of $TMSCF_3$ and that the carbonyl group is somehow associated with the positively charged nitrogen of the catalyst.[530] However, a more reasonable interpretation is that the sodium enolate of the ketone is silylated by $TMSCF_3$ to form a trifluoromethyl anion cinchoninium cation pair which serves to distinguish the enantiotopic faces of the ketone.



77

R^1	Time (h)	Yield (%)	er
2-FC_6H_4	19	47	84.0:16.0
3-ClC_6H_4	19	96	84.0:16.0
4-ClC_6H_4	19	83	80.5:19.5
4-BrC_6H_4	48	43	80.0:20.0
3-$O_2NC_6H_4$	48	30	84.0:16.0 (*R*)
4-$O_2NC_6H_4$	24	64	75.0:25.0
3-$MeOC_6H_4$	96	38	79.0:21.0
4-MeC_6H_4	3	70	83.5:16.5
(*E*)-PhCH=CH	22	31	79.5:20.5
1-naphthyl	6	98	91.0:9.0
2-naphthyl	6	96	90.5:9.5 (*R*)

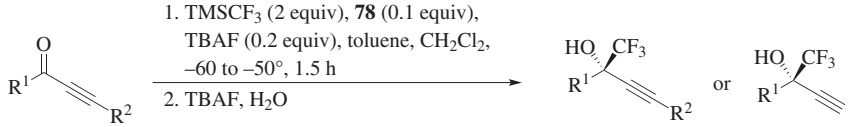
Scheme 210



107

Scheme 211

Highly enantioselective catalytic trifluoromethylations of alkynyl ketones using $TMSCF_3$ and bis-cinchona alkaloid **78** afford products that are important chiral building blocks for pharmaceuticals (Scheme 212).[531] This protocol, however, proved unsuitable for the synthesis of the HIV treatment drug Efavirenz. Instead, catalyst screening identified a cinchonine-derived catalyst **77** that provides the required intermediate in high yield and with 75.0:25.0 er (Scheme 213).[315]

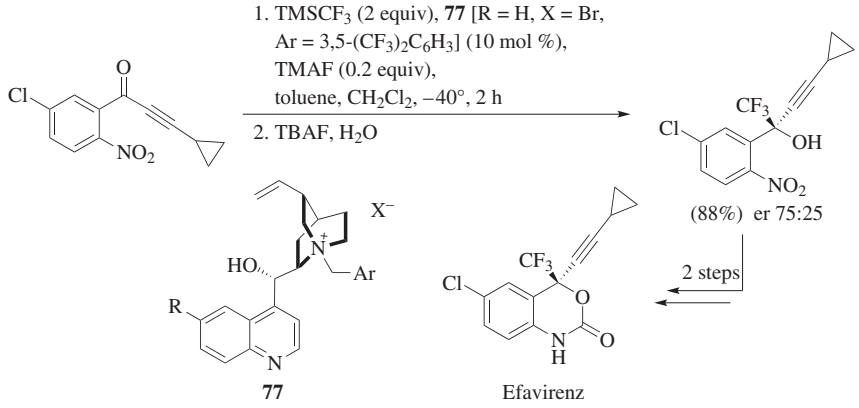


R^1 = aryl, PhCH=CH
R^2 = *t*-Bu, $BnOMe_2C$, $(4\text{-}BrC_6H_4)CH_2OMe_2C$, Ph_2CHOMe_2C, TIPS

(53–93%)
er 75.5:24.5 to 97.5:2.5

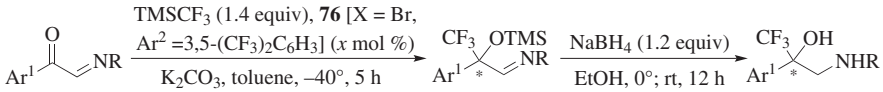
for R^2 = TIPS

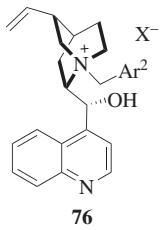
Scheme 212



Scheme 213

α-Imino ketones derived from aryl glyoxals are trifluoromethylated with $TMSCF_3$ in the presence of catalyst **76** to form *O*-silylated β-imino alcohols. Subsequent reduction with sodium borohydride affords trifluoromethylated alcohols **108** with moderate to good enantioselectivities and in high yields (Scheme 214).[532]

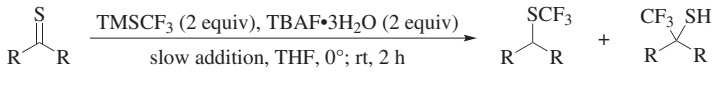




Ar[1]	R	*x*	**108** Yield (%)	**108** er
Ph	*i*-Pr	10	75	80.5:19.5
Ph	*i*-Pr	15	87	82.0:18.0
4-$O_2NC_6H_4$	*i*-Pr	15	81	66.0:34.0
4-$MeOC_6H_4$	*i*-Pr	15	78	82.0:18.0
Ph	*t*-Bu	15	85	83.5:16.5
4-$O_2NC_6H_4$	*t*-Bu	15	94	65.0:35.0
4-MeC_6H_4	*t*-Bu	15	89	85.5:14.5
benzofuran-2-yl	*t*-Bu	15	92	84.0:16.0
7-ethylbenzofuran-2-yl	*t*-Bu	15	87	75.0:25.0

Scheme 214

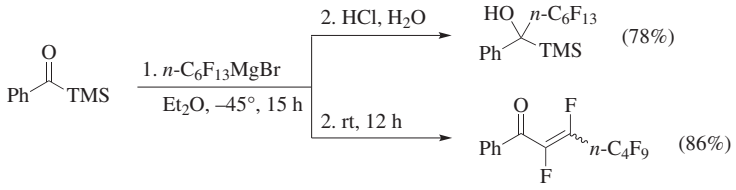
Thioketones. In contrast to ketones, thioketones contain two electrophilic centers: the carbon and sulfur atoms of the thioketone moiety. Aromatic thioketones react with an excess of $TMSCF_3$ and TBAF•$3H_2O$ in both thiophilic and carbophilic manners to provide moderate yields of (trifluoromethylthio)diarylmethanes **109** and 1,1-diaryl-2,2,2-trifluoroethanethiols **110** (Scheme 215).[533] The use of TBAF under anhydrous conditions affords a mixture of product **109**, tetraarylthiirane, and small amounts of 1,1-difluoro-2,2-diarylethene and tetraarylethene.[476] For the formation of product **109** an excess of TBAF•$3H_2O$ is used to promote protonation of the intermediate formed by the addition of $TMSCF_3$ to the diaryl thioketone.[476]



R	**109** Yield (%)	**110** Yield (%)
Ph	30	10
4-$MeOC_6H_4$	10	—

Scheme 215

Acylsilanes. Acylsilanes are electrophilic substrates amenable to attack by nucleophilic perfluoroalkyl reagents. Reaction of benzoyltrimethylsilane with *n*-$C_6F_{13}MgBr$ in diethyl ether at –45° affords, after acidic hydrolysis at this temperature, the corresponding carbinol adduct in 78% yield.[534] However, if the reaction mixture is allowed to warm to room temperature, the Brook rearrangement (1,2-carbon to oxygen migration of silicon) occurs, followed by fluoride elimination to generate an α,β-unsaturated ketone (Scheme 216).[534] Using $TMSCF_3$ or perfluoroalkyllithium reagents also leads to rearrangement and fluoride elimination products.[534–537]

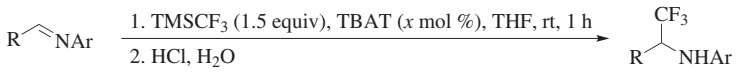


Scheme 216

Imines and Iminium Salts. Nucleophilic perfluoroalkyl addition to imines and iminium salts is a very attractive process because it provides perfluoroalkyl-bearing amines, which are important building blocks for pharmaceutical research and asymmetric synthesis. Nucleophilic trifluoromethylation of C=N bonds was reviewed in 2011.[538] *N*-Alkyl aldimines or ketimines are much less electrophilic than aldehydes and ketones and are usually unreactive in nucleophilic perfluoroalkyl additions. The electrophilicity of imines can be increased by (1) attachment of an electron-withdrawing group on nitrogen or the carbon atoms, (2) the use of a Lewis acid for coordination of the imine nitrogen, or (3) conversion to iminium salts.

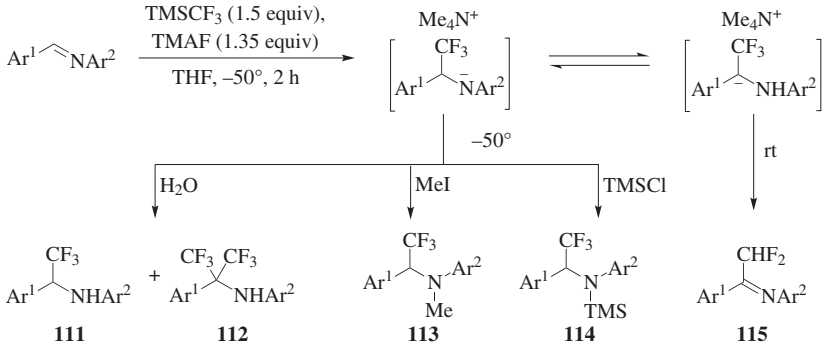
Unactivated Imines. *N*-Arylaldimines can be conveniently trifluoromethylated with $TMSCF_3$ and a small amount of TBAT at room temperature (Scheme 217)[539] or with an equivalent amount of TMAF at –50° in THF (Scheme 218).[540] In the case of TMAF as the fluoride source, the intermediate amide anions react with various electrophiles at low temperature to generate trifluoromethylated amines **111–115**.

However, in the absence of an electrophile, HF elimination takes place upon warming to room temperature to afford difluoromethyl ketimines **115** (Scheme 218).[540]



R	Ar	*x*	Yield (%)
t-Bu	Ph	5	trace
c-C_6H_{11}	Ph	5	47
Ph	Ph	15	75
2-FC_6H_4	Ph	5	74
4-FC_6H_4	Ph	5	67
4-ClC_6H_4	Ph	5	54
2,4-$Cl_2C_6H_3$	Ph	5	77
2-BrC_6H_4	Ph	5	83
4-BrC_6H_4	Ph	5	50
4-$MeOC_6H_4$	Ph	15	38
4-MeC_6H_4	Ph	15	46
Ph	4-$MeOC_6H_4$	15	72

Scheme 217

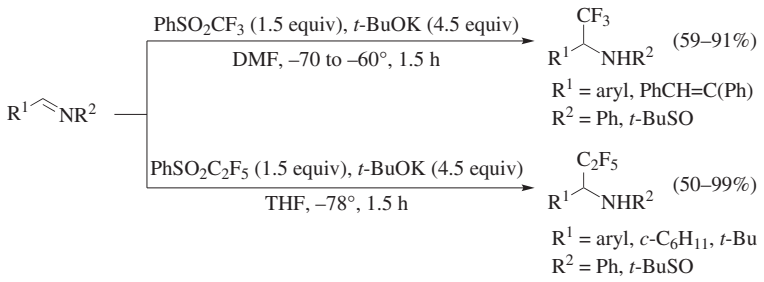


Ar^1	Ar^2	**111** Yield (%)	**112** Yield (%)	**113** Yield (%)	**114** Yield (%)	**115** Yield (%)
Ph	Ph	89	—	91	76	79
Ph	3-FC_6H_4	83	—	—	—	47
4-$Me_2NC_6H_4$	4-FC_6H_4	65	25	—	—	—
4-MeC_6H_4	4-FC_6H_4	72	—	79	84	66

Scheme 218

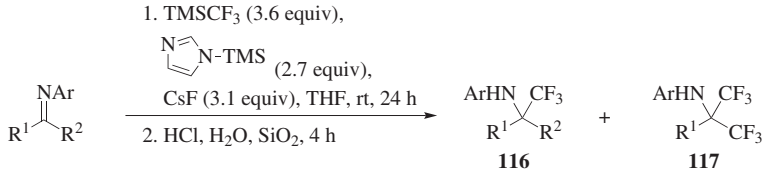
N-Arylaldimines can be perfluoroalkylated using the $PhSCF_3/Et_3GeNa$ system in THF/HMPA at –60° in nearly quantitative yields[171] or with $PhSO_2R_F$ ($R_F = CF_3$, C_2F_5) using *t*-BuOK at low temperature (Scheme 219).[180] *N*-Phenylaldimines are trifluoromethylated with two equivalents of $TMSCF_3$ in the presence of 20 mol % of

tris(2,4,6-trimethoxyphenyl)phosphine in DMF or DMPU to afford trifluoromethylated amines in moderate to good yields.[141]



Scheme 219

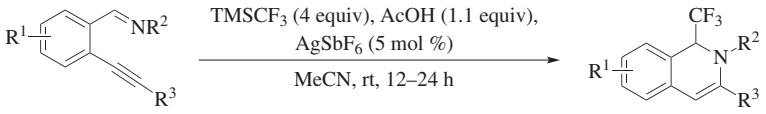
The reactivity of non-activated imines—initially considered to be unreactive toward $TMSCF_3$—can be enhanced by the addition of the auxiliary silylating agent *N*-trimethylsilylimidazole. Under these conditions, aldimines and trifluoromethyl-containing ketimines undergo trifluoromethyl addition in moderate to good yields to provide the trifluoromethylated amines **116**. In the case of aldimines, product **116** is often contaminated by double-addition side products **117** (Scheme 220).[541] Non-fluorinated ketimines provide only traces of products.



R^1	R^2	Ar	**116** Yield (%)	**117** Yield (%)
2-furyl	H	Ph	54	2
–$(CH_2)_5$–		Ph	2	—
Ph	H	Ph	55	4
Ph	H	3-$CF_3C_6H_4$	26	4
3-$MeOC_6H_4$	H	Ph	42	4
PhCH=CH	H	Ph	19	—
2-naphthyl	H	Ph	57	10
Ph	CF_3	Ph	64	—

Scheme 220

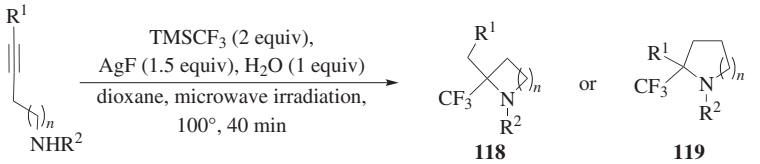
Structurally diverse 1-(trifluoromethyl)-1,2-dihydroisoquinolines are synthesized by the reaction of 2-alkynylaryl aldimines with $TMSCF_3$ in the presence of acetic acid and small amounts of silver(I) salts (Scheme 221).[542] The reaction is initiated by nucleophilic addition of $TMSCF_3$ to the imine followed by 6-*endo-dig* cyclization of the formed amide. A similar two-step process through an isoquinolinium intermediate has been described.[543]



R^1 = H, F, Cl, Me, MeO
R^2 = *n*-Bu, *t*-Bu, Ph, Bn
R^3 = alkyl, aryl, TMS

Scheme 221

Saturated five- to seven-membered nitrogen heterocycles containing a CF_3 group on a quaternary α-carbon are efficiently prepared by tandem silver-mediated 5-*exo-dig* cyclization followed by nucleophilic trifluoromethylation of the imine or enamine intermediate (Scheme 222).[544] The reaction requires heating under microwave irradiation and the true nucleophilic species is believed to be $AgCF_3$.[544]



118 5-, 6-, or 7-*exo-dig* **119** 5-*endo-dig*

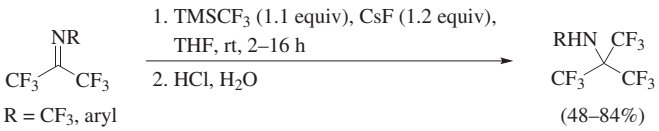
R^1	R^2	*n*	**118** Yield (%)
H	Ph	4	95
H	Bn	2	92
H	Bn	3	88
H	(*R*)-Ph(Me)CH	3	90[a]
n-Bu	allyl	4	87
n-Bu	Ph	4	89
n-Bu	Bn	4	92

[a] The product has 77:23 dr.

R^1	R^2	*n*	**119** Yield (%)
n-Bu	Ph	1	90
n-Bu	Bn	1	91

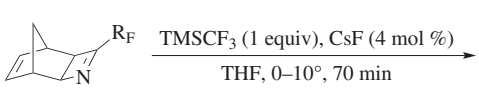
Scheme 222

Activated Imines. Perfluoroalkyl-substituted ketimines undergo efficient trifluoromethylations with $TMSCF_3$ (Schemes 223 and 224).[545,546]



R = CF_3, aryl

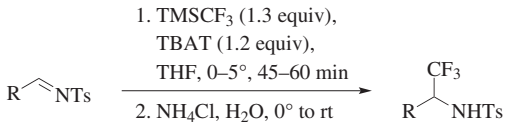
Scheme 223



R_F	Yield (%)
CF_3	85
C_2F_5	73
n-C_3F_7	68

Scheme 224

Sulfonylimines represent another class of activated imines, which in the presence of an equimolar amount of a fluoride source (CsF or TBAT) react with $TMSCF_3$ to afford the corresponding trifluoromethylated sulfonamides in good to excellent yields (Scheme 225).[547] Aliphatic sulfonylaldimines afford lower yields because of their inherent instability. Sulfonylaldimines are also successfully trifluoromethylated using $TMSCF_3$ with t-Bu_3P (1 equivalent),[140] sodium phenolate (1.2 equivalents) and TBAB (catalytic) (PTC, phase transfer catalysis conditions),[548] lithium phenolate (catalytic),[131,549] lithium acetate (catalytic),[131,549] or tris(2,4,6-trimethoxyphenyl)phosphine (catalytic).[141]

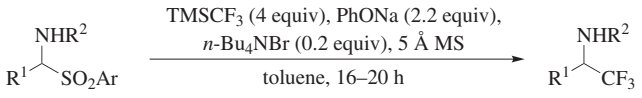


R	Yield (%)
Me	45
n-C_3H_7	50
c-C_6H_{11}	80
Ph	90
4-ClC_6H_4	87
4-$MeOC_6H_4$	85
(*E*)-PhCH=CH	83
2-naphthyl	95

Scheme 225

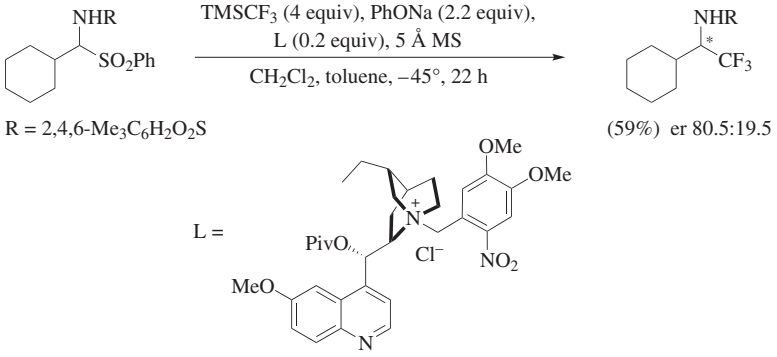
N-Tosylimines derived from aromatic aldehydes react with CF_3I/TDAE to provide very good yields of the trifluoromethylated adducts.[550] Analogous introduction of perfluoroethyl and perfluorobutyl groups is somewhat less efficient.[386] Trifluoromethylation of benzophenone *N*-tosylimine occurs in satisfactory 54% yield; irradiation with a sun lamp does not enhance the reaction rate.[550] Non-enolizable *N*-tosylaldimines are trifluoromethylated in excellent yields using $CF_3B(OMe)_3^-\ K^+$ in DMF under heating.[102]

N-Tosylimines can be generated in situ from α-amido sulfones, and undergo nucleophilic trifluoromethylation using $TMSCF_3$ in the presence of sodium phenolate and a small amount of TBAB in nonpolar solvent (PTC conditions) (Scheme 226).[548] One example of the enantioselective variant of the reaction is reported wherein TBAB is replaced by a cinchona alkaloid derived chloride salt; the observed enantioinduction is moderate (Scheme 227).[548]



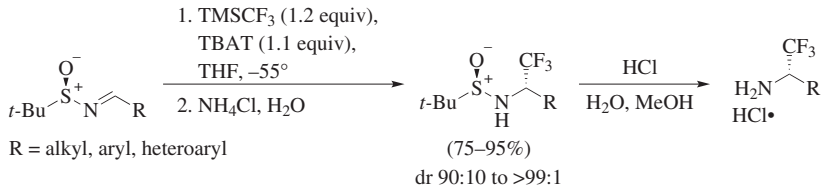
R^1	R^2	Ar	Temp (°)	Yield (%)
n-Pr	Ts	4-MeC_6H_4	–55	78
i-Pr	Ts	4-MeC_6H_4	–55	76
c-C_6H_{11}	Cbz	Ph	0	53
c-C_6H_{11}	Ts	4-MeC_6H_4	–55	91
c-C_6H_{11}	4-$MeOC_6H_4O_2S$	Ph	–30	39
c-C_6H_{11}	2,4,6-$(MeO)_3C_6H_2O_2S$	Ph	–30	75
Ph	Cbz	Ph	rt	75
$Ph(CH_2)_2$	Ts	4-MeC_6H_4	–55	59

Scheme 226

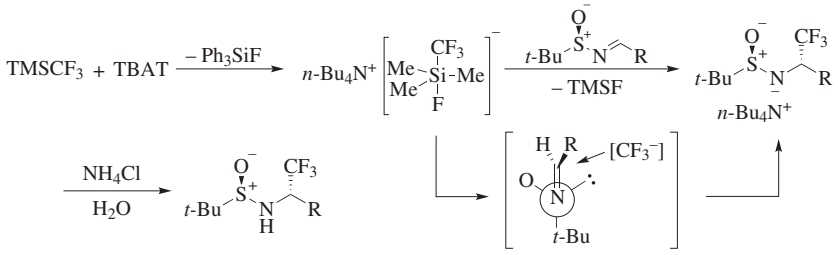


Scheme 227

Sulfinimines are chiral compounds due to the presence of the stereogenic sulfur atom. Direct enantioselective synthesis of trifluoromethylated amines is achieved by the highly diastereoselective reaction of chiral *N-tert*-butylsulfinimines with $TMSCF_3$ in the presence of TBAT in THF followed by hydrolysis of the intermediate adduct to the chiral amine salts (Scheme 228).[36,551] In contrast, when a stoichiometric amount of CsF is used the trifluoromethylated sulfinamides are obtained in only 50–65% yields with moderate diastereoselectivity. The highly diastereoselective addition of the trifluoromethyl group takes place through the non-chelated Cram open transition structure, affording the *anti*-sulfinamide as the main isomer (Scheme 229).[551] The more economical Bu_4N^+ AcO^- can substitute for TBAT.[552]

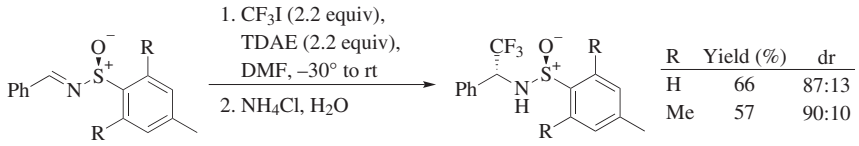


Scheme 228



Scheme 229

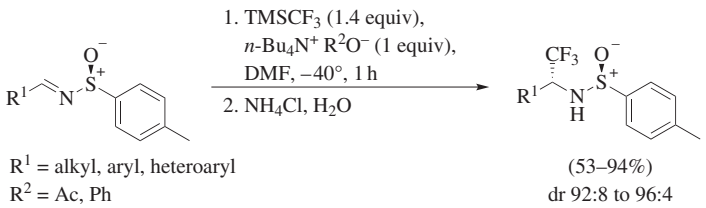
Enantiopure sulfinimines, easily prepared from the respective aldehydes and menthyl 4-toluenesulfinate, are trifluoromethylated with CF_3I/TDAE in good yields and diastereoselectivities. A wide variety of substrates give acceptable results, including the tolylsulfinimine derived from *n*-heptanal (48% yield, 72:28 dr). Unfortunately, only a modest increase in diastereoselectivity is observed when the mesityl rather than the tolylsulfinimine is used, as exemplified for the reactions with benzaldehyde in Scheme 230.[550]



R	Yield (%)	dr
H	66	87:13
Me	57	90:10

Scheme 230

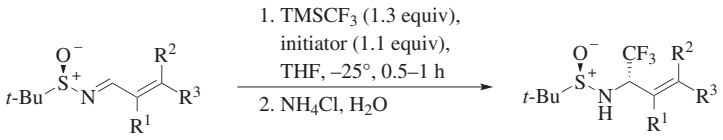
Higher yields and diastereoselectivities in the trifluoromethylation of enantiopure *N*-tolylsulfinimines are achieved by using $TMSCF_3$ in the presence of a Lewis base. An equimolar amount of tetrabutylammonium acetate initiates the reaction in the case of sulfinimines without α-protons, whereas those with α-protons require tetrabutylammonium phenolate as the catalyst (Scheme 231).[553]



Scheme 231

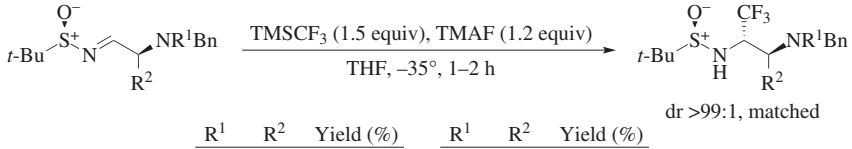
Highly diastereoselective additions of $TMSCF_3$ to α,β-unsaturated *N-tert*-butylsulfinimines proceed in a 1,2-fashion in the presence of TBAT or TMAF. Hydrolysis of the adducts gives access to chiral trifluoromethylated allylic amines (Scheme 232).[554] The diastereoselectivity and efficiency of the nucleophilic addition depends on the electrophilicity of the substrates but also on the size of the nucleophile. For α-branched imine substrates ($R^1 \neq H$) complete diastereoselectivity but lower yields are observed with TBAT, whereas the yields increase when the sterically less demanding TMAF is used.

A very high, matched, double diastereoselectivity is observed in the addition of $TMSCF_3$ to α-amino *N-tert*-butylsulfinimines derived from L-amino aldehydes (Scheme 233).[555] However, the corresponding sulfinimine derived from the D-amino aldehyde affords the corresponding adduct in 60% yield and with 80:20 dr (Scheme 234).[555] These observations suggest that the sulfinimido moiety dominates the stereochemical course of the addition to the *Re* face of the imine.



R^1	R^2	R^3	Initiator	Yield (%)	dr
H	H	furyl	TBAT	76	92:8
H	H	Ph	TBAT	55	90:10
Me	H	Ph	TBAT	73	>99:1
n-C_5H_{11}	Ph	H	TBAT	25	>99:1
n-C_5H_{11}	Ph	H	TMAF	82	90:10
Ph	Ph	H	TMAF	62	93:7
H	Ph	Ph	TBAT	62	>99:1

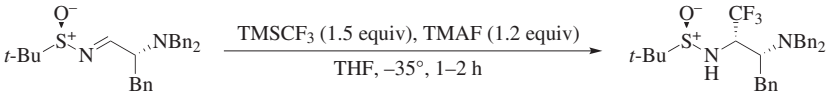
Scheme 232



dr >99:1, matched

R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
$-(CH_2)_3-$		79	Bn	n-Pr	85
Bn	Me	86	Bn	i-Bu	71
Bn	i-Pr	66	Bn	Bn	81

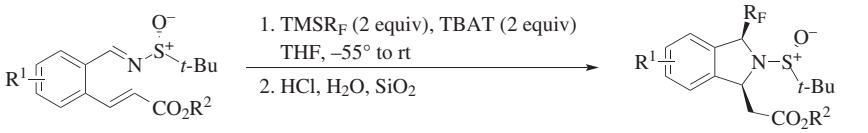
Scheme 233



(60%) dr 80:20, mismatched

Scheme 234

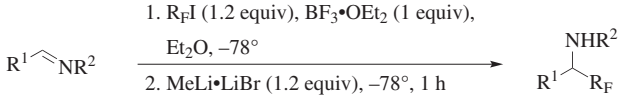
Reaction of $TMSCF_3$ and higher analogues with sulfinimines **120** causes nucleophilic addition and intramolecular aza-Michael reaction to form cyclized products **121** in good yields and high diastereoselectivities (Scheme 235).[556] This strategy allows the construction of chiral fluorinated isoindolines.



120 **121** (37–94%) dr 95:5 to 99:1

Scheme 235

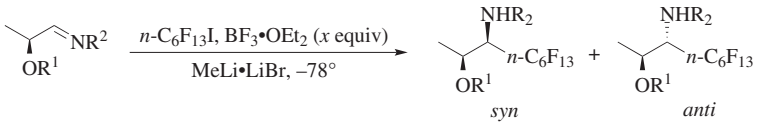
The activation of imines with Lewis acids such as $BF_3{\bullet}OEt_2$ is widely applied in the perfluoralkylation with perfluoroalkyllithium reagents[313,197] (Scheme 236).[313]



R^1	R^2	R_F	Yield (%)
Me(MeO)CH	*n*-Pr	*n*-C_6F_{13}	46
i-Pr	*i*-Bu	*n*-C_6F_{13}	84
Ph	Et	C_2F_5	91
Ph	Et	*i*-C_3F_7	0
Ph	Et	*n*-C_4F_9	80
Ph	Et	*n*-C_6F_{13}	88
Ph	Et	*n*-C_8F_{17}	79
Ph	*t*-Bu	*n*-C_6F_{13}	68
Ph	*c*-C_6H_{11}	*n*-C_6F_{13}	69
Ph(Me)CH	*n*-Pr	*n*-C_6F_{13}	81

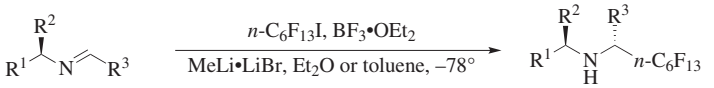
Scheme 236

Imines derived from enantiomerically pure chiral aldehydes readily react with perfluoro-*n*-hexyllithium in the presence of BF_3•OEt_2. The nature of the solvent and the amount of Lewis acid has considerable influence on the observed product diastereoselectivity, with the *anti* product as the major diastereomer (Schemes 237 and 238).[197] However, reverse diastereoselectivity is observed for α-silyloxy imines (Scheme 237).[197]



R^1	R^2	Solvent	*x*	Yield (%)	*syn*/*anti*
Me	*n*-Pr	Et_2O	1.2	46	37:63
Me	*n*-Pr	toluene	1.2	47	19:81
Me	*n*-Pr	toluene	2	40	25:75
MOM	*n*-Pr	Et_2O	1.2	52	19:81
MOM	*n*-Pr	toluene	1.2	42	3:97
MOM	allyl	Et_2O	1.2	40	19:81
TBS	allyl	Et_2O	1.2	81	85:15

Scheme 237

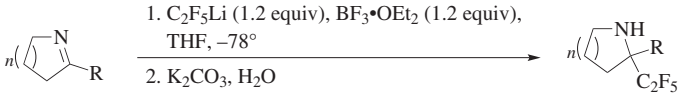


R^1 = Me, *i*-Pr, *i*-Bu, Bn
R^2 = MeO_2C, EtO_2C, Ph
R^3 = *n*-BuO_2C, *i*-Pr, MeCH=CH, Ph

(43–90%) dr 77:23 to 97:3

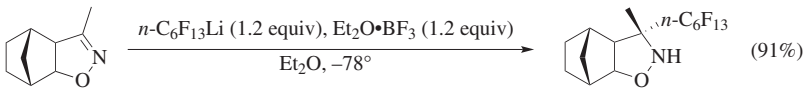
Scheme 238

Cyclic imines, when activated with BF_3•OEt_2, are also good substrates for nucleophilic perfluoroalkylation using perfluoroalkyllithium reagents (Scheme 239).[196] Structurally similar 2-isoxazolines can also be activated with BF_3•OEt_2 and undergo nucleophilic attack by R_FLi (Scheme 240).[557,558]



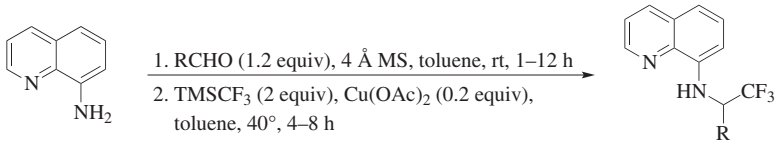
R	*n*	Yield (%)	R	*n*	Yield (%)
t-Bu	1	65	Ph	2	59
t-Bu	2	48	Ph	3	43
t-Bu	3	55	4-$MeOC_6H_4$	1	55
n-Bu	1	58	4-FC_6H_4	1	59
2-furyl	1	43	4-$CF_3C_6H_4$	1	49
Ph	1	52			

Scheme 239



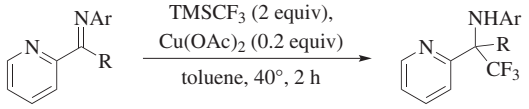
Scheme 240

Aldimines derived from 8-aminoquinoline undergo nucleophilic trifluoromethyl addition using $TMSCF_3$ and a small amount of copper(II) acetate (Scheme 241).[559] Presumably the Lewis acidic $Cu(OAc)_2$ coordinates with the imine as an *N,N*-bidentate ligand, activating the imine for nucleophilic addition. The departing acetate ligand in turn activates $TMSCF_3$. Similarly, imines bearing a 2-pyridyl moiety as shown in Scheme 242 undergo smooth reaction to afford trifluoromethylated amines.[559]



R	Yield (%)	R	Yield (%)
2-furyl	61	4-BrC_6H_4	71
2-pyridyl	61	4-$O_2NC_6H_4$	72
3-pyridyl	72	4-$MeOC_6H_4$	69
c-C_6H_{11}	62	4-MeC_6H_4	67
Ph	81	(*E*)-PhCH=CH	53

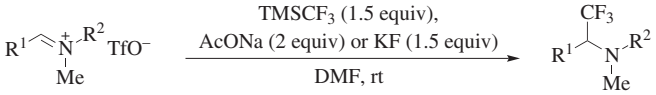
Scheme 241



R	Ar	Yield (%)
H	Ph	74
Ph	4-MeC$_6$H$_4$	53

Scheme 242

Iminium Salts. Another widely exploited strategy for the activation of imines toward nucleophilic addition is their conversion into iminium salts. Thus, iminium triflates, generated by the coupling of aldehydes with *N*-trimethylsilylamines and TMSOTf or by the methylation of imines with MeOTf, smoothly react with $TMSCF_3$ to afford the corresponding trifluoromethylated tertiary amines. The nucleophilic addition step is promoted by sodium acetate or potassium fluoride in DMF (Scheme 243)[560,561] Alternative conditions for this transformation use $CF_3B(OMe)_3^-\ K^+$ and heating in DMF.[102]

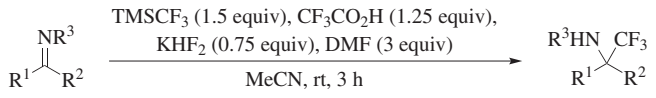


R^1 = alkyl, alkenyl, aryl, heteroaryl
R^2 = Me, allyl, Bn, aryl

(58–99%)

Scheme 243

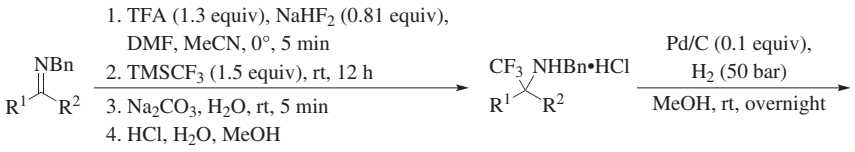
Surprisingly, nucleophilic trifluoromethylation of imines with $TMSCF_3$ can be carried out under strongly acidic conditions. *N*-Aryl- or *N*-alkylaldimines as well as -ketimines in the presence of strong acids (CF_3CO_2H or CF_3SO_3H) and KHF_2 provide the trifluoromethylated amines in good to excellent yields (Scheme 244).[490] Reactions are conducted in acetonitrile (in some cases with a small amount of DMF added) at room temperature. Furthermore, with careful choice of reaction conditions chemoselective trifluoromethylation of either the imine or ketone moiety of 2-(4-(benzyliminomethyl)phenoxy]-1-phenylethanone can be achieved (Scheme 183).[490]



R^1	R^2	R^3	Yield (%)
i-Pr	H	Bn	82
2-thienyl	H	*c*-Pr	50
2-furyl	H	*c*-C_6H_{11}	75
t-Bu	H	Bn	90
Et	Et	Bn	75
–$(CH_2)_5$–		Bn	62
Ph	H	Bn	90
Ph	Me	*i*-Pr	67

Scheme 244

N-Benzylimines are trifluoromethylated on 10–30 g scale under acidic conditions to afford, after palladium-mediated hydrogenation, α-trifluoromethylamine hydrochlorides in good to high yields (Scheme 245).[562]

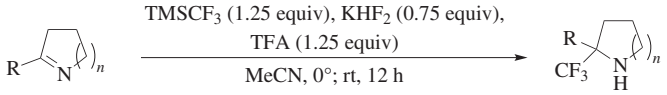




R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
Me	$MeOCH_2$	55	Me	*c*-Pr	41
Me	Et	72	$-(CH_2)_2O(CH_2)_2-$		76
$-(CH_2)_3-$		42	$-(CH_2)_4-$		81
H	*t*-Bu	91	H	*c*-C_5H_9	93
Et	Et	56	H	*c*-C_6H_{11}	50

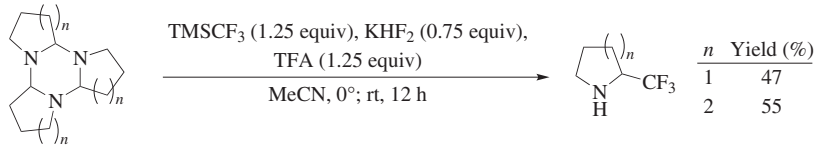
Scheme 245

Five- to seven-membered cyclic imines react with $TMSCF_3$ under acidic conditions to afford the corresponding α-trifluoromethylated derivatives of nitrogen heterocycles in good yields (Scheme 246).[563] Unsubstituted five- and six-membered cyclic imines are reactive and oligomerize to trimers, which are trifluoromethylated under acidic conditions to form α-trifluoromethylated pyrrolidine and piperidine, respectively (Scheme 247).[563]



n	R	Yield (%)	*n*	R	Yield (%)
1	Me	49	2	*t*-Bu	56
1	*n*-Bu	57	2	2-furyl	65
1	2-thienyl	71	2	3-pyridyl	67
1	2-furyl	60	2	Ph	49
1	3-pyridyl	68	3	*t*-Bu	56
1	*c*-C_6H_{11}	68	3	2-furyl	56
1	4-BrC_6H_4	61	3	3-pyridyl	56
1	4-$MeOC_6H_4$	49	3	Ph	44

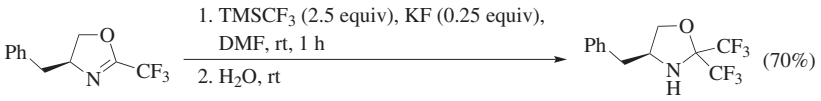
Scheme 246



n	Yield (%)
1	47
2	55

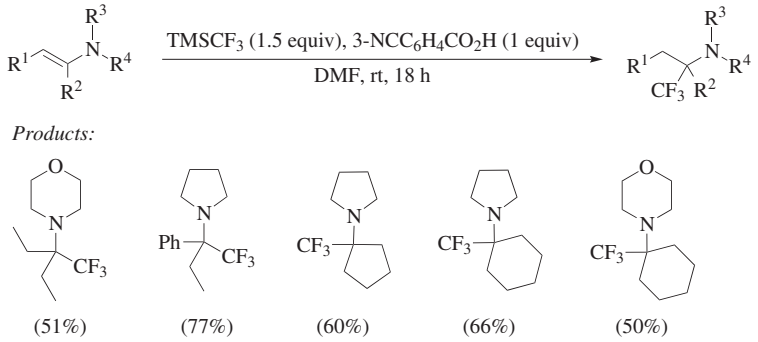
Scheme 247

(*S*)-4-Benzyl-2-trifluoromethyl-1,3-oxazoline reacts with a variety of nucleophiles to yield ring-opened products. However, the reaction with $TMSCF_3$/KF leads to the product of addition to the carbon–nitrogen double bond (Scheme 248).[564]



Scheme 248

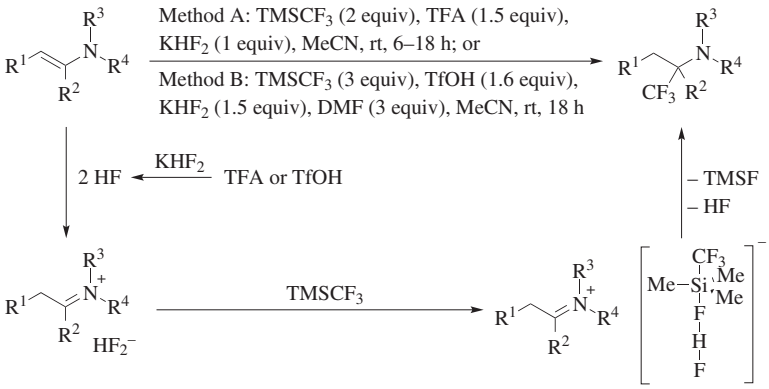
Enamines react with carboxylic acids to afford iminium carboxylates and subsequent reaction with $TMSCF_3$ in DMF provide α-trifluoromethyl-substituted amines in good yields. These compounds are difficult to access by other methods. The carboxylate counterion plays the role of Lewis base activator of $TMSCF_3$ and there is a delicate balance between the acidity of the carboxylic acid and nucleophilicity of the corresponding carboxylate. 3-Cyanobenzoic acid has been identified as the optimal promoter of the reaction (Scheme 249).[565]



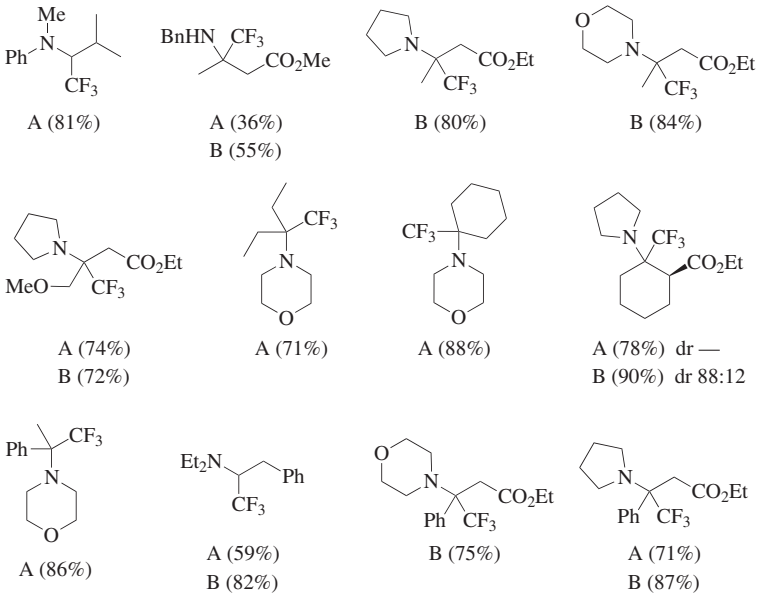
Scheme 249

Improved conditions for trifluoromethylation of enamines under acidic conditions use KHF_2 in combination with either trifluoroacetic acid for more reactive substrates (method A) or triflic acid for the less reactive ones (method B). A variety of enamines are trifluoromethylated with these conditions, including those containing ester groups, to afford α-trifluoromethylated amines (Scheme 250).[566] The enamine is speculated to convert to the iminum hydrogen fluoride under the acidic conditions. The HF_2^- anion acts as a nucleophilic activator of the silane, followed by transfer of the trifluoromethyl group from the silicon atom to the iminium electrophile (Scheme 250).[538]

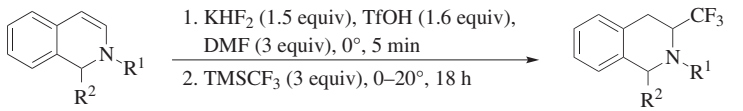
Enamines **122**, prepared by alkylation of dihydroisoquinoline at the nitrogen atom followed by reaction with Grignard reagents, undergo trifluoromethylation under acidic conditions to provide trifluoromethyl-substituted 1,2,3,4-tetrahydroisoquinolines (Scheme 251).[567] Similarly, unstable enamines **123**, derived from 4-methylpyridine by N-alkylation and reaction with Grignard reagents, afford trifluoromethylated 1,2,3,6-tetrahydropyridines (Scheme 252).[567]



Products:



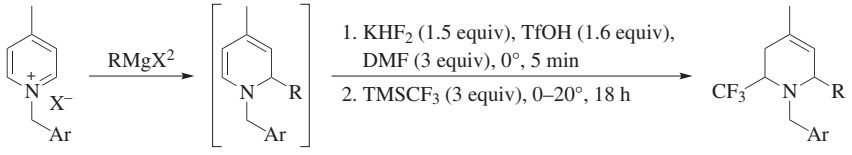
Scheme 250



122

R^1	R^2	Yield (%)	dr
Me	H	13	—
Me	Me	50	50:50
Me	*i*-Pr	64	50:50
PMB	*i*-Pr	54	56.5:43.5

Scheme 251

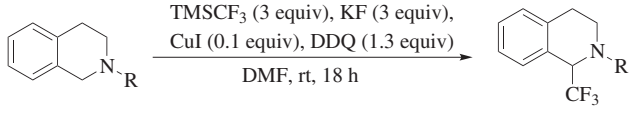


123

Ar	X^1	R	X^2	Yield (%)	dr
Ph	Br	Ph	Cl	58	60:40
4-MeC_6H_4	Cl	Me	I	34	56.5:43.5

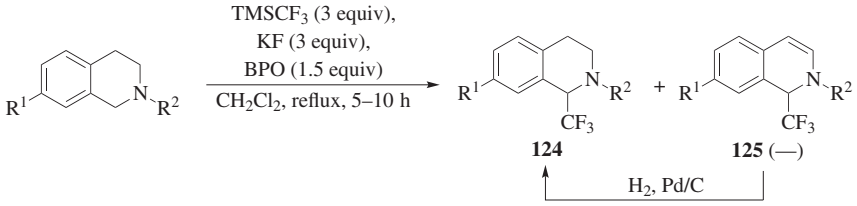
Scheme 252

Another variant of trifluoromethylation of iminium salts is the reaction of a cyclic tertiary amine, usually of tetrahydroisoquinoline type, with an oxidant to produce the iminium salt that undergoes trifluoromethylation, most often using the $TMSCF_3$/KF system. Thus, *N*-aryl or *N*-alkyl tetrahydroisoquinolines are trifluoromethylated with $TMSCF_3$ in the presence of DDQ (Scheme 253),[568] BPO (benzoyl peroxide) (Scheme 254),[569] or Rose Bengal dye under visible light irradiation (Scheme 255).[570,571]



R	Yield (%)
2-pyridyl	11
Ph	81
3-$MeOC_6H_4$	57
4-$MeOC_6H_4$	73
4-BrC_6H_4	69
4-$CF_3C_6H_4$	41
1-naphthyl	46

Scheme 253



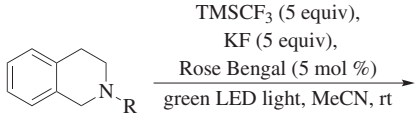
124 **125** (—)

R^1	R^2	**124** Yield (%)	**124/125**
H	Me	46[a]	—
H	allyl	39[a]	—
H	Bn	52[a]	—
H	Ph	82[b]	77:23
H	3-FC_6H_4	60[b]	67:33
H	4-ClC_6H_4	82[b]	77:23
H	3-$MeOC_6H_4$	87[b]	93:7

R^1	R^2	**124** Yield (%)	**124/125**
H	4-$MeOC_6H_4$	89[b]	97:3
H	4-MeC_6H_4	85[a]	82:18
H	3-$CF_3C_6H_4$	73[b]	67:33
H	4-$CF_3C_6H_4$	87[a]	79:21
Br	Ph	73[a]	55:45
2-pyridyl	Ph	67[b]	69:31

[a] Isolated yield of **124** after column chromatography.
[b] Isolated yield of **124** after hydrogenation of **124** + **125** mixture.

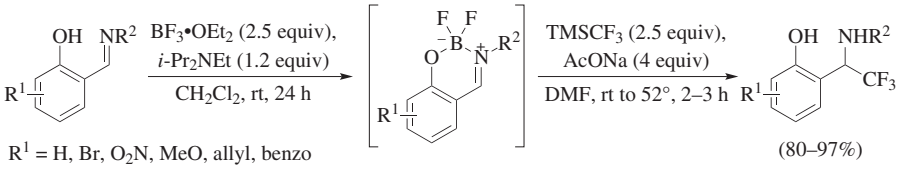
Scheme 254



R	Time (h)	Yield (%)
Me	72	52
allyl	48	58
Bn	48	60
Ph	36	67
4-BrC_6H_4	48	71
4-$MeOC_6H_4$	30	69
1-naphthyl	40	65

Scheme 255

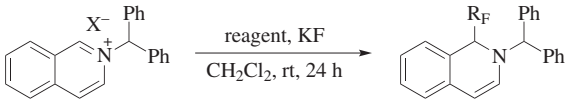
Other. *N*-Aryl and *N*-alkyl salicylaldimines are trifluoromethylated using $TMSCF_3$ activated with sodium acetate. The reaction proceeds via the initial generation of a boron chelate (Scheme 256).[572,573]



R^1 = H, Br, O_2N, MeO, allyl, benzo
R^2 = alkyl, allyl, aryl, 4-morpholinyl, 4-piperidinyl

Scheme 256

A three-step protocol for the trifluoromethylation of azines has been developed. It consists of alkylation with 4-methoxybenzyl bromide to form *N*-4-methoxybenzylazinium bromides, reaction with $TMSCF_3$/KF in the presence of a catalytic amount of Ph_3SnF to form 2-trifluoromethyl dihydroazines, and deprotection/oxidation with ceric ammonium nitrate to provide 2-trifluoromethylazines in overall 18–68% overall yields.[574] A similar process starting from *N*-alkyl azinium bromides or chlorides enables installation of a heptafluoroisopropyl group starting from hexafluoropropene and KF (Scheme 257).[575]

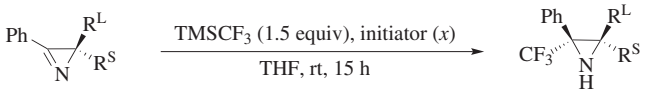


X	Reagent	R_F	Yield (%)
Br	$TMSCF_3$ (1.3 equiv) + Ph_3SnF (0.3 equiv)	CF_3	85
Cl	$CF_3CF{=}CF_2$	*i*-C_3F_7	85

Scheme 257

Azirines. Azirines undergo efficient trifluoromethylation using $TMSCF_3$ and a fluoride source (TBAF or TEAF, tetraethylammonium fluoride) (Scheme 258).[576]

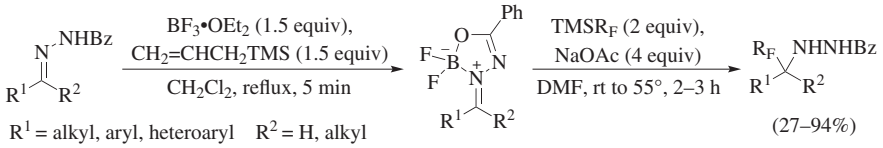
The high strain release upon addition of 'CF_3' most probably compensates for the formation of the thermodynamically unfavorable silicon–nitrogen bond (compared to favorable Si–O bonds in additions to carbonyl compounds), thus rendering the reaction catalytic. Single isomers of aziridines are observed, consistent with the nucleophilic attack from the side of the smaller substituent.



R^L	R^S	Initiator	*x*	Yield (%)
Me	H	TEAF	cat.	51
Me	Me	TBAF	1 equiv	41
MeO_2C	H	TBAF	cat.	67
Ph	H	TEAF	cat.	86

Scheme 258

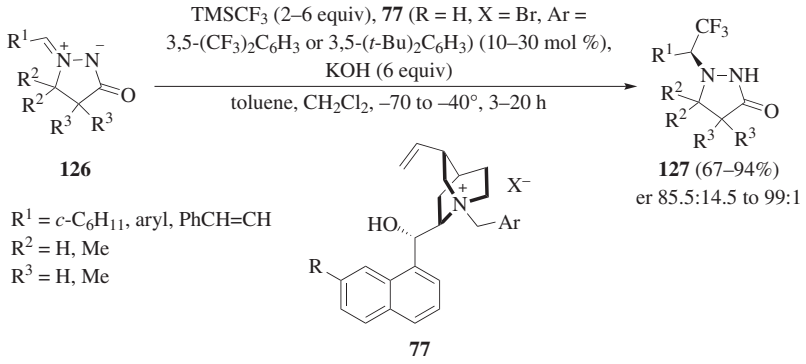
Hydrazones. Nucleophilic trifluoromethylation and pentafluoroethylation of *N*-benzoylhydrazones with $TMSCF_3$ or $TMSC_2F_5$ and an excess of sodium acetate is possible after activation of the hydrazones with boron trifluoride in the presence of allyltrimethylsilane to form a zwitterionic difluoroboron complex (Scheme 259).[577,573]



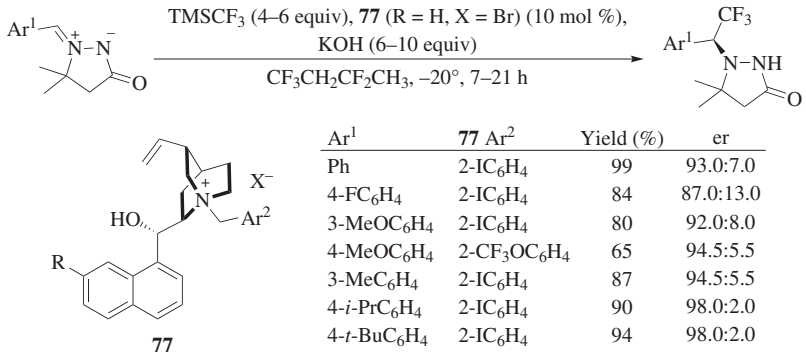
R^1 = alkyl, aryl, heteroaryl R^2 = H, alkyl
$R_F = CF_3, C_2F_5$

Scheme 259

Azomethine imines **126** are sterically demanding imine equivalents with a constrained conformation. They react with $TMSCF_3$ in the presence of chiral cinchona alkaloid derived salts **77** (R = H, X = Br) as phase-transfer catalysts to afford enantioenriched adducts **127**. The reaction is performed at low temperature in nonpolar solvents in the presence of KOH. High chemical yields and enantioselectivities are obtained especially with aryl azomethine imines and catalyst **77** with bulky aryl substituents (Scheme 260).[578] Adducts **127** are transformed in two steps to enantiopure trifluoromethylated amines. Further optimization studies of the reaction performed in Solkane 365mfc reveals that catalyst **77** (R = H, X = Br, $Ar^2 = 2\text{-}IC_6H_4$) provides the best enantioselectivity (Scheme 261), while catalyst **77** (R = H, X = Br, $Ar^2 = 4\text{-}IC_6H_4$) provides the lowest enantioselectivity.[579] Solkane 365mfc ($CF_3CH_2CF_2CH_3$) is an environmentally benign nonpolar solvent.



Scheme 260

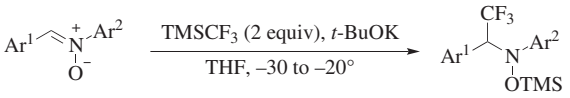


Ar^1	**77** Ar^2	Yield (%)	er
Ph	2-IC_6H_4	99	93.0:7.0
4-FC_6H_4	2-IC_6H_4	84	87.0:13.0
3-$MeOC_6H_4$	2-IC_6H_4	80	92.0:8.0
4-$MeOC_6H_4$	2-$CF_3OC_6H_4$	65	94.5:5.5
3-MeC_6H_4	2-IC_6H_4	87	94.5:5.5
4-*i*-PrC_6H_4	2-IC_6H_4	90	98.0:2.0
4-*t*-BuC_6H_4	2-IC_6H_4	94	98.0:2.0

Scheme 261

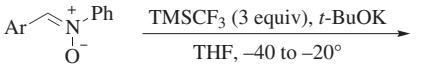
Aldazines (bisimines of hydrazine) undergo nucleophilic addition with perfluoroalkyllithium reagents. After reduction with lithium aluminum hydride, mono- or disubstituted perfluoroalkyl hydrazines are obtained.[197]

Nitrones. Generally, nitrones are strongly electrophilic substrates and readily accept perfluoroalkyl nucleophiles. Potassium *tert*-butoxide initiated nucleophilic trifluoromethylation of nitrones with $TMSCF_3$ leads to α-(trifluoromethyl)hydroxylamines protected as *O*-trimethylsilyl ethers. The reaction works best with α,N-diaryl nitrones (Scheme 262).[580,581] Acidic deprotection of the nitrone/$TMSCF_3$ adducts generates α-(trifluoromethyl)hydroxylamines, whereas catalytic hydrogenation of the adducts produces α-(trifluoromethyl)amines. Nitrones with strong electron-withdrawing groups on the α-aryl ring or with α-heterocyclic groups undergo an addition–elimination–addition sequence to generate α,α-bis(trifluoromethyl)amines (Scheme 263).[580,581]



Ar^1	Ar^2	Yield (%)	Ar^1	Ar^2	Yield (%)
Ph	Ph	85–93	2-$MeOC_6H_4$	Ph	59–74
Ph	4-ClC_6H_4	52–59	2-furyl	Ph	18–43
Ph	4-$MeOC_6H_4$	62–79	2-pyridyl	Ph	<5
4-$O_2NC_6H_4$	Ph	10–22	4-pyridyl	Ph	<5
4-ClC_6H_4	Ph	71–90	1-naphthyl	Ph	83–90

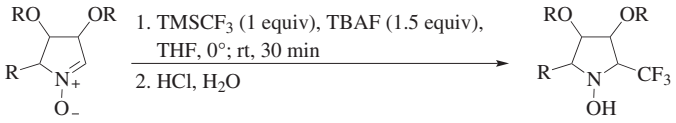
Scheme 262



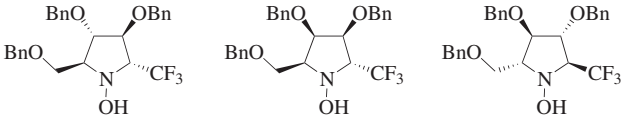
Ar	Yield (%)
2-furyl	78–82
2-pyridyl	51–76
3-pyridyl	72–75
4-$O_2NC_6H_4$	64–77

Scheme 263

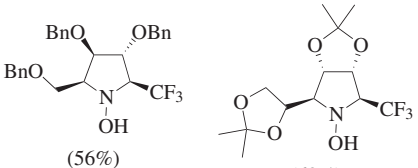
Sugar-derived cyclic nitrones undergo trifluoromethylation with $TMSCF_3$ to afford cyclic hydroxylamines in good yields and with complete diastereoselectivities (Scheme 264).[582]



Products:



(60%) (69%) (60%)

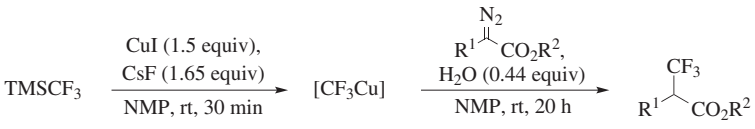


(56%) (63%)

Scheme 264

Nitrones with alkyl groups on the dipole fail to react with $TMSCF_3$, but this limitation can be circumvented by the trifluoromethylation of β,γ-unsaturated nitrones followed by reduction of the double bond. In all cases, trifluoromethylation of nitrones requires the addition of an external anionic initiator.

Diazo Compounds. α-Trifluoromethyl esters can be accessed via the reaction of electrophilic α-diaz oesters and CF_3Cu (Scheme 265).[583] A proposed mechanism involves formation of a copper carbenoid that undergoes migratory insertion of the CF_3 group and protonation by water, which is added to the reaction mixture (Scheme 265 and Scheme 266).[583]

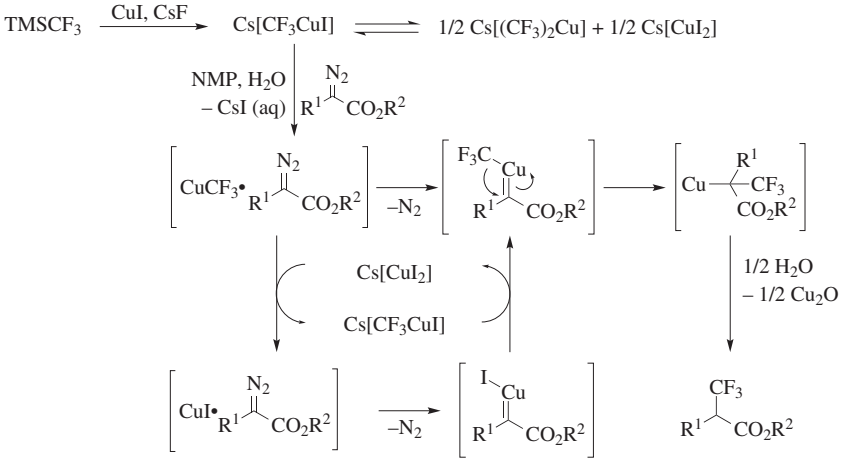


R^1	R^2	Yield (%)
Ph	Et	82
3,4-$Cl_2C_6H_3$	Et	87
4-$O_2NC_6H_4$	Et	81[a]
4-$MeOC_6H_4$	Me	96

R^1	R^2	Yield (%)
4-$MeOC_6H_4$	allyl	88
Bn	Et	81
1-naphthyl	Et	75

[a] The conditions used were $[CF_3Cu]$ (2 equiv), H_2O (1 equiv), 60°.

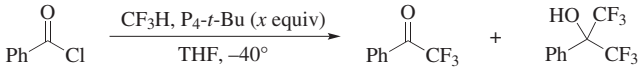
Scheme 265



Scheme 266

This reaction displays a broad scope and is applicable even to diazoesters with a methylene group in the α-position to the diazo group. However, in the absence of a proton source, such as water, the predominant pathway after the migration of CF_3 group becomes β-fluoride elimination and formation of difluoroalkenes.[583,584]

Acid Halides. Benzoyl chloride reacts with fluoroform in the presence of P_4-*t*-Bu superbase to afford trifluoroacetophenone or 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, depending on the stoichiometry and reaction time (Scheme 267).[81]



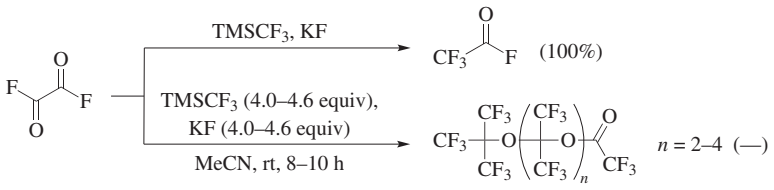
x	Time (h)	Ketone Yield (%)	Alcohol Yield (%)
1.2	1.5	72	trace
1.2	3	72	14
2.4	1	81	7
2.4	10	13	60
2.4	24	0	90

Scheme 267

Both carboxylic acid fluorides and chlorides react with (perfluoroalkyl)trimethylsilanes in the presence of fluoride to initially afford perfluoroalkyl ketones and subsequently bis(perfluoroalkyl) carbinols. Acid fluorides generally require only small amounts of the fluoride initiator, whereas in the reaction with acid chlorides at least an equimolar amount of a fluoride source is necessary.

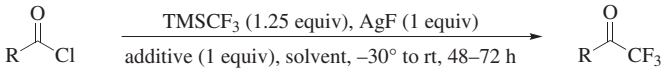
Formyl fluoride reacts with an excess of $TMSCF_3$ in the presence of excess KF in acetonitrile to afford high yields of perfluoro *tert*-butanol.[397,465,466] When identical conditions are employed with phosgene, no trifluoromethyl-containing product is formed.[465] Treatment of fluorophosgene with excess $TMSCF_3$ and a catalytic amount of KF results in the formation of perfluoro *tert*-butyl trifluoroacetate in good yield.[397] Acetyl fluoride reacts with $TMSCF_3$ in the presence of a catalytic amount of KF in acetonitrile to provide $MeC(CF_3)_2OAc$ in 80% yield.[397] Propionyl fluoride affords ethyl perfluorooctyl ketone upon treatment with n-$C_8F_{17}TMS$ in the presence of small amounts of $(Me_2N)_3SF$.[326] Similarly, benzoyl fluoride reacts with $TMSR_F$ (R_F = n-C_6F_{13}, n-C_8F_{17}) and CsF to afford perfluoroalkyl phenyl ketones.[326] Analogous ketone formation is observed for n-$C_3F_7OCF(CF_3)COF$ [326] and perfluoroglutaryl and perfluorosuccinyl fluorides.[585,586] Trifluoroacetyl fluoride reacts with two equivalents of $TMSCF_3$ and substoichiometric amounts of KF to provide $CF_3CO_2C(CF_3)_3$ in more than 65% yield.[397] Other perfluoro acid fluorides R_FCOF (R_F = C_2F_5, n-C_3F_7, n-C_7F_{15}, C_6F_5) react with an excess of $TMSCF_3$ and KF or CsF to form alcoholates $R_F(CF_3)_2CO^-$, sometimes accompanied by $R_FCO_2C(CF_3)_2R_F$ ester formation.[465,466,587]

Oxalyl fluoride displays unique behavior; reaction with $TMSCF_3$ and KF results in the quantitative formation of trifluoroacetyl fluoride rather than the expected diketone (Scheme 268).[397] This can be rationalized by carbon–carbon bond cleavage after nucleophilic addition. Surprisingly, when a large excess of $TMSCF_3$ and KF is used, a mixture of branched-chain polyether oligomers is obtained (Scheme 268).[397]



Scheme 268

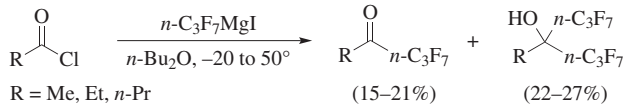
The combination of $TMSCF_3$ and silver fluoride is an efficient reagent for the synthesis of trifluoromethyl ketones from acid chlorides (Scheme 269).[588] In this case it is presumed that the formed CF_3Ag reacts with the acid chloride without subsequent addition to the perfluoroalkyl ketone.



R	Additive	Solvent	Yield (%)
2-furyl	DMAP	CH_2Cl_2	61
2-FC_6H_4	DMAP	CH_2Cl_2	71
4-ClC_6H_4	DMAP	CH_2Cl_2	78
4-BrC_6H_4	DMAP	CH_2Cl_2	61
4-$O_2NC_6H_4$	DMAP	CH_2Cl_2	50
4-$MeOC_6H_4$	—	EtCN	73
(*E*)-$PhCH{=}CH_2$	—	EtCN	50

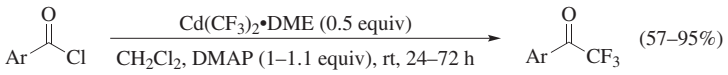
Scheme 269

Acid halides react with R_FMgX,[204,199] R_FAg,[588] $(R_F)_2Cd$,[589] R_FCu,[590] R_FZnX,[591] and other perfluoroalkyl organometallic reagents. In most cases the major product of the coupling is the corresponding perfluoroalkyl ketone. Reactive R_FMgX reagents produce significant amounts of tertiary alcohols as side products (Scheme 270).[204,199]



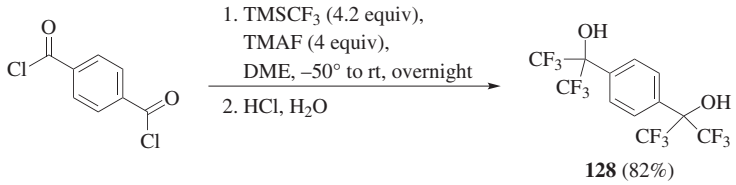
Scheme 270

Benzoyl chloride reacts with $TMSCF_3$ (1.2 equivalent) and more than one equivalent of TBAF in THF to provide a mixture of phenyl trifluoromethyl ketone and $Ph(CF_3)_2COTMS$.[122] However, with two equivalents of both $TMSCF_3$ and TMAF in DME, alcohol $Ph(CF_3)_2COH$ is obtained in 77% yield after acidification.[592] Aryl and heteroaryl carboxylic acid chlorides can be converted into the corresponding perfluoroalkyl ketones in good yields by the reaction of acid halides with the $Cd(CF_3)_2$•DME complex. If pyridine is used as the base, products of acylation–nucleophilic addition to the pyridine ring also form along with the expected trifluoromethyl ketones.[589] Substitution of pyridine with DMAP in CH_2Cl_2 helps to avoid undesirable side reactions and provides access to high yields of the trifluoromethyl ketones (Scheme 271).[589] Reaction of tris(trifluoromethyl)bismuth with benzoyl chloride proceeds smoothly at room temperature using pyridine as the catalyst and affords trifluoroacetophenone in 69% yield.[168]



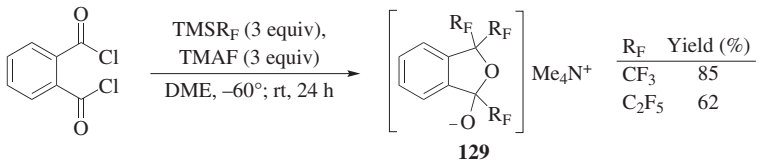
Scheme 271

Terephthaloyl chloride reacts with an excess of $TMSCF_3$ and TMAF with the formation of diol **128** after acidification (Scheme 272).[592] In contrast, phthaloyl dichloride under similar conditions yields alcoholates **129** (Scheme 273).[593] In this case the perfluoroalkyl nucleophile first substitutes the chloride atoms, then attacks the intermediate ketone to form the tertiary alcoholate which reacts with the proximal carbonyl.



128 (82%)

Scheme 272

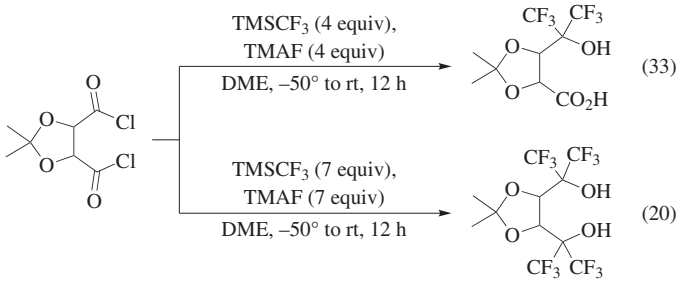


R_F	Yield (%)
CF_3	85
C_2F_5	62

129

Scheme 273

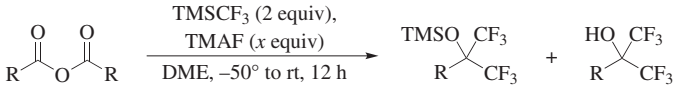
Trifluoromethylation of isopropylidenetartaric acid dichloride using $TMSCF_3$ forms the semitrifluoromethylated tartaric acid derivative or the trifluoromethyl analogue of TADDOL (2,2-dimethyl-α,α,α′,α′-tetraphenyldioxolane-4,5-dimethanol) depending on the amount of $TMSCF_3$ used (Scheme 274).[594]



Scheme 274

Perfluoroalkylations of acid halides using perfluoroalkyl bromides or iodides and $(Et_2N)_3P$,[595–598] perfluoroalkyl iodides and TDAE,[599] non-metallic perfluoroalkyl salts,[101] and sodium trifluoroacetate in the presence of CuI have been described.[600]

Anhydrides. Anhydrides react with two equivalents of $TMSCF_3$ and TMAF to form $RC(CF_3)_2OTMS$ (**130**) or the corresponding alcohols **131** depending on the amount of TMAF used (Scheme 275).[592] Only one carbonyl residue is converted to the tertiary alcohol, the other one departs as an alkanecarboxylate. The reaction proceeds through the trifluoromethyl ketone intermediates, which unlike the starting anhydrides are capable of reaction with $TMSCF_3$, initiated by RCO_2NMe_4, a byproduct of the first addition. The exception is trifluoroacetic anhydride, which requires two equivalents of TMAF for clean conversion into the alcohol due to the reduced nucleophilicity of trifluoroacetate.[592]



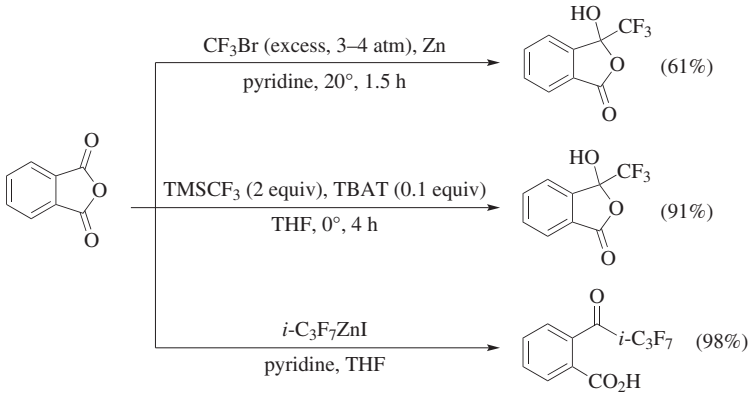
130 **131**

R	*x*	**130** Yield (%)	**131** Yield (%)
t-BuO	1	50	—
Me	1	62	—
Ph	1	82	—
1-naphthyl	1	88	—
CF_3	2	—	87[a]
Ph	2	—	81[b]

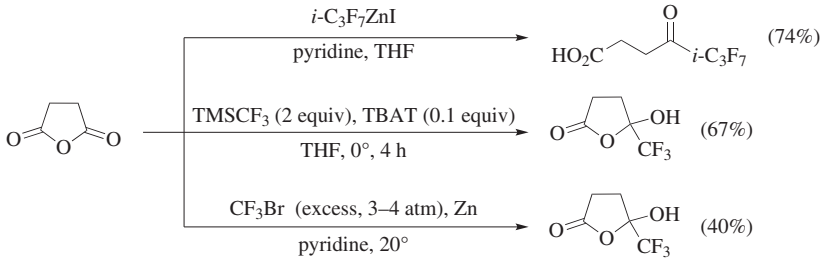
[a] The product was obtained after acidification with H_2SO_4.
[b] The product was obtained after acidification with HCl.

Scheme 275

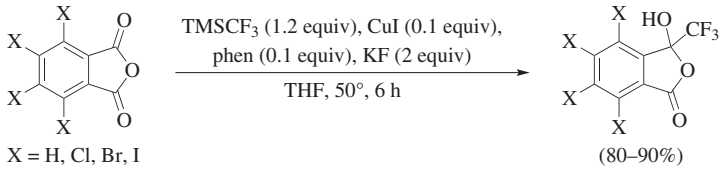
Butyric anhydride can be converted into trifluoromethyl *n*-propyl ketone in 20% yield by reaction with CF_3Br/Zn in pyridine.[601] Similar reaction conditions applied to phthalic anhydride afford the product of addition of a trifluoromethyl group to one of the carbonyl groups without anhydride ring opening;[600–602] however a better yield is obtained using $TMSCF_3$ and TBAT as the catalyst (Scheme 276).[603] On the other hand, reaction of phthalic anhydride with *i*-C_3F_7ZnI affords 2-perfluoroisobutyroyl benzoic acid in 98% yield (Scheme 276).[591] Similar ring opening takes place in the case of succinic anhydride in 74% yield (Scheme 277).[591] In contrast, 5-trifluoromethyl-5-hydroxy-γ-butyrolactone forms in good yield in the reaction of succinic anhydride with $TMSCF_3$ and a substoichiometric amount of TBAT or TBAF[604,603] (Scheme 277).[603] Phthalic anhydride derivatives are efficiently trifluoromethylated with $TMSCF_3$ in the presence of a copper catalyst (Scheme 278).[605]



Scheme 276

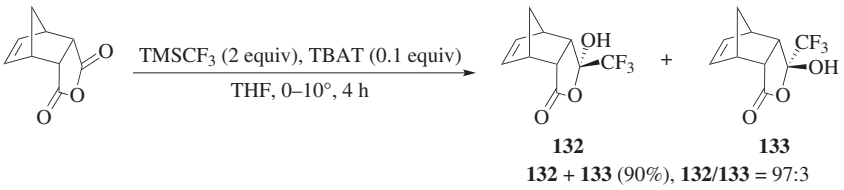


Scheme 277



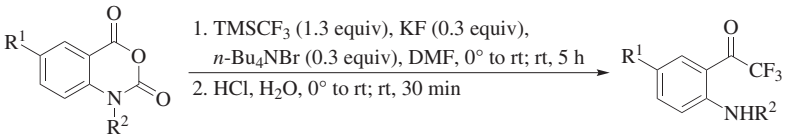
Scheme 278

The Diels–Alder adduct of cyclopentadiene and maleic anhydride undergoes trifluoromethylation with $TMSCF_3$ under standard conditions to provide adducts **132** and **133** in high yield and *exo* selectivity (Scheme 279).[606]



Scheme 279

N-substituted isatoic anhydrides are converted to *N*-substituted 2-trifluoroacetylanilines upon reaction with $TMSCF_3$ followed by acidic and basic workup for consecutive desilylation and decarboxylation of intermediates (Scheme 280).[607]

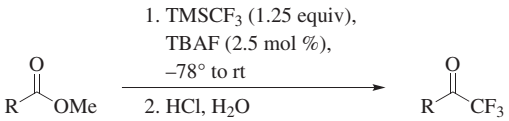


R^1	R^2	Yield (%)
Br	Me	85
H	Me	87
H	allyl	90
H	Ph	74
H	4-FC_6H_4	67
H	4-$MeOC_6H_4$	83
H	Bn	85
H	4-$(Ph_2CH)C_6H_4$	77[a]

[a] The reaction time for step 1 was 10 h.

Scheme 280

Esters and Lactones. Methyl and ethyl formate and methyl benzoate are trifluoromethylated with equimolar amounts of fluoroform in the presence of KHMDS[77] or P_4-*t*-Bu superbase[81] in toluene or THF to form trifluoromethyl ketones (or hemiacetals) in low to moderate yields. Non-activated carboxylic esters are unreactive toward $TMSCF_3$ in THF in the presence of TBAF hydrate.[122] However, the use of small amounts of anhydrous TBAF (solution in THF added at –78°) and dry nonpolar solvents such as pentane, dichloromethane, or toluene transforms various methyl esters into trifluoromethyl ketones in high yields (Scheme 281).[608] Tetrabutylammonium acetate also acts as an efficient initiator in these reactions.[131]

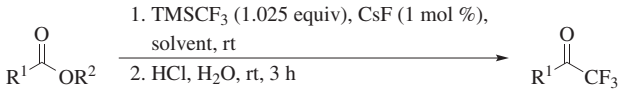


R	Solvent	Time (h)	Yield (%)
t-Bu	pentane	72	68
c-C_6H_{11}	pentane	48	72
Ph	toluene	18	95
4-$O_2NC_6H_4$	CH_2Cl_2	18	81
(*E*)-PhCH=CH	pentane	24	85
1-adamantyl	pentane	72	70
n-$C_{13}H_{27}$	pentane	24	75

Scheme 281

Non-enolizable, enolizable, as well as sterically hindered esters are reactive. In the case of methyl 3-phenylpropynoate the desired ketone cannot be isolated because of extensive polymerization. However, trifluoromethyl ketones are isolated in high yields in the reaction of methyl and ethyl 3-phenylpropynoates and other

non-activated esters in the reaction of $TMSCF_3$ and a catalytic amount of CsF in DME or without solvent (Scheme 282).[470]

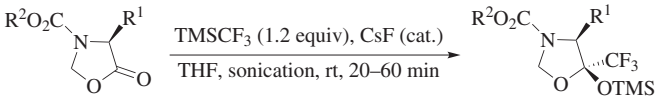


R^1	R^2	Solvent	Time (h)	Yield (%)
Me	Et	neat	1	86
CH_2=CMe	Me	neat	3	84
Ph	Me	neat	1	90
(*E*)-PhCH=CH	Me	DME	3	90
Ph–C≡C	Me	neat	3	86
$Ph(CH_2)_2$	Et	neat	4	90

Scheme 282

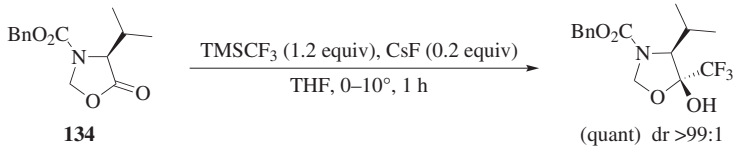
N-Protected acyclic or cyclic amino esters react with $TMSCF_3$ and CsF in DME to afford, after hydrolysis with hydrochloric acid, *N*-protected amino trifluoromethyl ketones as hydrated hydrochloride salts.[609] Activated esters such as hexyl trifluoroacetate or pentafluorophenyl carboxylates are reactive toward an excess of $TMSCF_3$ and equimolar amounts of TBAF or TMAF to provide trimethylsilyl-protected bis-trifluoromethylated alcohols.[122,592] Trifluoromethylation of di-*tert*-butyl oxalate with $TMSCF_3$ in the presence of TBAF in THF affords trifluoropyruvic acid monohydrate in 78% yield.[610]

Five- and six-membered ring lactones react smoothly with $TMSCF_3$ under fluoride catalysis to produce trifluoromethyl-containing silylated hemiketals in good yields. The four-membered ring adduct undergoes rapid decomposition, whereas the seven-membered ring lactone affords side-products arising from fluoride-mediated ring opening.[122,604] Addition of $TMSCF_3$ to amino acid derived *N*-substituted oxazolidin-5-ones is highly diastereoselective[611–615] (Scheme 283).[611] Trifluoromethyl group addition to chiral oxazolidin-5-one **134** derived from valine proceeds with quantitative yield and complete diastereoselectivity (on 73 kg scale) (Scheme 284).[616] The analogous oxazolidin-5-one derived from L-phenylalanine is trifluoromethylated in 97% yields and with complete diastereoselectivity.[387]



R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
$BnSCH_2$	*t*-Bu	77	*n*-Bu	*t*-Bu	98
Me	Bn	69	*i*-Bu	*t*-Bu	95
Me	*t*-Bu	85	Bn	Bn	95
i-Pr	*t*-Bu	84			

Scheme 283

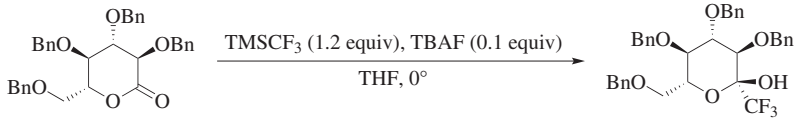


134

(quant) dr >99:1

Scheme 284

Several sugar 1,4-lactones are trifluoromethylated to produce mixtures of diastereomeric hemiketals.[406,617,618] Six-membered-ring sugar lactone **135** undergoes diastereoselective trifluoromethylation to afford trifluoromethyl glucopyranose **136** (Scheme 285).[619]

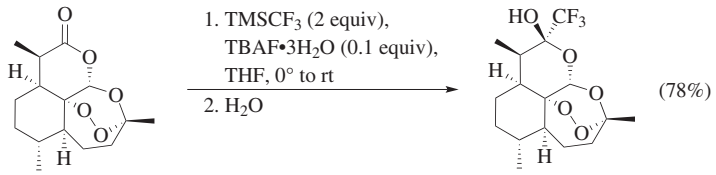


135

136 (72%)

Scheme 285

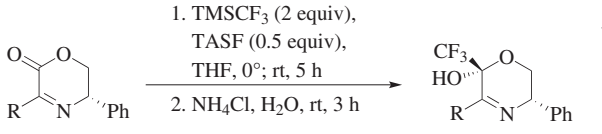
Trifluoromethylation of artemisinin works well even in the presence of TBAF trihydrate. The trifluoromethylated hemiketal is isolated as a single diastereomer[620,442] (Scheme 286).[442]



(78%)

Scheme 286

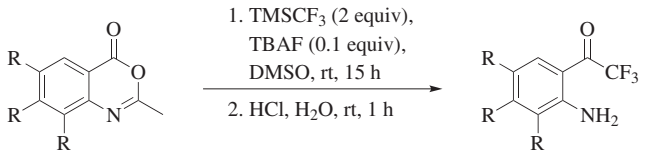
The Ruppert–Prakash reagent adds diastereoselectively to oxazin-2-ones exclusively on the lactone carbonyl, leaving the imino function unaffected (Scheme 287).[621,622]



R	Yield (%)
Me	72
$MeO_2C(CH_2)_2$	74
t-Bu	65
$CH_2{=}CH(CH_2)_3$	69
Ph	32
$Ph(CH_2)_2$	75

Scheme 287

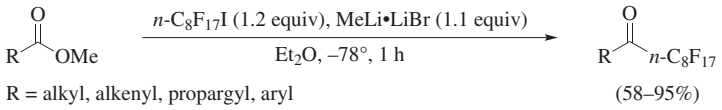
Substituted benzoxazinones undergo nucleophilic trifluoromethylation with $TMSCF_3$ to afford 2-amino-1,1,1-trifluoroacetophenones in moderate yields (Scheme 288).[623]



Scheme 288

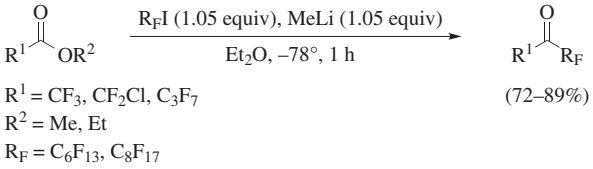
Perfluoroalkyllithium and Grignard reagents react with esters of carboxylic acids. In the reactions of most esters with n-C_3F_7MgI, the perfluoropropyl ketones are the major products along with the bis(perfluoroalkyl) tertiary alcohols and perfluoroalkyl secondary alcohols.[204] With pentafluoroethyllithium, depending on the substrate and the number of equivalents of the nucleophilic reagent, the major products are either the corresponding ketones or alcohols formed via second addition to the intermediate ketones.[391]

Good to excellent yields of perfluorooctyl ketones are formed from methyl esters and in situ generated perfluorooctyllithium (Scheme 289).[624,625]



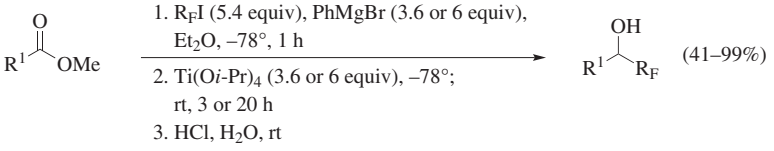
Scheme 289

Esters of perfluoroalkanoic acids react readily with long-chain perfluoroalkyllithium reagents, generated from methyllithium and perfluoroalkyl iodides, to provide unsymmetrical perfluorinated ketones (Scheme 290).[626]



Scheme 290

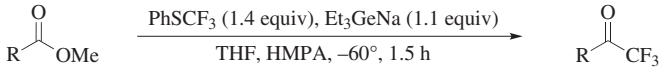
Interestingly, perfluoroalkyl titanate-type reagents prepared from perfluoroalkyl Grignard reagents and titanium(IV) isopropoxide convert methyl or phenyl esters into perfluoroalkyl-containing secondary alcohols in high yields. Formation of these products can be rationalized by the Meerwein–Ponndorf–Verley reduction of the ketone intermediate by isopropoxide (Scheme 291).[627]



R^1 = alkyl, alkenyl, aryl
R_F = C_4F_9, C_6F_{13}

Scheme 291

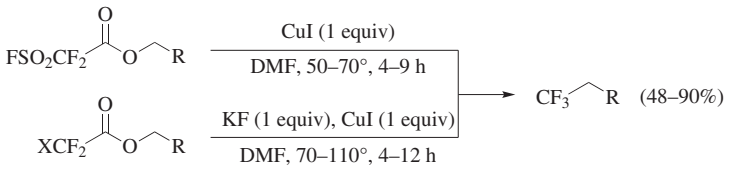
A combination of $PhSCF_3$ and Et_3GeNa chemoselectively transforms methyl esters into trifluoromethyl ketones (Scheme 292).[172] Other functionalities such as longer alkyl esters, acetals, or epoxides are not affected.



R = aryl, alkyl
(93–98%)

Scheme 292

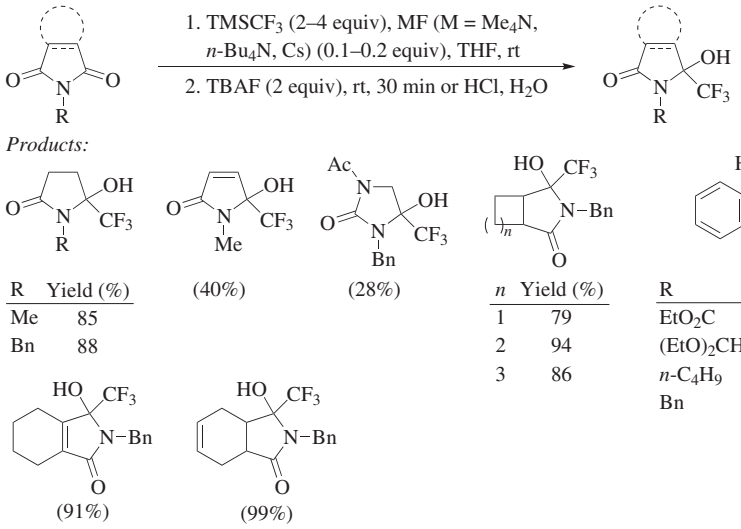
Several copper-mediated rearrangements can be considered as nucleophilic perfluoroalkyl additions because such rearrangements may involve formation of trifluoromethyl copper species. An example is the formation of RCH_2CF_3, when $FSO_2CF_2CO_2CH_2R$ is heated in DMF in the presence of CuI (Scheme 293).[245] A similar rearrangement is observed for $XCF_2CO_2CH_2R$ (X = Cl, Br) in DMF in the presence of KF and CuI. Good yields are reported for both protocols (Scheme 293).[245]



X = Cl, Br
R = CH_2=CH, HC≡C, Ar, PhCH=CH

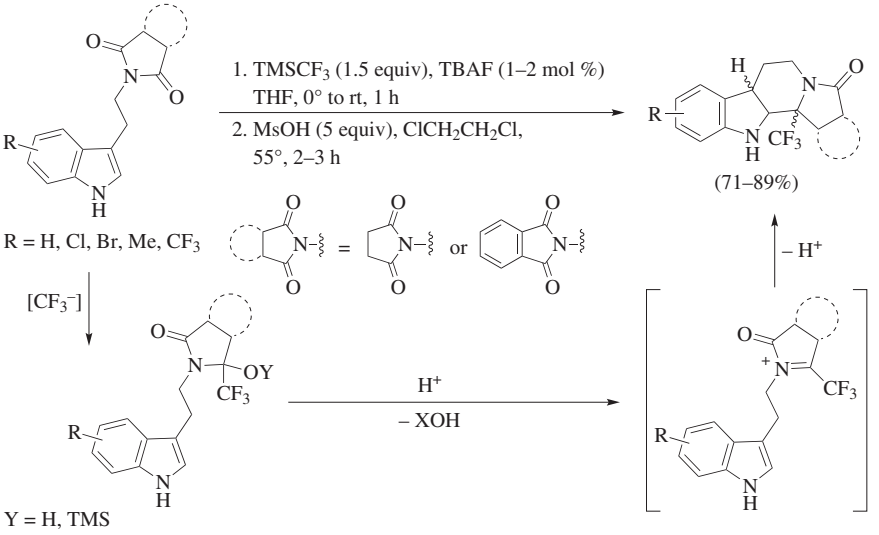
Scheme 293

Imides. N-Protected succinimides, maleimides, phthalimides, and related bicyclic structures undergo trifluoromethylation reactions with $TMSCF_3$ in the presence of substoichiometric amounts of TBAF or CsF to afford trifluoromethylated lactams after hydrolysis (Scheme 294).[289,628] The reaction fails with succinimide,[289] open-chain imides such as *N*-methyl bisacetimide,[289] with barbituric acid,[289] glutarimide,[628] and six-membered homophthalimide[628] due to the presence of an acidic hydrogen leading to the formation of trifluoromethane. Efficient trifluoromethylation of *N*-protected phthalimides proceeds with $TMSCF_3$ and substoichiometric amounts of $(t\text{-Bu})_3P$[140] or KF/TBAB,[457] and also with hemiaminal **8** (Scheme 23) in the presence of *t*-BuOK.[110] Diastereoselective trifluoromethylations of certain unsymmetrically functionalized bi- and tricyclic imides using $TMSCF_3$ and substoichiometric amounts of CsF have been achieved.[628,629]

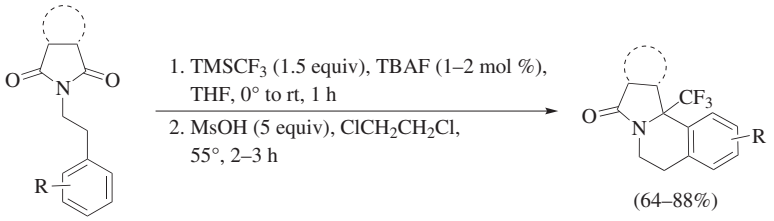


Scheme 294

Tryptamine- and phenylethylamine-derived imides are selectively trifluoromethylated using $TMSCF_3$. Subsequent methanesulfonic acid mediated cyclization of the intermediate hemiaminals affords α-trifluoromethylated amine derivatives via the formation of trifluoromethylated acyliminium ions in one pot. The strategy is applicable to both intra- (Scheme 295 and Scheme 296)[630] and intermolecular (Scheme 297)[630] versions.

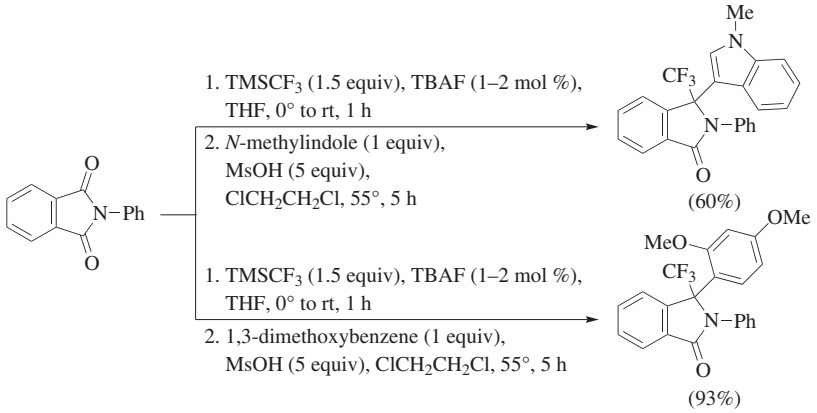


Scheme 295



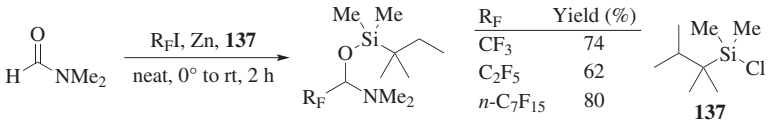
R = H, Cl, Br, I, MeO, Me

Scheme 296



Scheme 297

Amides. Only a limited number of nucleophilic additions of perfluoroalkyl groups to amides are known. For example, simple non-activated amides are unreactive with (perfluoroalkyl)trimethylsilanes with or without a fluoride initiator.[289] However, the use of DMF provides hemiaminal adducts $CF_3CH(OSiR_3)NMe_2$ in moderate yields starting from R_3SiCF_3 (R = Me, Et) in the presence of a fluoride[75] or cyanide[137] catalyst. With an undivided cell and a sacrificial metal (Mg, Al, or Zn) anode and Ni cathode, bromotrifluoromethane is electrochemically reduced in DMF to afford trifluoroacetaldehyde isolated as the diacetate. The best yield (77.5%) is obtained when an Al anode and an excess of $BF_3{\bullet}OEt_2$ are used.[93] Reaction between perfluoroalkyl iodides and zinc in DMF in the presence of chlorosilane **137** gives access to silylated hemiaminals in good yields (Scheme 298).[631]

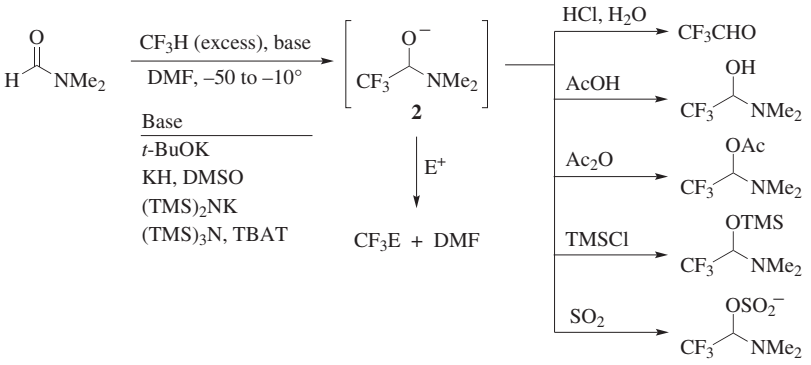


R_F	Yield (%)
CF_3	74
C_2F_5	62
n-C_7F_{15}	80

137

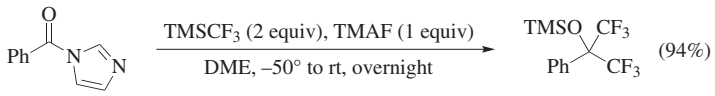
Scheme 298

The addition of fluoroform at low temperature (–50 to –10°) to a mixture of *t*-BuOK, potassium dimsylate, or $(TMS)_2NK$ in DMF, generates the trifluoromethyl anion which is trapped in situ by DMF to form the amino alcoholate **2** (Scheme 12).[72,71] This intermediate is a relatively stable synthetic equivalent of the trifluoromethyl anion at temperatures below –10°,[48] compared to CF_3K, which is unstable even at –78°.[188,199,632–634] Amino alcoholate **2** reacts with strong electrophiles such as aldehydes, ketones, or disulfides to form the trifluoromethylated products and DMF is regenerated. Alternatively, hydrolysis or reaction with other suitable electrophiles affords fluoral and its derivatives (Scheme 299).[48,71,72,75,76] Other dialkyl formamides such as *N*-formylmorpholine can replace DMF in stabilizing the trifluoromethyl anion.

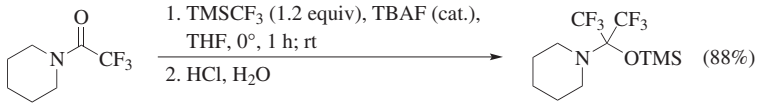


Scheme 299

Reaction between *N*,*N*-dimethylbenzamide and *n*-$C_6F_{13}Li$ under $BF_3{\bullet}OEt_2$ activation affords phenyl perfluoro-*n*-hexyl ketone in 66% yield.[197] Activated amides such as 1-benzoylimidazole (Scheme 300)[592] or 2,2,2-trifluoro-1-(piperidin-1-yl)ethanone (Scheme 301)[289] readily react with $TMSCF_3$ with fluoride activation.



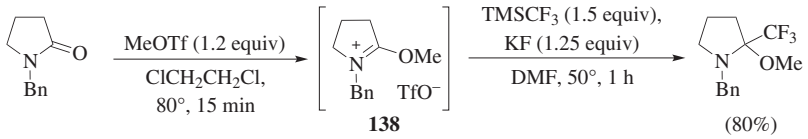
Scheme 300



Scheme 301

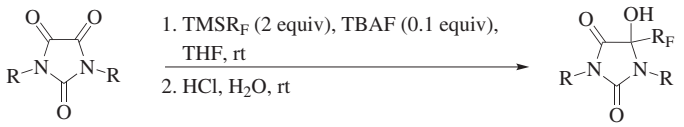
N-Benzyl-2-pyrrolidone reacts with methyl triflate to generate the salt **138**, which undergoes trifluoromethylation with $TMSCF_3$/KF to form 1-benzyl-2-methoxy-2-trifluoromethylpyrrolidine in high yield (Scheme 302).[635] The product is unstable

at room temperature and the methoxy group can be replaced with various carbon nucleophiles including TMSCN to give the corresponding products in good yields.[635]



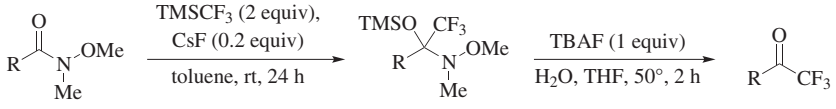
Scheme 302

Lactams undergo nucleophilic addition of n-$C_6F_{13}Li$ followed by elimination of water, such as the transformation of *N*-methylpyrrolidone to 5-perfluoro-*n*-hexyl-1-methyl-2,3-dihydro-1*H*-pyrrole in 55% yield.[197] Imidazolidinetriones react in the presence of TBAF with (perfluoroalkyl)trimethylsilanes to afford 5-perfluoroalkyl-5-hydroxyimidazolidine-2,4-diones (Scheme 303).[636]



Scheme 303

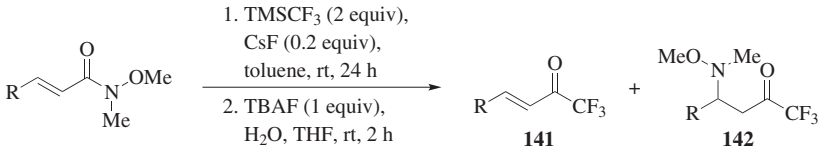
N-Methoxy-*N*-methylamides (Weinreb amides) react readily with $TMSCF_3$ to provide adducts **139**, which in the presence of TBAF preferentially eliminate the *N*-methoxy-*N*-methylamine group over the CF_3 group to provide trifluoromethyl ketones **140** in good yields (Scheme 304).[637] However, 2-substituted aromatic Weinreb amides as well as α-substituted aliphatic amides and those with acidic α-hydrogens are not compatible. α,β-Unsaturated Weinreb amides afford a mixture of products **141** and **142**, the latter formed by 1,4-addition of the eliminated *N*-methoxy-*N*-methylamine to **141** (Scheme 305)[637] The analogous nucleophilic addition of C_2F_5Li to an α,β-unsaturated Weinreb amide has also been reported.[638]



R	**140** Yield (%)	R	**140** Yield (%)
4-pyridyl	90[a]	3,5-$(MeO)_2C_6H_3$	99
3-$O_2NC_6H_4$	78	n-C_7H_{15}	59
3-BrC_6H_4	72	$Ph(CH_2)_2$	76
4-$MeOC_6H_4$	88	1-naphthyl	84

[a] Isolated yield of stable hydrate.

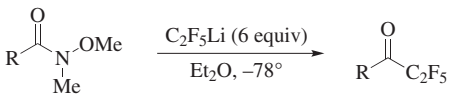
Scheme 304



R	**141** Yield (%)	**141/142**
2-furyl	51	71:29
Ph	22	25:75
4-FC_6H_4	41	41:59
4-$MeOC_6H_4$	47	55:45

Scheme 305

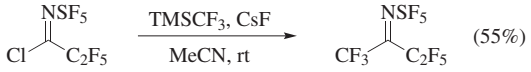
N-Methoxy-*N*-methylamides and *N*-morpholineamides also react with C_2F_5Li generated from C_2F_5I and MeLi. The ketone is usually the major product in these reactions, and these conditions work well for both enolizable and non-enolizable substrates (Scheme 306).[190]



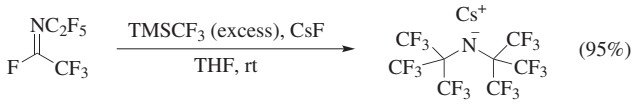
R	Yield (%)
(*E*)-PhCH=CH	74
$Ph(CH_2)_4$	98

Scheme 306

Imidoyl Halides. Imidoyl halides are electrophilic substrates amenable to nucleophilic trifluoromethylations. Examples are shown in Schemes 307[639] and 308.[545] Related tris(dimethylamino)sulfonium triazinates react with an excess of $TMSCF_3$ in acetonitrile at –40° to generate a mixture of trifluoromethyl-containing triazinates.[640]



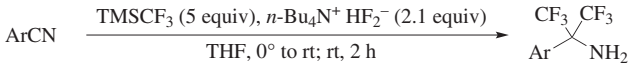
Scheme 307



Scheme 308

Imino Esters. Reaction of cyclic imino esters with pentafluoroethane and *n*-butyllithium in the presence of $BF_3{\bullet}OEt_2$ at –78° affords moderate yields of cyclic pentafluoroethyl imines.[196]

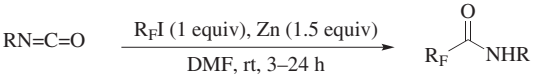
Nitriles. Acetonitrile and trifluoroacetonitrile react with CF_3MgI to afford trifluoroacetone and hexafluoroacetone, respectively, in low yields.[199] However, this transformation was never reproduced. Aromatic nitriles are efficiently trifluoromethylated with an excess of $TMSCF_3$ in the presence of tetrabutylammonium bifluoride to form α,α-bistrifluoromethylated amines (Scheme 309).[641]



Ar	Yield (%)
Ph	58
3-BrC_6H_4	76
4-$MeOC_6H_4$	52
4-$Me_2NC_6H_4$	18

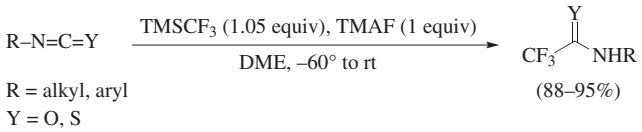
Scheme 309

Cyanates, Thiocyanates, and Their Isoforms. Aryl cyanates afford perfluoroalkylnitriles in the reaction with perfluoroalkyl Grignard reagents.[394] On the other hand, alkyl or aryl thiocyanates react with nucleophilic perfluoroalkylating reagents on sulfur with elimination of cyanide anion to afford perfluoroalkyl sulfides (see section on Perfluoroalkyl Additions to Heteroatom Electrophiles – Sulfur Electrophiles). Isocyanates undergo nucleophilic addition of perfluoroalkylzinc halide reagents; the corresponding amides of perfluoroalkyl carboxylic acids are formed in moderate yields (Scheme 310).[642]



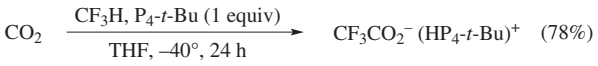
Scheme 310

Isocyanates and isothiocyanates also react with $TMSCF_3$ in the presence of an equimolar amount of a fluoride source to produce the corresponding trifluoroacetamides or trifluorothioacetamides, respectively, in high yields (Scheme 311).[643]



Scheme 311

Other Carboxylic Acid Derivatives. Carbon dioxide reacts with fluoroform in the presence of P_4-*t*-Bu superbase to afford the trifluoroacetate salt of the superbase in 78% yield (Scheme 312).[81]



Scheme 312

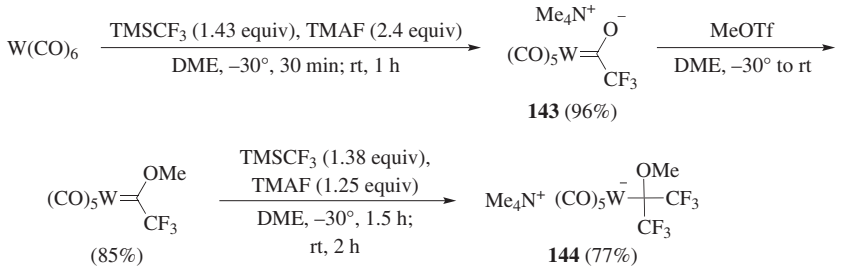
Carbon dioxide also reacts with $TMSR_F$ ($R_F = CF_3$, C_2F_5) in the presence of an equimolar amount of CsF or TMAF in DME to afford perfluoroalkylcarboxylate salts in nearly quantitative yields.[644,645] These reactions do not proceed in the absence of solvent. Only the monoaddition product is formed even when using an excess of $TMSR_F$. Addition of an equimolar amount of anhydrous hydrochloric acid provides trifluoroacetic acid ($R_F = CF_3$) in 90% yield and pentafluoropropionic acid ($R_F = C_2F_5$) in 85% yield,[644] respectively. Perfluoroalkanoic acids are also produced in moderate to good yields by reaction of carbon dioxide with various perfluoroorganometallic reagents (R_FM, M = Li, Cu, Ag, MgX, ZnX, MnI).[130,189,316,646–648]

Reaction of carbonyl sulfide (COS) with $TMSCF_3$ and an equimolar amount of CsF or TMAF affords cesium or tetramethylammonium trifluorothioacetate in 97% yield, which can be either acidified to form a mixture of $CF_3C(S)OH$ and $CF_3C(O)SH$[644] or combined with ethyl iodide to afford $CF_3C(O)SEt$ in 95% yield.[645]

The reaction of carbon disulfide with $TMSR_F$ ($R_F = CF_3$, C_2F_5, n-C_4F_9) in the presence of TMAF or CsF in DME affords perfluorodithioacetates in almost quantitative yields. Subsequent alkylation provides alkyl perfluorodithioacetates in high yields.[645,649]

The outcome of the perfluoroalkylation of carbonates is strongly dependent on the type of metal in the perfluoroalkyl organometallics and on the reaction conditions. The reaction of diethyl carbonate with an equimolar amount of perfluoro-*n*-octyl magnesium bromide at –60° over 20 hours affords ethyl perfluoro-*n*-nonanoate in 94% yield. The more reactive perfluoro-*n*-octyllithium (2.3 equivalents) provides bis(perfluorooctyl) ketone in 55% yield at –78°.[650]

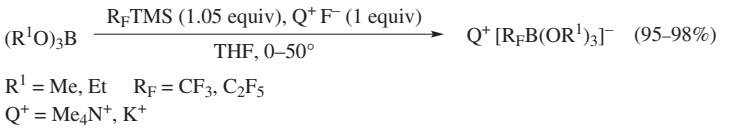
Other. Tetramethylammonium fluoride initiated addition of $TMSCF_3$ to hexacarbonyltungsten affords Fisher carbene complex salt **143** in high yield, which after methylation on oxygen adds another trifluoromethyl group to form the stable bis(trifluoromethyl)-containing tungsten salt **144** (Scheme 313).[651]



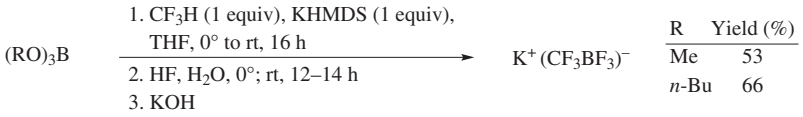
Scheme 313

Perfluoroalkyl Addition to Heteroatom Electrophiles

Boron Electrophiles. Reaction of boron trifluoride with (trifluoromethyl)tributyltin generates tributyltin (trifluoromethyl)trifluoroborate in high yield.[652] Boron halides X_2BNR_2 (X = Cl, Br) can be trifluoromethylated with the $CF_3Br/(Et_2N)_3P$ or CF_3I/TDAE system to provide trifluoromethylborane amine complexes $(CF_3)_3B{\bullet}NHR_2$.[653–655,89] Trimethyl or triethyl borates react with (perfluoroalkyl)trimethylsilanes in the presence of fluoride to afford (perfluoroalkyl)trialkoxyborates in excellent yields (Scheme 314).[656,657] Trimethyl and tri(*n*-butyl) borates react with fluoroform in the presence of KHMDS base to form (trifluoromethyl)trialkoxyborates which are transformed into $K^+(CF_3BF_3)^-$ in good yields (Scheme 315).[77]

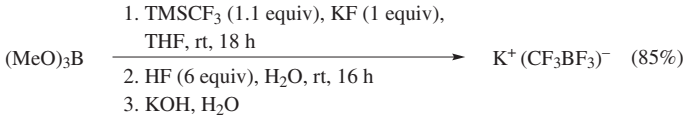


Scheme 314



Scheme 315

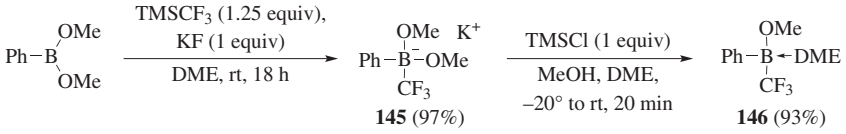
Tribenzyl, tris(2-methoxyethyl), and tris(tetrahydrofuryl)borates are also reactive with $TMSCF_3$ and provide the corresponding potassium (trifluoromethyl)trialkoxyborates in moderate to good yield.[103] However, the more sterically demanding $(i\text{-PrO})_3B$, $(t\text{-BuO})_3B$, and $(PhO)_3B$ are unreactive. Addition of aqueous hydrogen fluoride to intermediate $K^+[CF_3B(OMe)_3]^-$ affords potassium (trifluoromethyl)trifluoroborate $K^+(CF_3BF_3)^-$ (Scheme 316).[658] Analogous long-chain (perfluoroalkyl)trialkoxyborates and (perfluoroalkyl)trifluoroborates are prepared using perfluoroalkyllithium or Grignard reagents.[659–662]



Scheme 316

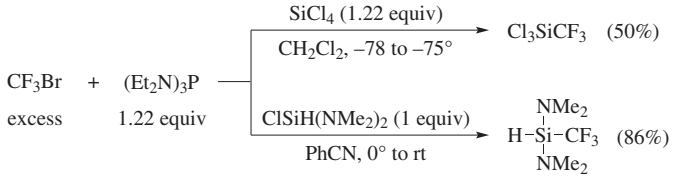
Dimethyl phenylboronate upon trifluoromethylation with $TMSCF_3$ affords potassium borate **145**, a stable solid that upon treatment with TMSCl in DME affords stabilized borane **146** (Scheme 317).[663] Because of the increased Lewis acidity of

boron this compound reacts rapidly with α-diazocarbonyl compounds to afford the products of transfer of the organic group (Ph) from boron. Alkyl-, aryl-, vinyl-, and alkynylboronic esters can be used in this reaction.[663]



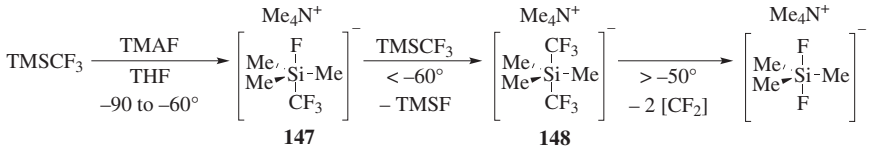
Scheme 317

Silicon Electrophiles. Perfluoroalkyl addition reactions to trialkylchlorosilanes to form (perfluoroalkyl)trialkylsilanes are covered in the section on Perfluoroalkylsilicon reagents. Other chlorosilanes and halogenated dialkylaminosilanes undergo nucleophilic trifluoromethylation using CF_3Br and $(Et_2N)_3P$[90,664,665] (Scheme 318)[664] or CF_3I and TDAE.[89]



Scheme 318

Trifluoromethylsilicates are thought to be the intermediates in the fluoride-initiated trifluoromethylation with $TMSCF_3$. Some of these unstable species have been prepared and characterized spectroscopically. The hypercoordinate silicon species $Me_4N^+[Me_3Si(CF_3)_2]^-$ (**148**) and $Me_4N^+[Me_3Si(CF_3)F]^-$ (**147**) form by the reaction of $TMSCF_3$ with TMAF in THF at –90 to –60° (Scheme 319).[63] With less than 1 equivalent of TMAF salt, compound **148** is obtained, whereas with more than 1 equivalent of TMAF salt compound **147** is generated. Addition of $TMSCF_3$ to a solution of salt **147** produces salt **148**, whereas addition of TMAF to **148** does not give any evidence for the formation of **147**. Salts **147** and **148** cannot be isolated in pure state but are stable in solution at –60° and are characterized spectroscopically.

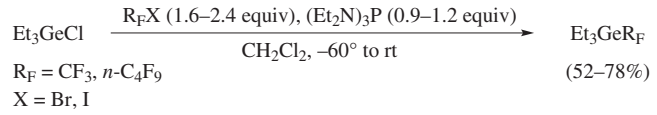


Scheme 319

The reaction of an excess of $TMSCF_3$ with $(Me_2N)_3S^+[Me_3SiF_2]^-$, Q^+F^-, or $Q^+[HF_2]^-$ [$Q^+ = Me_4N^+$, $(Me_2N)_3C^+$, $(Me_2N)_4P^+$] in DME at –55° or THF at –78° generates the hypervalent silicon species $[(CF_3)_2SiMe_3]^-$, which is stable in solution up to –10°. The molecular structure determined by X-ray crystallography shows a trigonal-bipyramidal geometry with apical Si–CF_3 and equatorial C–Me bonds.[64]

Reaction of $TMSCF_3$ with CsF and 15-crown-5 proceeds up to a temperature of 5° with mainly the formation of $[(CF_3)_2SiMe_3]^-$.[145]

Germanium Electrophiles. Germanium tetraiodide reacts with $Cd(CF_3)_2$•DME to produce a mixture of $Ge(CF_3)_4$ and $Ge(CF_3)_3I$. Solvent effects appear to be an important factor.[230] Perfluoroalkylation of chlorotriethylgermane with CF_3Br, CF_3I, or n-C_4F_9Br proceeds in a similar fashion as the reaction with TMSCl (Scheme 320).[666] Reaction with $(CF_3)_3CI$ affords only Et_3GeF.[666]



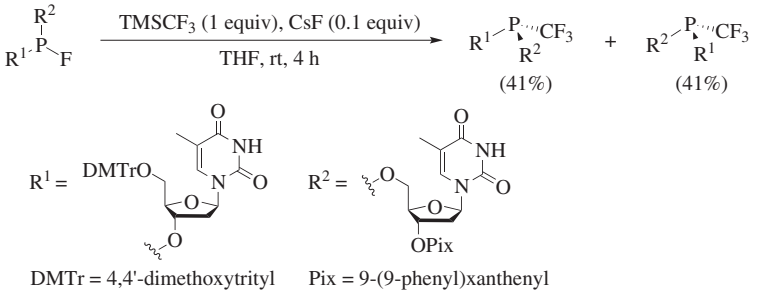
Scheme 320

Tin Electrophiles. Tin tetrabromide reacts with the $Cd(CF_3)_2$•DME complex to produce a mixture of $Sn(CF_3)_4$, $Sn(CF_3)_3Br$, and $Sn(CF_3)Br_3$.[230] (Trifluoromethyl)trimethyltin is prepared by nucleophilic trifluoromethylation of Me_3SnCl and different nucleophilic reagents; however, yields are not reported.[154,169,231,667] Perfluoroalkylation of trimethyltin trifluoroacetates with cadmium reagents results in the formation of (perfluoroalkyl)trimethyltin in good yields.[153] Treatment of bis(tributyltin) oxide with $TMSCF_3$ and substoichiometric amounts of TBAF provides (trifluoromethyl)tributyltin (Bu_3SnCF_3) in 95% yield.[150]

Lead Electrophiles. Good yields of (perfluoroalkyl)trimethyllead are obtained by reaction of trimethyllead acetate with perfluoroalkylcadmium reagents.[153] Although this is an example of a seemingly nucleophilic process the reaction may proceed via a radical pathway.

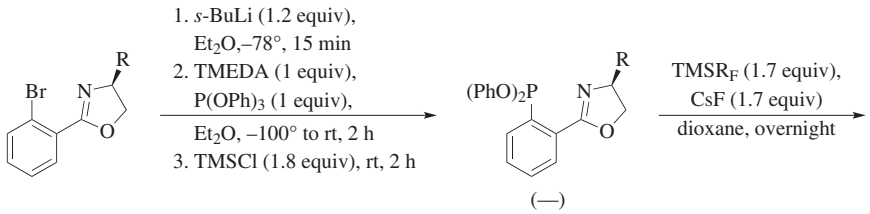
Nitrogen Electrophiles. Perfluoronitrosoalkanes can be prepared in high yields from nitrosyl chloride (NOCl) and $TMSR_F$ (R_F = CF_3, C_2F_5) in the presence of CsF[644] or from NOF or NOCl and non-metallic perfluoroalkyl salts.[68] Nitrosotrifluoromethane (CF_3NO) can also act as a trifluoromethylating reagent. Nitrosobenzene reacts with $TMSCF_3$ in the presence of TBAF to afford the *O*-silylated hydroxylamine $PhN(CF_3)OTMS$ quantitatively. However, the adduct decomposes to unidentified materials.[13] Reaction between non-metallic perfluoroalkyl salts and 4-nitrophenyldiazonium hexafluorophosphate provides azo compounds ($ArN{=}NR_F$) in 89% yields.[68]

Phosphorus Electrophiles. *N,N,N′,N′*-Tetraethyl-1-(trifluoromethyl)phosphinediamine [$(Et_2N)_2PCF_3$] is easily available by the three-component reaction of $(Et_2N)_3P/PCl_3/CF_3Br$ in 70% yield. The reaction proceeds through $(Et_2N)_2PCl$ as an intermediate.[668,669] Triiodophosphine (PI_3) reacts with the $(CF_3)_2Cd$•DME complex and in 30 minutes a mixture of $(CF_3)_3P$ and $(CF_3)_2PI$ (2:3) is formed.[230] Chlorophosphines R_2PCl and $RPCl_2$ (R = Me, *i*-Pr, NEt_2) are trifluoromethylated with $TMSCF_3$ to yield R_2PCF_3 and $RP(CF_3)_2$,[669] whereas the use of pentafluoroethyllithium at low temperature provides pentafluoroethyl-containing phosphines in good yields.[670,671] The dinucleoside trifluoromethylphosphine derived from deoxythymidine can be prepared from the corresponding fluorophosphine (Scheme 321).[672]



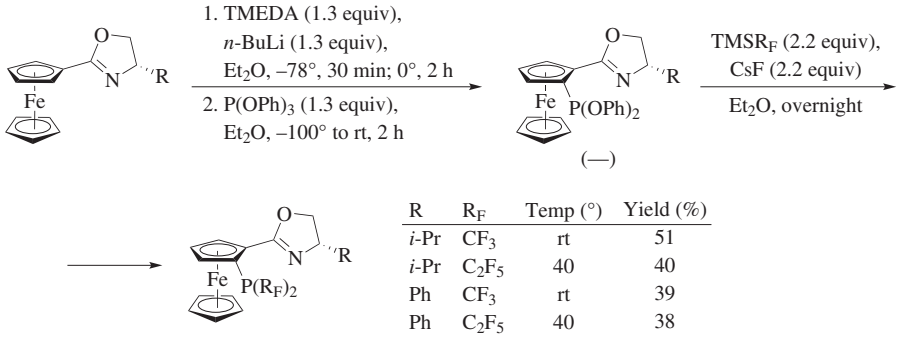
Scheme 321

The tertiary phosphine $(CF_3)_3P$ is prepared in high yield from $P(OPh)_3$ and $TMSCF_3$ or $CF_3Br/(Et_2N)_3P$.[673–675] Further reaction of $(CF_3)_3P$ with TMAF and an excess of $TMSCF_3$ in DME at –60° yields $Me_4N^+[P(CF_3)_4]^-$.[64] Bis(perfluoroalkyl)phosphines are prepared from diphenyl phosphonites (Scheme 322 and Scheme 323).[676] using perfluoroalkylsilanes and are used as ligands for transition metal complexes.[676–678] A similar synthetic protocol is applied in the synthesis of bis(trifluoromethyl)phosphino naphthalenes and acenaphthenes.[675]



R	R_F	Temp (°)	Yield (%)
i-Pr	CF_3	rt	65
i-Pr	C_2F_5	40	45
Ph	CF_3	rt	61
Ph	C_2F_5	40	41

Scheme 322



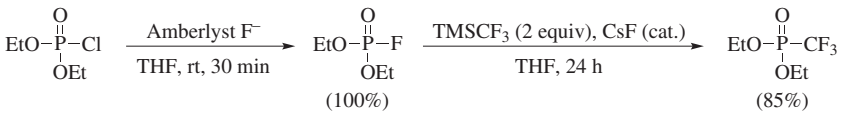
(—)

R	R_F	Temp (°)	Yield (%)
i-Pr	CF_3	rt	51
i-Pr	C_2F_5	40	40
Ph	CF_3	rt	39
Ph	C_2F_5	40	38

Scheme 323

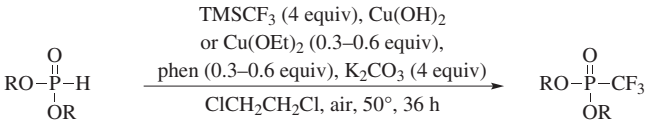
Cyanophenylphosphines, Ph_2PCN or $PhP(CN)_2$, undergo trifluoromethylation with $TMSCF_3$ in the presence of substoichiometric amounts of fluoride or cyanide ions to yield Ph_2PCF_3 (70%) or $PhP(CF_3)_2$ (75%), respectively.[137]

Four-coordinate phosphorus fluorides such as dibutyl phosphorofluoridate undergo trifluoromethylation with $TMSCF_3$ in the presence of substoichiometric amounts of KF to afford dibutyl (trifluoromethyl)phosphonate in nearly quantitative yield.[679] Similarly, diethyl phosphorochloridate is transformed into diethyl (trifluoromethyl)phosphonate in two steps (Scheme 324).[680]



Scheme 324

Copper-catalyzed aerobic oxidative trifluoromethylation of dialkyl phosphites using $TMSCF_3$ has been described (Scheme 325).[681] The mechanism is unknown but most probably involves the formation of a ligated CF_3Cu species.

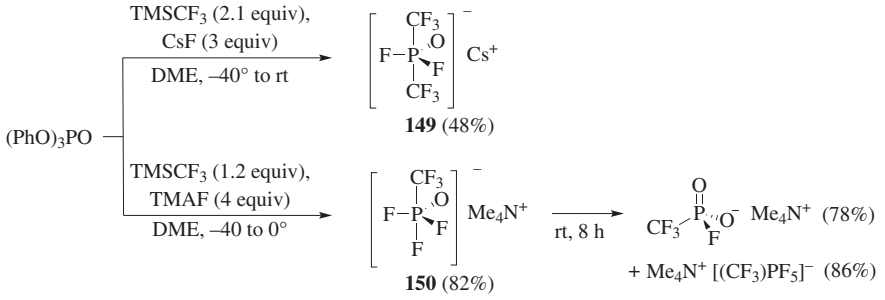


R = Et, *n*-Pr, *n*-Bu, *i*-Bu, $Cl(CH_2)_4$, *n*-C_6H_{13}, *c*-C_6H_{11}

Scheme 325

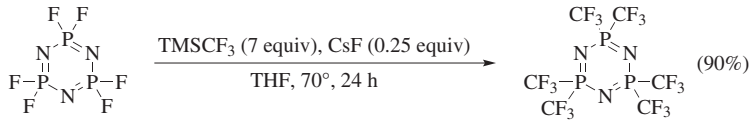
Trialkyl phosphates react with a two-fold excess of perfluoroalkyl iodides in the presence of a Zn/Cu couple at 60–80° to produce bis(perfluoroalkyl)phosphinates. With a three-fold excess of perfluoroalkyl iodides at 90–100° perfluoroalkylphosphine oxides are produced.[682] Reaction of triphenyl phosphate with $TMSCF_3$

and a fluoride ion source (CsF or TMAF) gives rise to novel salts **149** and **150**. Compound **149** is stable at room temperature, whereas salt **150** dismutates above 0° (Scheme 326).[683]



Scheme 326

Several phosphazenes can also be trifluoromethylated with $TMSCF_3$;[684,685] one example is shown in Scheme 327.[684]



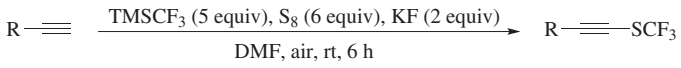
Scheme 327

Arsenic Electrophiles. The formation of Ph_2AsCF_3 from Ph_2AsCl, CF_3Br, and $P(NEt_2)_3$ has been described.[667]

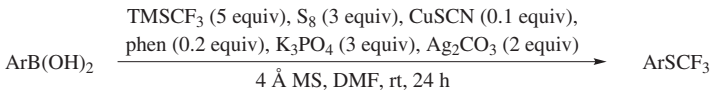
Antimony Electrophiles. Antimony halides SbX_3 (X = Cl, Br, I) react with the $Cd(CF_3)_2$•2MeCN complex at low temperature in acetonitrile to provide high yields of $(CF_3)_3Sb$.[686] The formation of Me_2SbCF_3 from Me_2SbCl, CF_3Br, and $P(NEt_2)_3$ has also been reported.[667]

Bismuth Electrophiles. Bismuth trichloride reacts with the CF_3ZnBr•2MeCN complex in dichloromethane to generate tris(trifluoromethyl)bismuth in 70% yield,[687] which can be converted into tetrakis(trifluoromethyl)bismuthate $Me_4N^+[(CF_3)_4Bi]^-$ in nearly quantitative yield by the action of $TMSCF_3$ in the presence of TMAF at –70 to –50°. At higher temperatures the formation of $Me_4N^+[(CF_3)_3BiF]^-$ is observed. Hypercoordinate anionic bismuth species are solids stable at low temperature in dry nitrogen and act as trifluoromethylating reagents.[169] Reactions of $ArBiBr_2$ or Ar_2BiCl with $Cd(CF_3)_2$•2MeCN complex at room temperature provide a mixtures of $(CF_3)_3Bi$, $ArBi(CF_3)_2$, and Ar_2BiCF_3.[168]

Sulfur Electrophiles. Trifluoromethanesulfonic acid is formed in 18% conversion in the reaction of fluoroform with elemental sulfur in the presence of KHDMS base in THF at –78°. The formed $[CF_3S_n^-]$ ($n = 1, 2 \ldots$) species are oxidized with 30% aqueous solution of hydrogen peroxide in concentrated sulfuric acid to form CF_3SO_3H.[77] Reaction of elemental sulfur with $TMSCF_3$ in the presence of a fluoride source [TMAF or CsF(benzo-15-crown-5)$_2$] produces trifluoromethanethiolates as oxygen-sensitive solids in excellent yields.[688] Reaction of $TMSCF_3$ with elemental sulfur and KF under air provides CF_3SK, which efficiently transfers the trifluoromethylthio group to terminal alkynes to afford alkynyl trifluoromethyl sulfides (Scheme 328).[689] Reaction of elemental sulfur with $TMSCF_3$ in the presence of silver salts and a catalytic amount of copper salts effects trifluoromethylthiolation of aryl boronic acids (Scheme 329).[690] The reaction does not involve CF_3Cu species.[690] $TMSCF_3$ can be substituted by CF_3CO_2Na but the reaction requires heating to 130°.[691]

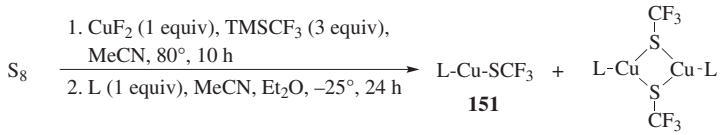


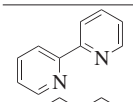
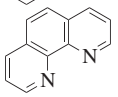
Scheme 328



Scheme 329

Stable phosphine- and nitrogen-ligated copper(I)–trifluoromethylthiolate complexes **151** and **152** have been prepared and investigated for nucleophilic trifluoromethylthiolation of aryl halides and allylic bromides (Scheme 330).[692,693]

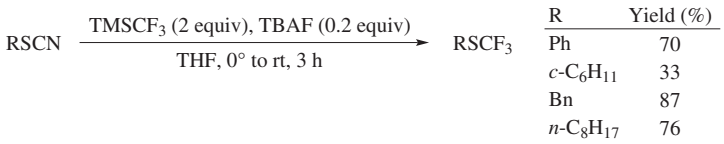


L	**151** Yield (%)	**152** Yield (%)
	44	0
	0	49

Scheme 330

Aryl trifluoromethyl sulfides are obtained by trifluoromethylation of the corresponding aryl sulfenyl chlorides using $TMSCF_3$ in the presence of TASF in moderate

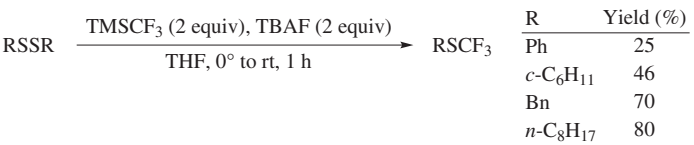
to good yields.[694,695] Replacing TASF with TBAF•3H_2O in this reaction provides much lower yields due to competing hydrolysis of the starting material. A more efficient procedure starts from thiocyanates. A small amount of TBAF is required in this case and good yields of the trifluoromethyl sulfides are obtained[696,697] (Scheme 331).[696] Using this method, trifluoromethylthio sugar derivatives[698] and an SCF_3-containing β-cyclodextrin[699] can be prepared from their thiocyanate precursors.



R	Yield (%)
Ph	70
c-C_6H_{11}	33
Bn	87
n-C_8H_{17}	76

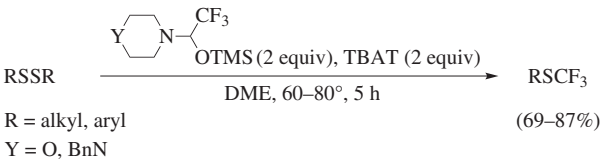
Scheme 331

Alkyl and aryl trifluoromethyl sulfides are formed by trifluoromethylation of disulfides using a variety of methods including (1) $TMSCF_3$/TBAF (Scheme 332),[695] (2) fluoroform and *t*-BuOK[73,76,700] or P_4-*t*-Bu organo-superbase,[82] (3) hemiaminals **9** or **10** (Scheme 23) in combination with TBAT (Scheme 333),[111] (4) potassium trifluoroacetate[701] with *t*-BuOK, (5) salt of hexafluoroacetone (**11**) with *t*-BuOK,[107] or (6) phenyl trifluoromethyl sulfone with *t*-BuOK.[179] A very efficient method for the conversion of disulfides into trifluoromethyl sulfides uses the combination of CF_3I and TDAE. In the presence of an excess of CF_3I both sulfur atoms of the starting disulfide can be utilized to form the trifluoromethyl sulfides (Scheme 334).[386]

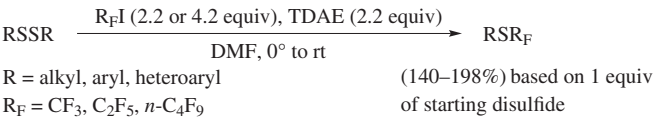


R	Yield (%)
Ph	25
c-C_6H_{11}	46
Bn	70
n-C_8H_{17}	80

Scheme 332

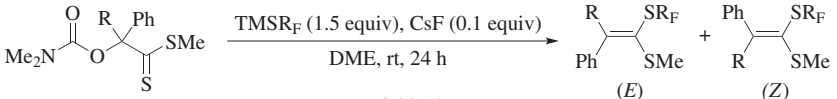


Scheme 333



Scheme 334

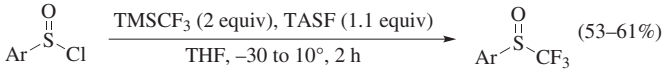
α-Substituted dithioesters such as α-carbamoyloxy dithioesters undergo thiophilic attack by $TMSR_F$ in the presence of a catalytic amount of CsF to afford ketene dithioacetals in high yields (Scheme 335).[702]



R	R_F	Yield (%)	(*E*)/(*Z*)
Me	CF_3	79	82:18
Me	C_2F_5	83	86:14
Et	CF_3	91	87:13
Et	C_2F_5	90	88:12

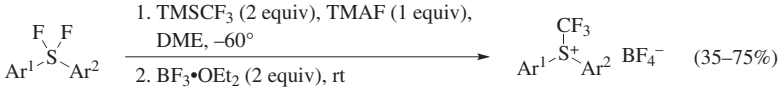
Scheme 335

A number of sulfur(IV) compounds have been perfluoroalkylated. Reaction of $TMSCF_3$ or $TMSC_2F_5$ with sulfur dioxide and CsF in equimolar ratios in DME leads to the formation of R_FSO_2Cs in 95% yield.[644] Sulfur dioxide also reacts with perfluoroalkyl organometallic reagents and the resulting perfluoroalkanesulfinates are usually oxidized to derivatives of perfluoroalkanesulfonic acids. Thus, reaction with pentafluoroethyllithium followed by oxidation with hydrogen peroxide generates $C_2F_5SO_3H$ in 80% yield,[703] or reaction with a perfluorooctylcopper reagent followed by oxidation with chlorine provides *n*-$C_8F_{17}SO_2Cl$ in 52–75% yield.[646] Thionyl chloride (or thionyl fluoride) and $CF_3S(O)F$ react with $TMSCF_3$ in acetonitrile in the presence of substoichiometric amounts of TBAF or KF to provide $CF_3S(O)F$ and $(CF_3)_2S{=}O$, respectively, in yields ranging from 75–95%.[397] Aryl sulfinyl chlorides react with 2 equivalents of $TMSCF_3$ and 1.1 equivalents of TASF to furnish aryl trifluoromethyl sulfoxides in moderate yields (Scheme 336).[694]



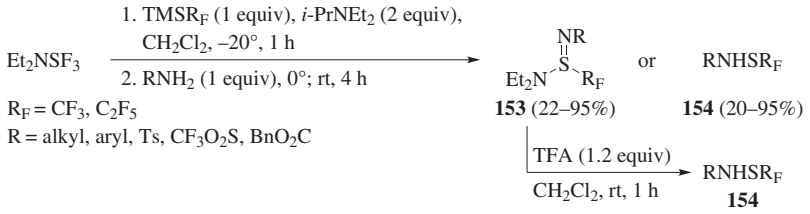
Scheme 336

By analogy to carbonyl compounds, DMSO undergoes trifluoromethylation with $TMSCF_3$ in the presence of TBAF in THF to afford $Me_2(CF_3)SOTMS$.[397] Dimethyl sulfite affords $(CF_3)_2S{=}O$ in 77% yield.[470] Diaryltrifluoromethylsulfonium salts are prepared from diaryl difluorosulfuranes in moderate to good yields by the action of an excess of $TMSCF_3$ and one equivalent of TMAF (Scheme 337).[704] The products are useful electrophilic trifluoromethylating reagents.[704,705]



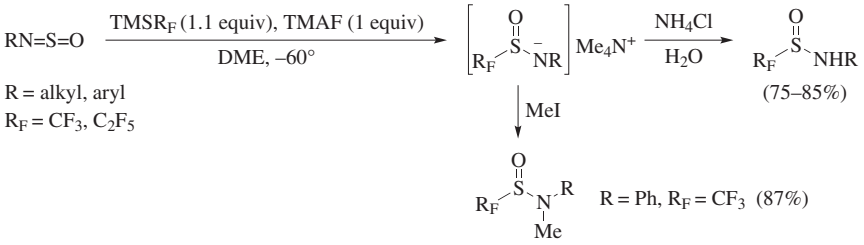
Scheme 337

Sulfimides such as $CF_3N{=}SF_2$ react with $TMSCF_3$ in the presence of CsF in acetonitrile to afford $CF_3N{=}S(CF_3)_2$ in 68% yield.[639] The action of DAST on $TMSCF_3$ provides unisolable intermediates that can then react with various primary amines to afford perfluoroalkanesulfinamidines **153** or perfluoroalkanesulfenamides **154** (Scheme 338).[706]



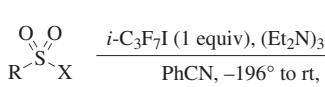
Scheme 338

Similarly, *N*-sulfinylamines form perfluoroalkanesulfinamides in high yields[707–709] (Scheme 339).[707]



Scheme 339

Compounds containing a sulfur(VI) electrophilic center are also reactive in nucleophilic perfluoroalkyl additions. Sulfur trioxide reacts with $TMSCF_3$ to generate CF_3SO_3TMS in 83% yield.[710] Sulfuryl chloride and fluoride in the presence of $TMSCF_3$ and substoichiometric amounts of KF afford CF_3SO_2F.[397] Perfluoroisopropyl addition to methanesulfonyl chloride or trifluoromethanesulfonyl fluoride using $i\text{-}C_3F_7I$ and $(Et_2N)_3P$ provides fluorinated sulfones (Scheme 340).[596]

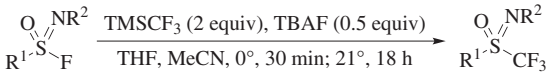


R	X	Yield (%)
Me	Cl	66
CF_3	F	90

Scheme 340

Arylsulfonyl fluorides react with $TMSCF_3$ or Me_3SnCF_3 in the presence of TASF to afford aryl trifluoromethyl sulfones in very good yields.[161,694,711] Methyl sulfonates RSO_3Me (R = Me, Ph) provide trifluoromethyl sulfones RSO_2CF_3 in 85–88% yield.[470]

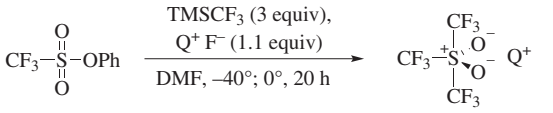
N-Protected trifluoromethyl-subsituted sulfoximines are prepared by the treatment of sulfonimidoyl fluorides with $TMSCF_3$ in the presence of TBAF (Scheme 341).[712]



R^1	R^2	Yield (%)
Ph	Ts	72
Ph	Bz	79
4-ClC_6H_4	Bz	74
4-MeC_6H_4	Boc	75
4-*t*-BuC_6H_4	Ts	70

Scheme 341

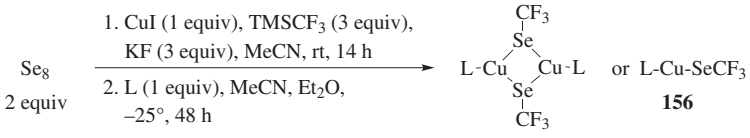
The treatment of phenyl triflate with a three-fold excess of $TMSCF_3$ and equimolar amounts of fluoride salts gives rise to hypercoordinate sulfuranide dioxide salts, which themselves show trifluoromethylation reactivity toward various electrophiles (Scheme 342).[155]

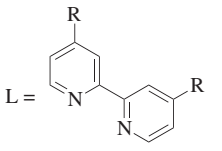


$Q^+ F^-$	Yield (%)
KF(18-crown-6)	50
TMAF	79
TASF	65

Scheme 342

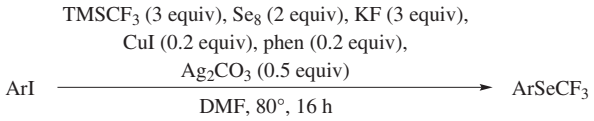
Selenium Electrophiles. Tetramethylammonium trifluoromethylselenate is conveniently prepared from $TMSCF_3$ and TMAF and red selenium in 70% yield. The product is a slightly light-sensitive solid. No reaction is observed using metallic selenium.[713,714] Air-stable copper(I) trifluoromethylselenolate dimeric complex **155** or monomeric complex **156** (in the case of a bulky ligand) are formed in moderate yield by the reaction of elemental selenium and $TMSCF_3$ in the presence of CuI and KF (Scheme 343).[715] These complexes are useful for trifluoromethylselenolation of aryl and alkyl halides.[715] Cu(I) and Ag(I) salts catalyze trifluoromethylselenolation of aryl iodides (Scheme 344)[716] and alkyl bromides (Scheme 345)[716] by employing $TMSCF_3$, elemental selenium, and KF. The reaction is believed to start with the formation of $AgSeCF_3$, which transmetallates to copper to form the catalytically active (phen)$Cu(SeCF_3)_2$ complex. Radical species are probably not involved.[716]





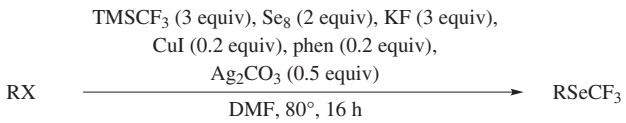
R	**155** Yield (%)	**156** Yield (%)
H	54	0
t-Bu	0	46

Scheme 343



Ar	Yield (%)	Ar	Yield (%)
2-thienyl	68	4-*t*-BuC_6H_4	83
2-pyridyl	53	1-naphthyl	75
4-$MeOC_6H_4$	64	4-PhC_6H_4	70
4-NCC_6H_4	91		

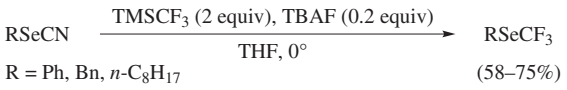
Scheme 344



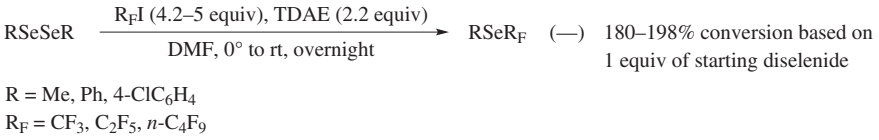
R	X	Yield (%)
4-$MeC_6H_4S(CH_2)_3$	Br	94
$PhO(CH_2)_4$	Br	91
$AcO(CH_2)_5$	Br	80
$NC(CH_2)_6$	Br	90
4-$MeC_6H_4CH_2$	Br	64
$PhCH_2CHCH_3$	I	89
n-$C_{12}H_{25}$	Br	85

Scheme 345

Trifluoromethyl selenides can be prepared either from selenocyanates by reaction with $TMSCF_3$ and TBAF (Scheme 346)[717,696] or from diselenides in a number of ways: (1) using fluoroform in the presence of base,[73,75] (2) using $TMSCF_3$ and an excess of TBAF,[717,695] (3) using piperazine-derived hemiaminals and TBAT initiators,[111] and (4) using an excess of perfluoroalkyl iodides and TDAE. The last is the method of choice, since it utilizes both selenium atoms of the starting diselenide[546,386] (Scheme 347).[386]



Scheme 346



Scheme 347

Dimethylselenite ($(MeO)_2Se{=}O$) reacts with $TMSCF_3$ and a substoichiometric amount of CsF at 50° to afford $(CF_3)_2Se{=}O$ in 84% yield.[470]

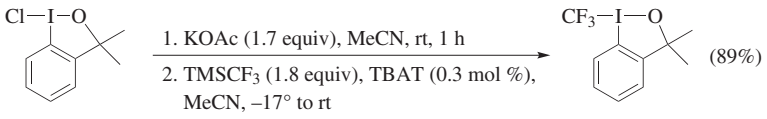
Tellurium Electrophiles. Elemental tellurium reacts with iodoperfluorohexane and copper at 180° to afford bis(perfluorohexyl)tellurium in good yield.[718] Elemental Te also reacts with $TMSCF_3$ or $TMSC_2F_5$ in the presence of TMAF to give perfluoroalkyltellurates(0) as moderately light-sensitive solids, which can be handled open to air for a short period of time.[719,720] bis(Trifluoromethyl)tellurium is susceptible to attack by $TMSCF_3$ and TMAF (THF, –78°) to form the reactive solid $Me_4N^+[Te(CF_3)_3]^-$ in quantitative yield.[721] This tellurate(II) decomposes in solution above –30° to yield fluoroform and $Te(CF_3)_2$, but in pure state is stable up to 110° tetrakis(trifluoromethyl)tellurium is prepared by the trifluoromethylation of $Te(CF_3)_2F_2$ with $TMSCF_3$[185] or from $Te(CF_3)_2Cl_2$ and the $Cd(CF_3)_2$•DME complex.[722] Tellurium(II) dithiocarbamates can be perfluoroalkylated with (perfluoroalkyl)trimethylsilanes to provide air- and light-stable Te(II) salts in quantitative yields.[719]

Chlorine Electrophiles. Reaction of chlorine with $Zn(CF_3)_2$•2Py provides CF_3Cl.[723] The non-metallic salt n-$C_3F_7(CF_3)_2C^-\ {}^+S(NMe_2)_3$, which is stable up to 60°, reacts with chlorine in benzonitrile at 0° to afford n-$C_3F_7(CF_3)_2CCl$ in 77% yield.[68]

Bromine Electrophiles. 1-Bromoheptafluoropropane is prepared in 44% yield by the reaction of bromine with perfluoropropylzinc iodide in dioxane at reflux.[213] Similar to chlorine, reaction of bromine with n-$C_3F_7(CF_3)_2C^-\ {}^+S(NMe_2)_3$ provides n-$C_3F_7(CF_3)_2CBr$ in almost quantitative yield.[68]

Iodine Electrophiles. 1-Iodoheptafluoropropane is formed in 77% yield from iodine and perfluoropropylzinc iodide in refluxing dioxane.[213] Reaction of heptafluoroisopropylsilver with iodine affords 2-iodoheptafluoropropane in 42% yield.[724] The hypervalent iodine salt $Me_4N^+[I(CF_3)_2]^-$ is a highly reactive solid which decomposes between 0° and room temperature. It can be prepared in quantitative yield from CF_3I and $TMSCF_3$ in the presence of TMAF at low temperature.[721]

A family of hypercoordinate iodine(III) compounds are synthesized by ligand-exchange reaction from methoxy or acetoxy compounds or in an improved procedure starting from a chloro compound (see example Scheme 348).[725] The resulting trifluoromethyl or pentafluoroethyl[726] iodine species are mostly stable solids with T-shaped geometry and are capable of direct electrophilic transfer of the trifluoromethyl moiety onto organic nucleophiles (see section on Comparison with Other Methods – Electrophilic Perfluoroalkyl Additions).[725,727–729]



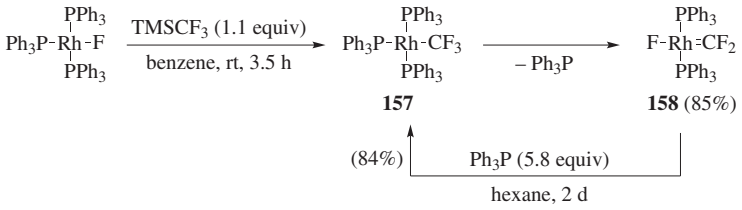
Scheme 348

Xenon Electrophiles. Reaction of $Cd(CF_3)_2$ with C_6F_5XeF in dichloromethane produces low yields of $C_6F_5XeCF_3$ apart from C_6F_5H, fluoroform, and $CFCl_3$.[730]

Transition-Metal Electrophiles. A number of transition-metal complexes with halogen or alkoxy ligands can be trifluoromethylated using $TMSCF_3$. These reactions can be significantly more complex than simple nucleophilic processes.

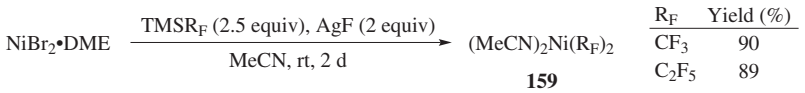
Titanium Complexes. Cp_2TiF_2 reacts with an excess of $TMSCF_3$ in the presence of CsF to afford the thermally sensitive $Cp_2Ti(CF_3)F$ in 60% yield.[731]

Rhodium Complexes. Rhodium(I) perfluoroalkyl complexes $[Rh(R_F)(COD)(PR_3)]$ are prepared by combining the corresponding fluoro complexes with (perfluoroalkyl)trimethylsilanes.[732,733] Complex $[Rh(\mu\text{-}OH)(COD)]_2$ reacts with isocyanate and $TMSCF_3$ to provide $(CF_3)Rh(CNR)_3$[734] or with $TMSR_F$ ($R_F = CF_3$, n-C_3F_7) and PMe_2Ph or $PMePh_2$ to provide $[(R_F)Rh(PR_3)_3]$.[735] These reactions take place without the need of a fluoride initiator. Treatment of $(Ph_3P)_3RhF$ with $TMSCF_3$ in benzene results in red-orange crystals of difluorocarbene–fluoride complex **158**, which probably stems from complex **157** by an α-fluoride elimination upon loss of one phosphine ligand (Scheme 349).[736] In fact, complex **157** can be prepared in high yield from complex **158** by addition of excess triphenylphosphine. Both complexes are fully characterized, including by NMR and X-ray crystallography.[736]



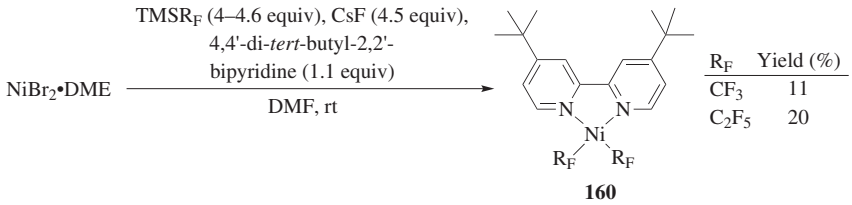
Scheme 349

Nickel Complexes. Nickel bromide reacts with $TMSR_F$ ($R_F = CF_3$, C_2F_5) to form various square-planar complexes. With AgF in acetonitrile, complexes **159** are formed (Scheme 350),[737] which readily exchange MeCN ligands for nitrogen bidentate or tridentate ligands. With CsF and a bipyridine ligand, complexes **160** are prepared (Scheme 351).[738]



R_F	Yield (%)
CF_3	90
C_2F_5	89

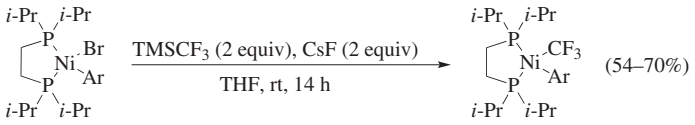
Scheme 350



160

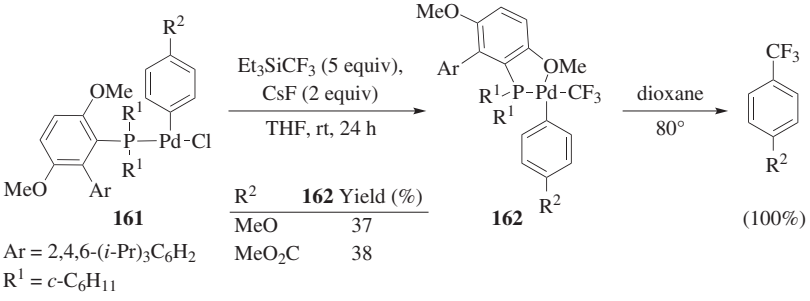
Scheme 351

A variety of Ni(aryl)(CF_3) complexes supported by a chelating bisphosphine ligand have been prepared (Scheme 352).[739] These complexes are thermally stable and do not produce trifluoromethyl aromatic compounds under thermal conditions. Trifluoromethyl and pentafluoroethyl pincer nitrogen tridentate nickel complexes are synthesized by perfluoroalkylation of the corresponding nickel chloride complexes using $TMSR_F$ ($R_F = CF_3$, C_2F_5).[740,741]



Scheme 352

Palladium Complexes. A series of palladium complexes $(L)_2Pd(Ar)(CF_3)$ (L_2 = dppe, dppp, tmeda, Xantphos, (*t*-Bu)$_2$-bipy, L = Ph_3P, 4-methylpyridine) are synthesized from the corresponding iodo or fluoro complexes using excess $TMSCF_3$ and CsF.[742−746] Some of those complexes upon oxidation to Pd(IV) undergo thermolysis to $ArCF_3$. Stable Pd(II) complexes **162** with square-planar geometry at palladium are prepared in moderate yields by the reaction of the chloro complexes **161** with Et_3SiCF_3 and CsF. Complexes **162** undergo quantitative thermolysis in dioxane at 80° with a half life of about 20 minutes to form trifluoromethylated aromatic compounds (Scheme 353).[747] These complexes are presumed to function as true catalytic species in palladium-catalyzed trifluoromethylations of aryl and heteroaryl chlorides.[747]



161

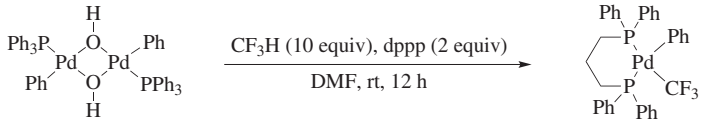
Ar = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$

R^1 = *c*-C$_6$H$_{11}$

162

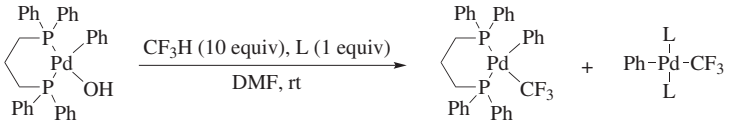
Scheme 353

Dinuclear palladium complex **163** in the presence of bidentate phosphine ligand dppp (1,3-bis(diphenylphosphino)propane) is capable of activating fluoroform at room temperature with the formation of trifluoromethyl Pd(II) complex **164** (Scheme 354).[748] The same complex is formed in the reaction of mononuclear complex **165** with phosphine ligands such as *n*-Bu_3P or dppp and fluoroform (Scheme 355).[748] Combined experimental and computational studies have identified a new mechanism of this fluoroform activation based on nucleophilic attack of the phosphine ligand on palladium and hydrogen bonding of the OH ligand with fluoroform.



163 dppp = 1,3-bis(diphenylphosphino)propane **164** (81%)

Scheme 354



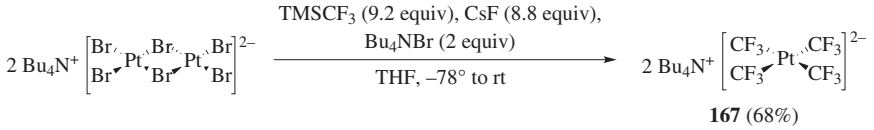
165 **164** **166**

L	Time (h)	**164** Yield (%)	**166** Yield (%)
n-Bu_3P	0.5	83	16
dppp	24	76	—

Scheme 355

Palladates(II) $Me_4N^+[Pd(CF_3)_3PPh_3)]^-$ and $Me_4N^+[(CF_3)_4Pd]^-$ are prepared from $[Cl_2Pd\ (PPh_3)_2]$, $TMSCF_3$, and TMAF.[749]

Platinum Complexes. Platinates(II) $Me_4N^+[(CF_3)_3Pt(PPh_3)]^-$ and $Me_4N^+[(CF_3)_4Pt]^-$ are prepared from $[Cl_2Pt(PPh_3)_2]$, $TMSCF_3$, and TMAF.[749] Related complex **167** is prepared from $[(Br_2Pt)_2(\mu\text{-}Br)_2]^{2-}$ salt (Scheme 356).[750]



167 (68%)

Scheme 356

Copper Complexes. Alkoxycopper(I) complexes $ROCu(PPh_3)_3$ (R = Ph, $CH(CF_3)_2$) react with $TMSCF_3$ at 50° to form $CF_3Cu(PPh_3)_3$.[751] Trifluoromethylcopper(I) complexes **32** are prepared from *tert*-butoxy complexes **31** (Scheme 54).[277,278] In the case of complex **33**, an equilibrium with cuprate salt **34** is observed (Scheme 55).[278] For the preparation of R_FCu complexes please refer to the Perfluorocopper Reagents section.

Silver Complexes. The reaction of $TMSCF_3$ with silver fluoride leads to CF_3Ag.[154,282,379] AgC_2F_5•pyridine is available in high yield by the reaction of $TMSC_2F_5$ with silver fluoride in pyridine.[752]

Gold Complexes. Gold(I) chloride reacts with $TMSCF_3$ in the presence of TMAF or CsF to form $Ag(CF_3)_2^-$ salts with linear geometry.[753,754] Gold(III) chloride reacts with $TMSCF_3$ in the presence of CsF and Ph_4PBr to afford a mixture of $[Ph_4P][(CF_3)_2Au]$ and $[Ph_4P][(CF_3)_4Au]$, the latter complex having a square-planar geometry.[753] Alkoxygold(I) complexes $[Au(OR^1)(PR^2{}_3)]$ (R^1 = Ph, $CH(CF_3)_2$; R^2 = Ph, *c*-C_6H_{11}) react with $TMSCF_3$ to generate trifluoromethylgold(I) complexes $[(CF_3)Au(PR^2{}_3)]$.[751] Gold(III) complexes $[Me_2Au(CF_3)L]$ (L = PMe_3, PEt_3, $PMePh_2$, PMe_2Ph) are prepared by trifluoromethylation of the corresponding phenoxy complexes with $TMSCF_3$.[751]

Zinc and Cadmium Complexes. Transmetallation between Me_2M (M = Cd, Zn) and $MeTeCF_3$ or $(CF_3)_3Te$ in DME has been observed. Depending on the reagent used and the stochiometry, $MeMCF_3$•DME or $M(CF_3)_2$•DME complexes are prepared quantitatively.[222]

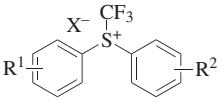
COMPARISON WITH OTHER METHODS

Synthetic methods leading to trifluoromethyl- or perfluoroalkyl-containing molecules can be broadly divided into three types: (1) reactions involving direct introduction of perfluoroalkyl groups (nucleophilic, eletrophilic, radical perfluoroalkyl additions, or additions using transition metals), (2) transformations of compounds already containing perfluoroalkyl groups, and (3) fluorination methods. Herein, we describe only direct additions of perfluoroalkyl groups, other than nucleophilic additions.

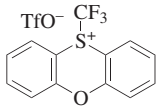
Electrophilic Perfluoroalkyl Additions

The trifluoromethyl and perfluoroalkyl groups can act as electrophiles when they are attached to highly electron-deficient atoms or electron-withdrawing groups. Several classes of electrophilic perfluoroalkylating reagents have been developed: the trifluoromethylchalcogen salts **168–171** (oxonium, sulfonium, selenonium, telluronium, thiophenium), iodonium salts **172–174**, and the CF_3 analog of Johnson's reagent **175**. Trifluoromethylation and perfluoroalkylation of carbanions, alkenes, alkynes, silyl enol ethers, allyl silanes, enamines, alcohols, sulfonic acids, anilines, phosphines, thiols, aromatics, and other nucleophiles has been achieved with these reagents. Recent reviews on the topic exist, including enantioselective electrophilic perfluoroalkyl additions.[6,36,705,755–758,705]

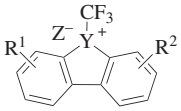
Additionally, electrophilic perfluoroalkyl additions to enamines, silyl enol ethers or α,β-unsaturated ketones with R_FX (X = Br, I) in the presence of zinc powder or Et_2Zn and a substoichiometric amount of Cp_2TiCl_2 or Wilkinson's catalyst have been described.[299,759–763] The perfluoroalkylating reagent in this case is the intermediate transition-metal complex containing the perfluoroalkyl group bound to the metal center. Carbanions, enamines, and thiolate anions are trifluoromethylated in low to moderate yields with neutral S–CF_3 reagents **176**.[764]



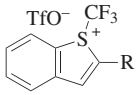
168 X = OTf, SbF_6



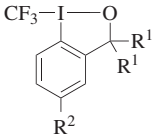
169



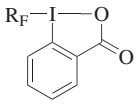
170 Y = O, S, Se, Te
Z = BF_4, OTf, PF_6, SbF_6, Sb_2F_{11}



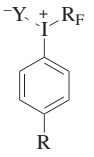
171



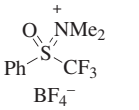
172 R^1 = Me, CF_3
R^2 = H, Me



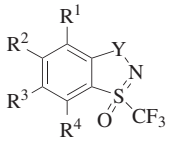
173 R_F = CF_3, C_2F_5, *n*-C_3F_7



174 R = H, F, Me
Y = Cl, OTf, BF_4, CF_3CO_2, OSO_3H



175



176 Y = OC, O_2S

Radical Perfluoroalkyl Additions

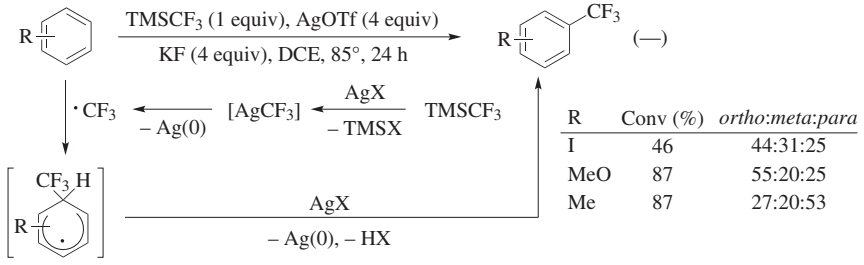
Radical perfluoroalkyl addition is an important method for the introduction of perfluoroalkyl groups. Several recent reviews covering the topic are available.[6,8,36,765,766] Unlike methyl radical, which is planar, the trifluoromethyl radical is pyramidal (nearly tetrahedral) and shows a large barrier for inversion.[765] Perfluoroalkyl radicals are more electrophilic than alkyl radicals and their electrophilicity increases from primary to tertiary radicals. In comparison with alkyl radicals, the perfluoroalkyl radicals are more destabilized and significantly more reactive. For example, styrene reacts 440 times faster with the trifluoromethyl radical than with the methyl radical.[766] Several factors such as branching can dramatically stabilize perfluoroalkyl radicals kinetically. For example, Scherer's radicals $[(CF_3)_2CF]_2(C_2F_5)C\bullet$ and $[(CF_3)_2CF]_3C\bullet$ are very stable.[767] The first radical has a half-life of 1 hour at 100° and the second one does not react even with pure F_2 at room temperature.[767]

Perfluoroalkyl radicals can be generated in a number of ways: (1) from perfluoroalkyl halides photochemically, electrochemically, reductively (using metals, low-valent metal salts, dithionites, etc.) or using radical initiators such as silanes,

stannanes, or trialkylboranes, (2) from perfluoroacyl peroxides by thermal or photochemical fragmentation, (3) from perfluoroalkylsulfonyl chlorides or bromides by photochemical or thermal fragmentation, (4) from perfluoroalkyl sulfinates (such as the Langlois reagent: CF_3SO_2Na)[768] by oxidative fragmentation or electrochemical oxidation, (5) by photolysis of perfluoroazoalkanes, (6) by photochemical fragmentation of in situ formed Barton esters from perfluoroacyl chlorides and thiopyridone *N*-oxide, and other ways.[6,765,766] Other sources of the trifluoromethyl radical are trifluoromethanethiosulfonates (CF_3SO_2SR) or trifluorothioacetates (CF_3COSR), acetylenic triflones ($RC{\equiv}CSO_3CF_3$), *S*-trifluoromethyl xanthates, *N*-trifluoromethyl-*N*-nitrososulfonamides,[262,769] $M(CF_3)_2$ (M = Hg, Cd, Te), $Sb(CF_3)_3$, $AgCF_3$, and the $Bi(CF_3)_3/Cu(OAc)_2$ system.[8] Trifluoromethyl radicals are also formed by SET reduction of electrophilic trifluoromethylating reagents. For example, Togni reagents are reduced with Cu(I) salts or TEMPONa to form CF_3 radicals for addition onto alkenes.[726,770,771,772,773] Umemoto sulfonium reagent is reduced by SO_2 radical anion from $HOCH_2SO_2Na$, and the resulting trifluoromethyl radical can add to styrenes.[774] On the other hand, SET reduction of the nucleophilic reagent $TMSCF_3$ with silver triflate provides $AgCF_3$, which decomposes upon heating to elemental silver and trifluoromethyl radicals, that then add to arenes.[775]

Perfluoroalkyl radicals add to electron-rich alkenes, aromatic and heteroaromatic compounds, enolates, silyl enol ethers, enamines, unsaturated potassium organotrifluoroborates, etc.[765,766,776,777] Several diastereoselective trifluoromethylations and perfluoroalkylations using R_FX (X = Br, I) have been reported.[36] Enantioselective α-trifluoromethylation and α-perfluoroalkylation of various aldehydes using perfluoroalkyl iodides as sources of perfluoroalkyl radicals and a combination of iridium photocatalyst and a chiral imidazolidinone organocatalyst has recently been reported.[790] The new stereogenic center is formed upon reaction of the chiral enamine intermediate (from the reaction of the aldehyde with the organocatalyst) with the perfluoroalkyl radical. Enantioselective radical trifluoromethylation at the α-position of 2-phenylcyclohexanone through the corresponding lithium enolate coordinated with a chiral bidentate ligand has also been reported.[36,778]

Most of the perfluoroalkylsilver reactions are likely to proceed via radical pathways. Thus, Sanford reports radical trifluoromethylation of arenes with CF_3Ag formed from $TMSCF_3$ and AgOTf in the presence of potassium fluoride (Scheme 357).[775] This process usually produces mixtures of constitutional isomers, with ratios dependent on the substituents on the arene ring.



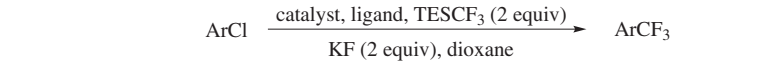
R	Conv (%)	*ortho*:*meta*:*para*
I	46	44:31:25
MeO	87	55:20:25
Me	87	27:20:53

Scheme 357

Transition-Metal-Assisted Perfluoroalkyl Additions

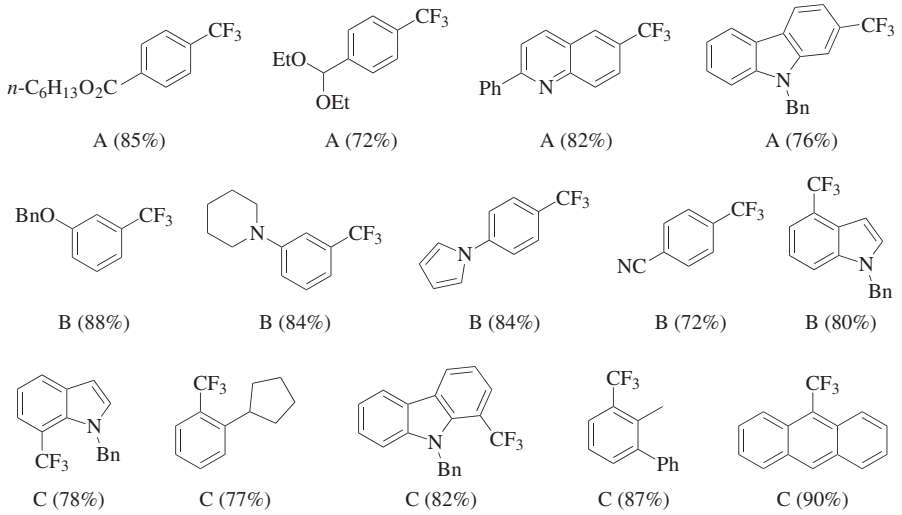
Transition-metal-catalyzed trifluoromethylation and perfluoroalkylation is a rapidly growing field which has been covered in recent reviews.[32,779,780,791] Owing to the limited current knowledge of the mechanistic aspects of some transition-metal-catalyzed reactions it is difficult to classify many of them as nucleophilic processes. However, recent advances in this field are briefly discussed because of their importance.

Palladium-catalyzed trifluoromethylation of aryl chlorides has been reported by Buchwald.[747] In this ground-breaking process $[(allyl)PdCl]_2$ or $Pd_2(dba)_3$ undergoes oxidative addition with the carbon–chloride bond of the aryl halide, and the halogen is subsequently replaced by CF_3^- generated from Et_3SiCF_3 and a fluoride source. Reductive elimination to form trifluoromethylarenes is notoriously slow due to the strong bonding between Pd and CF_3 and the activation energy is close to 22 kcal mol^{-1}.[781] However, when BrettPhos or RuPhos ligands are used this elimination becomes feasible and moderate to excellent yields of trifluoromethylarenes can be obtained (Scheme 358).[747] Similar trifluoromethylation conditions are reported for naphthyl bromide and substituted phenyl bromides using $[(cinnamyl)PdCl_2]$ and BrettPhos.[782]



Method	Cat.	Ligand	Temp (°)
A	$[(allyl)PdCl_2]$ (3 mol %)	BrettPhos (9 mol %)	120–130
B	$Pd(dba)_2$ (6 mol %)	BrettPhos (9 mol %)	130
C	$[(allyl)PdCl_2]$ (4 mol %)	RuPhos (12 mol %)	140

Products and method:



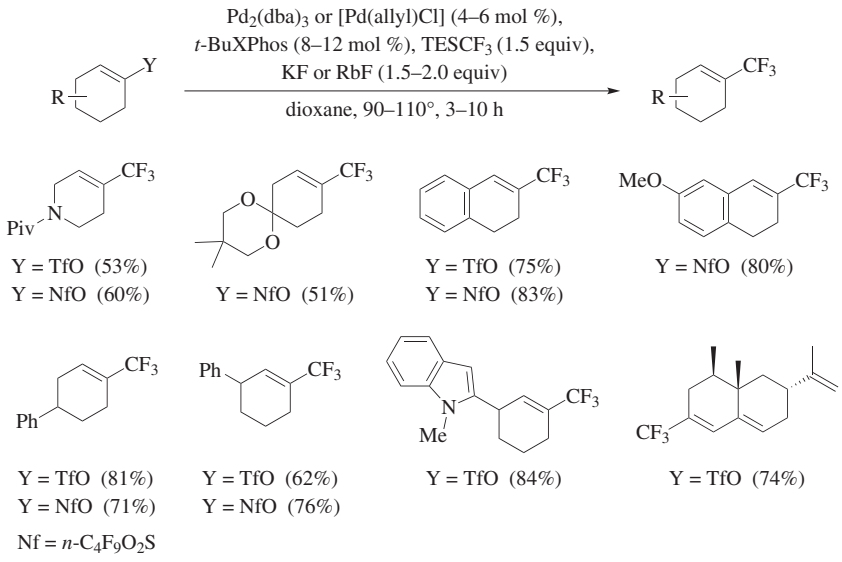
A (85%) A (72%) A (82%) A (76%)

B (88%) B (84%) B (84%) B (72%) B (80%)

C (78%) C (77%) C (82%) C (87%) C (90%)

Scheme 358

Palladium-catalyzed trifluoromethylation of vinyl triflates and nonaflates has also been reported. Using $Pd_2(dba)_3$ or $[Pd(allyl)Cl]_2$ with *t*-BuXPhos in dioxane and the $TMSCF_3/F^-$ system, trifluoromethylalkenes can be prepared from the corresponding triflates or nonaflates at elevated temperatures (Scheme 359).[783] Trifluoromethylation of vinyl chlorides or bromides does not occur under these conditions. Another limitation of this process is the sluggish reaction of cyclohexenyl sulfonates with substitution at the 2-position. Also, compared to six-membered fluoroalkylsulfonates, the analogous five-membered substrates demonstrate significantly reduced reactivity under these conditions.[783]

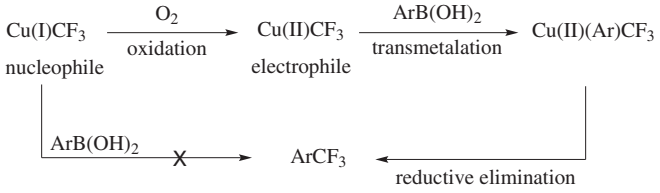


Scheme 359

Oxidative copper-catalyzed coupling of aryl, alkenyl, and alkylboronic acids with trifluorosilanes and perfluoroalkyl iodides has been reported by several research groups. All of these processes involve formation of the R_FCu species followed by the oxidative coupling with boronic acid.[352,354] A one-pot preparation of pinacol boronic esters via C–H activation and coupling with $[(phen)Cu(R_F)]$ allows access to perfluoroalkylated arenes.[356] In the reaction between R_FI and arylboronic acids, R_FCu species are suggested to be formed via a radical pathway. The arylboronic acid reacts with Cu(0) in the presence of oxygen to produce ArCu species which undergo copper–halogen exchange with R_FI to produce R_FCu.[352] The mechanism of these oxidative couplings is not yet fully understood.

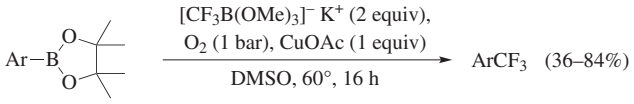
The reaction between fluoroform-derived CF_3Cu and boronic acids under aerobic conditions constitutes a complementary low-cost process to the protocols mentioned above. Nucleophilic $Cu(I)CF_3$ species are suggested to undergo air-oxidation to form

electrophilic $Cu(II)CF_3$ species that undergo transmetalation with boronic acids to produce $Cu(II)(Ar)CF_3$, which then reductively eliminate to produce trifluoromethylarenes (Scheme 360).[362]



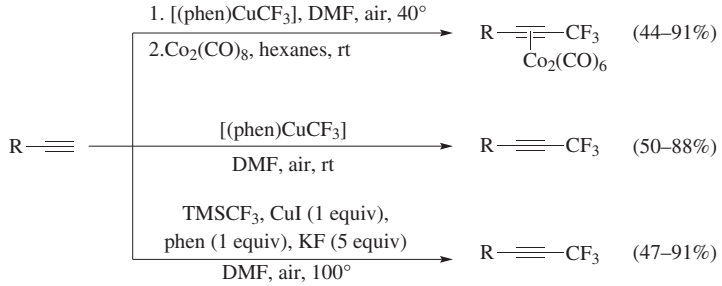
Scheme 360

Oxidative coupling of arylboronates with the shelf-stable potassium (trifluoromethyl)trimethoxyborate proceeds with comparable yields of trifluoromethylated products (Scheme 361).[363] The same reagent is used for the trifluoromethylation of aryl iodides.[103]



Scheme 361

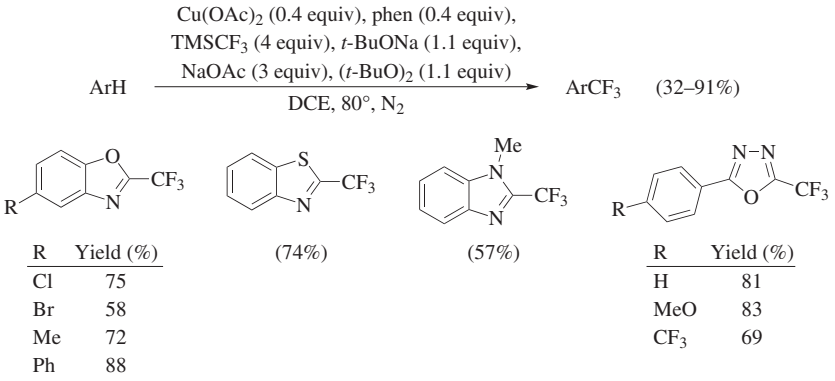
Several reports demonstrate the utility of $[(phen)CuCF_3]$ in oxidative couplings with alkynes to access trifluoromethylated alkynes (Scheme 362),[357,359–361] which are otherwise available via electrophilic trifluoromethylation of alkynes. Often, addition of the alkyne via syringe pump is required to achieve good yields.



Scheme 362

The mechanism of such oxidative coupling reactions is proposed to involve molecular oxygen coordination to the CF_3Cu complex, followed by coordination of the acetylene with the formation of a Cu(III) complex, reductive elimination of the trifluoromethylated alkyne, and regeneration of the Cu(I) species.[358,360]

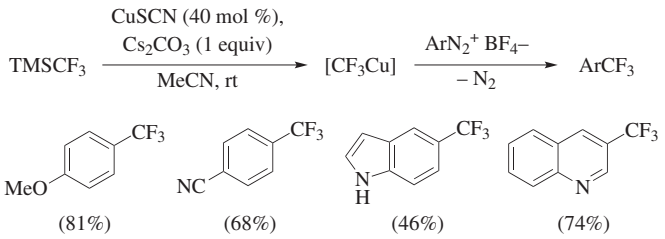
As was seen with terminal alkynes, heterocycles and electron-deficient arenes undergo copper-mediated C–H oxidative trifluoromethylation (Scheme 363).[784] This reaction employs an oxidant, and most likely proceeds through Cu(III) species, which reductively eliminate to produce the trifluoromethylated product.



Scheme 363

Palladium-catalyzed trifluoromethylation processes involving Pd(II)/Pd(IV) species are outside of the scope of this review.[744,746,785,786] Importantly, it is known that Pd(IV) complexes can participate in reductive elimination reactions that are challenging at other metal centers.

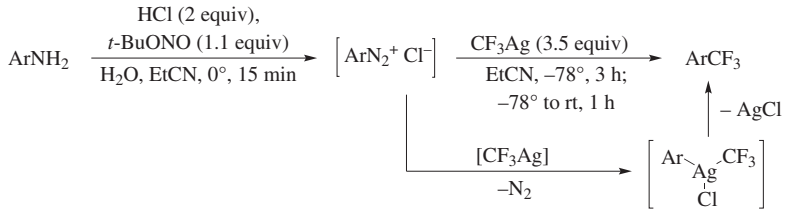
Trifluoromethylcopper undergoes smooth reaction with diazonium salts in a process similar to the Sandmeyer reaction. Although various Cu(I) salts can be used in this reaction to generate CF_3Cu in situ, CuSCN provides the best yields of the trifluoromethylated arenes (Scheme 364).[787] This process is an interesting alternative to trifluoromethylation of aryl iodides because of its wide functional group tolerance.



Scheme 364

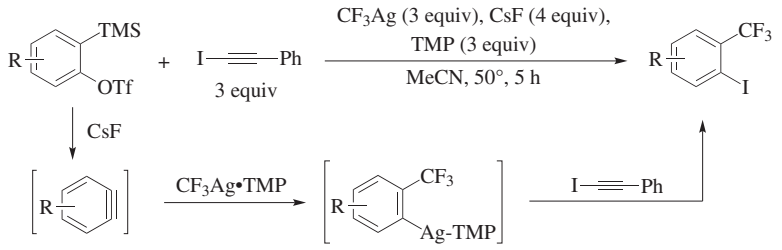
A similar process is reported employing CF_3Ag prepared from $TMSCF_3$ and AgF. This process operates at lower temperatures and is influenced by the counterion of the diazonium salt. Bromide and trifluoroacetate afford results similar to chloride, whereas tetrafluoroborate affords a diminished yield, and *t*-butoxide affords only a trace of the product. Radical trapping experiments and the use of SET inhibitors

suggest that the CF_3 radical is unlikely to be involved in the trifluoromethylation pathway with $AgCF_3$. Silver(III) intermediates are proposed for this process (Scheme 365).[788]



Scheme 365

Silver-mediated trifluoromethylation–iodination of arynes has been reported and involves the formation of a benzyne intermediate that is reactive toward CF_3Ag (Scheme 366).[789] After insertion, the phenylsilver intermediate is trapped by an electrophilic iodinating agent to produce trifluoromethylated iodoarenes. This seemingly radical process is not inhibited by TEMPO, suggesting that a mechanism involving a radical pathway is less likely.[789] Interestingly, neither $(CF_3)_2Zn$ nor CF_3Cu can be used as the trifluoromethyl source in this reaction, and only CF_3Ag undergoes smooth addition to the benzyne intermediate.



Scheme 366

EXPERIMENTAL CONDITIONS

General Comments

The most widely used reagents for nucleophilic perfluoroalkyl additions are (trifluoromethyl)trimethylsilane, perfluoroalkyllithium, perfluoroalkylmagnesium, and perfluoroalkylcopper reagents. In this section, the preferred solvents, initiators, and other reaction conditions for the above-listed reagents and different substrates are described.

Reactions with (Trifluoromethyl)trimethylsilane

(Trifluoromethyl)trimethylsilane is a very popular and general reagent for nucleophilic addition of the CF_3 group to a variety of electrophilic substrates under mild conditions. Typically a small excess of $TMSCF_3$ is used and the choice of the initiator and solvent is very important. For reactive substrates such as aldehydes, ketones, sulfonimines, sulfinimines, and lactones substoichiometric amounts (1–10 mol %) of fluoride ions are used such as TBAF, TMAF, TBAT, or TASF, which are soluble in ethereal solvents such as diethyl ether, THF, or DME. Dry solvents (commercial quality) are typically acceptable and should be employed to minimize hydrolysis of the nucleophilic hypercoordinate silicon intermediate. However, small amounts of protic impurities (HA) are usually not a problem. The reaction of $TMSCF_3/F^-$ in the presence of small amounts of HA produces CF_3H (gas) and A^-, which can act as a nucleophilic initiator for $TMSCF_3$. For example, the use of small amounts of TBAF in its hydrated form does not have a detrimental effect on the reaction. Reactions proceed well at room temperature; however, with reactive substrates such as aldehydes or activated ketones, the reactions are often started at 0° and then warmed to room temperature for better control of the rate and to avoid possible side reactions. Other efficient initiators include metal fluorides such as KF or CsF, or oxygen nucleophiles such as K_2CO_3, LiOPh, or NaOAc in a polar aprotic solvent such as DMF or DMSO. Dry DMSO in the presence of molecular sieves is also able to act as an initiator.[136] A general method for the trifluoromethylation of imines using $TMSCF_3$ employs strongly acidic conditions.[490] The reaction is promoted by HF generated in situ from KHF_2 and either trifluoroacetic acid or triflic acid. Acetonitrile, sometimes with added DMF (3 equivalents), is used as the solvent and the reaction is conducted at room temperature. Because esters are much less reactive than aldehydes or ketones, substoichiometric amounts of anhydrous TBAF or tetrabutylammonium acetate in dry, nonpolar solvents such as pentane, toluene, or dichloromethane (–78° to room temperature) are used.[131,608] Alternatively, $TMSCF_3$ with substoichiometric amounts of CsF in DME or without solvents efficiently converts alkyl esters into trifluoromethyl ketones.[470] Primary alkyl iodides or bromides undergo trifluoromethylation using an excess of a fluoride source (TMAF, TASF, or Cs(15-crown-5)$_2$F) in DME or Et_2O.[317]

Reactions with Perfluoroalkyllithium Reagents

Trifluoromethyllithium is unstable, but pentafluoroethyllithium and other perfluoroalkyllithium reagents are widely used. They are usually prepared in situ by halogen–lithium exchange at low temperatures (rapid decomposition starts at –75°) in diethyl ether. The majority of perfluoroalkylation reactions with R_FLi are carried out by rapid generation of the perfluoroalkyllithium species quickly followed by capture with an appropriate electrophile.

Reactions with Perfluoroalkylmagnesium Reagents

In contrast to perfluoroalkyllithium reagents, the direct reaction between perfluoroalkyl halides and magnesium metal usually provides good yields of the corresponding Grignard reagents. Magnesium free of traces of other metals should be used. However, halogen–RMgX exhange is a preferred method for the preparation of perfluoroalkylmagnesium reagents.[204,206,207] This exhange is rapid and usually quantitative at low temperatures (–70°). Diethyl ether provides better stability of the R_FMgX reagents compared to THF. Perfluoroalkylmagnesium reagents generally should not be handled at temperatures above –30°.

Reactions with Perfluoroalkylcopper Reagents

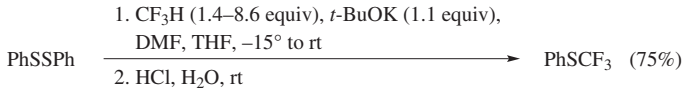
These reagents can be prepared in a variety of ways. The most popular is 1,10-phenanthroline-stabilized perfluoroalkylcopper because of its stability and simple preparation from $TMSR_F$.[54] Direct reaction of the perfluoroalkyl halide (usually bromide or iodide) with an excess of copper metal at elevated temperatures or decarboxylation of perfluoroalkylcarboxylates in the presence of Cu(I) salts are also widely used methods for the preparation of perfluoroalkylcoppers. However, these methods do not provide quantitative yields of R_FCu reagents and often require filtration of excess copper. The best yields for these protocols are obtained in dipolar aprotic solvents such as DMF, DMA, DMSO, HMPA, etc.

One of the most-often used perfluoroalklylcopper reagents is CF_3Cu. However this reagent is not very stable at room temperature without stabilizing ligands or additives and must be used shortly after preparation. Several routes are available for this important reagent. The most useful and high-yielding protocols do not require heating above ambient temperature. Direct formation of CF_3Cu species from fluoroform is another useful method to access these species under mild conditions using CuCl and *t*-BuOK in DMF or NMP.[56] Excellent stability of the perfluoroalkylcopper complexes is achieved by the addition of $Et_3N•(HF)_3$ or $Py•(HF)_n$.[56,57] Another protocol is the in situ metathesis of trifluoromethylcadmium or -zinc reagents with CuX (X = Cl, Br, I, CN) to afford CF_3Cu in 90–100% yields.[273] These reactions are usually carried out in DMF to stabilize the intermediate difluorocarbene, which is presumably formed in the course of the reaction between difluorodihalomethane and Zn(Cd) metal. Interestingly, the exchange between trifluoromethylcadmium is fast even at –30°, while the methathesis of trifluoromethylzinc requires higher temperatures. Another method of in situ preparation of CF_3Cu is the generation of the trifluoromethyl anion from $TMSCF_3$ and KF,[344] which is immediately captured by CuI. The most common solvents for this preparation are DMF and NMP.

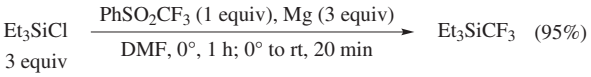
EXPERIMENTAL PROCEDURES

This section is organized according to the type of nucleophilic perfluoroalkyl reagent in the same order as in the section Overview and Preparation of Nucleophilic Perfluoroalkyl Reagents (starting with fluoroform, then perfluoroalkyl halides,

$TMSCF_3$, sulfur reagents, and finishing with a copper-catalyzed trifluoromethylation).



Phenyl Trifluoromethyl Sulfide [Trifluoromethylation of Diphenyl Disulfide Using Trifluoromethane].[73] Trifluoromethane (200–600 mg, 1.4–8.6 mmol) was bubbled at –15° into a solution of diphenyl disulfide (218 mg, 1 mmol) in DMF (2 mL). Then, a solution of *t*-BuOK (123 mg, 1.1 mmol) in THF (1.1 mL) was added dropwise at the same temperature. The reaction mixture was stirred at –15° for 5.5 h, then was warmed to rt and stirred for 12 h. Water (2 mL) and aqueous HCl (1 M, 0.5 mL) were added, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with brine and water, dried (Na_2SO_4), and evaporated under vacuum. The residual oil was purified by column chromatography (silica gel, petroleum ether) to afford phenyl trifluoromethyl sulfide (134 mg, 75%): bp 140°; ^{1}H NMR ($CDCl_3$) δ 7.34–7.47 (m, 3H), 7.66 (dd, J = 7.9, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 129.5, 130.8, 136.5 (q, J = 0.9 Hz); EIMS (*m/z*) 178 (M^+), 159, 109, 108, 77, 69; ^{19}F NMR ($CDCl_3$) δ –43.37 (s).



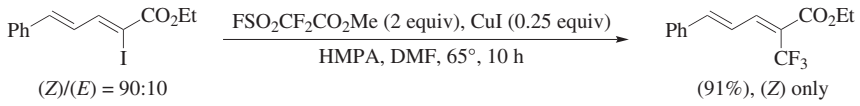
(Trifluoromethyl)triethylsilane [Preparation from Trifluoromethyl Phenyl Sulfone].[125] Into a flame-dried Schlenk flask containing magnesium turnings (1.03 g, 43 mmol) and DMF (30 mL) under argon was added trifluoromethyl phenyl sulfone (3.0 g, 14 mmol) at 0°. After the mixture was stirred for 5 min, triethylsilyl chloride (6.45 g, 43 mmol) was added dropwise via syringe. The color of the reaction mixture slowly turned yellow. The progress of the reaction was monitored by ^{19}F NMR spectroscopy periodically. After 1 h, the mixture was slowly warmed to rt over a 20-minute period and the reaction mixture was washed with ice-water (50 mL). After the excess Mg was removed, the solution was extracted with pentane (3 × 30 mL). The pentane phase was washed carefully with cold 98% sulfuric acid (4 × 30 mL) to remove most of the siloxane and silanol. Subsequently, the organic phase was washed with cold water (2 × 30 mL), $NaHCO_3$ solution (2 × 30 mL), and water (2 × 20 ml), and dried ($MgSO_4$). The solvent was removed under vacuum (~100 mm Hg), and the crude product containing diphenyl disulfide was purified by small-scale fractional distillation to provide (trifluoromethyl)triethylsilane (2.48 g, 95%): bp 56–58°/60 mm Hg; ^{1}H NMR ($CDCl_3$) δ 0.79 (q, J = 7.9 Hz, 6H), 1.04 (t, J = 7.9 Hz, 9H); ^{13}C NMR ($CDCl_3$) δ 0.8, 6.4, 132.2 (q, J = 323.5 Hz); ^{19}F NMR ($CDCl_3$) δ –61.3; ^{29}Si NMR ($CDCl_3$) δ 7.74 (q, J = 32.0 Hz); EIMS (*m/z*): M^+ 184, [M – Et] 155, [Et_3Si^+] 115.

$$Et_3SiCl \xrightarrow[Et_2O,\ -78^\circ,\ 2\ h;\ -78^\circ\ to\ rt;\ rt,\ 1\ h]{CF_3H\ (1\ equiv),\ KHMDS\ (1\ equiv)} Et_3SiCF_3 \quad (71\%)$$

(Trifluoromethyl)triethylsilane [Trifluoromethylation of Chlorotriethylsilane Using Trifluoromethane].[77] To a 250-mL, round-bottomed flask with magnetic stirrer under argon was added Et_2O (140 mL); the reaction flask was cooled to –78° and the solvent was stirred at that temperature for 10 min. Trifluoromethane (2.5 g total was added at the rate of 52.5 mL/min) was bubbled into the Et_2O solution for 16 min 17 sec to obtain a 0.25 M solution in Et_2O. Chlorotriethylsilane (5.32 g) was added dropwise and the resulting reaction mixture was stirred at –78° for 10 min. A solution of KHMDS in Et_2O (7.4 g in 52 mL, 0.625 M) was added dropwise, and the resulting yellowish mixture was stirred at –78° for 2 h and then was gradually warmed to rt and stirred at rt for 1 h. The solvent was removed under vacuum and the residue obtained was dissolved in pentane (150 mL). The pentane layer was washed with water (30 mL) and with cold concentrated sulfuric acid (98%) (4 × 15 mL) to remove most of the siloxane and silanols formed in the reaction. The organic layer was then washed with water (5 × 50 mL) until the pH of the water layer showed neutral. After drying (Na_2SO_4), the pentane was removed under vacuum to obtain the crude product which was distilled under vacuum to obtain pure (trifluoromethyl)triethylsilane (4.6 g, 71%): ^{1}H NMR ($CDCl_3$) δ 0.79 (q, J = 7.9 Hz, 6H), 1.04 (t, J = 7.9 Hz, 9H); ^{13}C NMR ($CDCl_3$) δ 0.86, 6.53, 132.24 (q, J = 324 Hz); ^{19}F NMR ($CDCl_3$) δ –61.3 (s); ^{29}Si NMR ($CDCl_3$) δ 7.7 (q, J = 32 Hz).

$$TMSCl \xrightarrow[PhCN,\ -60^\circ\ to\ rt,\ 17.5\ h]{CF_3Br\ (3\ equiv),\ (Et_2N)_3P\ (1.2\ equiv)} TMSCF_3 \quad (75\%)$$

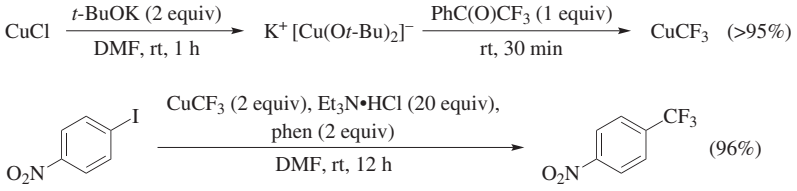
(Trifluoromethyl)trimethylsilane [Trifluoromethylation of TMSCl Using CF_3Br].[91] This preparation is described in *Organic Syntheses*.[91]



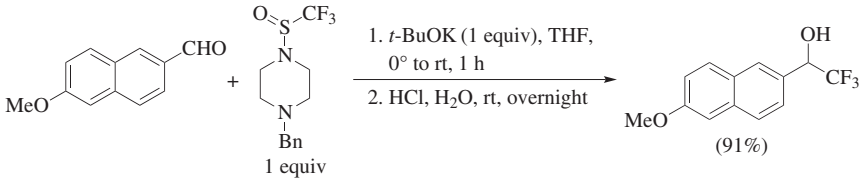
(*Z*)/(*E*) = 90:10 (91%), (*Z*) only

Ethyl 5-Phenyl-2-trifluoromethylpenta-2,4-dienoate [Trifluoromethylation of a Vinyl Iodide with $FSO_2CF_2CO_2Me$].[328] A solution of $FSO_2CF_2CO_2Me$ (0.5 mL, 4 mmol) in DMF (10 mL) was added dropwise over 3 h to a mixture of ethyl 2-iodo-5-phenylpenta-2,4-dienoate (656 mg, 2 mmol), CuI (96 mg, 0.5 mmol), and HMPA (1 mL) in DMF (15 mL) at 65°. The reaction mixture was stirred at 65° for 10 h before being cooled to rt. Saturated aqueous NH_4Cl (30 mL) was added and the mixture was extracted with Et_2O. The extracts were washed with brine, dried over Na_2SO_4, and the solvent was removed under vacuum. Purification of the residue by column chromatography on silica gel (hexane/EtOAc, 25:1) provided

the pure product as an oil (492 mg, 91%): IR (neat) 2987, 1724, 1623, 1290, 1257, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, J = 7.1 Hz, 3H), 4.33 (q, J = 7.1 Hz, 2H), 7.11 (d, J = 15.2 Hz, 1H), 7.41 (m, 4H), 7.53 (m, 2H), 7.72 (d, J = 11.9 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ –20.7 (s); EIMS (*m/z*): [M^+ + 1] 271 (50), M^+ 270 (100), 225 (26), 69 (12).

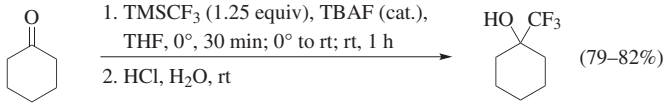


1-Nitro-4-(trifluoromethyl)benzene [Trifluoromethylation of an Iodoarene with CF_3Cu Prepared from 2,2,2-Trifluoroacetophenone].[280] A mixture of CuCl (50 mg, 0.50 mmol) and *t*-BuOK (112 mg, 1.0 mmol) in DMF (1 mL) was stirred for 1 h at rt under argon atmosphere. To the mixture was added dropwise 2,2,2-trifluoroacetophenone (0.068 mL, 0.50 mmol) at rt. After the reaction mixture was stirred for 30 min, CF_3Cu was observed by ^{19}F NMR analysis using benzotrifluoride as an internal standard (>95% yield). ^{13}C NMR (75 MHz, DMF-d_7) δ 150.3 (q, J = 342.0 Hz); ^{19}F NMR (282 MHz, DMF-d_7) δ –25.2 (s). The solution of CF_3Cu in DMF (0.4–0.5 M, 0.4–0.5 mL, 0.2 mmol) neutralized with Et_3N•HCl (275 mg, 2 mmol) was added to a solution of 1-iodo-4-nitrobenzene (0.1 mmol) and 1,10-phenanthroline (36 mg, 0.2 mmol) in DMF (1 mL) at rt under argon. After stirring for 12 h, the reaction mixture was quenched with HCl (1 M, 5 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 5 mL); the combined organic layer was washed with brine (10 mL), dried (Na_2SO_4), and evaporated. The resulting crude product was purified by silica gel column chromatography (pentane/Et_2O, 10:1) to afford the product as a colorless liquid (18.3 mg, 96%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 8.37 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.9 (q, J = 271.5 Hz), 124.1, 126.8 (q, J = 3.5 Hz), 136.1 (q, J = 33.2 Hz), 150.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.1 (s).

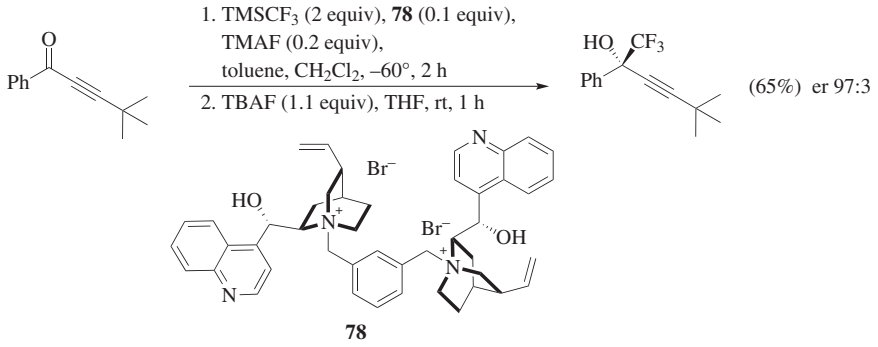


2,2,2-Trifluoro-1-(6-methoxynaphthalen-2-yl)ethanol [Trifluoromethylation of an Aromatic Aldehyde Using a Sulfur-Based Trifluoromethylating Reagent].[181] To a solution of 1-benzyl-4-trifluoromethanesulfinylpiperazine (292 mg, 1 mmol) and 6-methoxynaphthalene-2-carbaldehyde (186 mg, 1 mmol) in THF (1 mL), cooled to 0°, was added dropwise a solution of *t*-BuOK (112 mg,

1 mmol) in THF (1 mL). The temperature was allowed to rise to rt over 1 h. The crude mixture was hydrolyzed with aqueous HCl (1 M, 1 mL) overnight and was then extracted with Et_2O. The organic phase was dried (Na_2SO_4) and the solvent was evaporated under vacuum. The crude product was purified by chromatography (silica gel) to afford 2,2,2-trifluoro-1-(6-methoxynaphthalen-2-yl)ethanol (233 mg, 91%): ^{1}H NMR ($CDCl_3$) δ 3.23 (s, 1H), 3.93 (s, 3H), 5.16 (q, J = 6.7 Hz, 1H), 7.18 (m, 2H), 7.53 (d, J = 8.5 Hz, 1H), 7.75 (t, J = 8.2 Hz, 2H), 7.84 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 55.8, 73.4 (q, J = 32.0 Hz), 106.1, 119.8, 124.9 (q, J = 282.0 Hz), 124.3, 127.6, 127.7, 128.8, 129.6 (q, J = 1.2 Hz), 130.2, 135.4, 158.7; ^{19}F NMR ($CDCl_3$) δ −78.2 (d, J = 6.7 Hz).



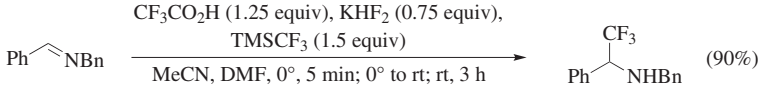
1-(Trifluoromethyl)cyclohexanol [Trifluoromethylation of an Enolizable Ketone Using $TMSCF_3$ and TBAF].[91] This preparation is described in *Organic Syntheses*.[91]



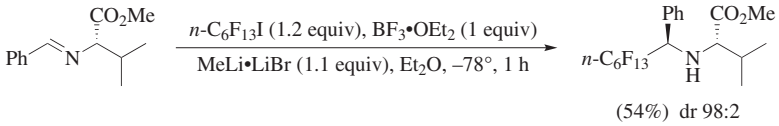
78

(*S*)-1,1,1-Trifluoro-5,5-dimethyl-2-phenylhex-3-yn-2-ol [Enantioselective Trifluoromethylation of a Non-Enolizable Ketone Using $TMSCF_3$ and a Chiral Phase-Transfer Catalyst].[531] To a stirred solution of 4,4-dimethyl-1-phenylpent-2-yn-1-one (36.1 mg, 0.20 mmol), catalyst **78** (17.0 mg, 20 μmol) and TMAF (3.7 mg, 40 μmol) in toluene/CH_2Cl_2 (2:1, 0.5 mL) was added $TMSCF_3$ (59.1 μL, 0.40 mmol) at −60° under a nitrogen atmosphere. After stirring the reaction mixture at −60° for 2 h, saturated aqueous NH_4Cl was added. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was treated with TBAF (57.5 mg, 0.22 mmol) in THF (1.5 mL) at rt for 1 h. The resulting mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, *n*-hexane/acetone, 9:1) to afford the product as a pale yellow oil (32.4 mg, 64%, er 97:3): $[\alpha]_D^{25}$ = −2.2 (*c* 0.65, $CHCl_3$); ^{1}H

NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 9H), 2.87 (s, 1H), 7.39–7.42 (m, 3H), 7.71–7.74 (m, 2H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 27.6, 30.4, 72.7 (q, J = 32.2 Hz), 74.8, 97.5, 123.4 (q, J = 285.2 Hz), 127.2, 128.1, 129.2, 135.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ –81.3 (s, 3F); IR (neat) 3481, 3067, 2973, 2871, 2244, 1698, 1453, 1364, 1254, 1182, 1023, 935, 908, 877, 765, 709, 665 cm^{-1}; EIMS (*m/z*): M^+ 256; HRMS (EI) (*m/z*): calcd for $C_{14}H_{15}F_3O$, 256.1075; found, 256.1093. The er was determined by HPLC using three OJ-H columns (*n*-hexane/*i*-PrOH, 95:5, flow rate 0.5 mL/min, λ = 207 nm, t_R (*S*) = 32.7 min, t_R (*R*) = 34.9 min).

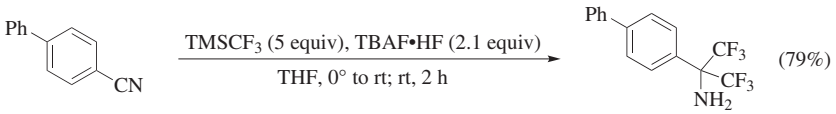


Benzyl (2,2,2-Trifluoro-1-phenylethyl)amine [Trifluoromethylation of an Imine Using $TMSCF_3$ under Acidic Conditions].[490] Trifluoroacetic acid (96 μL, 1.25 mmol) was added to a mixture of *N*-benzylidene benzylamine (195 mg, 1 mmol) and KHF_2 (59 mg, 0.75 mmol) in acetonitrile (2 mL) and DMF (232 μL, 3 mmol) at 0°, and the suspension was stirred for 5 min. $TMSCF_3$ (221 μL, 1.5 mmol) was added, the cooling bath was removed, and the mixture was stirred for 3 h at rt. Saturated aqueous Na_2CO_3 (0.5 mL) was added dropwise, the mixture was stirred for an additional two min, diluted with water (7 mL), and extracted with Et_2O/hexane (1:1, 3 × 5 mL). The combined organic phase was filtered through Na_2SO_4 and concentrated under vacuum, and the crude product was chromatographed on silica gel (hexanes/EtOAc, 10:1), affording benzyl(2,2,2-trifluoro-1-phenylethyl)amine as an oil (239 mg, 90%): ^1H NMR ($CDCl_3$) δ 2.09 (br s, 1H), 3.71 (d, J = 13.2 Hz, 1H), 3.88 (d, J = 13.2 Hz, 1H), 4.19 (q, J = 7.7 Hz, 1H), 7.27–7.54 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 51.0, 63.3 (q, J = 28.8 Hz), 125.4 (q, J = 281.4 Hz), 127.3, 128.1, 128.5, 128.6, 128.7, 129.0, 134.2 (q, J = 1.7 Hz), 138.9; ^{19}F NMR ($CDCl_3$) δ –74.6 (d, J = 7.7 Hz). Anal. Calcd for $C_{15}H_{14}F_3N$: C, 67.91; H, 5.32; N, 5.28. Found: C, 67.99; H, 5.33; N, 5.21.



(*S,*R**)-Methyl 3-Methyl-2-[(1-phenyl-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)amino]butanoate [Diastereoselective Perfluorohexylation of an Imine with Perfluoro-*n*-hexyllithium].**[197] A solution of the imine (219 mg, 1 mmol) and perfluoro-*n*-hexyl iodide (446 mg, 1.2 mmol) in dry Et_2O (10 mL) was stirred and cooled to –78°. BF_3•OEt_2 (0.13 mL, 1 mmol) was added and soon the BF_3–imine complex precipitated. An ethereal solution of MeLi•LiBr (1.1 mmol) was added at –78° over 10 min. The mixture became clear near the end of the addition. After the mixture was stirred for 1 h at –78°, aqueous $NaHCO_3$ was added.

The organic phase was separated and the aqueous phase was extracted with Et_2O; the combined extracts were washed with brine and dried over Na_2SO_4. The pure product was obtained by distillation (291 mg, 54%): bp 106° (oven temp)/0.2 mm Hg; IR (neat) 3040, 2968, 1738, 1366, 1300–1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (d, J = 6.7 Hz, 3H), 0.90 (d, J = 6.7 Hz, 3H), 1.92 (m, 1H), 2.42 (br s, 1H), 2.78 (d, J = 5.8 Hz, 1H), 3.71 (s, 3H), 4.32 (t, J = 12.7 Hz, 1H), 7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.0, 19.3, 31.5, 51.6, 61.8 (dd, J = 22, 21 Hz), 63.2, 100–125 (6C), 128.5, 129.3, 129.8, 132.8, 174.5; CIMS (*m/z*): [M^+ + 1] 540 (100), 520, 480, 437, 409, 220, 140. Anal. Calcd for $C_{19}H_{18}F_{13}NO_2$: C, 42.31; H, 3.36; N, 2.60. Found: C, 42.26; H, 3.38; N, 2.65.



2-Biphenyl-4-yl-1,1,1,3,3,3-hexafluoropropan-2-amine [Trifluoromethylation of a Nitrile Using $TMSCF_3$].[641] Biphenyl-4-carbonitrile (110 mg, 0.61 mmol) was dissolved in THF (4 mL); $TMSCF_3$ (0.45 mL, 3.05 mmol) was added under nitrogen at 0°. To this mixture was then added TBAF•HF (360 mg, 1.28 mmol) solution in THF (4 mL). The cooling bath was removed, and the reaction mixture was stirred at rt for 2 h. The reaction mixture was concentrated under rotary vacuum to afford a light yellow gum. Column chromatography of the residue (silica gel, hexane/EtOAc, 5:1) provided 2-biphenyl-4-yl-1,1,1,3,3,3-hexafluoropropan-2-amine (154 mg, 79%) as a white solid: ^1H NMR (400 MHz, $CDCl_3$) δ 2.20 (br s, 2H), 7.35–7.42 (m, 1H), 7.42–7.50 (m, 2H), 7.56–7.63 (m, 2H), 7.63–7.69 (m, 2H), 7.83 (d, J = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 65.4 (sept, J = 27.8 Hz), 124.3 (q, J = 286.9 Hz), 127.6, 127.7, 128.2, 128.3, 129.3, 129.7, 140.3, 143.2. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{12}F_6N$, 320.08684; found, 320.08670.

TABULAR SURVEY

The tables include nucleophilic perfluoroalkyl additions that have appeared in the literature up to the first quarter of 2014. Tables 1–27 describe perfluoroalkyl addition to carbon electrophiles, while Tables 28–34 describe perfluoroalkyl additions to heteroatom electrophiles. The tables are arranged in a similar order as the text discussion. Entries in the tables are arranged in the order of increasing carbon count, although protecting groups, chiral auxiliaries, and small groups attached to heteroatoms are omitted from the carbon count to facilitate comparison of similar substrates. In Tables 28–34, all groups attached by carbon to the activating heteroatom (as determined by the table title) are included in the carbon count. The symbol (—) indicates that no yield was reported.

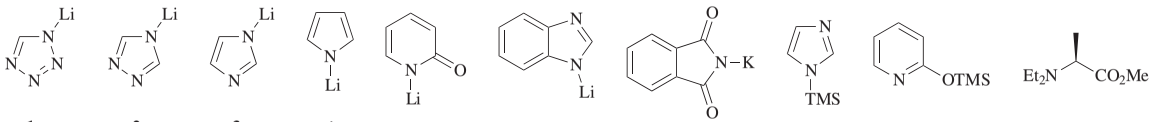
The tables are preceded by a chart showing the structures of catalysts, reagents, and initiators that are used in the tables. Bold numbers in the table entries indicate these structures. Solid, anhydrous potassium carbonate is used unless stated otherwise. The

notation (*xy* eq) means *x* times *y*. In addition to those listed in "*The Journal of Organic Chemistry Standard Abbreviations and Acronyms*", the following abbreviations are used in the Tabular Survey:

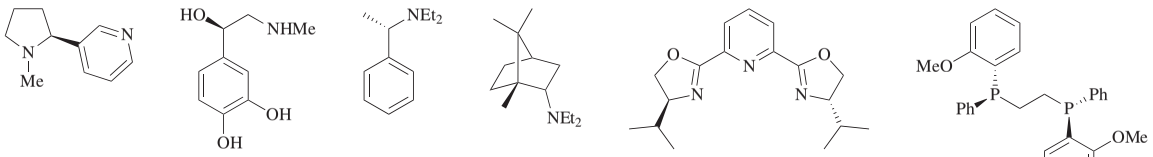
15-c-5	15-crown-5
bipy	2,2′-bipyridine
BOM	(benzyloxy)methyl
BPO	benzoyl peroxide
Brettphos	2-(dicyclohexylphosphino)-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-bipheryl (**161**)
C_4H_3O	furyl
C_4H_3S	thienyl
c-C_4H_7	cyclobutyl
c-C_5H_9	cyclopentyl
c-C_6H_{11}	cyclohexyl
$C_{10}H_7$	naphthyl
conv	conversion
DAST	*N*,*N*-diethylamino sulfurtrifluoride
diglyme	bis(2-methoxyethyl) ether
DMED	*N*,*N*′-dimethylethylenediamine
DMEU	*N*,*N*-dimethylethylenurea (1,3-dimethyl-2-imidazolidinone)
DMI	1,3-dimethyl-2-imidazolidinone
DMTr	4,4′-dimethoxytrityl
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
dtbpy	4,4′-di-*t*-butyl-2,2′-bipyridine
EDCI	1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
KHMDS	potassium bis(trimethylsilyl)amide
Nf	nonafluorobutanesulforate (nonaflate)
Ns	*P*-nitrobenzenesulforate (nosylate)
o/n	overnight
phen	1,10-phenanthroline
Pix	9-(9-phenyl)xanthenyl
PMP	4-methoxyphenyl
py	pyridine
quant	quantitative
R_F	perfluoroalkyl (C_nF_{2n+1}, $n = 1, 2, 3 \ldots$)
rt	room temperature
Ruphos	2-Dicyclohexylphosphino-2′,6′-diisopropyloxy bipheryl
TASF	tris(dimethylamino)sulfonium fluoride

TBAB	tetrabutylammonium bomide
TBAT	tetrabutylammonium triphenyldifluorosilicate
TBD	1, 5, 7-triazabicyclo[4.4.0]dec-5-ene
TBDPS	*tert*-butyldiphenylsilyl
TC	thiophene-2-carboxylate
TDAE	tetrakis(dimethylamino)ethylene
TEAF	tetraethylammonium fluoride
TEMPO	2,2,6,6-tetramethyl-*N*-oxypiperidinyl radical
tetraglyme	tetraethyleneglycol dimethyl ether
TMAF	tetramethylammonium fluoride
TMP	2,2,6,6-tetramethylpiperidine
Tol	tolyl (methylphenyl)
TPAP	tetrapropylammonium perruthenate
t_r	residence time in a flow reactor
Xantphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (**30**)

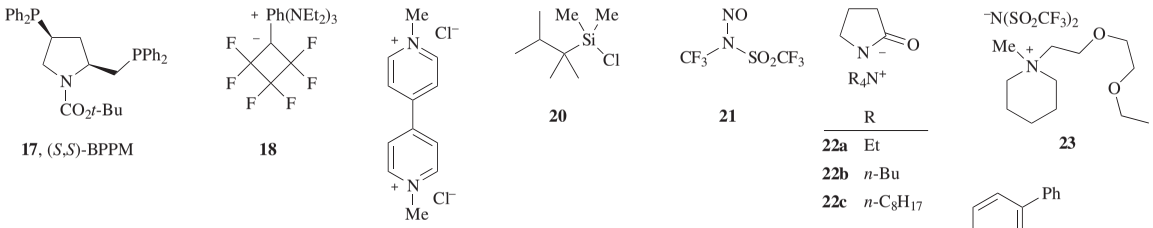
CHART 1. CATALYSTS, REAGENTS, AND INITIATORS USED IN TABLES



1 **2** **3** **4** **5** **6** **7** **8** **9** **10**



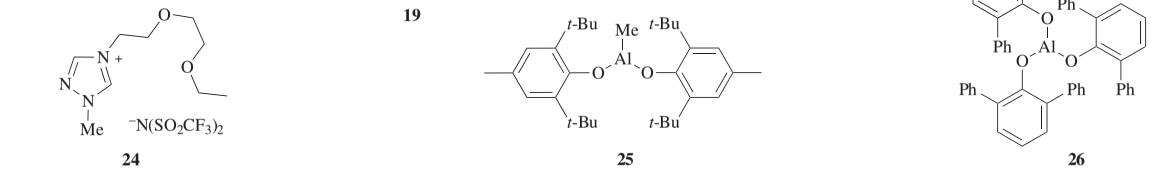
11, nicotine **12**, epinephrine **13** **14** **15**, (*S*,*S*)-ip-pybox **16**, (*S*,*S*)-DIPAMP



17, (*S*,*S*)-BPPM **18** **19** **20** **21**

	R
22a	Et
22b	*n*-Bu
22c	*n*-C_8H_{17}

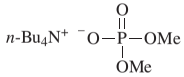
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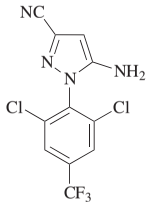
24 **25** **26**



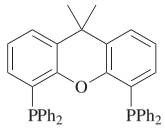
	R
27a	1-adamantyl
27b	$MeSO_2$
27c	*t*-Bu
27d	2,6-*i*-$Pr_2C_6H_3$



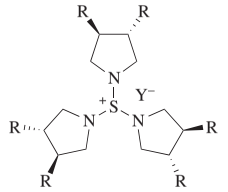
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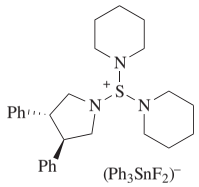
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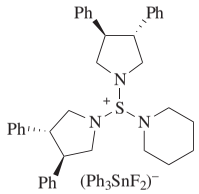
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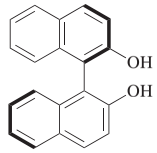
	R	Y
31a	Ph	F
31b	Ph	Ph_3SnF_2
31c	4-$MeOC_6H_4$	Ph_3SnF_2
31d	4-$CF_3C_6H_4$	Ph_3SnF_2
31e	3,5-$Me_2C_6H_3$	Ph_3SnF_2



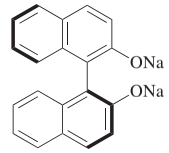
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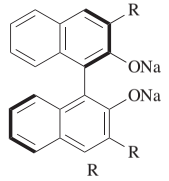
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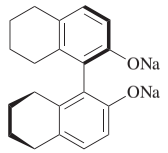
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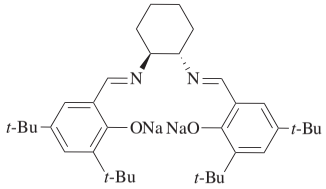
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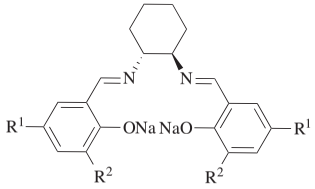
	R
36a	H
36b	$SiPh_3$



37

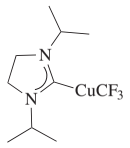


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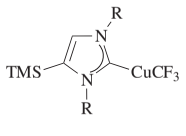


	R^1	R^2
39a	H	Ph
39b	*t*-Bu	*t*-Bu
39c	*t*-Bu	1-adamantyl

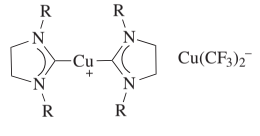
CHART 1. CATALYSTS, REAGENTS, AND INITIATORS USED IN TABLES (*Continued*)



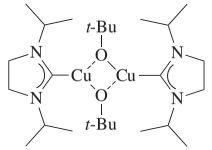
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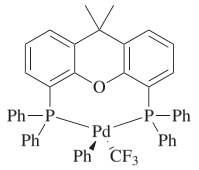
41 R = 2,4,6-$Me_3C_6H_2$



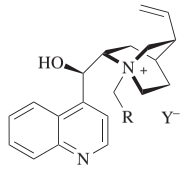
42 R = 2,4,6-$Me_3C_6H_2$



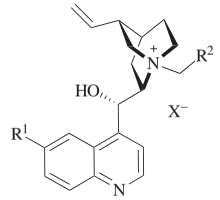
43



44

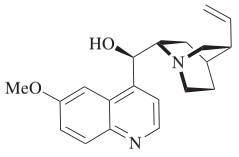


	R	Y
45a	Ph	PhO
45b	2,6-$F_2C_6H_3$	PhO
45c	3,5-$(MeO)_2C_6H_3$	PhO
45d	3,5-$(CF_3)_2C_6H_3$	PhO
45e	3,5-$(CF_3)_2C_6H_3$	Br
45f	1-$C_{10}H_7$	PhO
45g	2-$C_{10}H_7$	PhO
45h	3,5-(*t*-Bu)$_2C_6H_3$	PhO
45i	3,5-$Ph_2C_6H_3$	PhO
45j	3,5-[3,5-$(CF_3)_2C_6H_3$]$_2C_6H_3$	PhO
45k	3,5-[3,5-(*t*-Bu)$_2C_6H_3$]$_2C_6H_3$	PhO

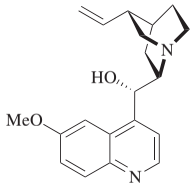


	R^1	R^2	X
46a	H	Ph	F
46b	H	Ph	Br
46c	H	2-IC_6H_4	Br
46d	H	3-$MeOC_6H_4$	F
46e	H	4-$MeOC_6H_4$	F
46f	H	2-$CF_3OC_6H_4$	Br
46g	H	3,5-$(MeO)_2C_6H_3$	F
46h	H	2-$CF_3C_6H_4$	Br
46i	H	3-$CF_3C_6H_4$	Br
46j	H	4-$CF_3C_6H_4$	F
46k	H	4-$CF_3C_6H_4$	Br
46l	H	2,4-$(CF_3)_2C_6H_3$	F

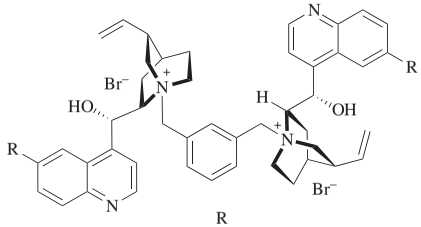
	R^1	R^2	X
46m	H	2,4-$(CF_3)_2C_6H_3$	Br
46n	H	2,5-$(CF_3)_2C_6H_3$	Br
46o	H	3,5-$(CF_3)_2C_6H_3$	F
46p	H	3,5-$(CF_3)_2C_6H_3$	Cl
46q	H	3,5-$(CF_3)_2C_6H_3$	Br
46r	MeO	3,5-$(CF_3)_2C_6H_3$	Br
46s	H	1-$C_{10}H_7$	F
46t	H	4-PhC_6H_4	F
46u	H	3,5-(*t*-Bu)$_2C_6H_3$	Br
46v	H	9-anthryl	F
46w	MeO	3,5-[3,5-$(CF_3)_2C_6H_3$]$_2C_6H_3$	Br



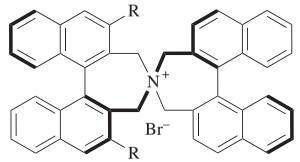
47, quinine



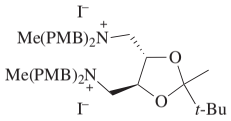
48, quinidine



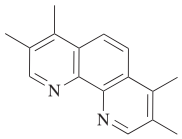
	R
49a	H
49b	MeO



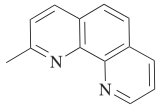
50 R = 3,4,5-$(CF_3)_3C_6H_2$



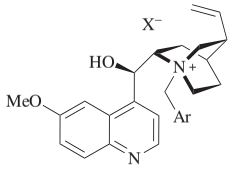
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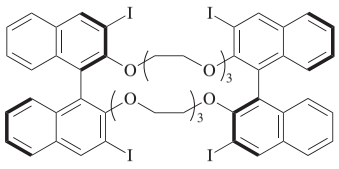
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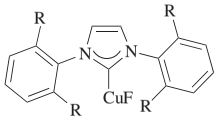
53



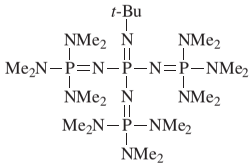
	Ar	X
54a	3,5-$(MeO)_2C_6H_3$	Cl
54b	3,5-$(CF_3)_2C_6H_3$	Br
54c	3,5-(*t*-Bu)$_2C_6H_3$	Br
54d	9-anthryl	Br



55

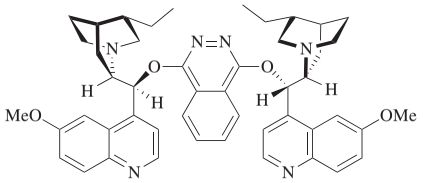


56 R = *i*-Pr

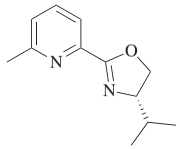


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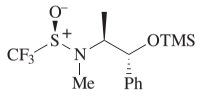
CHART 1. CATALYSTS, REAGENTS, AND INITIATORS USED IN TABLES (*Continued*)



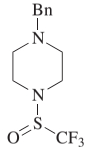
58, $(DHQD)_2PHAL$



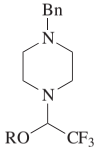
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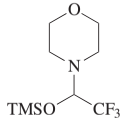
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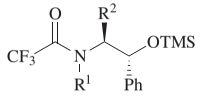
61



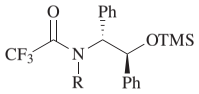
	R
62a	H
62b	TMS



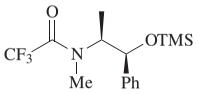
63



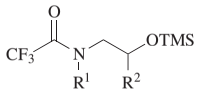
	R^1	R^2
64a	Me	Me
64b	n-C_5H_{11}	Me
64c	Me	Ph
64d	Bn	Me
64e	Bn	Ph



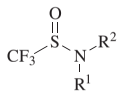
	R
65a	Me
65b	Bn



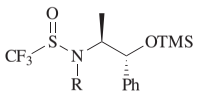
66



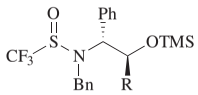
	R^1	R^2
67a	Me	H
67b	Me	Ph
67c	Bn	H



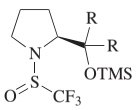
	R^1	R^2
68a	Me	Ph
68b	Bn	Bn



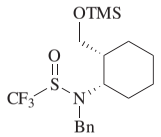
	R	dr
69a	Me	100:0
69b	Bn	92:8



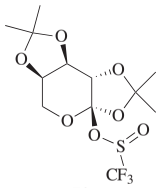
	R	dr
70a	H	92:8
70b	Ph	73:27



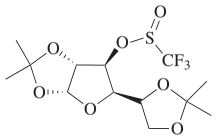
	R	er
71a	H	62:38
71b	Ph	100:0



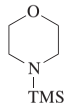
72 dr 92:8



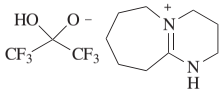
73



74



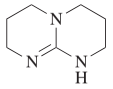
75



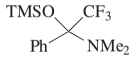
76



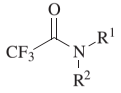
77



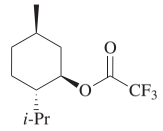
78



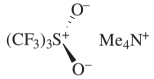
79



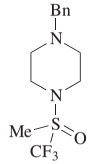
	R^1	R^2
80a	Me	Me
80b	$-(CH_2)_2O(CH_2)_2-$	
80c	$-(CH_2)_5-$	
80d	*i*-Pr	*i*-Pr
80e	*n*-Bu	*n*-Bu
80f	Me	Bu



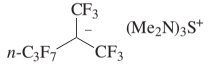
81



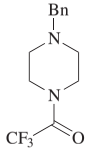
82



83



84



85

TABLE 1. PERFLUOROALKYL ADDITION TO ALKENES

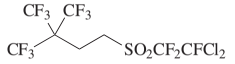
Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_2



$(CF_3)_3CH$ (1 eq), Et_3N (2.5 mol %), rt, 24 h

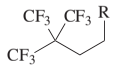


(61) 87

C_3

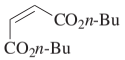


$(CF_3)_3CH$ (1.05 eq), Et_3N (*x* eq)

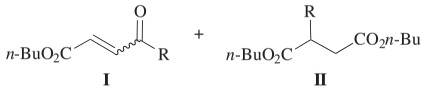


R	*x*	Temp (°)	Time		
NC	0.24	100	77 h	(66)	85, 86
CHO	0.14	0	o/n	(20)	
MeO_2C	0.46	100	20 d	(30)	

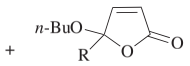
C_4



RX, MeLi/LiBr, additive, Et_2O, –78°, 1 h



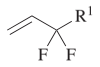
I + **II**



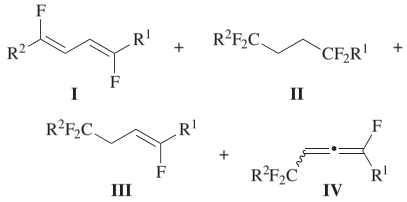
+ **III** (—) 625

R	X	Additive	**I**	(*E*)/(*Z*)	**II**	**I/II/III**
n-C_8F_{17}	I	—	(46)	10:1	(21)	—
n-C_6F_{13}	I	BF_3•Et_2O (1 eq)	(91)	5:6	(—)	56:24:5
n-C_4F_9	$Sa(n\text{-}Bu)_3$	—	(—)	10:1	(—)	33:10:0

$C_{4–10}$



R^2CF_2I, Cu, DMF

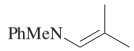


I + **II** + **III** + **IV**

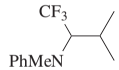
792

R^1	R^2	Temp (°)	Time (h)	**I**	**II**	**III**	**IV**
CF_3	*n*-C_5F_{11}	150	18	(8)	(77)	(—)	(—)
CF_3	*n*-C_5F_{11}	100	48	(25)	(15)	(45)	(—)
n-C_5F_{11}	*n*-C_3F_7	150	—	(—)	(—)	(—)	(—)
n-C_5F_{11}	*n*-C_5F_{11}	150	—	(—)	(—)	(—)	(—)
n-C_5F_{11}	*n*-C_5F_{11}	100	48	(10)	trace	(—)	(60)
n-C_5F_{11}	*n*-C_7F_{15}	150	—	(—)	(—)	(—)	(—)
n-C_7F_{15}	*n*-C_3F_7	150	—	(—)	(—)	(—)	(—)
n-C_7F_{15}	*n*-C_7F_{15}	150	—	(—)	(—)	(—)	(—)

C_4



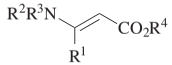
$TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 18 h



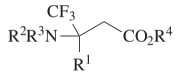
(81)

566

$C_{4–9}$



A: $TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 18 h; *or*
B: $TMSCF_3$ (3 eq), TfOH (1.6 eq), KHF_2 (1.5 eq), DMF (3 eq), MeCN, rt, 18 h



566

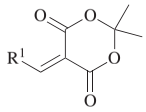
R^1	R^2	R^3	R^4	**A**	**B**
Me	H	Bn	Me	(36)	(55)
Me	$-(CH_2)_3-$		Me	(—)	(80)
Me	$-(CH_2)_2O(CH_2)_2-$		Me	(—)	(84)
$MeOCH_2$	$-(CH_2)_3-$		Me	(74)	(72)
Ph	$-(CH_2)_3-$		Et	(71)	(87)
Ph	$-(CH_2)_2O(CH_2)_2-$		Et	(—)	(75)

TABLE 1. PERFLUOROALKYL ADDITION TO ALKENES (*Continued*)

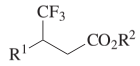
Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{4–12}$



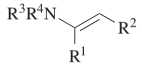
1. $PhSO_2CF_3$ (2.5 eq), $HgCl_2$ (6 mol %), Mg (2.5 eq), DMF, rt; 75°, 3 h
2. 7 M HCl, rt; 118°, 1 h
3. R^2X, K_2CO_3, DMF, rt, 2 h



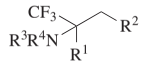
178

R^1	R^2	X		R^1	R^2	X	
MeO	Bn	Br	(53)	4-$O_2NC_6H_4$	Me	I	(32)
2-furyl	Me	I	(52)	4-$MeOC_6H_4$	Me	I	(69)
2-thienyl	Me	I	(54)	2-MeC_6H_4	Me	I	(65)
Ph	Me	I	(63)	4-MeC_6H_4	Me	I	(68)
4-FC_6H_4	Me	I	(45)	2,6-$Me_2C_6H_3$	Me	I	(53)

$C_{5–8}$



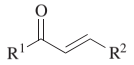
A: $TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 18 h; *or*
B: $TMSCF_3$ (3 eq), TfOH (1.6 eq), KHF_2 (1.5 eq), DMF (3 eq), MeCN, rt, 18 h



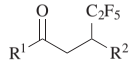
566

R^1	R^2	R^3	R^4	**A**	**B**
Et	Me	$–(CH_2)_2O(CH_2)_2–$		(71)	(—)
H	Ph	Et	Et	(59)	(82)
Ph	H	$–(CH_2)_2O(CH_2)_2–$		(86)	(—)

$C_{5–9}$



C_2F_5Li, **26** (1.5 eq), hexane, CH_2Cl_2, –78°



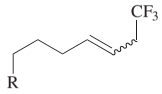
793

R^1	R^2	Time (h)	
$–(CH_2)_2–$		0.5	(51)
$–(CH_2)_3–$		1	(68)
Ph	H	1	(78)

C_{6-18}

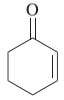


$TMSCF_3$ (4 eq), $PhI(OAc)_2$ (2 eq),
CuTC (30 mol %), NMP, 80°, 24 h

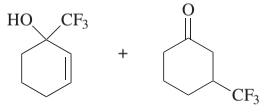


R		(*E*)/(*Z*)	
2-furylCO$_2$	(67)	88:12	298
4-O$_2$NC$_6$H$_4$O	(54)	94:6	
PhCO$_2$	(87)	100:0	
4-BrC$_6$H$_4$CO$_2$	(76)	93:7	
2-phthalimidyl	(63)	86:14	
	(34)[a]	—	
MeO$_2$C(CH$_2$)$_4$	(81)	90:10	
1-C$_{10}$H$_7$	(56)	87:13	
1-indolylCO(CH$_2$)$_3$	(74)	88:12	

C_6



1. $TMSCF_3$ (*x* eq), initiator (*y* eq),
Lewis acid (1 eq)
2. HCl, H_2O



I (—) **II**

290

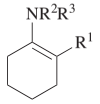
x	Initiator	*y*	Lewis Acid	Solvent	Temp (°)	Time (h)	Conv **I** (%)	Conv **II** (%)	**II**
2	TMAF	1	—	THF	rt	4	84	—	(—)
3	TMAF	2.5	$(PhO)_3Al$	CH_2Cl_2	rt	4	59	—	(—)
3	TMAF	2.5	**25**	CH_2Cl_2	rt	18	3	5	(—)
3	TMAF	1	**26**	CH_2Cl_2	rt	4	—	25	(—)
3	TMAF	2	**26**	CH_2Cl_2	rt	4	—	48	(—)
3	TMAF	3	**26**	CH_2Cl_2	–35	5	3	53	(—)
3	TMAF	3	**26**	CH_2Cl_2	rt	4	1	55	(—)
2	*t*-BuOK	3	**26**	CH_2Cl_2	rt	19	—	56	(46)

TABLE 1. PERFLUOROALKYL ADDITION TO ALKENES (*Continued*)

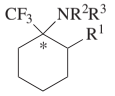
Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{6-7}



A: $TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 18 h; *or*
B: $TMSCF_3$ (3 eq), TfOH (1.6 eq), KHF_2 (1.5 eq), DMF (3 eq), MeCN, rt, 18 h



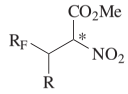
566

R^1	R^2	R^3	**A**	**B**	*CF_3/R^1 *trans/cis*
H	$-(CH_2)_2O(CH_2)_2-$		(88)	(—)	—
EtO_2C	$-(CH_2)_3-$		(78)	(90)	88:12

C_{7-13}



$TMSR_F$ (1.5 eq), activator (1.2 eq), 3 h



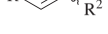
287

R	dr	R_F	Activator	Solvent	Temp (°)		*dr
2-furyl	55:45	CF_3	NaOAc	DMF	rt	(<1)	—
2-furyl	55:45	CF_3	$(n\text{-Bu})_4NOAc$	CH_2Cl_2	–20	(37)	55:45
2-thienyl	57:43	CF_3	NaOAc	DMF	rt	(32)	62:38
2-thienyl	57:43	CF_3	$(n\text{-Bu})_4NOAc$	CH_2Cl_2	–20	(68)	45:55
Ph	62:38	CF_3	NaOAc	DMF	rt	(67)	50:50
Ph	62:38	CF_3	$(n\text{-Bu})_4NOAc$	CH_2Cl_2	–20	(82)	50:50
Ph	62:38	C_2F_5	NaOAc	DMF	rt	(88)	58:42
Ph	62:38	C_6F_5	NaOAc	DMF	rt	(99)	55:45
4-ClC_6H_4	96:4	CF_3	$(n\text{-Bu})_4NOAc$	CH_2Cl_2	–20	(84)	55:45
4-$MeOC_6H_4$	52:48	CF_3	NaOAc	DMF	rt	(67)	50:50
4-$MeOC_6H_4$	52:48	CF_3	$(n\text{-Bu})_4NOAc$	CH_2Cl_2	–20	(82)	50:50
1-$C_{10}H_7$	63:37	CF_3	$(n\text{-Bu})_4NOAc$	CH_2Cl_2	–20	(70)	50:50

C_{8-10}



R^2I, Cu, DMF, 120°, 20 h

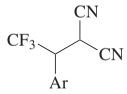


R^1	R^2		
n-C_6F_{13}	n-C_4F_9	(66)	
n-C_6F_{13}	n-C_6F_{13}	(70)	794
n-C_6F_{13}	n-C_8F_{17}	(60)	
n-C_8F_{17}	n-C_4F_9	(70)	
n-C_8F_{17}	n-C_8F_{17}	(60)	

C_{8-12}



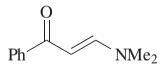
1.$PhSO_2CF_3$ (2 eq), $HgCl_2$ (6 mol %), Mg (2 eq), DMF, –50°; rt, 3 h
2. HCl



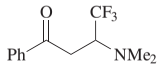
178

R		R		R	
2-furyl	(59)	4-FC_6H_4	(63)	3-MeC_6H_4	(76)
2-thienyl	(60)	4-$O_2NC_6H_4$	(52)	4-MeC_6H_4	(70)
Ph	(64)	4-$MeOC_6H_4$	(77)	3-$CF_3C_6H_4$	(60)
2-FC_6H_4	(57)	2-MeC_6H_4	(73)	2,6-$Me_2C_6H_3$	(60)
3-FC_6H_4	(58)				

C_9



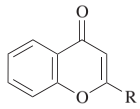
CF_3H, $(TMS)_3N$ (1.5 eq), TMAF (1.5 eq), DMF, –10°, 1 h



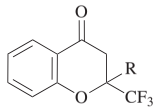
(36)

73

C_{9-10}



1. $TMSCF_3$ (2 eq), initiator (3 eq), **26** (1 eq), CH_2Cl_2, rt
2. HCl, H_2O



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R	Initiator	Time (h)	Conv (%)	
H	t-BuOK	12	48	(30)
CF_3	TMAF	16	72	(—)

TABLE 1. PERFLUOROALKYL ADDITION TO ALKENES (*Continued*)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{9-10}

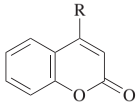


TMSCF$_3$ (4 eq), PhI(OAc)$_2$ (2 eq), CuTC (30 mol %), NMP, 80°, 24 h

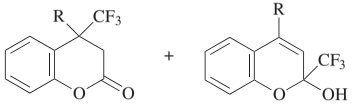


R		(*E*)/(*Z*)
4-MeOC$_6$H$_4$	(61)	100:0
Bn	(76)	91:9

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1. TMSCF$_3$ (2 eq), initiator (*x* eq), Lewis acid (1 eq)
2. HCl, H$_2$O

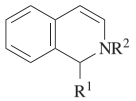


I + **II** (—)

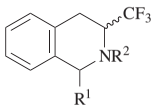
290

R	Initiator	*x*	Lewis Acid	Solvent	Temp (°)	Conv **I** (%)	**I**	Conv **II** (%)
H	TMAF	1	—	DME	–30 to rt	8	(—)	53
H	*t*-BuOK	3	**26**	CH_2Cl_2	rt	35	(20)	—
CF_3	TMAF	1	—	DME	–30 to rt	1	(—)	44
CF_3	TMAF	1	**26**	CH_2Cl_2	rt	61	(—)	6

C_{9-15}



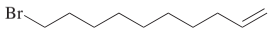
1. KHF_2 (1.5 eq), MeCN, DMF, rt
2. TfOH (1.6 eq), 0°, 5 min
3. TMSCF$_3$ (3 eq), 0°; 20°, 18 h



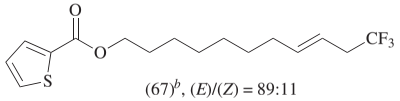
R^1	R^2		*trans*/*cis*
H	Me	(17)	—
Me	Me	(50)	1:1
i-Pr	Me	(64)	1:1
i-Pr	PMB	(54)	1.3:1
Ph	Me	(52)	1.5:1

567

C_{10}

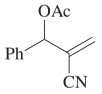


TMSCF$_3$ (4 eq), PhI(OAc)$_2$ (2 eq), CuTC (30 mol %), NMP, 80°, 24 h

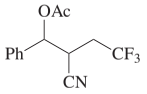


(67)[b], (*E*)/(*Z*) = 89:11

298

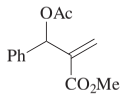


1. TMSCF$_3$ (1.5 eq), (*n*-Bu)$_4$NOAc (5 mol %), MeCN, –20°; 0°, 18 h
2. HCl

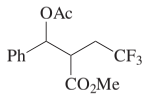


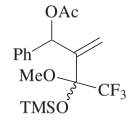
(40)

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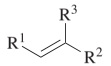


1. $TMSCF_3$ (1.5 eq), $(n\text{-}Bu)_4NOAc$ (5 mol %), DMF, –20°, 18 h
2. HCl

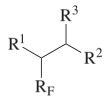


(15) +  (15) 295

$C_{10–14}$



$TMSR_F$ (1.5 eq), NaOAc (2 eq), DMF, rt, 3 h

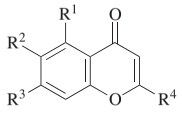


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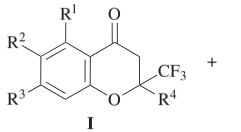
R^1	R^2	R^3	R_F	
Ph	NC	NC	CF_3	(94)
Ph	NC	NC	C_2F_5	(97)
3-BrC_6H_4	NC	NC	CF_3	(83)
4-$O_2NC_6H_4$	NC	NC	CF_3	(75)
2-$MeOC_6H_4$	NC	NC	CF_3	(96)
4-$MeOC_6H_4$	NC	NC	CF_3	(95)

R^1	R^2	R^3	R_F	
Ph	NC	MeO_2C	CF_3	(66)[c]
3,4-$(MeO)_2C_6H_3$	NC	NC	CF_3	(98)
Ph	MeO_2C	MeO_2C	CF_3	trace
(*E*)-PhCH=CH	NC	NC	CF_3	(87)
1-$C_{10}H_7$	NC	NC	CF_3	(84)

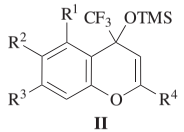
$C_{10–11}$



1. $TMSCF_3$ (1.4 eq), TMAF (cat.), THF
2. HCl, H_2O, rt, 15 min



I

+ 

II

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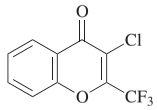
R^1	R^2	R^3	R^4	Temp (°)	Time (h)	**I**	**II**
H	H	H	CF_3	–10	4	(86)	(11–12)
H	MeO	H	CF_3	–30	24	(76)	(—)
H	H	MeO	CF_3	–30	24	(67)	(—)
H	MeO	H	CF_2H	–30	24	(50)	(—)
MeO	H	MeO	CF_3	–30	24	(64)	(—)
H	Me	H	CF_3	–10	4	(61)	(11–12)

TABLE 1. PERFLUOROALKYL ADDITION TO ALKENES (*Continued*)

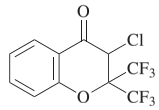
Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

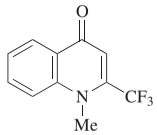
C_{10}



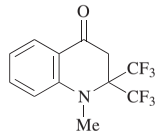
1. $TMSCF_3$ (1.4 eq), TMAF (cat.), THF, rt, 24 h
2. HCl, H_2O, rt, 15 min



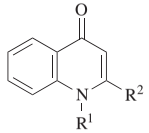
(58) 292



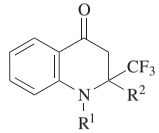
1. $TMSCF_3$ (1.4 eq), TMAF (cat.), THF, –30°, 24 h
2. HCl, H_2O, rt, 15 min



(53) 292



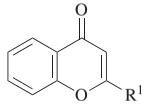
1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°; rt, 12 h
2. HCl, H_2O, rt, 15 min



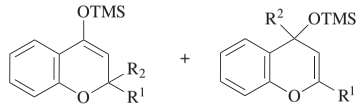
R^1	R^2	
Me	CF_3	(53)
Ph	CF_2H	(42)
Ph	CF_3	(48)

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C_{10-11}



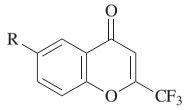
$TMSR^2$ (1.2 eq), TMAF (2 mol %), THF, 4 h



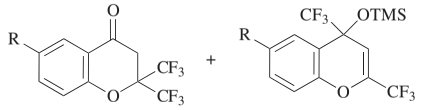
I (—) + **II** (—)

R^1	R^2	Temp (°)	**I/II**
CF_3	CF_3	–30	92:8
CF_3	CF_3	0	90:10
CF_3	CF_3	rt	87:13
CF_3	C_2F_5	–30	82:18
CF_3	C_2F_5	0	77:23
CF_3	C_2F_5	rt	72:28
C_2F_5	CF_3	0	73:27

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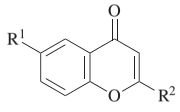
1. $TMSCF_3$, TMAF, THF, –10°, 4 h
2. HCl, H_2O



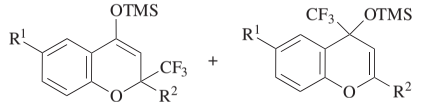
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I **II** (—)

R	**I**	**I/II**
H	(86)	—
Me	(61)	90:10



$TMSCF_3$ (1.4 eq), initiator (3–4 mol %), THF, 4–24 h

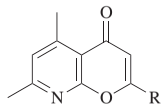


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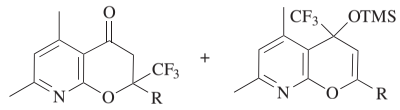
I (—) **II** (—)

R^1	R^2	Initiator	Temp (°)	**I/II**
H	CF_2H	TMAF	–30	100:0
MeO	CF_3	*t*-BuOK	–30	47:53
MeO	CF_3	TMAF	–30	93:7
H	C_2F_5	TMAF	–30	80:20
H	C_2F_5	TMAF	0	73:27
MeO	C_2F_5	TMAF	–30	86:14

C_{11}



1. $TMSCF_3$ (1.56 eq), TMAF (cat.), THF, –30°; rt, 12 h
2. HCl, H_2O, rt, 15 min

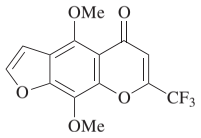
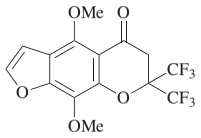
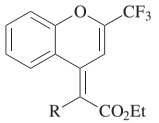
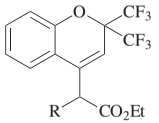
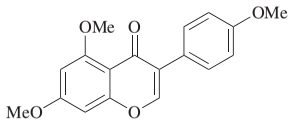
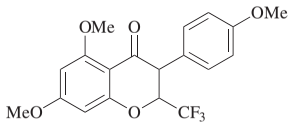
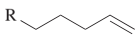
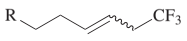
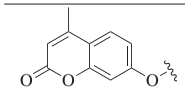
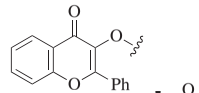
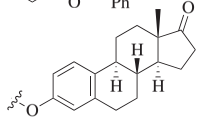


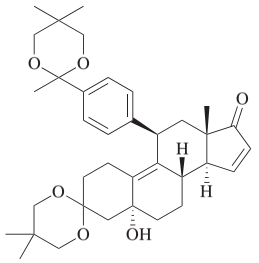
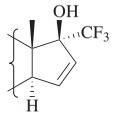
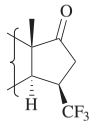
291

I **II** (—)

R	**I**	**I/II**
CF_2H	(35)	—
CF_3	(27)	55:45

TABLE 1. PERFLUOROALKYL ADDITION TO ALKENES (*Continued*)

Alkene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{12} 	1. $TMSCF_3$ (1.4 eq), TMAF (cat.), THF, –30°, 24 h 2. HCl, H_2O, rt, 15 min	 (70)	292
C_{13} 	1. $TMSCF_3$ (2 eq), TMAF (1.5 eq), THF, –30°, 24 h 2. HCl, H_2O, 0°	 R: NC (71); EtO_2C (80)	294
C_{15} 	1. $TMSCF_3$, TMAF (cat.), 0°, 24 h 2. HCl, H_2O	 (—)	258
C_{15-23} 	$TMSCF_3$ (4 eq), $PhI(OAc)_2$ (2 eq), CuTC (30 mol %), NMP, 80°, 24 h	 R: (48) 86:14;  (71) 100:0;  (72) 89:11; 	298

C_{26}		$TMSCF_3$ (4 eq), TBAF (2 eq), THF, 0°; rt, 3 h		(14)	+		(33)	526

[a] The yield was determined by ^{19}F NMR spectroscopy.

[b] The yield is based on the catalyst.

[c] The product was formed as a mixture of diastereomers in a 2.2:1 ratio.

TABLE 2. PERFLUOROALKYL ADDITION TO ALKYNES

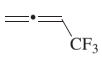
Alkyne	Conditions	Product(s) and Yield(s) (%)	Refs.

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

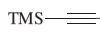
C_3



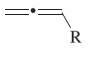
CF_3CdBr, CuI, DMF, –78 to 20°



(43) 267

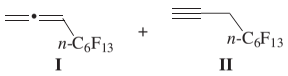


"RCu"[a], DMSO, 15–20°



(70–75) R = *n*-C_6F_{13}, *n*-C_8F_{17} 301

1. "*n*-$C_6F_{13}Cu$"[a], DMSO, 15–20°
2. (*n*-Bu)$_4$NF, THF or MeCN, 0°



I + **II** (49), **I**/**II** = 1:1 301

$C_{3–8}$

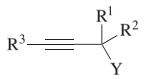


R^2I, Zn, CuI, THF, ultrasound, 2 h

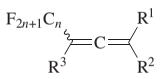


R^1	R^2		(*E*)/(*Z*)
$HOCH_2$	CF_3	(61)	32:68
$HOCH_2$	*i*-C_3F_7	(65)	33:67
$HOCH_2$	*n*-C_3F_7	(66)	30:70
$HOCH_2$	*n*-C_4F_9	(74)	27:73
$HOCH_2$	*n*-C_6F_{13}	(55)	25:75
n-Bu	CF_3	(71)	24:76
Ph	CF_3	(65)	28:72
Ph	*i*-C_3F_7	(52)	31:69

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"*n*-$C_nF_{2n+1}Cu$", DMF (*n* = 1) or DMSO (*n* = 3, 6, 8), overnight



R^1	R^2	R^3	Y	Temp (°)	*n* = 1	*n* = 3	*n* = 6	*n* = 8
H	H	H	TsO	0 to rt	(68)	(41)	(49)	(30)
H	Me	H	TsO	0 to rt	(65)	(67)	(58)	(55)
Me	Me	TMS	Cl	–78 to rt	(52)	(—)	(—)	(—)
Me	Me	H	Cl	0 to rt	(73)	(68)	(66)	(60)
Me	Me	EtO_2C	Cl	–20 to rt	(57)	(—)	(—)	(—)
–$(CH_2)_5$–		H	Cl	0 to rt	(66)	(64)	(54)	(54)

300

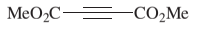
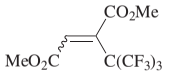
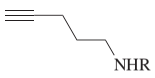
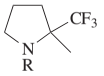
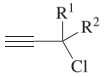
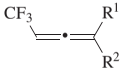
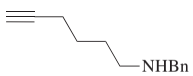
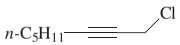
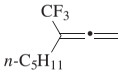
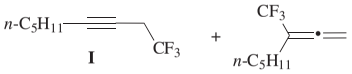
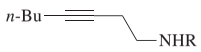
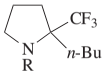
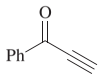
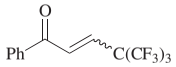
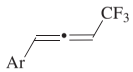
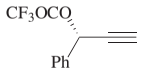
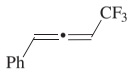
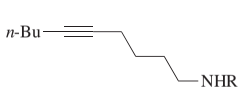
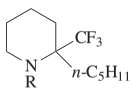
C_4 	$(CF_3)_3CH$ (1.3 eq), Et_3N (0.37 eq), Et_2O, rt, 2.5 h		(92)	88
$C_{5–13}$ 	$TMSCF_3$ (2 eq), AgF (1.5 eq), H_2O (1 eq), dioxane, MW, 100°, 40 min		R: Ph (95) —; Bn (92) —; (*R*)-PhCHMe (90) 77:23	544
$C_{5–10}$ 	$(PPh_3)_3CuCF_3$ (1 eq), THF, 16 h		R^1 / R^2 / Temp (°): Me Me 50 (86)[b]; –$(CH_2)_4$– 22 (87); Bn H 22 (92)	303
C_6 	$TMSCF_3$ (2 eq), AgF (1.5 eq), H_2O (1 eq), dioxane, MW, 100°, 40 min		(88)	544
C_8 	$(PPh_3)_3CuCF_3$ (1 eq), THF, 22°, 16 h		(67)	303
	$TMSCF_3$ (1.5 eq), KF (1.5 eq), CuTC (5 mol %), THF	 **I** + **II**	Temp / Time (h) / **I** / **II**: rt 72 (89) (5); 60° 20 (79) (6)	302
	$TMSCF_3$ (2 eq), AgF (1.5 eq), H_2O (1 eq), dioxane, MW, 100°, 40 min		R: Ph (90); Bn (91)	544

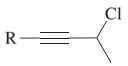
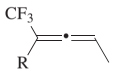
TABLE 2. PERFLUOROALKYL ADDITION TO ALKYNES (*Continued*)

Alkyne	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_9 	$(CF_3)_3CH$ (1.86 eq), Et_3N (0.3 eq), benzene, 1.5 h	 (50)	88
C_{9-13} 	$(PPh_3)_3CuCF_3$ (1 eq), THF, 22°, 16 h		303

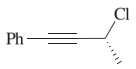
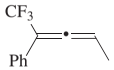
Ar	Y	
Ph	Cl	(68)[c]
Ph	CF_3CO_2	(85)[c]
4-FC_6H_4	CF_3CO_2	(86)
4-BrC_6H_4	CF_3CO_2	(63)[c]
4-$MeOC_6H_4$	CF_3CO_2	(52)
4-*t*-BuC_6H_4	CF_3CO_2	(58)[c]

C_9  er 95.0:5.0	$(PPh_3)_3CuCF_3$ (1 eq), THF, 4°, 16 h	 (70) er 85.0:15.0	303
C_{10} 			544

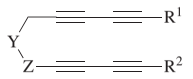
R	
CH_2=$CHCH_2$	(87)
Ph	(89)
Bn	(92)

C_{10-12} 	$TMSCF_3$ (1.5 eq), KF (1.5 eq), CuTC (5 mol %), THF		302

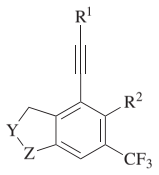
R	Temp (°)	Time (h)	
Ph	60	20	(89)
4-ClC_6H_4	60	20	(81)
4-$MeOC_6H_4$	40	48	(77)
4-MeC_6H_4	60	20	(79)
$PhCH_2CH_2$	60	20	(71)

C_{10} 	$TMSCF_3$ (1.5 eq), KF (1.5 eq), CuTC (5 mol %), THF, 60°, 20 h	 (83) no chirality transfer	302

$C_{10–42}$

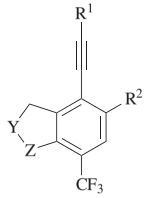


1. AgF (1.5 eq), $TMSCF_3$ (2 eq), toluene, rt, 30 min
2. Substrate (1 eq), MeCN, 90°, 4 h



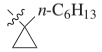
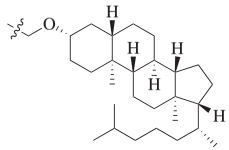
I

+

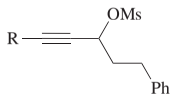


II

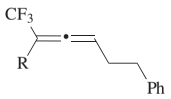
311

R^1	R^2	Y	Z	**I + II**	**I/II**
TMS	TMS	TsN	CH_2	(0)	—
H	*n*-Bu	CH_2	TsN	(<10)	—
n-Bu	*n*-Bu	CH_2	TsN	(76)	60:40
$Cl(CH_2)_3$	Ph	CH_2	TsN	(75)	100:0
n-Pr	4-$CF_3C_6H_4$	CH_2	TsN	(78)	100:0
n-C_6H_{13}	*n*-C_6H_{13}	O	CH_2	(76)	50:50
	Ph	CH_2	TsN	(0)	—
	*n*-Bu	CH_2	TsN	(67)	100:0

$C_{11–15}$



$TMSCF_3$ (2 eq), CuI (1.1 eq), KF (2 eq), DMF/HMPA (1:1), 60°, 4 h



R	
TMS	(70)
Me	(89)
n-Bu	(93)

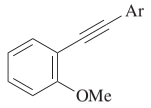
323

TABLE 2. PERFLUOROALKYL ADDITION TO ALKYNES (*Continued*)

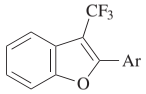
Alkyne	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{14–20}$

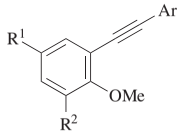


1. Iodine (1 eq), 40°, 6 h
2. $TMSCF_3$ (5 eq), CuI (1 eq), KF (2 eq), DMF, 100°, 16 h

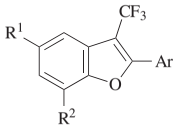


Ar		Refs.
Ph	(89)	795
3-FC_6H_4	(55)	
4-FC_6H_4	(61)	
3-ClC_6H_4	(57)	
4-ClC_6H_4	(64)	
3-$MeOC_6H_4$	(68)	
4-$MeOC_6H_4$	(76)	
3-MeC_6H_4	(67)	
4-MeC_6H_4	(72)	
4-*t*-BuC_6H_4	(67)	
4-PhC_6H_4	(57)	

$C_{14–18}$



1. Iodine (1 eq), 40°, 6 h
2. $TMSCF_3$ (5 eq), CuI (1 eq), KF (2 eq), DMF



795

R^1	R^2	Ar	Temp (°)	Time (h)	
F	F	Ph	100	16	(51)
Cl	H	Ph	100	16	(61)
MeO	H	Ph	100	16	(72)
MeO	H	4-MeC_6H_4	100	16	(70)
Me	H	Ph	100	16	(81)
NC	H	Ph	140	36	(49)
MeO_2C	H	Ph	100	16	(62)
t-Bu	H	Ph	100	16	(74)

[a] The reagent is a perfluoroalkylcopper species that contains R_FCu, sometimes in equilibrium with $[(R_F)_2Cu]^-$ and $[R_FCuX]^-$ (X = halogen).

[b] The yield was determined by NMR spectroscopy.

[c] At 50° the propargyl isomer was formed; see Table 5A.

TABLE 3. PERFLUOROALKYL ADDITION TO ARENES

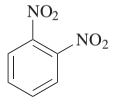
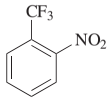
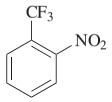
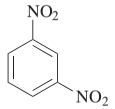
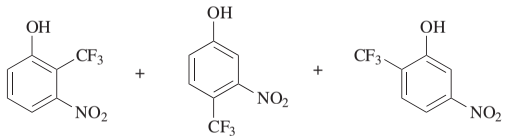
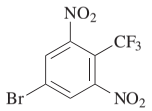
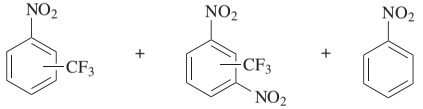
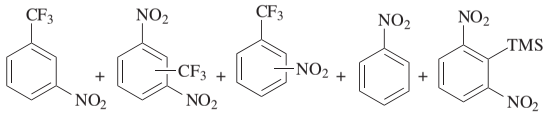
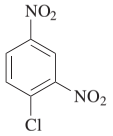
Arene	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_6			
	$TMSCF_3$ (2.8 eq), KF (5 eq), DMA, 50°, "few" min	 (—) 16% conv	306
	$TMSCF_3$, KF, DMA	 (16)	305
	1. $TMSCF_3$ (1.2 eq), TASF (1 eq), THF, pyridine, –70°, 5 min 2. H_2O (1 eq), DMDO (1.2 eq), acetone, 15 min 3. HCl, H_2O	 (47) (18) (13)	307
	1. $TMSCF_3$ (1.2 eq), TASF (1 eq), THF, pyridine, –70°, 5 min 2. Br_2 (1.2 eq), THF, –70°, 5 min 3. Et_3N (7.2 eq)	 (46)	307
	$TMSCF_3$ (2.8 eq), KF (5 eq), DMA, 50°, "few min"	 two isomers (—) 14% and 1% conv; two isomers (—) 6% and 4% conv; trace	306
	$TMSCF_3$, KF, DMA	 (—) (—) (—) (—) (—)	305

TABLE 3. PERFLUOROALKYL ADDITION TO ARENES (*Continued*)

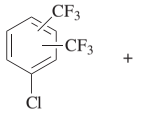
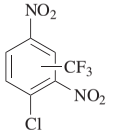
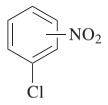
Arene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_6

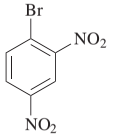


TMSCF$_3$ (2.8 eq), KF (5 eq), DMA, 50°, "few" min

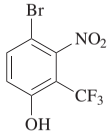
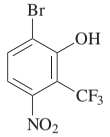
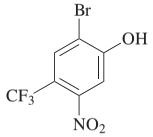

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+


(—) 5% conv (—) 18% conv (—) 5% conv

306

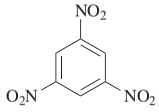


1. TMSCF$_3$ (1.2 eq), TASF (1 eq), THF, pyridine, –70°, 5 min
2. H_2O (1 eq), DMDO (1.2 eq), acetone, 15 min
3. HCl, H_2O

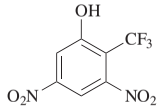
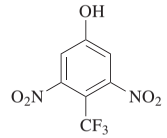
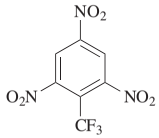

+

+


(29) (6) (11)

307



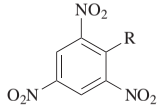
1. TMSCF$_3$ (1.2 eq), TASF (1 eq), THF, pyridine, –70°, 5 min
2. H_2O (1 eq), DMDO (1.2 eq), acetone
3. HCl, H_2O


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+


(22) (31) (33)

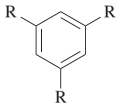
307

1. RCO_2K (3 eq), DMF or DMSO, 150°, 1 h
2. *t*-BuOCl
3. HCl, H_2O

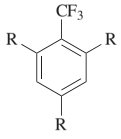


R	
CF_3	(40)
C_2F_5	(—)

796

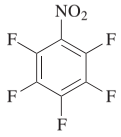


1. TMSCF$_3$ (*x* eq), Me_4NF (1.2 eq), DME, –60°; –50°, 1 h; to rt, o/n
2. *t*-BuOCl (1.3 eq), DME, 5°, 5–10 min; to rt

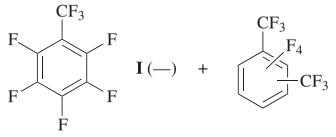


R	*x*	Step 1	Step 2
O_2N	1.3	(95)	(85)
FO_2S	2.5	(65)[a]	(75)
$CF_3CH_2O_3S$	1.3	(95)	(90)

308

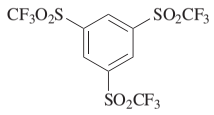


TMSCF$_3$, TBAF (1 eq), THF, 0°

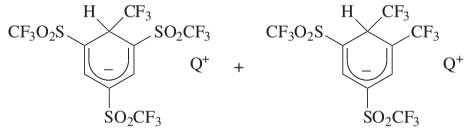


I (—) + **II** (—), **I/II** = 9:1

304



QA, DME, –60°

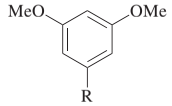


I **II**

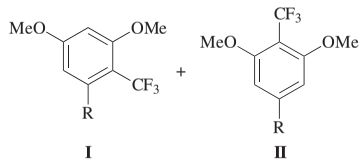
QA	Conv (**I** + **II**) (%)	**I** + **II**	**I/II**
[Me$_3$Si(CF$_3$)$_2$] [Me$_4$N]	60	(—)[b]	4:1
[Me$_3$Si(CF$_3$)$_2$] [Cs(15-c-5)$_2$]	95	(65)[a,b]	4:1

308

C$_{6-8}$



1. Pb(OAc)$_4$ (1.2 eq), K$_3$PO$_4$ (2.4 eq), benzoquinone (20 mol %), 4 Å MS, MeCN, inverse addition
2. TMSCF$_3$ (2.4 eq), 85°, 6 h

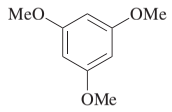


I **II**

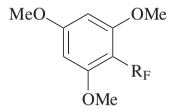
R	**I** + **II**	**I/II**
H	(59)	58:42
Cl	(79)	76:24
Br	(50)	50:50
AcO	(56)	60:40
Ac	(56)	77:23

797

C$_6$



1. Pb(OAc)$_4$ (1.2 eq), K$_3$PO$_4$ (2.4 eq), benzoquinone (20 mol %), 4 Å MS, MeCN, inverse addition
2. TMSR$_F$ (2.4 eq), 85°, 6 h



R$_F$	
CF$_3$	(78)
n-C$_3$F$_7$	(86)

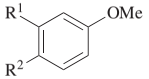
797

TABLE 3. PERFLUOROALKYL ADDITION TO ARENES (*Continued*)

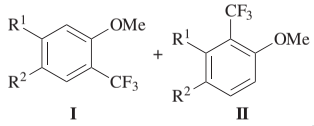
Arene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_6



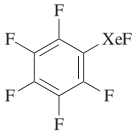
1. $Pb(OAc)_4$ (1.2 eq), K_3PO_4 (2.4 eq), benzoquinone (20 mol %), 4 Å MS, MeCN, inverse addition
2. $TMSCF_3$ (2.4 eq), 85°, 6 h



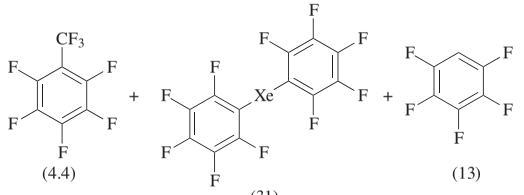
I **II**

R^1	R^2	**I + II**	**I/II**
MeO	MeO	(73)	92:8
–OCH_2O–		(43)	89:11

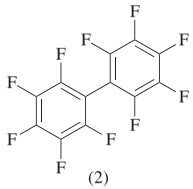
797



$TMSCF_3$ (1 eq), TMAF (0.3 eq), CH_2Cl_2, –78°



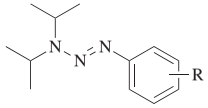
(4.4) (31) (13)



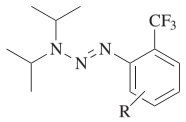
(2)

730

$C_{6–10}$



$TMSCF_3$ (2 eq), AgF (4 eq), *n*-C_6F_{14}, 100°, 4 h



I

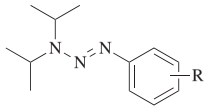
+ 3- and/or 4-mono- and 2,6-bis(trifluoromethyl)ated products

798

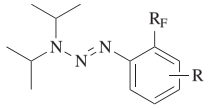
R	**I**
4-F	(62)
4-Cl	(59)
2-Br	(56)
4-Br	(65)
2-I	(46)
4-I	(64)

R	**I**
2-MeO	(39)
4-EtO_2C	(53)
4-NC-6-Me	(74)
4-*t*-Bu	(56)

C_{6-8}

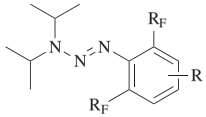


$TMSR_F$ (2 eq), AgF (4 eq), *n*-C_6F_{14}, 100°, 4 h



I

+



II

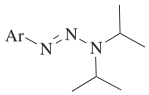
799

R	R_F	**I**	**II**
4-F	C_2F_5	(64)	trace
4-F	*n*-C_3F_7	(49)	(7)
4-Cl	C_2F_5	(43)	(12)
4-Cl	*n*-C_3F_7	(52)	(8)
4-Br	C_2F_5	(53)	(10)

R	R_F	**I**	**II**
4-Br	*n*-C_3F_7	(64)	(13)
2-I	C_2F_5	(43)	(—)
2-I	*n*-C_3F_7	(41)	(—)
4-I	C_2F_5	(62)	(17)
4-I	*n*-C_3F_7	(50)	(19)

R	R_F	**I**	**II**
4-EtO_2C	C_2F_5	(45)	(11)
4-EtO_2C	*n*-C_3F_7	(43)	(18)
2-Me-4-NC	C_2F_5	(69)	(—)
2-Me-4-NC	*n*-C_3F_7	(70)	(—)

C_{6-13}



1. MeI (6 eq), 110°, 5–16 h
2. $TMSCF_3$ (1.2 eq), CuI (1.5 eq), KF (1.4 eq), NMP, 60°, 16 h

$ArCF_3$

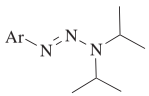
351

Ar	
4-ClC_6H_4	(33)[a]
2-BrC_6H_4	(26)[a]
4-$O_2NC_6H_4$	(0)
2-MeO-4-$O_2NC_6H_3$	(63)
2-$MeOC_6H_4$	(54)[a]
3-Cl-4-MeC_6H_3	(66)[a]

Ar	
2-O_2N-6-MeC_6H_3	(37)
3-O_2N-4-MeC_6H_3	(57)[a]
4-NCC_6H_4	(0)
4-$EtO_2CC_6H_4$	(67)
2,6-$Me_2C_6H_3$	(46)[a]
2-O_2N-4,5-$Me_2C_6H_2$	(48)[a]

Ar	
2-Me-4-NCC_6H_3	(88)
3,5-$(MeO_2C)_2C_6H_3$	(32)
2,4,6-$Me_3C_6H_2$	(38)[a]
4-Br-1-$C_{10}H_7$	(70)
2-PhC_6H_4	(55)
2-Bz-4-ClC_6H_3	(43)

C_{6-8}



1. MeI (6 eq), 110°, 5–16 h
2. $TMSC_2F_5$ (1.2 eq), CuI (1.5 eq), KF (1.4 eq), DMF, 60°, 16 h

ArC_2F_5

Ar	
2-MeO-4-$O_2NC_6H_3$	(62)
2-Me-4-NCC_6H_3	(46)

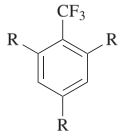
351

TABLE 3. PERFLUOROALKYL ADDITION TO ARENES (*Continued*)

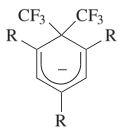
Arene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

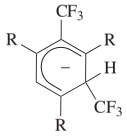
C_7



TMSCF$_3$ (*x* eq), Me$_4$NF (1.2 eq), DME, –60°; –50°, 1 h; to rt, o/n



Me$_4$N$^+$ +

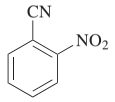


Me$_4$N$^+$

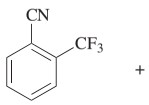
I **II**

R	*x*	**I**	**I + II**[a]	**I/II**
O_2N	1.15	(—)	(70)	1:9
FO_2S	2.54	(—)	(85)	1:2
$CF_3CH_2O_3S$	1.15	(65)	(95)	9:1

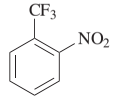
308



TMSCF$_3$ (2.8 eq), KF (5 eq), DMA, 50°, "few" min



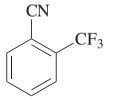
+



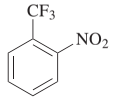
(—) 10% conv (—) 5% conv

306

TMSCF$_3$, KF, DMA

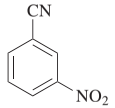


(10) +

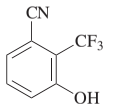


(5)

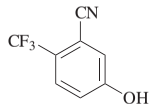
305



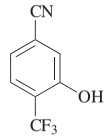
1. TMSCF$_3$ (1.2 eq), TASF (1 eq), THF, pyridine, –70°, 5 min
2. H_2O (1 eq), DMDO (1.2 eq), acetone, 15 min
3. HCl, H_2O



+

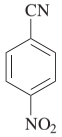


+

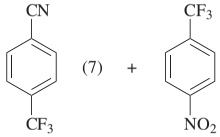


(22) (4) (23)

307

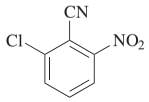


$TMSCF_3$, KF, DMA

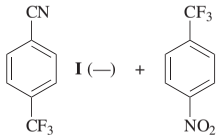


(7) + trace

305



$TMSCF_3$ (2.8 eq), KF (*x* eq), DMA, "few" min

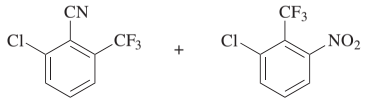


I (—) + **II** (—)

x	Temp (°)	Conv **I** (%)
2	rt	2
5	50	7
10	rt	10
10	50	13

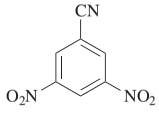
306

$TMSCF_3$ (2.8 eq), KF (5 eq), DMA, 50°, "few" min



(—) 51% conv (—) 20% conv

306



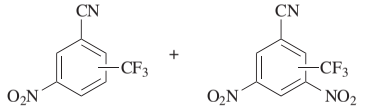
$TMSCF_3$, KF, DMA



(51) + 20)

305

$TMSCF_3$ (2.8 eq), KF (5 eq), DMA, 50°, "few" min

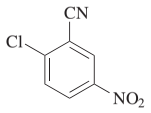
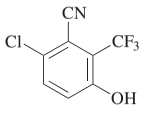
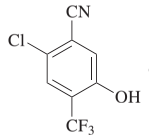
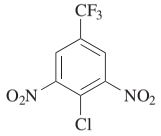
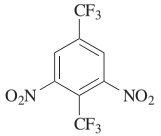
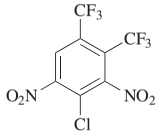
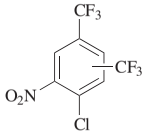
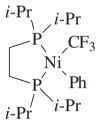
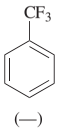
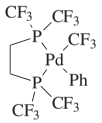
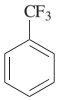
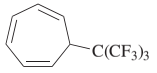


two isomers (—) 2% and 3% conv

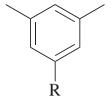
two isomers (—) 5% and 9% conv

306

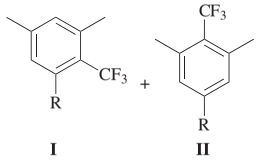
TABLE 3. PERFLUOROALKYL ADDITION TO ARENES (*Continued*)

Arene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_7 	1. $TMSCF_3$ (1.2 eq), TASF (1 eq), THF, pyridine, –70°, 5 min 2. H_2O (1 eq), DMDO (1.2 eq), acetone, 15 min 3. HCl, H_2O	 (47) +  (16)	307
	$TMSCF_3$ (2.8 eq), KF (5 eq), DMA, 50°, "few" min	 +  +  (—) 3% conv (—) 4% conv two isomers (—) 2% and 4% conv	306
	Additive (x mol %), solvent	 (—) Additive x Solvent Temp Time (h) Conv (%) H_2O 100 toluene 80° 5 22 $ZnBr_2$ 5 THF rt 14 19 PhZnBr 25 THF rt 72 11	739
	$(CF_3)_2PCH_2CH_2P(CF_3)_2$, benzene, 80°, 100 min	 (—) 100% conv	678
 Br^-	$(CF_3)_3CH$ (2.3 eq), Et_3N (2.5 eq), 3 h	 (53)	83

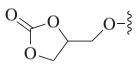
C_{8-9}



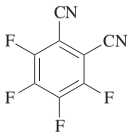
1. $Pb(OAc)_4$ (1.2 eq), K_3PO_4 (2.4 eq), benzoquinone (20 mol %), 4 Å MS, MeCN, inverse addition
2. $TMSCF_3$ (2.4 eq), 85°, 6 h



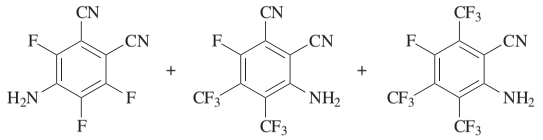
I **II**

R	I + II	I/II	
MeO	(72)	60:40	
Me	(95)[a]	—	797
	(55)	57:33	

C_8

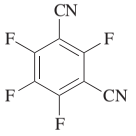


1. $TMSCF_3$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, NMP, 80°, 8 h
2. NH_4OH, H_2O

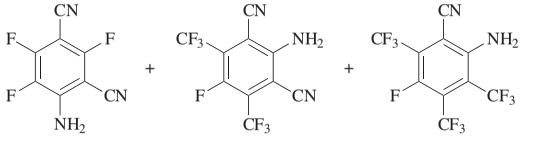


(—) 53% conv (—) 6% conv (—) 3% conv

334



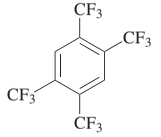
1. $TMSCF_3$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, NMP, 80°
2. NH_4OH, H_2O



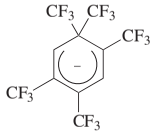
(—) 28% conv (—) 16% conv (—) 3% conv

334

C_{10}

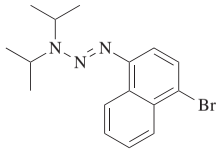


$TMSCF_3$ (1 eq), TASF (1 eq), THF, –30°, 1.5–2 h

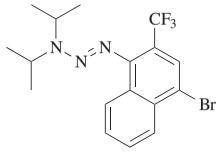


$(Me_2N)_3S^+$ (60)

309



$TMSCF_3$ (2 eq), AgF (4 eq), n-C_6F_{14}, 100°, 4 h



+ 3- and/or 4-mono- and 2,6-bis(trifluoromethyl)ated products

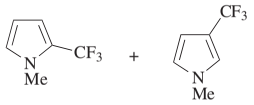
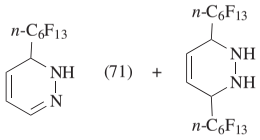
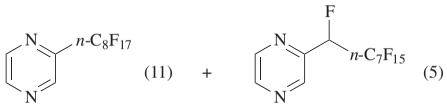
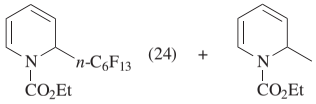
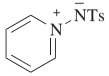
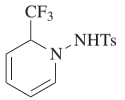
798

(51)

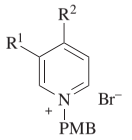
[a] The yield was determined by ^{19}F NMR spectroscopy.

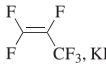
[b] The products could not be isolated but were characterized by ^{1}H and ^{19}F NMR spectroscopy.

TABLE 4. PERFLUOROALKYL ADDITION TO HETEROARENES

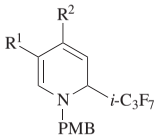
Heteroarene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_4			
	1. $Pb(OAc)_4$ (1.2 eq), K_3PO_4 (2.4 eq), benzoquinone (20 mol %), 4 Å MS, MeCN, inverse addition 2. $TMSCF_3$ (2.4 eq), 85°, 6 h	 **I** + **II** (94), **I**/**II** = 6.4:1	797
	n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, –78°	 (71) + (2)	800
	n-$C_8F_{17}I$, MeLi/LiBr, BF_3•OEt_2, Et_2O, –78°	 (11) + (5)	800
C_5			
	n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, $ClCO_2Et$, –78°	 (24) + (17)	800, 312
	$TMSCF_3$, CsF, DMF, H_2O	 (79)	314

C_{5-12}

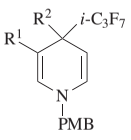




CF_3, KF, DMF, rt, 2 h



+



575

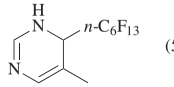
I **II**

R^1	R^2	**I**	**II**	**I**[a]	**II**[a]
Cl	H	(—)	(—)	(—)	(74)
O_2N	EtO	(74)	(—)	(36)	(—)
NC	H	(62)	(22)	(67)	(22)
H	NC	(50)	(—)	(53)	(—)
MeO_2C	H	(44)	(40)	(39)	(33)
PhCO	H	(81)	(18)	(—)	(—)

C_5

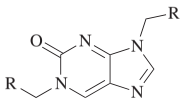


n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, –78°

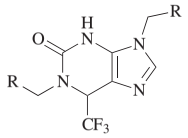


(57)

800



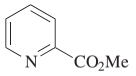
$TMSCF_3$ (5 eq), K_2CO_3 (5 eq), DMF, 0° to rt, 17 h



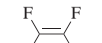
R	
Ph	(58)
TBSO	(62)

310

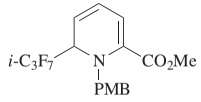
C_6



1. PMBBr, $AgBF_4$, MeCN, rt



2. CF_3, KF, MeCN, rt, 2 h



(37)

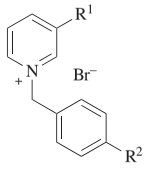
575

TABLE 4. PERFLUOROALKYL ADDITION TO HETEROARENES (*Continued*)

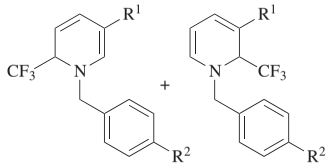
Heteroarene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{6-12}



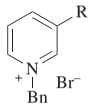
$TMSCF_3$ (1.2 eq), KF (1.5 eq), Ph_3SnF (0.3 eq), CH_2Cl_2, rt, 24 h



I **II**

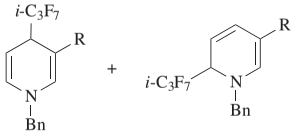
R^1	R^2	**I**	**II**	Refs.
Me	H	(41)	(—)	
NC	MeO	(29)	(20)	574
MeO_2C	MeO	(40)	(30)	
PhCO	MeO	(44)	(36)	

C_6





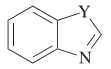
CF_3, KF, solvent, rt



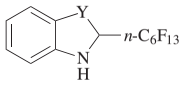
I **II**

R	Solvent	Time (h)	**I**	**II**	Refs.
Me	DME	13	(90)	(—)	575
NC	DMF	2	(22)	(57)	
MeO_2C	DMF	2	(42)	(39)	

C_7

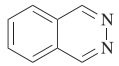


n-$C_6F_{13}I$, MeLi/LiBr, $BF{\bullet}OEt_2$, –78°

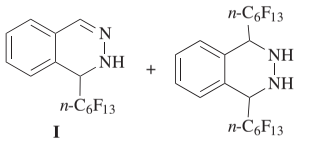


Y		Refs.
O	(24)	800
S	(6)	

C_8

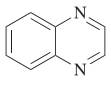


n-$C_6F_{13}I$ (x eq), MeLi/LiBr, $BF{\bullet}OEt_2$, Et_2O, –78°, 1 h

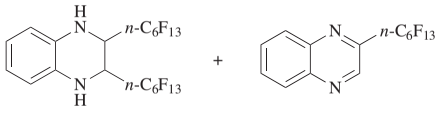


I **II**

x	**I**	**II**	Refs.
2.0	(71)	(11–16)	800
0.9–1.1	(61)	(—)	



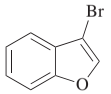
n-$C_6F_{13}I$ (*x* eq), MeLi/LiBr, BF_3•OEt_2, Et_2O, –78°, 1 h



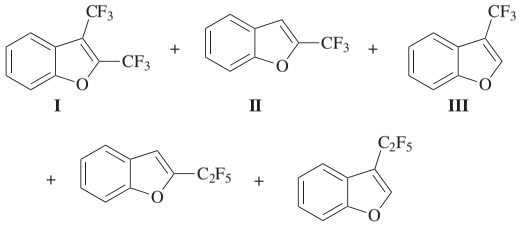
I **II**

x	**I**	**II**
2.0	(88)	(—)
0.9–1.1	(11)	(55)

800



CF_3I, Cu, solvent, 140°

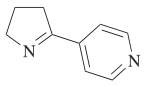


I **II** **III** **IV** **V**

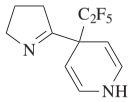
Solvent	**I**	**II**	**III**	**IV**	**V**
pyridine	(45)	(27)	(9)	(9)	(9)
DMF	(—)	(11)	(66)	(9)	(14)

336

C_9



C_2F_5H (1.5 eq), *n*-BuLi (1.2 eq), BF_3•OEt_2, (1.2 eq), THF, –78°, 6 h



(—)

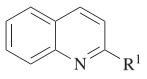
196

TABLE 4. PERFLUOROALKYL ADDITION TO HETEROARENES (*Continued*)

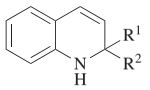
Heteroarene	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{9-17}



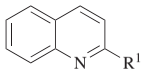
R^2I (*x* eq), MeLi/LiBr (2 eq), BF_3•OEt_2, Et_2O, –78°, 1 h



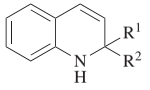
800

R^1	R^2	*x*		R^1	R^2	*x*		R^1	R^2	*x*	
H	C_2F_5	2	(93)	Me	C_2F_5	2	(72)	*n*-Bu	*n*-C_6F_{13}	2	(96)
H	*n*-C_4F_9	2	(99)	Me	*n*-C_4F_9	2	(51)	Ph	*n*-C_6F_{13}	2	trace
H	*n*-C_6F_{13}	2	(90)	Me	*n*-C_6F_{13}	2	(72)	*n*-C_6F_{13}	*n*-C_6F_{13}	4	(—)
H	*n*-C_8F_{17}	2	(84)	Me	*n*-C_8F_{17}	2	(70)	PhCH=CH	*n*-C_6F_{13}	2	(—)

C_{9-10}



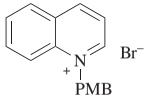
R^2I (2 eq), MeLi/LiBr, BF_3•OEt_2 (2 eq), Et_2O, –78°, 1 h



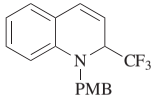
R^1	R^2	
H	C_2F_5	(93)
H	*n*-C_4F_9	(99)
H	*n*-C_8F_{17}	(84)
Me	C_2F_5	(91)
Me	*n*-C_6F_{13}	(72)

312

C_9

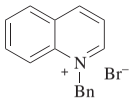


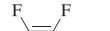
$TMSCF_3$ (1.2 eq), KF (1.5 eq), catalyst (0.33 eq), solvent, rt



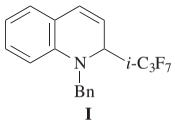
Catalyst	Solvent	Time (h)	
—	CH_2Cl_2	2.5	(25)
Ph_3SnF	CH_2Cl_2	2.5	(44)
Ph_3SnF	CH_2Cl_2	24	(76)
Ph_3SnF	DME	24	trace

574





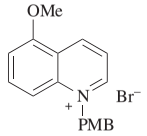
CF_3, KF, solvent, rt



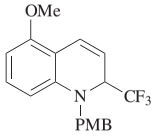
I + **II**

Solvent	Time (h)	**I**	**II**
CH_2Cl_2	24	(70)	trace
DMF	2	(85)	(10)

575

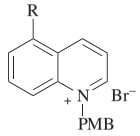


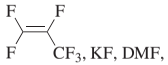
$TMSCF_3$ (1.2 eq), KF (1.5 eq), Ph_3SnF (0.3 eq), CH_2Cl_2, rt, 24 h



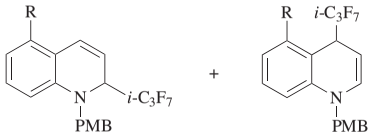
(76)

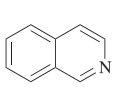
574



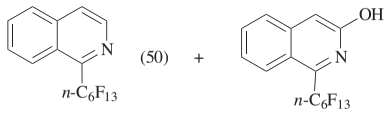


CF_3, KF, DMF, rt, 2 h



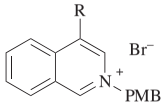


n-$C_6F_{13}I$ (2 eq), MeLi/LiBr, BF_3•OEt_2 (2 eq), Et_2O, –78°, 1 h



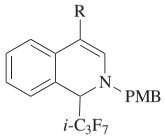
(50) + (15)

312, 800



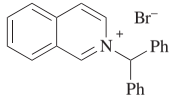


F, KF, DMF, rt, 2 h

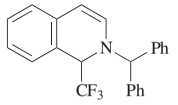


R		
H	(36)	
Br	(87)	

575



$TMSCF_3$ (1.2 eq), KF (1.5 eq), Ph_3SnF (0.3 eq), CH_2Cl_2, rt, 24 h



(85)

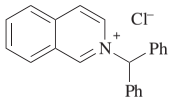
574

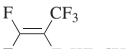
TABLE 4. PERFLUOROALKYL ADDITION TO HETEROARENES (*Continued*)

Heteroarene	Conditions	Product(s) and Yield(s) (%)	Refs.

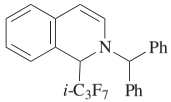
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_9



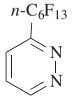


F, KF, CH_2Cl_2, rt, 24 h

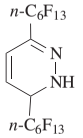


(85) 575

C_{10}

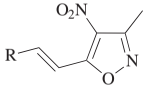


n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, –78°

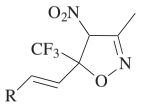


(82) 800

$C_{10–16}$



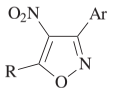
1. $TMSCF_3$ (2 eq), NaOAc (1.5 eq), n-$C_{16}H_{33}NMe_3Br$ (30 mol %), DMF, rt, time 1
2. HCl, rt



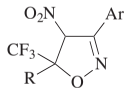
315

R	Time 1 (h)		R	Time 1 (h)	
2-furyl	8	(86)	2-Cl-5-$O_2NC_6H_3$	4	(67)
Ph	8	(87)	4-$O_2NC_6H_4$	6	(84)
2-ClC_6H_4	3	(88)	4-$MeOC_6H_4$	8	(82)
3-ClC_6H_4	3	(90)	4-MeC_6H_4	5	(84)
4-ClC_6H_4	4	(96)	1-$C_{10}H_7$	6	(81)
4-BrC_6H_4	7	(88)	2-$C_{10}H_7$	8	(85)

$C_{10–19}$



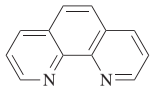
1. $TMSCF_3$ (2 eq), NaOAc (1.5 eq), n-$C_{16}H_{33}NMe_3Br$ (30 mol %), DMF, rt, time 1
2. HCl, rt



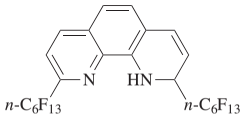
315

R	Ar	Time 1 (h)		R	Ar	Time 1 (h)	
Me	Ph	5	(72)	3-ClC_6H_4	4-BrC_6H_4	3	(97)
Me	4-MeC_6H_4	5	(64)	4-ClC_6H_4	Ph	6	(99)
Ph	Ph	6	(95)	Ph	4-MeC_6H_4	6	(85)
Ph	4-ClC_6H_4	6	(90)	3-MeC_6H_4	Ph	8	(90)
4-BrC_6H_4	Ph	5	(92)	2-$C_{10}H_7$	Ph	7	(90)

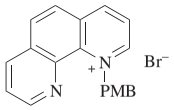
C_{12}



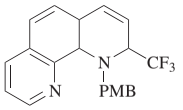
n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, –78°



(5) 800

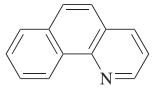


$TMSCF_3$ (1.2 eq), KF (1.5 eq), Ph_3SnF (0.3 eq), CH_2Cl_2, rt, 24 h

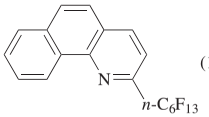


(88) 574

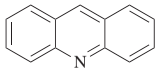
C_{13}



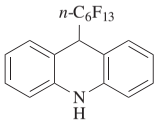
n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2 (2.4 eq), air, –78°



(16) 800

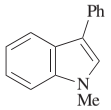


n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2 (2.4 eq), –78°

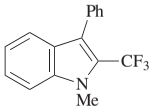


(6) 800

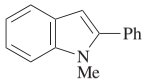
C_{14}



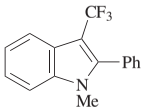
1. $Pb(OAc)_4$ (1.2 eq), K_3PO_4 (2.4 eq), benzoquinone (20 mol %), 4 Å MS, MeCN, inverse addition
2. $TMSCF_3$ (2.4 eq), 85°, 6 h



(72) 797

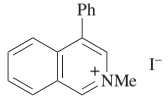
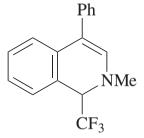
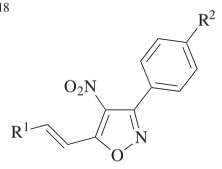
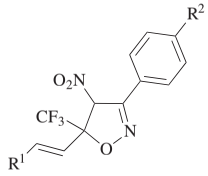


1. $Pb(OAc)_4$ (1.2 eq), K_3PO_4 (2.4 eq), benzoquinone (20 mol %), 4 Å MS, MeCN, inverse addition
2. $TMSCF_3$ (2.4 eq), 85°, 6 h



(62) 797

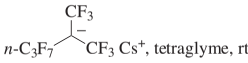
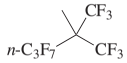
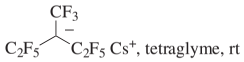
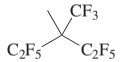
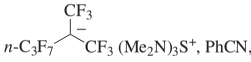
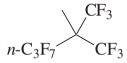
TABLE 4. PERFLUOROALKYL ADDITION TO HETEROARENES (*Continued*)

Heteroarene	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{15} 	$TMSCF_3$ (1.5 eq), KF (1.5 eq), DMF, –20°, 4 h	 (91)	567
$C_{17–18}$ 	1. $TMSCF_3$ (2 eq), NaOAc (1.5 eq), *n*-$C_{16}H_{33}NMe_3Br$ (30 mol %), DMF, rt, time 1 2. HCl, rt		315

R^1	R^2	Time 1 (h)	
Ph	H	5	(90)
Ph	Me	5	(95)
4-ClC_6H_4	H	5	(96)
4-MeC_6H_4	H	9	(90)

[a] The starting salts were prepared in situ.

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES

Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_1			
MeI	3 $CuCF_3$•Et_3N•3HF (1.5 eq), DMF, NMR tube, 50°	$MeCF_3$ (—)	56
		 (—)	67
		 (—)	67
$MeOSO_2F$		 (60)	67, 68
C_{1-8}			
RX^1	$X^2CF_2CO_2Me$ (2 eq), KF (1 eq), CuI (1 eq), CdI_2 (1 eq), HMPA, 6–8 h	RCF_3 + CO_2 + $MeX^1(X^2)$	242

R	X^1	X^2	Temp (°)	Conv (%)	[a]
Me	I	Cl	110	74	(81)
Me	I	Br	90	71	(75)
CH_2I	I	Cl	120	81	(78)
n-Bu	Br	Cl	120	41	(67)
n-Bu	I	Cl	120	75	(74)
c-C_6H_{11}	Br	Br	90	43	(68)

R	X^1	X^2	Temp (°)	Conv (%)	[a]
n-C_6H_{13}	Br	Cl	120	37	(72)
n-C_7H_{15}	Br	Cl	120	43	(73)
n-C_7H_{15}	Br	Br	95	44	(69)
n-C_8H_{17}	I	Cl	120	71	(77)
n-C_8H_{17}	I	Br	90	70	(72)

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

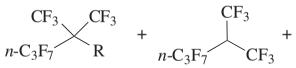
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

C_{1-4}

RX

I

1. $CF_3CF{=}CFCF(CF_3)_2$ (1 eq), MF (*x* eq), solvent
2. H_2O

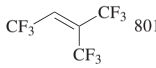


II

+

III

+



IV

801

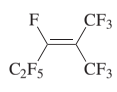
R	X	MF	*x*	Solvent	Temp (°)	Time (h)	Conv **II** (%)	**I**/**II**/(**III** + **IV**)
Me	Br	CsF	1.15	DMF	18	48	99	0:99:1
Me	I	KF	1.7	diglyme	60	18	26.1	4.4:30.3:65.3
Me	I	KF	1.7	DMF	60	18	77.1	0:98.2:0.8
Me	I	KF	1.7	DMF	20	66	18.8	1.7:25.2:73.1
Me	I	CsF	1.15	diglyme	20	18	78.8	0:91.6:8.5
Me	I	CsF	1.15	DMF	20	20	77.5	0:90.5:9.5
Et	Br	CsF	1.15	DMF	18	48	17	3.5:19.1:77.4
Et	I	KF	1.7	diglyme	150	18	—	0:0:100
Et	I	KF	1.7	DMF	60	18	35.6	12.2[b]:39.3:37.2
Et	I	CsF	1.15	diglyme	60	18	87.6	3.3:93.6:3.1
Et	I	CsF	1.15	diglyme	20	18	80.3	4.3:86:9.7
Et	I	CsF	1.15	DMF	60	18	87.5	5.5:90.9:3.6
Et	I	CsF	1.15	DMF	20	18	67.8	3.9:78.6:17.5
n-Pr	I	KF	1.7	DMF	60	18	7.6	36.6[b]:8.6:23.2
n-Pr	I	CsF	1.15	diglyme	20	18	43.2	11.2:50:37.7
n-Pr	I	CsF	1.15	DMF	60	18	75.7	9.6:81.2:10.2
n-Pr	I	CsF	1.15	DMF	20	18	42	17.5:52.4:30.1
i-Pr	I	CsF	1.15	DMF	60	18	—	20.9[b]:0:60.6
$CH_2{=}CHCH_2$	Cl	KF	1.7	DMF	60	18	7.5	21.9[b]:11.2:31.3
$CH_2{=}CHCH_2$	Br	KF	1.7	DMF	60	18	44	13[b]:48.7:27.5
$CH_2{=}CHCH_2$	Br	KF	1.7	DMF	60	42	70.2	2.1[b]:74.9:4
$CH_2{=}CHCH_2$	I	KF	1.7	DMF	60	18	63.7	5.6[b]:68.4:18.3
$CH_2{=}CHCH_2$	I	KF	1.7	DMF	60	36	70.8	5.5[b]:75.3:14.5
n-Bu	I	CsF	1.15	DMF	20	18	43	11:47.9:41.1
n-Bu	I	CsF	1.15	DMF	60	18	74.8	10.9:72.6:16.5
i-Bu	I	CsF	1.15	DMF	60	18	6.2	35.6:11.7:52.7

C_1





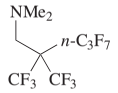
F (*x* eq), solvent



+



+



99

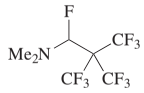
I **II** **III**

x	Solvent	Temp (°)	Time (h)	**I**	**II**	**III**
1.1	—	rt	4	(28)	(32)	(—)
1.1	diglyme	40	5	(18)	(28)	(4)
1.8	diglyme	60	5	(29)	(59)	(—)





F (2 eq), diglyme, rt, 24 h



(35) 100

$(Me_2N)_3C–F$ $TMSCF_3$ (2.69 eq), Et_2O, –50°, 1 h; rt $(Me_2N)_3C–CF_3$ (96) 319, 64

$C_{2–12}$

R^1X R_FTMS (1.7 eq), CsF (1.7 eq), 15-c-5 (3.4 eq), DME, –18° to rt $R^1–R_F$ 317

R^1	X	R_F	Time (h)	Conv (%)	
Et	Br	CF_3	1	>98	(—)
Et	I	CF_3	1	>98	(—)
Et	I	C_2F_5	16	>98	(—)
$Cl(CH_2)_3$	I	CF_3	1	—	(61)[c]
$Cl(CH_2)_3$	I	C_2F_5	16	>98	(—)

R^1	X	R_F	Time (h)	Conv (%)	
n-C_8H_{17}	I	CF_3	1	—	(70)
n-C_8H_{17}	I	C_2F_5	16	—	(78)
n-$C_{12}H_{25}$	I	CF_3	1.5	—	(78)
n-$C_{12}H_{25}$	I	C_2F_5	16	—	(82)

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{2-7}

RX[1]

$X^2CF_2CO_2Me$ (2 eq), CuI (1 eq), KF (1 eq), DMF, 8 h

$RCF_3 + CO_2 + MeX$

R	X^1	X^2	Temp (°)		Refs.
EtO_2CCH_2	Cl	Cl	110–120	(5)	243, 244
CH_2=$CHCH_2$	Br	Cl	110–120	(82)	243, 244
CH_2=$CHCH_2$	Br	Br	85–90	(70)	243
CH_2=$CHCH_2$	I	Cl	110–120	(85)	243, 244
CH_2=$CHCH_2$	I	Br	85–90	(73)	243
Bn	Cl	Cl	110–120	(46)	243, 244
Bn	Cl	Br	85–90	(41)	243
Bn	Br	Cl	110–120	(84)	243, 244
Bn	Br	Br	85–90	(61)	243

RX

$FSO_2CF_2CO_2Me$ (*x* eq), Cu, DMF, 80° RCF_3

R	X	*x*	Time (h)	Conv (%)		Refs.
Et_2NCOCH_2	Br	0.67	5	100	(76)	252
Bn	Br	0.5	3	100	(70)	
Bn	Br	0.5	3	62	(70)[d]	
Bn	I	0.5	3	100	(80)	

$FSO_2CF_2CO_2Me$ (*x* eq), Cu (0.12 eq), additive, DMF

$RCF_3 + SO_2 + CO_2 + CH_4$

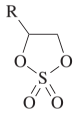
R	X	*x*	Additive	Time (h)		Refs.
Et_2NCOCH_2	Br	0.67	—	5	(76)	252
Bn	Br	0.5	—	3	(70)	
Bn	Br	0.5	1,4-$(O_2N)_2C_6H_4$ (0.2 eq)	3	(70)	
Bn	I	0.5	—	3	(80)	

C_{2-9}

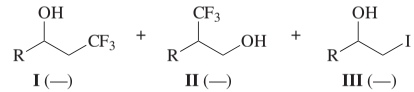
R^1X^1 — R_FX^2, AgBr/Li, THF, ultrasound — $R^1{-}R_F$ — 316

R^1	X^1	R_F	X^2		R^1	X^1	R_F	X^2	
Et	I	n-C_8F_{17}	I	(64)	Bn	Br	CF_3	I	(42)
$MeCH{=}CHCH_2$	Br	n-C_4F_9	I	(52)	Bn	Br	CF_3	Br	(45)
$MeCH{=}CHCH_2$	Br	n-C_4F_9	Br	(36)	$PhCH{=}CHCH_2$	Br	CF_3	Br	(31)
$MeCH{=}CHCH_2$	Br	n-C_6F_{13}	I	(47)					

C_{2-6}



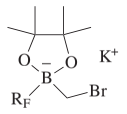
1. CF_3I (x eq), TDAE (1 eq), solvent, –20°; rt, 4 h
2. H_2SO_4, H_2O



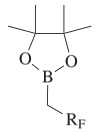
325

R	x	Solvent	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)	R	x	Solvent	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)
H	2.2	THF	45	—	55	Me	5	THF	56	1	—
Me	2.2	DMF	8	—	—	Et	2.2	THF	49	0.5	33
Me	2.2	THF	55	1	30	n-Pr	2.2	THF	51	0.2	31
Me	3	THF	62	1	—	n-Bu	2.2	THF	50	0.5	40

C_{2-3}



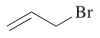
DMF



R_F	Temp (°)	Time (h)	
CF_3	70	1.5	(45)
C_2F_5	50	1	(80)

104

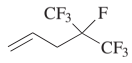
C_3



CF_3CdBr, CuI, DMF, –78 to 20°

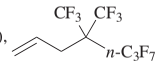
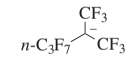
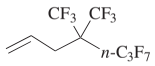
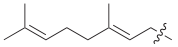
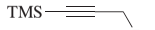
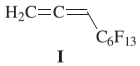
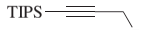
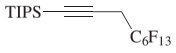
(66) — 267

i-C_3F_7Ag (0.67 eq), MeCN, 20°, 48 h



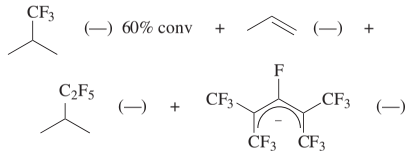
(50) — 647

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_3 	$(CF_3)_2C{=}CFCF_2CF_3$ (0.5 eq), MF (0.66 eq), solvent, 50–60°, 5 h	 MF / Solvent: KF / diglyme (39); CsF / MeCN (31); CsF / DME (61); CsF / diglyme (80)	802
	 tetraglyme, rt	 (—)	67
$C_{3–13}$	$(Ph_3P)_3CuCF_3$ (1.1 eq), $CDCl_3$, rt, 18 h	R / X: PhMe2Si / Cl (41); *c*-C6H11[e] / Cl (59); Ph / Cl (76); Ph / CF3CO2 (53); 4-ClC6H4 / Cl (85); 4-O2NC6H4 / Cl (51); 4-MeOC6H4 / Cl (79); PhCH2CH2 / Cl (75);  / Br (90)	322
C_3 	1. "$C_6F_{13}Cu$", DMSO, 15–20° 2. $(n\text{-Bu})_4NF$, THF or MeCN, 0°	 **I** +  **II** **I + II** (49) **I/II** = 1:1	301
	"$C_6F_{13}Cu$", DMSO, 15–20°	 (50)	301



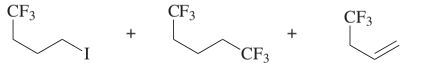
TMSCF$_3$ (1.7 eq), CsF (1.7 eq), 15-c-5 (3.4 eq), DME, −18° to rt, 1 h



317

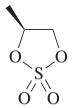


TMSCF$_3$ (3.4–4 eq), CsF (3.4 eq), 15-c-5 (3.4 eq), DME, −18° to rt, 1 h

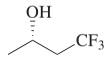


(—) 50% conv (—) 45% conv (—) 5% conv

317



1. CF_3I (2.2 eq), TDAE (2.2 eq), THF, −20°; rt, 4 h
2. H_2SO_4, H_2O



(—) 43% conv, er >99.75:0.25

325

C_{3-9}

RX

[$CuCF_3$]•bipy, 80–120°, DMF

RCF_3

R	X	
CH_2=$CHCH_2$	Cl	(50)
Bn	Br	(90)
Ph(Me)CH	Br	trace
2-Me$C_6H_4CH_2$	Br	(32)
PhCH=$CHCH_2$	Br	(90)

234

C_{3-7}

RX

FSO_2CF_2I (*x* eq), Cu (*y* eq), DMF

RCF_3

259

R	X	*x*	*y*	Temp (°)	Time (h)	Conv (%)	
CH_2=$CHCH_2$	Br	0.33	0.73	60	6	100	(74)
CH_2=$CHCH_2$	I	0.33	0.73	60	6	100	(78)
Bn	Br	0.4	0.9	90	6.5	83	(72)
Bn	I	0.5	1.1	90	5.5	100	(79)
4-$O_2NC_6H_4CH_2$	Br	0.5	1.1	90	7	98	(84)

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-7}

RX

$FSO_2CF_2CO_2Me$ (*x* eq), CuI (12 mol %), DMF

RCF_3

R	X	*x*	Temp (°)	Time (h)	Conv (%)	
CH_2=$CHCH_2$	Br	0.33	60	4	100	(70)
CH_2=$CHCH_2$	I	0.33	60	4	100	(74)
Bn	Cl	0.5	80	4	95	(53)
Bn	Br	0.4	80	3.5	100	(72)
Bn	I	0.5	70	2	100	(81)

250

$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI, DMF, 120°, 8 h

RCF_3

R	X	
CH_2=$CHCH_2$	Br	(81)
Bn	Cl	(42)
Bn	Br	(61)

249

ICF_2CO_2Me (2 eq), CuI (1 eq), KF (1 eq), DMF, 80°, 5 h

RCF_3 (—) + CO_2 + MeX

R	X	Conv (%)
CH_2=$CHCH_2$	Br	82
Bn	Cl	32
Bn	Br	62

243

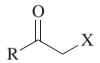
$FSO_2CF_2CF_2OCF_2CO_2K$ (1.2 eq), CuI (1 eq), DMF, 45°, 6–8 h

RCF_3

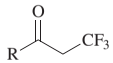
R	X	
CH_2=$CHCH_2$	Br	(57)
Bn	Br	(68)

247

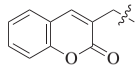
C_{4-14}



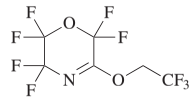
[3 $CuCF_3$•Et_3N•3HF (Table 34, C_0) + Et_3N•3HF (*x* mol %)] (1.3 eq), DMF, rt



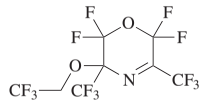
324

R	X	*x*	Time (min)	
Et	Br	20	20	(86)[f]
t-Bu	Br	20	120	(87)[f]
2-thienyl	Br	20	15	(96)
2-pyridyl	Br	30	15	(52)
c-C_6H_{11}	Br	20	30	(88)[f]
Ph	Br	20	15	(93)
4-FC_6H_4	Cl	20	60	(89)
2-ClC_6H_4	Br	20	15	(84)[f]
4-ClC_6H_4	Cl	20	60	(93)[f]
4-ClC_6H_4	Br	20	15	(85)
2,4-$Cl_2C_6H_3$	Br	20	15	(80)
3-BrC_6H_4	Br	20	15	(91)
4-$O_2NC_6H_4$	Br	20	15	(83)[f]
2-$MeOC_6H_4$	Br	20	15	(94)
3-$MeOC_6H_4$	Br	20	15	(95)
4-$MeOC_6H_4$	Br	20	15	(96)
4-MeC_6H_4	Br	20	15	(94)
2-$CF_3C_6H_4$	Br	20	15	(87)
2,4-$Me_2C_6H_3$	Br	20	15	(93)
3,5-$(CF_3)_2C_6H_3$	Br	20	15	(77)
	Br	20	15	(57)
1-adamantyl	Br	20	60	(97)[f]
2-$C_{10}H_7$	Br	20	15	(94)
4-PhC_6H_4	Br	20	15	(95)

C_4

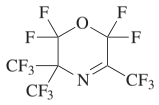


$TMSCF_3$ (1.05 eq), KF (0.2 eq), 0°, 1 h; rt, 20 h



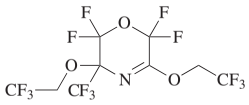
(—) 9% conv

+



(—) 5% conv

+ 803



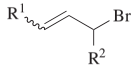
(—) 3% conv

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

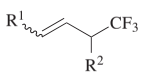
Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{4-9}



CF_3CdBr, CuI, DMF, –78 to 20°



R^1	R^2	
EtO_2C	H	(68)
Me_2NCO	H	(62)
$-(CH_2)_3-$		(54)
Ph	H	(74)

267

C_5

n-$C_5H_{11}I$ — $C_2F_5CO_2Na$, CuI, NMP, 170°, 3 h — *n*-$C_5H_{11}C_2F_5$ (22) — 59

C_6

n-$C_6H_{13}Br$ — CF_3H, PhI (3 eq), $(n\text{-}Bu)_4NBF_4$ (8 mol %), DMF, e^-, Mg or Al anode, Ni/Cd cathode, 5–10° — *n*-$C_6H_{13}CF_3$ (—) 60% conv — 70

C_7

BnBr — $TMSCF_3$ (*x* eq), additive (*y* eq), solvent, rt, 112 h — $BnCF_3$ (—) — 277

x	Additive	*y*	Solvent	Conv (%)
—	CuI, KF	—	DMF	29
0.65	**43**	0.2	THF	20
0.4	**43**	0.2	DMF	58

See table. — $BnCF_3$ (—)

Conditions	Conv (%)
40 (0.2 eq), THF, rt, 112 h	54
42, DMI, benzene, 50°, 20 h	36

277, 278

C_{7-9}

RX — $TMSCF_3$ (1.1–1.2 eq), KF (1.2 eq), CuI (1.5 eq), solvent, 80° — RCF_3 — 339

R	Solvent	Time (h)	
Bn	**23** (1 eq)	8	(90)
Bn	**23** (2 eq)	8	(89)
Bn	**23** (0.5 eq)	24	(65)
Bn	**24** (1 eq)	12	(70)

R	Solvent	Time (h)	
3-$BrC_6H_4CH_2$	**23** (1 eq), DMF	8	(81)
n-C_8H_{17}	**23** (1 eq)	8	(27)
$Ph(CH_2)_3$	**23** (1 eq)	8	(36)
(*E*)-PhCH=$CHCH_2$	**23** (1 eq), DMF	8	(42)

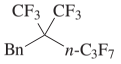
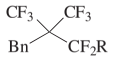
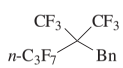
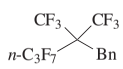
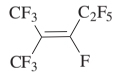
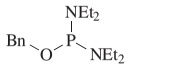
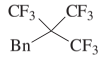
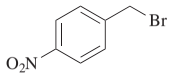
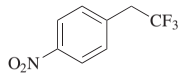
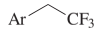
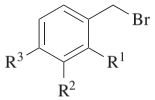
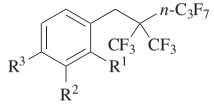
C_7 BnBr	$TMSC_2F_5$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, 60°, 24 h	BnC_2F_5 (—)	90% conv		275
C_{7-9} RBr	Et_3SiCF_3 (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, NMP, 80°, 24 h	RCF_3 (—)	R: Bn; $PhCH{=}CHCH_2$	Conv (%): 73; 23	275
C_7 BnBr	$ClCF_2CO_2Me$, KF, CuI, solvent, 8 h	$BnCF_3$	Solvent: DMF; NMP	Temp (°): 120; 80 (84); (68)	247
	1. CF_3H (1 eq) (inverse addition), THF, –40°, 20 min 2. KHMDS (1 eq), –40°, 1 h; rt, 10 h	$BnCF_3$ (10)[f]			77
	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI, solvent	$BnCF_3$	Solvent (s): DMF; DMF, HMPA; NMP	Temp (°): 120; 80; 90	Time (h): 8 (62); 4 (70); 10 (63)	247
	$FSO_2CF_2CO_2Me$, CuI, solvent	$BnCF_3$	Solvent: DMF; NMP	Temp (°): 70; 55	Time (h): 2.5 (72); 8 (70)	247
	1.  (0.83 eq), CsF (1 eq), diglyme, 50–60°, 1 h 2. Alkyl halide (1 eq), 50–60°, overnight		(90)			804
	 R, CsF, diglyme, 20°		R: F; C_2F_5	(88); (87)		321

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

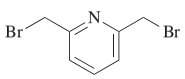
Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_7			
BnBr	n-$C_3F_7CF(CF_3)^-$ $(Me_2N)_3S^+$, MeCN, rt	 (66)	68
	n-$C_3F_7CF(CF_3)^-$ Cs^+, tetraglyme, rt or 80°	 (—) +  (—)	67
	$(CF_3)_3CBr$, –30°	 (81)	805
	$(CF_3)_2Hg$/Cu, solvent, 140–150°, 5 h		261
C_{7-13}			
	TMSCF_3 (2 eq), CuI (1.1 eq), KF (2 eq), DMF/HMPA (1:1), 60°, 4 h		323
C_7			
	n-$C_3F_7CF(CF_3)^-$ Cs^+, sulfolane, 60°, 6 d		806

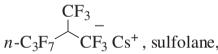
Solvent

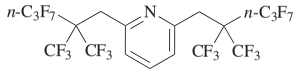
NMP	(58)
DMA	(32)

Ar		Ar	
Ph	(76)	4-$CF_3C_6H_4$	(80)
4-FC_6H_4	(75)	3-NCC_6H_4	(81)
3,5-$Cl_2C_6H_5$	(72)	4-$MeO_2CC_6H_4$	(68)
4-BrC_6H_4	(78)	2-$C_{10}H_7$	(78)
4-$O_2NC_6H_4$	(40)	4-PhC_6H_4	(79)

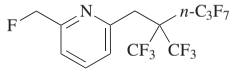
R^1	R^2	R^3	
H	H	H	(58)
Br	H	H	(34)
H	Br	H	(64)
H	H	Br	(62)
H	NO_2	H	(64)
H	H	NO_2	(60)







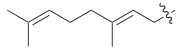
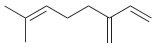
(20) + 806



(33)

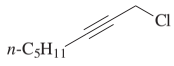
C_{7-10}

RX | "$CuCF_3$", HMPA | RCF_3 | 53

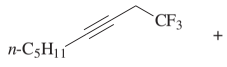
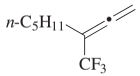
R	X	Temp (°)	Time (h)	
Bn	Br	rt	12	(65)
$PhCH{=}CHCH_2$	Br	rt	12	(37)
$n\text{-}C_{10}H_{21}$	Br	45–70	62	(13)[g] + $n\text{-}C_{10}H_{21}F$ (32)[g]
$n\text{-}C_{10}H_{21}$	I	50	32	(48) + $n\text{-}C_{10}H_{21}F$ (6)[g]
	Br	50	12	(50)[g] +  (3.7)[g]

C_8

$n\text{-}C_8H_{17}OSO_2CF_3$ | $TMSCF_3$ (2 eq), TASF (1 eq), THF, –10°, 1 h | $n\text{-}C_8H_{17}CF_3$ (60) + $n\text{-}C_8H_{17}F$ (—) 7% conv + $n\text{-}C_6H_{13}CH{=}CH_2$ (—) 5% conv + $n\text{-}C_8H_{17}OH$ (—) 7% conv | 320



$TMSCF_3$ (1.5 eq), CuTC (5 mol %), KF (1.5 eq), THF

 + 

302

I **II**

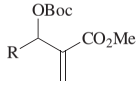
Temp	Time (h)	**I**	**II**
rt	72	(89)	(5)
60°	20	(79)	(6)

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

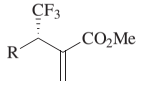
Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{8-18}



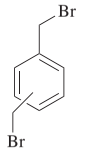
TMSCF$_3$ (2.5 eq), **58** (15 mol %), KF (10 mol %), DME/MeCN, rt

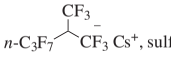


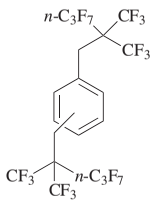
297

R	DME/MeCN	Time (h)		er	R	DME/MeCN	Time (h)		er
5-methyl-2-thiazolyl	4:1	56	(84)	95.0:5.0	4-$O_2NC_6H_4$	4:1	56	(83)	96.5:3.5
2-furyl	4:1	48	(70)	93.5:6.5	4-AcBocNC$_6$H$_4$	4:1	120	(47)	79.0:21.0
2-thienyl	1:1	120	(54)	74.0:26.0	4-$MeOC_6H_4$	1:1	120	(51)	95.0:5.0
5-TBSOCH$_2$-2-furyl	4:1	48	(79)	96.5:3.5	4-CH_2=$CHCH_2OC_6H_4$	4:1	110	(80)	97.0:3.0
c-C_6H_{11}	4:1	15	(72)	—	(*E*)-PhCH=CH	4:1	56	(61)	81.0:19.0
Ph	4:1	60	(72)	97.0:3.0	4-*i*-PrC_6H_4	4:1	120	(32)	93.5:6.5
3-ClC_6H_4	4:1	60	(69)	97.0:3.0	2-quinolyl	4:1	58	(81)	88.5:11.5
4-ClC_6H_4	4:1	60	(70)	96.5:3.5	4-(*E*)-PhCH=CHC_6H_4	4:1	72	(86)	96.0:4.0

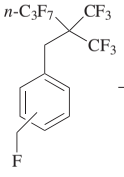
C_8







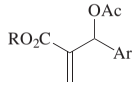
+



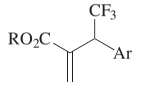
Isomer	I	II	
1,2	(12)	(66)	806
1,3	(56)	(21)	
1,4	(59)	(22)	

I **II**

C_{8-14}



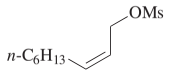
TMSCF$_3$ (2 eq), DABCO (10 mol %), THF, rt, 12 h



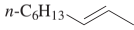
296

Ar	R		Ar	R		Ar	R	
2-furyl	*t*-Bu	(87)	2-BrC_6H_4	*t*-Bu	(67)	3-$MeOC_6H_4$	*t*-Bu	(92)
2-pyridyl	*t*-Bu	(85)	3-BrC_6H_4	*t*-Bu	(99)	4-$MeOC_6H_4$	Me	(90)
Ph	Me	(96)	4-BrC_6H_4	Me	(96)	3-MeC_6H_4	*t*-Bu	(99)
3-ClC_6H_4	*t*-Bu	(98)	4-BrC_6H_4	*t*-Bu	(98)	4-MeC_6H_4	*t*-Bu	(91)
4-ClC_6H_4	*t*-Bu	(95)	3,5-Br_2-4-$MeOC_6H_2$	*t*-Bu	(93)	1-$C_{10}H_7$	*t*-Bu	(85)
3,4-$Cl_2C_6H_3$	*t*-Bu	(93)	4-$O_2NC_6H_4$	*t*-Bu	(87)	2-$C_{10}H_7$	*t*-Bu	(92)

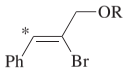
C_9



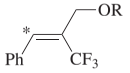
$TMSCF_3$ (2 eq), CuI (1.1 eq), KF (2 eq), DMF/HMPA (1:1), 60°, 4 h



(87), (*E*)/(*Z*) = 23:1 — 323



$(CF_3)_2Hg$/Cu, DMA, 140°, 2 h

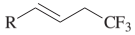


R	*Config		
Ac	(*Z*)	(93)	
Ac	(*E*)	(91)	329
n-Bu	(*E*)	(95)	

C_{9-11}

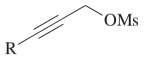


$(PPh_3)_3CuCF_3$ (1.1 eq), $CDCl_3$, 55°, 18 h

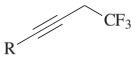


R	X		
Ph	CF_3CO_2	(61)	322
4-$O_2NC_6H_4$	Cl	(62)	
$PhCH_2CH_2$	CF_3CO_2	(30)	

C_{9-10}

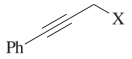


$TMSCF_3$ (2 eq), CuI (1.1 eq), KF (2 eq), DMF/HMPA (1:1), 60°, 4 h

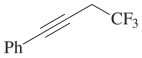


R		
Ph	(50)	323
n-C_7H_{15}	(64)	

C_9

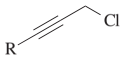


$TMSCF_3$ (*x* eq), CuTC (5 mol %), KF (*y* eq), THF, 60°, 20 h

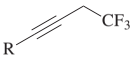


X	*x*	*y*		
Cl	1.5	1.5	(73)	
Cl	3	3	(72)[h]	302
HO	3	3	(7)[h]	
MsO	3	3	(47)[h]	
Br	3	3	(35)[h]	
I	3	3	(48)[h]	

C_{9-13}



$TMSCF_3$ (1.5 eq), CuTC (*x* mol %), KF (1.5 eq), THF, 60°



302

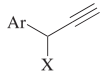
R	*x*	Time (h)		R	*x*	Time (h)	
Ph	5	20	(73)	4-$CF_3C_6H_4$	10	48	(75)
4-ClC_6H_4	5	20	(71)	Bn	5	20	(80)
2-$MeOC_6H_4$	5	20	(84)	$PhCH_2CH_2$	5	20	(93)
4-$MeOC_6H_4$	5	20	(79)	1-$C_{10}H_7$	5	20	(86)
3-MeC_6H_4	5	20	(62)	2-$C_{10}H_7$	5	20	(72)
4-MeC_6H_4	5	20	(83)				

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

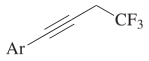
Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{9-13}

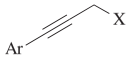


$(PPh_3)_3CuCF_3$ (1 eq), THF, 50°, 16 h

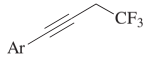


Ar	X	*i*
Ph	Cl	(82)
Ph	CF_3CO_2	(74)
4-BrC_6H_4	CF_3CO_2	(87)
4-*t*-BuC_6H_4	CF_3CO_2	(73)

303



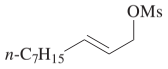
$(PPh_3)_3CuCF_3$ (1 eq), THF, 22°, 16 h



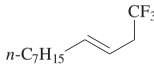
Ar	X	
Ph	Cl	(74)
2-$C_{10}H_7$	Br	(86)

303

C_{10}

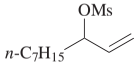


$TMSCF_3$ (2 eq), CuI (1.1 eq), KF (2 eq), DMF/HMPA (1:1), 60°, 4 h

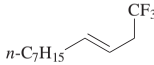


(78), (*E*)/(*Z*) = 32:1

323

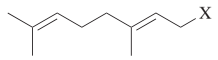


$TMSCF_3$ (2 eq), CuI (1.1 eq), KF (2 eq), DMF/HMPA (1:1), 60°, 4 h

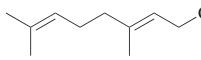


(80), (*E*)/(*Z*) = 32:1

323

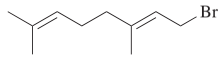


$TMSCF_3$ (3 eq), CuTC (2 mol %), KF (3 eq), THF, rt, 48 h

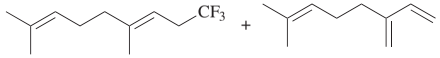


X	
Cl	(59)
Br	(45)

61

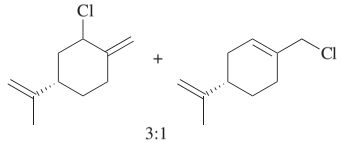


$CuCF_3$, HMPA, 50°, 12 h



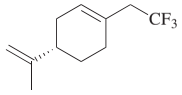
(50) (3.7)

53



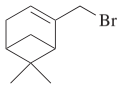
3:1

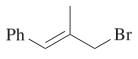
$(PPh_3)_3CuCF_3$ (1.1 eq), $CDCl_3$, 55°, 18 h



(56)

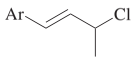
322



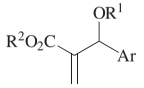


(*E*)/(*Z*) = 20:1

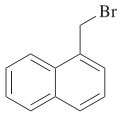
C_{10-11}



C_{10}



C_{11}



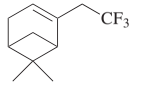
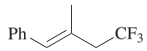
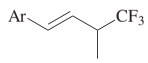
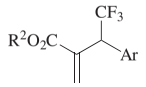
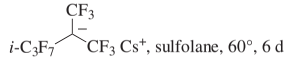
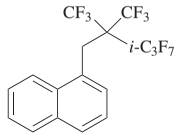
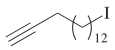
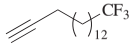
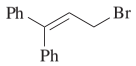
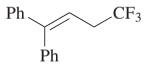
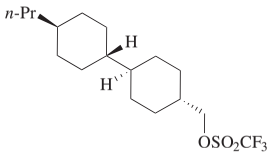
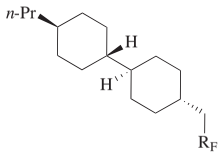
$TMSCF_3$ (3 eq), CuTC (2 mol %), KF (3 eq), THF, 60°, 48 h		(81)	61
$TMSCF_3$ (3 eq), CuTC (2 mol %), KF (3 eq), THF, 60°, 20 h		(73)	61
$TMSCF_3$ (3 eq), CuTC (10 mol %), KF (3 eq), THF, 40°, 20 h		Ar: Ph (44); 4-MeC_6H_4 (45)	61
$TMSCF_3$ (5 eq), **58** (10 mol %), THF, 60°, 120 h		Ar / R^1 / R^2: Ph / Ac / *t*-Bu, trace, —; Ph / Boc / Me, (52), 97.0:3.0 er; Ph / Boc / *t*-Bu, (39), 96.0:4.0 er; 2-BrC_6H_4 / Boc / *t*-Bu, (37), 94.0:6.0 er; 4-BrC_6H_4 / Boc / *t*-Bu, (60), 95.0:5.0 er	296
		(58)	806

TABLE 5A. PERFLUOROALKYL ADDITION TO ALKYL HALIDES AND PSEUDOHALIDES (*Continued*)

Alkyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{15} 	1. CsF (2 eq), 15-c-5 (2 eq), DME, –20°, 5 min 2. Alkyl halide (1 eq), $TMSCF_3$ (2 eq), DME, –20°; 10°, 4 h	 (88)	318
	$TMSCF_3$ (3 eq), CuTC (2 mol %), KF (3 eq), THF, 60°, 20 h	 (60)	61
C_{16} 	$TMSR_F$ (2.9 eq), TMAF (1.2 eq), DME, –30°, 3 h; 0°, 1.5 h	 R_F: CF_3 (71); C_2F_5 (80)	320

[a] The isolated yield was based on % conversion.

[b] A number of unidentified products were also present.

[c] The product contained about 15% of Et_2O.

[d] The reaction was performed in the presence of 1,4-dinitrobenzene (0.2 eq).

[e] The linear to branched ratio in the substrate was 6:1.

[f] The number is the conversion which was determined by ^{19}F NMR spectroscopy.

[g] The yield was determined by gas chromatography.

[h] The yield was determined by ^{1}H NMR spectroscopy.

[i] At 22° the allene isomer was formed; see Table 2.

TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES

Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_2

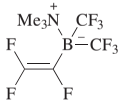
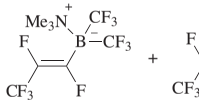
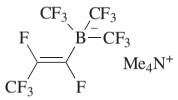
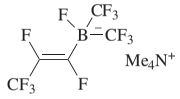
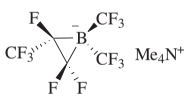
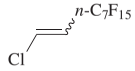
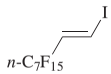
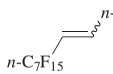
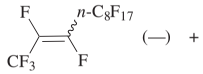
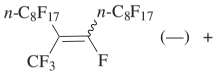
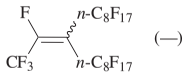
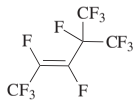
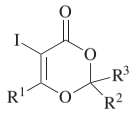
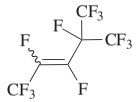
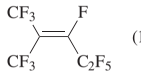
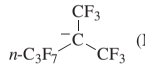
CH_2=CHBr	XCF_2CO_2Me (2 eq), CuI (1 eq), KF (1 eq), DMF	CH_2=$CHCF_3$ + CO_2 + MeX X Temp (°) Time (h) Cl 100 10 (56) Br 85–90 5 (68)	243, 244 243
	Me_3N, DMF, 60°	$(C_2F_4)_n$ n = 2–6 (—)	97
	CsF, diglyme, 100°, 80 h	oligomers (—)	807
	HgF_2, 100°, 4 h	n-$C_6F_{13}HgF$ (—)	808
	$TMSCF_3$ (6.5 eq), TMAF (2.8 eq), THF, –60 to 0°, 7 h	 +  Me_4N^+ + (—) 45% conv (—) 40% conv  Me_4N^+ +  Me_4N^+ (—) 10% conv (—) 5% conv	809
	n-$C_7F_{15}I$, Cu, pyridine, 100°	 (65)	810, 330
	1. n-$C_8F_{17}I$, Cu, DMF or DMA, 100–120°, 16 h 2. KOH	n-C_8F_{17}—≡ (71)	811

TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES (*Continued*)

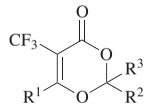
Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_2			
	*n*-C_7F_{15}I (0.5 eq), Cu, DMF, 120°, 56 h	 (32)	812
	*n*-C_7F_{15}I, Cu, pyridine, 100°	 (50)	810, 330
C_{3-9}			
	$FSO_2CF_2CO_2Me$, CuI (0.1 eq), 75–80°	 R: EtO$_2$C, Time 12 h, (72); *n*-Bu, 9 h, (80); Ph, 8 h, (91); 4-MeC_6H_4, 10 h, (90)	251
C_{3-8}			
RCH=CHBr	R_FX, AgBr/Li, THF, ultrasound	RCH=CHR_F: Me, *n*-C_4F_9, I, (52); Me, *n*-C_4F_9, Br, (36); Me, *n*-C_6F_{13}, I, (47); Ph, CF_3, Br, (31)	316
C_3			
	*n*-C_8F_{17}TMS (0.25 eq), CsF (0.7 mol %), DME, –50°, 40 min; –40°, 15 min; –30°, 15 min; –20°, 15 min; 0°, 1 h	 (—) +  (—) +  (—)	326
	KF, MeCN, rt	 (95%)	801

C_{3-9}



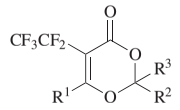
TDAE (5 mol %), rt		(100)	97
TDAE (5 mol %), 60°		(100)	97
TASF (excess)		$(Me_2N)_3S^+$ (—)	68
n-C_3F_7MgBr	perfluoropolymer of unknown structure	(—)	202

"$CuCF_3$", HMPA, 50–60°, 1 h



I

+

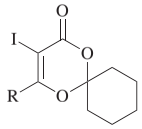


II

813

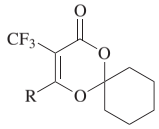
R^1	R^2	R^3	**I**	**II**
H	Me	Me	(64)	(—)
H	$-(CH_2)_5-$		(89)	(—)
Me	Me	Me	(71)	(—)

R^1	R^2	R^3	**I**	**II**
Me	$-(CH_2)_5-$		(54)	(23)
Ph	Me	Me	(95)	(—)
Ph	$-(CH_2)_5-$		(62)	(—)



R = H, Me, Ph

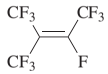
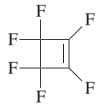
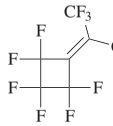
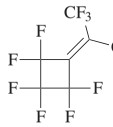
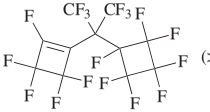
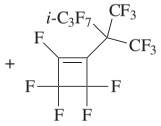
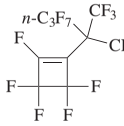
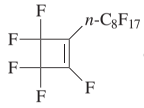
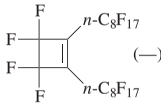
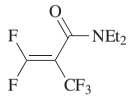
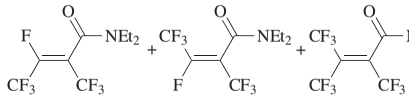
"$CuCF_3$", HMPA, 50°

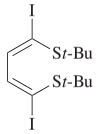


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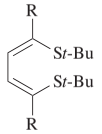
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TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES (*Continued*)

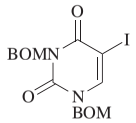
Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_4			
	CF_3Br, $(Et_2N)_3P$, CH_2Cl_2, –78°	 (—) + $C_{10}F_{18}$[a] (—)	332
	 CF_3, CsF, DMF, rt, 10 d	 (30)	815
	 CF_3, CsF, DMF, rt, 3 h	 (6) +  (>30)	815
		+  (>20) +  (—)	
	n-C_8F_{17}TMS (0.5 eq), CsF (2.2 mol %), THF, –78°; –40°, 1 h; 0°, 1 h; rt	 (—) +  (—)	326
	CF_3Br, $(Et_2N)_3P$, CH_2Cl_2, –78°	 **I** **II** **III** (—) **I** + **II** (34)	332



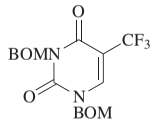
"RCd", CuI, DMF, HMPA



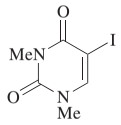
R	Temp (°)	Time (h)		
CF_3	–20	1.5	(51)	270
C_2F_5	rt	4	(61)	



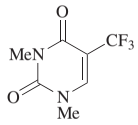
(phen)$CuCF_3$ (1.5 eq), DMF, 50°, 18 h



(78) 54

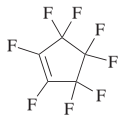


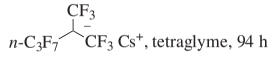
1. CuCl (1 eq), KO*t*-Bu (2 eq), DMF, rt, 1 h
2. $PhCOCF_3$ (1 eq), rt, 30 min
3. $Et_3N{\bullet}HCl$ (1 eq)
4. Substrate (0.5 eq), phen (1 eq), 50°, 12 h



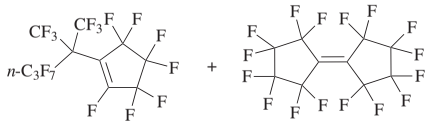
(78) 280

C_5





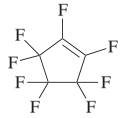
n-C_3F_7, CF_3 Cs^+, tetraglyme, 94 h

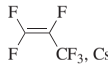


67

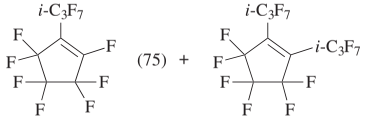
I **II**

Temp (°)	**I**	**II**
rt	(32)	(22)
70	(23)	(71)



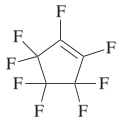
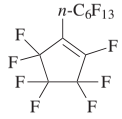
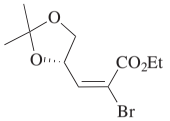
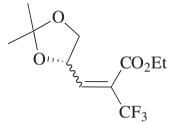
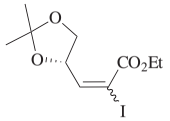
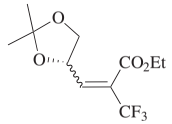
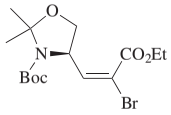
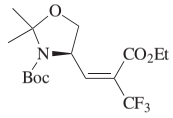
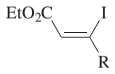
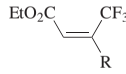
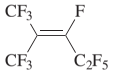
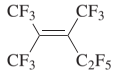


CF_3, CsF, DMF, rt, 3 h



(75) + (10) 815

TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES (*Continued*)

Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_5 	*n*-C_6F_{13}TMS (0.64 eq), CsF (3.2 mol %), DME, –40°, 20 min; –30°, 45 min; 0°	 (—) + $C_{17}F_{32}$ (—)	326
 (*E*)	$FSO_2CF_2CO_2Me$, CuI, DMF, HMPA, 70°	 (61), (*E*)/(*Z*) = 24:1	255, 256
 (*E*)/(*Z*) = 89:11	$FSO_2CF_2CO_2Me$, CuI, DMF, HMPA, 70°	 (61), (*E*)/(*Z*) = 90:10	328
	$FSO_2CF_2CO_2Me$, CuI, DMF, HMPA, 70°	 (56)	255, 256
C_{5-9} 	$TMSCF_3$ (2 eq), CuI (1.7 eq), KF (1.5 eq), DMPU, 80°, 16 h	 R: Et (86); Ph (88)	331
C_6 	CF_3Br, $(Et_2N)_3P$, CH_2Cl_2, –78°	 (45)	332

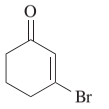
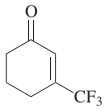
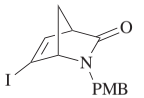
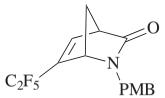
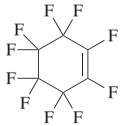
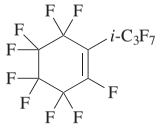
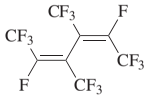
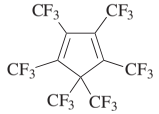
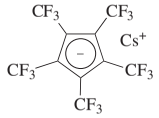
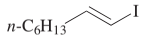
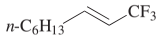
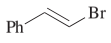
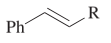
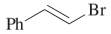
	CF_3Cu, HMPA, 30°, 12 h		(40)	53
	$TMSC_2F_5$ (5 eq), CuI (2 eq), KF (5 eq), DMF, NMP, 80°, 48 h		(57)	816
	 CF_3, CsF, DMF, rt, 6 h		(—)	815
C_8 	$CF_3CH{=}CF_2$, CsF, MeCN, rt		(74)	817
	$CF_3CH{=}CFCF_3$, CsF, MeCN, 100°		(43)	817
	(phen)$CuCF_3$ (1.5 eq), DMF, 50°, 18 h		(99)[b]	54
 (*E*)/(*Z*) = 86:14	Et_3SiCF_3 (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, NMP, 80°, 24 h	 **I** (—) **II** (—) **III** (—) 14% conv (**I** + **II**) 51% conv, **I**/**II** = 83:17		275
	RI, Cu, pyridine, 100°, 1–12 h		R n-C_3F_7 (82) n-C_7F_{15} (95)	810 330

TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES (*Continued*)

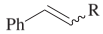
Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_8



1. *n*-$C_6F_{13}I$, Cu, DMF or DMA, 100–120°, 16 h
2. Br_2, Freon 113, rt, 1–4 h
3. KOH

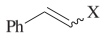

(84)

811

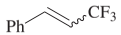
RX, AgBr/Li, THF, ultrasound

R	X		(*E*)/(*Z*)
CF_3	I	(48)	62:38
CF_3	Br	(36)	58:42
C_2F_5	I	(45)	56:44
i-C_3F_7	I	(37)	66:34
n-C_4F_9	I	(51)	61:39
n-C_4F_9	Br	(42)	63:37

316



See table.

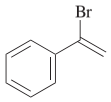


X	Conditions	Conv (%)		Refs.
Cl	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI, DMF, 120°, 8 h	—	(67)	249
Br	"$CuCF_3$", HMPA, 50°, 24 h	—	(65)	53
Br	[$CuCF_3$]•bipy, 80–120°, DMF	—	(98)	234
Br	FSO_2CF_2I (0.5 eq), Cu (1.1 eq), DMF, 80°, 7 h	100	(74)	259
Br	$FSO_2CF_2CO_2Me$ (0.33 eq), CuI (12 mol %), DMF, 70°, 4 h	100	(62)	250
Br	$FSO_2CF_2CO_2Me$ (0.5 eq), CuI (12 mol %), DMSO, 70°, 3 h	95	(68)	250
Br	$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI, DMF, 120°, 8 h	—	(67)	249
Br	$FSO_2CF_2CF_2OCF_2CO_2K$ (1.2 eq), CuI (1 eq), DMF, 45°, 6–8 h	—	(65)	247
Br	$FSO_2CF_2CO_2Me$ (0.5 eq), Cu, DMF, 60°, 4 h	100	(72)	252
Br	$ClCF_2CO_2Me$ (2 eq), CuI (1 eq), KF (1 eq), DMF, 110–120°, 8 h	—	(81)	243, 244
Br	CF_3Br, Cu anode, DMF, TMEDA, 80°	—	(90)	234

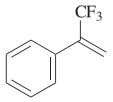
PhCH=CHBr

$FSO_2CF_2CO_2Me$ (0.5 eq), Cu (0.12 eq), DMF, 60°, 4 h — $PhCH=CHCF_3$ (72) 100% conv + SO_2 + CO_2 + CH_4 — 252

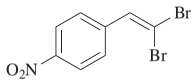
$C_2F_5CO_2Na$, CuI, NMP, 170°, 3 h — $PhCH=CHC_2F_5$ (53) — 59



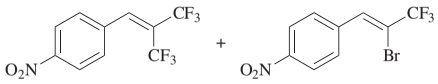
See table.



Conditions		
$[CuCF_3]$•bipy, DMF, 80–120°	(98)	234
CF_3Br, Cu anode, DMF, TMEDA, 80°	(90)	234
$TMSCF_3$ (2 eq), CuI (1.7 eq), KF (1.5 eq), DMPU, 80°, 16 h	(23)	331

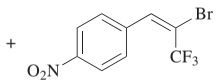


$FSO_2CF_2CO_2Me$, CuI, catalyst, DMF, HMPA, 70°, 24 h



I (82) **II** (—) 253

Catalyst	**I/II/III**
—	2:1:1
$PdCl_2$ (5 mol %)	12:1:1
$Pd(PPh_3)_4$ (1 mol %)	1:0:0



III (—)

$C_{8–14}$



I

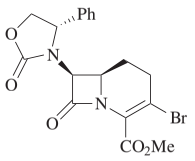
$TMSCF_3$ (2 eq), CuI (1.7 eq), KF (1.5 eq), DMPU, 80°, 16 h



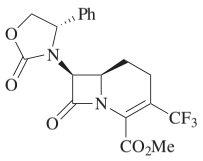
II

R^1	R^2	(*E*)/(*Z*) **I**		(*E*)/(*Z*) **II**	
n-Pr	*n*-Pr	1.0:0	(>99)[c]	1.0:0	
Ph	H	5.8:1	(>99)	5.8:1	331
2-BrC_6H_4	H	1.0:0	(>99)	1.0:0	
Ph	MeO_2C	1.6:1	(66)	1.4:1	
Ph	Ph	2.2:1	(58)	5:1	

C_8



$CF_3M/(CF_3)_2M$ (M = Zn or Cd), Cu(I), DMF



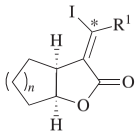
(—) 266

TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES (*Continued*)

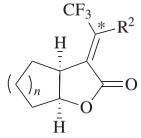
Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{8-9}



"$CuCF_3$", HMPA, DMF, 30–40 min

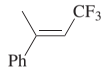


n	R^1	*Config	Temp (°)	R^2		Refs.
1	H	(*E*)	rt	H	(80)	
1	H	(*E*)	60	H	(98)	
1	H	(*Z*)	60	H	(90)	327
1	Me	(*E*)	60	Me	(75)	
1	Me	(*Z*)	60	Me	(94)	
2	H	(*E*)	rt	H	(95)	
2	H	(*E*)	60	H	(89)	
2	H	(*Z*)	60	H	(84)	
2	TMS	(*E*)	60	H	(98)	

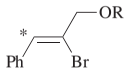
C_9



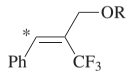
$TMSCF_3$ (2 eq), CuI (1.7 eq), KF (1.5 eq), DMPU, 80°, 16 h



(78) 331

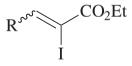


$(CF_3)_2Hg$/Cu, DMA, 140°, 2 h



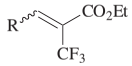
R	*Config		Refs.
Ac	(*Z*)	(93)	
Ac	(*E*)	(91)	329
n-Bu	(*E*)	(95)	

C_{9-11}



I

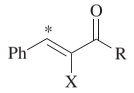
$FSO_2CF_2CO_2Me$, CuI, DMF, HMPA, 70°, 10 h



II

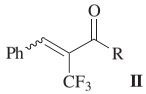
R	(*E*)/(*Z*) **I**		(*E*)/(*Z*) **II**	Refs.
Ph	81:19	(96)	86:14	
4-$O_2NC_6H_4$	84:16	(82)	84:16	328
2,6-$Cl_2C_6H_3$	96:4	(92)	95:5	
3-BrC_6H_4	83:17	(92)	82:18	
(*E*)-PhCH=CH	90:10	(91)	100:0	

C_{9-10}



I

$(CF_3)_2Hg/Cu$, DMA, 2 h

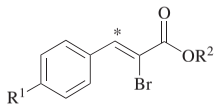


II

R	X	*Config **I**	Temp (°)		(*E*)/(*Z*) **II**
H	Br	(*Z*)	140	(90)	75:25
H	Br	(*E*)	140	(75)	77:23
H	I	(*Z*)	140	(87)	77:23
H	I	(*Z*)	100	(93)	84:16
Me	Br	(*Z*)	140	(87)	75:25
Me	Br	(*E*)	140	(90)	74:26

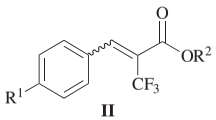
329

C_9



I

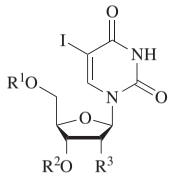
$(CF_3)_2Hg/Cu$, DMA, 140°, 2 h



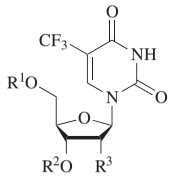
II

R^1	R^2	*Config **I**		(*E*)/(*Z*) **II**
H	Me	(*Z*)	(92)	5:95
H	Me	(*E*)	(88)	98:2
O_2N	Et	(*Z*)	(93)	23:77
O_2N	Et	(*E*)	(86)	95:5
O_2N	CF_3CH_2	(*Z*)	(92)	81:19
O_2N	CF_3CH_2	(*E*)/(*Z*) = 2:1	(89)	82:18

329



CF_3I, Cu, HMPA



R^1	R^2	R^3	Temp (°)	Time (h)	
Ac	Ac	H	110	40	(38)
Ac	Ac	AcO	110	40	(54)
Tr	H	TrO	45	12	(62)
Tr	Tr	H	45	12	(89)

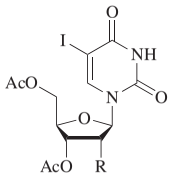
368

TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES (*Continued*)

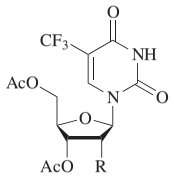
Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_9

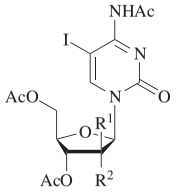


CF_3I, Cu, HMPA, 110°, 40 h

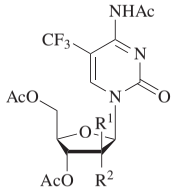


R		
H	(54)	
AcO	(38)	

818

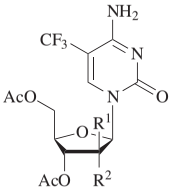


CF_3I, Cu, HMPA, 45°, 12 h



I

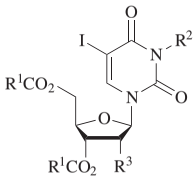
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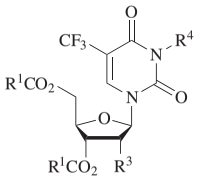
II

R^1	R^2	**I**	**II**
H	H	(—)	(62)
H	AcO	(—)	(59)
AcO	H	(11)	(39)

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$(CF_3)_2Hg$/Cu, DMA, 2 h



R^1	R^2	R^3	Temp (°)	R^4	
Ph	H	$PhCO_2$	140	H	(—)
Ph	Me	$PhCO_2$	140	Me	(94)
Ph	Bz	$PhCO_2$	140	H	(49)
4-MeC_6H_4	PMP	H	110	PMP	(90)

329

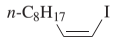
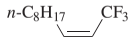
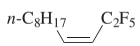
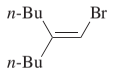
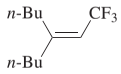
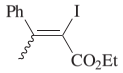
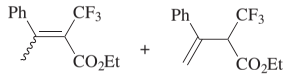
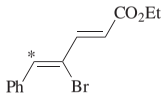
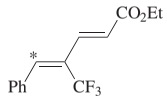
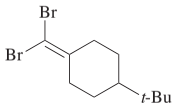
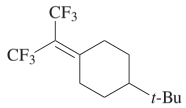
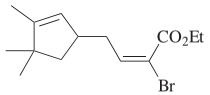
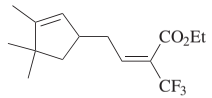
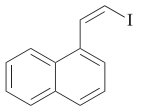
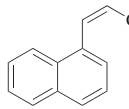
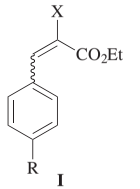
C_{10}				
	Et_3SiCF_3 (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, NMP, 80°, 24 h		(—) 90% conv	275
	$TMSC_2F_5$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, 60°, 24 h		(—) 77% conv	275
	"$CuCF_3$", HMPA, rt, 12 h		(62)	53
	$TMSCF_3$ (2 eq), CuI (1.7 eq), KF (1.5 eq), DMPU, 80°, 16 h	 (78) + (22)		331
C_{11}				
 **I**	$(CF_3)_2Hg$/Cu, DMA, 140°, 2 h	 **II**	*Config **I** (*Z*) (85) *(*Z*)/(*E*) **II** 100:0; (*E*) (92) 1:99	329
	"CF_3Cu", HMPA, rt to 50°, 20 h		(81)	53
C_{12}				
	$FSO_2CF_2CO_2Me$, CuI, DMF, HMPA, 70°		(46)	255
	$(CF_3)_2Hg$/Cu, DMA, 140°, 2 h		(93)	329

TABLE 5B. PERFLUOROALKYL ADDITION TO ALKENYL HALIDES AND PSEUDOHALIDES (*Continued*)

Alkenyl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

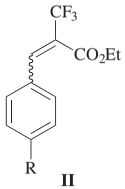
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{15}



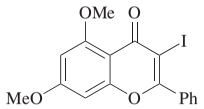
I

$FSO_2CF_2CO_2Me$, CuI, DMF, HMPA, 70°

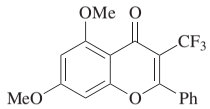


II

R	X	(*E*)/(*Z*) **I**		(*E*)/(*Z*) **II**	Refs.
H	Br	1:0	(92)	28:1	
O_2N	Br	24:1	(91)	24:1	255, 256
O_2N	I	0:1	(—)	0:1	
MeO	Br	25:1	(65)	11:1	

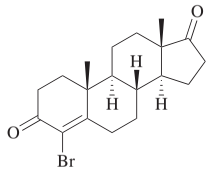


$FSO_2CF_2CO_2Me$, CuI

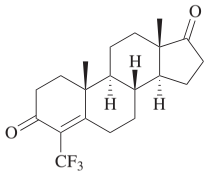


(—) 258

C_{19}

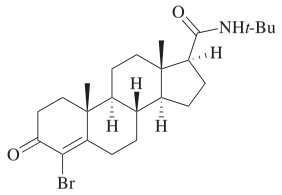


$FSO_2CF_2CO_2Me$, CuI, DMF, 75°

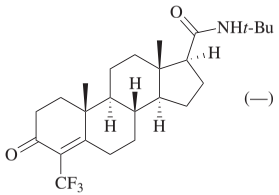


(—) 819

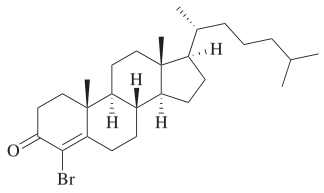
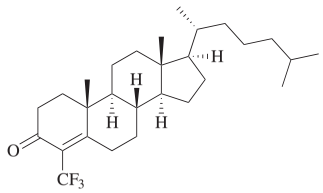
C_{20}



$FSO_2CF_2CO_2Me$, CuI, DMF, 75°



(—) 819

C_{27}		$FSO_2CF_2CO_2Me$, CuI, DMF, 75°		(—)	819

[a] Refers to perfluorodiene dimers with general formula $C_{10}F_{18}$.

[b] The yield was determined by ^{19}F NMR spectroscopy.

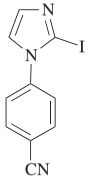
[c] The yield was determined by GC/MS.

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES

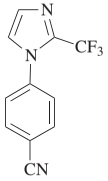
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

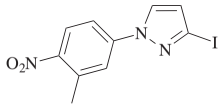
C_3



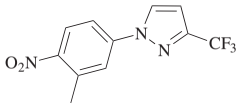
TMSCF$_3$ (1.5 eq), initiator (1.5 eq), CuI (1.5 eq), DMF, NMP, 80°, 1 h



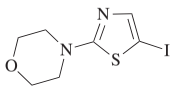
Initiator	Time (h)		Refs.
CsF	1	(22)	820
KF	41	(37)	369



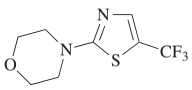
CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min



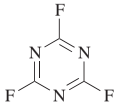
(65) 338



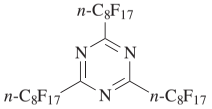
1. Substrate (1 eq), KF (6 eq), DMF/NMP, rt, 5 min
2. TMSCF$_3$ (1.3 eq), 50°, 4 h



(36) 821

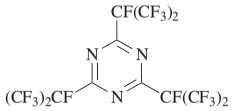


n-C_8F_{17}TMS (3.66 eq), CsF (1.36 eq), Et_2O, MeCN, –5°; 0°, 22 h; rt, 1 h



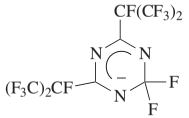
(57) 335

CF_2=$CFCF_3$ (3.2 eq), Me_3N (0.23 eq), 60°, 48 h



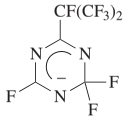
(—) 95% conv 97

CF_2=$CFCF_3$ (3 eq), Me_3N (0.46 eq), 60°, 48 h



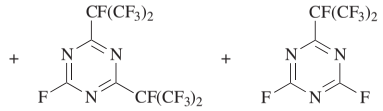
$Me_3N^+CF{=}CF_2$
(—) 40% conv

+



$Me_3N^+CF{=}CF_2$
(—) 29% conv

97



(—) 16% conv (—) 11% conv

C_{3-9}

1. CuCl (x eq), t-BuOK (2x eq), DMF, rt, 0.5 h
2. HCF_3 (1.1x eq), rt over 1 h; rt, 1 h
3. $Et_3N{\bullet}3HF$ (xy eq)
4. ArX (1 eq), temp 1, time 1; temp 2, time 2

ArX $\rightarrow$ $ArCF_3$

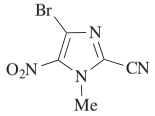
Ar	X	x	y	Temp 1 (°)	Time 1 (h)	Temp 2 (°)	Time 2 (h)		
2-thiazolyl	Br	1.0	0.33	rt	24	50	15	(35)[a]	78
5-O_2N-2-thiazolyl	Br	1.0	0.33	50	18[b]	—	—	(55)[a]	78
2-pyrimidyl	Br	1.5	0.53	rt	18	—	—	(95)[a]	78
5-pyrimidyl	Br	1.5	0.53	50	18	—	—	(24)[a]	78
2-thienyl	I	1.5	0.53	50	18	—	—	(87)[a,c]	78, 56
2-pyridyl	Br	2.0	0.53	80	8[d]	—	—	(90)[a]	78, 56
2-pyridyl	I	1.5	0.33	50	16	—	—	(95–99)[a]	56
3-pyridyl	Br	1.5	0.53	60	15	—	—	(35)[a]	78
3-pyridyl	I	2.0	0.53	rt	24	50	24	(8)[a]	78
4-pyridyl	Br	3.0	0.53	rt	24	50	15	(74)[a]	78
5-O_2N-2-pyridyl	Br	1.5	0.53	rt	15	—	—	(91)	78
3-Me-2-pyridyl	Br	1.0 + 1.0	0.53	50	15	—	18	(88)[a]	78
4-Me-2-pyridyl	Br	1.0 + 1.0	0.53	50	15	—	18	(80)[a]	78
5-Me-2-pyridyl	Br	1.0 + 1.0	0.53	50	15	—	18	(77)[a]	78
6-Me-2-pyridyl	Br	1.0 + 1.0	0.53	50	15	—	18	(73)[a]	78
2-Me-3-pyridyl	Br	1.5	0.53	60	15	—	—	(20)[a]	78
4-Me-3-pyridyl	Br	1.5	0.53	60	15	—	—	(17)[a]	78
3-Me-5-O_2N-2-pyridyl	Br	1.5	0.53	rt	15	—	—	(92)	78
3-formyl-2-pyridyl	Br	1.5	0.53	rt	12	—	—	(94)[a]	78
3-MeO_2C-2-pyridyl	Br	1.5	0.53	rt	12	—	—	(91)	78
2-quinolinyl	Br	1.5	0.53	rt	48	—	—	(80)	78

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

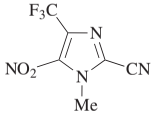
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_4



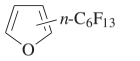
CF_3CdBr, CuI, HMPA, 70°, 6 h



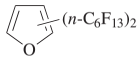
(60) 268, 269



n-$C_6F_{13}I$ (1.2 eq), Cu (2.73 eq), DMSO, 125–130°, 22 h



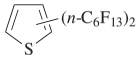
(31) +



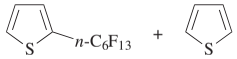
(—) 365



n-$C_6F_{13}I$ (1.1 eq), Cu (2.3 eq), DMSO, 125–130°



+



+

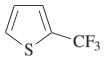
365

I (—) **II** **III** (—)

Time (h)	**II**
1.5	(57)
17	(45)



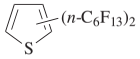
CF_3CO_2Na, CuI, NMP, 160°, 4 h



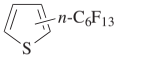
(46) 59



n-$C_6F_{13}I$ (1.1 eq), Cu (2.3 eq), DMSO, 125–130°, 19 h

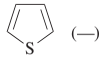


(—) +



(42) 365

+



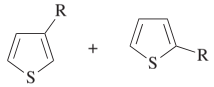
(—) +



(—)

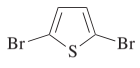


R_FI (1.2 eq), Cu (3.2 eq), DMF, 120–130°, 16–20 h

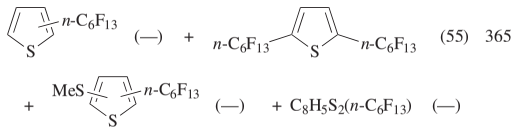


I **II**

X	R_F	**I + II**	**I/II**	
I	CF_3	(17)	**I** only	370
Br	n-C_4F_9	(30)	82:18	
I	n-C_8F_{17}	(50)	96:4	
Br	n-C_8F_{17}	(40)	82:18	



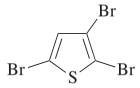
n-$C_6F_{13}I$ (2.4 eq), Cu (5 eq), DMSO, 125–130°, 3 h



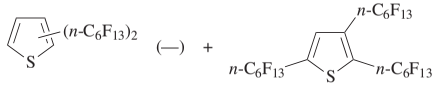
(—) + (55) 365

+ $C_8H_5S_2(n\text{-}C_6F_{13})$ (—)

+ $C_8H_4S_2(n\text{-}C_6F_{13})_2$ (—)



n-$C_6F_{13}I$ (3.6 eq), Cu (7.5 eq), DMSO, 125–130°, 22 h



(—) + (20) 365



(—) + $C_8H_4S_2(n\text{-}C_6F_{13})_4$ (—)

+ $C_8H_2S_2Br(C_6H_{13})_3$ (—)

$C_{4–10}$

ArI

$(MeO)_3BCF_3K$ (3 eq), CuI (20 mol %), 1,10-phenanthroline (20 mol %), DMSO, 60°, 16 h

$ArCF_3$ 103

Ar		Ar		Ar		Ar	
2-thienyl	(85)	4-BrC_6H_4	(93)	2-$MeSC_6H_4$	(91)	2-NC-3-FC_6H_3	(76)
3-pyridyl	(82)	4-$Me_2NC_6H_4$	(52)	2-MeC_6H_4	(70)	2-$MeO_2CC_6H_4$	(96)
5-Br-2-pyridyl	(81)	4-AcMeNC_6H_4	(96)	3-MeC_6H_4	(92)	4-$MeO_2CC_6H_4$	(84)
Ph	(91)	4-$O_2NC_6H_4$	(81)	4-MeC_6H_4	(74)	4-$Et_2NCOC_6H_4$	(95)
4-FC_6H_4	(81)	2-$MeOC_6H_4$	(83)	4-(1,3-dioxolan-2-yl)C_6H_4	(84)	2,6-$Me_2C_6H_3$	(59)
4-ClC_6H_4	(75)	4-$MeOC_6H_4$	(77)	4-NCC_6H_4	(95)	1-$C_{10}H_7$	(97)

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{4-8}

ArX — $[CF_3Cu]$•ligand, 80–120°, DMF — $ArCF_3$ — 234

Ar	X	Ligand		Ar	X	Ligand		Ar	X	Ligand	
2-thienyl	I	bipy	(95)	4-$O_2NC_6H_4$	Cl	PBu_3	(55)	3-NCC_6H_4	Br	bipy	(34)
2-thienyl	Br	bipy	(30)	3,5-$Cl_2C_6H_3$	Br	PBu_3	(20)	4-NCC_6H_4	Br	PPh_3	(74)
2-pyridyl	Br	PBu_3	(90)	4-$MeOC_6H_4$	I	PBu_3	(93)	2-AcC_6H_4	Br	bipy	(75)
2-$O_2NC_6H_4$	Br	bipy	(95)	4-$MeOC_6H_4$	Br	PBu_3	(15)	3-AcC_6H_4	Br	bipy	(25)
4-$O_2NC_6H_4$	Br	PPh_3	(70)	2-NCC_6H_4	Br	bipy	(62)	4-AcC_6H_4	Br	bipy	(60)

C_{4-7}

ArX — $C_2F_5CO_2Na$, CuI, NMP, 170°, 3 h — ArC_2F_5 — 59

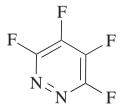
Ar	X	Conv. (%)	
2-thienyl	I	28	(—)
Ph	I	86	(—)
4-IC_6H_4	I	83[a]	(—)
4-$O_2NC_6H_4$	I	51	(—)
4-ClC_6H_4	I	75	(54)
2-ClC_6H_4	I	62	(14)
4-$CF_3C_6H_4$	Br	71	(19)

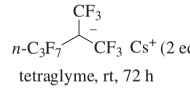
C_{4-6}

ArX — 1. $TMSCF_3$ (1.33 eq), AgF (1 eq), DMF, rt, 0.33 h; 2. Cu (1.67 eq), rt , 4 h; 3. Substrate (*x* eq) — $ArCF_3$ — 379

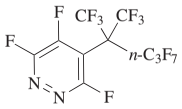
Ar	X	*x*	Temp (°)	Time (h)	
2-pyrimidyl	Br	1	20	12	(75)
2-pyridyl	Br	1	90	5	(79)
5-Br-2-pyridyl	Br	0.5	75	4	(92)
Ph	I	1	20	6	(84)
C_6F_5	I	1	50	3	(~85)[e]

C_4



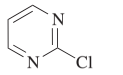


n-C_3F_7 CF_3 CF_3 Cs^+ (2 eq), tetraglyme, rt, 72 h

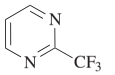


(83)

67



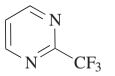
CF_2Br_2, Cu, DMA, 100°, 8 h

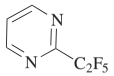


(46)

51

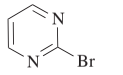
CF_2Br_2, Cu (6 eq), DMA, 100°, 8 h



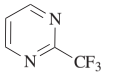
(46) + 

(50)

367



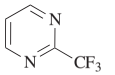
42, benzene, DMI, 50°, 20 h



(—) 77% conv

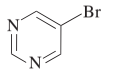
278

CF_3CO_2Na, CuI, NMP, 160°, 4 h

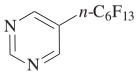


(34)

59



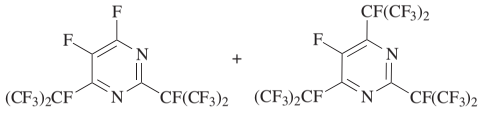
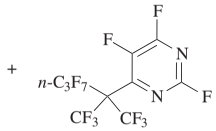
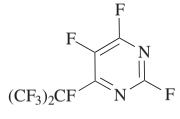
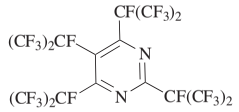
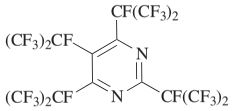
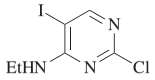
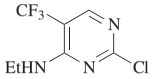
n-$C_6F_{13}I$ (1.2 eq), Cu (2.3 eq), DMSO, 125–130°, 2 h

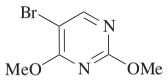
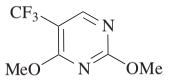
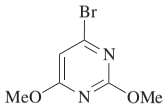
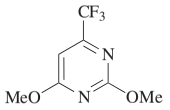
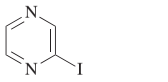
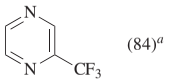
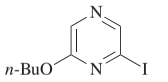
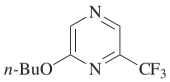
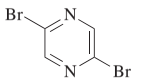
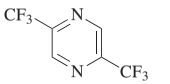
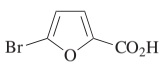
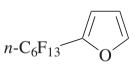
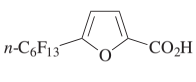


(71)

365

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_4			
	$CF_2{=}CFCF_3$ (3 eq), TDAE (3.8 eq), 60°, 48 h	 (—) 41% conv + (—) 40% conv	97
		+  (—) 8% conv +  (—) 2% conv	
		+  (—) 2% conv	
	$CF_2{=}CFCF_3$ (excess), TDAE (0.1 eq), MeCN, rt, 48 h	 (quant)	97
	1. CuI (1.2 eq), KF (1.2 eq), 150°, reduced pressure, 2 h 2. $TMSCF_3$ (1.2 eq), DMF/NMP (1:1), rt, 0.5 h 3. Substrate (1 eq), 35°, 48 h	 (69)	822

	CF_3I, Cu, HMPA, 110°, 40 h		(42)		368
	CF_3I, Cu, HMPA, 110°, 40 h		(31)		368
	1. CF_3I (5 eq), Zn (2 eq), DMPU, rt, 2 h 2. Substrate, Cu (10 mol %), 50°, 24 h		(84)[a]		62
	CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min		(64)		338
	1. CuCl (3 eq), *t*-BuOK (6.1 eq), DMF, rt, 0.5 h 2. Add HCF_3 (3.3 eq) at rt over 1 h; rt, 1 h 3. $Et_3N{\bullet}3HF$ (1.6 eq) 4. Substrate (1 eq), rt, 24 h		(94)[a]		78
C_5 	*n*-$C_6F_{13}I$ (*x* eq), Cu (*y* eq), DMSO, 125–130°		**I**	+  **II**	365

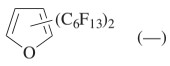
x	*y*	Time (h)	**I**	**II**	
1.1	2.3	4	(—)	(45)	
1.2	2.7	4	(—)	(23)	+  (—)
1.2	2.7	21	(51)	(—)	

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

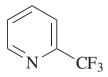
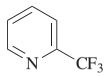
C_{5-10}

ArI	**63** (2 eq), CsF (2 eq), CuI (10 mol %), phen (10 mol %), diglyme, 80°, 24 h	$ArCF_3$	377

Ar		Ar	
5-Me-2-thienyl	(75)	4-$HOCH_2C_6H_4$	(44)
3,4-$Cl_2C_6H_3$	(97)	4-NCC_6H_4	(93)
4-BrC_6H_4	(53)	3-$EtO_2CC_6H_4$	(60)
2-$O_2NC_6H_4$	(47)	4-AcC_6H_4	complex mixture
3-$O_2NC_6H_4$	(90)	4-*n*-BuC_6H_4	(40)
4-$O_2NC_6H_4$	(77)	1-$C_{10}H_7$	(97)
4-$EtOC_6H_4$	(57)	2-$C_{10}H_7$	(95)

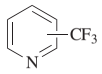
	$TMSCF_3$ (2 eq), KF (2 eq), CuI (10 mol %), phen (10 mol %), NMP/DMF (1:1), 60°, 24 h	$ArCF_3$	Ar		376
			5-Me-2-thienyl	(63)[a]	
			5-Cl-3-pyridyl	(69)[a]	
			4-ClC_6H_4	(63)[a]	
			3-$O_2NC_6H_4$	(63)	
			4-$O_2NC_6H_4$	(70)	
			4-NCC_6H_4	(80)[a]	
			4-$EtO_2CC_6H_4$	(89)[a]	
			4-*n*-BuC_6H_4	(44)[a]	

C_5

	"CF_3Cu", DMF, ligand (*x* eq), 90°, 3 h		Ligand	*x*	364
			PBu_3	2 (90)	
			TMEDA	10 (98)	
	CF_3CO_2Na, CuI, NMP, 140–160°, 4 h		(41)		58



CF_3Br, e^-, Cu anode, DMF, TMEDA, Bu_4NBr, 95°, 7 h; heating, 2 h

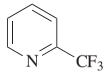


Isomer	
2-	(95)
3-	(98)

364



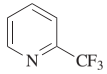
$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), DMF, NMP, rt, 16 h



(23) 45% conv

349

$(CF_3)_2Hg$/Cu, solvent, 140–150°, 5 h

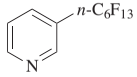


Solvent	
NMP	(74)
DMA	(57)[f]

261

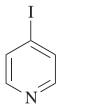


n-$C_6F_{13}I$ (x eq), Cu (y eq), DMSO, 125–130°

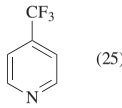


x	y	Time (h)	
1.1	2.2	1.5	(71)
2.2	4.6	4	(82)

365



$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), DMF, NMP, rt, 16 h



(25) 48% conv

349

C_{5-7}

ArX

$FSO_2CF_2CF_2OCF_2CO_2Me$, CuI, DMF, 8 h

ArCF$_3$

249

Ar	X	Temp (°)	
2-pyridyl	Cl	120	(64)
2-pyridyl	Br	120	(70)
Ph	Cl	110–120	(52)
Ph	Br	110	(73)
Ph	I	100	(80)
4-$O_2NC_6H_4$	Cl	120	(67)

Ar	X	Temp (°)	
3-$O_2NC_6H_4$	Cl	120	(72)
4-$MeOC_6H_4$	Cl	120	(34)
2-MeC_6H_4	Cl	120	(32)
4-MeC_6H_4	Cl	120	(56)
4-$CHOC_6H_4$	Cl	120	(37)
4-$EtO_2CC_6H_4$	Cl	120	(52)

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions		Product(s) and Yield(s) (%)				Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*							
C_{5-10}							
			Ar	X			
ArX	$FSO_2CF_2CF_2OCF_2CO_2K$ (1.2 eq), CuI (1 eq), DMF, 45°, 6–8 h	$ArCF_3$	2-pyridyl	Br	(52)		247
			Ph	I	(72)		
			Ph	Br	(61)		
			2,4-$(O_2N)_2C_6H_3$	Cl	(55)		
			2,4-$(O_2N)_2C_6H_3$	I	(78)		
			1-$C_{10}H_7$	I	(61)		
C_{5-8}							
			Ar	X	Conv (%)		
ArX	CF_3Br, Cu anode, DMF, TMEDA, 80°	$ArCF_3$	2-pyridyl	Br	95	(80)	234
			3-pyridyl	Br	98	(60)	
			2-$O_2NC_6H_4$	Br	100	(—)	
			3-$O_2NC_6H_4$	Br	92	(—)	
			4-$O_2NC_6H_4$	Br	100	(—)	
			4-$O_2NC_6H_4$	Cl	60	(—)	
			3,5-$Cl_2C_6H_3$	Br	70	(—)	
			4-$MeOC_6H_4$	I	100	(90)	
			4-$MeOC_6H_4$	Br	32	(—)	
			2-NCC_6H_4	Br	80	(77)	
			3-NCC_6H_4	Br	85	(80)	
			4-NCC_6H_4	Br	91	(85)	
			CH_2=C(Ph)	Br	84	(—)	
			PhCH=CH[ff]	Br	90	(88)[fff]	

C_{5-10}

ArX — CF_3CO_2Na (4 eq), CuI (2 eq), NMP, 140–160°, 4 h — $ArCF_3$ — 58

Ar	X	Conv (%)	
2-pyridyl	Br	41	(—)
Ph	I	72	(—)
4-ClC_6H_4	I	68	(—)
4-$O_2NC_6H_4$	I	47	(39)
3-$MeOC_6H_4$	I	59	(42)
3-MeC_6H_4	Br	58	(—)
3-MeC_6H_4	I	88	(—)
1-$C_{10}H_7$	I	82	(78)

C_{5-7}

ArX — CF_3CO_2Me (5 eq), CsF (2.5 eq), CuI (1 eq), solvent, 8 h — $ArCF_3$ — 120

Ar	X	Solvent	Temp (°)	Conv (%)	
2-pyridyl	Br	DMF	180	45	(42)
Ph	I	DMF	180	69	(—)
4-ClC_6H_4	I	DMF	180	82	(50)
4-$O_2NC_6H_4$	I	sulfolane	140	63	(62)
4-$MeOC_6H_4$	Br	DMF	180	—	(56)
4-MeC_6H_4	I	DMF	180	71	(65)

ArI — Catalyst (1 eq), DMF, 80° — $ArCF_3$ — 55

1.1 eq

Ar	Catalyst	Time (h)	
2-pyridyl	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(85)[a]
2-pyridyl	[(Ph_3P)$_3$CuCF$_3$]	2–7	(75)[a]
Ph	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(65)[a]
Ph	[(Ph_3P)$_3$CuCF$_3$]	22	(60–65)[a]
4-FC_6H_4	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(60)[a]
4-FC_6H_4	[(Ph_3P)$_3$CuCF$_3$]	2–7	(60)[a]
4-ClC_6H_4	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(80)[a]
4-ClC_6H_4	[(Ph_3P)$_3$CuCF$_3$]	22	(60)[a]
4-$O_2NC_6H_4$	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(70)[a]
4-$O_2NC_6H_4$	[(Ph_3P)$_3$CuCF$_3$]	2–7	(90)[a]
4-$MeOC_6H_4$	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(65)[a]
4-$MeOC_6H_4$	[(Ph_3P)$_3$CuCF$_3$]	22	(70–75)[a]
4-MeC_6H_4	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(60)[a]
4-MeC_6H_4	[(Ph_3P)$_3$CuCF$_3$]	22	(55)[a]
4-$CF_3C_6H_4$	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(60)[a]
4-$CF_3C_6H_4$	[(Ph_3P)$_3$CuCF$_3$]	2–7	(75)[a]
4-NCC_6H_4	[(phen)Cu(Ph_3P)$_3CF_3$]	16	(85)[a]
4-NCC_6H_4	[(Ph_3P)$_3$CuCF$_3$]	2–7	(70)[a]

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-10}

ArX

[CuC_2F_5•Et_3N•3HF (Table 34, C_0) + *x* mol % Et_3N•3HF] (*y* eq), DMF

ArC_2F_5

279

Ar	X	*x*	*y*	Temp (°)	Time (h)	
2-pyridyl	I	53	1.2	rt	24	(95)[a]
3-pyridyl	Br	20	2	80	48	(80)[a]
Ph	Br	20	2	80	72	(95)[a]
Ph	I	53	1.2	50	24	(95)[a]
4-ClC_6H_4	Br	20	2	80	72	(96)[a]
4-ClC_6H_4	I	53	1.2	rt	16	(94)[a]
4-BrC_6H_4	I	53	1.2	rt	16	(90)[a,g]
4-$O_2NC_6H_4$	Br	20	1.5	80	18	(98)[a]
4-$O_2NC_6H_4$	I	53	1.2	rt	24	(96)[a]
2-$MeOC_6H_4$	Br	20	1.5	90	24	(99)[a]
3-$MeOC_6H_4$	Br	20	2	90	36	(97)[a]
4-$MeOC_6H_4$	Br	20	2	80	60	(94)[a]
4-$MeOC_6H_4$	I	53	1.2	rt	16	(97)[a]
3,4-$(OCH_2O)C_6H_3$	Br	20	2.5	90	24	(86)
2,4-$(MeO)_2C_6H_3$	I	53	1.2	rt	16	(98)[a]
3-MeC_6H_4	Br	20	2	80	72	(96)[a]
4-$CF_3C_6H_4$	I	53	1.2	rt	16	(95)[a]
4-NCC_6H_4	I	53	1.2	rt	24	(94)[a]
3-$OHCC_6H_4$	I	53	1.2	rt	16	(99)[a]
4-$EtO_2CC_6H_4$	Br	20	1.5	80	36	(99)[a]
4-$EtO_2CC_6H_4$	I	53	1.2	rt	16	(97)[a]
2-$H_2NCOC_6H_4$	I	53	1.2	rt	0.5	(92)[a]
4-AcC_6H_4	I	53	1.2	rt	16	(99)[a]
2-quinolinyl	Br	20	1.5	50	72	(85)
3-quinolinyl	Br	20	2	80	72	(97)
4-*t*-BuC_6H_4	I	53	1.2	rt	16	(96)[a]
1-$C_{10}H_7$	I	53	1.2	rt	16	(97)[a]
2-$C_{10}H_7$	Br	20	2	80	60	(82)

ArI

1. CuCl (*x* eq), *t*-BuOK (2*x* eq), DMF, rt, 1 h
2. $PhCOCF_3$ (*x* eq), rt, 0.5 h
3. Et_3N•HCl (*x* eq)
4. Substrate (0.5 eq), phen (*y* eq), temp, 12 h

$ArCF_3$

280

Ar	*x*	*y*	Temp (°)	
3-pyridyl	1	1	rt	(85)[a]
2-BrC_6H_4	1	1	50	(93)
4-$O_2NC_6H_4$	0.5	0.5	rt	(95)
4-$MeOC_6H_4$	1	1	50	(65)
4-$CF_3C_6H_4$	1	1	rt	(91)[a]
2-$EtO_2CC_6H_4$	1	1	rt	(87)
4-AcC_6H_4	1	1	rt	(80)
4-*t*-BuC_6H_4	1	1	50	(71)
1-$C_{10}H_7$	1	1	50	(91)

ArX (phen)$CuCF_3$ (1 eq), DMF, 18 h $ArCF_3$ 54

5 eq

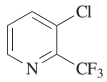
Ar	X	Temp	
3-pyridyl	I	rt	(92)[a,h]
Ph	I	rt	(88)[a,h]
2-ClC_6H_4	I	rt	(89)[a,h]
4-BrC_6H_4	I	rt	(92)[a,h]
2-$MeOC_6H_4$	I	rt	(90)[a,h]
4-$MeOC_6H_4$	I	rt	(86)[a,h]
2,6-$(MeO)_2C_6H_3$	I	rt	(96)[a,h]
4-$Me_2NC_6H_4$	I	rt	(88)[a,h]
2-MeC_6H_4	I	rt	(88)[a,h]
4-$HOCH_2C_6H_4$	I	rt	(75)[a,h]
4-$OHCC_6H_4$	Br	110°	(66)[a,h]
4-$OHCC_6H_4$	I	rt	(92)[a,h]
4-NCC_6H_4	Br	110°	(60)[a,h]
4-$EtO_2CC_6H_4$	Br	110°	(61)[a,h]
4-AcC_6H_4	I	rt	(87)[a,h]
2,6-$Me_2C_6H_3$	I	rt	(87)[a,h]
4-*n*-BuC_6H_4	I	rt	(83)[a,h]

C_{5-12}

ArX $TMSCF_3$ (*x* eq), additive 1 (*y* eq), additive 2, solvent, rt, 112 h $ArCF_3$ (—) 277

Ar	X	*x*	Additive 1	*y*	Additive 2	Solvent	Conv (%)
3-pyridyl	I	—	CuI	—	KF	DMF	3[i]
3-pyridyl	I	0.4	**43**	0.2	—	DMF	94
3-pyridyl	I	0.65	**43**	0.2	—	THF	44
4-pyridyl	I	—	CuI	—	KF	DMF	70
4-pyridyl	I	0.4	**43**	0.2	—	DMF	99
4-pyridyl	I	0.65	**43**	0.2	—	THF	79
Ph	I	—	CuI	—	KF	DMF	25
Ph	I	0.4	**43**	0.2	—	DMF	94
Ph	I	0.65	**43**	0.2	—	THF	16
4-$MeOC_6H_4$	I	—	CuI	—	KF	DMF	62
4-$MeOC_6H_4$	I	0.4	**43**	0.2	—	DMF	91
4-$MeOC_6H_4$	I	0.65	**43**	0.2	—	THF	12
Bn	Br	—	CuI	—	KF	DMF	29
Bn	Br	0.4	**43**	0.2	—	DMF	58
Bn	Br	0.65	**43**	0.2	—	THF	20
4-PhC_6H_4	I	—	CuI	—	KF	DMF	41
4-PhC_6H_4	I	0.4	**43**	0.2	—	DMF	99
4-PhC_6H_4	I	0.65	**43**	0.2	—	THF	19

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)			Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*					
$C_{5–10}$					
ArI	Bu_3SnCF_3 (2 eq), CuI (2 eq), KF (2 eq), NMP/DMF (1:1), 80°, 24 h	$ArCF_3$	Ar		157
			3-pyridyl	(96)[a]	
			4-ClC_6H_4	(95)[a]	
			4-$O_2NC_6H_4$	(87)[a]	
			4-$Ph(CH_2)_3OC_6H_4$	(87)[a]	
			4-MeC_6H_4	(99)[a]	
			4-$BnO_2CC_6H_4$	(91)[a]	
			2-CH_2=$CHCH_2C_6H_4$	(90)[a]	
			4-*t*-BuC_6H_4	(82)[a]	
			1-$C_{10}H_7$	(98)[a]	
$C_{5–12}$					
ArX	**40** (0.2 eq), THF, rt, 112 h	$ArCF_3$	(—)	Ar: X: Conv (%)	277
				3-pyridyl: I: 59	
				4-pyridyl: I: 80	
				Ph: I: 20	
				4-$MeOC_6H_4$: I: 14	
				4-PhC_6H_4: I: 45	
	42, benzene, DMI, 50°, 20 h	$ArCF_3$	(—)	Ar: X: Conv (%)	278
				3-pyridyl: I: 88	
				4-pyridyl: I: 57	
				Ph: I: 86	
				4-$MeOC_6H_4$: I: 89	
				4-*t*-BuC_6H_4: I: 70	
				4-PhC_6H_4: I: 93	
C_5					
	1. $TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, 50°, 6 h 2. NH_3, H_2O		(46)		348

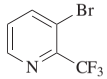
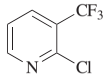
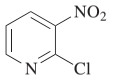
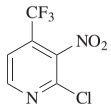
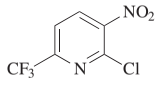
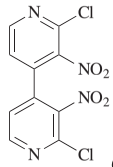
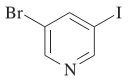
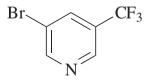
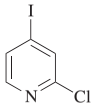
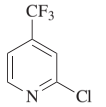
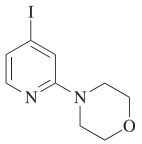
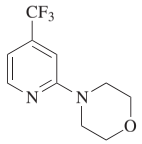
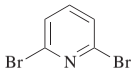
	$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, rt, 3–6 h		(74)	350
	$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, DMF, rt, 16 h		(67) 91% conv	349
	1. $TMSCF_3$ (1.2 eq), TASF (1 eq), THF, pyridine, –70°, 5 min 2. DMDO (1.2 eq), H_2O (1 eq), acetone, 15 min 3. HCl, H_2O	 (28) +  (29) +  (6)		307
	$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, DMF, rt, 16 h		(48) 72% conv	349
	$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, DMF, rt, 16 h		(68) 90% conv	349
	CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min		(91)	338

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

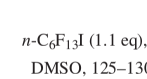
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_5

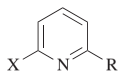


n-$C_6F_{13}I$ (1.1 eq), Cu (2.3 eq), DMSO, 125–130°, 1.5 h

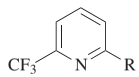


(89)[ii]

365

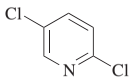


$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, DMF, rt, 16 h

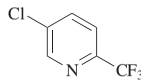


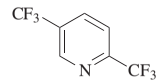
X	R		Conv (%)
I	H	(68)	92
Br	Cl	(32)	39
Br	Br	(28)	34
I	Cl	(59)	89
I	Br	(79)	93

349



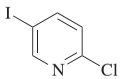
CF_3CO_2Na, CuI, NMP, 160°, 4 h



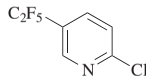
(85) + 

(7)

59

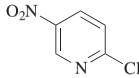


$CF_3CF_2CO_2Na$, CuI, NMP, 170°, 3 h

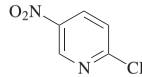


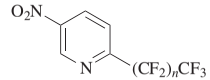
(30)

59



Cu (0.6 eq), CF_2Br_2 (0.2 eq), DMF, 100°, 8 h



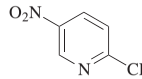
(35) + 

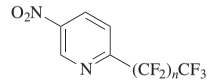
n = 1–3

(7)

274

Cu (6 eq), CF_2Br_2 (2 eq), charcoal (1 g/10 mmol CF_2Br_2), DMF, 100°, 8 h

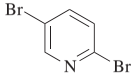


(45) + 

n = 1–3

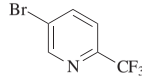
(45)

274



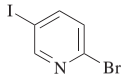
I

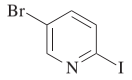
$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, DMF, rt, 20 h

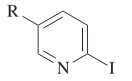


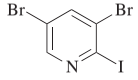
II (—), **I**/**II** = 1:1

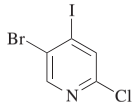
350



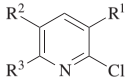


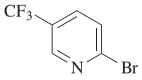
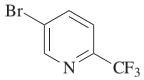
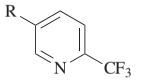
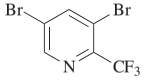
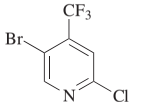
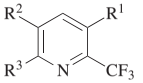
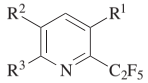






C_{5-6}



$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, DMF, rt, 16 h		(29)	42% conv				349
$TMSCF_3$ (*x* eq), KF (*y* eq), CuI (*z* eq), NMP, DMF, rt		*x*	*y*	*z*	Time (h)	Conv (%)	
		—	—	—	16	— (87)	347
		1	1.1	1.1	16	85 (69)	349
		1	1.1	1.1	3–6	— (69)	350
1. Zn (2 eq), CF_3I (5 eq), DMPU, rt, 2 h 2. Substrate, Cu (10 mol %), 50°, 24 h		R					62
		H	(96)[a]				
		Br	(90)				
$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, DMF, rt, 16 h		(59)	87% conv				349
$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, 50°, 20.75 h		(64)					346
CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h	 **I** +  **II**						367

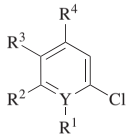
R^1	R^2	R^3	**I**	**II**
H	H	H	(13)	(23)
H	O_2N	H	(48)	(18)
O_2N	H	H	(93)	(—)
H	H	CF_3	(9)	(9)
CF_3	H	H	(19)	(13)

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

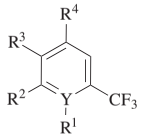
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-13}



CF_2Br_2, Cu, solvent



51

R^1	R^2	R^3	R^4	Y	Solvent	Temp (°)	Time (h)	
—	H	H	H	N	DMA	100	8	(13)
—	H	O_2N	H	N	DMA	100	8	(48)
O_2N	H	O_2N	H	C	DMA	100	4	(93)
O_2N	H	O_2N	H	C	DMF	100	8	(88)
O_2N	H	O_2N	H	C	NMP	100	4	(83)
O_2N	H	O_2N	H	C	DMPU	90	8	(93)
O_2N	H	O_2N	H	C	DMSO	100	8	(97)
O_2N	H	H	H	C	DMF	100	8	(59)
H	O_2N	H	H	C	DMF	100	8	(0)
H	H	O_2N	H	C	DMF	100	8	(5)
H	O_2N	O_2N	H	C	DMF	100	8	(8)
H	O_2N	CF_3	O_2N	C	DMF	100	0.5	(83)
MeO_2C	H	H	H	C	DMF	100	8	(17)
Bz	H	O_2N	H	C	DMF	100	8	(47)

C_5



$TMSCF_3$, TASF, THF, 20°, 2–3 h



(—) 40–70% conv

333

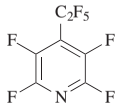
$Me_4N^+ B(CF_3)_4^-$, –78°



(—)

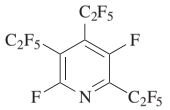
169

$CF_2{=}CF_2$ (3.15 eq), Me_3N (0.19 eq), DMF, 60°, 48 h



(—) 60% conv

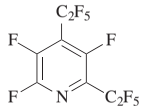
+



(—) 25% conv

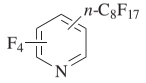
97

+



(—) 10% conv

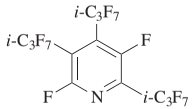
n-C_8F_{17}TMS (0.8 eq), CsF (2.7 mol %), DME, 40 min



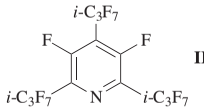
(—)

326

$CF_2{=}CFCF_3$, KF, tetrahydrothiophene dioxide



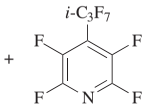
I +



II 823

Temp (°)	Time (h)	**I** + **II**	**III**
102	0.75	(19)	(53)
136	1	(32)	(19)
102	1.5	(36)	(34)
118	1.5	(50)	(23)
90	2	(37)	(42)
78	3	(35)	(38)
102	3	(79)	(9)

+



III

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

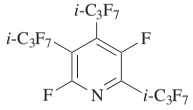
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_5

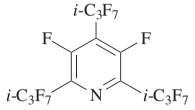


CF_2=$CFCF_3$ (2.76 eq), TDAE (5.6 mol %), 60°, 48 h



(—) 7% conv

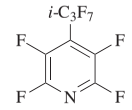
+



(—) 35% conv

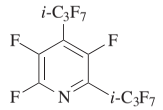
97

+

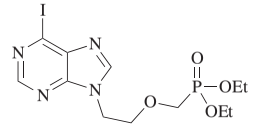


(—) 21% conv

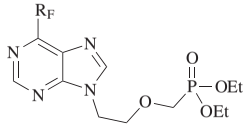
+



(—) 10% conv

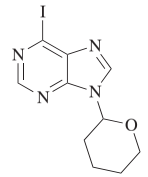


$TMSR_F$ (*x* eq), KF (1.4 eq), CuI (1.6 eq), NMP, DMF, 60°

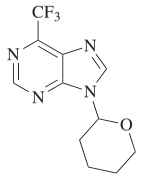


R_F	*x*	Time (h)	
CF_3	1.4	24	(92)
n-C_3F_7	1.7	48	(46)

371



$TMSCF_3$ (1.4 eq), KF (1.4 eq), CuI (1.6 eq), NMP, 60°, 24 h



(85)

371

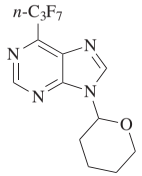
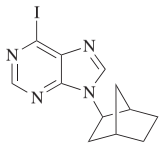
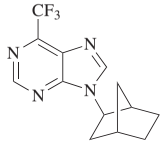
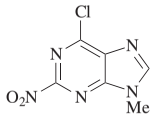
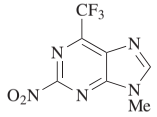
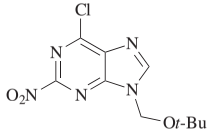
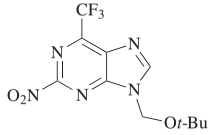
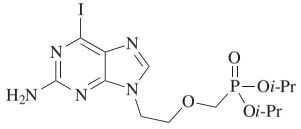
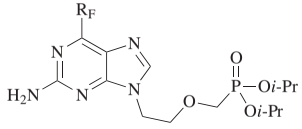
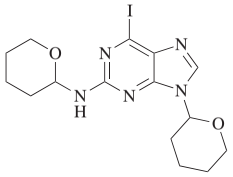
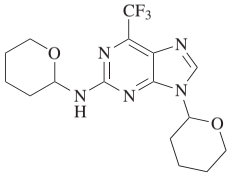
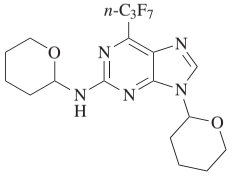
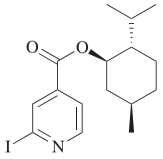
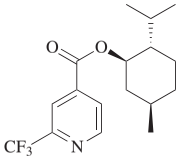
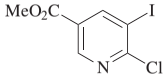
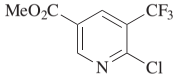
	n-C_3F_7TMS (1.7 eq), KF (1.4 eq), CuI (1.6 eq), NMP, DMF, 60°, 48 h		(35)	371
	$TMSCF_3$ (1.5 eq), KF (1.5 eq), CuI (1.7 eq), NMP, DMF, 80°, 40 h		(81)	824
	$TMSCF_3$ (2 eq), CsF (4 eq), THF, 0°, 5 min; rt, 16 h		(30)	825
	$TMSCF_3$ (3 eq), CsF (1.5 eq), THF, 0°, 5 min; rt, 5 h		(31)	825
	1. $TMSR_F$ (2 eq), KF (1.4 eq), CuI (1.6 eq), NMP, DMF, rt, 4 d 2. $Na_2S_2O_3$, H_2O		R_F / CF_3 (28) / *n*-C_3F_7 (21)	375

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_5			
	$TMSCF_3$ (1.4 eq), KF (1.4 eq), CuI (1.6 eq), NMP, 60°, 24 h	 (30)	371
	n-C_3F_7TMS (1.7 eq), KF (1.4 eq), CuI (1.6 eq), NMP, DMF, 60°, 48 h	 (23)	371
C_6			
	CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min	 (75)	338
 7 kg	1. CuI (1.5 eq), KF (1.1 eq), NMP, 120° 2. ClF_2CO_2Me (4.7 eq) over 1 h at 120°; 120°, 2 h 3. $HO_2CCO_2H•H_2O$, H_2O, 30–40°	 (68) 92.3% pure	826

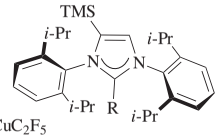
PhI	$FSO_2(CF_2)_2OCF_2CO_2Me$, CuI, solvent	$PhCF_3$	Solvent (s) / Temp (°) / Time (h) / (%): DMF / 120 / 8 / (80); DMF, HMPA / 80 / 4 / (72); NMP / 90 / 10 / (62)	247
	$FSO_2CF_2CO_2Me$, CuI, solvent	$PhCF_3$	Solvent / Temp (°) / Time (h) / (%): DMF / 70 / 2.5 / (84); NMP / 55 / 8 / (70)	247
	$ClCF_2CO_2Me$, KF, CuI, solvent, 8 h	$PhCF_3$	Solvent / Temp (°) / (%): DMF / 120 / (83); NMP / 80 / (61)	247
	$FSO_2(CF_2)_2OCF_2CO_2K$, CuI, solvent	$PhCF_3$	Solvent (s) / Temp (°) / Time (h) / (%): DMF / 45 / 8 / (70); NMP / 45 / 6 / (68); HMPA / 40 / 2 / (74); DMF, HMPA / 40 / 3 / (72)	247
	$PhSO_2CF_3$, *t*-BuOK, CuI, 80°, 20 h	$PhCF_3$	(26)	179
	41, rt, 44 h	$PhCF_3$	(33)	277
	41, heat	$PhCF_3$	(—) +  (—) R = CuC_2F_5	277
	n-$C_3F_7CO_2Na$ (4 eq), CuI (2 eq), NMP, 132°, 3 h	*n*-C_3F_7Ph	(30)	59

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_6

PhI — *i*-C_3F_7I, Cu, DMF, 90°, 15 h — *i*-C_3F_7Ph (54) — 827

— CF_3Br, Cu, HMPA, 130°, 20 h — $PhCF_3$ (11) — 828

PhX — RY (*x* eq), Cu (*y* eq) — PhR **I** + Ph–Ph **II** + PhBr **III** — 337

X	R	Y	*x*	*y*	Solvent	Temp (°)	Time (h)	**I**	**II**	**III**
I	CF_3	I	0.71	2.71	DMF	150	12	(45)	(—)	(—)
I	*n*-C_3F_7	I	0.5	1	DMSO	120	1	(65)	(—)	(—)
I	*i*-C_3F_7	I	0.5	3.6	DMF	125	1.5	(40)	(—)	(—)
I	*n*-C_7F_{15}	I	1	2.4	DMSO	110	2	(70)	(—)	(—)
I	*n*-C_7F_{15}	Br	0.23	2	DMF	188	50	(40)	(25)	(25)
Br	*n*-C_7F_{15}	I	1	2	DMSO	120	1.5	(12)	(80)	(—)

C_{6-7}

ArI — CF_3I, Cu, DMF — $ArCF_3$ — 366

Ar	Temp (°)	Time (h)	
Ph	120–130	14	(72)
4-$O_2NC_6H_4$	135	30	(51)
4-$MeOC_6H_4$	130–140	20	(86)
2-MeC_6H_4	130–140	11	(28)
3-MeC_6H_4	130–140	20	(68)
2-$CF_3C_6H_4$	140	24	(80)
3-$CF_3C_6H_4$	130–140	20	(62)

ArX — CF_2X_2, M, CuY, DMF, –80° to rt; X = Br, Cl; M = Cd, Zn; Y = I, Br, Cl, CN — $ArCF_3$ — 273

Ar	
Ph	(100)
2-$O_2NC_6H_4$	(95)
3-$O_2NC_6H_4$	(88)
4-$O_2NC_6H_4$	(81)
2-ClC_6H_4	(96)
4-BrC_6H_4	(95)
2-$MeOC_6H_4$	(78)
4-MeC_6H_4	(95)

C_6

ArX — CF_3I, Cu, pyridine, 140° — $ArCF_3$ **I** + ArC_2F_5 **II** + ArH **III** — 336

Ar	X	**I**	**II**	**III**	**I/II/III**
Ph	I	(100)	(—)	(—)	—
Ph	Br	(—)	(—)	(—)	1:1:1
4-$O_2NC_6H_4$	I	(—)	(—)	(—)	—
4-$O_2NC_6H_4$	Cl	(—)	(—)	(—)	9:1:0
2-$MeOC_6H_4$	I	(100)	(—)	(—)	—
3-$MeOC_6H_4$	Br	(—)	(—)	(—)	1:1:1
4-$MeOC_6H_4$	I	(—)	(—)	(—)	—

C_{6-10}

ArI

1. CuCl (*x* eq), *t*-BuOK (2*x* eq), DMF, rt, 0.5 h
2. HCF_3 (1.1*x* eq) at rt over 1 h; rt, 1 h — $ArCF_3$
3. $Et_3N{\bullet}3HF$ (*xy* eq)
4. ArI (1 eq), temp 1, time 1; temp 2, time 2

Ar	*x*	*y*	Temp 1	Time 1 (h)	Temp 2 (°)	Time 2 (h)		
Ph	1.5	0.53	rt	24	50	18	(96)[a]	78
4-FC_6H_4	1.5	0.33	50°	25	—	—	(75)[a]	56
4-ClC_6H_4	1.5	0.33	50°	25	—	—	(90–95)[a]	56
2-BrC_6H_4	1.3	0.53	rt	24	50	18	(95)[a,j]	78
4-BrC_6H_4	1.5	0.53	rt	24	50	18	(96)[a,k]	78
4-$O_2NC_6H_4$	1.5	0.53	rt	20	—	—	(83)	78
2-$MeOC_6H_4$	1.5	0.53	rt	24	50	18	(87)	78
3-$MeOC_6H_4$	2.0	0.53	rt	24	50	24	(97)[a]	78
4-$MeOC_6H_4$	2.0	0.53	rt	24	50	24	(88)	78, 56
3,4-$(MeO_2)C_6H_3$	1.5	0.53	rt	72	—	—	(97)	78
2-MeC_6H_4	1.5	0.53	rt	24	50	18	(94)[a]	78
3-MeC_6H_4	2.0	0.53	rt	24	50	24	(99)[a]	78
4-MeC_6H_4	1.5	0.53	rt	24	50	18	(97)[a]	78, 56
4-NCC_6H_4	1.5	0.53	rt	24	50	18	(94)	78
3-$OHCC_6H_4$	1.5	0.53	rt	24	50	18	(99)[a]	78
2-$H_2NCOC_6H_4$	1.1	0.53	rt	0.25	—	—	(81)	78

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{6–10}$

ArI

1. CuCl (x eq), t-BuOK ($2x$ eq), DMF, rt, 0.5 h
2. HCF_3 ($1.1x$ eq) at rt over 1 h; rt, 1 h
3. $Et_3N•3HF$ (xy eq)
4. ArI (1 eq), temp 1, time 1; temp 2, time 2

$ArCF_3$

Ar	x	y	Temp 1	Time 1 (h)	Temp 2 (°)	Time 2 (h)		
4-$EtO_2CC_6H_4$	1.5	0.53	rt	24	50	18	(96)	78
2,4-$Me_2C_6H_3$	1.5	0.53	rt	24	50	18	(97)[a]	78
4-AcC_6H_4	1.5	0.53	rt	18	—	—	(95)[a]	78
4-t-BuC_6H_4	2.0	0.53	rt	24	50	24	(95)	78
1-$C_{10}H_7$	1.5	0.53	rt	24	50	18	(98)	78

$C_{6–8}$

ArBr

1. CuCl (x eq), t-BuOK ($2x$ eq), DMF, rt, 0.5 h
2. HCF_3 ($1.1x$ eq) at rt over 1 h; rt, 1 h
3. $Et_3N•3HF$ ($0.53x$ eq)
4. ArBr (1 eq), temp 1, time 1; temp 2, time 2

$ArCF_3$ — 78

Ar	x	Temp 1	Time 1 (h)	Temp 2 (°)	Time 2 (h)	
2-$O_2NC_6H_4$	1.3	rt	18	—	—	(88)
3-$O_2NC_6H_4$	1.5	rt	24	50	24	(22)[a]
4-$O_2NC_6H_4$	2.0	80°	4	—	2[l]	(60)[a]
2-NCC_6H_4	1.5	rt	72	—	—	(30)[a]
4-NCC_6H_4	1.5	rt	72	—	—	(31)[a]
2-$OHCC_6H_4$	2.0	rt	24	50	24	(83)[a,m]
2-$HO_2CC_6H_4$	1.1	rt	0.25	—	—	(77)[n]
2-$MeO_2CC_6H_4$	2.0	rt	24	50	24	(95)
2-HO_2C-4-BrC_6H_3	1.1	rt	0.2	—	—	(82)[n]
2-HO_2C-4-$MeOC_6H_3$	1.1	rt	0.2	—	—	(79)[a,n]
2-AcC_6H_4	1.3	rt	18	—	—	(92)
2,4-$(HO_2C)_2C_6H_3$	1.1	rt	0.3	—	—	(60)[a]

C_{6-10}

ArX

$ClCF_2CO_2Me$ (2 eq), CuI (1 eq), KF (*x* eq), solvent, 8 h

$ArCF_3$ **I** + CO_2 + MeX

Ar	X	*x*	Solvent	Temp (°)	**I**	
Ph	Br	1	DMF	110–120	(60)	243, 244
Ph	I	—	DMF	110–120	(10)	243
Ph	I	1	HMPA	100	(80)	243, 244
Ph	I	1	DMF	120	(88)	243, 244
4-ClC_6H_4	I	1	DMF	100	(81)	243, 244
4-$O_2NC_6H_4$	I	1	DMF	100	(89)	243, 244
1-$C_{10}H_7$	I	1	DMF	110–120	(94)	243, 244

$BrCF_2CO_2Me$ (2 eq), CuI (1 eq), KF (*x* eq), solvent, 85–90°, 5 h

$ArCF_3$ **I** + CO_2 + MeX — 243

Ar	X	*x*	Solvent	**I**
Ph	Br	1	DMF	(67)
Ph	I	—	DMF	(25)
Ph	I	1	HMPA	(79)
Ph	I	1	DMF	(81)
4-$O_2NC_6H_4$	I	1	DMF	(80)
1-$C_{10}H_7$	Br	1	DMF	(71)
1-$C_{10}H_7$	I	1	DMF	(84)

C_6

PhX

ICF_2CO_2Me (2 eq), CuI (1 eq), KF (1 eq), DMF, 80°, 5 h

$PhCF_3$ **I** (—) + CO_2 + MeX — 243

X	Conv **I** (%)
Br	61
I	75

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{6-10}

ArX

FSO_2CF_2I (*x* eq), Cu (*y* eq), DMF, 80°

$ArCF_3$ 259

Ar	X	*x*	*y*	Time (h)	Conv (%)	
Ph	I	0.5	1.1	7	100	(80)
4-$O_2NC_6H_4$	I	0.4	0.9	6	100	(83)
4-ClC_6H_4	I	0.5	1.1	6	91	(79)
4-ClC_6H_4	I	3	6.6	6	92	(84)
4-$Cl(CF_2)_4C_6H_4$	I	0.56	1.23	7	100	(90)
1-$C_{10}H_7$	Br	0.4	0.9	7	100	(78)
1-$C_{10}H_7$	I	0.5	1.1	7	100	(84)

ArI **I**

$FSO_2CF_2CO_2Me$ (*x* eq), Cu (0.12 eq), DMF

$ArCF_3$ **II** + SO_2 + CO_2 + CH_4 252

Ar	*x*	Temp (°)	Time (h)	Conv **I** (%)	**II**
Ph	0.4	65	4	93	(84)
Ph	0.4	65	4	43	(56)[o]
Ph	0.4	65	4	48	(54)[p]
4-ClC_6H_4	0.5	70	3	90	(70)
4-$O_2NC_6H_4$	0.5	65	3	100	(82)
4-$O_2NC_6H_4$	0.5	65	3	53	(77)[q]
4-$Cl(CF_2)_4C_6H_4$	0.5	70	3	90	(68)
$C_{10}H_7$	0.5	80	4	100	(90)

ArX

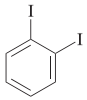
$FSO_2CF_2CO_2Me$ (*x* eq), CuI (12 mol %), solvent

$ArCF_3$

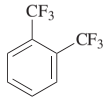
250

R	X	*x*	Solvent	Temp (°)	Time (h)	Conv (%)	
Ph	I	0.5	DMF	70	2.5	100	(84)
Ph	I	0.5	DMSO	60	2.5	100	(84)
Ph	Br	0.4	DMF	80	3	100	(61)
4-$O_2NC_6H_4$	I	0.5	DMF	65	3	95	(80)
4-$O_2NC_6H_4$	I	0.5	DMF	65	3	95	(80)[o]
4-ClC_6H_4	I	0.5	DMF	70	4	100	(78)
4-ClC_6H_4	I	3.5	DMF	70	4.5	95	(90)
4-[$Cl(CF_2)_4$]C_6H_4	I	0.5	DMF	80	4	100	(92)
1-$C_{10}H_7$	Br	0.5	DMF	80	4	94	(70)
1-$C_{10}H_7$	I	0.67	DMF	80	6	100	(74)

C_6

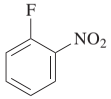


CF_3I, Cu, DMF, 140°, 24 h

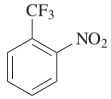


(40)

366



$TIPSCF_3$ (0.09 eq), 18-crown-6 (0.2 eq), *t*-BuOK (0.2 eq), THF, –78°, 1 h; to rt

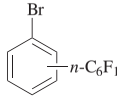


(7)[j]

80



n-$C_6F_{13}I$, Cu, bipy, DMSO, C_6F_6



Isomer	
1,2–	(—)
1,3–	(—)
1,4–	(—)

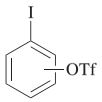
829

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

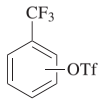
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_6

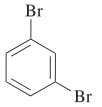


$FSO_2CF_2CO_2Me$, CuI, HMPA, DMF, 70°, 4 h

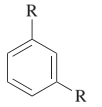


Isomer	
1,2–	(84)
1,3–	(64)
1,4–	(88)

254

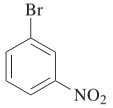


RI, Cu, DMF, 15 h

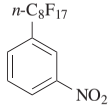


R	Temp (°)	
i-C_3F_7	90	(67)
n-C_4F_9	100	(70)

827

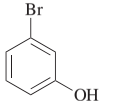


n-$C_8F_{17}I$ (1.3 eq), Cu (2.73 eq), DMSO, 125–135°, 22 h

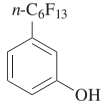


(81)

830

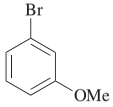


n-$C_6F_{13}I$ (1.2 eq), Cu (2.53 eq), DMSO, 125–135°, 4.5 h

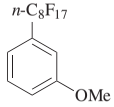


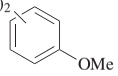
(57)

830

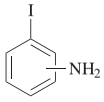


n-$C_8F_{17}I$ (1.25 eq), Cu (2.5 eq), DMSO, 125–135°, 4 h

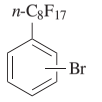


(86) +  (11)

830

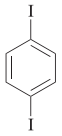


1. *n*-$C_8F_{17}I$, Cu, DMF, 120°
2. *t*-BuONO, $CuBr_2$, MeCN, –5° to rt

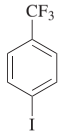


Isomer	
1,3–	(51)
1,4–	(53)

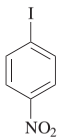
831



TMSCF$_3$ (1.1–1.2 eq), KF (1.2 eq), CuI (1.5 eq), **23** (1 eq), 80°, 8 h

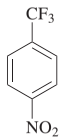


(38) 339

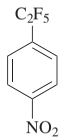


I

Et$_3$SiCF$_3$ (1.2 eq), initiator (*x* eq), additive (*y* eq), solvent, 80°, 24 h



II (—) +



III (—) 275

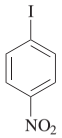
Initiator	*x*	Additive	*y*	Solvent (s)	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)
KF	1.2	CuCN	1	DMF	11	65	2
KF	1.2	CuCl	1	DMF	13	84	3
KF	1.2	CuBr	1	DMF	38	58	—
KF	1.2	CuI	1	DMF	11	85	4
KF	1	CuI	0.5	DMF	30	40	—
NaF	1.2	CuI	1	DMF	78	15	—
CsF	1.2	CuI	1	DMF	71	22	—
TBAF	1.2	CuI	1	DMF, THF	83	—	—
KF	1.2	CuI	1	NMP	23	70	—
KF	1.2	CuI	1	HMPA	27	70	—
KF	1.2	CuI	1	DMI	18	77	—
KF	1.2	CuI	1	DMSO	30	40	—
KF	1.2	CuI	1.5	DMF, NMP	—	99	<1

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

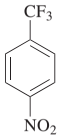
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_6



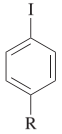
$[CF_3P(NMe_2)_3]^+Br^-$ (1 eq), KF (1 eq), CuI (1 eq), DMF, 0°, 3 h; HMPA, 60°, 5 h



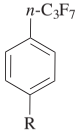
(98)

166

C_{6-12}



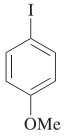
(phen)Cu(*n*-C_3F_7) (1.5 eq), DMF, 18 h



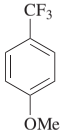
R	
O_2N	(88)
BnO	(99)
Ph	(99)

54

C_6



1. CF_3H (2 eq), $MeSOCH_2K$ (4 eq), DMF, DMSO, –40°; –25°, 1 h
2. CuI (2 eq), DMEU, rt; 60°, 1 h
3. NH_3, NH_4Cl, H_2O, rt

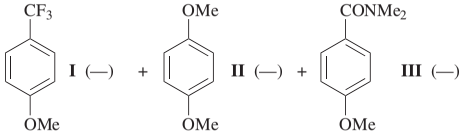


(—)

DMF/DMEU	Conv (%)
2:1	20
1:1	40

48

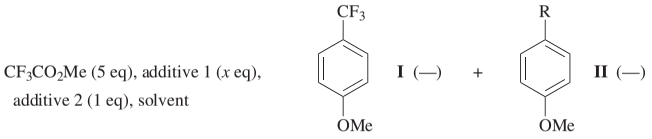
1. CF_3CO_2Me (*x* eq), CsF (*y* eq), CuI (1 eq), solvent, 130°, 2 h
2. Solvent, 180°, 4 h



I (—) + **II** (—) + **III** (—)

120

x	*y*	Solvent	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)
1	1	sulfolane	23	35	—
3	1	DMF	11	2	51
3	1	sulfolane	71	1–2	—
5	1	DMF	12	5.5	35
5	1	sulfolane	80	4	14
5	2.5	DMF	40.5	6	14



CF_3CO_2Me (5 eq), additive 1 (*x* eq), additive 2 (1 eq), solvent

120

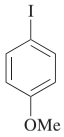
Additive 1	*x*	Additive 2	Solvent	Temp (°)	Time (h)	Conv **I** (%)	R	Conv **II** (%)
KF	2.5	CuI	DMF	180	4	35	Me_2NCO	12
KI	1	CuI	DMF	180	4	33	—	—
CsF	1.5	CuI	DMF	180	4	46	Me_2NCO	37
CsF	2.5	CuI	DMF	180	4	75	Me_2NCO	8
CsF	2.5	CuBr	DMF	180	4	61	Me_2NCO	11
CsF	2.5	CuBr	DMF	180	4	61	Br	15
CsF	2.5	Cu	DMF	180	4	14	Me_2NCO	47
CsF	2.5	Cu	DMF	180	4	14	H	4
CsF	2.5	CuI	DMA	180	4	16	H	17
CsF	2.5	CuI	NMP	180	4	23	H	46
CsF	2.5	CuI	sulfolane	140	8	53	—	—
CsF	2.5	CuI	sulfolane	160	8	66	—	—
CsF	2.5	CuI	sulfolane	180	4	79	—	—
CsCl	1	CuI	DMF	180	4	60	Cl	12
CsCl	2.5	CuI	DMF	180	4	55	Cl	8
CsBr	1	CuI	DMF	180	4	32	Br	27
CsI	1	CuI	DMF	180	4	46	—	—
Me_4NI	2.5	CuI	DMF	180	4	25	—	—

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

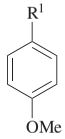
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

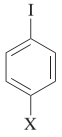
C_6



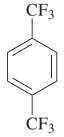
$R^1CO_2R^2$ (5 eq), CsX (2.5 eq), CuI (1 eq), solvent, 180°, 8 h



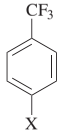
R^1	R^2	X	Solvent		
CF_3	Et	Cl	DMF	(26)	120
CF_3	CF_3CO	F	sulfolane	(30)[r]	
C_2F_5	Me	F	sulfolane	(50)	



$FSO_2(CF_2)_2OCF_2CO_2Me$ (*x* eq), CuI (*y* eq), DMF, 100°, 8 h



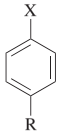
I +



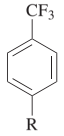
II

X	*x*	*y*	**I**	**II**	
Cl	1	2	(—)	(82)	249
Cl	2	4	(52)	(—)	
I	1	2	(62)	(—)	

C_{6-7}



"CF_3Cu", ligand (*x* eq), DMF, 90°, 3 h



R	X	Ligand	*x*		
O_2N	Br	PPh_3	2	(70)	
O_2N	Cl	PBu_3	2	(55)	364
O_2N	Cl	TMEDA	10	trace	
MeO	I	TMEDA	10	(50)	
MeO	I	bipy	5	(67)	
MeO	I	PBu_3	2	(92)	
MeO	I	PPh_3	2	(75)	
MeO	Br	PBu_3	2	(15)	
NC–	Br	PPh_3	2	(72)	
EtO_2C	Br	PBu_3	4	(52)	

C_{6-10}

ArI

Et_3SiCF_3 (1.2 eq), KF (1.2 eq), CuI (1.5 eq), NMP, DMF, 80°, 24 h

$ArCF_3$ **I** (—) + ArC_2F_5 **II** (—) 275

Ar	Conv **I** (%)	Conv **II** (%)
4-ClC_6H_4	35	—
4-$MeOC_6H_4$	48	18
2-MeC_6H_4	86	—
3-MeC_6H_4	78	—
4-MeC_6H_4	82	—
4-$EtO_2CC_6H_4$	94	4
2-$C_{10}H_7$	94	—

C_6

ArX

CF_2Br_2, Cu (6 eq), DMA, 100°, 8 h

$ArCF_3$ + ArC_2F_5

I **II**

Ar	X	**I**	**II**
$2\text{-}O_2NC_6H_4$	Cl	(59)	(—)
$2\text{-}O_2NC_6H_4$	Br	(30)	(—)
$2\text{-}O_2NC_6H_4$	I	(6)	(—)
$4\text{-}O_2NC_6H_4$	Cl	(5)	(1)

367

ArI

$C_2F_5CO_2M$ (1.5–2 eq, M = Na or K), CuI (2 eq), DMF, toluene, 145–150°

ArC_2F_5

Ar	Conv (%)	
$4\text{-}O_2NC_6H_4$	75	(58)
$4\text{-}MeOC_6H_4$	90	(72)
$4\text{-}MeC_6H_4$	83	(—)
$1\text{-}C_{10}H_7$	90	(68)

832

$TMSR_F$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, 60°, 24 h

ArR_F (—)

Ar	R_F	Conv (%)
$4\text{-}O_2NC_6H_4$	C_2F_5	86
$4\text{-}O_2NC_6H_4$	$n\text{-}C_3F_7$	41
$2\text{-}MeC_6H_4$	C_2F_5	92
$3\text{-}MeC_6H_4$	C_2F_5	89
$4\text{-}MeC_6H_4$	C_2F_5	86
$4\text{-}EtO_2CC_6H_4$	C_2F_5	86
$2\text{-}C_{10}H_7$	C_2F_5	68

275

C_{6-7}

ArX

CF_3CO_2Na, CuI, NMP, 140–160°, 4 h

$ArCF_3$

Ar	X	
$4\text{-}O_2NC_6H_4$	I	(47)
$4\text{-}ClC_6H_4$	I	(68)
$4\text{-}MeOC_6H_4$	I	(59)
$3\text{-}MeC_6H_4$	I	(88)
$3\text{-}MeC_6H_4$	Br	(58)

58

C_6

ArX

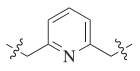
21, Cu, MeCN, solvent, 100°, 18–19 h

$ArCF_3$

Ar	X	Solvent	
$4\text{-}O_2NC_6H_4$	I	HMPA	(68)
$4\text{-}ClC_6H_4$	I	NMP	(74)
$4\text{-}BrC_6H_4$	I	HMPA	(53)
$2\text{-}MeOC_6H_4$	I	NMP	(88)
$3\text{-}MeOC_6H_4$	I	NMP	(72)
$4\text{-}MeOC_6H_4$	I	NMP	(66)
$4\text{-}MeOC_6H_4$	I	HMPA	(71)
$4\text{-}MeOC_6H_4$	Br	HMPA	(5)

262

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions		Product(s) and Yield(s) (%)				Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*							
C_{6-7}							
ArX	1. $TMSCF_3$ (1 eq), AgF (1 eq), EtCN, rt, 20 min 2. Cu (2 eq), rt, 4 h 3. Substrate (*x* eq), rt, 6 h; 75–80°, 12 h	$ArCF_3$	Ar	X	*x*		379
			4-$O_2NC_6H_4$	I	1	(54)	
			2,4-$(O_2N)_2C_6H_3$	Cl	1	(59)	
			4-$O_2NC_6H_4CH_2$	I	1	(60)	
			4-$EtO_2CC_6H_4$	Br	1	(72)	
				Br	0.5	(53)	
C_{6-10}							
ArX	CF_3Br, e^-, Cu anode, TMEDA, Bu_4NBr, DMF, 95°, 7 h; heat, 2 h	$ArCF_3$	Ar	X			364
			3,5-ClC_6H_3	Br	(70)		
			4-ClC_6H_4	Br	(32)		
			4-$O_2NC_6H_4$	Br	(98)		
			2-$MeOC_6H_4$	Br	(32)		
			3-$MeOC_6H_4$	Br	(23)		
			4-$MeOC_6H_4$	Br	(32)		
			4-$MeOC_6H_4$	I	(90)		
			4-NCC_6H_4	Br	(91)		
			4-NCC_6H_4	Cl	(3)		
			2-$MeO_2CC_6H_4$	Br	(54)		
			4-$EtO_2CC_6H_4$	Br	(56)		
			1-$C_{10}H_7$	I	(98)		

C_{6-14}

ArI — CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min — $ArCF_3$ — 338

Ar	
3,5-$Cl_2C_6H_3$	(80)
4-(1-pyrrolyl)C_6H_4	(90)
3-(1-piperidinyl)C_6H_4	(81)
3,4,5-$(MeO)_3C_6H_2$	(86)
4-$Et_2NSO_2C_6H_4$	(93)
2-Me-4-$O_2NC_6H_3$	(85)
3-(4-morpholinyl)C_6H_4	(83)
4-$EtO_2CC_6H_4$	(93)
4-*n*-$C_6H_{13}O_2CC_6H_4$	(96)
1-$C_{10}H_7$	(87)
4-PhC_6H_4	(87)
4-*n*-$C_7H_{15}C_6H_4$	(89)
9-phenanthrenyl	(91)

C_{6-12}

ArI — (phen)$CuCF_3$ (1.5 eq), DMF, 18 h — $ArCF_3$ — 54

Ar	Temp (°)	
4-$AcNHC_6H_4$	50	(85)
4-$AcNHC_6H_4$	rt	(100)
4-$O_2NC_6H_4$	50	(100)[a]
4-$MeOC_6H_4$	50	(96)[a]
2-CH_2=$CHCH_2OC_6H_4$	50	(91)
4-$BnOC_6H_4$	50	(89)
4-$BnOC_6H_4$	50	(95)[s]
4-(4'-BrC_6H_4)CH_2OCH_2	50	(89)

Ar	Temp (°)	
4-$OHCC_6H_4$	50	(89)[a]
6-AcO-5-MeO-3-$OHCC_6H_4$	50	(68)
4-$EtO_2CC_6H_4$	50	(94)[a]
6-Cl-2-$EtO_2CC_6H_3$	50	(69)
4-AcC_6H_4	50	(93)[a]
4-AcC_6H_4	50	(85)[a,s]
4-PhC_6H_4	50	(83)
4-PhC_6H_4	50	(89)[s]

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{6-10}

ArI

1. CuI (10 mol %), *t*-BuONa (30 mol %), NMP, rt, 10 min
2. Ligand (20 mol %), rt, 2 min
3. Substrate (1 eq), AgF (1.3 eq), $TMSCF_3$ (2 eq), 90°, 30 min

$ArCF_3$

Ar	Ligand		Refs.
3-$O_2NC_6H_4$	phen	(60)[a]	378
4-$O_2NC_6H_4$	DMED	(98)	
2-$MeOC_6H_4$	DMED	(66)[a]	
2-MeC_6H_4	DMED	(59)[a]	
4-MeC_6H_4	DMED	(73)[a]	
2-$CF_3C_6H_4$	DMED	(61)[a]	
4-$CF_3C_6H_4$	DMED	(64)[a]	
3-NCC_6H_4	phen	(74)[a]	
4-NCC_6H_4	DMED	(89)[a]	
2,4-$Me_2C_6H_3$	DMED	(76)	
1-$C_{10}H_7$	DMED	(75)	
2-MeO-1-$C_{10}H_6$	DMED	(47)[a]	

C_{6-7}

ArI

1. CF_3I (2.5 *x* eq), Zn (*x* eq), DMPU, rt, 2 h
2. Substrate, Cu (*y* mol %), additive (*y* mol %), 50°

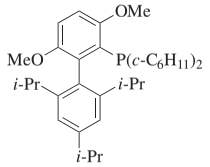
$ArCF_3$ **I** + ArC_2F_5 **II** — 62

Ar	*x*	*y*	Additive	Time (h)	**I**	**II**
4-$O_2NC_6H_4$	4	2	phen	48	(80)[a]	(—)
2,4-$(O_2N)_2C_6H_3$	2	10	phen	24	(90)[a]	(—)
4-$MeOC_6H_4$	2	10	phen	24	(6)[a]	(—)
4-$OHCC_6H_4$	2	10	phen	24	(44)[a]	(—)
4-NCC_6H_4	4	2	phen	48	(60)[a]	(—)
2-$EtO_2CC_6H_4$	2	2	none	24	(97)[a]	(3)[a]
2-CF_3-4-NCC_6H_3	2	10	none	24	(70)	(—)

C_{6-14}

ArBr

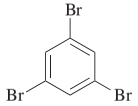
$TMSCF_3$ (2 eq), cyclohexylBrettPhos (10 mol %), cinnamylPdCl$_2$ (2 mol %), CsF (2 eq), Na dodecyl sulfate, toluene, turbine agitator, 110°, 12 h



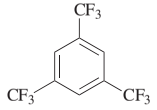
cyclohexylBrettPhos

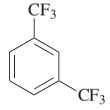
$ArCF_3$	Ar		
	2-HOC_6H_4	(74)	782
	4-HOC_6H_4	(70)	
	2-$H_2NC_6H_4$	(70)	
	4-$H_2NC_6H_4$	(71)	
	3-Me-4-$O_2NC_6H_3$	(77)	
	2-OHC-4-HOC_6H_4	(68)	
	1-$C_{10}H_7$	(88)	
	3-Ph-4-$H_2NC_6H_3$	(72)	
	9-anthryl	(80)	

C_6



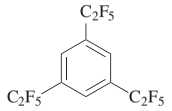
CF_3CO_2Na (3 eq), CuI, NMP, 160°, 4 h



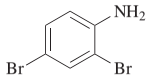
(48) + 

(41) 59

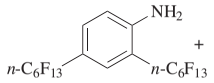
$C_2F_5CO_2Na$, CuI, NMP, 170°, 3 h



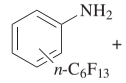
(31) 59



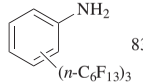
n-$C_6F_{13}I$ (2.4 eq), Cu (5.47 eq), DMSO, 125–135°, 20 h



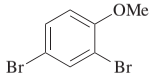
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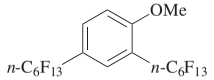
(2) +



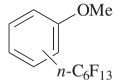
(12) 830



n-$C_6F_{13}I$ (2.33 eq), Cu (5.47 eq), DMSO, 125–135°, 22 h



(94) +



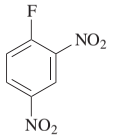
(5) 830

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

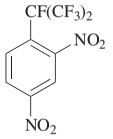
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_6

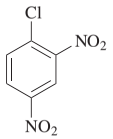


CF_2=$CFCF_3$ (3.7 eq), TDAE (6.2 mol %), MeCN, 60°, 3 d

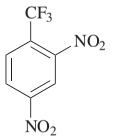


(11) 85% conv

97

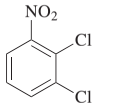


CF_3SO_2Cl, Cu, DMA

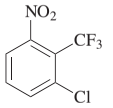


(—)

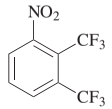
260



CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h

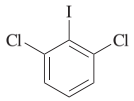


(86) +

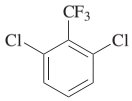


(5)

367



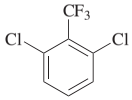
$TMSCF_3$, KF, CuI



(98)

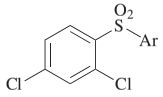
343

$TMSCF_3$ (1 eq), KF (1.1 eq), CuI (1.1 eq), NMP, 50°, 6 h



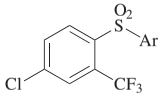
(69)

342

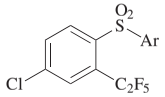


Ar = 4-FC_6H_4

CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h

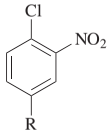


(6.4) +

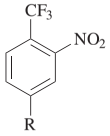


(10.1)

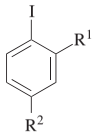
367



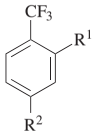
CF_2Br_2 (2 eq), Cu (6 eq), additive (1 g/10 mmol CF_2Br_2), DMF, 100°, 4 h



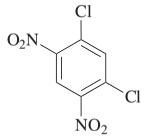
R	Additive		
H	none	(24)	274
H	charcoal	(89)	
O_2N	none	(21)	
O_2N	charcoal	(87)	



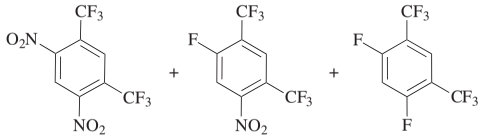
CF_3HgY/Cu, solvent, 5 h



R^1	R^2	Y	Solvent		
H	H	CF_3	NMP	(65)	261
H	O_2N	CF_3	NMP	(60)	
H	O_2N	CF_3	NMP	(88)[f]	
H	O_2N	CF_3	DMA	(73)	
H	O_2N	I	NMP	(65)	
H	O_2N	CF_3O_2C	NMP	(38)	
H	O_2N	CF_3O_2C	DMA	(28)	
O_2N	O_2N	CF_3	NMP	(71)[f]	

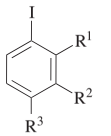


CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h

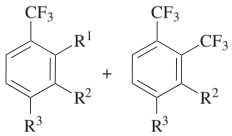


(—) (—) (—) 367

C_{6-7}



CF_3I (15 eq), Zn, $CuSO_4$, DMF, 130–140°



I **II**

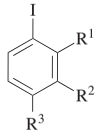
R^1	R^2	R^3	**I**	**II**	
H	H	O_2N	(51)	(—)	52
H	Me	H	(68)	(—)	
I	H	H	(—)	(32)	
Me	H	H	(28)	(—)	
CF_3	H	H	(80)	(—)	

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

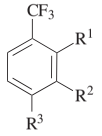
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{6-7}

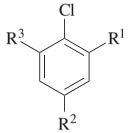


$ClCF_2CO_2Me$ (1 eq), KF (5 eq), CuI (1 eq), DMPU or HMPA, 120°, 4 h

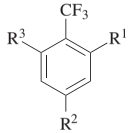


R^1	R^2	R^3	
H	H	H	(62)
O_2N	H	H	(64)
H	H	Me	(73)
H	CF_3	H	(76)
Me	H	H	(52)

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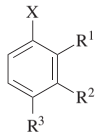


$FSO_2CF_2CO_2Me$ (2 eq), CuI (cat.), solvent, 70–80°

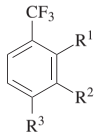


R^1	R^2	R^3	Solvent	Time (h)	
H	O_2N	H	DMF	12	(95)
O_2N	O_2N	H	DMF	8	(90)
O_2N	O_2N	O_2N	DMF	5	(80)
O_2N	CF_3	H	DMF	10	(90)
O_2N	CF_3	O_2N	DMF	5	(93)
O_2N	CF_3	O_2N	HMPA	5	(94)

248



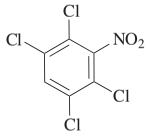
CF_3CO_2Na (1 eq), CuI, NMP, 160°, 4 h



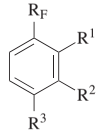
R^1	R^2	R^3	X	
H	H	H	I	(87)
H	H	H	Br	(68)
H	H	H	Cl	(—)
H	H	O_2N	I	(64)
H	H	Cl	I	(98)
Cl	H	H	I	(87)
H	H	CF_3	Br	(62)
H	H	CF_3	I	(73)
H	Me	H	Br	(78)

59

C_6



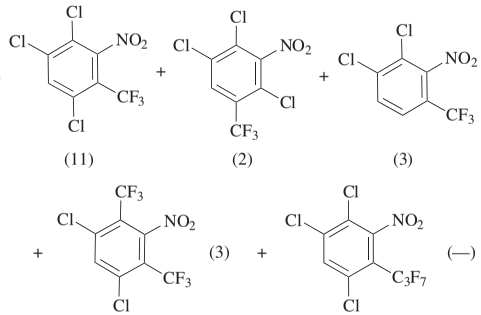
R_FI (x eq), Cu (y eq), solvent



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R^1	R^2	R^3	X	R_F	x	y	Solvent	Temp (°)	Time (h)	
H	H	$MeSO_3$	I	n-C_7F_{15}	1.1	4	DMSO	115–120	4.83	(14)
H	NH_2	H	I	n-C_9F_{19}	1.05	4	DMF	105–120	3.5	(45)
H	AcO	H	I	n-C_3F_7	0.52	2.13	DMF	125–135	0.83	(65)
O_2N	H	H	Cl	n-C_3F_7	0.17	0.51	DMF	175	14	(17)
H	H	HO_2C	I	n-C_5F_{11}	1.1	3.2	DMF	105–120	3.5	(65)
H	H	MeO_2C	I	n-C_7F_{15}	1	4	DMSO	125	3	(70)

CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h



(11) (2) (3) + (3) + (—)

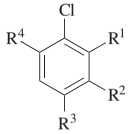
367

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

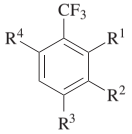
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

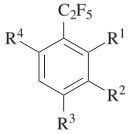
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*

C_{6-13}



CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h

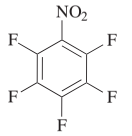


I +  **II**

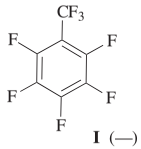
367

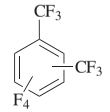
R^1	R^2	R^3	R^4	**I**	**II**
H	O_2N	O_2N	H	(8)	(8)
O_2N	H	O_2N	H	(100)	(—)
O_2N	H	CF_3	H	(97)	(3)
O_2N	H	CHO	H	(100)	(—)
O_2N	H	CF_3	O_2N	(53)	(—)
O_2N	H	Ac	H	(95)	(—)
Bz	H	NO_2	H	(100)	(—)

C_6



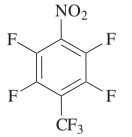
$TMSCF_3$, TBAF (1 eq), THF, 0°

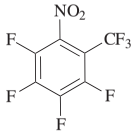


I (—) +  **II** (—) **I/II** = 9:1

304

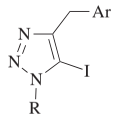
$TMSCF_3$ (1.33 eq),
n-$Bu_4N^+Ph_3SnF_2^-$ (1 eq),
THF, 0°, 0.5 h; rt, 12 h



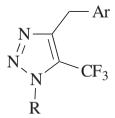
I (—) +  **II** (—) **I** + **II** 60% conv

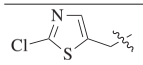
289

C_{7-10}

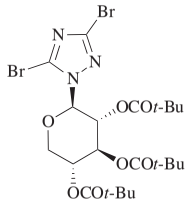


TMSCF$_3$ (3 eq), KF (3 eq), CuI (1 eq), phen (1 eq), Ag$_2$CO$_3$ (2 eq), DMF, 100°, 2–3 h

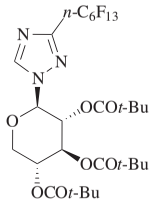


R	Ar		
	4-MeC$_6$H$_4$O	(74)	
			
Bn	4-PhOC$_6$H$_4$	(89)	380
Bn	4-MeC$_6$H$_4$	(82)	

C_7

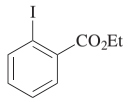


n-C$_6$F$_{13}$I (8 eq), Cu (16 eq), I$_2$ (cat.), DMSO, 110°, 15–20 h

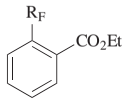


(37)

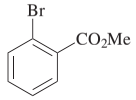
833



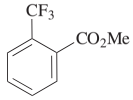
R$_F$H (*x* eq), (TMP)$_2$Zn (1.5 eq), CuCl (0.1 eq),[*t*] phenathroline (2 eq), DMPU



R$_F$	*x*	Temp (°)	Time (h)		
CF$_3$	—	65	23	(51)	382
C$_2$F$_5$	—	90	11	(96)	
n-C$_3$F$_7$	—	90	13	(83)	
n-C$_6$F$_{13}$	3	90	14	(87)	
n-C$_{10}$F$_{21}$	3	90	3	(81)	



"CF$_3$Cu", PBu$_3$ (4 eq), DMF, 90°, 3 h



(98)

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TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-13}

ArCl

CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h

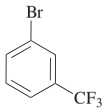
$ArCF_3$ + ArC_2F_5

I **II**

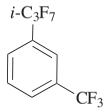
Ar	**I**	**II**
2-$HOCC_6H_4$	(16)	(22)
2-$MeO_2CC_6H_4$	(38)	(10)
2-AcC_6H_4	(17)	(17)
2-BzC_6H_4	(7)	(1.3)
4-BzC_6H_4	(—)	(3)

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C_7

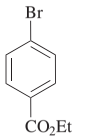


i-C_3F_7I (1.37 eq), Cu (3.3 eq), DMF, 90°, 15 h

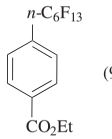


(63)

827

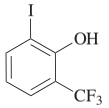


n-$C_6F_{13}I$ (1.2 eq), Cu (2.73 eq), DMSO, 125–135°, 4 h

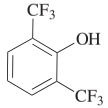


(99)

830

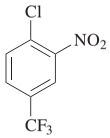


CF_2Br_2 (6 eq), Cd (9 eq), CuBr (3 eq), DMF, HMPA, 60°, 1.5 h

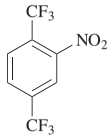


(47)

834



Cu (6 eq), CF_2Br_2 (2 eq), additive (1 g/10 mmol CF_2Br_2), DMF, 100°, 4 h



Additive	
none	(41)
charcoal	(98)

274

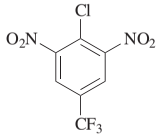
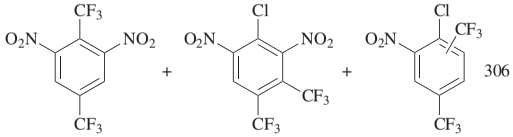
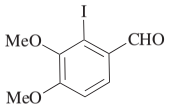
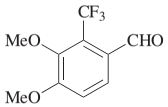
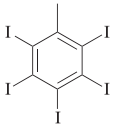
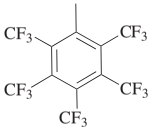
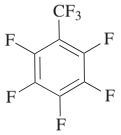
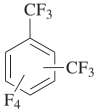
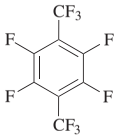
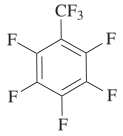
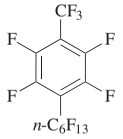
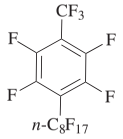
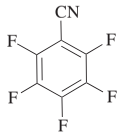
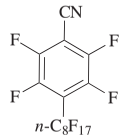
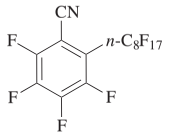
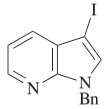
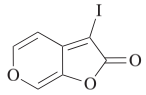
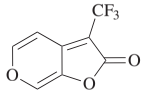
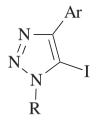
	$TMSCF_3$ (2.8 eq), KF (5 eq), DMA, air, 50°, "few min"	 (—) 3% conv + (—) 4% conv + two isomers (—) 2% and 4% conv	306
	CF_3CO_2Na, CuI, NMP, 175°, 4 h	 (25.1)	238
	$TMSCF_3$ (6 eq), CuBr (7.9 eq), KF (6 eq), NMP, DMF, 65–70°, 14 h	 (41)	276
	CF_3Br, $(Et_2N)_3P$, CH_2Cl_2, –78°	 (7)	332
	$TMSCF_3$, TASF, THF, rt, 2–3 h	 (—) 40–70% conv	333

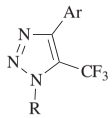
TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

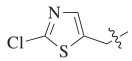
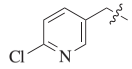
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_7 	*n*-C_6F_{13}TMS (0.5 eq), CsF, DME, –20°, 1 h; 0°, 1 h; rt, 18 h	 (—) + $C_{13}F_{20}$ (—)	326
	n-C_8F_{17}TMS (0.5 eq), CsF (2.5 mol %), DME, –20°, 0.75 h; 0°, 2 h; rt, 18 h	 (—) 34% conv	326
	*n*-C_8F_{17}TMS (0.83 eq), CsF (2.8 mol %), DME, <29°, 18 h	 (—) major +  (—) minor	326
	CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min	 (83)	338
	Et_3SiCF_3, KF, CuI, NMP	 (45)	835

C_{8-16}

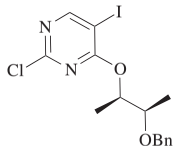


$TMSCF_3$ (3 eq), KF (3 eq), CuI (1 eq), phen (1 eq), Ag_2CO_3 (2 eq), DMF, 100°, 2–3 h

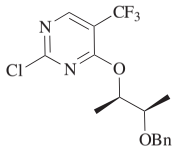


R	Ar		
Bn	Ph	(90)	380
Bn	4-FC_6H_4	(81)	
Bn	4-$MeOC_6H_4$	(85)	
4-$ClC_6H_4CH_2$	Ph	(77)	
4-$MeC_6H_4CH_2$	Ph	(87)	
2-$NCC_6H_4CH_2$	Ph	(52)	
$PhCH_2CH_2$	Ph	(87)	
$PhCH_2CH_2$	4-$MeOC_6H_4$	(85)	
$Ph(CH_2)_3$	Ph	(84)	
$Ph(CH_2)_3$	4-$MeOC_6H_4$	(83)	
Bn	4-MeC_6H_4	(88)	
Bn	4-EtC_6H_4	(85)	
	Ph	(71)	
2-furylmethyl	Ph	(55)	
	Ph	(70)	
"	4-MeC_6H_4	(75)	
"	4-EtC_6H_4	(77)	

C_8



$TMSCF_3$ (1.5 eq), KF (1.5 eq), CuI (1.8 eq), NMP, THF, rt; 80°, 5.5 h



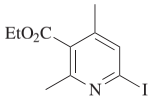
(54) 835a

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

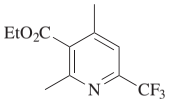
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

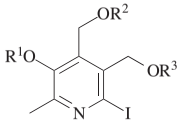
C_8



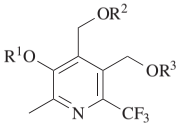
$TMSCF_3$, KF, CuI, 70°, o/n



(>45) — 836

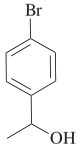


$TMSCF_3$ (1.2 eq), KF (1.2 eq), CuI (1 eq), NMP/DMF (1:1), dark, 80°, 24 h

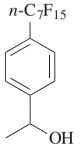


R^1	R^2	R^3	
H	Ac	Ac	(12)
Ac	Ac	Ac	(40)
H	H	Bn	(100)
H	Bn	Bn	(100)
Bn	Bn	Bn	(96)

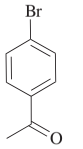
837



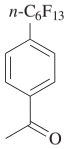
n-$C_7F_{15}I$ (1 eq), Cu (4 eq), DMSO, 125°, 12 h



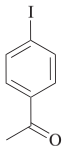
(65) — 337



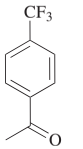
n-$C_6F_{13}I$ (1.2 eq), Cu (2.73 eq), DMSO, 125–135°, 2.5 h



(99) — 830

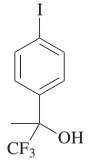


Et_3SiCF_3 (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, NMP, 80°, 24 h



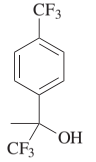
(—) 45% conv

+



(—) 17% conv

+



(—) 6% conv

275

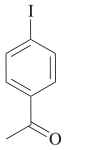
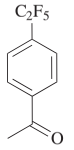
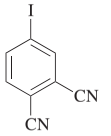
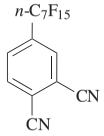
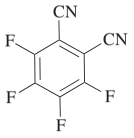
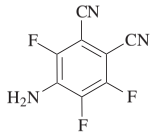
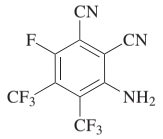
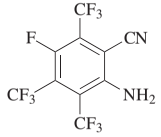
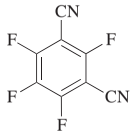
	$TMSC_2F_5$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, 60°, 24 h	 (—) 61% conv	275
	*n*-$C_7F_{15}I$, Cu, DMSO, 115–120°, 2 h	 (56)	838
	1. $TMSCF_3$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), NMP, DMF, 80°, 8 h 2. NH_4OH, H_2O	 (—) 53% conv +  (—) 6% conv +  (—) 3% conv	334

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

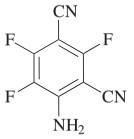
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_8

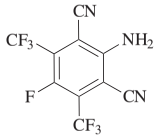


1. $TMSCF_3$ (1.2 eq), KF (1.2 eq), CuI (1.5 eq), NMP, DMF, 80°
2. NH_4OH, H_2O



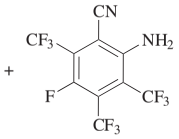
(—) 28% conv

+



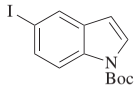
(—) 16% conv

+

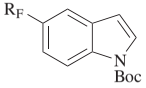


(—) 3% conv

334

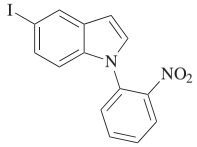


(phen) CuR_F (*x* eq), DMF, 50°, 18 h

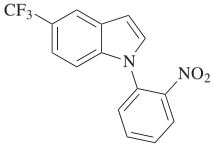


R_F	*x*	
CF_3	2	(99)
CF_3	2	(83)[a]
n-C_3F_7	1.5	(92)

54

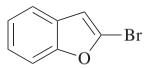


CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min

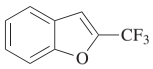


(84)

338

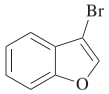


CF_3I, Cu, DMF, 110–130°, 20 h

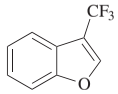


(53)

839

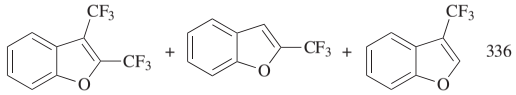


CF_3I, Cu, DMF, 110–130°, 20 h



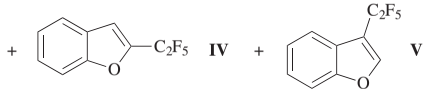
(60) 839

CF_3I, Cu, solvent, air, 140°

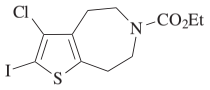


I **II** **III** 336

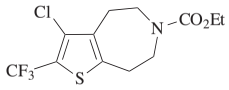
Solvent	**I**	**II**	**III**	**IV**	**V**
pyridine	(45)	(27)	(9)	(9)	(9)
DMF	(—)	(11)	(66)	(9)	(14)



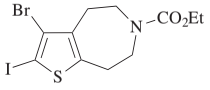
IV **V**



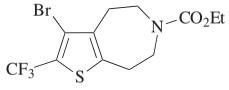
$TMSCF_3$ (5 eq), KF (2.2 eq), CuI (1.1 eq), NMP, DMF, 80°, 12 h



(12) 840

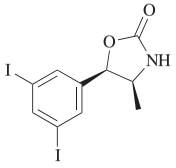


$TMSCF_3$ (5 eq), KF (1.1 eq), CuI (1.1 eq), bipy (1.3 eq), NMP, DMF, 80°, 16 h

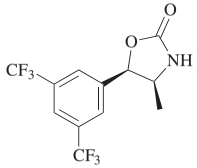


(23) 840

C_9



1. CuCl (4 eq), *t*-BuOK (4 eq), phen (4 eq), DMF, rt, 1 h
2. $TMSCF_3$ (4 eq), rt, 1 h
3. Substrate (1 eq), 50°, 18 h



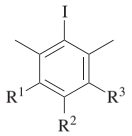
(78) 841

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

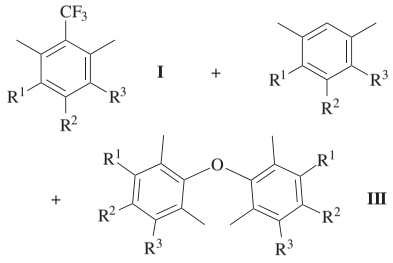
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*

C_{9-11}



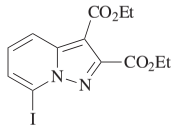
CF_3CO_2Na (2.5 eq), CuI (1.5 eq), HMPA, 150–180°, 15 h

R^1	R^2	R^3	**I**	**II**	**III**
H	Me	H	(41)	(35)	(14)
Me	Me	H	(38)	(36)	(13)
Me	H	Me	(32)	(36)	(15)
Me	Me	Me	(38)	(37)	(9)

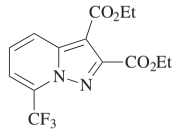


239

C_9

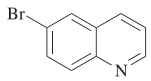


$FSO_2CF_2CO_2Me$, CuI, DMF, 80°

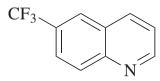


(89)

314

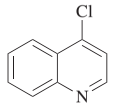


CF_3I (15 eq), Zn, $CuSO_4$, DMF, 130–140°

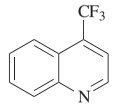


(28)

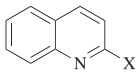
52



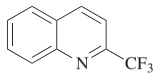
See Table.



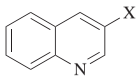
Conditions		
CF_3I, Cu, DMF, 140°, 36 h	(11)	366
CF_3I (15 eq), Zn, $CuSO_4$, DMF, 130–140°	(11)	52



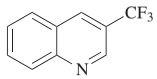
See Table.



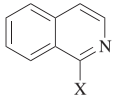
X	Conditions		
Cl	CF_3I (15 eq), Zn, $CuSO_4$, DMF, 130–140°	(10)	52
Cl	CF_3I, Cu, DMF, 120–130°, 24 h	(10)	366
I	CF_3I (15 eq), Zn, $CuSO_4$, DMF, 130–140°	(60)	52
I	CF_3I, Cu, DMF, 135°, 20 h	(60)	366
I	$TMSCF_3$ (2 eq), KF (2 eq), CuI (10 mol %), phen (10 mol %), NMP/DMF (1:1), 60°, 24 h	(95)	376



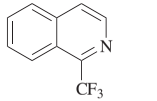
See Table.



X	Conditions		
Br	CF_3I, Cu, HMPA, 130–140°, 20 h	(74)	366
Br	CF_3Br, Cu, HMPA, 130°, 20 h	(22)	828
Br	CF_3Br, e^-, Cu anode, DMF, TMEDA, Bu_4NBr, 95°, 7 h; heat, 2 h	(98)	364
I	CF_3I, Cu, MeCN, 120°, 20 h	(30)	366
I	CF_3I (15 eq), Zn, $CuSO_4$, DMF, 130–140°	(11)	52



See Table.



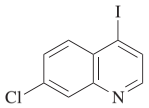
X	Conditions		
Cl	CF_3I (15 eq), Zn, $CuSO_4$, DMF, 130–140°	(30)	52
Cl	CF_3I, Cu, DMF, 135–140°, 20 h	(30)	366
I	CF_3I, Cu, DMF, 130–140°, 20 h	(8.5)	366
I	CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min	(66)	338

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

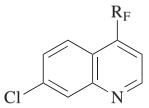
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_9

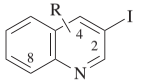


(phen)CuR_F (x eq), DMF, rt, 18 h

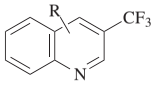


R_F	x		
CF_3	2	(92)[s]	
n-C_3F_7	1.5	(92)	

54

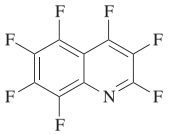


$TMSCF_3$ (x eq), KF (y eq), CuI (z eq), NMP, 50°, 20 h

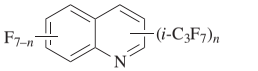


R	x	y	z	
2-Cl	1	1.1	1.1	(80)
4-Cl	1.1	1.1	1.1	(79)
2-Cl-8-Br	1.5	1.5	1.5	(64)

350



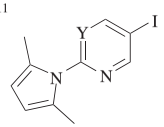
CF_2=$CFCF_3$, CsF, KF, glymes, rt



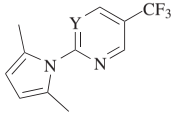
(4–53) n = 1–3

842, 823

C_{10-11}



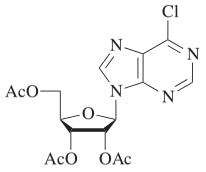
CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min



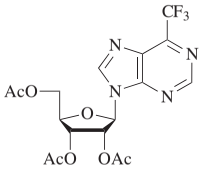
Y		
N	(63)	
CH	(82)	

338

C_{10}

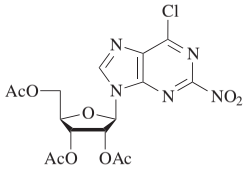


CF_3I, Cu, HMPA, 60°, 60 h

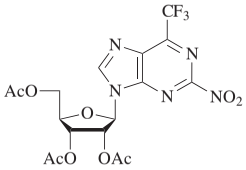


(29)

368

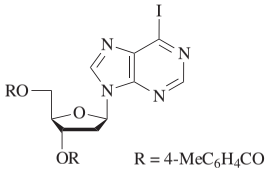


$TMSCF_3$ (1.6 eq), CsF (1.6 eq), THF, 0°, 5 min; rt, 19 h



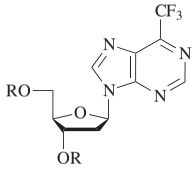
(25)

825



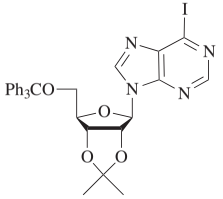
R = 4-MeC$_6$H$_4$CO

TMSCF$_3$ (2.8 eq), KF (2.8 eq), CuI (1.6 eq), NMP, DMF, 60°, 24 h

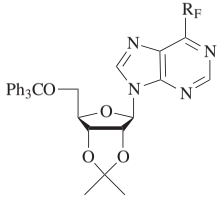


(58)

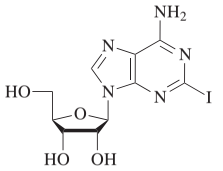
374



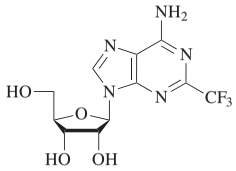
TMSR$_F$ (*x* eq), KF (1.4 eq), CuI (1.6 eq), NMP, 60°



R_F	*x*	Time (h)		
CF_3	1.4	24	(75)	371
n-C_3F_7	1.7	48	(47)	

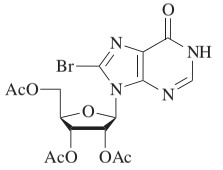


CF_3ZnBr, CuBr, HMPA, DMF, 70°, 4 h

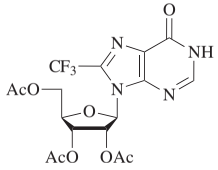


(51–84)

264, 265



CF_3I, Cu, HMPA, 45°, 24 h



(42)

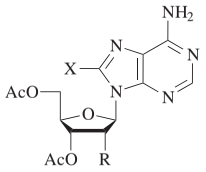
368

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

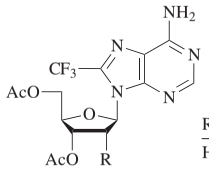
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{10}

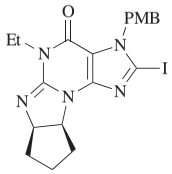


CF_3I, Cu, HMPA

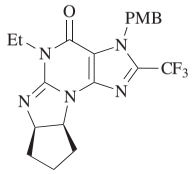


R	X	Temp (°)	Time (h)	
H	Br	45	24	(64)
AcO	I	rt	12	(46)

368

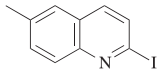


CF_2Br_2, Zn, CuBr, HMPA, DMF, 60–70°, 30–40 min

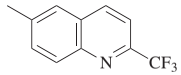


(—)

271

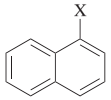


CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min

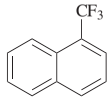


(79)

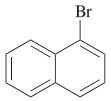
338



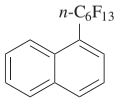
See Table.



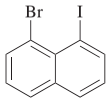
X	Condtions		
Br	**21**, Cu, HMPA/MeCN (5:2),100°, 18–19 h	(16)	262
Br	**21**, Cu, NMP/MeCN (5:2), 100°, 18–19 h	(3)	262
I	CF_3CO_2Na, CuI, NMP, 140–160°, 4 h	(82)	58
I	CF_3CO_2Na (4 eq), CuI (4 eq), DMA, 160°, 4 h	(69)	843



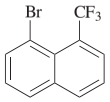
n-$C_6F_{13}I$ (1.2 eq), Cu (2.4 eq), DMSO, 125–135°, 3.5 h



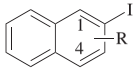
(78) 830



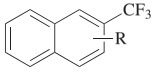
$TMSCF_3$ (1 eq), KF (1 eq), CuI (1 eq), NMP, 75°, 20.75 h



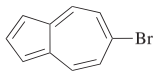
(92) 344



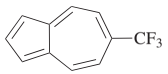
See Table.



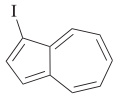
R	Conditions		
H	CF_3CO_2Na (4 eq), CuI (4 eq), DMA, 160°, 4 h	(86)	843
1-Br	$TMSCF_3$ (1 eq), KF (1 eq), CuI (1 eq), NMP, 50°, 20 h	(61)	344
3-Br	$TMSCF_3$ (1 eq), KF (1 eq), CuI (1 eq), NMP, 50°, 20 h	(48)	344
1-Cl-4-Br	$TMSCF_3$ (1 eq), KF (1 eq), CuI (1 eq), NMP, 50°, 20 h	(54)	344



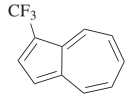
CF_3CO_2Na (6 eq), CuI (4 eq), DMA, 160°, 4 h



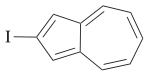
(55) 843



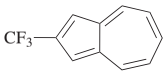
CF_3CO_2Na (6 eq), CuI (4 eq), DMA, 160°, 4 h



(42) 843

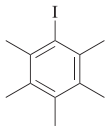
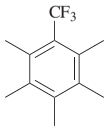
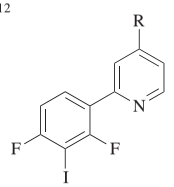
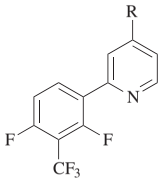
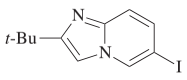
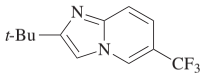
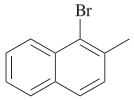
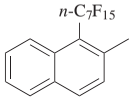
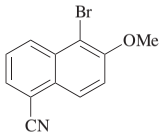
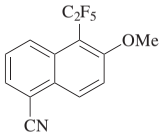


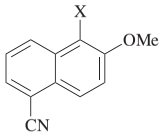
CF_3CO_2Na (4 eq), CuI (4 eq), DMA, 160°, 4 h



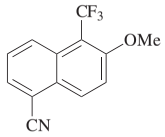
(90) 843

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_{11} 	CF_3CO_2Na (1 eq), CuI, NMP, 160°, 4 h	 (60)	59
C_{11-12} 	$TMSCF_3$, CuI, KF, NMP	 R: H (32), Me (33)	341
C_{11} 	CF_3CO_2K (2 eq), CuI (2 eq), pyridine (2.4 eq), NMP, 200–210°, flow system, t_r = 16 min	 (65)	338
	n-$C_7F_{15}I$ (1 eq), Cu (4 eq), HMPA, 155–160°, 40 min	 (17)	337
	$C_2F_5CO_2M$ (1.5–2 eq, M = Na or K), CuI (2 eq), DMF, toluene, 145–150°	 (70)	832

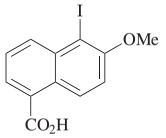


1. CF_3CO_2Na, CuI, toluene, reflux
2. DMA, 150–155°

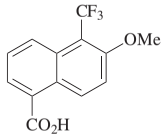


X	Time (h)	
Br	6	(82)
I	4	(73)
I	4[j]	(90)

240

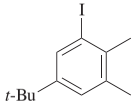


CF_3I, Cu, pyridine, 1 h

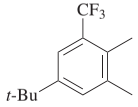


(—) 240

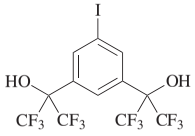
C_{12}



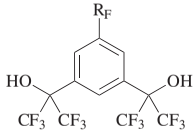
CF_3CO_2Na (2 eq), CuI (2 eq), NMP, 160°, 24 h



(41) 844a



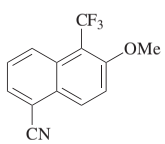
R_FI, Cu, DMSO, 120–145°, 10–16 h



• DMSO

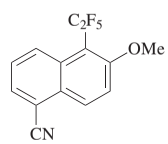
R_F	
n-C_3F_7	(87)
i-C_3F_7	(—)
n-C_6F_{13}	(78)
n-C_7F_{15}	(91)
n-C_8F_{17}	(88)

845



CF_3CO_2R (x eq), CuI (2.1 eq), toluene, DMF, 156°, 2 h

I (—) +



II (—) 844

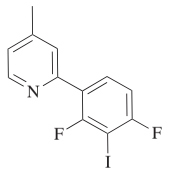
R	x	Conv **I** (%)	Conv **II** (%)
Na	4	80.9	4.9
Me_4N	1.5	87.1	—
Bu_4N	1.5	82.3	—

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

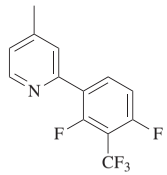
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{12}

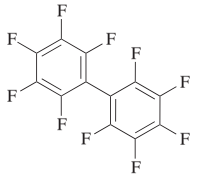


1. CuI (1.5 eq), KF (1.5 eq), heat under reduced pressure
2. Substrate (1 eq), $TMSCF_3$ (2 eq), NMP, rt, 24 h

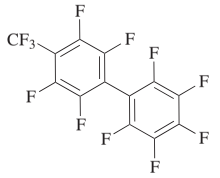


(53)

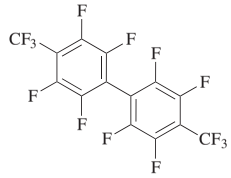
846, 847, 848



$TMSCF_3$, TASF, THF, rt, 2–3 h



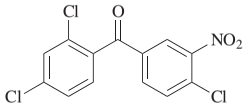
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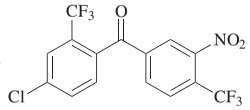
333

I **I + II** (—) 40–70% conv, **I/II** = 2:1 **II**

C_{13}



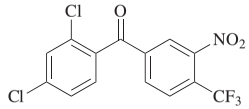
CF_2Br_2(2.2 eq), Cu (6 eq), DMA, 100°, 8 h



(21.5)

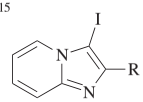
367

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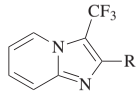


(68)

$C_{13–15}$



$TMSCF_3$ (2.05 eq), KF (1.54 eq), CuI (1.54 eq), NMP, rt, 24 h



R	
Ph	(65)
2,4-$F_2C_6H_3$	(57)
4-$CF_3C_6H_4$	(83)
3,5-$(CF_3)_2C_6H_3$	(39)

849

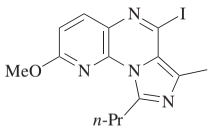
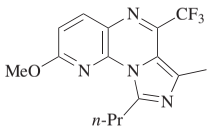
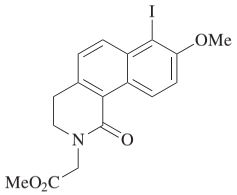
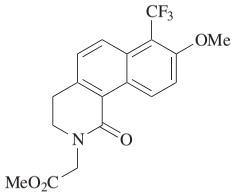
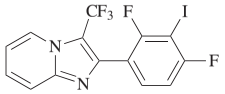
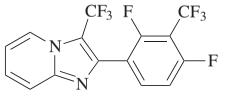
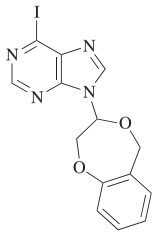
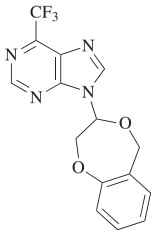
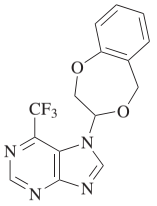
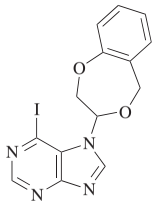
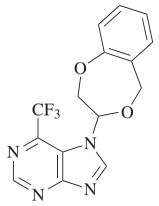
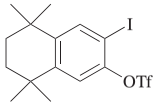
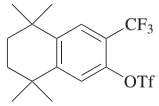
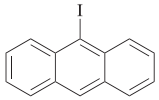
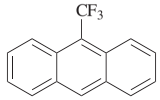
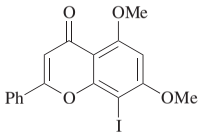
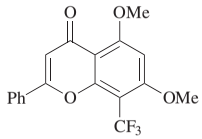
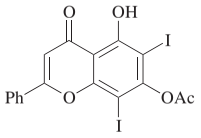
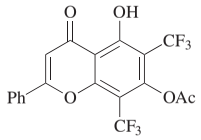
C_{13}		1. KF (1.3 eq), CuI (1.3 eq), heat 2. $TMSCF_3$ (1.2 eq), NMP, rt; 50°, 0.75 h 3. Substrate (1 eq), rt; 50°, 20 h		(58)	850
		$(CF_3)_2Hg$, Cu, DMA, 150–155°, 1 h		(99)	851
C_{14}		$TMSCF_3$ (2.05 eq), KF (1.54 eq), CuI (1.54 eq), NMP, rt, 24 h		(31)	849
		$TMSCF_3$ (1.4 eq), KF (1.4 eq), CuI (1.6 eq), NMP, DMF, 60°, 24 h	 (49) + 	(20)	372

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{14} 	$TMSCF_3$ (1.4 eq), KF (1.4 eq), CuI (1.6 eq), NMP, DMF, 60°, 24 h	 (14)	372
	$FSO_2CF_2CO_2Me$, CuI, HMPA, DMF, 70°, 4 h	 (89)	254
	CF_3CO_2Na, CuI, NMP, 150–160°, 6 h	 (17)	241
C_{15} 	$FSO_2CF_2CO_2Me$, CuI, DMF	 (—)	257
	$FSO_2CF_2CO_2Me$, CuI, DMF	 (—)	257

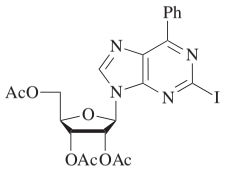
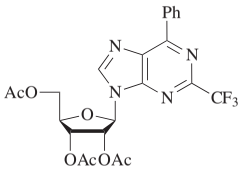
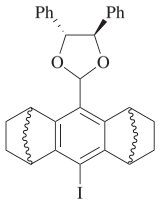
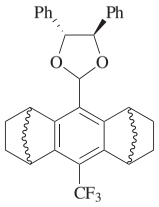
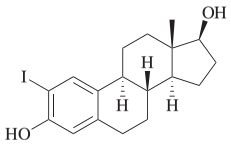
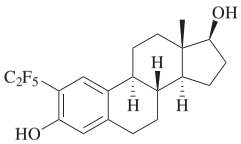
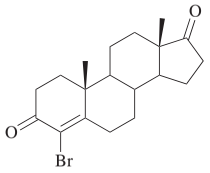
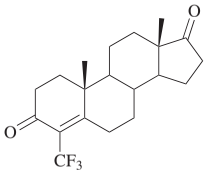
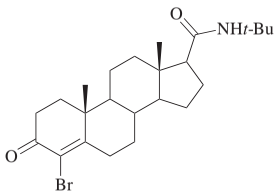
C_{16}		$TMSCF_3$ (1.4 eq), KF (1.4 eq), CuI (1.6 eq), NMP, DMF, 60°, 24 h		(48)	373
C_{17}		$TMSCF_3$, KF, CuI		Config (1*S*,4*R*,5*R*,8*S*) (96) (1*R*,4*S*,5*S*,8*R*) (96)	345
C_{18}		C_2F_5I (1.2 eq), Cu (2.5 eq), DMSO, 80°, 16 h		(41)	525
C_{19}		$FSO_2CF_2CO_2Me$, CuI, DMF, 75°		(—)	819

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

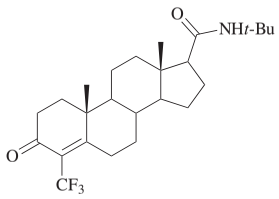
Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{20}

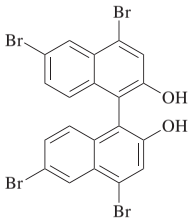


$FSO_2CF_2CO_2Me$, CuI, DMF, 75°

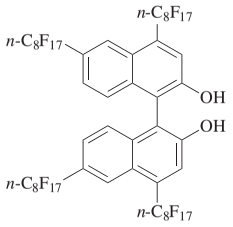


(—)

819

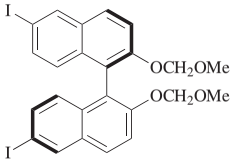


n-$C_8F_{17}I$, Cu, DMSO, 160°

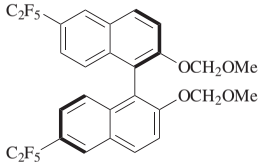


(46)

852

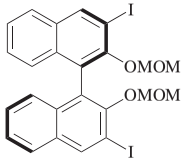


$TMSC_2F_5$ (4 eq), KF (4 eq), CuI (3 eq), DMF, 100°, 24 h

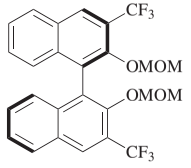


(82)

340



(phen) $CuCF_3$ (1.5 eq), DMF, rt, 18 h



(97)

54

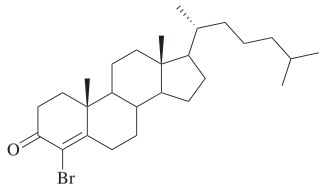
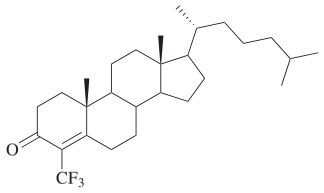
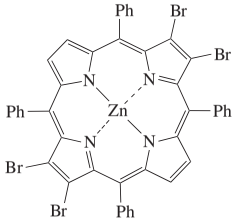
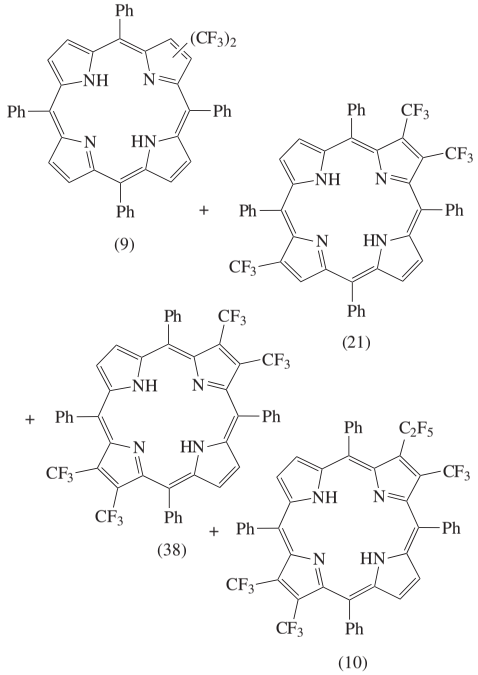
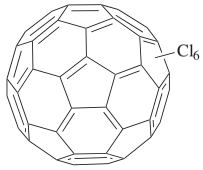
C_{27} 	$FSO_2CF_2CO_2Me$, CuI, DMF, 75°		(—)	819
C_{44} 	CF_3CdBr (2.8 eq), CuBr (14 eq), HMPA, DMF, 90°, 7 h			272

TABLE 5C. PERFLUOROALKYL ADDITION TO ARYL AND HETEROARYL HALIDES AND PSEUDOHALIDES (*Continued*)

Aryl or Heteroaryl Halide or Pseudohalide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{60} 	C_2F_5Li (3 eq), Et_2O, –95° to rt	$C_{60}(C_2F_5)_2$ + $C_{60}(C_2F_5)_4$ + $C_{60}(C_2F_5)H$ + $C_{60}(C_2F_5)_3H$ + $C_{60}(C_2F_5)_5H$ (5–10% each)	853

[a] The yield was determined by ^{19}F NMR spectroscopy.

[b] The reagent was added over 12 h and the mixture was then stirred another 6 h.

[c] Thiophene (4%) was also formed.

[d] The reagent was added over 6 h and the mixture was then stirred another 2 h.

[e] The product was a mixture of perfluorotoluene and C_6F_5H.

[f] The "CF_3Cu" solution was filtered.

[ff] (*E*)/(*Z*) = 85:15.

[fff] (*E*)/(*Z*) = 93:7.

[g] 1,4-$(C_2F_5)_2C_6H_4$ was produced in 8% yield.

[h] The yield is based on the catalyst.

[i] A white precipitate was observed.

[ii] The yield as reported in the reference is likely based on 1.1 eq of perfluoroalkylating reagent per reacting center.

[j] 1,2-$(CF_3)_2C_6H_4$ was formed in 3% yield.

[k] 1,4-$(CF_3)_2C_6H_4$ was formed in 4% yield.

[l] The reagent was added over 4 h and the mixture was then stirred another 2 h.

[m] Benzaldehyde was formed in 2% yield.

[n] About 10% of the corresponding phenol was also formed.

[o] The reaction was performed in the dark.

[p] The reaction was performed in the presence of oxygen.

[q] The reaction was performed in the presence of 1,4-dinitrobenzene (0.2 eq).

[r] 1,4-Dimethoxybenzene was formed as a side product.

[s] The reagent (phen)$CuCF_3$ was prepared in situ.

[t] Some reagents were added in different order and at different pre-generation times and temperatures. See the original literature for details.

[u] The reaction was carried out in air.

TABLE 6. PERFLUOROALKYL ADDITION TO ALCOHOLS

Alcohol	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-9}

ROH

XCF_2CO_2R (2 eq), KF (1 eq), CuI (1 eq), DMF

RCF_3

R	X	Temp (°)	Time (h)		Refs.
CH_2=$CHCH_2$	Cl	100	6	(71)	245
Bn	Cl	100	10	(43)	
Bn	Br	90	8	(39)	
Bn	FSO_2	70	9	(47)	
4-$BrC_6H_4CH_2$	Cl	100	10	(40)	
PhCH=$CHCH_2$	Cl	100	7	(64)	
PhCH=$CHCH_2$	Br	90	10	(72)	
PhCH=$CHCH_2$	FSO_2	65	7	(63)	

C_7

CF_2Br_2 (2 eq), Cu (6 eq), DMF, 80–85°



R		Refs.
Ph	(39)	383
2-ClC_6H_4	(12)	
2-$O_2NC_6H_4$	(19)	
3-$O_2NC_6H_4$	(45)	
4-$O_2NC_6H_4$	(27)	

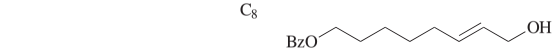
BnOH

CF_2Br_2 (2 eq), Cu (6 eq), solvent, 100°, 8–24 h

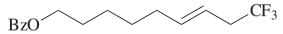
$BnCF_3$ (**I**) + BnC_2F_5 (**II**)

Solvent	**I**	**II**	Refs.
DMF	(27)	(—)	383
DMA	(5)	(—)	
NMP	(12)	(14)	

C_8



CF_2Br_2 (2 eq), Cu (6 eq), DMF, 80–85°

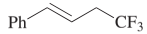

(28)

383

C_9



CF_2Br_2 (2 eq), Cu (6 eq), DMF, 80–85°


(29)

383

TABLE 7. PERFLUOROALKYL ADDITION TO EPOXIDES

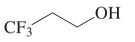
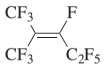
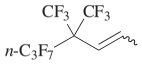
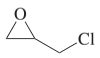
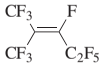
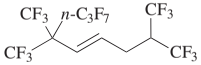
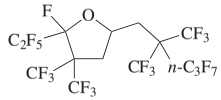
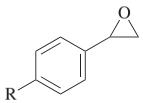
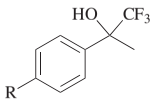
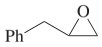
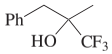
Epoxide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_2 	CF_3MgI, *n*-Bu_2O, 0°, 12 h; 40°, 30 h	 (57)	199
C_{2-3} 	 , CsF, diglyme, 130°, 100 h	 R: H (82); Me (28)	321
C_3 	 , CsF, diglyme, 130°, 80 h	 (—) +  (—)	321
C_{8-9} 	CHF_3, **57** (1.2 eq), 40°, o/n	 R: H (51); MeO (37); CF_3 (69)	81
C_9 	CHF_3, **57** (1.2 eq), 40°, o/n	 (53)	81

TABLE 8. PERFLUOROALKYL ADDITION TO AMINES

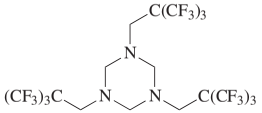
Amine	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_6

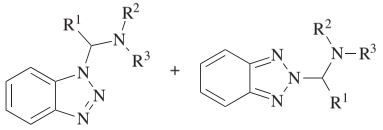


$(CF_3)_3CH$, Et_3N (1.1 eq), 100°, 27 h

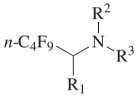


(24) 84

$C_{7–15}$



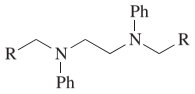
1. *n*-C_4F_9MgX[a]
   Et_2O, –78°
2. BF_3•OEt_2, –78° to rt



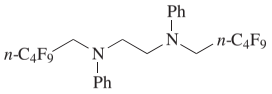
384

R^1	R^2	R^3	
H	Ph	Me	(73)
i-Pr	Ph	Me	(60)
i-Pr	Bn	Bn	(56)
Ph	Ph	Me	(45)
4-$O_2NC_6H_4$	–$(CH_2)_2O(CH_2)_2$–		(61)
$PhCH_2CH_2$	Bn	Bn	(64)

C_{16}



1. *n*-C_4F_9MgX[a] (2 eq), Et_2O
2. BF_3•OEt_2 (2 eq), –78° to rt



(60) 384

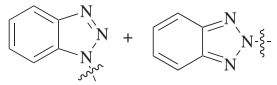
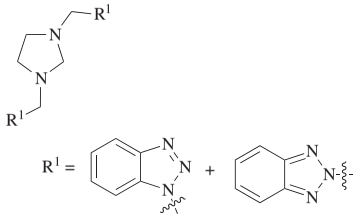
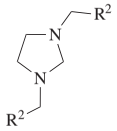
R = 

TABLE 8. PERFLUOROALKYL ADDITION TO AMINES (*Continued*)

Amine	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{17} 	1. R^2MgX[a](2 eq), Et_2O, THF, –40°, 1 min 2. BF_3•OEt_2 (2 eq), –78° to rt		384

R^2	
n-C_4F_9	(31)
n-C_6F_{13}	(50)

[a] X is not specified

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES

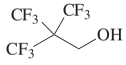
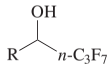
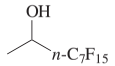
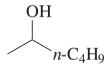
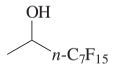
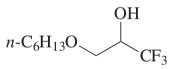
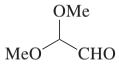
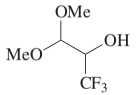
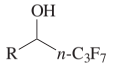
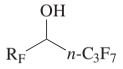
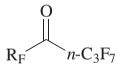
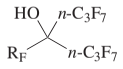
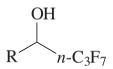
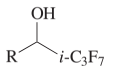
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_1			
$(CH_2O)_n$	$(CF_3)_3CH$, Et_3N (0.2 eq), 100°, 55 h	 (—)	84
$C_{1–2}$			
RCHO	*n*-C_3F_7MgI, *n*-Bu_2O, –25°, 8 h; –25° to rt, o/n; rt to 60°	 R: H (42); Me (37)	202
C_2			
MeCHO	*n*-$C_7F_{15}I$, *n*-BuLi (1–1.5 eq), Et_2O, pentane, –95°, 0.5 h	 (70) 60% conv +  (17) + *n*-$C_5F_{11}CF{=}CF$(*n*-C_4H_9) (5)	189
	n-$C_7F_{15}I$ (0.96 eq), *n*-BuLi (0.96 eq), Et_2O, –95°	 (64)	189
	1. $TMSCF_3$ (1.05 eq), CsF (cat.), THF, 1 h 2. HCl, H_2O, 1 h	 (80)	854
	1. $TMSCF_3$ (1.87 eq), TBAF (1.9 mol %), THF, –20°; 0°, 0.5 h; rt, 5 h 2. HCl, H_2O, 3 h	 (38)	435
$C_{2–9}$			
RCHO	1. $TMSCF_3$ (1.025 eq), CsF (1 mol %), solvent, rt 2. HCl, H_2O, rt, 2 h	 R: Me — 1 (85); Ph — 6 (88); (*E*)-PhCH=CH DME 1.5 (92)	470

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{2-4}			
RCHO	*n*-C_3F_7MgI, *n*-Bu_2O, –50°, 41 h; –50° to rt, 24 h; 60°, 1 h	 R: Me (41); Et (45); *n*-Pr (40)	204
R_FCHO	*n*-C_3F_7MgI, *n*-Bu_2O, –20°, 8 h; –20° to rt, 4 h; rt, 24 h	 R_F: CF_3 (38); C_2F_5 (42); *n*-C_3F_7 (43)	204
	n-C_3F_7MgI, *n*-Bu_2O, –20°, 25 h; –20° to rt, 12–15 h; 50°,0.5 h	 **I** +  **II** R_F: CF_3 (36) (11); C_2F_5 (41) (13); *n*-C_3F_7 (31) (16)	204
RCHO	*n*-C_3F_7MgBr, Et_2O, –50° to rt	 R: Me (30); *n*-Pr (45.5)	855
C_{2-5}			
RCHO *x* eq	*i*-C_3F_7M (1 eq), Et_2O, conditions		217

R	*x*	M	Conditions	
Me	1.85	MgBr	–40° to rt, 6 h	(22.7)
Et	1.45	Li	–78° to rt, 6 h	(53)
Et	1.45	MgBr	–78° to rt, 6 h	(17.5)
n-Bu	2.0	MgBr	–50° to rt, 1 h; reflux, 0.25 h	(37)

C_3

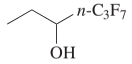


RH (R = *n*-C_3F_7, *i*-C_3F_7), MeLi, Et_2O, –70° or –40 to 20°, 2 h



(—) 195

n-C_3F_7I, MeLi, Et_2O, –40° to rt, 3 h; reflux, 1 h



(50) 188

$C_{3–9}$



R_FI, Zn, **19** (3.2 mol %), MeCN, rt



R	R_F	Time (h)		
Et	*n*-C_8F_{17}	24	(53)	390
n-C_5H_{11}	CF_3	15	(48)	
n-C_5H_{11}	*n*-C_4F_9	25	(42)	
Ph	CF_3	15	(52)	
Ph	C_2F_5	21	(57)	
Ph	*n*-C_4F_9	14	(42)	
Ph	*n*-C_6F_{13}	13	(65)	
Ph	*n*-C_8F_{17}	14	(52)	
n-C_7H_{15}	*n*-C_6F_{13}	48	(68)	
$Ph(CH_2)_2$	C_2F_5	17	(51)	
$Ph(CH_2)_2$	*n*-C_6F_{13}	39	(57)	

$C_{3–7}$

1. R_FI (*x* eq), TDAE (1 eq), solvent
2. HCl, H_2O, rt



127

R	R_F	*x*	Solvent	Temp (°)	Time (h)	
Et	C_2F_5	1.2	CH_2Cl_2	–40 to –20	2 h	(24)
Et	*n*-C_4F_9	1.2	DMF	–20 to –10	8 h	(35)
c-C_6H_{11}	CF_3	1.3	DMF	–20 to –10	2 h	(62)
c-C_6H_{11}	*n*-C_4F_9	1.2	THF	–40 to –30	2 h	(30)
Ph	*n*-C_3F_7	1.2	DME	–40 to –30	1.5 h	(30)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-7}

RCHO

R_FX, $MnCl_2$/Na, DMF, ultrasound



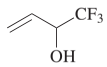
316

R	R_F	X		R	R_F	X	
Et	*n*-C_8F_{17}	I	(46)	Ph	CF_3	I	(52)
Et	*n*-C_8F_{17}	Br	(38)	Ph	CF_3	Br	(48)
MeCH=CH	*n*-C_6F_{13}	I	(51)	Ph	C_2F_5	I	(46)
n-C_5H_{11}	CF_3	I	(32)	Ph	*i*-C_3F_7	I	(41)
n-C_5H_{11}	CF_3	Br	(37)	Ph	*n*-C_4F_9	I	(44)
n-C_5H_{11}	*n*-C_4F_9	I	(52)	Ph	*n*-C_4F_9	Br	(51)
n-C_5H_{11}	*n*-C_4F_9	Br	(40)	Ph	*n*-C_6F_{13}	I	(54)

C_3



1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt
2. HCl, H_2O



(80)

289

C_{3-7}

RCHO

$TMSR_F$ (1.1 eq), KF (0.17 eq), $Me[O(CH_2)_2O]_4Me$, 20–30°

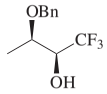


R	R_F	Time (h)		Refs.
CH_2=CH	CF_3	18	(75)	126
Ph	CF_3	5	(90)	
Ph	*i*-C_3F_7	18	(67)	

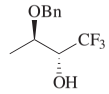
C_3



1. $TMSCF_3$ (1.3 eq), TBAF (cat.), THF, 0°, 0.25 h; rt, 0.75 h
2. HCl, H_2O, rt, o/n



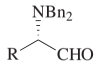
(29) +



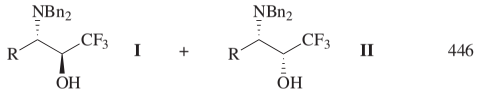
(33)

856

C_{3-9}



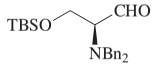
1. $TMSCF_3$ (1.5 eq), TBAF (5 mol %), THF, 0°; rt
2. TBAF (0.2 eq), rt, 1 h



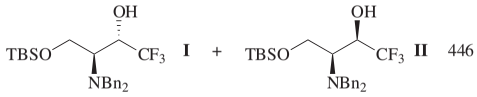
446

R	Time (h)	**I** + **II**	**I**/**II**
Me	2	(74)	80:20
i-Pr	3	(63)	84:16
i-Bu	3	(81)	72:28
Ph	3	(40)	46:54
Bn	2	(72)	76:24

C_3



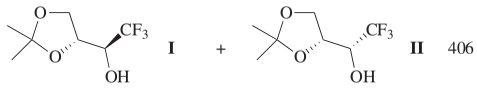
1. $TMSCF_3$ (1.5 eq), TBAF (5 mol %), THF, 0°; rt, 2 h
2. TBAF (1 eq), rt, 1 h



446

I + **II** (52), **I**/**II** = 62:38

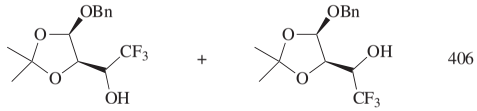
1. $TMSCF_3$ (1.1 eq), TEAF (1–5 mol %), THF, 0°, 0.25 h
2. TEAF (1.1 eq), THF, 0.25 h



406

I + **II** (53), **I**/**II** = 3:2

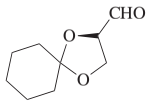
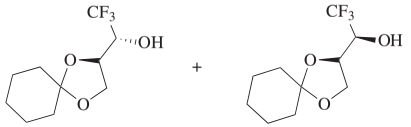
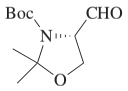
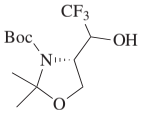
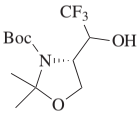
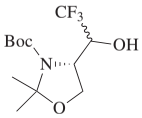
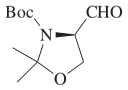
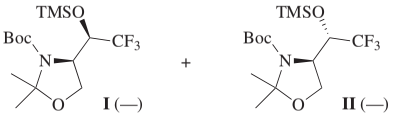
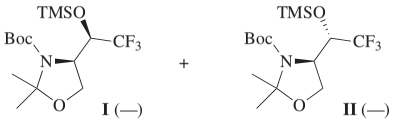
1. $TMSCF_3$ (1.1 eq), TEAF (1–5 mol %), THF, 0°, 0.25 h
2. TEAF (1.1 eq), THF, 0.25 h



406

I (45) **I**/**II** = 55:45 **II** (37)

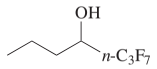
TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_3			
	CF_3I, Zn, DMF, ultrasound	 **I** **I + II** (70), **I/II** = 3:2 **II**	214
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°; rt, 24 h 2. TBAF (2 eq), rt, 24 h	 (70)	857
	1. $TMSCF_3$ (3 eq), Amberlyst A-27 resin (F– form), THF, rt, 1–19 h 2. Amberlyst A-15 resin (H^+ form) 3. Aminomethylated polystyrene resin	 (100)	858
	1. $TMSCF_3$ (1.2 eq), TBAF (2 mol %), THF, 0°; rt, 2.5 d 2. TBAF (2.1 eq), rt, 6 h	 (92)	448
	$TMSCF_3$ (1.2 eq), AcOLi (5 mol %), DMF, 0°, 0.5 h	 **I** (—) + **II** (—) **I + II** 77% conv, **I/II** or **II/I** = 58:42	131
	$TMSCF_3$ (1.2 eq), *n*-Bu_4NOAc (5 mol %), toluene, 0°, 0.5 h	 **I** (—) + **II** (—) **I + II** 86% conv, **I/II** or **II/I** = 62:38	131

C_4



n-C_3F_7I, Mg, Et_2O, –40°, 39 h; –30°, 72 h; –20°, 17 h; rt, 36 h



(16)

201

$C_{4–8}$

RCHO

CF_3CO_2Na, CuI, DMF, 170°, 2 h



R	
n-Pr	(85.8)
Ph	(99.2)
4-ClC_6H_4	(98.6)
4-MeC_6H_4	(96)

600

1. CF_3CO_2Na (x eq), catalyst (y eq), DMF, temp 1, time 1
2. HCl, H_2O, temp 1, time 2



(—)

R	x	Catalyst	y	Temp 1 (°)	Time 1 (h)	Time 2 (h)	Conv (%)	
n-Pr	4	CuI	1	170	2	4	85.8	859
c-C_6H_{11}	4	CuI	1	170	2	4	95.7	859, 860
Ph	4	—	—	170	2	4	59.8	859, 860
Ph	4	Cu	1	170	2	4	82.5	860
Ph	4	CuCl	1	170	2	4	96.9	859, 860
Ph	4	CuBr	1	170	2	4	98.1	859, 860
Ph	4	$CuBr_2$	1	170	2	4	96.8	860
Ph	4	CuI	0.5	170	2	4	85.1	860
Ph	2	CuI	1	170	2	4	56.9	859
Ph	4	CuI	1	120	2	4	71	859
Ph	4	CuI	1	140	2	4	92.3	859
Ph	4	CuI	1	170	2	4	99.2	859, 860
Ph	4	CuI	1	170	1	1	75.5	859
Ph	4	CuI	1	170	1	2	85.8	859
2-ClC_6H_4	4	CuI	1	170	2	4	96.7	859, 860
3-ClC_6H_4	4	CuI	1	170	2	4	86.8	860
4-ClC_6H_4	4	CuI	1	170	2	4	98.6	859, 860
2-MeC_6H_4	4	CuI	1	170	2	4	92.4	859, 860
3-MeC_6H_4	4	CuI	1	170	2	4	82.7	860
4-MeC_6H_4	4	CuI	1	170	2	4	96	859, 860

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{4-8}

RCHO

1. CF_3CO_2Na (4 eq), catalyst (*x* eq), solvent, 170°, 2 h
2. HCl, H_2O, 170°, 4 h



600

R	Catalyst	*x*	Solvent	
n-Pr	CuI	1	DMF	(85.8)
Ph	—	—	DMF	(59.8)
Ph	Cu	1	DMF	(82.5)
Ph	Zn	1	DMF	(82.2)
Ph	CuCl	1	DMF	(96.9)
Ph	CuBr	1	DMF	(98.1)
Ph	$CuBr_2$	1	DMF	(96.8)
Ph	CuI	0.5	DMF	(85.1)
Ph	CuI	1	DMF	(99.2)
Ph	CuI	1	MeCN	trace
Ph	CuI	1	THF	trace
Ph	CuI	1	THF/DMF (1:1)	(42.7)
Ph	CuI	1	NMP	(41.9)
Ph	CuI	1	pyridine	trace
4-ClC_6H_4	CuI	1	DMF	(98.6)
4-MeC_6H_4	CuI	1	DMF	(96)

C_{4-9}

RCHO

1. CF_3Br, Zn, pyridine
2. H_3O^+



R	Temp (°)		
n-Pr	0–10	(30)	601
2-C_4H_3O	20	(26)	
2-pyridyl	20	(65)	
c-C_6H_{11}	20	(30)	
Ph	20	(52)	
4-FC_6H_4	20	(60)	
4-ClC_6H_4	40	(46)	
4-$MeOC_6H_4$	20	(47)	
4-MeC_6H_4	20	(53)	
4-NCC_6H_4	40	(43)	
(*E*)-PhCH=CH	20	(55)	

C_{4-15}

RCHO

CF_3Br, Zn, pyridine, 1–2 h



R	Temp (°)		
n-Pr	0–10	(30)	861
2-pyridyl	20	(65)	
Ph	20	(52)	
4-FC_6H_4	20	(60)	
PhCH=CH	20	(55)	
9-anthryl	20	(37)	

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{4–11}$

RCHO

CF_3I (2.2 eq), TDAE (2.2 eq), solvent, *h*ν, –20° to rt, 12 h



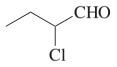
R	Solvent	Conv (%)		Refs.
n-Pr	DMF	15	(—)	385
i-Pr	DMF	52	(48)	385
2-furyl	DMF	82	(78)	385
3-thienyl	DMF	74	(68)	385
4-pyridyl	DMF	—	(73)	385
c-C_6H_{11}	DMF	68	(53)	385
Ph	DMF	80	(78)	385, 386
4-FC_6H_4	DMF	95	(90)	385
4-ClC_6H_4	DMF	89	(81)	385
2-BrC_6H_4	DMF	91	(86)	385
4-NCC_6H_4	DMF	89	(82)	385
PhCH=CH	DMF	—	(78)	385
2-$MeOC_6H_4CH$=CH	DMF	83	(79)	385
1-$C_{10}H_7$	DMF	100	(93)	385, 386
1-$C_{10}H_7$	DME	—	(53)	385
1-$C_{10}H_7$	DME/HMPA (1:1)	—	(72)	385

R_FI (2.2 eq), TDAE (2.2 eq), DMF, –15° to rt; *h*ν, 1 h; rt, 12 h

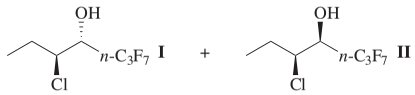


R	R_F		Refs.
n-Pr	C_2F_5	(5)	386
Ph	C_2F_5	(75)	
Ph	*n*-C_4F_9	(35)	
(*E*)-2-$MeOC_6H_4CH$=CH	C_2F_5	(80)	
1-$C_{10}H_7$	C_2F_5	(90)	

C_4

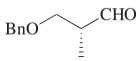


n-C_3F_7MgBr, Et_2O, –30°, 1 h; –30 to 0°

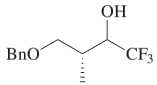


I + **II** (68), **I**/**II** = 63:37

862

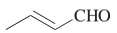


1. $TMSCF_3$, CsF
2. TBAF

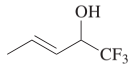


(—)

863



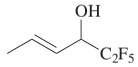
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt
2. HCl, H_2O



(50)

289

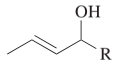
C_2F_5MgBr, Et_2O, –40 to rt, o/n



(60)

393

RX, Zn, DMF, ultrasound



R	X	Time (h)	
CF_3	I	0.5	(62)
CF_3	Br	3	(41)
C_2F_5	I	0.5	(40)
n-C_4F_9	Br	2	(58)

299

$C_{4–9}$

RCHO

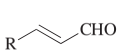
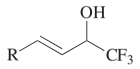
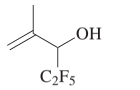
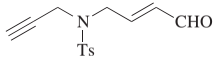
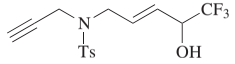
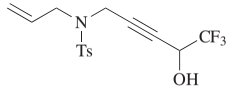
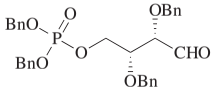
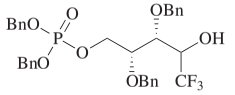
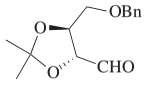
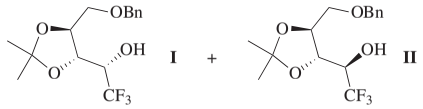
CF_3I, Zn, DMF, ultrasound, 0.5 h

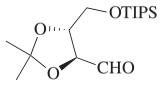


R	
MeCH=CH	(62)
n-C_5H_{11}	(61)
Ph	(72)
PhCH=CH	(68)

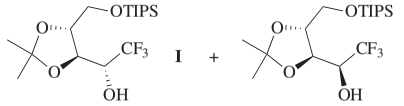
396

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
$C_{4–10}$  R = $BnOCH_2$, *n*-Pr, (*E*)-EtCH=CH, *n*-C_5H_{11}, Ph, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$	1. $TMSCF_3$ (1.2 eq), TBAF (5 mol %), THF, 0° to rt 2. HCl, H_2O	 (—)	864
C_4 	C_2F_5MgBr, Et_2O, –40 to rt, o/n	 (60)	393
	1. $TMSCF_3$ (1.2 eq), CsF (5 mol %), DME, rt, 0.5 h 2. HCl, H_2O	 (39)	865
	1. $TMSCF_3$ (1.25 eq), TBAF (5 mol %), THF, 0°, 0.25 h 2. HCl, H_2O	 (65)	865
	1. $TMSCF_3$, CsF 2. TBAF, THF	 (72)	424
	1. $TMSCF_3$ (1.1 eq), TEAF (cat.), THF, rt 2. TEAF (1 eq), THF, rt	 **I** + **II** **I** + **II** (82), **I**/**II** = 1:1	618

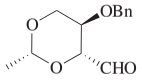


1. $TMSCF_3$ (1.1 eq), *t*-BuOK (cat.), THF, 0°, 2 h
2. TBAF (2.1 eq), THF, 0°, 2 h

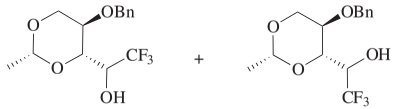


I + **II** (80), **I/II** or **II/I** = 3:2

866

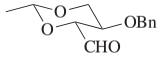


1. $TMSCF_3$ (1.1 eq),
   TEAF (1–5 mol %),
   THF, 0°, 0.25 h
2. TEAF (1.1 eq), THF, 0.25 h

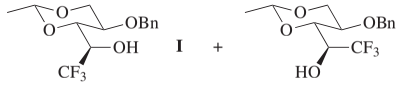


I (43) **I/II** = 3:2 **II** (28)

406



1. $TMSCF_3$ (1.1 eq), TEAF (cat.), THF, –10°, 5 min
2. HCl, EtOH, rt, 5 min



I + **II** (71), **I/II** = 3:2

617, 618

C_{5-9}

RCHO

1. **60** (1 eq, dr 60:40), initiator (0.1 eq), solvent
2. TBAF (1 eq), THF, 1 h



182

R	Initiator	Solvent	Time (h)	
n-Bu	CsF	DME	24	(30)
t-Bu	CsF	DME	24	(63)
2-C_4H_3O	CsF	DME	24	(90)
Ph	CsF	DME	24	(73)
Ph	TBAT	THF	6	(84)
(*E*)-PhCH=CH	CsF	DME	24	(70)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
$C_{5–7}$			
RCHO	R_FI, $SnCl_2$, pyridine, DMF, rt		867

R	R_F	Time (h)	
n-Bu	CF_3	24	(21)
n-Bu	*n*-C_3F_7	12	(68)
n-C_5H_{11}	*i*-C_3F_7	5	(67)
Ph	CF_3	24	(18)
Ph	*n*-C_3F_7	12	(72)
Ph	*i*-C_3F_7	5	(86)
Ph	*n*-C_6F_{13}	24	(66)
4-$MeOC_6H_4$	*i*-C_3F_7	5	(82)

$C_{5–11}$			
RCHO	CHF_3, **57** (1.2 eq), THF, –40°, 3 h		81

R		
t-Bu	(81)	
n-C_6H_{13}	(48)	
c-C_6H_{11}	(53)	
1-$C_{10}H_7$	(65)	
2-$C_{10}H_7$	(56)	
1-Br-2-$C_{10}H_6$	(65)	

$C_{5–8}$			
RCHO	R_FH, PhI (2–3 eq), e^-, Bu_4NBF_4 (8 mol %), DMF, Mg or Al anode, Ni/Cd cathode, 5–10°		70

R	R_F		
t-Bu	CF_3	(46)	
Ph	CF_3	(71)	
Ph	C_2F_5	(40)	
4-ClC_6H_4	CF_3	(51)	
2-$MeOC_6H_4$	CF_3	(12)	
4-$MeOC_6H_4$	CF_3	(73)	
2-MeC_6H_4	CF_3	(53)	
3-MeC_6H_4	CF_3	(66)	
4-MeC_6H_4	CF_3	(76)	

C_{5-7}

RCHO

CF_3Br, Zn anode, Bu_4NBr, DMF



R		
t-Bu	(80)	234
n-C_6H_{13}	(80)	
c-C_6H_{11}	(70)	
Ph	(95)	
4-ClC_6H_4	(90)	
4-$PhOC_6H_4$	(90)	

CF_3Br, e^-, Ni (cathode),
Bu_4NBr (0.5 eq),
DMF, –10°, 4–12 h



R	Anode		
t-Bu	Zn	(80)	868
2-C_4H_3O	Zn	(50)	
n-C_6H_{13}	Zn	(80)	
c-C_6H_{11}	Zn	(70)	
Ph	Zn	(95)	
Ph	Al	(21)	
Ph	Mg	(33)	
4-ClC_6H_4	Zn	(90)	
3-$PhOC_6H_4$	Zn	(90)	

C_{5-13}

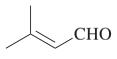
RCHO

1. $PhSO_2CF_3$ (2 eq), *t*-BuOK (2.5 eq),
DMF, –50° to rt
2. H_2O

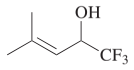


R	Conv (%)		
t-Bu	79	(—)	179
Ph	—	(77)	
4-EtC_6H_4	—	(83)	
2-$C_{10}H_7$	—	(62)	
4-PhC_6H_4	—	(76)	

C_5

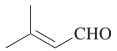
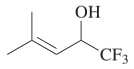
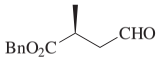
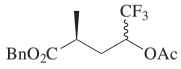


1. $TMSCF_3$ (1.2 eq), TBAF (cat.),
THF, 0°, 1 h; rt
2. HCl, H_2O



(90) 289

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_5			
	1. $TMSCF_3$ (1.2 eq), *n*-$Bu_4N^+Ph_3SnF_2^-$ (cat.), THF, rt, 2 h 2. HCl, H_2O	 (60)	289
	1. $TMSCF_3$ (1.5 eq), TBAF (10 mol %), THF, 0°, 1 h 2. Ac_2O (1.1 eq), 4-dimethylaminopyridine (10 mol %), CH_2Cl_2, 0°; rt, 80 min	 (65) dr 1.5:1	869
C_{5-11}			
RCHO	$TMSCF_3$ (1.2 eq), 4 Å MS (0.5 g/mmol), DMSO, rt	 (—)	136

R	Time (min)	Conv (%)
$BnOCH_2Me_2C$	20	99
c-C_6H_{11}	20	91
Ph	15	100
4-BrC_6H_4	10	97
4-$MeOC_6H_4$	15	100
4-$TBSOC_6H_4$	15	99
4-$Me_2NC_6H_4$	30	53
2-MeC_6H_4	15	91
3-MeC_6H_4	15	86
4-MeC_6H_4	15	98
4-$MeO_2CC_6H_4$	15	98
$Ph(CH_2)_2$	20	81
(*E*)-PhCH=CH	30	85
2,4,6-$Me_3C_6H_2$	15	100
1-$C_{10}H_7$	10	100
2-$C_{10}H_7$	10	100

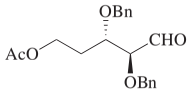
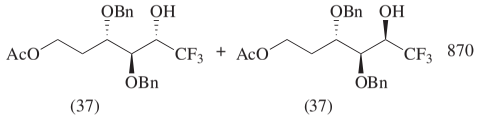
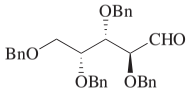
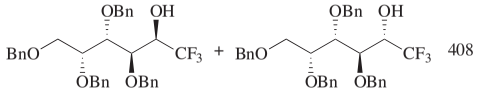
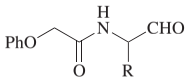
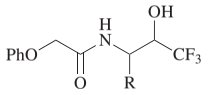
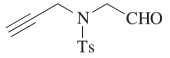
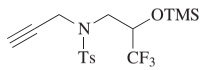
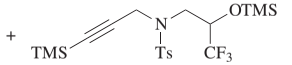
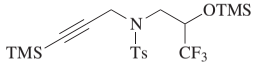
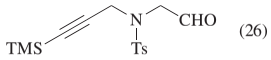
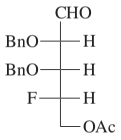
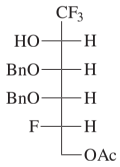
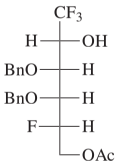
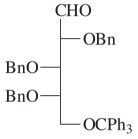
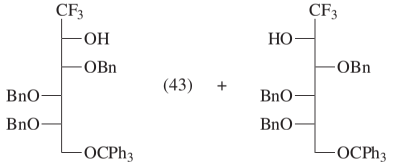
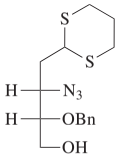
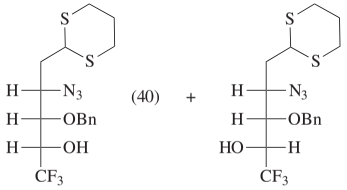
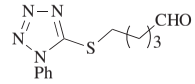
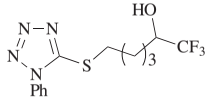
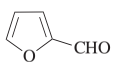
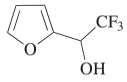
C_5 	1. $TMSCF_3$ (1.49 eq), TBAF (0.1 eq), THF, 0°, 0.5 h; rt, 1.5 h 2. AcOH, H_2O, 50°, 1.5 h	 (37) (37)	870
	1. $TMSCF_3$, TBAF (cat.), THF, 0° to rt, 2 h 2. HCl, H_2O, rt, 4 h	 **I** **I + II** (79), **I/II** = 1:1 **II**	408
C_{5-11} 	1. $TMSCF_3$, CsF (cat.), THF, sonication 2. HCl	 R: Me (40–50); Bn (40–44)	613, 614
C_5 	$TMSCF_3$ (2.7 eq), CsF (2 mol %), THF, rt, 6 h	 (33) +  (37)	414
	$TMSCF_3$ (2.7 eq), KF (2 mol %), DMF, rt, 3 h	 (59) +  (26)	414
	1. $TMSCF_3$ (1.6 eq), TBAF (0.1 eq), 1,3-dioxolane, rt, 1 h 2. AcOH, H_2O, 50°, 3 h	 (39) +  (29)	871

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_5			
	1. $TMSCF_3$ (2 eq), TBAF (5 mol %), THF, 2 h 2. TBAF (1 eq), THF, 5 h	 (43) + (42)	409
	1. $(COCl)_2$ (2.02 eq), DMSO (3.03 eq), CH_2Cl_2, –78°, 40 min 2. *i*-Pr_2NEt (5.06 eq), –78°, 0.5 h; 0°, 1.5 h 3. NH_4Cl, H_2O, 0° 4. $TMSCF_3$ (1.8 eq), TBAF (0.1 eq), 1,3-dioxolane, –40°, 10 min 5. TBAF (1 eq), 1,3-dioxolane, 0°, 10 min	 (40) + (31)	402
	1. $TMSCF_3$ (1.2 eq), TBAF (0.1 eq), THF, 0° to rt, 1 h 2. HCl, rt, 1 h	 (87)	872
	1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O	 (94)	398

C_{5-7}

RCHO

1. CF_3H (2 eq), $MeSOCH_2K$ (2 eq), DMSO, DMF, –40°, 1 h
2. HCl, H_2O, 0°



R		
2-C_4H_3O	(42)	48
c-C_6H_{11}	(45)	
Ph	(65)	
4-$MeOC_6H_4$	(72)	
2,3-$(MeO)_2C_6H_3$	(52)	
3,4-$(MeO)_2C_6H_3$	(51)	
4-$Me_2NC_6H_4$	(70)	
3,4,5-$(MeO)_3C_6H_2$	(45)	
3-$PhOC_6H_4$	(61)	

C_{5-15}

RCHO

1. CF_3H (1 eq, inverse addition), THF, –40°, 20 min
2. *t*-BuOK (1 eq), –40°, 1 h; rt, 10 h



R		
2-furyl	(43)	77
Ph	(49)	
4-$MeOC_6H_4$	(42)	
3-MeC_6H_4	(34)	
9-anthryl	(51)	

C_{5-12}

RCHO

$PhSCF_3$ (1.9 eq), Et_3GeNa (1.1 eq), THF, HMPA, –60°, 0.5 h



R	Conv (%)		
2-furyl	96	(—)	170
4-ClC_6H_4	—	(92)	
4-$MeOC_6H_4$	—	(91)	
(*E*)-PhCH=CH	—	(93)	
(*E*,*E*)-$C_5H_{11}CH$=CHCH=CH	—	(92)	
2-$C_{10}H_7$	—	(91)	
n-$C_{11}H_{23}$	—	(86)	
(*E*)-*n*-$C_9H_{19}CH$=CH	—	(96)	

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-8}

RCHO

1. **79** (2 eq), CsF (0.1 eq), THF, reflux, 20 h
2. HCl, H_2O, rt, 3 h



R		Refs.
2-furyl	(73)	116, 117
Ph	(89)	
4-BrC_6H_4	(82)	
4-$MeOC_6H_4$	(71)	
4-MeC_6H_4	(69)	

C_{5-11}

RCHO

1. $TMSCF_3$ (2 eq), catalyst (0.1 eq), ligand (0.1 eq), solvent, rt
2. $NaHCO_3$, H_2O



135

R	Catalyst	Ligand	Solvent	Time (h)	
2-furyl	$Cu(OAc)_2$	dppe	toluene	1	(55)
2-thienyl	$Cu(OAc)_2$	dppe	toluene	2	(99)
Ph	$Cu(OAc)_2$	dppe	toluene	1	(96)
4-BrC_6H_4	$Cu(OAc)_2$	dppe	toluene	0.5	(92)
4-$MeOC_6H_4$	$Cu(OAc)_2$	dppe	toluene	1	(93)
4-$O_2NC_6H_4$	$Cu(OAc)_2$	dppe	toluene	1	(94)
n-C_7H_{15}	$Cu(OAc)_2$	dppe	toluene	0.5	(95)
4-MeC_6H_4	$Cu(OAc)_2$	dppe	toluene	0.5	(96)
(*E*)-PhCH=CH	$Cu(OAc)_2$	dppe	toluene	2	(99)
2-$C_{10}H_7$	$Cu(OAc)_2$	dppe	CH_2Cl_2	14	(71)
2-$C_{10}H_7$	$Cu(OAc)_2$	dppp	toluene	<1	(97)
2-$C_{10}H_7$	$Cu(OAc)_2$	dppe	toluene	<1	(99)
2-$C_{10}H_7$	CuF_2	dppe	toluene	<1	(99)

C_{5-9}

RCHO

$TMSCF_3$ (1.5 eq),
$[2,4,6\text{-}(MeO)_3C_6H_2]_3P$ (5 mol %),
THF, rt, 0.5 h



R		
2-furyl	(82)	141
c-C_6H_{11}	(81)	
Ph	(85)	
4-ClC_6H_4	(91)	
4-$O_2NC_6H_4$	(90)	
4-$MeOC_6H_4$	(86)	
n-C_8H_{17}	(91)	
$Ph(CH_2)_2$	(85)	
(*E*)-PhCH=CH	(90)	
1-$C_{10}H_7$	(83)	
2-$C_{10}H_7$	(86)	

1. $TMSCF_3$ (1.5 eq), PhONa (0.1 eq),
solvent, 0°, 0.5 h; rt
2. HCl, H_2O, 0°



R	Solvent		
2-furyl	THF	(85)	134
Ph	THF	(92)	
Ph	—	(100)	
2-FC_6H_4	THF	(100)	
2-ClC_6H_4	THF	(93)	
4-BrC_6H_4	THF	(93)	
4-$O_2NC_6H_4$	THF	(99)	
4-$MeOC_6H_4$	THF	(90)	
(*E*)-PhCH=CH	THF	(84)	

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-13}

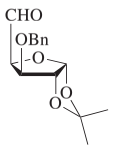
RCHO

1. *n*-Bu_3SnCF_3 (*x* eq), CsF, (20 mol %), rt
2. NH_4Cl, H_2O

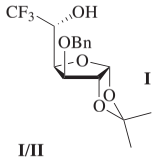


R	*x*	Time (h)		
2-furyl	1.3	9	(>95)[a]	156
Ph	1.1	8	(>95)[a]	
4-BrC_6H_4	1.1	9	(70)	
4-$O_2NC_6H_4$	1.1	9	(49)	
4-$Me_2NC_6H_4$	1.1	22	(70)	
4-$MEMOC_6H_4$	1.3	8	(67)	
4-$THPOC_6H_4$	1.3	8	(64)	
4-$TrOC_6H_4$	1.3	8	(68)	
9-anthryl	1.1	8	(83)	

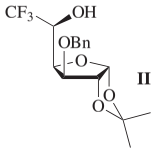
C_5



1. $TMSCF_3$ (1.2 eq), catalyst (5 mol %), solvent, 10 min
2. TBAF

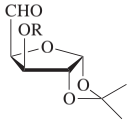


I (—) +

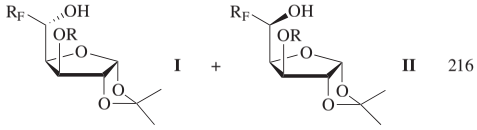


II (—) 131

Catalyst	Solvent	Temp (°)	Conv **I** + **II** (%)	**I/II**
AcOLi	DMF	0	55	75:25
n-Bu_4NOAc	CH_2Cl_2	0	84	62:38
n-Bu_4NOAc	DMF	–20	65	77:23
n-Bu_4NOAc	DMF	0	37	75:25
n-Bu_4NOAc	Et_2O	0	87	68:32
n-Bu_4NOAc	toluene	0	92	73:27

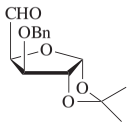


1. $TMSR_F$ (1.1 eq),
n-$Bu_4N^+Ph_3SnF_2^-$ (cat.), CH_2Cl_2
2. HCl, H_2O or TBAF, MeOH

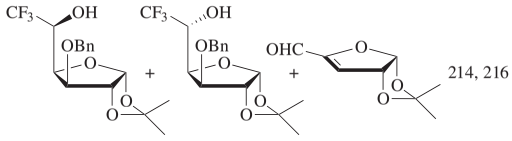


I + **II** 216

R	R_F	Temp (°)	**I** + **II**	**I**/**II**
CH_2=$CHCH_2$	CF_3	0 to rt	(98)	88:12
Bn	CF_3	0 to rt	(95)	80:20
Bn	n-C_4F_9	0 to rt	(65)	85:15
Bn	n-C_4F_9	–45	(—)	80:20



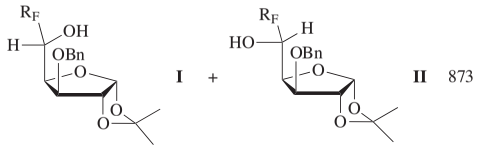
CF_3I, Zn, DMF, ultrasound



I **II** **III** (—) 214, 216

I + **II** (47), **I**/**II** = 1:2.5

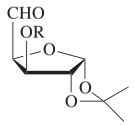
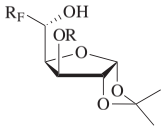
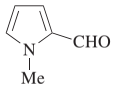
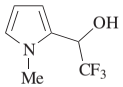
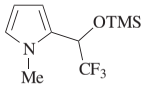
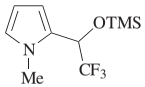
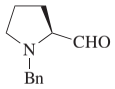
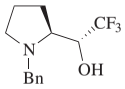
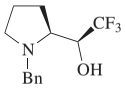
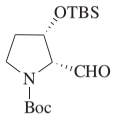
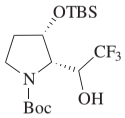
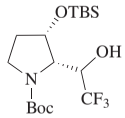
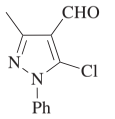
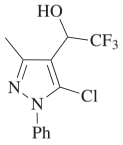
R_FI (2 eq), Zn (2 eq), DMF, rt

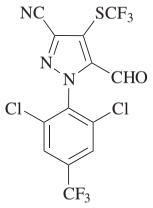


I + **II** 873

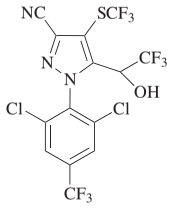
R_F	Time (h)	**I**	**II**
n-C_4F_9	1.5	(36)	(17)
n-C_6F_{13}	3	(38)	(12)
n-C_8F_{17}	8	(27)	(12)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

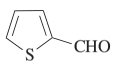
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_5			
	1. R_FMgBr (1.2 eq), Et_2O, –45° 2. H_3O^+	 L-ido/D-gluco > 95:5 R = CH_2=$CHCH_2$, R_F = *n*-C_4F_9 (64) R = CH_2=$CHCH_2$, R_F = *n*-C_6F_{13} (57) R = Bn, R_F = *n*-C_4F_9 (68) R = Bn, R_F = *n*-C_6F_{13} (60)	216
	1. **61**(1 eq), *t*-BuOK (1 eq), THF, 0° to rt, 1 h 2. HCl, H_2O, o/n	 (75) 86% conv	181
	63 (2 eq), CsF (0.1 eq), DME, 80°, 5 h	 (92) 98% conv	74
	1. **62a** (2 eq), *t*-BuOK (2 eq), THF, rt, 24 h 2. TMSCl	 (96) 100% conv	110
	1. $TMSCF_3$ (1.5 eq), TBAF (5 mol %), THF, 0°, to completion 2. TBAF (20 mol %), rt, 1 h	 (33) +  (27)	447
	1. $TMSCF_3$ (1.03 eq), CsF (1 mol %), rt, 24 h; 50°, 5 h 2. HCl, H_2O, rt, o/n	 (50) +  (8)	411
	1. $TMSCF_3$ (3 eq), Amberlyst A-27 resin (F^- form), THF, rt, 1–19 h 2. Amberlyst A-15 resin (H^+ form) 3. Aminomethylated polystyrene resin	 (79)	858



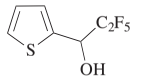
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 21 h
2. $TMSCF_3$ (1.2 eq), 5 d
3. HCl, H_2O



(47) 874

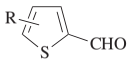


1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h
2. HCl, H_2O, rt, 12 h

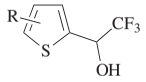


(63.3) 398

C_{5-11}



1. $TMSCF_3$ (1.2 eq), CsF (10 mol %), THF, rt, 2 h
2. HCl, H_2O



R		
5-Br	(95)	875
4-Ph	(—)	

C_{5-15}

RCHO

CHF_3 (excess), **57** (1.5 eq), THF, –30°, 2 h



R		
2-thienyl	(65)	82
Ph	(75)	
4-ClC_6H_4	(86)	
4-BrC_6H_4	(80)	
4-$O_2NC_6H_4$	(52)	
4-MeC_6H_4	(76)	
2-$C_{10}H_7$	(88)	
9-anthryl	(74)	

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-7}

RCHO

63 (2 eq), CsF (0.1 eq), DME, 80°, 5 h



R	Conv (%)		Refs.
3-thienyl	95	(80)	74
Ph	99	(95)	

C_{5-9}

RCHO

1. $TMSCF_3$ (1.2 eq), KF (0.1 eq), (n-$Bu_3MeN)^+(HSO_4)^-$ (0.1 eq), Ph_3SnF (0.1 eq), CH_2Cl_2
2. HCl, H_2O, 0.25 h



R	Temp (°)	Time (h)		Refs.
2-thienyl	rt	o/n	(81)	405
Ph	0 to rt	1	(81)	
4-ClC_6H_4	0 to rt	1	(65)	
3-$O_2NC_6H_4$	rt	1	(93)	
4-$O_2NC_6H_4$	0 to rt	1	(89)	
4-$MeOC_6H_4$	0 to rt	1	(98)	
(*E*)-PhCH=CH	0 to rt	4	(30)	

1. $TMSCF_3$ (1.2 eq),
$K^+(Ph_3SnF_2)^-$ (5 mol %), DMF, 1 h
2. HCl, H_2O, 0.25 h

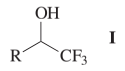


R	Temp (°)		Refs.
2-thienyl	rt	(71)	405
3-pyridyl	rt	(39)	
Ph	0 to rt	(90)	
4-ClC_6H_4	0 to rt	(93)	
3-$O_2NC_6H_4$	rt	(87)	
4-$O_2NC_6H_4$	0 to rt	(85)	
4-$MeOC_6H_4$	0 to rt	(78)	
(*E*)-PhCH=CH	0 to rt	(20)	

C_{5-13}

RCHO

1. $TMSCF_3$ (2 eq), **34** (0.1 eq), NaOH (0.35 eq), **46r** (0.1 eq), 4 Å MS, Et_2O
2. HCl, H_2O, rt



I +


II

459

R	**I**	**II**	er **I**	er **II**
2-thienyl	(—)	(68)	—	72.5:27.5
Ph	(72)	(—)	78.0:22.0	—
4-FC_6H_4	(—)	(86)	—	78.5:21.5
3-ClC_6H_4	(—)	(95)	—	78.0:22.0
4-ClC_6H_4	(72)	(—)	75.0:25.0	—
4-$MeOC_6H_4$	(87)	(—)	70.5:29.5	—
3-MeC_6H_4	(—)	(88)	—	79.0:21.0
4-MeC_6H_4	(87)	(—)	80.0:20.0	—
4-PhC_6H_4	(73)	(—)	78.0:22.0	—

C_{5-15}

RCHO

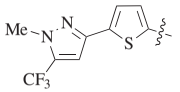
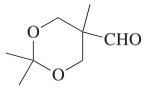
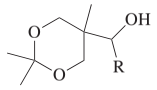
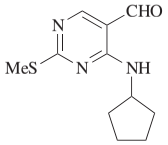
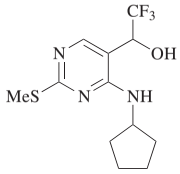
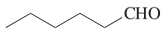
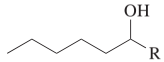
1. $TMSCF_3$, K_2CO_3, DMF, rt, 4 h
2. H_3O^+, 4 h

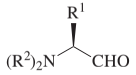


R	
5-Br-3-thienyl	(93)
5-Me-2-furyl	(99)
4-Cl-2-pyridyl	(96)
5-Br-2-pyridyl	(93)
5-Br-3-pyridyl	(93)
6-Br-3-pyridyl	(92)
6-Bz-3-pyridyl	(96)
2-CF_3-5-Br-4-pyridyl	(93)
1-Boc-2-indolyl	(93)
5-Br-2-benzofuryl	(91)
5-Br-2-benzothienyl	(99)

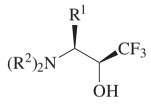
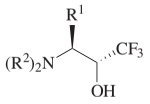
389

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

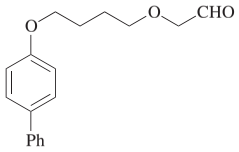
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{5-10}			
RCHO	In a microreactor:[b] 1. $TMSCF_3$ (1.2 eq), monolithic fluoride column, 40°, 100 min residence time 2. Amberlyst 15	 R: (87), (88), 3-pyridyl (86), $2\text{-}BrC_6H_4$ (80) R: $2\text{-}O_2NC_6H_4$ (84), $3,4\text{-}OCH_2O\text{-}6\text{-}O_2NC_6H_2$ (76),  (88), 1-Me-2-indolyl (79), 2-benzofuryl (84), $PhCHMeCH_2$ (83)	432
C_5 	RMgBr, Et_2O, –40 to –10°, 2 h	 R: $n\text{-}C_4F_9$ (48), $n\text{-}C_6F_{13}$ (49), $n\text{-}C_8F_{17}$ (72), $n\text{-}C_{10}F_{21}$ (61)	876
	1. $TMSCF_3$ (6 eq), CsF (cat.), THF, rt, 48 h 2. HCl, H_2O	 (25)	877
C_6 	RX, Zn, DMF, ultrasound	 R, X, Time (h): CF_3 I 0.5 (61); CF_3 Br 3 (47); C_2F_5 I 1 (54); $n\text{-}C_4F_9$ I 0.5 (71); $n\text{-}C_4F_9$ Br 2 (52); $n\text{-}C_8F_{17}$ I 0.5 (62)	299



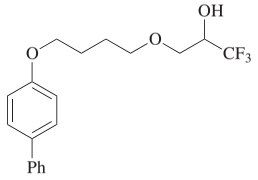
1. $TMSCF_3$ (1.5 eq), TBAF (5 mol %), THF, 0°, to completion
2. TBAF (20 mol %), rt, 1 h

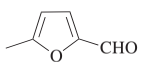

I + 
II 447

R^1	R^2	**I**	**II**
s-Bu	Me	(37)	(7)
s-Bu	Bn	(49)	(8)
t-Bu	Bn	(53)	(6)

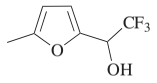


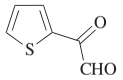
$TMSCF_3$, TBAF, THF, 0°


(94) 878

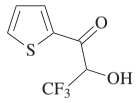
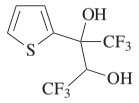


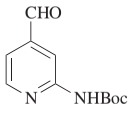
1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h
2. HCl, H_2O


(92) 398



1. $TMSCF_3$ (2.05 eq), CsF (2 mol %), DME, 0°, 1 h; rt, 5 h
2. HCl, H_2O, THF, rt, 3 h


(78) + 
(—) 438



1. $TMSCF_3$ (2 eq), TBAF (2 eq), THF, 4 Å MS, rt, o/n
2. NH_4Cl, H_2O

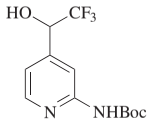
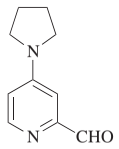
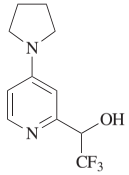
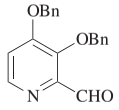
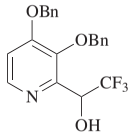

(66) 878a

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_6 	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°; rt, 0.25 h 2. HCl, H_2O, 0.5 h	 (84)	879
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°; rt, 1 h 2. HCl, H_2O	 (92)	880
C_{6-11} RCHO	1. $TMSCF_3$ (2 eq), catalyst (*x* mol %), **56** (*x* mol %), toluene 2. TBAF (1 eq), THF, rt, to full conv		462, 461

R	Catalyst	*x*	Temp (°)	Time (h)		er
2-pyridyl	**46r**	2	–78	2	(89)	71.0:29.0
Ph	**46r**	2	–20	2	(80)	80.0:20.0
3-FC_6H_4	**46r**	2	–20	2	(87)	75.5:24.5
4-FC_6H_4	**46r**	2	–20	2	(79)	72.5:27.5
3-ClC_6H_4	**46r**	2	–20	2	(83)	75.5:24.5
4-ClC_6H_4	**46r**	2	–20	2	(83)	75.5:24.5
3-BrC_6H_4	**46r**	2	–78	2	(82)	76.0:24.0
4-BrC_6H_4	**46r**	2	–78	2	(81)	78.5:21.5
2-$MeOC_6H_4$	**46r**	2	–78	1	(88)	86.5:13.5
3-$MeOC_6H_4$	**46r**	2	–78	1	(89)	87.0:13.0
4-$MeOC_6H_4$	**46r**	2	–78	1	(85)	83.5:16.5
3,4-$OCH_2OC_6H_3$	**46r**	2	–78	2	(92)	90.5:9.5
3,4-$O(CH_2)_2OC_6H_3$	**46r**	2	–78	2	(92)	89.5:10.5

4-CH_2=$CHCH_2OC_6H_4$	**46r**	2	–78	2	(80)	83.5:16.5
4-$EtSC_6H_4$	**46r**	2	–78	2	(85)	86.5:13.5
3-$PhOC_6H_4$	**46r**	2	–78	1	(87)	80.0:20.0
4-MeC_6H_4	**46r**	2	–78	1	(88)	84.0:16.0
1-$C_{10}H_7$	**46r**	2	–78	2	(88)	80.0:20.0
2-$C_{10}H_7$	**46r**	2	–78	1	(90)	87.5:12.5
2-$C_{10}H_7$	**46r**	10	–78	1	(92)	84.5:15.5
2-$C_{10}H_7$	**46w**	10	–78	1	(86)	81.5:18.5
6-MeO-2-$C_{10}H_6$	**46r**	2	–78	2	(83)	76.5:23.5
4-PhC_6H_4	**46r**	2	–78	1	(90)	83.0:17.0

$C_{6–15}$

RCHO

$TMSCF_3$ (1.2 eq), AcOLi (5 mol %), DMF, 0°, 10 min



(—)

R	Conv (%)	
2-pyridyl	92	131
c-C_6H_{11}	81	131, 132
Ph	91	131, 132
4-BrC_6H_4	94	131
4-$O_2NC_6H_4$	97	131, 132
4-$Me_2NC_6H_4$	97	131, 132
4-$MeO_2CC_6H_4$	91	132
4-$MeO_2CC_6H_4$	97	131
$Ph(CH_2)_2$	70	132
$Ph(CH_2)_2$	77	131
(*E*)-PhCH=CH	93	131, 132
2-$C_{10}H_7$	98	131
9-anthryl	99	131

$C_{6–11}$

RCHO

1. $TMSCF_3$ (3 eq), Amberlyst A-27 resin (F^- form), THF, rt, 1–19 h
2. Amberlyst A-15 resin (H^+ form)
3. Aminomethylated polystyrene resin



R		
3-pyridyl	(89)[c]	
Ph	(100)	858
4-FC_6H_4	(98)	
4-ClC_6H_4	(97)	
4-$O_2NC_6H_4$	(75)	
4-$MeOC_6H_4$	(100)	
(*E*)-PhCH=CH	(100)	
n-$C_{10}H_{21}$	(100)	
2-$C_{10}H_7$	(97)	

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-9}

RCHO

1. $TMSCF_3$ (0.83 eq), initiator (*x* mol %), DMF
2. HCl, H_2O



(—)

R	Initiator	*x*	Temp	Time (h)	Conv RCHO (%)	Conv $TMSCF_3$ (%)	
n-C_6H_{13}	Et_3N	17	rt	7	60	100	138
n-C_6H_{13}	Et_3N	20	rt	7	60	100	139
n-C_6H_{13}	Ph_3P	8.3	50°	24	53	100	138
c-C_6H_{11}	Et_3N	17	rt	24	64	98	138
c-C_6H_{11}	Et_3N	20	rt	24	64	98	139
4-ClC_6H_4	Et_3N	17	rt	5	82	100	138
4-ClC_6H_4	Et_3N	20	rt	5	82	100	139
4-$MeOC_6H_4$	Et_3N	17	rt	7	56	100	138
4-$MeOC_6H_4$	Et_3N	20	rt	7	56	100	139
(*E*)-PhCH=CH	Et_3N	17	rt	24	67	100	138
(*E*)-PhCH=CH	Et_3N	20	rt	24	67	100	139

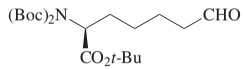
1. $TMSCF_3$ (*x* eq), **27a** (*y* mol %), DMF
2. HCl, H_2O, rt

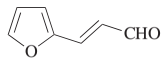


142

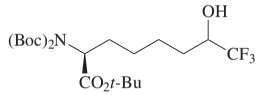
R	*x*	*y*	Temp (°)	Time (h)	
CH_2=$CHCH_2(Me_2)C$	3	1	rt	4	(71)
c-C_6H_{11}	3	0.5	–25 to rt	1	(81)
Ph	2.8	0.5	rt	0.75	(73)
4-ClC_6H_4	2.8	0.5	–25 to rt	1	(86)
4-$MeOC_6H_4$	3	0.5	–25 to rt	1	(90)
n-C_7H_{15}	3	1	rt	2.17	(81)
4-NCC_6H_4	3	0.5	–25 to rt	1	(87)
4-$HO_2CC_6H_4$	5	0.5	rt	0.5	(84)
$Ph(CH_2)_2$	3	1	rt	3	(80)
(*E*)-PhCH=CH	3	0.5	–25 to rt	1	(89)

C_7



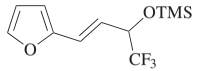


$TMSCF_3$, TBAF, 0°, 1 h



(76) 881

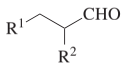
$TMSCF_3$ (x eq), catalyst (y mol %), DMF, rt



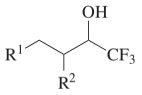
65

x	Catalyst	y	Time (min)	
2	Me_3NO	5	12	(76)
1.2	K_2CO_3	1	10	(87)
1.2	**28**	2	10	(91)

C_{7-10}



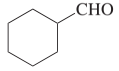
1. $TMSCF_3$ (1.3 eq), TBAF (1 mol %), THF, 0°, 10 min; rt, 6 h
2. TBAF (10 mol %), THF, H_2O



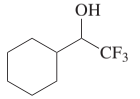
R^1	R^2	
2-furyl	H	(85)
c-C_6H_{11}	H	(65)
Ph	Me	(70)

882

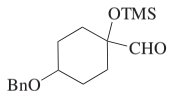
C_7



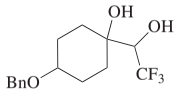
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h
2. HCl, H_2O, rt, 1 h



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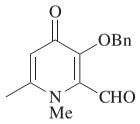
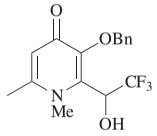


1. $TMSCF_3$ (1.1 eq), TBAF (0.5–1 mol %), THF, rt, 0.5–2 h
2. TBAF (2 eq), THF, rt, 10 min



(87) 883

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_7 	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°; rt, 1 h 2. HCl, H_2O	 (—)	880
C_{7-11} RCHO	1. CHF_3 (2 eq), KH (2 eq), DMSO, rt, 0.75 h 2. DMF, –45°, 0.5 h; rt 3. HCl, H_2O		72
		R: c-C_6H_{11} (45); Ph (60); 2,4-$(MeO)_2C_6H_3$ (45); 3,4,5-$(MeO)_3C_6H_2$ (20); 2,4,6-$Me_3C_6H_2$ (20); 2-$C_{10}H_7$ (50)	
C_{7-9} RCHO	CHF_3 (7 eq), base (x eq), additive (6 eq), DMF, –50°, 10 min; –10°, 5 h		69

R	Base	x	Additive	
c-C_6H_{11}	**22b**	3	$(TMS)_2NH$	(23)
Ph	NaH	1.5	—	(28)
Ph	t-BuOK	1.5	—	(40)
Ph	**22a**	1.5	—	(34)
Ph	**22b**	1.5	—	(74)
Ph	**22c**	1.5	—	(80)
4-$MeOC_6H_4$	**22b**	3	—	(92)
3,4-$(MeO)_2C_6H_3$	**22b**	3	—	(78)
4-EtC_6H_4	**22b**	3	—	(60)

TMSCF$_3$ (2 eq), base (5 mol %), solvent, rt



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R	Base	Solvent	Time (h)	
c-C_6H_{11}	1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	1	(92)
Ph	1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	0.5	(90)
4-ClC_6H_4	1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	0.5	(91)
4-$O_2NC_6H_4$	1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	0.5	(82)
4-$MeOC_6H_4$	1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	0.5	(90)
4-$MeOC_6H_4$	1,5,7-triazabicyclo[4.4.0]dec-5-ene	THF	24	(65)
4-$MeOC_6H_4$	1,5,7-triazabicyclo[4.4.0]dec-5-ene	MeCN	24	(71)
4-$MeOC_6H_4$	7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	4	(75)
4-$MeOC_6H_4$	tetramethylguanidine	DMF	4	(62)
4-$MeOC_6H_4$	DBU	DMF	4	(68)
$PhCH_2CH_2$	1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	0.5	(92)
(*E*)-PhCH=CH	1,5,7-triazabicyclo[4.4.0]dec-5-ene	DMF	1	(85)

C_{7-11}

RCHO

1. $TMSCF_3$ (1.2 eq), **31b** (0.1 eq), Et_2O, –78°, 24 h
2. HCl, H_2O, THF, rt, 1 h



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R		er
c-C_6H_{11}	(88)	55.0:45.0
4-ClC_6H_4	(93)	65.0:35.0
4-$MeOC_6H_4$	(97)	68.5:31.5
2-MeC_6H_4	(98)	66.5:33.5
4-$CF_3C_6H_4$	(90)	62.0:38.0
(*E*)-PhCH=CH	(99)	59.0:41.0
1-$C_{10}H_7$	(71)	56.0:44.0

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-11}

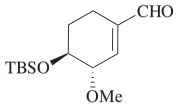
RCHO

$R_FB(OMe)_3K$ (1.2 eq), DMF, 50°, 1 h

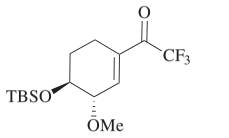


R	R_F		Refs.
c-C_6H_{11}	CF_3	(33)	102
Ph	CF_3	(97)	
Ph	C_2F_5	(93)	
4-$O_2NC_6H_4$	CF_3	(87)	
4-$MeOC_6H_4$	CF_3	(85)	
4-$MeO_2CC_6H_4$	CF_3	(78)	
(*E*)-PhCH=CH	CF_3	(97)	
1-$C_{10}H_7$	CF_3	(96)	

C_7

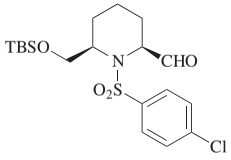


1. $TMSCF_3$ (1.5 eq), TBAF (0.1 eq), THF, 0°, 1 h
2. TFA (0.2 eq), THF, H_2O, 0°, 6 h
3. Dess–Martin periodinane (1.2 eq), CH_2Cl_2, 0°, 16 h
4. $NaHCO_3$, $Na_2S_2O_3$, H_2O, 0°, 1 h

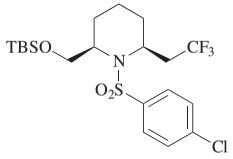


(55)

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1. $TMSCF_3$, BF_3•OEt_2
2. *n*-BuLi, PhOC(S)Cl
3. Bu_3SnH, AIBN



(—)

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PhCHO

I

1. CF_3H (9.5 eq), *t*-BuOK (*x* eq), DMF, 1 h
2. AcOH, rt



+ $PhCH_2OH$ + $PhCO_2H$ 71

II (—) **III** (—) **IV** (—)

x	Temp (°)	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)	Conv **IV** (%)
1	–10	88	64	3	—
1	–50	94	67	2	—
2	–10	100	19	—	trace
2.2	–50	97	67	—	—

PhCHO

CHF_3 (1 eq), base, DMF, –40°



I + $PhCH_2OH$ **II** + $PhCO_2H$ **III** 48

Base	**I**	**II**	**III**
t-BuOK	(40)	(22)	(30)
KH	(1)	(—)	(—)
KH, DMSO	(65)	(—)	(—)
NaH, DMSO	(10)	(—)	(—)

PhCHO **I**

1. CHF_3 (*x* eq), *t*-BuOK (*y* eq), solvent
2. AcOH



II (—) + $PhCH_2OH$ **III** (—) 76

x	*y*	Solvent (s)	Temp (°)	Time (h)	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)
—	0.2	DMF, H_2O	–50	—	98	70	6
—	1	DMF	–10	—	88	73	3
—	1.5	DMF	–10	—	100	19	—
—	2.2	DMF	–50	—	97	69	—
9.8	1.14	DMF, THF	–40	1	67	46	trace
11.7	0.83	DMF, THF	–50	0.5	74	60	0.3

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

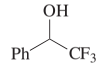
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7

PhCHO **I**

1. CHF_3 (*x* eq), base (*y* eq), additive (*z* eq), DMF, 1–1.5 h
2. AcOH

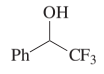


II (—) + $PhCH_2OH$ **III** (—)

x	Base	*y*	Additive	*z*	Temp (°)	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)	Refs.
7.8	KH	1.2	—	—	rt	70	9	11	76
8.7	KH	1.15	DMSO	—	–15	91	66	3	76
9	*t*-BuOLi	1.1	—	—	–20	32.5	13	trace	76, 75
9	*t*-BuONa	1.1	—	—	–20	83	59	trace	76, 75
9	*t*-BuOK	1.1	—	—	–15	88	64	3	76, 75
9	*t*-BuOK	1.1	—	—	–20	88	64	trace	76
9	NaH	1.3	DMSO	—	0	94	50	—	76
9.3	NaH	1.3	15-crown-5	1	–10	96	65	—	76

PhCHO

1. CHF_3 (9.74 eq), *t*-BuOK (1.07 eq), solvent, –10°, 1.5 h
2. AcOH



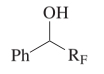
(—)

Solvent	Conv (%)
THF	25
DMF	57
N-formylpiperidine	5

Refs. 76, 75

PhCHO **I**

1. R_FH (*x* eq), *t*-BuOK (1 eq), DMF, –40°, 1 h
2. AcOH

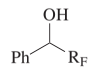


II (—)

R_F	*x*	Conv **I** (%)	Conv **II** (%)	Refs.
CF_3	8.6	94	67	76, 75
C_2F_5	4	98.5	71	

PhCHO

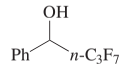
1. R_FH (4 eq), *t*-BuOK (1 eq), DMF, –40°, 1.5 h
2. AcOH, rt



R_F	
CF_3	(67)
C_2F_5	(71)

Refs. 71

$CF_3CF_2CHF_2$, *n*-BuLi, Et_2O, –80°, 2 h



(70) Refs. 128

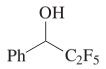
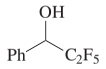
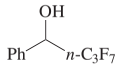
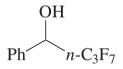
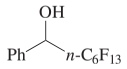
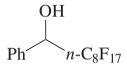
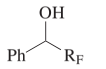
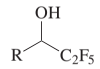
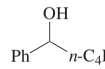
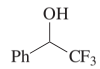
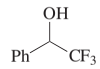
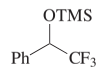
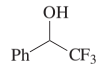
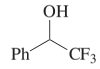
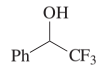
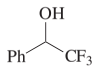
C_2F_5I (1 eq), Ca/Hg, THF, –40°, 20 h		(68)	210
C_2F_5I (1,84 eq), MeLi (1.46 eq), LiBr, Et_2O, –78°, 0.5 h		(91)	392, 391
n-C_3F_7I, Li/Na, Et_2O, –40°, 48 h; –40° to rt		(—)	187
n-C_3F_7I, MeLi, Et_2O, –74° to rt, 3 h; reflux, 1 h		(54.4)	188
n-$C_6F_{13}I$ (2 eq), MeLi, LiBr, Et_2O, –78°, 0.5 h		(73)	197
n-$C_8F_{17}I$, PhMgBr, THF, –70° to rt, 1.5 h		(60)	395
R_FX, Zn, DMF, ultrasound		R_F X Time (h) CF_3 I 0.5 (72) CF_3 Br 3 (56) C_2F_5 I 0.5 (67) *n*-C_3F_7 I 0.5 (58) *i*-C_3F_7 I 0.5 (56) *n*-C_4F_9 I 0.5 (61) *n*-C_4F_9 Br 3 (49) *n*-C_6F_{13} I 0.5 (66) *n*-C_8F_{17} I 0.5 (58) *n*-C_8F_{17} Br 2 (32)	299

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_7			
RCHO R = Ph, 4-ClC_6H_4, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$	C_2F_5Li	 (—)	886
PhCHO	1. *n*-$C_4F_9Ti(Oi\text{-}Pr)_4MgBr$ (1.2 eq), Et_2O, rt, 2 h 2. HCl, H_2O	 (93)	627
	CF_3CO_2K (*x* eq), solvent, 140°, 3.5 h	 *x* Solvent 1.67 NMP (15) 1.7 DMF (20)	887
	CF_3CO_2K (1.66 eq), MeCN, 140°, 3.5 h	 (2.5) + PhCH=CHCN (main product)	887
	1. $TMSCF_3$ (1.2 eq), *n*-$Bu_4N^+Ph_3SnF_2^-$ (cat.), THF, rt, 2 h 2. HCl, H_2O	 (80)	289
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h 2. HCl, H_2O, rt, 1 h	 (85)	288
	1. $TMSCF_3$ (1.1 eq), CsF (0.1 eq), **23** (1 eq), rt, 3 h 2. HCl, H_2O, rt, 3 h	 (88)	339
	1. $TMSCF_3$ (1.1 eq), Ph_3P (0.1 eq), **23** (1 eq), 35°, 24 h 2. HCl, H_2O, rt, 3 h	 (91)	339

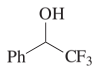
1. $TMSCF_3$ (3 eq), catalyst (*x* mol %), solvent
2. HCl, H_2O



(—) 142

Catalyst	*x*	Solvent	Temp	Time (h)	Conv (%)
TBAF	0.5	THF	rt	0.5	100
TBAF	0.5	DMF	rt	0.5	100
27a	0.1	DMF	rt	24	62
27a	0.5	DMF	rt	0.75	98
27a	0.5	THF	rt	5	79
27a	10	DMF	rt	0.33	100
27a	10	THF	0°	1	100
27b	0.5	DMF	rt	0.5	100
27c	0.5	DMF	rt	0.5	93
27d	0.5	DMF	rt	0.33	100

1. $TMSCF_3$ (1.2 eq), catalyst (*x* eq), solvent, –78°
2. HCl, H_2O, THF, rt, 1 h



453

Catalyst	*x*	Solvent	Time (h)		er
31a	0.1	Et_2O	5	(91)	55.5:45.5 (*S*)
31b	0.1	toluene	24	(88)	58.0:42.0 (*S*)
31b	0.1	Et_2O	24	(96)	76.0:24.0 (*S*)
31c	0.1	Et_2O	24	(23)	52.0:48.0 (*S*)
31d	0.1	Et_2O	24	(64)	52.5:47.5 (*R*)
31e	0.1	Et_2O	24	(92)	63.0:37.0 (*S*)
32	0.2	toluene	65	(75)	51.0:49.0 (*S*)
33	0.2	toluene	65	(82)	52.0:48.0 (*S*)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_7			
PhCHO	1. $TMSCF_3$ (1.1 eq), KF (0.17 eq), $Me[O(CH_2)_2O]_4Me$, rt to 30°, 5 h 2. H_2O, 80°	 (88)	126
	$TMSCF_3$ (2 eq), *t*-Bu_3P (5 mol %), DMF, rt, 20 min	 (96)	140
	$TMSCF_3$ (0.91–0.95 eq), Et_4NBF_4 (cat.), e^-, steel cathode, Al anode, DMF	 (84)	144
	1. $TMSCF_3$ (1.2 eq), **18** (4.9 mol %), THF, 40°, 1 h 2. HCl, H_2O, THF, rt, 8 h	 (65)	888
	i-Pr_3SiCF_3 (0.45 eq), 18-crown-6 (1 eq), *t*-BuOK (1 eq), THF, –78°, 1 h; to rt	 (68)[d]	80
	$TMSCF_3$ (1.2 eq), additive (*x* mg/mmol), solvent, rt		136

Additive	*x*	Solvent	Time (h)	Conv (%)	
—	—	DMSO	6	48	(—)
H_2O	18	DMSO	6	5	(—)
$MgSO_4$	167	DMSO	1	85	(—)
3 Å MS	167	DMSO	1	94	(—)
4 Å MS	33	DMSO	1	83	(—)
4 Å MS	167	DMSO	1	96	(—)
4 Å MS	167	DMF	1	86	(—)
4 Å MS	167	MeCN	1	7	(—)
4 Å MS	333	DMSO	1	98	(—)
4 Å MS	500	DMSO	1	100	(98)
5 Å MS	167	DMSO	1	90	(—)
13X MS	167	DMSO	1	70	(—)

$TMSCF_3$ (1.5 eq), R_3P (5 mol %), solvent, rt, 0.5 h



(—)

R	Solvent	Conv (%)	
n-Bu	THF	trace	141
t-Bu	THF	trace	
Ph	THF	trace	
4-$MeOC_6H_4$	THF	45	
2,4,6-$(MeO)_3C_6H_2$	MeCN	80	
2,4,6-$(MeO)_3C_6H_2$	DMPU	95	
2,4,6-$(MeO)_3C_6H_2$	DMF	96	
2,4,6-$(MeO)_3C_6H_2$	THF	95	

1. $TMSCF_3$ (0.83 eq.), Et_3N (*x* eq), solvent, rt
2. HCl, H_2O



(—)

x	Solvent	Time (h)	Conv PhCHO (%)	Conv $TMSCF_3$ (%)	
0.083	THF	24	trace	low	138
0.083	toluene	24	trace	low	138
0.083	DMF	10	59	100	138
0.1	DMF	10	59	100	139
0.167	DMF	10	66	100	138
0.2	DMF	10	66	100	139
0.42	DMF	10	61	100	138
0.5	DMF	10	61	100	139

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7

PhCHO

1. $TMSCF_3$ (0.83 eq), Ph_3P (*x* eq), DMF
2. HCl, H_2O



(—)

x	Temp (°)	Time (h)	Conv PhCHO (%)	Conv $TMSCF_3$ (%)	Refs.
0.083	rt	24	60	51	138
0.083	50	12	70	100	138
0.1	rt	24	60	51	139
0.1	50	12	70	100	139
0.167	rt	96	45	89	138
0.167	50	12	79	100	138
0.42	rt	24	58	100	138

1. $TMSCF_3$ (0.83 eq), initiator (*x* eq)
   DMF, rt
2. HCl, H_2O



(—)

Initiator	*x*	Time (h)	Conv PhCHO (%)	Conv $TMSCF_3$ (%)	Refs.
pyridine	0.42	8	37	100	138
pyridine	0.5	8	37	100	139
TMEDA	0.042	3	82	100	138
TMEDA	0.042	2	82	100	138
n-Bu_2NH	0.083	5	68	100	138
n-Bu_2NH	0.1	5	68	100	139
Ph_3As	0.083	24	49	83	138
Ph_3As	0.1	24	49	83	139
Ph_3Sb	0.083	24	44	51	138
Ph_3Sb	0.1	24	44	51	139

1. $TMSCF_3$ (1.4 eq), sodium alginate (5 mol %), DMF, rt, to completion
2. HCl



(42) 889

1. $TMSR_F$ (1.2 eq), TBAF (cat.), THF, 0° to rt
2. TBAF, THF, 0° to rt, 5 h



R_F	
C_2F_5	(86)
n-C_3F_7	(66)

122

1. $R^1R^2{}_2SiCF_3$ (0.83 eq), catalyst (x mol %), DMF
2. HCl, H_2O



(—)

R^1	R^2	Catalyst	x	Temp	Time (h)	Conv PhCHO (%)	Conv Si (%)	er	
Me	Me	**10**	4.2	rt	24	78	85	53.5:46.5	138
Me	Me	**11**	8.3	rt	12	57	100	52.0:48.0	138
Me	Me	**12**	4.2	rt	24	52	96	51.0:49.0	138
Me	Me	**13**	4.2	rt	24	75	100	52.5:47.5	138
Me	Me	**14**	4.2	rt	3	72	100	52.5:47.5	138
Me	Me	**15**	2.1	rt	24	26	35	54.5:45.5	138
Me	Me	**16**	8.3	rt	5	79	100	50.0:50.0	138
Me	Me	**17**	8.3	rt	120	53	100	51.5:48.5	138
Me	Me	**47**	4.2	rt	3	49	100	54.5:45.5	138, 139
Me	Me	**47**	8.3	0°	5	36	100	54.5:45.5	138
Me	Me	**47**	8.3	rt	5	42	100	53.0:47.0	138
Me	Me	**48**	8.3	rt	3	58	100	51.0:49.0	138
Et	Et	**47**	4.2	rt	24	24	46	60.5:39.5	138, 139
i-Pr	*i*-Pr	**47**	4.2	rt	24	trace	37	—	138, 139
Ph	Me	**47**	4.2	rt	24	39	93	53.0:47.0	138, 139
Me	Ph	**47**	4.2	rt	24	35	93	56.0:44.0	138, 139

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_7			
PhCHO	1. $TMSR_F$ (0.83 eq), Et_3N (*x* eq), DMF, rt 2. HCl, H_2O	 (—)	

R_F	*x*	Time (h)	Conv PhCHO (%)	Conv $TMSR_F$ (%)	Refs.
C_2F_5	0.17	24	51	85	138
C_2F_5	0.2	—	43	—	139
n-C_3F_7	0.17	24	75	85	138
n-C_3F_7	0.2	—	64	—	139

Conditions	Product(s) and Yield(s) (%)			Refs.
1. $CF_3CH(OH)NR_2$ (1.1 eq), *t*-BuONa (*x* eq), DMF, THF, 0°, 0.5 h 2. PhCHO (1.eq), 0°, 1.5 h 3. AcOH (1.21 eq), 0° to rt	 (—)	*x*: 1.1, 1.3 Conv (%): 37, 48	R = Et, *n*-Bu	105
1. $CF_3CH(OH)NMe_2$ (1.06 eq), *t*-BuOK (1.3 eq), DMF, THF, 0°, 7.5 h 2. AcOH (1.7 eq), rt	 (—)	48% conv		75

1. Catalyst (1 eq),
initiator (0.1 eq), solvent, rt
2. TBAF (1 eq), THF, 1 h



42

Catalyst	Initiator	Solvent	Time (h)		er
64a	CsF	DME	24	(89)	50.0:50.0
64a	TBAT	THF	7	(83)	52.0:48.0
64b	CsF	DME	144	(15)	—
64b	TBAT	THF	144	(4)	—
64c	CsF	DME	24	(36)	50.0:50.0
64c	TBAT	THF	7	(82)	50.0:50.0
64d	CsF	DME	24	(32)	56.0:44.0
64d	TBAT	THF	7	(71)	55.0:45.0
64e	CsF	DME	24	(53)	50.0:50.0
64e	TBAT	THF	24	(83)	50.0:50.0
65a	CsF	DME	24	(46)	50.0:50.0
65a	TBAT	THF	7	(72)	50.0:50.0
65b	TBAT	THF	7	(86)	50.5:49.5
66	CsF	DME	24	(83)	51.5:48.5
66	TBAT	THF	7	(86)	52.5:47.5

1. **62a** (2 eq), *t*-BuOK (2 eq),
THF, rt, 24 h
2. TMSCl



(65) 72% conv

110

1. Catalyst (1 eq),
CsF (0.1 eq), DME
2. TBAF (1 eq), THF, 1 h



Catalyst	Temp (°)	Time (h)		
64a	rt	24	(89)	121
64a	50	6	(85)	
67a	80	24	(43)	
67b	80	24	(56)	
67c	80	24	(52)	

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_7			
PhCHO	1. $[CF_3P(NEt_2)_3]^+Br^-$ (1.2 eq), TASF (1 eq), CH_2Cl_2, THF, –30°; 20°, 0.5 h 2. HCl, H_2O, 2 h	 (81)	166
	$[CF_3P(NMe_2)_3]^+Br^-$ (1.18 eq), KF (1.18 eq), CuI (0.13 eq), pyridine, 1.5 h	 (55)	166
	$PhSCF_3$ (1.2 eq), $(R^1)_2R^2GeNa$ (1.1 eq), solvent		170
	1. $(CF_3)_3S^+ \; K^+$(18-crown-6) (1 eq), pyridine, –30°; rt, 24 h 2. H_3O^+	 (—) 48% conv	155
	1. $PhSOCF_3$ (2 eq), *t*-BuOK (2.5 eq), DMF, –50° to rt 2. H_2O	 (68)	179

R^1	R^2	Solvent	Temp (°)	
Et	Et	Et_2O	–60	(41)
Et	Et	*n*-C_6H_{14}	–60	(12)
Et	Et	THF, HMPA	–78	trace
Et	Et	THF, HMPA	–60	(92)
Et	Et	THF, HMPA	–50	(88)
Et	Et	THF, HMPA	–20	(12)
Et	Et	THF, HMPA	rt	trace
Et	Ph	THF, HMPA	–60	(20)
Ph	Ph	THF, HMPA	–60	(31)

1. **61** (1 eq), *t*-BuOK (1 eq), THF, 0° to rt, 1 h
2. HCl, H_2O, o/n



(80) 95% conv

181

1. Catalyst (1 eq), *t*-BuOK (1 eq), THF, 0°, 1 h
2. HCl, H_2O, o/n



(—)

Catalyst	Conv (%)
68a	21
68b	39

181

1. Catalyst (1 eq), CsF (0.1 eq), DME, rt, 24 h
2. TBAF (1 eq), THF, rt, 1 h



Catalyst		er
69a	(73)	50.0:50.0
69b	(68)	50.0:50.0

42

1. Catalyst (1 eq), initiator (0.1 eq), DME, 24 h
2. TBAF (1 eq), THF, rt, 1 h



Catalyst	Initiator	Temp		er
70a	CsF	0°	(49)	59.5:40.5
70a	CsF	rt	(65)	60.0:40.0
70a	**46a**	rt	(31)	65.0:35.0
70b	CsF	rt	(64)	50.0:50.0

42

1. Catalyst (1 eq), CsF (0.1 eq), DME, rt, 24 h
2. TBAF (1 eq), THF, rt, 1 h



Catalyst		er
71a	(3)	—
71b	(23)	50.5:49.5
72	(33)	58.5:41.5

42

1. Catalyst (1 eq), *t*-BuOK (1 eq), THF, 0°, 1 h
2. HCl, H_2O, o/n



(—)

Catalyst	Conv (%)
73	28
74	19

181

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

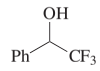
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7

PhCHO

1. $PhSO_2CF_3$ (x eq), base (y eq), solvent, temp 1, time 1; temp 2, time 2
2. H_2O

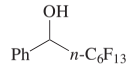


(—)

179

x	Base	y	Solvent	Temp 1 (°)	Time 1 (h)	Temp 2	Time 2 (h)	Conv (%)
0.33	*t*-BuOK	0.67	DMSO	rt	1	—	—	76
0.33	*t*-BuOK	0.67	DMF	–30 to rt	0.5	—	—	91
0.33	MeONa	1	DMF	–30 to rt	3	—	—	30
0.33	KOH	2.67	DMF	rt	20	—	—	45
1	*t*-BuOK	2	DMF	–50	1	—	—	71
1	*t*-BuOK	2	DMF	–50	1	rt	2	71
2	*t*-BuOK	2	DMF	–50 to rt	3	—	—	84

n-$C_6F_{13}I$ (1 eq), In (1 eq), LiCl (1 eq), DMF, rt, 2 h



(60)

235

MeLi (1.1 eq), R_FX, Et_2O, –78°, 1 min (batch); 0° (microreactor)



R_F	X	Batch	Microreactor
n-C_2F_5	I	—	(84)[d]
n-C_3F_7	I	—	(80)[d]
n-C_4F_9	I	—	(85)[d]
n-C_5F_{11}	I	—	(86)[d]
n-C_6F_{13}	Br	—	(71)[d]
n-C_6F_{13}	I	(67)[e]	(74)

198

C_{7-8}

RCHO

CF_3Br, e^-, Zn anode DMF, 0–30°



R	
Ph	(98)
n-C_7H_{15}	(90)

890

C_{7-11}

RCHO

62b (1 eq), CsF (0.1 eq), DME, 5 h



R	Temp (°)	Conv (%)		
Ph	60	95	(90)	109
2-$C_{10}H_7$	60	84	(—)	
2-$C_{10}H_7$	80	95	(84)	

1. $TMSCF_3$ (2 eq), **55** (1 mol %), PhOK (10 mol %), toluene
2. HCl



454

R	Temp (°)	Time (h)		er
Ph	–50	1	(84)	72.0:28.0
4-BrC_6H_4	–50 to –40	2	(87)	64.5:35.5
4-$MeOC_6H_4$	–50 to –40	14	(84)	71.5:28.5
4-MeC_6H_4	–50 to –40	14	(80)	69.5:30.5
$PhCH_2CH_2$	–50	4	(72)	62.0:38.0
(*E*)-PhCH=CH	–50 to –20	6	(90)	60.5:39.5
2-$C_{10}H_7$	–50	1	(88)	70.0:30.0

$TMSCF_3$ (2 eq), additive (*x* eq), solvent, rt



387

R	Additive	*x*	Solvent	Time (min)	
Ph	KOH	0.2	$CF_3CH_2CF_2Me$	15	(91)
4-BrC_6H_4	$CsOH•H_2O$	0.1	$CF_3CH_2CF_2Me$	20	(88)
4-$O_2NC_6H_4$	CsF	0.2	$CF_3CH_2CF_2Me$	20	(94)
2-$MeOC_6H_4$	$CsOH•H_2O$	0.1	$CF_3CH_2CF_2Me$	60	(80)
3-$MeOC_6H_4$	KOH	0.2	$CF_3CH_2CF_2Me$	60	(92)
4-$MeOC_6H_4$	KOH	0.2	$CF_3CH_2CF_2Me$	25	(94)
4-MeC_6H_4	KOH	0.2	$CF_3CH_2CF_2Me$	60	(90)
$PhCH_2CH_2$	CsF	0.2	$CF_3CH_2CF_2Me$	20	(82)
(*E*)-PhCH=CH	$CsOH•H_2O$	0.1	$CF_3CH_2CF_2Me$	20	(84)
1-$C_{10}H_7$	KOH	0.2	$CF_3CH_2CF_2Me$	30	(92)
2-$C_{10}H_7$	KOH	0.2	$CF_3CH_2CF_2Me$	20	(96)
2-$C_{10}H_7$	*t*-Bu_3P	0.1	DMF	30	(99)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-11}

RCHO

TMSCF_3 (2 eq), *t*-Bu_3P (0.1 eq), DMF, rt, 0.25–1 h



R	
Ph	(99)
2-ClC_6H_4	(99)
4-ClC_6H_4	(96)
4-BrC_6H_4	(94)
2-$O_2NC_6H_4$	(97)
3-$O_2NC_6H_4$	(91)
4-$O_2NC_6H_4$	(94)
4-$MeOC_6H_4$	(92)
n-C_7H_{15}	(62)
2-MeC_6H_4	(76)
4-MeC_6H_4	(80)
2,4-$Me_2C_6H_3$	(87)
$Ph(CH_2)_2$	(79)
(*E*)-PhCH=CH	(94)
2-$C_{10}H_7$	(99)

140

1. TMSCF_3 (2 eq), catalyst (0.1 eq), DMF, rt
2. $NaHCO_3$, H_2O



135

R	Catalyst	Time (h)	
Ph	TiF_4	4	(76)
Ph	Ti(O*i*-Pr)$_4$	2	(89)
4-BrC_6H_4	TiF_4	2	(89)
4-BrC_6H_4	Ti(O*i*-Pr)$_4$	2	(90)
4-$O_2NC_6H_4$	TiF_4	19	(99)
4-$O_2NC_6H_4$	Ti(O*i*-Pr)$_4$	4	(84)
4-$MeOC_6H_4$	TiF_4	19	(71)
4-$MeOC_6H_4$	Ti(O*i*-Pr)$_4$	4	(99)
n-C_7H_{15}	TiF_4	19	(75)

R	Catalyst	Time (h)	
(*E*)-PhCH=CH	Ti(O*i*-Pr)$_4$	4	(98)
2-$C_{10}H_7$	$Cu(OTf)_2$	24	(2)
2-$C_{10}H_7$	$NiClO_4$•$6H_2O$	24	(7)
2-$C_{10}H_7$	$Zn(OAc)_2$	24	(15)
2-$C_{10}H_7$	$Pd(OAc)_2$	24	(19)
2-$C_{10}H_7$	$Cu(OAc)_2$	24	(60)
2-$C_{10}H_7$	AgF	24	(10)
2-$C_{10}H_7$	ZnF_2	24	(23)
2-$C_{10}H_7$	CuF_2	24	(33)

n-C_7H_{15}	$Ti(Oi\text{-}Pr)_4$	6	(67)	2-$C_{10}H_7$	InF_3	24	(45)
4-MeC_6H_4	TiF_4	4	(62)	2-$C_{10}H_7$	TiF_4	4	(96)
4-MeC_6H_4	$Ti(Oi\text{-}Pr)_4$	0.5	(86)	2-$C_{10}H_7$	$MgCl_2$	16	(91)
(*E*)-PhCH=CH	TiF_4	4	(91)	2-$C_{10}H_7$	$Ti(Oi\text{-}Pr)_4$	2	(96)

1. $CF_3CH(OH)_2$•0.5 H_2O (1.5 eq), *t*-BuOK (6 eq), DMF, –50°, 0.5 h
2. Substrate (1 eq), –50°, 1 h; to rt



106

R		
Ph	(83)	
4-FC_6H_4	(51)	
4-ClC_6H_4	(58)	
4-BrC_6H_4	(56)	
4-$O_2NC_6H_4$	(0)[a]	
4-$Me_2NC_6H_4$	(94)	
2,4,6-$(MeO)_3C_6H_2$	(70)	
2-MeC_6H_4	(53)	
3-MeC_6H_4	(72)	
4-MeC_6H_4	(45)	
4-$CF_3C_6H_4$	(0)[a]	
n-C_8H_{17}	(0)[a]	
(*E*)-PhCH=CH	(0)[a]	
2-$C_{10}H_7$	(57)	

C_{7-15}

RCHO

$TMSCF_3$ (1.2 eq), catalyst (*x* mol %), DMF, rt



65

R	Catalyst	*x*	Time (min)		R	Catalyst	*x*	Time (min)	
Ph	K_2CO_3	1	5	(80)	4-MeC_6H_4	K_2CO_3	1	15	(78)
Ph	**28**	2	5	(77)	4-MeC_6H_4	**28**	2	15	(85)
4-BrC_6H_4	K_2CO_3	1	5	(80)	4-NCC_6H_4	K_2CO_3	1	5	(73)
4-BrC_6H_4	**28**	2	5	(70)	4-NCC_6H_4	**28**	2	5	(80)
4-$O_2NC_6H_4$	K_2CO_3	1	5	(81)	(*E*)-PhCH=CH	K_2CO_3	1	10	(90)
4-$O_2NC_6H_4$	**28**	2	5	(75)	(*E*)-PhCH=CH	**28**	2	10	(86)
2,6-$Cl_2C_6H_3$	K_2CO_3	1	10	(73)	2-$C_{10}H_7$	K_2CO_3	1	5	(85)
2,6-$Cl_2C_6H_3$	**28**	2	5	(87)	2-$C_{10}H_7$	**28**	2	5	(90)
4-$MeOC_6H_4$	K_2CO_3	1	15	(74)	9-anthryl	K_2CO_3	1	5	(86)
4-$MeOC_6H_4$	**28**	2	15	(87)	9-anthryl	**28**	2	5	(92)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-11}

RCHO

$TMSCF_3$ (2 eq), KF (0.1 eq), Bu_4NBr (0.1 eq), solvent



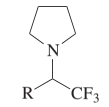
457

R	Solvent	Temp (°)	Time (h)	
Ph	toluene	rt	0.5	(91)
Ph	THF	0	0.5	(94)
4-BrC_6H_4	toluene	–20	0.5	(88)
4-BrC_6H_4	THF	–20	1	(99)
2-$O_2NC_6H_4$	toluene	–20	0.5	(90)
2-$O_2NC_6H_4$	THF	rt	6	(94)
4-$O_2NC_6H_4$	toluene	–20	1	(96)
4-$O_2NC_6H_4$	THF	–20	0.5	(88)
2-$MeOC_6H_4$	toluene	–20	0.5	(84)
2-$MeOC_6H_4$	THF	rt	1	(85)
4-$MeOC_6H_4$	toluene	–20	0.5	(88)
4-$MeOC_6H_4$	THF	0	0.5	(92)
n-C_7H_{15}	toluene	rt	0.5	(98)
n-C_7H_{15}	THF	–20	0.5	(79)
(*E*)-PhCH=CH	toluene	0	0.5	(94)
1-$C_{10}H_7$	toluene	0	1	(99)
1-$C_{10}H_7$	THF	0	0.5	(90)

C_7

RCHO

1. **77** (1.2 eq), TMSOTf (1.2 eq), CH_2Cl_2, 0° to rt, time 1
2. $TMSCF_3$ (1.5 eq), initiator (*x* eq), DMF, rt, time 2



560

R	Time 1 (h)	Initiator	*x*	Time 2 (h)	
Ph	0.5	NaF	1.5	1	(—)
Ph	0.5	KF	1.5	1	(76)
Ph	0.5	AcONa	2	1	(78)
4-$O_2NC_6H_4$	2	KF	1.5	18	(68)
4-$O_2NC_6H_4$	2	AcONa	2	18	(28)
4-$MeOC_6H_4$	0.5	AcONa	2	1	(70)

$C_{7–15}$

RCHO

1. $TMSCF_3$ (1.3 eq), catalyst (*x* mol %), additive, toluene, –78°, 2 h
2. HCl, H_2O



456

R	Catalyst	*x*	Additive	Conv (%)		er
Ph	**46j**	1	4 Å MS	>99	(—)	68.5:31.5 (*R*)
Ph	**46j**	10	—	>99	(—)	67.5:32.5 (*R*)
Ph	**46l**	20	—	>99	(—)	73.0:27.0 (*R*)
n-C_7H_{15}	**46j**	20	—	>99	(—)	57.5:42.5
9-anthracenyl	**46j**	10	—	—	(98)	72.5:27.5 (*R*)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-9}

RCHO

1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt,
2. HF, TMAF, H_2O, 5 h



R	Time (h)		Refs.
Ph	20	(97)	482, 891
3-MeO-4-HOC_6H_3	20	(95)	482, 891
3,4-$(MeO)_2C_6H_3$	24	(99)	482, 891
3,5-$(MeO)_2$-4-HOC_6H_2	24	(98)	482, 891
PhCH=CH	16	(99)	891
3-MeO-4-HOC_6H_3CH=CH	18	(99)	482, 891

C_{7-10}

RCHO

1. $TMSCF_3$ (1.5 eq), TBAF (1 eq), THF
2. HCl, H_2O



(—) 892

R	Conditions	Time	Conv (%)
Ph	microreactor	20 s	89
Ph	flask	5 h	76
4-$MeOC_6H_4$	microreactor	20 s	63
4-$CF_3C_6H_4$	microreactor	20 s	83
4-$CF_3C_6H_4$	flask	5 h	97
(*E*)-PhCH=CH	microreactor	20 s	12
n-C_9H_{19}	microreactor	20 s	74

C_{7-9}

RCHO

1. NaH (0.2 eq), THF, 0°, 10 min
2. $TMSCF_3$ (1.5 eq), 0°; rt
3. HCl, H_2O, 0°



(—)

R	Conv (%)
Ph	>99
2-FC_6H_4	87
2-ClC_6H_4	>99
4-BrC_6H_4	>99
4-$O_2NC_6H_4$	>99
4-$MeOC_6H_4$	>99
(*E*)-PhCH=CH	>99

134

1. $TMSCF_3$ (*x* eq), TMAF (*y* eq), THF, 0°, 0.5 h; rt, 24 h
2. TMAF (*z* eq), THF, rt, 24 h



483

R	*x*	*y*	*z*	
Ph	4.31	0.17	0.57	(97)
4-HOC_6H_4	4.96	0.2	0.66	(98)
3,4-$(HO)_2C_6H_4$	5.61	0.22	0.74	(99)
3-MeO-4-HOC_6H_3	6.18	0.24	0.82	(95)
3,4-$(MeO)_2C_6H_3$	6.75	0.27	0.89	(99)
3,5-$(MeO)_2$-4-HOC_6H_2	7.4	0.29	0.98	(98)
PhCH=CH	5.37	0.21	0.71	(99)
3-MeO-4-HOC_6H_3CH=CH	7.23	0.29	0.96	(99)

C_{7-11}

RCHO

CF_3I (5 eq), In (1 eq), LiCl (1 eq), ferrocene (1 eq), DMF, rt, 2 h



R	
Ph	(54)
n-C_8H_{17}	(43)
(*E*)-PhCH=CH	(50)
1-$C_{10}H_7$	(54)
2-$C_{10}H_7$	(41)

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TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-11}

RCHO

1. $TMSCF_3$, K_2CO_3, DMF, rt, 4 h
2. H_3O^+, 4 h



389

R		R	
Ph	(99)	"*N*,*N*-$Me_2C_6H_3$"	(99)
2-F-4-BrC_6H_3	(93)	4-$TBSOC_6H_4$	(94)
2-ClC_6H_4	(98)	2-$MeOC_6H_4$	(99)
3-ClC_6H_4	(99)	3-$MeOC_6H_4$	(97)
4-ClC_6H_4	(96)	4-$MeOC_6H_4$	(99)
2,4-$Cl_2C_6H_3$	(97)	3,4-$O(CH_2)_2O$-C_6H_3	(97)
2-BrC_6H_4	(98)	3-BzO-4-$MeOC_6H_3$	(96)
3-BrC_6H_4	(90)	3,4,5-$(MeO)_3C_6H_2$	(99)
4-BrC_6H_4	(94)	4-MeC_6H_4	(98)
2-$O_2NC_6H_4$	(99)	4-NCC_6H_4	(98)
3-$O_2NC_6H_4$	(99)	(*E*)-PhCH=CH	(94)
4-$O_2NC_6H_4$	(99)	1-$C_{10}H_7$	(96)

C_{7-15}

RCHO

$TMSCF_3$ (2 eq), Me_3NO (5 mol %), DMF, rt



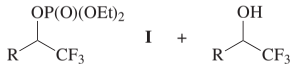
65

R	Time (min)	
Ph	12	(87)
4-BrC_6H_4	8	(89)
4-$O_2NC_6H_4$	8	(90)
2,6-$Cl_2C_6H_3$	24	(86)
4-MeC_6H_4	24	(90)
4-NCC_6H_4	12	(88)
2-$C_{10}H_7$	12	(88)
9-anthryl	12	(82)

C_{7-9}

RCHO

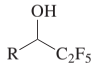
1. $(EtO)_2(O)PCF_3$ (1.2 eq), PhOK (2 eq), DMF, –40°; to rt, 1 h
2. HCl, rt



R	I	II
Ph	(65)	(9)[a]
4-ClC_6H_4	(86)	—
4-$MeOC_6H_4$	(0)	—
4-MeC_6H_4	(57)	—
$PhCH_2CH_2$	(53)	(16)[a]

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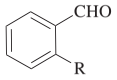
1. $PhSO_2C_2F_5$ (1.5 eq), *t*-BuOK (4.6 eq), THF, –75°; –70 to –75°, 1.5 h
2. HCl, –70 to –75°



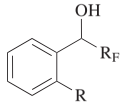
R	
Ph	(91)
4-BrC_6H_4	(85)
4-MeC_6H_4	(84)
(*E*)-PhCH=CH	(89)

180

C_7

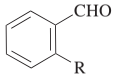


R_FI, Ca(Hg), THF, –20 to 40°, 2–20 h

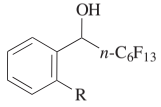


R	R_F	
H	C_2F_5	(70)
H	*n*-C_6F_{13}	(60)
HO	*n*-C_6F_{13}	(20)

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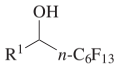
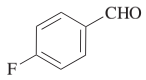
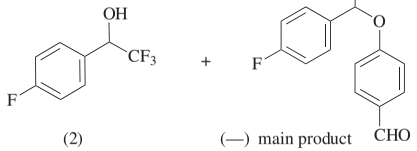
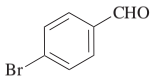
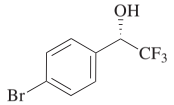
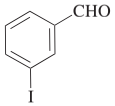
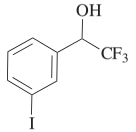
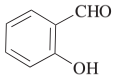
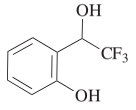
n-$C_6F_{13}I$ (1 eq), Ca/Hg, THF, –40°, 20 h

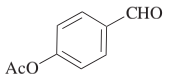


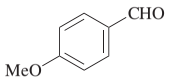
R	
H	(56)
HO	(21)

210

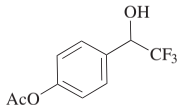
TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{7-8}			
R^1CHO	1. Me_2R^2Si-*n*-C_6F_{13} (1 eq), TBAF, 4 Å MS, THF, rt, 1 h 2. HCl, H_2O, rt, 1 h	 R^1 R^2 Ph Me (47) Ph *i*-Pr (55) *n*-C_7H_{15} Me (41) *n*-C_7H_{15} *i*-Pr (63)	893
C_7			
	CF_3CO_2K (1.62 eq), DMF, 140°, 4 h	 (2) (—) main product	887
	1. L-Menthol (0.2 eq), NaH (0.2 eq), THF, 0°, 10 min 2. $TMSCF_3$ (1.5 eq), 0°; rt, 8 h 3. HCl, H_2O, 0°	 (>99) er 53:47	134
	$TMSCF_3$ (1.25 eq), TBAF (20 mol %), THF, 0°; rt, 4 h	 (95), crude	894
	1. $TMSCF_3$ (1.5 eq), NaH (0.2 eq), $BnNEt_3Cl$ (0.15 eq), THF, 0°; rt, 24 h 2. HCl, H_2O, 0°	 (>99)	134



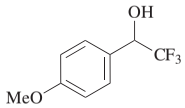


$TMSCF_3$, TBAF (cat.), THF



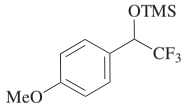
(80) 895

$TMSCF_3$ (0.625 eq), CsF (0.156 eq), CsOH (0.156 eq), THF, 0°, 20 h



(86) 896

$TMSCF_3$ (1.2 eq), catalyst (*x* mol %), solvent, 10 min



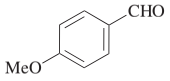
Catalyst	*x*	Solvent	Temp (°)	Conv (%)		
1	5	DMF	0	96	(—)	131
2	5	DMF	0	98	(—)	131
AcOLi	1	DMF	0	97	(—)	131, 132
AcOLi	5	DMF	0	98	(97)	131, 132
AcOLi	5	DMSO	rt	96	(—)	131, 132
AcONa	5	DMF	0	96	(—)	131, 132
AcOK	5	DMF	0	99	(—)	131, 132
AcOCs	5	DMF	0	98	(—)	131
3	5	DMF	0	96	(—)	131
$(CF_3)_2CHCOLi$	5	DMF	0	92	(—)	131
4	5	DMF	0	94	(—)	131
t-$BuCO_2Li$	5	DMF	0	98	(—)	131, 132
5	5	DMF	0	91	(—)	131
PhOLi	5	DMF	0	99	(—)	131
$PhCO_2Li$	5	DMF	0	98	(—)	131, 132
6	5	DMF	0	97	(—)	131
7	5	DMF	0	98	(—)	131

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

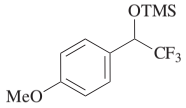
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7



TMSCF$_3$ (1.2 eq),
n-Bu$_4$NOAc (5 mol %),
solvent, 10 min



(—)

Solvent	Temp (°)	Conv (%)	Refs.
toluene	0	98	131, 132
DMSO	rt	95	131, 132
MeCN	0	70	131, 132
DMF	0	99	131
DMF	0	97	131, 132
THF	0	96	131, 132
CH_2Cl_2	0	95	131, 132
EtOAc	0	99	131, 132

RCHO

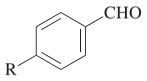
TMSCF$_3$ (1.5 eq),
catalyst (4 mol %), CH_2Cl_2, –50°



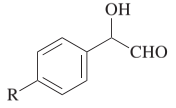
(—) 527

R	Catalyst	Conv (%)	er
2-MeOC$_6$H$_4$	**46g**	100	54.5:44.5
2-MeOC$_6$H$_4$	**46s**	100	54.5:45.5
3-MeOC$_6$H$_4$	**46g**	100	57.0:43.0
3-MeOC$_6$H$_4$	**46s**	100	53.0:47.0
4-MeOC$_6$H$_4$	**46g**	88	79.0:21.0
4-MeOC$_6$H$_4$	**46s**	100	54.5:45.5

C_{7-10}

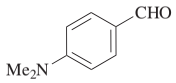


1. $TMSCF_3$ (1.4 eq), TBAF (cat.), THF, 0°; rt, 1 h
2. THF, HCl, H_2O, rt, 2 h

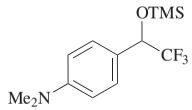


R		
MeO	(94)	897
Me	(95)	
i-Pr	(94)	

C_7

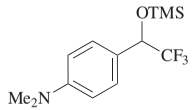


$TMSCF_3$ (1.2 eq), KF (0.1 eq), *n*-$Bu_3MeN^+HSO_4^-$ (0.1 eq), Ph_3SnF (0.1 eq), CH_2Cl_2, rt, 1 h

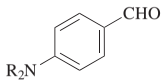


(64) 405

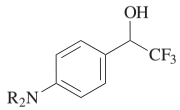
$TMSCF_3$ (1.2 eq), $K^+Ph_3SnF_2^-$ (5 mol %), DMF, rt, 1 h



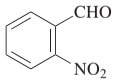
(66) 405



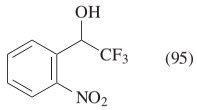
1. $TMSCF_3$ (1.05 eq), CsF (2 mol %), DME, 10°, 0.25 h; rt, 3 h
2. HCl, H_2O, THF, rt, 2 h



R		
Me	(95)	403
Et	(95)	



1. $TMSCF_3$ (1.2 eq), CsF (cat.), DME/THF, 0°; rt, 5 h
2. HCl



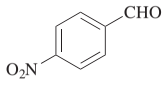
(95) 898

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

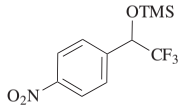
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7



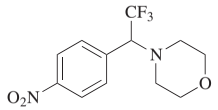
$TMSCF_3$ (1.2 eq),
K_2CO_3 (1 mol %), solvent, rt



65

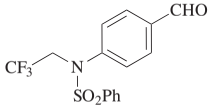
Solvent	Time	Conv. (%)	
DMF	5 min	100	(86)
DMSO	5 min	100	(78)
THF	o/n	60	(—)
THF/DMF (4:1)	10 h	100	(80)
CH_2Cl_2	48 h	<5	(—)
CH_2Cl_2/DMF (4:1)	1 h	100	(78)

1. **75** (1.2 eq), TMSOTf (1.2 eq),
CH_2Cl_2, rt, 1 h
2. $TMSCF_3$ (1.5 eq), KF (1.5 eq),
DMF, rt, 18 h

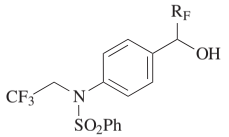


(35)

560

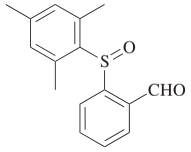


1. $TMSR_F$ (1.2 eq), TBAF (cat.),
THF, 0° to rt, o/n
2. HCl, H_2O, rt, 1 h

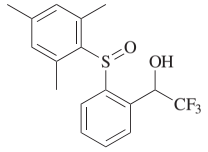


R_F	
CF_3	(85)
C_2F_5	(15)

415



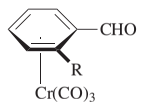
1. $TMSCF_3$ (3 eq), TMAF (3 eq),
CH_2Cl_2, 4 Å MS, –94°
2. HCl, H_2O



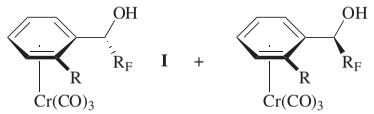
(65) dr 66.5:33.5

449

C_{7-8}



R_FI, Li/Na, Et_2O, –40°, 1–12 h

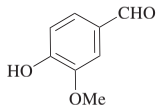


I + **II**

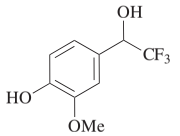
452

R	R_F	Time (h)	**I** + **II**	**I/II**
MeO	C_2F_5	1	(72)	99:1
MeO	*i*-C_3F_7	12	(—)	—
Me	C_2F_5	1	(87)	94:6
Me	*i*-C_3F_7	12	(40)	88:12

C_7

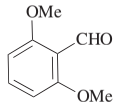


1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h
2. HCl, H_2O

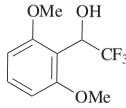


(69)

398

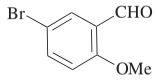


1. $TMSCF_3$ (1.21 eq), TBAF (0.7 mol %), THF, 0°; rt, 1.5 h
2. HCl, H_2O, 2 h

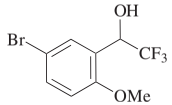


(96.4)

899

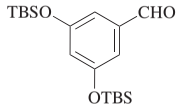


1. $TMSCF_3$ (1.2 eq), TBAF (0.41 eq), THF, 0°, to rt, 10 h
2. HCl, rt, 1 h

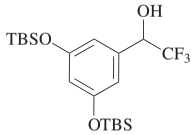


(70)

900



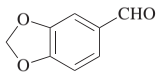
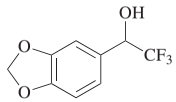
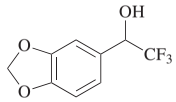
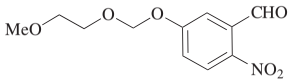
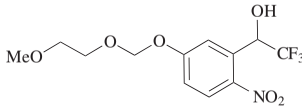
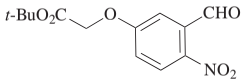
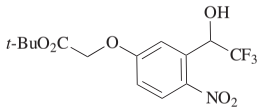
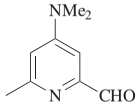
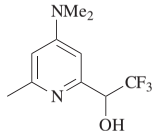
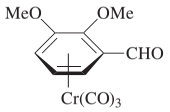
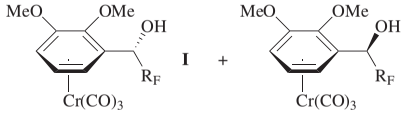
1. $TMSCF_3$ (5 eq), TBAF (1 mol %), THF, 0°, 5 min
2. HCl, H_2O, MeOH, rt, 5 min



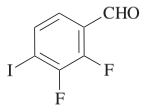
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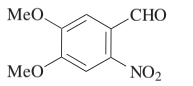
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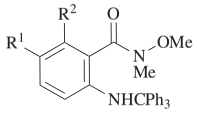
TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

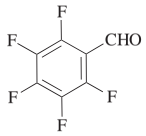
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_7			
	1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O	 (63)	398
	1. $TMSCF_3$ (2 eq), **34** (0.1 eq), **46r** (0.1 eq), NaOH (0.35 eq), Et_2O, 4 Å MS 2. HCl, H_2O, rt	 (95) er 56.5:43.5	459
	$TMSCF_3$ (1.73 eq), CsF (1.7 mol %), MeCN, rt, 10 min	 (93)	901
	1. $TMSCF_3$ (1.05 eq), CsF (cat.), DME, 0°; rt, 5 h 2. Acetone, $NaHSO_3$, H_2O, rt, 1 h	 (93)	902
	1. $TMSCF_3$ (1.2 eq), TBAF (0.41 eq), THF, 0°; rt, o/n 2. HCl (2 eq), H_2O, 1 h	 (65)	903
	R_FI, Li/Na, Et_2O, –40°	 **I** + **II**	452

R_F	Time (h)	**I + II**	**I/II**
C_2F_5	2	(72)	99:1
i-C_3F_7	12	(51)	99:1









C_{7-9}

RCHO

C_{7-11}

RCHO

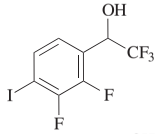
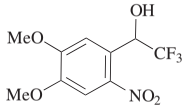
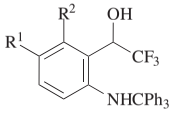
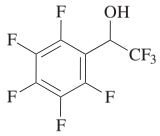
$TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°; to rt, 1 h		(85)	904
$TMSCF_3$, TBAF, THF		(80)	905
1. $LiAlH_4$, THF, –78° to rt, 1 h 2. $TMSCF_3$, TBAF, THF, 0°		R^1 R^2 F H (59–72) H O_2N (59–72)	906
1. $TMSCF_3$ (1 eq), TBAF (1.2 eq), THF, –30°, 2 h; rt, 10 h 2. H_3O^+		(62)	397
1. $TMSCF_3$ (1.05 eq), TBAF (2 mol %), THF, 10°, 10 min; to rt, 5 h 2. conc. HCl, THF, rt, 3 h		R 2,3-$OCH_2OC_6H_3$ (92) 2,6-Me_2-4-$MeOC_6H_2$ (94)	487
1. **76** (1.2 eq), *t*-BuOK (4.4 eq), *n*-Bu_4NCl (4.4 eq), –30°, 0.5 h 2. Substrate (1 eq), –30°, 1.5 h; to rt		R 4-$MeOC_6H_4$ (45) 4-$Me_2NC_6H_4$ (87) 4-(1-pyrrolidinyl)C_6H_4 (96) 2-Br-3,4-$OCH_2OC_6H_2$ (80) 3,4-$O(CH_2)_2OC_6H_3$ (84) 2,3,4-$(MeO)_3C_6H_2$ (95) 4-Me_2N-1-$C_{10}H_7$ (92)	107

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{7–15}$

RCHO

1. $TMSCF_3$ (2 eq), **46w** (5 mol %), Me_4NF (20 mol %), toluene/CH_2Cl_2 (2:1), 1 h
2. Substrate (1 eq)
3. HCl, H_2O, rt, 1 h



460

R	Temp (°)	Time (h)		er
3-ClC_6H_4	–60	2	(70)	77.5:22.5
3-BrC_6H_4	–60	1	(73)	79.0:21.0
3-$MeOC_6H_4$	–80	12	(82)	85.0:15.0
3,4-$(MeO)_2C_6H_3$	–60	3	(94)	75.0:25.0
3,4-$OCH_2OC_6H_3$	–60	1	(99)	81.5:18.5
3-MeC_6H_4	–60	12	(72)	81.5:18.5
4-MeC_6H_4	–60	8	(76)	80.0:20.0
3,4-$Me_2C_6H_3$	–60	3	(86)	78.0:22.0
2-$C_{10}H_7$	–60	1	(92)	83.0:17.0 (*R*)
9-anthryl	–60	12	(96)	75.0:25.0

$C_{7–9}$

RCHO

1. $TMSCF_3$ (1.05 eq), CsF (2 mol %), DME, 10°, 0.25 h; rt, 3 h
2. BBr_3 (3 eq), CH_2Cl_2, –78°, 15 h
3. NaCl, H_2O, 1 h



403

R	
2-$MeOC_6H_4$	(92)
3-$MeOC_6H_4$	(94)
4-$MeOC_6H_4$	(92)
3-Me-4-$MeOC_6H_3$	(93)
2,5-Me_2-4-$MeOC_6H_2$	(92)

C_{7-15}

RCHO

1. Me_3NO (0.5 eq), THF, rt, 0.5 h
2. $TMSCF_3$ (3 eq), rt, 12 h



R		
4-BrC_6H_4	(76)	143
2,4-$(MeO)_2C_6H_3$	(80)	
(*E*)-PhCH=CH	(74)	
$Ph(CH_2)_2$	(55)	
(*E*)-PhCH=CMe	(79)	
2-$C_{10}H_7$	(77)	
9-anthryl	(85)	

C_{7-13}

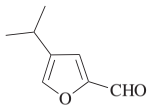
RCHO

1. $PhSO_2CF_3$ (2 eq), $HgCl_2$ (6 mol %), Mg (2 eq), DMF, −15°; to rt, 2 h
2. HCl

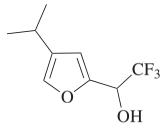


R		
2-ClC_6H_4	(60)	177
3-ClC_6H_4	(53)	
2,4-$Cl_2C_6H_3$	(45)	
4-$O_2NC_6H_4$	(28)	
4-$MeOC_6H_4$	(88)	
4-$BnOC_6H_4$	(78)	
3,4-$(MeO)_2C_6H_3$	(82)	
$Ph(CH_2)_2$	(45)	
4-*t*-BuC_6H_4	(69)	
1-$C_{10}H_7$	(60)	
2-$C_{10}H_7$	(55)	
4-PhC_6H_4	(72)	

C_8

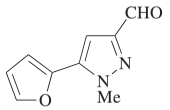
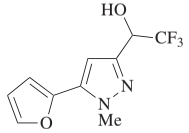
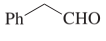
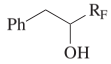
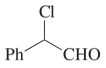
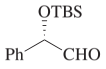
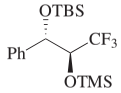
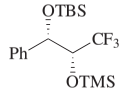
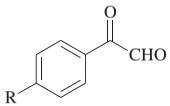
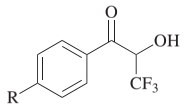
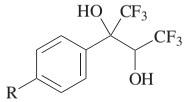


1. $TMSCF_3$, CsF (cat.), rt, 14 h
2. HCl, rt, 5 h

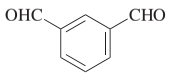


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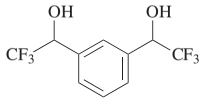
TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_8			
	1. $TMSCF_3$ (1.7 eq), TBAF (2 mol %), rt, 3.5 h 2. HCl, rt, 1 h	 (90)	907
	R_FMgBr, Et_2O, –40 to –10°, 2–3 h	 R_F: n-C_4F_9 (31–51); n-C_6F_{13} (44–55); n-C_8F_{17} (58); n-$C_{10}F_{21}$ (44)	876
	C_2F_5MgBr, Et_2O, –30°, 1 h; –30 to 0°	 **I** + **II** **I + II** (34), **I/II** = 1:1	862
	1. $TMSCF_3$ (1.2 eq), TBAF (0.4 mol %), THF, 0°, 0.75 h 2. H_2O	 **I** +  **II** **I + II** (92), **I/II** = 55:45	444
C_{8-9}			
	1. $TMSCF_3$ (2.05 eq), CsF (2 mol %), DME, 0°, 1 h; rt, 5 h 2. HCl, H_2O, THF, rt, 3 h	 +  **I**: R = H (82); MeO (70); Me (72). **II** (—)	438

C_8

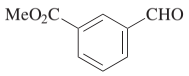


1. $TMSCF_3$ (2.2 eq), TBAF, THF, 0°; rt, o/n
2. HCl, rt, 5 h

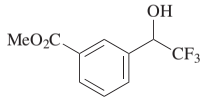


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908

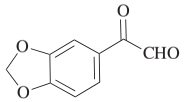


1. $TMSCF_3$ (1.3 eq), CsF (10 mol %), THF, sonication, rt, 0.5 h; rt, 5 h
2. HCl, H_2O, 0.25 h

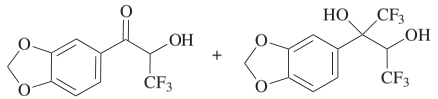


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908a

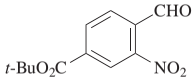


1. $TMSCF_3$ (2.05 eq), CsF (2 mol %), DME, 0°, 1 h; rt, 5 h
2. HCl, H_2O, THF, rt, 3 h

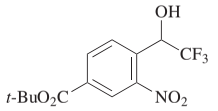


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438

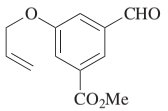


1. $TMSCF_3$ (1.0 eq), CsF (cat.), THF, 0°; rt, 5 h
2. HCl

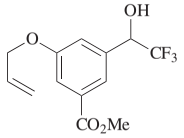


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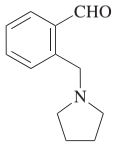


1. $TMSCF_3$ (1.2 eq), TBAF (1 mol %), THF, 0°, 5 min
2. MeOH, HCl, 5 min

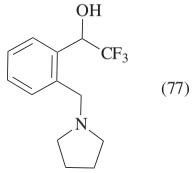


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910



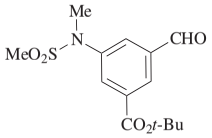
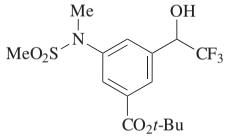
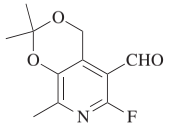
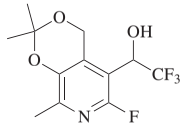
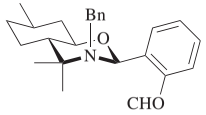
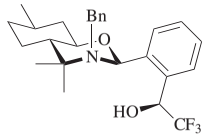
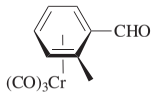
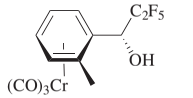
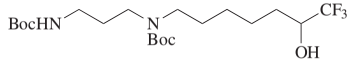
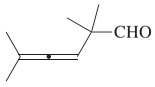
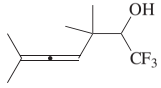
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°; rt, o/n
2. HCl (2 eq), H_2O, 1 h

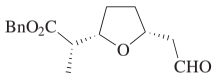


(77)

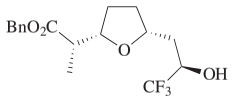
903

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

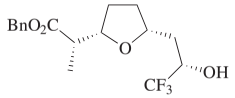
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_8			
	1. $TMSCF_3$ (1.2 eq), TBAF (0.1 eq), THF, 0° to rt, 6 h 2. HCl, H_2O	 (87)	911
	1. $TMSCF_3$ (1.47 eq), TBAF (cat.), THF, 0°; rt, 1 h 2. HCl, H_2O, 1 h	 (80)	912
	$TMSCF_3$ (1.1 eq), TBAF (cat.), THF, 0°, 0.75 h	 (96)	500
	C_2F_5Li, Et_2O, –40°	 (87) dr 94:6	451
C_9			
	1. $TMSCF_3$ (3 eq), TBAF (10 mol %), THF, rt, 2h 2. TBAF (1.5 eq), THF, H_2O, rt, 0.75 h	 (82)	913
	$TMSCF_3$, TBAF	 (—)	914



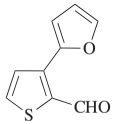
1. $TMSCF_3$ (1.5 eq), TBAF (12 mol %), 0°, 25 min
2. HCl



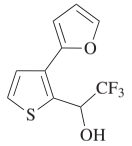
(44) 915



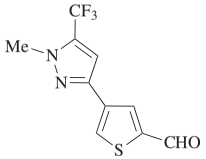
(41)



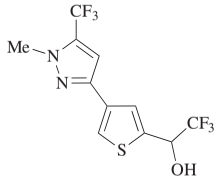
$TMSCF_3$ (1.2 eq), TBAF (10 mol %), THF, 0°; rt, 4 h



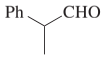
(90), crude 894



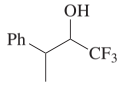
1. $TMSCF_3$ (3 eq), Amberlyst A-27 resin (F- form), THF, rt, 1–19 h
2. Amberlyst A-15 resin (H^+ form)
3. Aminomethylated polystyrene resin



(85) 858

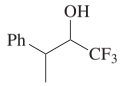


1. $TMSCF_3$ (0.83 eq), Et_3N (0.17 eq), DMF, rt, 10 h
2. HCl, H_2O



(—) 32% conv, dr 85:15 138

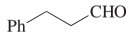
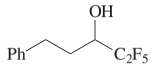
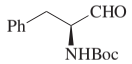
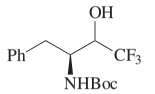
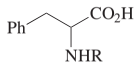
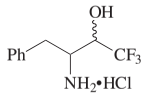
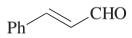
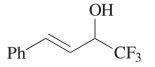
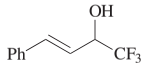
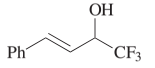
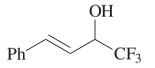
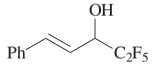
1. **60** (1 eq, dr 60:40), initiator (0.1 eq), solvent, 24 h
2. TBAF (1 eq), THF, 1 h



dr 1:1

Initiator	Solvent		
CsF	DME	(16)	182
TBAF	THF	(42)	

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_9			
	1. $TMSC_2F_5$ (1.2 eq), TBAF (1 mol %), THF, 0°, 10 min; rt, 6 h 2. TBAF (10 mol %), THF/H_2O	 (71)	882
	$TMSCF_3$ (1.19 eq), TBAF (1.6 mol %), THF, 0° to rt, 1 h	 (33), dr 1:1	916
 R = Boc, Cbz	1. MeNHOMe•HCl, EDCI, Et_3N, DMF 2. $LiAlH_4$, THF 3. $TMSCF_3$, CsF (cat.), THF 4. HCl	 (30)	614
	1. $TMSCF_3$, CsF (cat.), THF, rt 2. HCl, H_2O	 (90)	433
	1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O	 (58)	398
	1. $TMSCF_3$, CsF, DME, rt, 10 h 2. HCl, H_2O	 (82)	434
	1. $TMSCF_3$ (1 eq), TBAF (0.5 mol %), THF, –20 to 0°; 0°, 5 h; 20°, 2 h 2. HCl, H_2O, 3 h	 (97)	435
	1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h 2. HCl, H_2O, rt, 12 h	 (18.3)	398

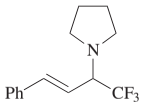
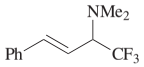
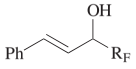
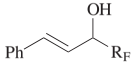
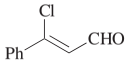
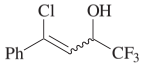
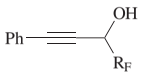
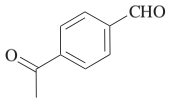
1. **77** (1.2 eq), TMSOTf (1.2 eq), CH_2Cl_2, rt, 0.5 h 2. $TMSCF_3$ (1.5 eq), AcONa (2 eq), DMF, rt, 2 h		(48) +  (12)	560
R_FMgBr, Et_2O, –40° to rt, o/n		R_F: C_2F_5 (70); n-C_6F_{13} (60); n-C_8F_{17} (60)	393
R_FX, Zn, DMF, ultrasound		R_F / X / Time (h): CF_3 I 0.5 (69); CF_3 Br 3 (45); C_2F_5 I 1 (48); n-C_3F_7 I 0.5 (60)	299
			
1. $TMSCF_3$ (1.2 eq), TBAF (1 eq), THF, 0°, 20 min; rt, 4 h 2. HCl, H_2O		(75)	436
			
1. $TMSR_F$ (1.25 eq), CsF or TBAF (5 mol %), DME or THF 2. HCl, H_2O		R_F / Temp (°) / Time (h): CF_3 rt — (90); C_2F_5 rt — (83); n-C_6F_{13} 50 15 (55); n-C_7F_{15} 50 15 (53); n-C_8F_{17} 50 15 (58)	437

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

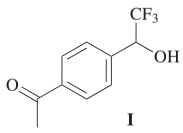
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_9

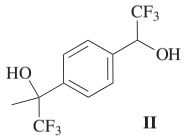


1. $TMSCF_3$ (*x* eq),
initiator (*y* mol %), solvent rt, 0.5 h
2. Hydrolysis



I

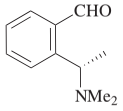
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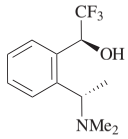
II

142

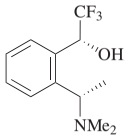
x	Initiator	*y*	Solvent	**I**	**I/II**
1	TBAF	—	DMF	(—)	1.9:1
1	TBAF	—	THF	(—)	3.6:1
1	TBAF	—	toluene	(—)	1:2.1
5	**27a**	0.5	DMF	(85)	**I** only



1. $TMSCF_3$ (1.2 eq),
TBAF (3.8 mol %), THF, 0°; rt, 4 h
2. HCl, H_2O, 1 h

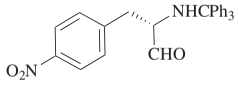


(61) +

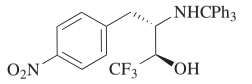


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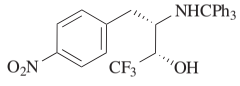
443



TMSCF$_3$, TBAF, THF



I +

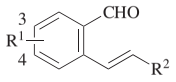


II

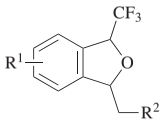
445

I + **II** (88),
I/II = 4.5:1

$C_{9–17}$



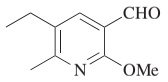
$TMSCF_3$ (1.5 eq), CsF (1.5 eq), THF, 0° to rt; rt



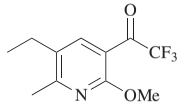
439

R^1	R^2	Time (h)		dr
H	O_2N	—	complex mixture	—
H	NC–	—	(80)	1.5:1
H	MeO_2C	10	(82)[f]	1.5:1
H	EtO_2C	12	(80)	2.1:1
H	*n*-BuO_2C	12	(91)	4.5:1
H	*t*-BuO_2C	12	(87)	1.8:1
H	Bz	7	(71)[e]	4.0:1
H	4-ClC_6H_4CO	12	(57)	2.0:1
H	4-$MeOC_6H_4CO$	9	(70)	1.9:1
H	3,4-$(MeO)_2C_6H_3CO$	9.5	(68)	2.7:1
4-O_2N	EtO_2C	24	(71)	2.5:1
3,4-OCH_2O	EtO_2C	18	(68)	2.2:1
H	4-MeC_6H_4CO	7	(77)	3.7:1

C_9



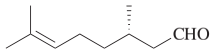
1. $TMSCF_3$, TBAF, THF
2. Dess–Martin periodinane



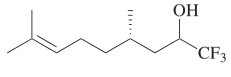
(—)

917

C_{10}



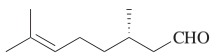
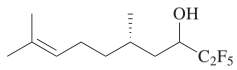
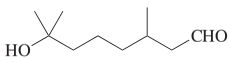
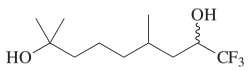
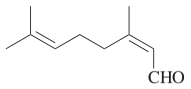
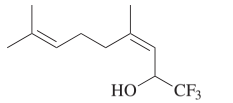
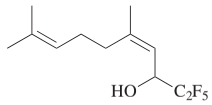
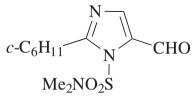
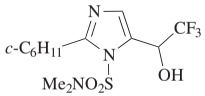
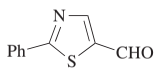
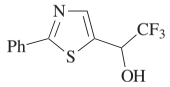
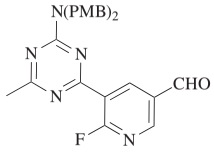
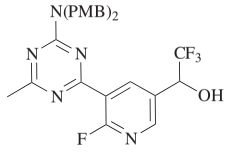
1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h
2. HCl, H_2O

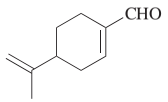
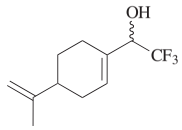
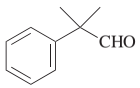
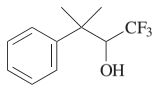
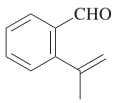
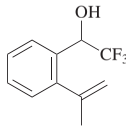
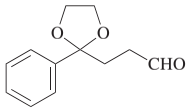
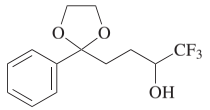
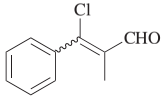
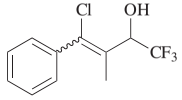
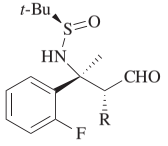
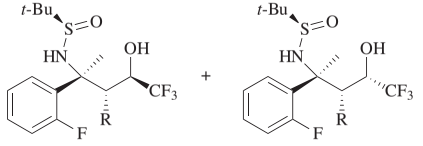


(54) dr 1:1

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TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

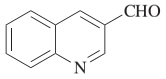
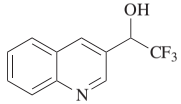
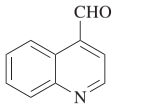
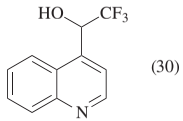
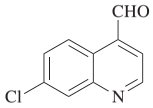
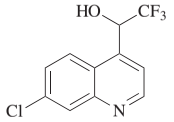
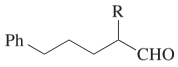
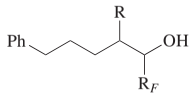
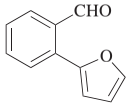
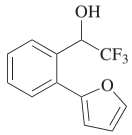
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{10}			
	1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h 2. HCl, H_2O, rt, 12 h	 (65.4) dr 1:1	398
	1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O	 (52)	398
	1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O	 (56)	398
	1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h 2. HCl, H_2O, rt, 12 h	 (64.3)	398
	$TMSCF_3$, TBAF, THF, 0° to rt, 2 h	 (73)	918
	1.$TMSCF_3$ (2 eq), CsF (20 mol %), THF, rt, 3 h 2. HCl, H_2O, rt, 0.5 h	 (—)	875
	$TMSCF_3$ (1.5 eq), CsF (20 mol %), THF, 0°, 10 min; rt, 3.5 h	 (91)	919

	1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O		(76)	398
	$TMSCF_3$ (1.2 eq), TBAF (10 mol %), THF, rt, 1 h		(66)	920
	1. $TMSCF_3$ (1.2 eq), TBAF (0.63 mol %), THF, 0°, 1 h; rt, o/n 2. HCl, 40°, 3 h		(93)	921
	1. $TMSCF_3$ (1.2 eq), TBAF (1 mol %), THF, 0°, 10 min; rt, 6 h 2. TBAF (10 mol %), THF/H_2O		(67)	882
	1. $TMSCF_3$ (1.2 eq), TEAF (1 eq), THF, 0°, 20 min; rt, 5 h 2. HCl, H_2O		(67)	436
	1. $TMSCF_3$ (2 eq), TBAF (0.1 eq), THF, 0°, 1 h 2. TBAF (0.9 eq), 0°, 1 h			922

I **II**

R	**I**	**II**
H	(13)	(25)
F	(35)	(22)

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{10}			
	1. **61** (1 eq), *t*-BuOK (1 eq), THF, 0° to rt, 1 h 2. HCl, H_2O, o/n	 (40) 55% conv	181
	1. **61** (1 eq), *t*-BuOK (1 eq), THF, 0° to rt, 1 h 2. HCl, H_2O, o/n	 (30) 35% conv	181
	1. $TMSCF_3$ (1.2 eq), TBAF (1 mol %), THF, 0° to rt, 2 h 2. HCl, H_2O, 0°; rt, 1 h	 (96)	923
C_{11}			
	1. R_FI (5 eq), MeLi•LiBr (5 eq), Et_2O, –78° 2. $KHSO_4$		190
	$TMSCF_3$ (1.2 eq), TBAF (1.5 mol %), THF, 0°; rt 4 h	 (81)	894

R	R_F	Time (h)		
H	C_2F_5	1.5	(98)	
H	n-C_3F_7	1.5	(85)	
F	C_2F_5	0.25	(73)	

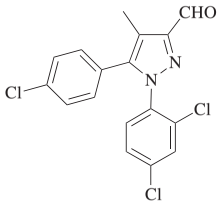
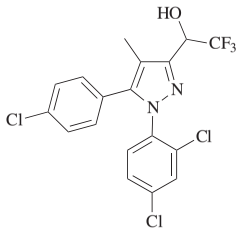
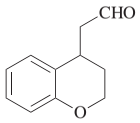
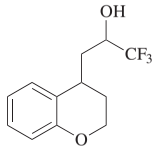
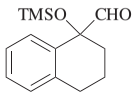
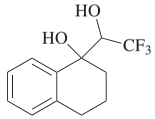
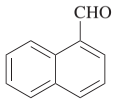
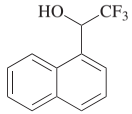
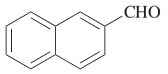
	1. $TMSCF_3$ (1.8 eq), TBAF (0.5 eq), THF, 0° to rt 2. TBAF (0.5 eq), rt, 0.25 h		(85)	924
	1. $TMSCF_3$, TBAF, THF, 0°, 1 h 2. TBAF		(—)	925
	1. $TMSCF_3$ (1.1 eq), TBAF (0.5–1 mol %), THF, rt, 0.5– 2 h 2. TBAF (2 eq), THF, rt, 10 min		(72)	883
	CF_3I (2.2 eq), TDAE (2.2 eq), DMF, –15° to rt; rt, 12 h		(69)	386

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

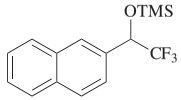
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{11}



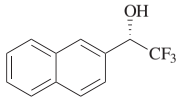
$TMSCF_3$ (x eq), catalyst (y mol %), solvent, rt



140

x	Catalyst	y	Solvent (s)	Time (h)	
1.1	P(t-Bu)$_3$	0.1	DMF	0.5	(94)
1.1	P(t-Bu)$_3$	1	DMF	0.5	(97)
1.1	P(t-Bu)$_3$	10	DMF	0.5	(97)
2	—	—	DMF	24	(22)
2	P(t-Bu)$_3$	10	MeCN	24	trace
2	P(t-Bu)$_3$	10	CH_2Cl_2	24	trace
2	P(t-Bu)$_3$	10	THF	24	trace
2	P(t-Bu)$_3$	10	Et_2O	24	trace
2	P(t-Bu)$_3$	10	HMPA	0.5	(86)
2	P(t-Bu)$_3$	10	DMSO	0.5	(94)
2	P(t-Bu)$_3$	10	DMA	1	(99)
2	P(t-Bu)$_3$	10	DMF	0.5	(99)
2	P(n-Bu)$_3$	10	DMF	0.5	(99)
2	PO(n-Bu)$_3$	10	DMF	16	(3)
2	P(c-C_6H_{11})$_3$	10	DMF/toluene	24	(16)
2	P(n-C_8H_{17})$_3$	10	DMF	0.5	(99)
2	PPh_3	10	DMF	17	(16)
2	$POPh_3$	10	DMF	5	(78)

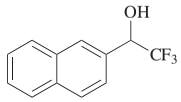
1. $TMSCF_3$ (2 eq), KF (5 mol %), **50** (0.1 eq), solvent
2. HCl, H_2O, THF, rt, 1 h



457

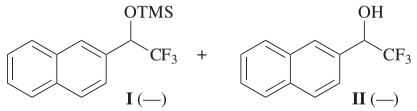
Solvent	Temp	Time (h)		er
toluene	rt	15	(76)	51.0:49.0
THF	–78° to rt	12	(9)	55.5:45.5

1. $TMSCF_3$, TBAF (cat.), 0° to rt, 2 h
2. TBAF



(95) 641

$TMSCF_3$ (2 eq), initiator (0.1 eq), additive (0.1 eq), solvent



457

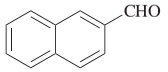
Initiator	Additive	Solvent	Temp (°)	Time (h)	Conv **I** (%)	Conv **I** + **II** (%)
KF	—	CH_2Cl_2	rt	12	trace	—
KF	—	MeCN	rt	12	trace	—
KF	—	DMF	–20	0.5	82	—
KF	—	THF	rt	12	12	—
KF	—	toluene	rt	12	trace	—
KF	Me_4NCl	toluene	0	0.5	77	—
KF	Me_4NCl	THF	–20	1	63	—
KF	Me_4NBr	toluene	–20	12	trace	—
KF	Me_4NBr	THF	–20	12	trace	—
KF	Et_4NCl	toluene	–20	1	85	—
KF	Et_4NCl	THF	0	6	81	—
KF	Et_4NBr	toluene	0	2	92	—
KF	Et_4NBr	THF	0	2	82	—
KF	Bu_4NCl	toluene	–20	2	—	80
KF	Bu_4NCl	THF	–20	2	—	83
—	Bu_4NBr	toluene	rt	12	tr	—
KF	Bu_4NBr	CH_2Cl_2	–20	0.5	89	—
KF	Bu_4NBr	MeCN	–20	0.5	87	—
KF	Bu_4NBr	THF	–20	0.5	82	—
KF	Bu_4NBr	toluene	–20	0.5	89	—
KF	*n*-$C_{16}H_{33}NMe_3Br$	toluene	–20	0.5	81	—
KF	*n*-$C_{16}H_{33}NMe_3Br$	THF	–20	0.5	90	—

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

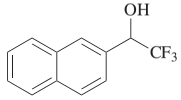
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{11}



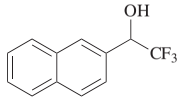
1. $TMSCF_3$ (2 eq), initiator (*x* mol %), additive (0.1 eq), Et_2O, –15°
2. HCl, H_2O, rt



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Initiator	*x*	Additive	Time (h)		er
35	20	**37**	24	(80)	69.0:31.0
36a	10	**37**	24	(86)	76.5:23.5
36a	20	**37**	24	(87)	75.0:25.0
36b	10	**37**	24	(52)	66.0:34.0
37	10	**37**	24	(27)	69.0:31.0
38	20	—	28	(37)	50.0:50.0
38	20	**37**	24	(93)	69.0:31.0
39a	10	**37**	24	(33)	71.0:29.0
39b	20	**37**	24	(80)	70.0:30.0
39c	10	**37**	24	(69)	72.0:28.0

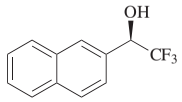
1. $TMSCF_3$ (2 eq), initiator (0.1 eq), **46r** (0.1 eq), additive (*x* eq)
2. HCl, H_2O, rt



459

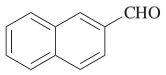
Initiator	Additive	*x*	Solvent		Temp (°)	Time (h)		er
34	NaOH	0.25	Et_2O	4 Å MS	–45	2	(76)	82.5:17.5
34	NaOH	0.25	Et_2O	4 Å MS	–15	2	(85)	85.5:14.5
34	NaOH	0.25	Et_2O	4 Å MS	0	2	(75)	81.5:18.5
36a	—	—	CH_2Cl_2	—	–15	24	(69)	64.5:35.5
36a	—	—	THF	—	–15	24	(77)	66.5:33.5
36a	—	—	Et_2O	3 Å MS	–15	3	(71)	78.5:21.5
36a	—	—	Et_2O	4 Å MS	–15	3	(62)	81.0:19.0
36a	—	—	Et_2O	5 Å MS	–15	3	(50)	77.5:22.5
36a	NaOH	0.15	Et_2O	4 Å MS	–15	3	(80)	84.5:15.5

1. $TMSCF_3$ (2 eq), KF (5 mol %), additive (0.1 eq), toluene
2. HCl, H_2O, THF, rt, 1 h

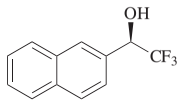


457

Additive	Temp	Time (h)		er
46b	rt	10	(67)	55.0:45.0
46h	rt	24	(44)	59.5:40.5
46i	rt	24	(67)	59.5:40.5
46k	0°	2	(81)	63.0:37.0
46m	rt	16	(58)	65.5:34.5
46n	rt	48	(34)	64.0:36.0
46p	0°	3.5	(90)	68.0:32.0
46q	rt	18	(54)	70.0:30.0
51	rt	48	(47)	51.0:49.0

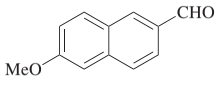


1. $TMSCF_3$ (2 eq), **49a** (0.1 eq), TMAF (0.1 eq), toluene/CH_2Cl_2 (2:1), –60 to –50°, 24 h
2. TBAF, H_2O, THF, rt, 1 h

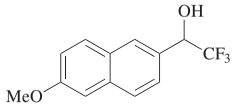


(93) er 70.5:29.5

458



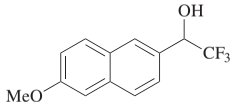
1. **61** (1 eq), *t*-BuOK (1 eq), THF, 0° to rt, 1 h
2. HCl, H_2O, o/n



(91) 95% conv

181

1. **60** (1 eq, dr 60:40), CsF (0.1 eq), DME, 24 h
2. TBAF (1 eq), THF, 1 h



(90) er 50.0:50.0

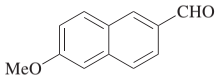
182

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

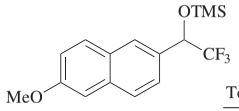
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{11}



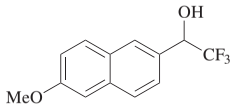
62b (1 eq), CsF (0.1 eq), DME, 5 h



109

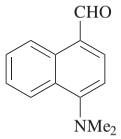
Temp (°)	Conv (%)	
60	78	(70)
80	80	(77)

1. **64a** (1 eq), CsF (0.1 eq), DME, rt
2. TBAF (1 eq), THF, 1 h

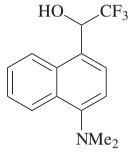


(93) er 50.0:50.0

121

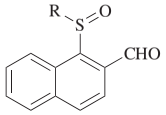


CF_3I (2.2 eq), TDAE (2.2 eq), DMF, *hν*, –20° to rt, 12 h

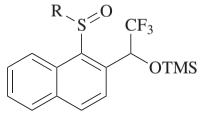


(86) 91% conv

385

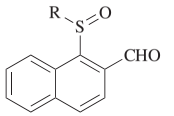
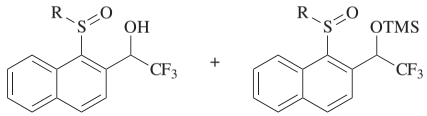
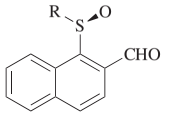
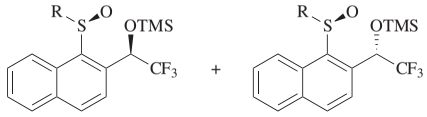


$TMSCF_3$ (*x* eq), TMAF (*y* eq), CH_2Cl_2



449

R	*x*	*y*	Temp (°)		*syn*/*anti*
4-MeC_6H_4	1.5	0. 2	–78	(85)	55:45
2,4,6-$Me_3C_6H_2$	1.5	0. 2	–78	(79)	79:21
2,4,6-*i*-$Pr_3C_6H_2$	1.5	0. 2	–94	(17)	92:8
2,4,6-*i*-$Pr_3C_6H_2$	1.5	0. 2	–78	(92)	85:15
2,4,6-*i*-$Pr_3C_6H_2$	1.5	1.5	–78	(89)	88:12
2,4,6-*i*-$Pr_3C_6H_2$	3	3	–94	(97)	90:10
2,4,6-*i*-$Pr_3C_6H_2$	3	3	–94	(96)[g]	91:9
2,4,6-*i*-$Pr_3C_6H_2$	3	3	–78	(97)	88:12

	R = 2,4,6-*i*-$Pr_3C_6H_2$	$TMSCF_3$ (1.5 eq), TBAF (0.2 eq), CH_2Cl_2, –78°	 (32) *syn*/*anti* = 79:21	449
	R = 2,4,6-*i*-$Pr_3C_6H_2$	$TMSCF_3$, TMAF, CH_2Cl_2, 4 Å MS, –94°	 **I** **I** + **II** (85), **I**/**II** = 88:12 **II**	449

C_{12}

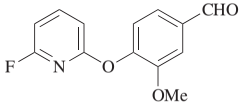
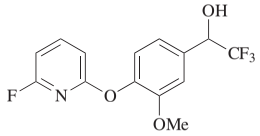
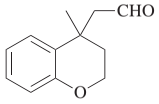
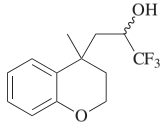
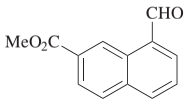
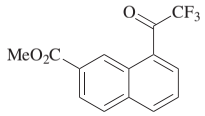
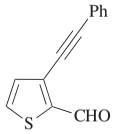
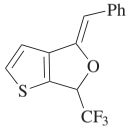
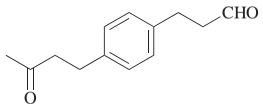
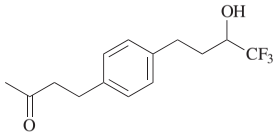
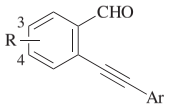
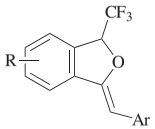
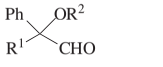
	1. $TMSCF_3$ (1.2 eq), TBAF (1 mol %), THF, 0°; rt, 2 h 2. HCl, rt, 2 h	 (88)	926
	1. $TMSCF_3$, TBAF (0.2 eq), THF, 1 h 2. TBAF	 (—)	927, 925
	1. $TMSCF_3$, TBAF (cat.), THF 2. HCl, H_2O 3. $(COCl)_2$, DMSO, CH_2Cl_2 4. Et_3N 5. LiOH, THF, H_2O	 (—)	928

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

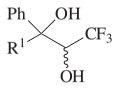
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{13} 	$TMSCF_3$ (3 eq), CsF (2 eq), TBAB (20 mol %), toluene, 80°, 6 h	 (93)	440
	1. $TMSCF_3$ (0.5 eq), THF, rt, 1 h 2. $TMSCF_3$ (0.5 eq) 3. TBAF (1.7 mol %), rt, 2 h 4. HCl, 0.5 h	 (47)	929
C_{13-16} 	$TMSCF_3$ (3 eq), CsF (2 eq), TBAB (20 mol %), toluene, 80°, 6 h		440

R	Ar	
H	2-thienyl	(83)
H	Ph	(88)
H	4-ClC_6H_4	(68)
H	4-BrC_6H_4	(78)
H	4-$MeOC_6H_4$	(72)
3-MeO	Ph	(61)
3-Cl	Ph	(62)
3-MeO	4-ClC_6H_4	(60)
3,4-OCH_2O	Ph	(55)
H	2-MeC_6H_4	(77)
H	3-MeC_6H_4	(82)
H	4-MeC_6H_4	(71)
H	4-NCC_6H_4	(53)
3-MeO	4-MeC_6H_4	(65)
3-CF_3	4-ClC_6H_4	(71)

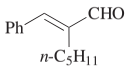
C_{14}



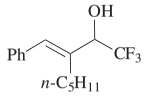
1. $TMSCF_3$ (1.1 eq),
TBAF (0.5–1 mol %), THF, rt, 0.5–2 h
2. TBAF (2 eq), THF, rt, 10 min



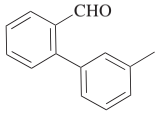
R^1	R^2		
n-C_6H_{13}	TMS	(95)	883
Ph	TBS	(94)	



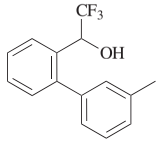
1. $TMSCF_3$ (1.5 eq), TBAF (cat.),
THF, rt, 24 h
2. HCl, H_2O



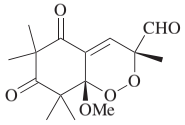
(66) 398



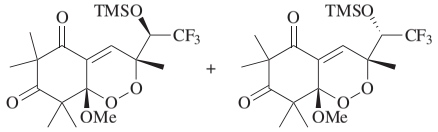
$TMSCF_3$ (1.2 eq), TBAF (1 mol %),
THF, 0°; rt, 4 h



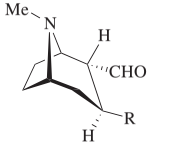
(44) 894



$TMSCF_3$, TBAF

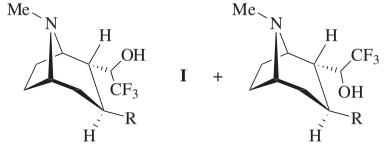


I **I** + **II** (80), **I**/**II** = 1:1 **II** 930



R = 4-ClC_6H_4

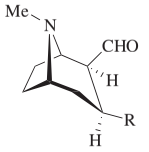
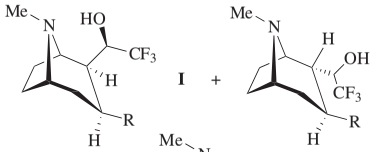
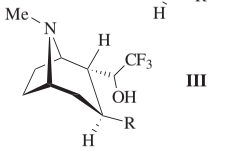
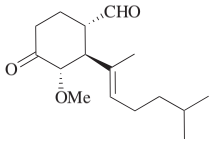
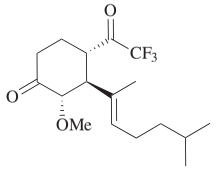
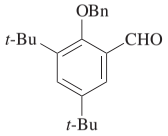
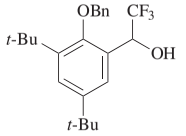
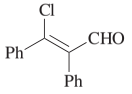
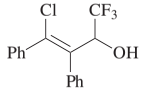
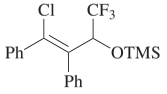
1. $TMSCF_3$, TBAF (cat.),
THF, rt, 2 h
2. TBAF, THF, rt, 1 h

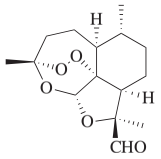


I + **II** **II** 931

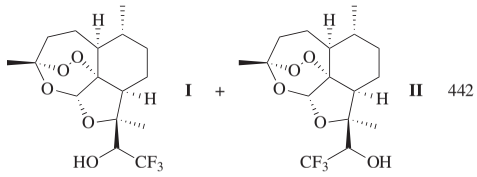
I + **II** (50), **I**/**II** or **II**/**I** = 2:1

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{14}  R = 4-ClC_6H_4	1. $TMSCF_3$, TBAF (cat.), THF, rt, 2 h 2. TBAF, THF, rt, 1 h	 **I** + **II** +  **III** **I** + **II** + **III** (40), **I**/(**II** + **III**) = 2:1	931
C_{15} 	1. $TMSCF_3$ (1.05 eq), TBAF (5 mol %), THF, 0°, 1 h 2. TBAF (1 eq), THF, 0.5 h 3. Dess–Martin periodinane (4 eq), CH_2Cl_2, 0°, 16 h 4. $NaHCO_3$, $Na_2S_2O_3$, H_2O, 0°, 1 h	 (40)	884
	1. $TMSCF_3$ (2 eq), Bu_3P (0.1 eq), DMF, rt, 1 h 2. TBAF, THF, rt, 2 h	 (71)	932
	1. $TMSCF_3$ (1.2 eq), TEAF (1 eq), THF, 0°, 20 min; rt, 28 h 2. HCl, H_2O	 (84) +  (11)	436

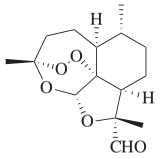


TMSCF$_3$ (1.9 eq), TBAF (0.3 eq), THF, 0°, 5 h

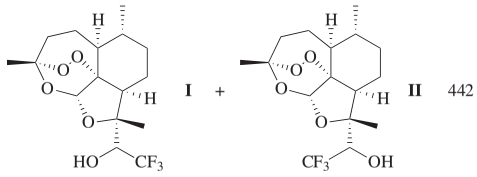


I + **II** 442

I + **II** (80), **I**/**II** or **II**/**I** = 38:62

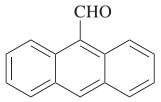


TMSCF$_3$ (1.9 eq), TBAF (0.3 eq), THF, 0°, 6 h

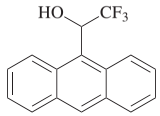


I + **II** 442

I + **II** (76), **I**/**II** or **II**/**I** = 88:12

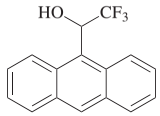


1. CF_3Br, Zn, pyridine, 0–40°
2. H_3O^+



(37) 601

1. TMSCF$_3$ (3 eq), Amberlyst A-27 resin (F^- form), THF, rt, 1–19 h
2. Amberlyst A-15 resin (H^+ form)
3. Aminomethylated polystyrene resin



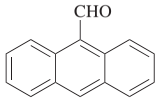
(67) 858

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

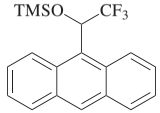
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{15}



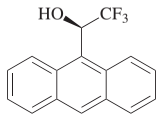
TMSCF$_3$ (*x* eq), catalyst (*y* mol %), DMF, rt



65

x	Catalyst	*y*	Time	Conv (%)	
1.2	Li_2CO_3	1	16 h	100	(—)
1.2	$NaHCO_3$	1	72 h	80	(—)
1.2	Na_2CO_3	1	0.5 h	100	(—)
1.2	$KHCO_3$	1	72 h	90	(—)
1.2	K_2CO_3	1	5 min	100	(—)
1.2	HCO_2Ag	1	0.25 h	100	(—)
1.2	$MeCO_2Na$	1	20 min	100	(—)
1.2	**28**	2	5 min	—	(92)
1.5	KH_2PO_4	5	16 h	—	(80)
1.5	$K_2HPO_4 \cdot 3H_2O$	5	0.5 h	—	(85)
1.5	K_3PO_4	5	2 h	—	(86)

1. TMSCF$_3$ (1.2 eq), **46a** (0.1 eq), solvent
2. HCl, H_2O



(—)

455

Solvent	Temp (°)	Time (h)	er
THF	rt	—	50.0:50.0
THF	–78 to rt	—	62.5:37.5
CH_2Cl_2	rt	—	52:5:47.5
CH_2Cl_2	–78; rt	5	97.5:2.5

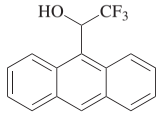
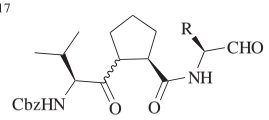
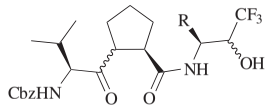
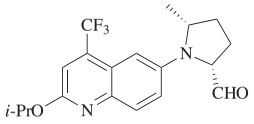
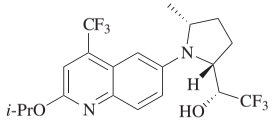
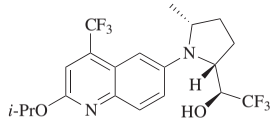
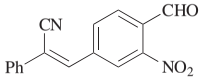
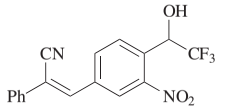
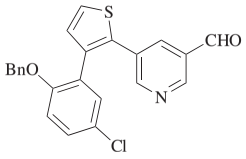
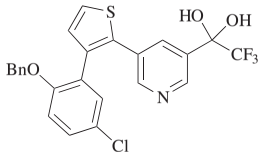
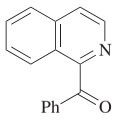
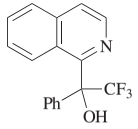
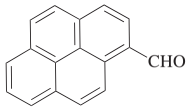
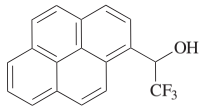
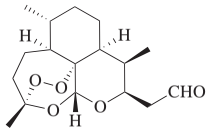
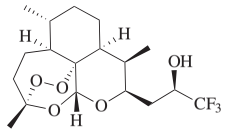
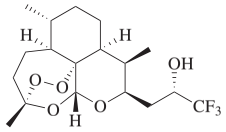
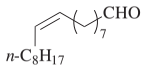
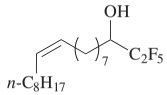
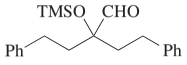
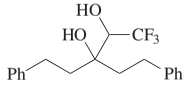
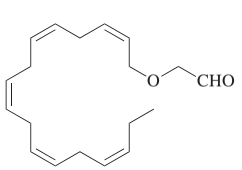
		1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 2 h 2. HCl, H_2O	 (74)	289
$C_{16–17}$		CF_3I, Zn, DMF, –20°, 1 h		R: *i*-Pr (50); *t*-Bu (—) 215
C_{16}		$TMSCF_3$ (1.45 eq), CsF (cat.), THF, –78° to rt, 18 h	 (48) +  (31)	933
		1. $TMSCF_3$ (1.2 eq), CsF (8 mol %), DME, 0°, rt, 2 h 2. HCl	 (88)	934
		1. $TMSCF_3$, TBAF 2. MnO_2	 (87)	935

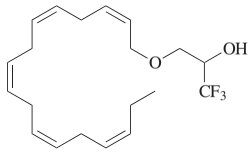
TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{16} 	1. $TMSCF_3$ (1.6 eq), TBAF (0.14 eq), THF, 0°; rt, 24 h 2. TBAF (2.5 eq), $CHCl_3$, rt, 10 min	 (—)	936
C_{17} 	1. $TMSCF_3$ (1.05 eq), TBAF (2 mol %), THF, 10°, 10 min; to rt, 24 h 2. conc. HCl, THF, rt, 3 h	 (96)	487
	1. $TMSCF_3$ (2 eq), TBAF (5 mol %), THF, rt, 1 h 2. HCl, H_2O, 1 h	 **I**	441
		I or **II** (53), **II** or **I** (38) +  **II**	
C_{18} 	1. C_2F_5I (5 eq), MeLi•LiBr (5 eq), Et_2O, –78°, 1.5 h 2. $KHSO_4$	 (78)	190
	1. $TMSCF_3$ (1.1 eq), TBAF (0.5–1 mol %), THF, rt, 0.5–2 h 2. TBAF (2 eq), THF, rt, 10 min	 (72)	883

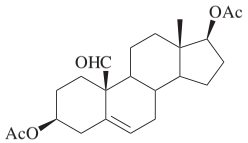
C_{19}



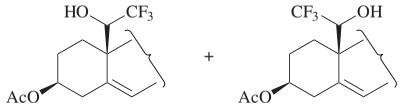
1. $TMSCF_3$ (1.2 eq), TBAF (0.1 eq), THF, 0° to rt, 1 h
2. HCl, H_2O, 10 min



(75) 937

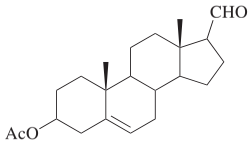


1. $TMSCF_3$ (2.22 eq), TBAF (1.86 eq), THF, 0°; rt, 9 h
2. $TMSCF_3$ (1.7 eq), 0°; rt, 15 h
3. HCl, H_2O, rt, 3 h

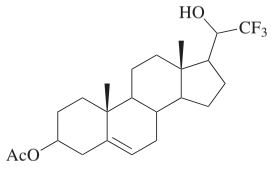


I **I** or **II** (54); **II** or **I** (6) **II** 938

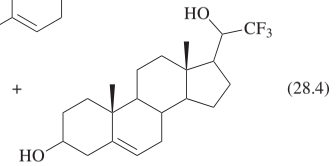
C_{20}



1. $TMSCF_3$ (2.22 eq), TBAF (2.37 eq), THF, 0°; rt, 9 h
2. $TMSCF_3$ (0.82 eq), 0°; rt, 12 h
3. HF, H_2O, rt, 3 h

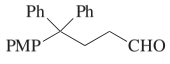


(62.1) 939

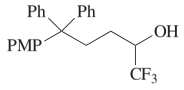


(28.4)

C_{22}

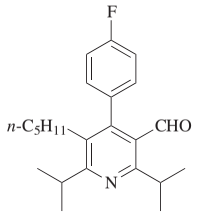
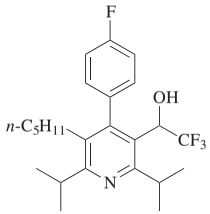
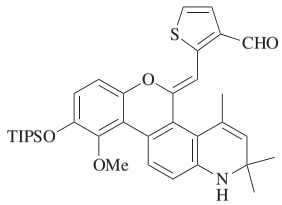
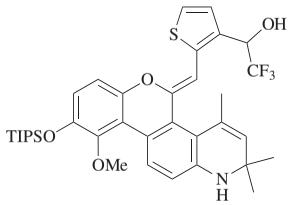
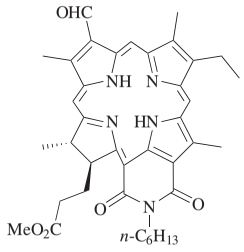
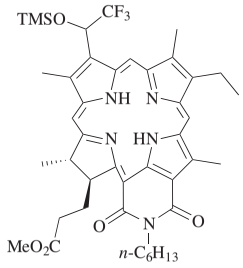


1. $TMSCF_3$ (2), TBAF (10 mol %), THF, 0°; rt, 18 h
2. TBAF (27 mol %), rt, 4.5 h

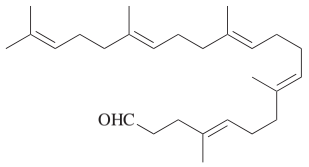


(77) 940

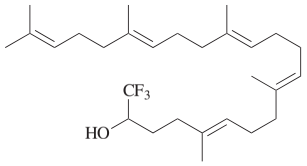
TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{23} 	$TMSCF_3$, TBAF, THF	 (70)	941
C_{25} 	$TMSCF_3$ (10 eq), TBAF (0.5 eq), THF, 0°, 0.4 h	 (55)	942
C_{26} 	$TMSCF_3$, TBAF (cat.)	 (93)	425

C_{27}

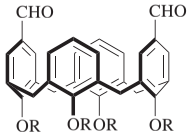


$TMSCF_3$, TBAF (1 eq), THF, 0°



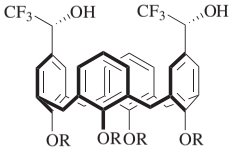
(91) 943

C_{30}

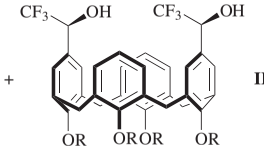


R = *n*-Pr

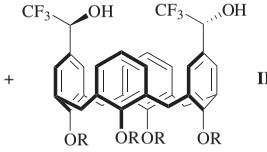
1. $TMSCF_3$, TBAF, THF
2. HCl, H_2O



I 944



\+ **II**



\+ **III** (meso)

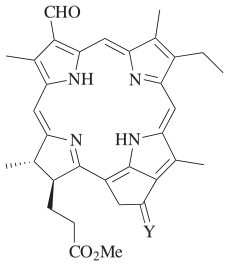
I + **II** + **III** (85), **I**/**II** = 1:1, (**I** + **II**)/**III** = 1:1

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

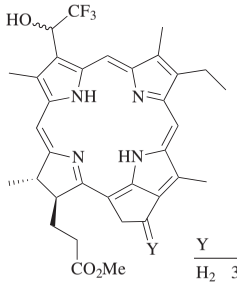
Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.

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

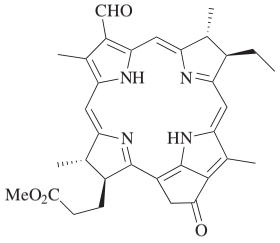
C_{32}



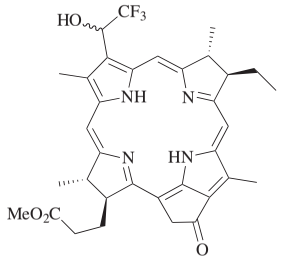
1. $TMSCF_3$ (*x* eq),
   $TBAF•3H_2O$ (*y* mol %), THF, rt
2. HCl, H_2O



Y	*x*	*y*	Time (min)		
H_2	3.1	20	—	(74)	429
O	7.5	2.3	5	(46)	426

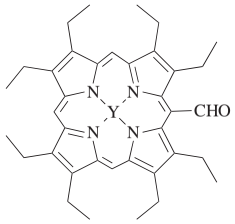


1. $TMSCF_3$ (8 eq),
   $TBAF•3H_2O$ (2.2 mol %),
   THF, rt, 1 min
2. HCl, H_2O, 10 min

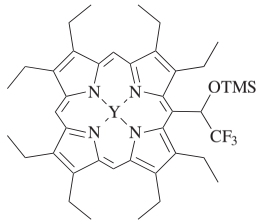


(31) 430

C_{37}



$TMSCF_3$, TBAF (cat.)



Y		
Ni	(98)	425
CH_2	(95)	

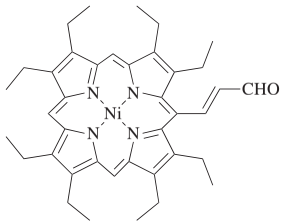
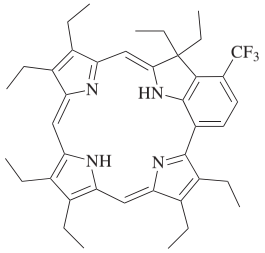
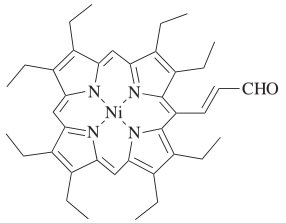
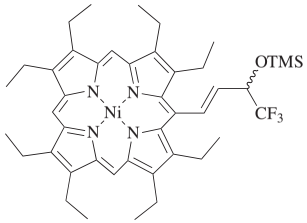
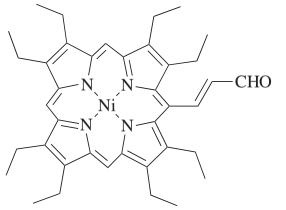
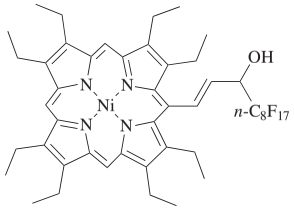
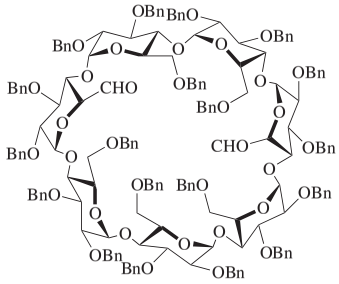
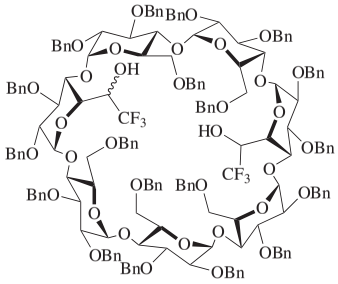
C_{39}		1. $TMSCF_3$ 2. H_2SO_4		(—)	428
		$TMSCF_3$ (2 eq), TBAF (8 mol %), THF, 0°, 0.5 h		(92)	427
		*n*-$C_8F_{17}Br$, *n*-$C_6H_{13}MgBr$, THF, –70°; –60°, 10 min		(81)	427

TABLE 9. PERFLUOROALKYL ADDITION TO ALDEHYDES (*Continued*)

Aldehyde	Conditions	Product(s) and Yield(s) (%)		Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_{42} 	1. $TMSCF_3$ (20 eq), **27a** (0.3 eq), DMF, rt, 1.5 h 2. TFA, EtOAc, MeOH, rt, 10 min		(27)	945

[a] The yield was determined by ^{19}F NMR spectroscopy.

[b] See the original literature for details.

[c] The product was recovered from the Amberlyst A-15 resin by washing with NH_3 in MeOH.

[d] The yield was determined by gas chromatography.

[e] The yield was 80% when the reaction was carried out at –20°.

[f] At –20° reaction temperature, only the initial, uncyclized product was formed in 91% yield.

[g] The reaction was carried out in the presence of 4 Å molecular sieves.

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES

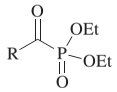
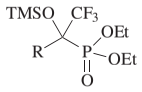
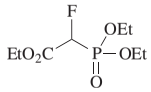
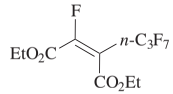
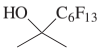
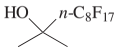
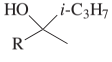
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{2-5} 	1. $TMSCF_3$ (1.5 eq), K_2CO_3 (0.2 eq), DMF, rt 2. NaCl, H_2O, rt	 R: Me (90); Et (88); *i*-Pr (70); *t*-Bu (89)	423
C_2 	1. *n*-BuLi, THF, –78° 2. EtO_2CCOCl, THF, –78°, 1 h; –10°, 5 h 3. *n*-C_3F_7MgBr, Et_2O, THF, –78° to rt, 6 h; rt, o/n	 (63)	946
C_3 	$TMSCF_3$, Et_4NCN	 (75)	137
	CF_3Br, Mg/Hg, Et_2O, –20°	 (—)	634
	n-C_3F_7I, Mg, Et_2O, rt to –80°, quickly; –80°, 58 h; rt	 (10)	201
	n-C_3F_7I, MeLi, Et_2O, –40° to rt, 3 h; reflux, 1 h	 (—)	188
	n-C_3F_7MgI, Et_2O, –30° to rt	 (48) 21% conv	203
	n-C_3F_7MgI, *n*-Bu_2O, –25°, 8 h; –25° to rt, o/n; rt to 60°	 (32)	202

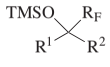
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_3 	*n*-$C_6F_{13}I$, Ca(Hg), THF	 (40) +  (30)	211
	n-$C_8F_{17}MgBr$, Et_2O, –78° to rt, 3h	 (90)	130
C_{3-8} 	1. CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 2 h 2. HCl, H_2O	 (—)	859
		R / Temp (°) / Time (h) / Conv (%) Me / 160 / 4 / 73.5 Et / 160 / 4 / 53.7 Pr / 170 / 4 / 43.9 Ph / 170 / 6 / 2.3	859 859 859 860
	1. CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 2 h 2. HCl, H_2O, 4 h		600
		R / Temp (°) Me / 160 / (73.5) Et / 160 / (53.7) Pr / 170 / (43.9) Ph / 180 / (2.3)	
	1. $TMSCF_3$ (1.025 eq), CsF (1 mol %), rt 2. HCl, H_2O, rt, 2 h		470
		R / Time (h) Me / 1.5 / (89) Ph / 5 / (93)	
C_{3-4} 	*i*-C_3F_7M, Et_2O, 6 h		217
		R / M / Temp (°) Me / Li / –78 to rt / (13) Me / MgBr / –78 to rt / (35) Et / MgBr / –40 to rt / (24.5)	

C_{3-13}

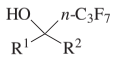


$TMSR_F$ (x eq), KF (0.17 eq), $Me[O(CH_2)_2O]_4Me$, 20–30°



R^1	R^2	R_F	x	Time (h)		
Me	Me	CF_3	1	6	(73)	126
i-Bu	Me	C_2F_5	1.1	18	(75)	
Ph	Me	C_2F_5	1.05	6	(85)	
Ph	CF_3	C_2F_5	1.1	18	(85)	
Ph	Ph	CF_3	1.1	18	(81)	

n-C_3F_7MgBr, Et_2O, –50° to rt

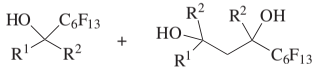


R^1	R^2		
Me	Me	(38)	855
$-(CH_2)_5-$		(90)	
Ph	Me	(77.4)	
Ph	Ph	(62)	

C_{3-9}



n-$C_6F_{13}I$ (1 eq), Ca/Hg, THF



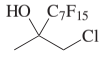
I **II** **III** 210

R^1	R^2	Temp (°)	Time (h)	**I**	**II**	**III**
Me	Me	–40	20	(37)	(28)	(—)
Me	Et	–30	18	(29)	(10)	(—)
Et	Et	–40	8	(66)	(—)	(—)
$-(CH_2)_5-$		–20	8	(58)	(—)	(—)
i-Pr	*i*-Pr	–40	18	(40)	(—)	(31)
n-Bu	*n*-Bu	–30	15	(22)	(—)	(—)

C_3



n-$C_7F_{15}MgBr$, Et_2O, –30°,1 h; –30° to 0°



(62) 862

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-13}



CF_3Br, e^-, Zn anode, Bu_4NBr, additive, solvent



234

R^1	R^2	Additive	Solvent (s)	
CH_2Cl	CH_2Cl	—	DMF	(31)
	$-(CH_2)_5-$	—	DMF	(5)
	$-(CH_2)_5-$	—	DMF/TMEDA (7:3)	(20)
Ph	Me	—	DMF	(5)
Ph	Me	$ZnBr_2$	DMF/TMEDA (7:3)	(37)
Ph	MeO_2C	—	DMF/TMEDA (7:3)	(45)
$Ph(CH_2)_2$	Me	—	DMF/TMEDA (7:3)	(33)
Ph	Ph	—	DMF	(57)

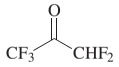
CF_3Br, e^-, Zn anode, Ni cathode, Bu_4NBr (0.5 eq), additive (2.5 eq), solvent, –10°, 4–12 h



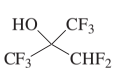
868

R^1	R^2	Additive	Solvent (s)	
CH_2Cl	CH_2Cl	—	DMF	(31)
Ph	Me	—	DMF	(5)
Ph	Me	—	pyridine	(5)
Ph	Me	—	DMF/TMEDA (7:3)	(16)
Ph	Me	$ZnBr_2$	DMF/TMEDA (7:3)	(37)
Ph	MeO_2C	—	DMF/TMEDA (7:3)	(45)
$Ph(CH_2)_2$	Me	—	DMF/TMEDA (7:3)	(33)
Ph	Ph	—	DMF	(57)

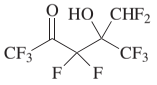
C_3



1. $TMSCF_3$ (0.96 eq), KF (1.1 eq), MeCN, –40° to rt
2. H_2SO_4



(17.1) +



(13.3) 465

C_{3-7}



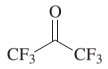
TMSCF$_3$ (1 eq), KF (*x* eq), additive (*y* eq), solvent



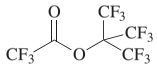
587

R^1	R^2	*x*	Additive	*y*	Solvent	Temp 1 (°)	Time 1 (h)	Temp 2 (°)	Time 2 (h)	
CF_3	CHF_2	2.17	—	—	MeCN	–40	15.5	19	0.75	(46)
CF_3	CF_2Cl	1.1	—	—	MeCN	–40	15.5	19	2.5	(91)
CF_3	CF_3	1.27	—	—	acetone	–40	19	18	3	(92.8)
i-C_3F_7	*i*-C_3F_7	1.13	18-crown-6	0.33	Et_2O	–10	–0.5	20	11.5	(13.2)

C_3



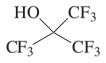
TMSCF$_3$ (1 eq), KF (cat.), MeCN, rt, 2–5 h



(>65)

397

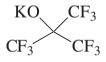
1. TMSCF$_3$ (0.63 eq), KF (0.8 eq), MeCN, –40°, 9 h; 18°, 3 h
2. H_2SO_4



(91.3) based on TMSCF$_3$ equivalents

465

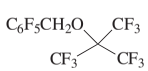
TMSCF$_3$ (0.61 eq), KF (1.05 eq), MeCN, –25° to rt, 16 h



(90.8) based on TMSCF$_3$ equivalents

465

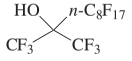
1. TMSCF$_3$ (1 eq), CsF (1.2 eq), MeCN, 60°, 20 h
2. $C_6F_5CH_2Br$ (1 eq), 90°, 48 h



(75)

466

n-$C_8F_{17}MgBr$, THF, –70° to rt, 4 h



(64)

130

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-8}

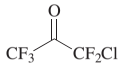


1. R_FI, TDAE (1 eq), solvent, 2 h
2. HCl, H_2O, rt

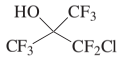


R	R_F	Solvent	Temp (°)		Refs.
CF_3	n-C_4F_9	DMF	–30 to –20	(42)	127
Ph	C_2F_5	THF	–40 to –20	(45)	
Ph	n-C_4F_9	DME	–40 to –30	(59)	

C_3

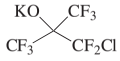


1. $TMSCF_3$ (0.63 eq), KF (0.69 eq), MeCN, –40° to rt, 18 h
2. H_2SO_4

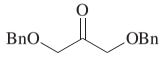


(88.6) based on $TMSCF_3$ equivalents — 465

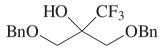
$TMSCF_3$ (0.63 eq), KF (0.69 eq), MeCN, –40° to rt, 18 h



(83) based on $TMSCF_3$ equivalents — 465

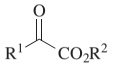


1. $TMSCF_3$ (1.46 eq), TBAF (1.1 eq), THF, <10°; rt, 18 h
2. HCl

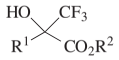


(81) — 947

C_{3-8}



1. $TMSCF_3$ (1.2 eq), TBAF (0.1 eq), THF, 0°, time 1; rt, time 2
2. HCl, H_2O, rt, time 3



418

R^1	R^2	Time 1 (h)	Time 2 (h)	Time 3 (h)	
Me	Me	3	4	3	(72)
Me	Et	3	4	3	(83)
i-Pr	Et	3	5	3	(76)
i-Bu	Et	3	60	18	(82)
Ph	Et	6	60	3	(70)



1. CF_3Br, Zn, pyridine, 20°
2. H_3O^+



R^1	R^2	
Me	EtO_2C	(35)
	$-(CH_2)_5-$	(20)
Ph	Me	(20)
Ph	EtO_2C	(30)

601

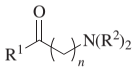
CF_3Br, Zn, pyridine, 1–2 h



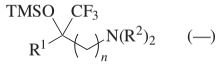
R^1	R^2	Temp (°)	
Me	EtO_2C	0–10	(35)
Ph	Me	20	(20)

861

C_{3-9}



$TMSCF_3$ (0.83 eq), DMF, rt

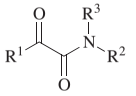


(—)

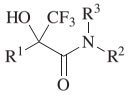
404

R^1	R^2	n	Time (h)	Conv Ketone (%)	Conv $TMSCF_3$ (%)
Me	Et	1	24	trace	43
Me	Et	2	3	82	100
Me	Et	3	3	78	87
Ph	Me	2	3	52	100

C_{3-8}



1. $TMSCF_3$ (1.2 eq), TBAF (2 mol %), THF, rt, 3 h
2. HCl, H_2O, rt, 2 h



R^1	R^2	R^3	
Me	Et	Et	(93)
Me	$-(CH_2)_5-$		(94)
Me	*i*-Bu	*i*-Bu	(92)
Ph	Et	Et	(91)
Ph	$-(CH_2)_2O(CH_2)_2-$		(95)
Ph	$-(CH_2)_5-$		(96)
Ph	*i*-Bu	*i*-Bu	(95)

498, 421

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-9}



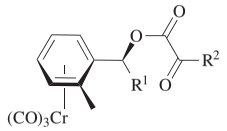
1. $TMSCF_3$ (1 eq), catalyst (*x* mol %), DMF
2. Hydrolysis



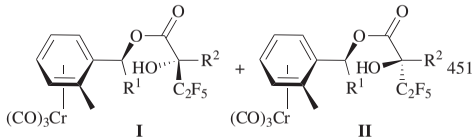
142

R^1	R^2	Catalyst	*x*	Temp	Time (h)	Hydrolysis	
c-$C_6H_{11}O_2C$	Me	**27a**	1	rt	0.5	TBAF, THF, rt, 10 min	(62)
4-$O_2NC_6H_4$	Me	**27b**	10	–25° to rt	1	HCl, H_2O, rt	(75)
$Ph(CH_2)_2$	EtO_2C	**27a**	1	rt	1	TBAF, THF, rt, 75 min	(54)

C_{3-8}



C_2F_5Li, Et_2O, –40°



I + **II**

451

R^1	R^2	**I** + **II**	**I/II**
C_2F_5	Me	(84)	92:8
C_2F_5	Ph	(95)	91.5:8.5
Et	Me	(87)	95:5
Et	Ph	(76)	94:6

C_3



$TMSCF_3$ (1.05 eq), CsF (1 mol %), unspecified solvent, rt, 10 h



(57)

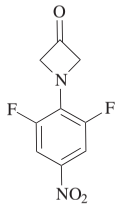
948

$TMSCF_3$ (1.65 eq), TBAF (10 mol %), THF, 20°, 2 h



(83)

949



$TMSCF_3$, TBAF, THF



(16) 950

C_4



$TMSCF_3$ (0.83 eq), Et_3N (1 eq), DMF, rt, 24 h



(—) 38% conv (ketone), 62% conv ($TMSCF_3$) 404



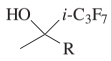
n-$C_6F_{13}I$, Ca(Hg), THF

(31) +  (10) 211

C_{4-8}



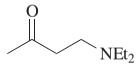
i-C_3F_7I, $SnCl_2$, pyridine, DMF, 70°



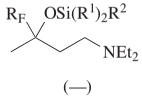
R	Time (h)	
Et	15	(46)
Ph	10	(37)

867

C_4



$R_FSi(R^1)_2R^2$, 100°



(—)

R_F	R^1	R^2	Conv (%)
C_2F_5	Me	Me	35
n-C_3F_7	Me	Me	49
CF_3	Me	Ph	45
CF_3	Ph	Me	56

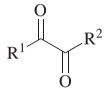
404

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

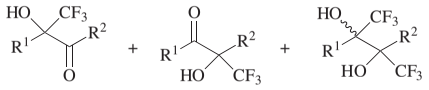
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{4-14}



1. $TMSCF_3$ (x eq), CsF (2 mol %), DME, 0–60°
2. HCl, H_2O, THF, rt, 3 h



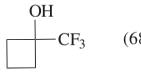
I + **II** + **III** — 438

R^1	R^2	x	**I** + **II**	**III**
Me	Me	>3	minor	major
Me	Et	>3	minor	major
Ph	Me	>3	(—)	(78)
Ph	Ph	2.25	(94)	(—)

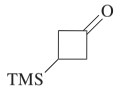
C_4



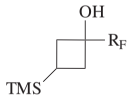
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 2 h
2. HCl, H_2O



(68) — 289

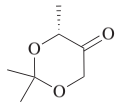


1. $TMSR_F$ (x eq), TBAF (1 mol %), THF, 0°, 5 min
2. TBAF (5 mol %), H_2O, 0° to rt, 0.5–3 h

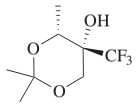


R_F	x	
CF_3	1.4	(80)
C_2F_5	1	(73)

951

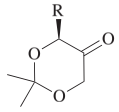


$TMSCF_3$ (1.5 eq), TBAF, THF, 0°

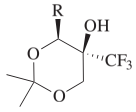


(59) dr >98:2, er >99:1 — 501

C_{4-6}



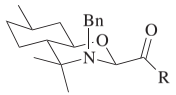
$TMSCF_3$ (1.5 eq), TBAF (1.5 eq), THF, 0°; rt



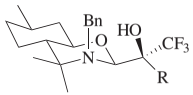
R		dr	er
Me	(69)	>98:2	>99:1
i-Pr	(75)	>98:2	96:4

501

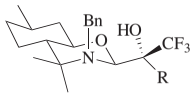
C_{4-8}



1. $TMSCF_3$ (1.5 eq), catalyst (2.5 mol %), solvent, 0°, 1.5–2 h
2. TBAF (1 eq), rt, 1 h


I

+


II

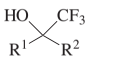
500

R	Catalyst	Solvent	**I**	**II**	**I/II**
Et	TBAF	THF	(82)	(6)	12:1
Et	CsF	THF	(90)	(—)	>50:1
i-Pr	TBAF	Et_2O	(85)	(3)	11:1
i-Pr	TBAF	THF	(87)	(2)	18:1
i-Pr	CsF	Et_2O	(93)	(—)	>50:1
i-Pr	CsF	THF	(95)	(—)	>50:1
n-Bu	TBAF	THF	(92)	(2)	32:1
n-Bu	CsF	THF	(94)	(—)	>50:1
2-furyl	CsF	THF	(96)	(—)	>50:1
Ph	TBAF	Et_2O	(80)	(—)	21:1
Ph	TBAF	THF	(82)	(—)	22:1
Ph	CsF	THF	(95)	(—)	>50:1
4-$MeOC_6H_4$	TBAF	THF	(85)	(—)	>50:1
4-$MeOC_6H_4$	CsF	THF	(93)	(—)	>50:1

C_{5-10}

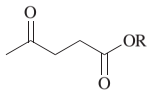
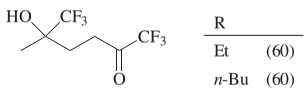
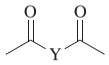


1. $TMSCF_3$ (0.833 eq), initiator (*x* eq), DMF
2. HCl, H_2O


(—)

R^1	R^2	Initiator	*x*	Temp	Time (h)	Conv Ketone (%)	Conv $TMSCF_3$ (%)	
Et	Et	Et_3N	17	rt	24	6	45	138
Et	Et	Et_3N	17	50°	24	11	39	138
Et	Et	Et_3N	20	rt	24	6	45	139
Ph	Me	Et_3N	43	rt	96	6	65	138
Ph	Me	Et_3N	50	rt	96	6	65	139
Ph	Me	Et_3N	83	rt	8	32	100	138
Ph	Me	Ph_3P	8.3	50°	24	trace	48	138
Ph	CF_3	Et_3N	17	rt	24	88	100	138
Ph	CF_3	Et_3N	20	rt	24	88	100	139
n-C_8H_{17}	CF_3	Et_3N	17	rt	5	68	100	138
n-C_8H_{17}	CF_3	Et_3N	20	rt	5	68	100	139

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

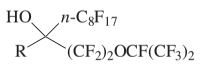
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{5-8} 	*n*-$C_6F_{13}I$, Ca(Hg), THF, –20° to 40°, 2–20 h	 R^1 R^2 (%): Et Et (70); *i*-Pr *i*-Pr (40); Ph Me (30)	211
C_{5-13} 	1. $TMSCF_3$ (1.2 eq), *n*-$Bu_4N^+Ph_3SnF_2^-$ (cat.), THF, rt, 2 h 2. HCl, H_2O	 **I** + **II** R^1 R^2 **I** **II**: *c*-C_3H_5 Me (60) (—); Ph Me (—) (65); Ph Ph (85) (—)	289
C_{5-8} 	CF_3I, Zn, DMF, ultrasound, 1 h	 R (%): CH_2=$CHCH_2$ (45); Ph (55)	396
C_5 	1. $TMSCF_3$ (2 eq), CsF (2 mol %), DME, 0° to rt, 6 h 2. HCl, H_2O, THF, rt, 3 h	 R (%): Et (60); *n*-Bu (60)	438
C_{5-16} 	1. $TMSCF_3$ (3.25 eq), CsF (2 mol %), DME, 2. HCl, H_2O, THF, rt, 3 h	 **I** + **II** Y Temp (°) **I** **II**: CH_2 60 (—) (—); $(CH_2)_2$ rt minor major; $(CH_2)_2$ 60 (—) (78); $(C_6H_4)_2$ 60 (—) (85)	438

C_5



R = $CF_3O[CF_2CF(CF_3)O]_2(CF_2)_2$

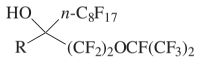
1. *n*-C_8F_{17}TMS (1.1 eq), CsF (1.1 eq), Et_2O, 0°
2. HCl, H_2O



Time (h)	Conv (%)
3	5
8	30
10	33

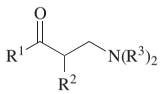
(—) 129

1. *n*-C_8F_{17}TMS (1.1 eq), CsF (1.1 eq), Et_2O/perfluoro-2-butyltetrahydrofuran, (3:1), 0°, 10 h; rt 16 h
2. HCl, H_2O

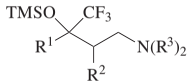


(30) 67% conv 129

C_{5-6}



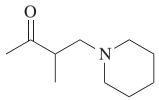
$TMSCF_3$ (0.83 eq), solvent, 3 h



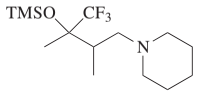
(—) 404

R^1	R^2	R^3	Solvent	Temp	Conv Ketone (%)	Conv $TMSCF_3$ (%)	dr
Me	Me	Me	DMF	rt	51	100	51:49
Me	Me	Me	DMF	0°	49	100	58:42
Me	Me	Me	—	rt	56	92	58:42
Me	Me	Et	DMF	rt	56	100	55.5:44.5
Me	Me	Et	—	50°	10	72	72:28
Me	Et	Me	DMF	rt	36	100	68:32
Me	Et	Me	DMF	0°	29	100	71:29
Me	Et	Me	—	rt	42	94	67.5:22.5
Et	Me	Me	DMF	rt	67	100	54.5:45.5

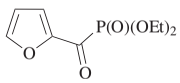
C_5



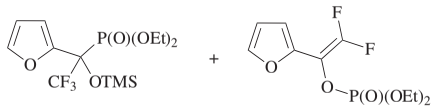
$TMSCF_3$ (0.83 eq), DMF, rt, 3 h



(—) 44% conv (ketone), 100% conv ($TMSCF_3$), dr 51.5:48.5 404

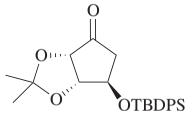
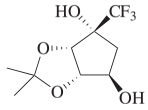
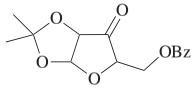
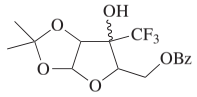
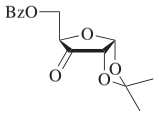
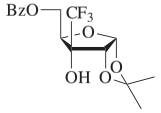
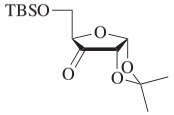
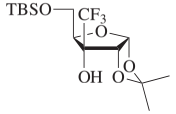
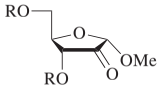
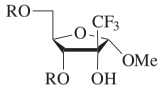
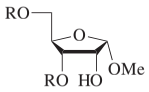
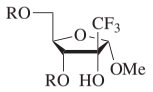


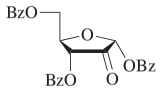
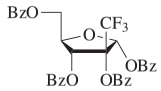
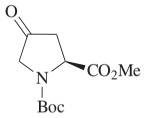
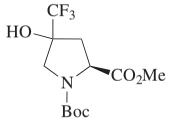
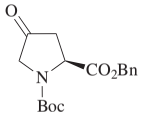
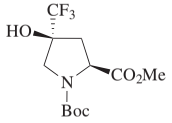
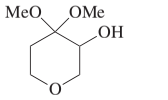
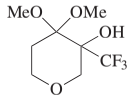
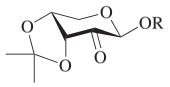
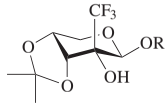
$TMSCF_3$, K_2CO_3, DMF, rt



I (—) **I/II** = 1:1 **II** (—) 423

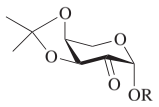
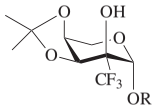
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)		Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_5				
	1. $TMSCF_3$, TBAF (cat.), THF, 0° 2. TBAF, rt		(81)	412
	$TMSCF_3$ (1.3 eq), TBAF (1.3 eq), THF, 0°; rt, 2 h		(70)	511
	$TMSCF_3$ (1.3 eq), TBAF (1.3 eq), THF, 0°; rt, 2 h		(63.2)	510
	1. $TMSCF_3$ (1.1 eq), TBAF (cat.), THF, rt 2. Na (0.1 eq), MeOH, 0°; rt, 1 h		(86)	512
	$TMSCF_3$, TBAF (cat.), THF, 0° to rt		(45) R = 3,5-$Cl_2C_6H_3CH_2$	407
	1. Dess–Martin periodinane (1.5 eq), CH_2Cl_2, 0°; rt, 48 h 2. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, 1 h 3. TBAF (1 eq), MeOH, THF, rt, 2 h		(67) R = 4-$ClC_6H_4CH_2$	515

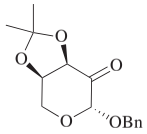
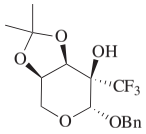
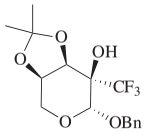
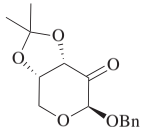
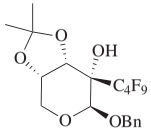
	1. $TMSCF_3$ (1.74 eq), TBAF (5 mol %), THF, rt, 18 h 2. TBAF (0.93 eq), THF, rt, 10 min 3. BzCl (3 eq), DMAP (1.5 eq), Et_3N, CH_2Cl_2, rt, 5 h		(73)	516
	$TMSCF_3$ (2 eq), TBAF (2.1 eq), 0° to rt, 24 h		(56) single diastereomer	952
	1. $TMSCF_3$ (1.07 eq), TBAF (3.5 mol %), THF, 0°; rt, o/n 2. NH_4Cl, H_2O, rt, 0.25 h 3. TBAF (1.6 eq), THF, rt, 1 h		(81)	504
	1. TPAP oxidation 2. $TMSCF_3$, TBAF, THF		(—)	953
	1. $TMSCF_3$ (1.2 eq), catalyst, solvent, 0°, 1 h; rt, 4 h 2. TBAF (1 eq), rt, 6 h			513

R	Catalyst	Solvent	
Me	TBAF	THF	(39)
Me	n-$Bu_4N^+SnPh_3F_2^-$	CH_2Cl_2	(64)
Bn	TBAF	THF	(40)
Bn	n-$Bu_4N^+SnPh_3F_2^-$	CH_2Cl_2	(65)

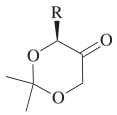
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_5 	1. $TMSCF_3$ (1.2 eq), catalyst, solvent, 0°, 1 h; rt, 4 h 2. TBAF (1 eq), rt, 6 h		513

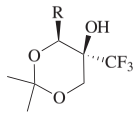
R	Catalyst	Solvent	
Me	TBAF	THF	(40)
Me	n-Bu_4N^+ $SnPh_3F_2^-$	CH_2Cl_2	(70)
Bn	TBAF	THF	(41)

	1. $TMSCF_3$ (1.1 eq), TBAF (0.2 eq), THF, 0°, 1 h; rt, 4 h 2. H_2O		(9)	514
	1. $TMSCF_3$ (1.1 eq), n-Bu_4N^+ $SnPhF_2$– (0.2 eq), CH_2Cl_2, 0°, 1 h; rt, 4 h 2. TBAF (1 eq), MeOH, 12 h		(25)	514
	n-C_4F_9I (19.7 eq), EtMgBr (19.8 eq), Et_2O, –45° to rt, 3 h		(20)	514

C_{5-9}



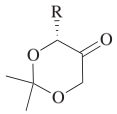
1. $TMSCF_3$ (1.5 eq),
   TBAF (5–10 mol %), THF, 0°; rt
2. TBAF (1.5 eq), 1 h



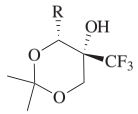
dr >98.2

R		er
Et	(86)	96.5:3.6
n-C_4H_9	(64)	97.0:3.0
n-C_6H_{13}	(94)	97.5:2.5

501



1. $TMSCF_3$ (1.5 eq),
   TBAF (5–10 mol %), THF, 0°; rt
2. TBAF (1.5 eq), 1 h

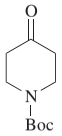


dr >98.2

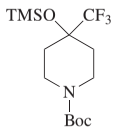
R		er
Et	(52)	96.5:3.5
i-Pr	(73)	96.5:3.5
n-C_4H_9	(73)	97.0:3.0
n-C_6H_{13}	(97)	98.0:2.0

501

C_5



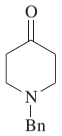
$TMSCF_3$ (1.2 eq),
catalyst (5 mol %),
solvent, 0° to rt, 1 h



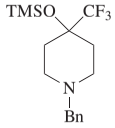
(—)

Catalyst	Solvent	Conv (%)
AcOLi	DMF	80
n-Bu_4NOAc	THF	96

132, 131



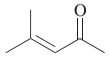
$TMSCF_3$ (1.2 eq),
4 Å MS (0.5 g/mmol),
DMSO, rt, 6 h



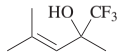
(98) 100% conv

136

C_6



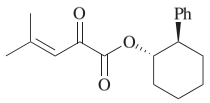
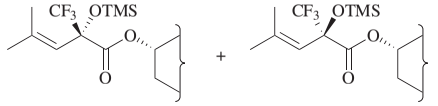
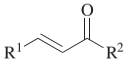
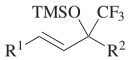
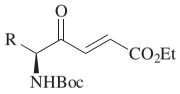
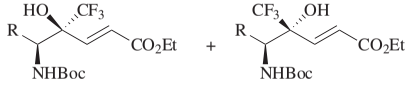
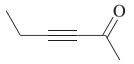
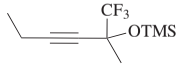
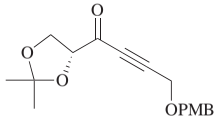
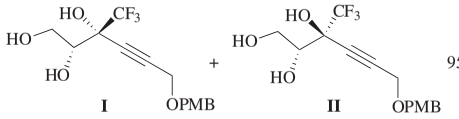
1. $TMSCF_3$ (1.2 eq), TBAF (cat.),
   THF, 0°, 1 h; rt
2. HCl, H_2O

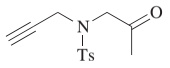


(78)

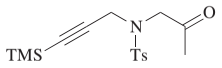
289

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

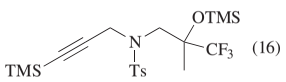
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6 	$TMSCF_3$, TBAF (0.1 eq), toluene	 **I** (—) + **I/II** = 3.5:1 **II** (—)	507
C_{6-15} 	$TMSCF_3$ (1.05 eq), CsF (2 mol %), DME, rt, 3 h	 R^1 R^2 (%): Me Et (97); 2-thienyl Me (98); Ph Me (98); Ph CF_3 (98); Ph Ph (99)	475
C_{6-12} 	1. $TMSCF_3$ (2.05 eq), Cs_2CO_3 (10 mol %), MeOH (20 mol %), DMA, 0°, 5 min 2. Substrate (1 eq), 0°; rt, 50 min	 **I** + **II** R: Me **I** (24) **II** (6); Bn **I** (63) **II** (4)	502
C_6 	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt 2. HCl, H_2O	 (70)	289
	1. $TMSCF_3$, TBAF (cat.), THF, rt, 1 h 2.TsOH. MeOH, rt, 20 h	 **I** + **II** (65), **I/II** 1.3:1	954



$TMSCF_3$ (1.6 eq),
KF (2 mol %), DMF, rt, 21 h



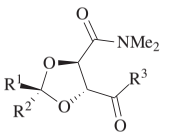
(72)



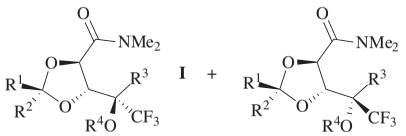
(16)

414

C_{6-10}



1. $TMSCF_3$, K_2CO_3 (cat.), DMF, rt
2. *t*-BuOK, R^4Cl, *n*-Bu_4NI (cat.)



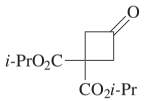
I +

II

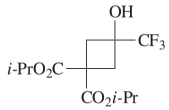
422

R^1	R^2	R^3	R^4	**I**	**II**	**I/II**
Me	Me	Et	Bn	(67)	(10)	82:18
H	Ph	Et	Bn	(53)	(—)	79:21
Me	Me	Ph	CH_2=$CHCH_2$	(73)	(—)	93:7
H	Ph	Ph	CH_2=$CHCH_2$	(58)	(—)	86:14

C_6

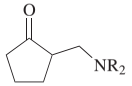


$TMSCF_3$ (1 eq), CsF (0.4 eq),
THF, 0° to rt, 15 h

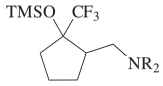


(90)

955



$TMSCF_3$ (0.83 eq), DMF, rt, 3 h

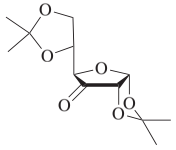
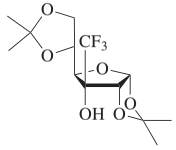
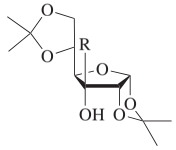
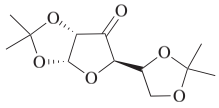
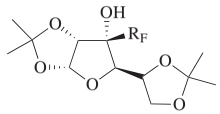
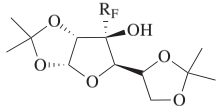
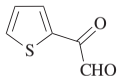
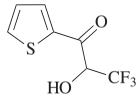
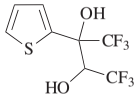


(—)

404

R	Conv Ketone (%)	Conv $TMSCF_3$ (%)	dr
Me	32	100	59:41
Et	24	100	63:37

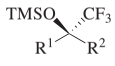
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6 	1. $TMSCF_3$ (1.1 eq), TBAF (cat.), THF, rt 2. TBAF (1 eq), MeOH, rt, 1 h	 (88)	512
	1. TMSR (1.1 eq), *n*-Bu_4N^+ $Ph_3SnF_2^-$ (cat.), CH_2Cl_2 2. HCl, H_2O or TBAF, MeOH	 R: CF_3 (88); *n*-C_4F_9 (70)	216
	1. R_FMgBr (1.2 eq), Et_2O, –45° 2. H_3O^+	 **I** R_F = *n*-C_4F_9 (68); *n*-C_6F_{13} (59); **I + II**; **I/II** = 78:22; 73:27 +  **II**	216
	1. $TMSCF_3$ (2.05 eq), CsF (2 mol %), DME, 0°, 1 h; rt, 5 h 2. HCl, H_2O, THF, rt, 3 h	 (78) +  (—)	438

C_{6-12}

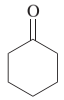


$TMSCF_3$ (1.4 eq), **45j** (0.1 eq), toluene/CH_2Cl_2 (7:3), –78°, 1 h



R^1	R^2		er	
2-thienyl	Me	(72)	66.5:33.5[a]	529, 528
3-pyridyl	Me	(90)	73.0:27.0	
4-pyridyl	Me	(93)	80.0:20.0	
3-BrC_6H_4	Me	(97)	80.5:19.5[a]	
4-BrC_6H_4	Me	(97)	72.0:28.0[a]	
2-$O_2NC_6H_4$	Me	(93)	85.5:14.5[a]	
3-$O_2NC_6H_4$	Et	(99)	82.0:18.0[a]	
4-$O_2NC_6H_4$	Me	(97)	86.5:13.5[a]	
3-$MeOC_6H_4$	Me	(90)	79.5:20.5[a]	
3-NCC_6H_4	Me	(96)	85.5:14.5[a]	
1-$C_{10}H_7$	Me	(91)	75.5:24.5[a]	
2-$C_{10}H_7$	Me	(95)	88.5:11.5[a]	

C_6



CF_3NO, TMS_2NNa, THF, –100°



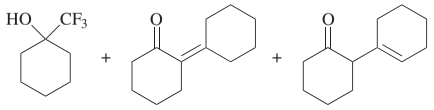
(30) 165

1. CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 170°, 2 h
2. HCl, H_2O, 170°, 4 h



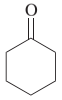
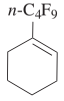
(—) 56.2% conv 860

CF_3CO_2K (1.69 eq), DMF, 140°, 5.5 h



I (10) **II** **II** + **III** (40) **III** 887

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6 	CF_3I (2.2 eq), TDAE (2.2 eq), DMF, *h*ν, –20° to rt, 12 h	 (76) 100% conv	385
	C_2F_5I (1.77 eq), MeLi (1.77 eq), LiBr, Et_2O, –78°, 8 min	 (100)	392, 391
	n-$C_6F_{13}I$, Ca(Hg), THF, –20 to 40°, 2–20 h	 (60)	211
	R_FI (2.2 eq), TDAE (2.2 eq), DMF, –15° to rt; *h*ν, 1 h; rt, 12 h	 R_F: CF_3 (50); C_2F_5 (50); *n*-C_4F_9 (20)	386
	1. *n*-C_4F_9I, Mg, Et_2O, –78°, sonication 2. Ac_2O, AcOH, *p*-TsOH (cat.) or AcCl, pyridine 3. 650–700° in flow	 (85)	956
	R_FMgBr, Et_2O, –78° to rt, 1 h	 R_F: *n*-C_3F_7 (75); *n*-C_8F_{17} (86)	206
	1. **64a** (1 eq), TBAT (0.1 eq), THF, rt 2. TBAF (1 eq), THF, 1 h	 (30)	121

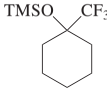
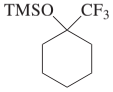
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h 2. HCl, H_2O, rt, 1 h		(77)	288
1. $TMSCF_3$ (1.25 eq), TBAF (0.12 mol %), THF, 0° to rt, 1.5 h 2. HCl, H_2O, rt, 8 h		(79–82)	91
$TMSCF_3$ (2 eq), *t*-Bu_3P (0.1 eq), DMF, rt, 0.25–1 h		(81)	140
1. $TMSCF_3$ (1.5 eq), TBAF (1 eq), THF, microreactor, 20 s 2. HCl, H_2O		(—) 7% conv	892
$TMSCF_3$ (2 eq), KF (0.1 eq), *n*-Bu_4NBr (0.1 eq), toluene, rt, 2 h		(48)	457
1. $TMSR_F$ (1.2 eq), TBAF (cat.), THF, 0° to rt 2. TBAF, THF, 0° to rt, 5 h		R_F / C_2F_5 (82) / *n*-C_3F_7 (81)	122

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

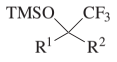
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{6-15}



$TMSCF_3$ (1.5 eq), $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$ (5 mol %), solvent, rt



R^1	R^2	Solvent	Time (h)	
$-(CH_2)_5-$		DMF	12	(78)
C_5H_{11}	Et	DMF	22	(76)
Ph	Me	DMF	0.5	(88)
Ph	Me	THF	14	(84)
$4\text{-}ClC_6H_4$	Me	DMF	0.5	(85)
$4\text{-}CF_3C_6H_4$	Me	DMF	0.5	(87)
Ph	Et	DMF	0.5	(80)
$Ph(CH_2)_2$	Me	DMF	4	(84)
(*E*)-PhCH=CH	Me	DMF	0.5	(92)
(*E*)-PhCH=CH	Ph	DMF	0.5	(75)

141

C_{6-13}



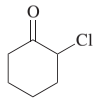
$TMSCF_3$ (2 eq), additive (*x* eq), $CF_3CH_2CF_2Me$, rt



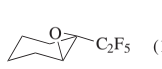
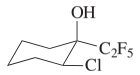
R^1	R^2	Additive	*x*	Time (min)	
$-(CH_2)_5-$		KOH	0.2	20	(72)
Me	Ph	$CsOH{\bullet}H_2O$	0.1	20	(89)
Me	$2\text{-}C_{10}H_7$	KOH	0.2	60	(97)
Ph	Ph	$CsOH{\bullet}H_2O$	0.1	120	(93)

387

C_6

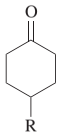


C_2F_5MgBr, Et_2O, –30°, 1 h; –30 to 0°

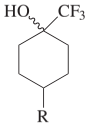

(17) +

(83)

862

C_{6-10}

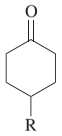


CF_3Br, e^-, Zn anode, Ni cathode, Bu_4NBr (0.5 eq), additive (2.5 eq), solvent, –10°, 4–12 h

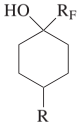


R	Additive	Solvent (s)		
H	—	DMF	(5)	868
t-Bu	—	DMF/TMEDA (7:3)	(25)	
t-Bu	$ZnBr_2$	DMF/TMEDA (7:3)	(32)	

C_{6-12}

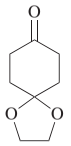


1. $TMSR_F$ (1.2 eq), TBAF (0.1 eq), THF, rt, 1 h
2. HCl, H_2O

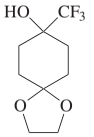


R	R_F		*trans*/*cis*	
H	CF_3	(77)	—	468
Me	CF_3	(71)	72:28	
Me	C_2F_5	(86)	69:31	
Et	CF_3	(73)	74:26	
i-Pr	CF_3	(77)	76:24	
i-Pr	C_2F_5	(84)	70:30	
t-Bu	CF_3	(68)	78:22	
Ph	CF_3	(89)	77:23	

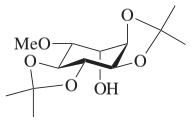
C_6



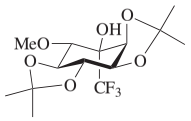
1. $TMSCF_3$ (1.1 eq), TBAF (3 mol %), THF, rt, 2 d
2. TBAF (1.1 eq), THF, 1 h



957



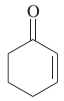
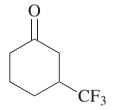
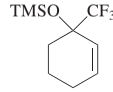
1. $(COCl)_2$, DMSO, *i*-Pr_2NEt, CH_2Cl_2, –73 to –30°, 1 h
2. $TMSCF_3$, TBAF (1 eq), THF, 1 h



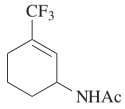
(38)

517

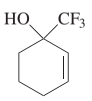
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6 	C_2F_5I (1.56 eq), MeLi (1.24 eq), LiBr, Et_2O, –78°, 0.5 h	 (81)	392, 391
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h 2. HCl, H_2O, rt, 15 h	 **I** +  **II** **I** + **II** (60), **I**/**II** > 9:1	288, 289
	$TMSCF_3$ (1.05 eq), CsF (2 mol %), DME, rt, 3 h	 (96)	475
	1. $TMSCF_3$ (1.1 eq), initiator (0.1 eq), **23** (1 eq) 2. HCl, H_2O, rt, 3 h		339

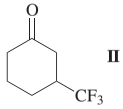
Initiator	Temp (°)	Time (h)	
CsF	rt	0.5 h	(98)
Ph_3P	35	24	(98)

	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF 2. HCl, H_2O or TBAF (1 eq), THF	 (—)	473
	1. $TMSCF_3$ (1.2 eq), TBAF (5 mol %), THF, rt 2. MeCN, H_2SO_4, reflux, 3 h	 (54)	467

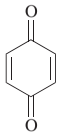
1. $TMSCF_3$ (x eq), initiator (y eq), Lewis acid (1 eq), solvent
2. HCl, H_2O



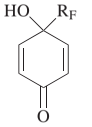
I (—) + **II** 290



x	Initiator	y	Lewis Acid	Solvent	Temp	Time (h)	Conv **I** (%)	Conv **II** (%)	**II**
2	TMAF	1	—	THF	rt	4	84	—	(—)
3	TMAF	2.5	$(PhO)_3Al$	CH_2Cl_2	rt	4	59	—	(—)
3	TMAF	2.5	**25**	CH_2Cl_2	rt	18	3	5	(—)
3	TMAF	1	**26**	CH_2Cl_2	rt	4	—	25	(—)
3	TMAF	2	**26**	CH_2Cl_2	rt	4	—	48	(—)
3	TMAF	3	**26**	CH_2Cl_2	–35°	5	3	53	(—)
3	TMAF	3	**26**	CH_2Cl_2	rt	4	1	55	(—)
2	*t*-BuOK	3	**26**	CH_2Cl_2	rt	19	—	56	(46)

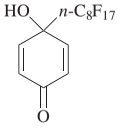


R_FI, MeLi/LiBr, Et_2O, –78°



(—) R_F = n-C_4F_9, n-C_6F_{13}, n-C_8F_{17} 958

n-$C_8F_{17}I$, MeLi/LiBr, Et_2O, –78°, 1 h



(50) 625

1. $TMSCF_3$, TBAF (0.1 eq)
2. H_3O^+



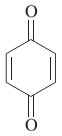
(—) 455

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

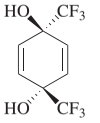
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

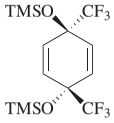
C_6



1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 6 h
2. TMAF, H_2O, 5 h



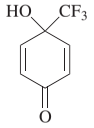
I (—) +



II (—) 482

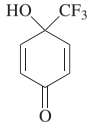
I + **II** (96)

Et_3SiCF_3 (1.18 eq), NH_4HF_2 (1.18 eq), MeCN, rt, 0.5 h



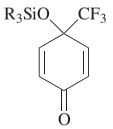
(42) 489

Et_3SiCF_3 (1.17 eq), KF (2.83 eq), AcOH (1.17 eq), MeCN, rt, 0.25 h



(34) 489

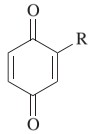
R_3SiCF_3 (*x* eq), initiator (*y* eq), solvent, rt



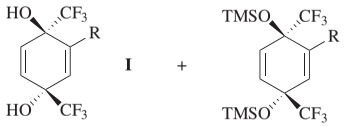
R	*x*	Initiator	*y*	Solvent	Time (h)		
Et	1	DMAP	0.05	MeCN	o/n	(50)	489
Et	1	K_2CO_3	2	DMF	1	(53)	489
Et	1.17	$(Et_2N)_3P$	—	MeCN	24	(63)	489
Et	1.17	*n*-Bu_4NHF_2	0.1	MeCN	0.5	(33)	489, 489a
Et	1.17	$(EtO)_3P$	0.2	MeCN	21	(51)	489
Et	1.17	NaOH	3	MeCN	2	(29)	489
Et	1.17	LiN_3	3	MeCN	22	(43)	489
Et	1.18	CsF	1	MeCN	o/n	(—)	489
Et	1.18	KHF_2	1.18	MeCN	2	(42)	489, 489a

Et	1.2	NaCN	0.2	MeCN	42	(41)	489
Et	1.2	KCN	3	MeCN	1	(64)	489
Et	1.53	KF	1.94	MeCN	1	(72)	489
n-Bu	1	K_2CO_3	0.2	DMF	1	(52)	489
n-Bu	1.17	*n*-Bu_4NHF_2	0.1	MeCN	0.5	(—)	489a
n-Bu	1.18	KHF_2	1.18	MeCN	2	(—)	489a
n-Bu	1.53	KF	1.94	MeCN	1	(59)	489

C_{6-7}



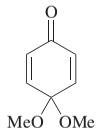
1. $TMSCF_3$ (*x* eq), TMAF (*y* eq), THF, 0°, 0.5 h; rt, 24 h
2. TMAF (*z* eq), THF, rt, 24 h



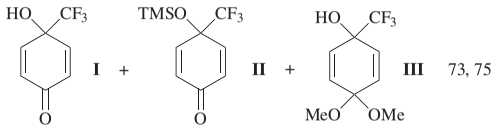
I + **II** 483

R	*x*	*y*	*z*	**I** + **II**
H	4.39	0.17	0.58	(96)
Me	4.96	0.2	0.66	(95)

C_6

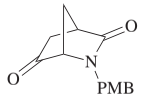


1. CF_3H, TMS_3N (1.5 eq), initiator (*x* eq), DMF, –10°
2. Work-up

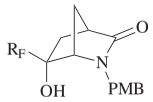


I + **II** + **III** 73, 75

Initiator	*x*	Work-up	**I**	**II**	**III**
TMAF	0.5	HCl, H_2O	(—)	(44)	(—)
TMAF	1.5	H_2O	(22)	(—)	(45)
TBAT	1.5	$NaHCO_3$, H_2O	(—)	(—)	(50)



$TMSR_F$ (1.5 eq), TBAF (0.1 eq), THF, rt, 2 h

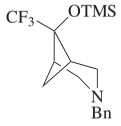


R_F	
CF_3	(94)
C_2F_5	(—)

816

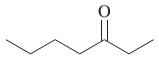
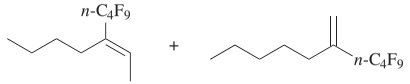
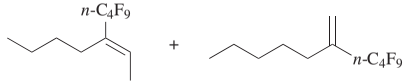
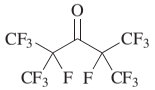
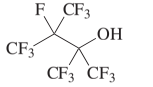
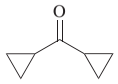
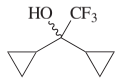
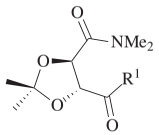
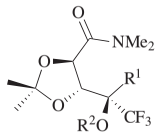
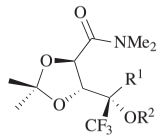


$TMSCF_3$ (1.4 eq), CsF (0.4 eq), THF, –5°; rt, 16 h



(100) 959

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_7			
	1. *n*-C_4F_9I, MeLi or Mg sonication, Et_2O, –78° 2. $SOCl_2$ (5 eq), pyridine (cat.), reflux, 4–10 h	 (25), (*E*)/(*Z*) = 97:3 (13)	956
	1. *n*-C_4F_9I, MeLi or Mg sonication, Et_2O, –78° 2. Ac_2O, AcOH, *p*-TsOH (cat.) or AcCl, pyridine 3. 650–700° in flow	 (38), (*E*)/(*Z*) = 98:2 (47)	956
	1. $TMSCF_3$ (1.1 eq), KF (1.13 eq), 18-crown-6 (0.3 eq), Et_2O, –10°, 0.5 h; 20°, 11.5 h 2. H_2SO_4	 (21.2)	465
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 2 h 2. HCl, H_2O	 (70)	289
$C_{7–10}$			
	1. $TMSCF_3$, K_2CO_3 (cat.), DMF, rt 2. *t*-BuOK, R^2Cl, *n*-BuN_4I (cat.)	 **I** +  **II**	422

R^1	R^2	**I**	**II**	**I + II**	**I/II**
c-C_3H_5	Bn	(—)	(—)	(82)	70:30
2-thienyl	CH_2=$CHCH_2$	(72)	(4)	(—)	89:11
4-FC_6H_4	CH_2=$CHCH_2$	(22)	(—)	(—)	91:9
3,5-$F_2C_6H_3$	CH_2=$CHCH_2$	(33)	(—)	(—)	77:23
2-$MeOC_6H_4$	CH_2=$CHCH_2$	(53)	(14)	(—)	79:21
4-$MeOC_6H_4$	CH_2=$CHCH_2$	(72)	(—)	(—)	94:6

$C_{7–12}$



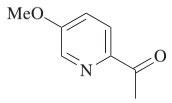
1. *n*-Bu_3SnCF_3 (*x* eq), CsF (20 mol %), rt
2. NH_4Cl, H_2O



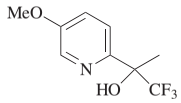
R^1	R^2	*x*	Time (h)	
2-pyridyl	Me	1.1	15	(41)
Ph	Me	1.1	24	(53)
Ph	CF_3	1.1	96	(66)[b]
4-ClC_6H_4	Me	1.3	24	(69)
4-$MeOC_6H_4$	Me	1.3	24	(72)
4-$MeO_2CC_6H_4$	Me	1.1	15	(71)
2-$C_{10}H_7$	Me	1.1	30	(78)

156

C_7

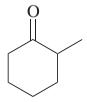


$TMSCF_3$, LiOAc, DMF, rt, 1.5 h

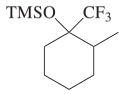


(87)

960



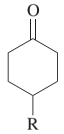
$TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° or –78°



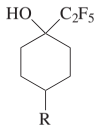
(—) dr 3:2

122

$C_{7–9}$



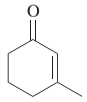
1. $TMSC_2F_5$ (1.2 eq), TBAF (1.1 mol %), THF, rt, 1 h
2. HCl, H_2O



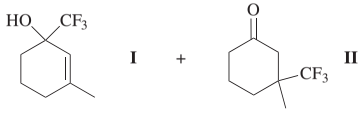
R	
Me	(86)
i-Pr	(84)

961

C_7



1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt
2. HCl, H_2O



I + **II** (57), **I**/**II** = 97:3

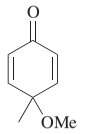
289

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

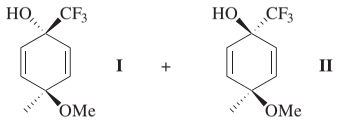
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7



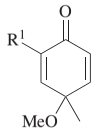
$TMSCF_3$, TBAF (cat.), 0°



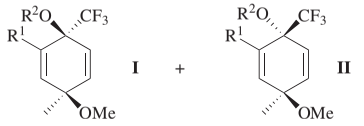
I + **II** (88), **I**/**II** = 1:1

962

C_{7-11}



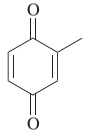
CF_3H, base (*x* eq), DMF, –10°



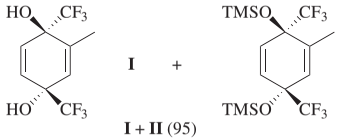
R^1	Base	*x*	R^2	Conv **I** (%)	**I**	Conv **II** (%)	**II**	*dr* **I**:**II**
H	*t*-BuOK	1.1	H	42	(42)	33	(33)	56.0:44.0
H	TMS_3N, TMAF	1.5, 0.2	TMS	38	(21)	26	(22)	59.5:40.5
t-Bu	*t*-BuOK	1.1	H	50	(47)	9	(9)	84.5:15.5
t-Bu	TMS_3N, CsF	1.5, 0.2	TMS	44	(26)	8	(7)	84.5:15.5

73, 75

C_7

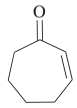


1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 7 h
2. TMAF, H_2O, 5 h

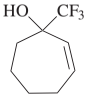


I + **II** (95)

482



1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF
2. HCl, H_2O or TBAF (1 eq), THF



(—)

473



1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt
2. HCl, H_2O



(89) 289

1. $TMSCF_3$ (1.1 eq), initiator (0.1 eq), **23** (1 eq)
2. HCl, H_2O, rt, 3 h



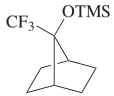
Initiator	Temp	Time (h)		
CsF	rt	1	(94)	339
Ph_3P	35°	24	(95)	

1. $TMSCF_3$ (1 eq), CsF (1 mol %), DME, rt, 1 h
2. HCl, H_2O, rt, 2 h



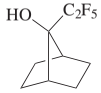
(90) 470

$TMSCF_3$ (1.25 eq), KF (0.2 eq), *t*-BuOK, THF, reflux, 5–10 min



(93–98) 92

C_2F_5I (1.5 eq), MeLi/LiBr, Et_2O, –78°, 0.5 h



(89–93) 92



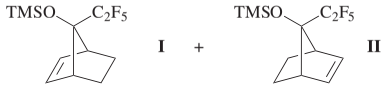
$TMSCF_3$ (1.25 eq), KF (0.2 eq), *t*-BuOK, THF, reflux, 5–10 min



I + **II** 92

I + **II** (91–97), **I/II** = 5:1

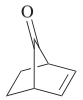
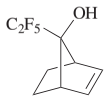
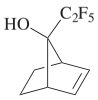
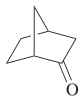
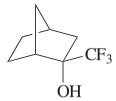
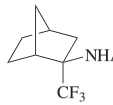
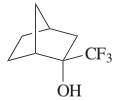
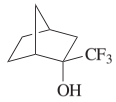
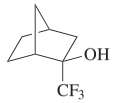
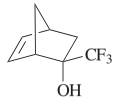
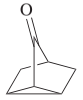
$TMSC_2F_5$ (1.25 eq), KF (0.2 eq), *t*-BuOK, THF, reflux, 5–10 min



I + **II** 92

I + **II** (91–97), **I/II** = 5:1

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_7 	C_2F_5I (1.19 eq), MeLi/LiBr, Et_2O, –78°, 0.75 h	 (84–95) +  (—)	92, 391, 392
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h 2. HCl, H_2O, rt, 4 h	 (92)	288
	1. $TMSCF_3$ (1.2 eq), TBAF (5 mol %), THF, rt 2. MeCN, H_2SO_4, AcOH, reflux, 24 h	 (32)	467
	1. $TMSCF_3$ (1 eq), CsF (1 mol %), DME, rt, 1.5 h 2. HCl, H_2O, rt, 2 h	 (95)	470
	$TMSCF_3$, TBAF, THF	 **I** +  **II** **I** + **II** (58), **I/II** = 98:2	469
	CF_3H (7 eq), **22b** (3 eq), TMS_2NH (6 eq), DMF, –50°, 10 min; –10°, 5 h	 (65)	69
	$TMSCF_3$ (1.25 eq), KF (0.2 eq), *t*-BuOK, THF, reflux, 5–10 min	 (92–96)	92

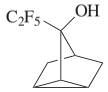
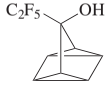
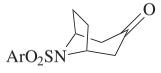
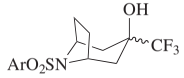
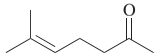
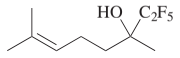
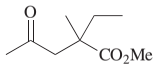
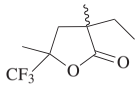
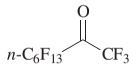
	C_2F_5I (1.5 eq), MeLi/LiBr, Et_2O, –78°, 0.5 h		(89–96)		92
	$TMSCF_3$ (1.25 eq), KF (0.2 eq), *t*-BuOK, THF, reflux, 5–10 min		(83–93)		92
	C_2F_5I (1.5 eq), MeLi/LiBr, Et_2O, –78°, 0.5 h		(92–98)		92
	$TMSCF_3$, TBAF, THF, 0° to rt		(—)	Ar = 4-*t*-BuC_6H_4	962
C_8 	C_2F_5I (1.5 eq), MeLi (1.3 eq), LiBr, Et_2O, –78°, 0.5 h		(86)		392, 391
	1. $TMSCF_3$ (1.38 eq), TBAF, THF, 0°; rt, 2 h 2. H_2SO_4, acetone, H_2O, o/n		(94)		494

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

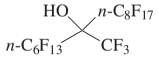
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_8



1. *n*-C_8F_{17}TMS (1.1 eq), CsF (*x* eq), solvent
2. HCl, H_2O

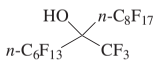


I + C_8F_{16} **II** (—) 129

x	Solvent	Temp (°)	Conv **I** (%)	**I**
0.06	Et_2O	0	5	(—)
1.07	MeCN	0	33	(—)
1.1	Et_2O	0	91	(60)
1.1	Et_2O	rt	60	(—)
1.21	THF	0	41	(—)

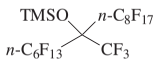
+ *n*-$C_8F_{17}H$ **III** (—) + $C_{16}F_{32}$ **IV** (—)

1. *n*-C_8F_{17}TMS (0.97 eq), CsF (0.98 eq), Et_2O, 0°, 8 h
2. Hydrolysis



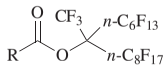
(75) 464

1. *n*-C_8F_{17}TMS (1.05 eq), CsF (1.16 eq), Et_2O, 0°, 20 h
2. TMSCl (1.68 eq), 0°; rt, 47 h



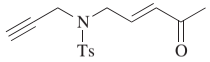
(70) 93% conv 464

1. *n*-C_8F_{17}TMS (*x* eq), CsF (*y* eq), Et_2O, 0°, 20 h
2. RCOX (*z* eq), 0°; rt

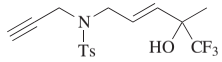


464

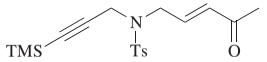
x	*y*	R	X	*z*	Time (h)	Conv (%)	
0.97	0.98	*n*-C_3F_7	Cl	1.04	5	48	(—)
1.05	1.19	Ph	Cl	1.68	48	82	(47)
1.06	1.18	*n*-$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$	F	—	89	70	(28)

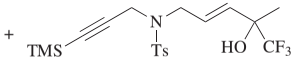


1. $TMSCF_3$ (1.2 eq), CsF (5 mol %), DME, rt, 3 h
2. HCl, H_2O

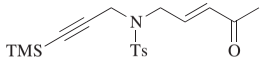

(21) 865

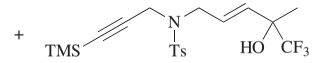
$TMSCF_3$ (1.6 eq), KF (2 mol %), DMF, rt, 18 h

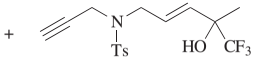

(74) 414


(11)

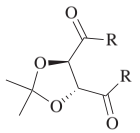
1. $TMSCF_3$, CsF
2. HCl


(28) 414

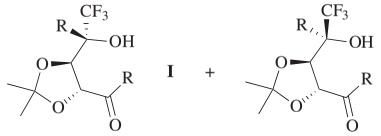

(42)


(29)

C_{8-18}

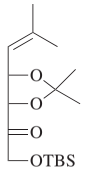
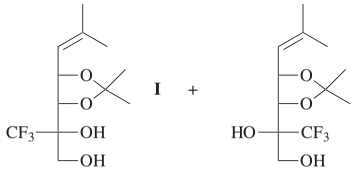
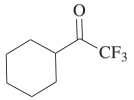
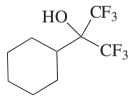
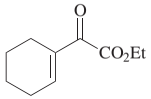
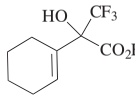
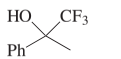
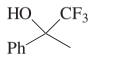
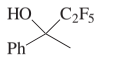
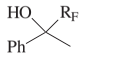


1. $TMSCF_3$ (1.05 eq), TBAF (8 mol %), THF, –40°
2. TBAF (1 eq), CH_2Cl_2, rt, 3 h


I + **II** 484

R	Time (h)	**I + II**	**I/II**
Et	1	(86)	99.5:0.5
Ph	1	(93)	99:1
2-$MeOC_6H_4$	3	(56)	60:40
4-$MeOC_6H_4$	3	(60)	87.5:12.5
4-MeC_6H_4	3	(20)	85:15
Bn	3	(91)	96:4

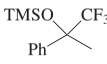
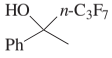
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_8 	$TMSCF_3$ (1.2 eq), TBAF (1.2 eq), THF, 0°, 1 h; rt, 2 h	 **I** + **II** **I + II** (69), **I/II** = 4:1	509
	CF_3CO_2K (1.6 eq), DMF or NMP, 140°, 5.5 h	 (25)	887
	1. $TMSCF_3$ (1.2 eq), TBAF (5 mol %), THF, rt, 2 h 2. TBAF (1 eq)	 (70)	472
	$TIPSCF_3$ (0.09 eq), 18-crown-6 (0.2 eq), *t*-BuOK (0.2 eq), THF, –78°, 1 h; to rt	 (22)[b]	80
	1. CF_3H, $(TMS)_3N$ (1.5 eq), TMAF (1.5 eq), DMF, –10° 2. AcOH	 (26)	73, 75
	C_2F_5I (1.51 eq), MeLi (1.4 eq), LiBr, Et_2O, –78°, 0.5 h	 (88)	392, 391
	R_FX, $MnCl_2$/Na, DMF, ultrasound		316

R_F	X	
CF_3	Br	(18)
n-C_4F_9	I	(14)

R_FX, Zn, catalyst (0.1 eq), DMF, ultrasound		R_F	X	Catalyst	Time (h)		299
		CF_3	I	—	1.5	(13)	
		CF_3	I	$(Cp)_2TiCl_2$	3	(36)	
		CF_3	Br	$(Cp)_2TiCl_2$	3	(33)	
		n-C_4F_9	I	—	2	(12)	
		n-C_4F_9	I	$(Cp)_2TiCl_2$	3	(38)	
CF_3CO_2Na, CuI, DMF, 170°, 2 h		(2.3)					600
1. $TMSCF_3$ (1.5 eq), PhONa (0.1 eq), THF, 0°, 0.5 h; rt 2. HCl, H_2O, 0°		(79)					134
1. $TMSCF_3$ (1.5 eq), TBAF (1 eq), THF, microreactor, t_r 20 s 2. HCl, H_2O		(—) 42% conv					892
1. NaH (0.2 eq), THF, 0°, 10 min 2. $TMSCF_3$ (1.5 eq), 0°; rt 3. HCl, H_2O, 0°		(—) 67% conv					134
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h 2. HCl, H_2O, rt, 6 h		(74)					288
1. $TMSCF_3$ (1.2 eq), AcOLi (5 mol %), DMF, –78° to rt, 2 h 2. Hydrolysis		(—) 84% conv					131
$TMSCF_3$ (4 eq), t-Bu_3P (0.1 eq), DMF, rt, 0.25–1 h		(84)					140

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_8 	$TMSCF_3$ (2 eq), KF (0.1 eq), *n*-Bu_4NBr (0.1 eq), toluene, rt, 0.5 h	 (89)	457
	1. PhOK (0.5 eq), 18-crown-6 (0.5 eq), THF, rt, 10 min; 0°, 5 min 2. Substrate (1 eq), $TMSCF_3$ (1.4 eq), 0°, 1 h	 (>99)	463
	1. $TMSC_2F_5$ (1.2 eq), TBAF (cat.), THF, 0° to rt 2. TBAF, THF, 0° to rt, 5 h	 (81)	122
	1. *n*-C_3F_7TMS (1.2 eq), TBAF (cat.), THF, 0° to rt 2. TBAF, THF, 0° to rt, 5 h	 (78)	122
C_{8-10} 	1. $TMSCF_3$ (1.3 eq), **46j** (0.2 eq), toluene, –78° 2. HCl, H_2O		456

R	Time (h)		er
Me	2	(91)	74.0:26.0
i-Pr	8	(87)	75.5:24.5

C_{8-15} 	CF_3H, **57** (*x* eq), additive (2.5 eq)		81

R	*x*	Additive	Temp (°)	Time (h)	
Me	1.2	none	40	3	(95)
Ph	0.5	TMS—≡—	–40	24	(80)
(*E*)-PhCH=CH	1.2	none	–40	3	(74)

C_{8-13}



$CF_3B(OMe)_3K$ (1.2 eq), DMF,1 h



I + **II**

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R	Temp (°)	**I**	**II**
Me	50	(43)	(15)
Ph	70	(90)	—

1. Catalyst (1 eq), CsF (0.1 eq), DME
2. TBAF (1 eq), THF, 1 h

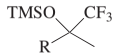


R	Catalyst	Temp (°)	Time (h)		
Me	**67a**	50	108	(21)	121
Me	**67a**	80	24	(41)	
Me	**67b**	80	24	(26)	
Me	**67c**	80	24	(28)	
Ph	**67a**	50	24	(59)	
Ph	**67a**	80	5	(60)	
Ph	**67b**	50	24	(44)	
Ph	**67b**	80	24	(54)	
Ph	**67c**	50	30	(50)	
Ph	**67c**	80	24	(50)	

C_{8-10}



$TMSCF_3$ (2 eq), **78** (10 mol %), DMF, rt



R	Time (h)		
Ph	1	(80)	388
4-ClC_6H_4	1	(82)	
$PhCH_2CH_2$	12	(80)	
(*E*)-PhCH=CH	4	(94)	

C_{8-12}



1. $TMSCF_3$ (2 eq), **55** (1 mol %), PhOK (10 mol %), toluene, –40 to –30°, 6 h
2. TBAF, THF, H_2O



R		er	
Ph	(66)	69.0:31.0	454
4-BrC_6H_4	(80)	65.5:34.5	
2-$C_{10}H_7$	(91)	67.0:33.0	

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{8-13}



1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, time 1
2. HF, TMAF, H_2O, time 2



482, 891

R^1	R^2	Time 1 (h)	Time 2 (h)	
Ph	Me	16	8	(96)
4-HOC_6H_4	Me	6	2	(98)
3-MeO-4-HOC_6H_3	Me	14	5	(96)
3,4-$(MeO)_2C_6H_3$	Me	14	5	(95)
3,5-$(MeO)_2$-4-HOC_6H_2	Me	18	2	(95)
Ph	Ph	16	5	(94)
4-$MeOC_6H_4$	4-$MeOC_6H_4$	16	5	(96)

1. $TMSCF_3$ (*x* eq), TMAF (*y* eq), THF, 0°, 0.5 h; rt, 24 h
2. TMAF (*z* eq), THF, rt, 24 h



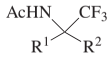
483

R^1	R^2	*x*	*y*	*z*	
Ph	Me	4.88	0.19	0.65	(96)
4-HOC_6H_4	Me	5.53	0.22	0.73	(98)
3-MeO-4-HOC_6H_3	Me	6.75	0.27	0.89	(96)
3,4-$(MeO)_2C_6H_3$	Me	7.32	0.29	0.97	(95)
3,5-$(MeO)_2$-4-HOC_6H_2	Me	7.97	0.32	1.05	(95)
Ph	Ph	7.4	0.29	0.98	(94)
4-$MeOC_6H_4$	4-$MeOC_6H_4$	9.84	0.39	1.3	(96)

C_{8-14}



1. $TMSCF_3$ (1.2 eq), TBAF (5 mol %), THF, rt
2. MeCN, H_2SO_4, AcOH, reflux

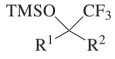


R^1	R^2	Time (h)		
Me	Ph	3	(54)	467
EtO_2C	Ph	48	(59)	
n-Bu	*n*-Bu	24	(32)	
Et	Bn	15	(49)	
Ph	Ph	5	(68)	
Ph	4-FC_6H_4	5	(57)	
Ph	4-$MeOC_6H_4$	5	(66)	
Ph	4-MeC_6H_4	5	(81)	

C_{8-15}



$TMSCF_3$ (*x* eq), 4 Å MS (0.5 g/mmol), DMSO, rt, 6 h



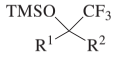
136

R^1	R^2	*x*	Conv (%)	
Ph	Me	1.5	82	(74)
Bn	Me	1.5	85	(81)
PhCH=CH	Me	1.2	89	(86)
PhCH=CH	Ph	1.2	96	(93)

C_{8-16}



$TMSCF_3$, catalyst (5 mol %), solvent, 0° to rt



(—)

R^1	R^2	Catalyst	Solvent	Time (h)	Conv (%)	
Ph	Me	AcOLi	DMF	2	84	132
4-$O_2NC_6H_4$	Me	AcOLi	DMF	1	95	132, 131
(*E*)-PhCH=CH	Me	AcOLi	DMF	2	91	131
(*E*)-PhCH=CH	Me	AcOLi	DMF	2	97	132
Ph	Ph	AcOLi	DMF	2	84	131
(*E*)-*t*-BuCH=CH	Ph	AcOLi	DMF	4	91	132
(*E*)-PhCH=CH	Ph	AcOLi	DMF	1	97	132, 131
(*E*)-PhCH=CH	Ph	*n*-Bu_4NOAc	THF	1	97	132, 131
(*E*)-PhCH=CH	4-MeC_6H_4	AcOLi	DMF	2	92	131

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{8–17}$



1. $CF_3CH(OH)_2$•0.5 H_2O (1.5 eq), *t*-BuOK (6 eq), DMF, –50°, 0.5 h
2. Substrate (1 eq), –50°, 1 h; to rt



Ar	R		Refs.
Ph	Me	(0)[b]	106
Ph	Ph	(90)	
4-$O_2NC_6H_4$	Ph	(45)	
Ph	1-adamantyl	(96)	
4-$MeOC_6H_4$	4-$MeOC_6H_4$	(80)	

$C_{8–13}$



CF_3H (7 eq), **46e** (3 eq), additive (6 eq), DMF, –50°, 10 min; –10°, 5 h



R^1	R^2	Additive		Refs.
Ph	Me	—	(tr)	69
Ph	Me	TMS_2NH	(60)	
Ph	*c*-C_3H_5	TMS_2NH	(73)	
n-C_9H_{19}	Me	—	(36)	
n-C_9H_{19}	Me	TMS_2NH	(83)	
n-C_5H_{11}	*n*-C_5H_{11}	TMS_2NH	(71)	
Ph	Ph	TMS_2NH	(84)	

$C_{8–17}$



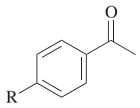
1. **64a** (1 eq), initiator (0.1 eq), solvent
2. TBAF (1 eq), THF, 1 h



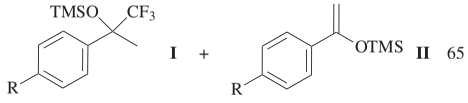
121

R^1	R^2	Initiator	Solvent	Temp	Time (h)	
Ph	Me	CsF	DME	rt	120	(58)
Ph	Me	TBAT	THF	rt	6	(60)
n-C_8H_{17}	Me	TBAT	THF	rt	6	(78)
n-C_5H_{11}	*n*-C_5H_{11}	TBAT	THF	rt	6	(90)
2-pyridyl	2-pyridyl	CsF	DME	rt	6	(60)
Ph	Ph	CsF	DME	rt	24	(76)
Ph	Ph	CsF	DME	50°	6	(71)
Ph	Ph	CsF	DME	80°	2	(74)
(*E*)-PhCH=CH	Ph	CsF	DME	rt	6	(68)
2-$C_{10}H_7$	Ph	CsF	DME	rt	6	(66)
(*E*)-PhCH=CH	(*E*)-PhCH=CH	CsF	DME	rt	6	(36)

C_{8-9}



$TMSCF_3$ (1.5 eq),
catalyst (*x* mol %), DMF, rt



I + **II** 65

R	Catalyst	*x*	Time (h)	**I**	**II**
H	K_2CO_3	10	3	(67)	(5–10)
H	**28**	5	2	(70)	(1–6)
Cl	K_2CO_3	10	3	(85)	(5–10)
Cl	**28**	5	1	(85)	(1–6)
CF_3	K_2CO_3	10	3	(65)	(5–10)
CF_3	**28**	5	0.5	(72)	(1–6)

C_{8-17}



1. **60** (1 eq, dr 60:40),
initiator (0.1 eq), solvent
2. TBAF (1 eq), THF, 1 h



182

R^1	R^2	Initiator	Solvent	Time (h)	
Ph	Me	CsF	DME	24	(30)
Ph	Me	TBAT	THF	6	(55)
n-C_8H_{17}	Me	TBAT	THF	6	(76)
n-C_5H_{11}	*n*-C_5H_{11}	TBAT	THF	6	(65)
2-pyridyl	2-pyridyl	TBAT	THF	6	(83)
Ph	Ph	CsF	DME	24	(73)
Bn	Bn	CsF	DME	24	(20)
Bn	Bn	TBAT	THF	6	(45)
(*E*)-PhCH=CH	Ph	CsF	DME	24	(61)
(*E*)-PhCH=CH	(*E*)-PhCH=CH	CsF	DME	24	(71)

C_8



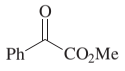
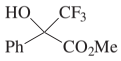
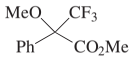
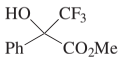
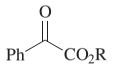
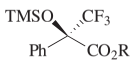
CF_3NO, $(TMS)_2NNa$, THF, –100°



(34)

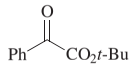
165

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

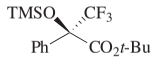
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_8 	1. CF_3H (12.3 eq), $MeSOCH_2K$ (1.67 eq), DMF, DMSO, –10°, 100 min 2. AcOH	 (44) 79% conv	76, 75
	1. **79** (2 eq), CsF (0.1 eq), THF, 110°, 20 h 2. HCl, H_2O, rt, 3 h	 (41)	116, 117
	1. $TMSCF_3$ (1.1 eq), TBAF (0.3 mol %), THF, rt, 3 h 2. MeONa (1.2 eq), MeOH, rt, 1 h 3. $(MeO)_2SO_2$ (1.35 eq), *t*-BuOMe, rt 4. NaOH, H_2O, 3 h	 (90)	491, 492
	1. $TMSCF_3$ (1.1 eq), AcOLi (5 mol %), DMF, 0° to rt, 1 h 2. Hydrolysis	 (87)	131
$C_{8–19}$ 	$TMSCF_3$ (1.4 eq), **45j** (0.1 eq), CH_2Cl_2, –78°, 1 h		528

R		er[a]
Me	(90)	65.5:34.5
Et	(86)	69.0:31.0
1-adamantyl	(90)	57.0:43.0
$Me_2C(CH_2)_2Ph$	(91)	66.5:33.5

C_8



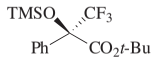
$TMSCF_3$ (1.4 eq),
catalyst (*x* mol %), CH_2Cl_2, –78°



528

Catalyst	*x*	Time (h)		er
45a	10	1	(86)	55.0:45.0
45b	10	1	(96)	51.5:48.5
45c	10	1	(77)	65.5:34.5
45d	10	1	(89)	65.5:34.5
45f	10	1	(92)	57.5:42.5
45g	10	1	(95)	60.0:40.0
45h	10	1	(77)	55.5:44.5
45i	10	1	(84)	68.5:31.5
45j	10	1	(99)	80.0:20.0
45j	5	6	(94)	79.0:21.0
45j	10	1	(95)	65.5:34.5

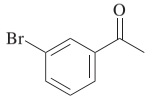
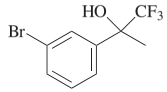
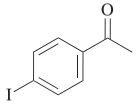
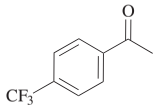
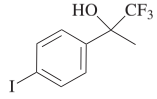
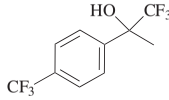
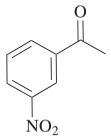
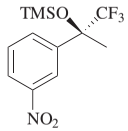
$TMSCF_3$ (1.4 eq), **45j** (0.1 eq),
solvent, 1 h



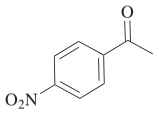
528

Solvent (s)	Temp (°)		er[a]
THF	–78	(99)	67.0:33.0
Et_2O	–60	(99)	74.5:25.5
AcOEt	–78	(98)	71.0:29.0
hexane/CH_2Cl_2 (1:1)	–65	(95)	72.5:27.5
toluene	–20	(99)	60.5:39.5

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_8			
	$TMSCF_3$ (2 eq), TBAF (1 eq), THF, 0° to rt	 (97)	963
	Et_3SiCF_3 (1.2 eq), KF (1.2 eq), CuI (1.5 eq), DMF, NMP, 80°, 24 h	 (—) 45% conv +  (—) 17% conv	275
		+  (—) 6% conv	
	$TMSCF_3$ (1.4 eq), catalyst (0.1 eq), CH_2Cl_2, –78°, 1 h		529, 228

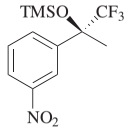
Catalyst		er[a]
45a	(93)	56.5:43.5
45b	(98)	54.0:46.0
45c	(97)	64.5:35.5
45d	(95)	67.0:33.0
45f	(99)	55.5:44.5
45g	(97)	63.0:37.0
45h	(96)	58.5:41.5
45i	(95)	75.0:25.0
45j	(99)	81.0:19.0
45k	(99)	80.5:19.5



C_{8-12}



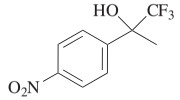
$TMSCF_3$ (1.4 eq), **45j** (*x* mol %), solvent, 1 h



529, 228

x	Solvent	Temp (°)		er[a]
3	toluene/CH_2Cl_2 (7:3)	–78	(56)	85.5:14.5
5	toluene/CH_2Cl_2 (7:3)	–78	(90)	89.5:10.5
10	toluene/CH_2Cl_2 (7:3)	–78	(98)	93.5:6.5
10	THF	–78	(92)	79.0:21.0
10	toluene	–20	(99)	89.5:10.5
10	EtCN	–20	(65)	59.5:40.5

$TMSCF_3$, TBAF, THF



(93)

964

$TMSCF_3$ (1.2 eq), NaH (50 mol %), **46q** (5 mol %), *i*-Pr_2O, –20°



530

Ar	Time (h)		er
4-FC_6H_4	19	(47)	84.0:16.0
3-ClC_6H_4	19	(96)	84.0:16.0
4-ClC_6H_4	19	(83)	80.5:19.5
4-BrC_6H_4	48	(43)	80.0:20.0
3-$O_2NC_6H_4$	48	(30)	84.0:16.0 (*R*)
4-$O_2NC_6H_4$	24	(64)	75.0:25.0
3-$MeOC_6H_4$	96	(38)	79.0:21.0
4-MeC_6H_4	3	(70)	83.5:16.5
(*E*)-PhCH=CH	22	(31)	79.5:20.5
1-$C_{10}H_7$	6	(98)	91.0:9.00
2-$C_{10}H_7$	6	(96)	90.5:9.5 (*R*)

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

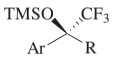
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{8–10}$



1. $TMSCF_3$ (2 eq), catalyst (0.1 eq), TMAF (*x* eq), additive, toluene/CH_2Cl_2 (2:1)
2. TBAF, H_2O, THF, rt, 1 h



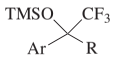
458

Ar	R	Catalyst	*x*	Additive	Temp (°)	Time (h)		er
4-FC_6H_4	Me	**49a**	0.1	—	–60 to –50	7	(96)	93.5:6.5
3-ClC_6H_4	Me	**49a**	0.2	—	–60 to –50	4	(80)	87.0:13.0
4-ClC_6H_4	Me	**49a**	0.1	—	–60 to –50	14	(71)	93.5:6.5
3-BrC_6H_4	Me	**49a**	0.1	—	–60 to –50	8	(73)	85.5:14.5
4-BrC_6H_4	Me	**46q**	0.1	—	–60 to –50	3	(71)	85.0:15.0
4-BrC_6H_4	Me	**49a**	0.1	—	–60 to –50	3	(81)	93.0:7.0
3-$O_2NC_6H_4$	Me	**46q**	0.1	4 Å MS	–60 to –50	7	(96)	82.0:18.0
4-$O_2NC_6H_4$	Me	**46q**	0.2	—	–60 to –50	3	(97)	76.0:24.0
4-$MeOC_6H_4$	Me	**49a**	0.2	—	–60 to –50	7	(84)	94.5:5.5
Ph	Et	**49a**	0.1	—	–60 to –50	14	(65)	91.0:9.0
4-BrC_6H_4	Et	**49a**	0.1	—	–80 to –70	12	(84)	96.5:3.5
4-MeC_6H_4	Me	**49a**	0.1	—	–60 to –50	12	(94)	94.0:6.0
$Ph(CH_2)_2$	Me	**49a**	0.1	—	–60 to –50	6	(37)	55.0:45.0
(*E*)-PhCH=CH	Me	**49a**	0.1	—	–60 to –50	3	(85)	85.0:15.0
Ph	Pr	**49a**	0.1	—	–60 to –50	7	(83)	88.0:12.0

C_{8-9}



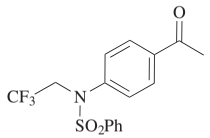
$TMSCF_3$ (1.5 eq), catalyst (4 mol %), CH_2Cl_2, –50°



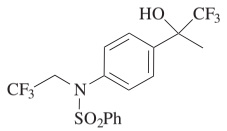
(—) 527

Ar	R	Catalyst	Conv (%)	er
4-$MeOC_6H_4$	Me	**46g**	100	64.0:36.0
4-$MeOC_6H_4$	Me	**46s**	96	63.5:36.5
4-$MeOC_6H_4$	Et	**46g**	96	66.0:34.0
4-$MeOC_6H_4$	Et	**46s**	96	71.5:28.5
2-MeC_6H_4	Me	**46g**	100	53.0:47.0
2-MeC_6H_4	Me	**46s**	100	52.5:47.5

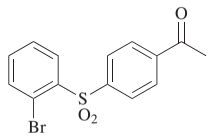
C_8



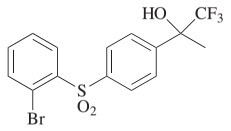
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, o/n
2. HCl, H_2O, rt, 1 h



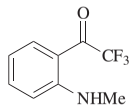
(25) 415



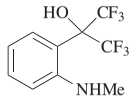
$TMSCF_3$, TBAF, THF



(59) 965



$TMSCF_3$ (2.8 eq), KF (0.34 eq), TBAF (0.34 eq), DMF, 0°; rt, 20 h



(55) 607

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

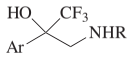
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{8–12}$



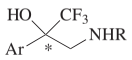
1. **46q** (15 mol %), K_2CO_3 (15 mol %), $TMSCF_3$ (1.4 eq), toluene, –40°, 17 h
2. H_2O
3. $NaBH_4$ (12 eq), EtOH, 0°; rt, 12 h



532

Ar	R		er
Ph	*i*-Pr	(87)	82.0:18.0
Ph	*t*-Bu	(85)	83.5:16.6
4-$MeOC_6H_4$	*i*-Pr	(78)	82.0:18.0
4-$MeOC_6H_4$	*t*-Bu	(89)	85.5:14.5
4-$O_2NC_6H_4$	*i*-Pr	(81)	66.0:34.0
4-$O_2NC_6H_4$	*t*-Bu	(94)	65.0:35.0
benzofuran-2-yl	*t*-Bu	(92)	84.0:16.0
7-Et-benzofuran-2-yl	*t*-Bu	(87)	75.0:25.0

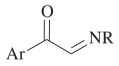
1. $TMSCF_3$ (1.1 eq), additive, solvent
2. $NaBH_4$, EtOH, 0°; rt, 12 h



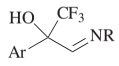
Ar	R	Additive	Solvent	Temp	Time (h)		*(2*R*,1'*S*)/(2*S*,1'*S*)[c]	
Ph	MeO	CsF (cat.)	DME	rt	1	(>69)	—	966
Ph	*i*-Pr	CsF (cat.)	DME	rt	1	(72)	—	967
Ph	*t*-Bu	CsF (cat.)	DME	rt	1	(90)	—	967
Ph	*t*-Bu	K_2CO_3 (cat.)	DMF	rt	3	(81)	—	967
Ph	*t*-Bu	4 Å MS	DMSO	rt	3	(75)	—	967
Ph	(*S*)-PhMeCH	CsF (cat.)	DME	rt	1	(75)	60:40	967
Ph	(*S*)-PhMeCH	CsF (cat.)	DME	–50°	1	(68)	65:35	967
Ph	(*S*)-PhMeCH	4Å MS	DMSO	rt	3	(70)	60:40	967
4-$O_2NC_6H_4$	*i*-Pr	CsF (cat.)	DME	rt	1	(78)	—	967
4-$O_2NC_6H_4$	*t*-Bu	CsF (cat.)	DME	rt	1	(82)	—	967
4-$O_2NC_6H_4$	*t*-Bu	K_2CO_3 (cat.)	DMF	rt	3	(76)	—	967
4-$O_2NC_6H_4$	*t*-Bu	4 Å MS	DMSO	rt	3	(84)	—	967
4-$MeOC_6H_4$	MeO	CsF (cat.)	DME	rt	1	(>78)	—	966

4-$MeOC_6H_4$	*i*-Pr	CsF (cat.)	DME	rt	1	(69)	—	967
4-$MeOC_6H_4$	*t*-Bu	CsF (cat.)	DME	rt	1	(73)	—	967
4-$MeOC_6H_4$	*t*-Bu	K_2CO_3 (cat.)	DMF	rt	3	(70)	—	967
4-$MeOC_6H_4$	*t*-Bu	4 Å MS	DMSO	rt	3	(75)	—	967
4-$MeOC_6H_4$	(*S*)-PhMeCH	CsF (cat.)	DME	rt	1	(78)	60:40	967
4-$CF_3C_6H_4$	*i*-Pr	CsF (cat.)	DME	rt	1	(72)	—	967
4-$CF_3C_6H_4$	*t*-Bu	CsF (cat.)	DME	rt	1	(89)	—	967
benzofuran-2-yl	*t*-Bu	CsF (cat.)	DME	rt	1	(70)	—	967
7-Et-benzofuran-2-yl	*t*-Bu	CsF (cat.)	DME	rt	1	(74)	—	967

C_{8-10}



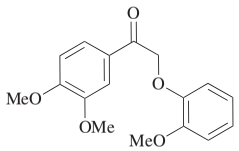
$TMSCF_3$ (1.1 eq), CsF (cat.), DME, rt, 1 h



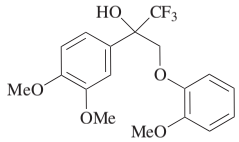
(—) 968

Ar/R = Ph/*i*-Pr; 4-$MeOC_6H_4$/*i*-Pr; 4-$O_2NC_6H_4$/*i*-Pr; 4-$O_2NC_6H_4$/*t*-Bu; benzofuran-2-yl/*t*-Bu

C_8

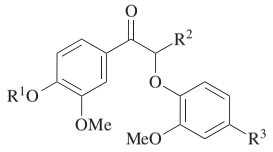


1. $TMSCF_3$ (1 eq), TBAF
2. HCl, H_2O

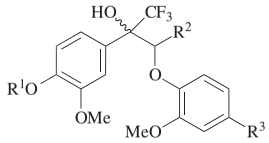


(46) 482

C_{8-9}



1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 24 h
2. HF, H_2O, MeCN, 24 h



482, 891

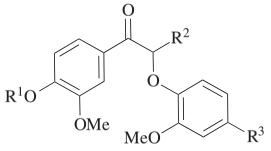
R^1	R^2	R^3	
Me	H	H	(96)
H	$HOCH_2$	Me	(93)
Me	$HOCH_2$	H	(95)

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

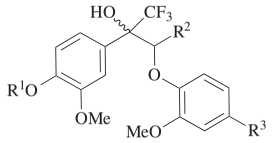
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{8-9}



1. $TMSCF_3$ (*x* eq), TMAF (*y* eq), THF, 0°, 0.5 h; rt, 24 h
2. TMAF (*z* eq), THF, rt, 24 h



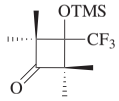
483

R^1	R^2	R^3	*x*	*y*	*z*	
Me	H	H	12.3	0.49	1.62	(96)
H	$HOCH_2$	Me	13.4	0.53	1.77	(93)
Me	$HOCH_2$	H	13.5	0.54	1.78	(95)

C_8



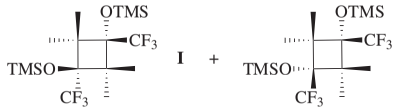
$TMSCF_3$ (1.25 eq), TBAF (2.5 mol %), 4 Å MS , THF, 0° or rt, 1 h



(74)

476, 477

$TMSCF_3$ (3 eq), TBAF (2.5 mol %), 4 Å MS, THF, rt, 5 min



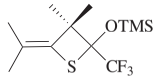
I + **II**

477

I + **II** (82), **I**/**II** = 2:1



$TMSCF_3$ (1.25 eq), TBAF (2.5 mol %), 4 Å MS, THF, 0–5°, 0.25 h

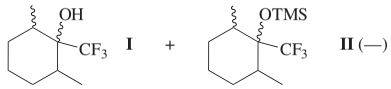


(70)

476

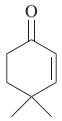


1. CF_3H, TMS_3N (1.5 eq), TMAF (*x* eq), DMF, –10°
2. AcOH

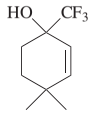


I + **II** (—)

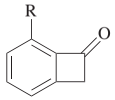
x	Time (h)	Conv **I** (%)	**I**	Conv **II** (%)	
0.2	1	—	(50)	—	73
0.2	240	3	(—)	42	75
1.5	1	36	(—)	14	75



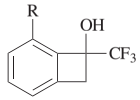
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF
2. HCl, H_2O or TBAF (1 eq), THF



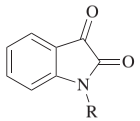
(—) 473



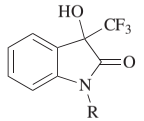
1. $TMSCF_3$ (1.36 eq), TBAF (1 mol %), THF, 0°; rt, 4 h
2. HCl, H_2O, THF, rt, 1.5 h



R		
F	(59)	969
Cl	(59)	
MeO	(54)	

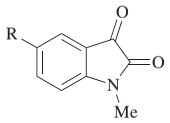


1. $TMSCF_3$ (1.5 eq), KF (0.2 eq), *t*-BuOK, THF, reflux; rt, 2 h
2. HCl, H_2O, THF, 0°, 0.25 h

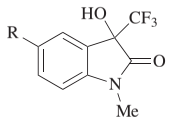


R		
H	(75)	495, 496
Me	(35)	

C_{8-9}

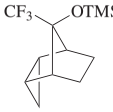
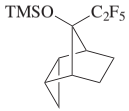
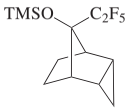
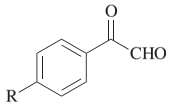
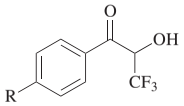
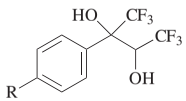
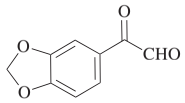
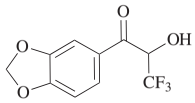
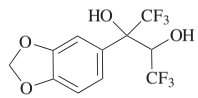


$TMSCF_3$ (2 eq), CsF (cat.), THF, rt, 24 h

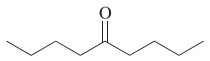


R		
H	(90)	497
Cl	(96)	
Br	(52)	
O_2N	(72)	
Me	(71)	

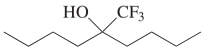
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_8 	$TMSCF_3$ (1.25 eq), KF (0.2 eq), *t*-BuOK, THF, reflux, 5–10 min	 **I** +  **II** **I + II** (93–98), **I/II** = 10:1	92
	$TMSC_2F_5$ (1.25 eq), KF (0.2 eq), *t*-BuOK, THF, reflux, 5–10 min	 **I** +  **II** **I + II** (93–98), **I/II** = 10:1	92
C_{8-9} 	1. $TMSCF_3$ (2.05 eq), CsF (2 mol %), DME, 0°, 1 h; rt, 5 h 2. HCl, H_2O, THF, rt, 3 h	 +  **I** **II** (—)	438
		R **I** H (82) MeO (70) Me (72)	
C_8 	1. $TMSCF_3$ (2.05 eq), CsF (2 mol %), DME, 0°, 1 h; rt, 5 h 2. HCl, H_2O, THF, rt, 3 h	 +  (80) (—)	438

C_9

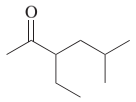


1. $TMSCF_3$ (1.2 eq), TBAF (cat), THF, 0° to rt, 1 h
2. HCl, H_2O, rt, 26 h

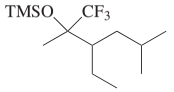


(87)

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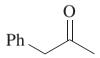


$TMSCF_3$ (0.83 eq), KF (0.1 eq), DMF, rt, 24 h

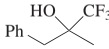


(—) 20% conv, dr 63:37

404

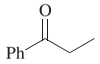


CF_3Br, e^-, Zn anode, DMF, 0–30°

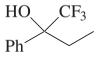


(20)

890

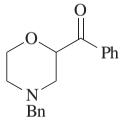


1. CF_3H, TMS_3N (1.5 eq), TMAF (1.5 eq), DMF, –10°
2. AcOH

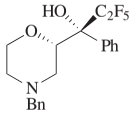


(28)

73, 75

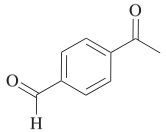


C_2F_5I (3.1 eq), MeLi (1.4 eq), Et_2O, –78°, 0.75 h

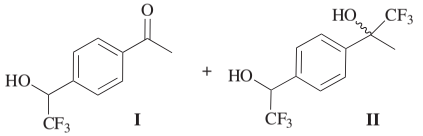


(91)

970



1. $TMSCF_3$ (*x* eq), initiator (*y* mol %), rt, 0.5 h
2. Hydrolysis



142

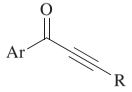
x	Initiator	*y*	Solvent	**I**	**I/II**
1	TBAF	—	DMF	(—)	1.9:1
1	TBAF	—	THF	(—)	3.6:1
1	TBAF	—	toluene	(—)	1:2.1
5	**27a**	0.5	DMF	(85)	1:0

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

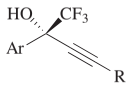
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{9–17}$



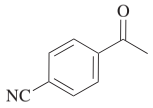
1. $TMSCF_3$ (2 eq), catalyst (10 mol %), Me_4NF (20 mol %), toluene/CH_2Cl_2 (2:1), temp, time
2. TBAF (1.1 eq), THF, rt, 1 h



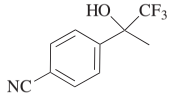
531

Ar	R	Catalyst	Temp (°)	Time (h)		er
Ph	H	**46q**	–60 to –50	1–5	(complex mixture)	—
Ph	TMS	**46q**	–60 to –50	1–5	(complex mixture)	—
Ph	Me	**46q**	–60 to –50	1–5	(complex mixture)	—
Ph	*t*-Bu	**49a**	–60	2	(65)	97.0:3.0
4-FC_6H_4	*t*-Bu	**49a**	–60	2	(81)	93.0:7.0
4-ClC_6H_4	*t*-Bu	**49a**	–60	1	(87)	93.0:7.0
3-$MeOC_6H_4$	*t*-Bu	**49a**	–60	1	(70)	95.0:5.0
4-$MeOC_6H_4$	*t*-Bu	**49a**	–60 to –50	2	(85)	97.5:2.5
4-MeC_6H_4	$BnO(Me)_2C$	**49a**	–60	2	(90)	95.5:4.5
2-MeC_6H_4	*t*-Bu	**49a**	–60 to –50	3	(75)	90.0:10.0
3-MeC_6H_4	*t*-Bu	**49a**	–60 to –50	4	(81)	96.0:4.0
4-MeC_6H_4	*t*-Bu	**49a**	–60 to –50	3	(70)	98.0:2.0
Ph	Ph	**46q**	–60 to –50	1–5	(54)	70.0:30.0
Ph	Ph	**49a**	–60 to –50	1–5	(91)	75.5:24.5
3,4-$Me_2C_6H_3$	*t*-Bu	**49a**	–60 to –50	2	(87)	96.0:4.0
(*E*)-PhCH=CH	*t*-Bu	**49a**	–60 to –50	2	(71)	91.5:8.5
2-$C_{10}H_7$	$BnO(Me)_2C$	**49a**	–60	2	(93)	91.5:8.5
2-$C_{10}H_7$	4-$BrC_6H_4CH_2O(Me)_2C$	**49a**	–60	4	(66)	89.0:11.0
2-$C_{10}H_7$	$Ph_2CHO(Me)_2C$	**49a**	–60	2	(99)	91.5:8.5
4-*t*-BuC_6H_4	*t*-Bu	**49a**	–60 to –50	2	(70)	97.0:3.0
2-$C_{10}H_7$	*t*-Bu	**49a**	–60	5	(78)	96.5:3.5
4-PhC_6H_4	*t*-Bu	**49a**	–60	2	(88)	95.5:4.5

C_9

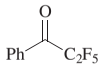


1. $TMSCF_3$ (1.3 eq), TBAF, THF, rt, 4 h
2. HCl, H_2O, 5.5 h

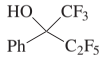


(82)

401



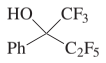
1. $TMSCF_3$ (1.05 eq), TBAF (0.4 mol %), THF, 0°; rt, 3 h
2. TBAF (6.4 mol %), H_2O, THF, rt, 20 h
3. HCl, H_2O



(88)

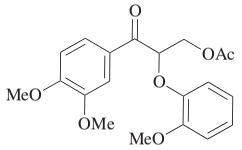
971

1. CF_3Br (1.2 eq), $(Et_2N)_3P$ (1.2 eq), CH_2Cl_2, –70°, 5 h
2. HCl (1.6 eq), –70° to rt
3. H_2O

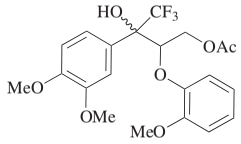


(56)

598

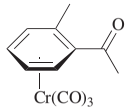


1. $TMSCF_3$ (1 eq), TBAF
2. HCl, H_2O

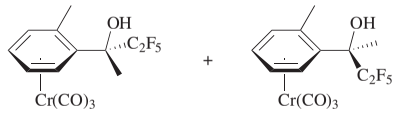


(46)

482

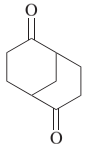


C_2F_5I, Li/Na, Et_2O, –40°, 0.5 h

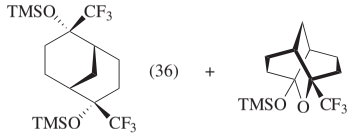


452

I **I + II** (95), **I/II** = 90:10 **II**



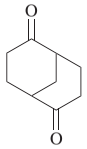
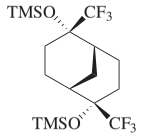
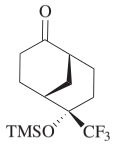
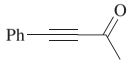
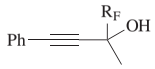
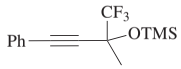
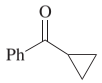
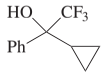
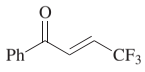
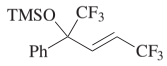
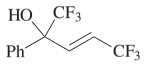
$TMSCF_3$ (2.58 eq), TBAF (0.9 mol %), THF, 0°, 0.5 h; rt, 24 h

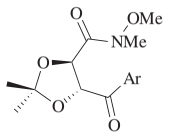


(36) + (37)

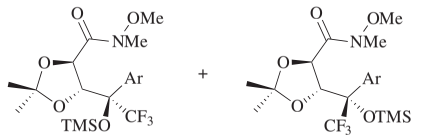
479

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_9 	1. $TMSCF_3$ (2.58 eq), TBAF (0.9 mol %), THF, 0°, 0.5 h; rt, 24 h 2. HCl, H_2O, Et_2O, 1 h	 (38) +  (38)	479
C_{10} 	1. $TMSR_F$ (1.25 eq), CsF (5 mol %) or TBAF (5 mol %), DME or THF 2. HCl, H_2O		437
		R_F / Temp (°) / Time (h): CF_3 rt — (88); C_2F_5 rt — (85); *n*-C_6F_{13} 50 15 (60); *n*-C_7F_{15} 50 15 (62); *n*-C_8F_{17} 50 15 (60–62)	
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt 2. HCl, H_2O	 (76)	289
	1. $TMSCF_3$ (1.2 eq), TBAF (cat), THF, 0° to rt, 1 h 2. HCl, H_2O, rt, 15 h	 (81)	288
	1. $TMSCF_3$, TMAF (cat.) 2. HCl, H_2O	 **I** +  **II** **I** + **II** (85), **I**/**II** = 92:8	292



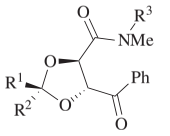
TMSCF$_3$ (1.3 eq),
TBAF•3H$_2$O (4 mol %),
THF, Ar, 0°, 7.5 h



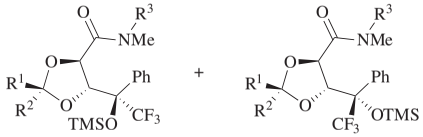
503

I (71) **I/II** = 95:5 **II** (—)

Ar = 4-MeOC$_6$H$_4$



TMSCF$_3$, initiator, solvent, 2 h



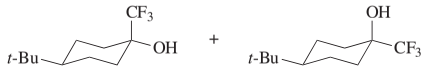
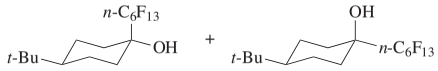
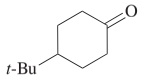
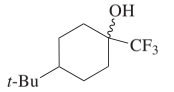
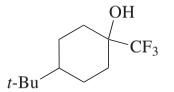
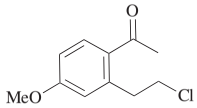
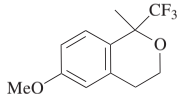
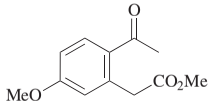
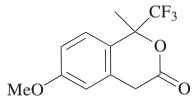
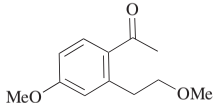
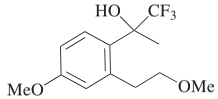
422

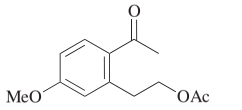
I (—) **I** + **II** >90% conv **II** (—)

R^1	R^2	R^3	Initiator	Solvent	Temp (°)	**I/II**
Me	Me	Me	KF	DMF	rt	92:8
Me	Me	Me	CsF	THF	–20	66:34
Me	Me	Me	CsF	THF	rt	68:32
Me	Me	Me	CsF	DMF	rt	91:9
Me	Me	Me	K_2HPO_4	DMF	rt	93:7
Me	Me	Me	K_2CO_3	DMF	rt	93:7
Me	Me	Me	AcONa	DMF	rt	93:7
Me	Me	Me	*t*-BuOK	DMF	rt	91:9
Me	Me	Me	TMAF	THF	–20	90:10
Me	Me	Me	TBAF•3H$_2$O	THF	–20	92:8
Me	Me	Me	*n*-Bu$_4$NPh$_3$SnF$_2$	THF	0	91:9

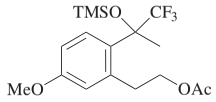
R^1	R^2	R^3	Initiator	Solvent	Temp (°)	**I/II**
Me	Me	MeO	CsF	THF	–20	68:32
Me	Me	MeO	K_3HPO_4	DMF	rt	94:6
Me	Me	MeO	K_2CO_3	DMF	rt	94:6
Me	Me	MeO	TMAF	THF	–20	92:8
Me	Me	MeO	TBAF•3H$_2$O	THF	–20	95:5
Me	Me	MeO	*n*-Bu$_4$NPh$_3$SnF$_2$	THF	0	94:6
H	Ph	Me	CsF	THF	–20	79:21
H	Ph	Me	K_2CO_3	DMF	rt	87:13
H	Ph	Me	TBAF•3H$_2$O	THF	–20	85:15
H	Ph	Me	*n*-Bu$_4$NPh$_3$SnF$_2$	THF	0	88:12

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

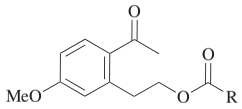
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{10}			
	$TMSCF_3$, TBAF, THF	 **I** **I + II** (58), **I/II** = 77:23 **II**	469
	n-$C_6F_{13}I$ (2 eq), MeLi/LiBr, Et_2O, –78°, 0.5 h	 **I** **I + II** (82), **I/II** = 85:15 **II**	197
	CF_3Br, e^-, Zn anode, Bu_4NBr, DMF/TMEDA (7:3)	 (32)	234
	1. *n*-Bu_3SnCF_3 (1.1 eq), CsF (20 mol %), rt, 15 h 2. NH_4Cl, H_2O	 (60) dr 85:15	156
	1. $TMSCF_3$, CsF, DMF 2. TBAF	 (—)	416
	1. $TMSCF_3$ (1.3 eq), CsF (7 mol %), DMF, 0°, 7 h 2. TBAF (1 eq), THF, 1 h	 (54)	416
	1. $TMSCF_3$ (1.3 eq), CsF (0.12 eq), DMF, 0°, 40 min 2. TBAF (1 eq), THF, 1 h 3. NaOH (1.15 eq), H_2O, rt	 (71)	416



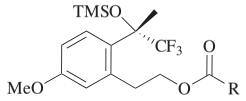
$TMSCF_3$ (1.31 eq), CsF (0.12 eq), DMF, 0°, 40 min



(100) 527



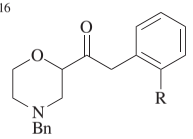
$TMSCF_3$ (2 eq), catalyst (0.2 eq), solvent



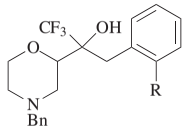
(—) 527

R	Catalyst	Solvent	Temp (°)	Conv (%)	er
Me	**46g**	CH_2Cl_2	–78	—	75.0:25.0
Me	**46j**	CH_2Cl_2	–78	70	74.0:26.0
t-Bu	**46g**	CH_2Cl_2	–78	—	69.0:31.0
Ph	**46g**	CH_2Cl_2	–78	—	80.0:20.0
4-BrC_6H_4	**46g**	CH_2Cl_2	–78	—	62.0:38.0
4-$MeOC_6H_4$	**46g**	CH_2Cl_2	–78	—	81.0:19.0
3,4-$(MeO)_2C_6H_3$	**46g**	CH_2Cl_2	–78	70	90.0:10.0
3,4-$(MeO)_2C_6H_3$	**46g**	CH_2Cl_2	–40	66	90.0:10.0
3,4-$(MeO)_2C_6H_3$	**46g**	CH_2Cl_2	–20	28	76.0:24.0
3,4-$(MeO)_2C_6H_3$	**46g**	CH_2Cl_2	0	<5	71.0.29.0
3,4-$(MeO)_2C_6H_3$	**46g**	DMF	–40	81	50.0:50.0

C_{10-16}



1. $TMSCF_3$ (*x* eq), CsF (0.5 eq), toluene, 0°; rt, 2 d
2. $TBAF{\bullet}3H_2O$, 0°; rt, 1 h

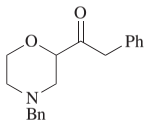
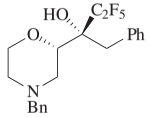
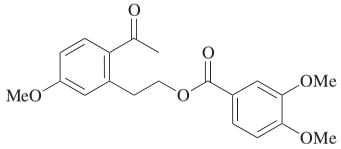
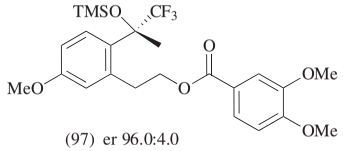
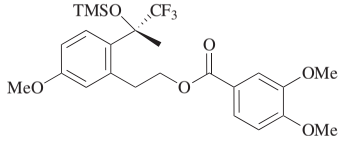


dr 1:1

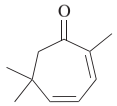
R	*x*	
H	5	(52)
MeO	4.8	(40)
Ph	5.7	(42)

970

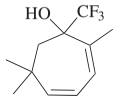
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{10} 	C_2F_5I (3.3 eq), MeLi (2.5 eq), Et_2O, –78°, 0.75 h		(52)	970
	$TMSCF_3$ (14.5 eq), **46s** (4 mol %), CH_2Cl_2, –50°, 3 h; rt, o/n	 (97) er 96.0:4.0		416
	$TMSCF_3$ (1.5 eq), catalyst (*x* mol %), CH_2Cl_2, –78°		(—)	527

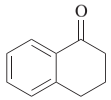
Catalyst	*x*	Conv (%)	er
46d	4	86	87.0:13.0
46e	4	88	79.0:21.0
46j	4	77	84.5:15.5
46g	50	27	84.5:15.5
46g	20	71	88.5:11.5
46g	10	96	91.0:9.0
46g	4	98	91.5:8.5
46o	4	21	85.0:15.0
46s	4	97	96.0:4.0
46v	4	95	92.5:7.5
46t	4	86	84.0:16.0



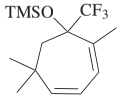
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF
2. TBAF (1 eq), THF



(60) 473

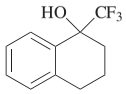


1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt
2. HCl, H_2O

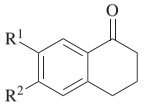


(56) 289

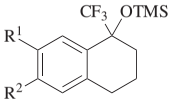
1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 2 h
2. HCl, H_2O



(88) 289



$TMSCF_3$ (1.5 eq), catalyst (4 mol %), CH_2Cl_2, –50°



(—) 527

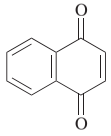
R^1	R^2	Catalyst	Conv (%)	er
H	MeO	**46g**	78	65.0:35.0
H	MeO	**46s**	65	69.5:30.5
MeO	H	**46g**	63	82.0:18.0
MeO	H	**46s**	88	62.5:37.5
O_2N	H	**46g**	100	64.0:36.0
O_2N	H	**46s**	100	50.5:49.5

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

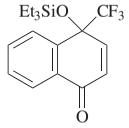
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

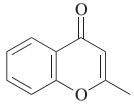
C_{10}



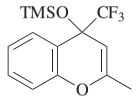
Et_3SiCF_3 (*x* eq), additive (*y* eq), solvent, rt



x	Additive	*y*	Solvent	Time (h)		
1	K_2CO_3	0.2	DMF	2	(41)	489
1.17	*n*-Bu_4NHF_2	0.1	MeCN	0.5	(—)	489a
1.18	KHF_2	1.18	MeCN	2	(—)	489a
1.53	KF	1.94	MeCN	1	(44)	489

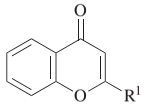


$TMSCF_3$ (1.4 eq), TMAF (cat.), THF, rt, 12 h

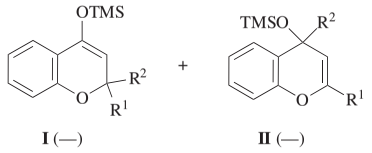


(—) 13% conv 292

C_{10-11}

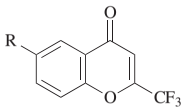


$TMSR^2$ (1.2 eq), TMAF (2 mol %), THF, 4 h

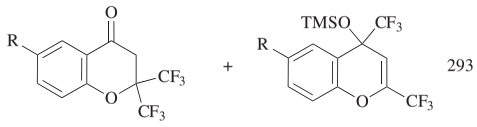


I (—) **II** (—) 293

R^1	R^2	Temp (°)	**I/II**
CF_3	CF_3	–30	92:8
CF_3	CF_3	0	90:10
CF_3	CF_3	rt	87:13
CF_3	C_2F_5	–30	82:18
CF_3	C_2F_5	0°	77:23
CF_3	C_2F_5	rt	72:28
C_2F_5	CF_3	0	73:27



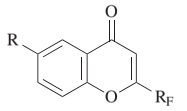
1. $TMSCF_3$, TMAF, THF, –10°, 4 h
2. HCl, H_2O



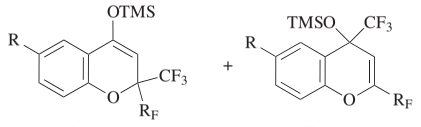
293

I **I/II** = 90:10 **II** (—)

R	**I**
H	(86)
Me	(61)



$TMSCF_3$ (1.4 eq),
initiator (3–4 mol %),
THF, 4–24 h



292

I (—) **II** (—)

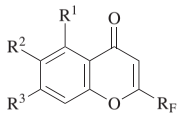
R	R_F	Initiator	Temp (°)	**I/II**
H	CHF_2	TMAF	–30	**I** only
MeO	CF_3	*t*-BuOK	–30	47:53
MeO	CF_3	TMAF	–30	93:7
H	C_2F_5	TMAF	–30	80:20
H	C_2F_5	TMAF	0	73:27
MeO	C_2F_5	TMAF	–30	86:14

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

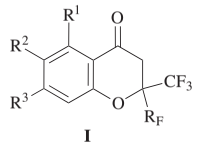
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{10-11}

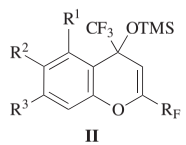


1. $TMSCF_3$ (1.4 eq), TMAF (cat.), THF
2. HCl, H_2O, rt, 0.25 h



I

+

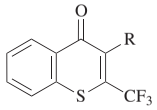


II

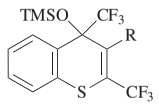
292

R^1	R^2	R^3	R_F	Temp (°)	Time (h)	**I**	**II**
H	H	H	CF_3	–10	4	(86)	(11–12)
H	H	MeO	CF_3	–30	24	(67)	(—)
H	MeO	H	CHF_2	–30	24	(50)	(—)
H	MeO	H	CF_3	–30	24	(76)	(—)
MeO	H	MeO	CF_3	–30	24	(64)	(—)
H	Me	H	CF_3	–10	4	(61)	(11–12)

C_{10-13}

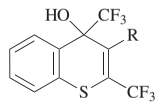


1. $TMSCF_3$ (1.49 eq), TMAF (cat.), THF, –30°, 5 h
2. H_2O



I

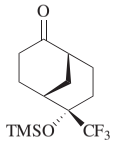
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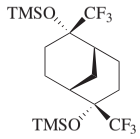
II (—) 291

R	**I**	**I/II**
H	(88)	—
n-Pr	(—)	70:30

C_{10}



TMSCF$_3$ (2.56 eq), TBAF (2.2 mol %), THF, 0°, 0.5 h; rt, 2 h



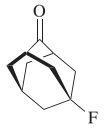
I (56)

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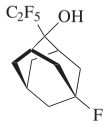


II (—) 479

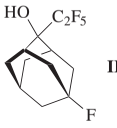
I/II = 4:1



C_2F_5I, MeLi/LiBr, Et_2O, –78°

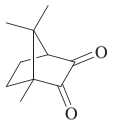


I (—) +

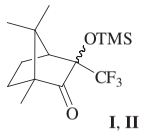


II (—) 972

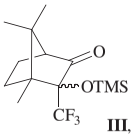
I/II = 3:1



$TMSCF_3$, CsF, DME, rt



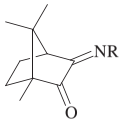
+



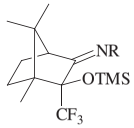
478

I, **II** (—) **III**, **IV** (—)

I/II/III/IV = 39:35:4:22

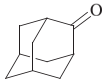


1. $TMSCF_3$ (1.1 eq), CsF (cat.), DME, rt, 1 h
2. H_2O

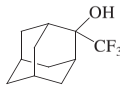


(—) 478

R = Me, Et, *i*-Pr, *t*-Bu, *c*-C_6H_{11}, Ph, 4-$MeOC_6H_4$, Ph(Me)CH

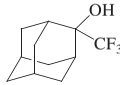


1. $TMSCF_3$ (1.2 eq), TBAF (cat), THF, 0° to rt, 24 h
2. HCl, H_2O, rt, 15 h



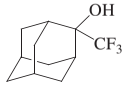
(72) 288

$TMSCF_3$



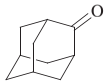
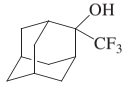
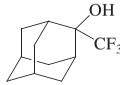
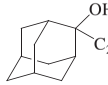
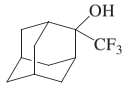
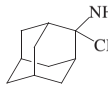
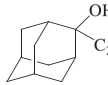
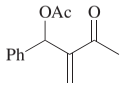
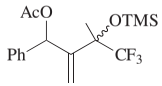
(—) 973

$TMSCF_3$, TBAF, THF

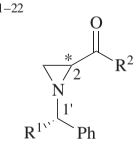


(94) 469

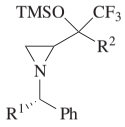
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{10} 	1. $PhSO_2CF_3$ (2 eq), *t*-BuOK (2.5 eq), DMF, –50° to rt 2. H_2O	 (82)	179
	1. $CF_3CH(OH)_2 \cdot 0.5H_2O$ (1.5 eq), *t*-BuOK (6 eq), DMF, –50°, 0.5 h 2. Substrate (1 eq), –50°, 1 h; to rt	 (95)	106
	1. $PhSO_2C_2F_5$ (1.5 eq), *t*-BuOK (4.6 eq), THF, –75°; –75 to –70°, 1.5 h 2. HCl, –75 to –70°	 (99)	180
	1. **79** (2 eq), CsF (0.1 eq), THF, reflux, 20 h 2. HCl, H_2O, rt, 3 h	 (87)	116
	1. $TMSCF_3$ (1.2 eq), TBAF (5 mol %), THF, rt 2. MeCN, H_2SO_4, AcOH, reflux, 24 h	 (40)	467
	C_2F_5I (1.61 eq), MeLi (1.44 eq), LiBr, Et_2O, –78°, 0.5 h	 (93)	392, 391
C_{11} 	1. $TMSCF_3$ (1.5 eq), Bu_4NOAc (5 mol %), MeCN, –20°; 18 h 2. HCl	 (48)	295

C_{11-22}



$TMSCF_3$ (1.6 eq), CsF (cat.), DME, rt, 1 h



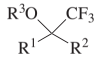
974

R^1	R^2	*Config.	More Polar Isomer	Less Polar Isomer
H	Me	(1'*S*,2—)	(49)	(10)
H	Ph	(1'*S*,2—)	(44)	(20)
Me	Me	(1'*S*,2*S*)	(18)[d]	(31)
Me	Ph	(1'*S*,2*S*)	(30)	(34)
Ph	Ph	(1'*S*,2*R*)	(2)[d]	(44)

C_{11-17}



1. **62a** (2 eq), t-BuOK (2 eq), THF, rt, 24 h
2. R^3Cl



110

R^1	R^2	R^3	Conv (%)	
3-thienyl	Ph	H	50	(47)
2-pyridyl	2-pyridyl	TMS	70	(60)
2-pyridyl	Ph	H	85	(80)
Ph	Ph	H	90	(80)
4-FC_6H_4	4-FC_6H_4	H	90	(75)
2-$C_{10}H_7$	Ph	H	94	(80)

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{11-13}



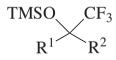
1. **85** (1 eq), *t*-BuOK (1 eq), solvent
2. HCl, H_2O, o/n



119

R^1	R^2	Solvent	Temp	Time (d)	Conv (%)	
2-thienyl	Ph	THF/DMF (1:1)	rt	1	13	(10)
2-pyridyl	2-pyridyl	THF/DMF (1:1)	rt	1	26	(20)
2-pyridyl	Ph	THF/DMF (1:1)	rt	1	100	(95)
Ph	Ph	THF	rt	7	50	(—)
Ph	Ph	THF	60°	1	20	(—)
Ph	Ph	THF, 18-crown-6 (1 eq)	rt	1	70	(—)
Ph	Ph	THF/DMF (1:1)	rt	1	100	(95)

62b (1 eq), CsF (0.1 eq), DME, 5 h



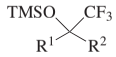
109

R^1	R^2	Temp (°)	Conv (%)	
2-pyridyl	2-pyridyl	60	78	(70)
2-pyridyl	2-pyridyl	80	79	(—)
2-pyridyl	Ph	60	64	(—)
2-pyridyl	Ph	80	83	(77)
Ph	Ph	40	28	(—)
Ph	Ph	50	57	(—)
Ph	Ph	60	85	(80)
Ph	Ph	80	86	(—)

C_{11-15}

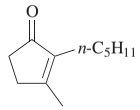


63 (*x* eq), CsF (0.1 eq), DME

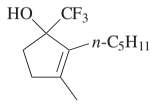


R^1	R^2	*x*	Temp (°)	Time (h)	Conv (%)		
2-pyridyl	2-pyridyl	2	80	5	91	(78)	74
Ph	Ph	1	60	20	58	(—)	74
Ph	Ph	1	80	5	79	(—)	74
Ph	Ph	2	40	5	19	(—)	109
Ph	Ph	2	40	25	50	(—)	74
Ph	Ph	2	50	5	55	(—)	109
Ph	Ph	2	50	24	71	(—)	74
Ph	Ph	2	60	5	70	(—)	74
Ph	Ph	2	80	5	81	(75)	74
(*E*)-PhCH=CH	Ph	2	80	9	80	(70)	74

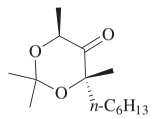
C_{11}



1. $TMSCF_3$ (1.5 eq), TBAF (cat), THF, rt, 24 h
2. HCl, H_2O

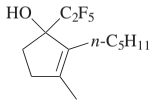


(56) 398



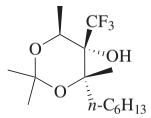
er >99:1

1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h
2. HCl, H_2O, rt, 12 h



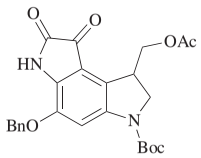
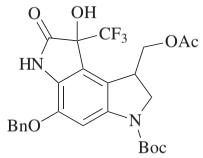
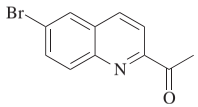
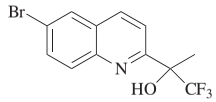
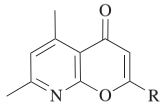
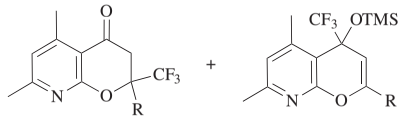
(64.7) 398

1. $TMSCF_3$ (1.5 eq), TBAF (7 mol %), THF, 0°; rt
2. TBAF (1.5 eq), 1 h

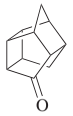
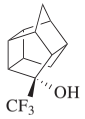
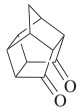
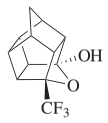


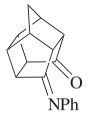
(77) dr >99:1 501

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

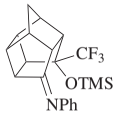
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{11} 	$TMSCF_3$, TBAF, THF, 0–10°	 (71) dr 3:1	975
	1. $TMSCF_3$, AcOLi (cat.), DMF 2. HCl, H_2O, THF	 (96)	976
	1. $TMSCF_3$ (1.56 eq), TMAF (cat.), THF, –30°; rt, 12 h 2. HCl, H_2O, rt, 0.25 h	 +	291

I R	**I**	**I/II**	**II** (—)
CHF_2	(35)	—	
CF_3	(27)	55:45	

	1. $TMSCF_3$ (1.1 eq), CsF (cat.), DME, rt, 1.5 h 2. HCl, H_2O, rt, 1 h	 (60)	471, 485
	1. $TMSCF_3$ (1.1 eq), CsF (cat.), DME, rt, 1.5 h 2. HCl, H_2O, rt, 1 h	 (65)[e]	471, 485

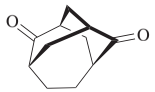


1. $TMSCF_3$ (1.25 eq), CsF (cat.),
DME, rt, 1.5 h
2. HCl, H_2O, rt, 1 h

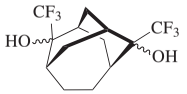


(48)

471, 485[f]



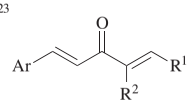
1. $TMSCF_3$ (4.1 eq), TBAF (cat.),
THF, 0°, 4 h
2. HCl, H_2O, o/n



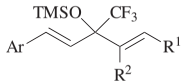
(66)

480

$C_{12–23}$



1. NaOAc (2 eq), DMF, rt, 5 min
2. $TMSCF_3$ (1.5 eq), rt, to completion



474

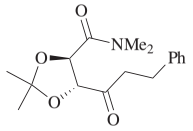
Ar	R^1	R^2	
4-ClC_6H_4	Me	H	(95)
Ph	Ph	H	(93)
2-FC_6H_4	2-FC_6H_4	H	(88)
4-FC_6H_4	Ph	H	(89)
4-FC_6H_4	4-FC_6H_4	H	(89)
4-ClC_6H_4	4-ClC_6H_4	H	(90)
4-ClC_6H_4	4-BrC_6H_4	H	(90)
2,4-$Cl_2C_6H_3$	2,4-$Cl_2C_6H_3$	H	(85)
4-BrC_6H_4	4-BrC_6H_4	H	(91)
4-$MeOC_6H_4$	4-$MeOC_6H_4$	H	(95)
4-FC_6H_4	4-MeC_6H_4	H	(92)
3-MeC_6H_4	3-MeC_6H_4	H	(94)
4-MeC_6H_4	4-MeC_6H_4	H	(95)
Ph	Ph	4-$MeOC_6H_4$	(86)

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

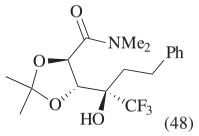
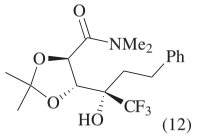
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{12}



1. $TMSCF_3$ (1.2 eq),
K_2CO_3 (10 mol %), DMF, rt, 1.5 h
2. TBAF (1.3 eq), CH_2Cl_2, rt, 3 h


(48)
+

(12)

508

C_{12-15}



1. **61** (1 eq), *t*-BuOK (1 eq),
THF, 1 h
2. HCl, H_2O, o/n



181

R	Temp (°)	Conv (%)	
2-pyridyl	0 to rt	91	(80)
Ph	0 to rt	85	(75)
Ph	rt	70	(—)
(*E*)-PhCH=CH	0 to rt	55	(53)

C_{12-13}



1. 
t-BuOK (*x* eq), rt, 20 min
2. HCl, H_2O, o/n



115

R	*x*	Solvent	Conv (%)	
2-pyridyl	2	THF/DMF (2:1)	100	(99)
Ph	1	THF	25	(—)
Ph	1	THF/DMF (1:1)	55	(—)
Ph	2	THF/DMF (2:1)	100	(98)

1. CF_3CO_2Me (*x* eq), *t*-BuOK (*x* eq),
THF/DMF (1:1), rt, 24 h
2. HCl, H_2O, o/n



119

R	*x*	Conv (%)	
2-pyridyl	2	27	(25)
Ph	1	42	(—)
Ph	2	77	(70)

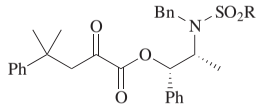
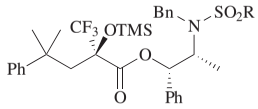
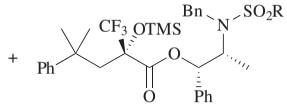
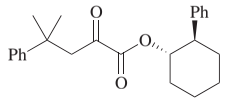
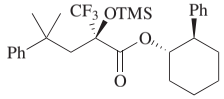
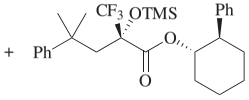
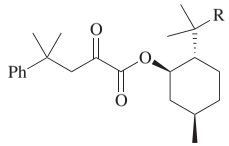
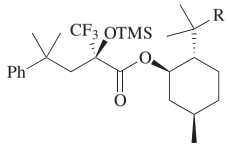
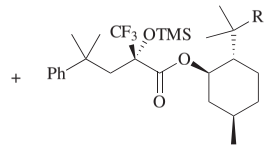
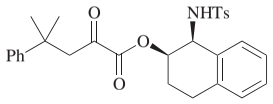
C_{12}  R = 2,4,6-$Me_3C_6H_2$	$TMSCF_3$, TBAF (0.1 eq), toluene	 **I** (—)  **II** (—) **I/II** = 58:42		507
	$TMSCF_3$, TBAF (0.1 eq), toluene	 **I** (—)  **II** (—) **I/II** = 78:22		507
	$TMSCF_3$, TBAF (0.1 eq), toluene	 **I** (—)  **II** (—)	R **I/II** H 56:44 Ph 67:33	507

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

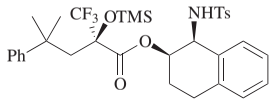
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

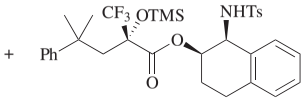
C_{12}



$TMSCF_3$, TBAF (0.1 eq), toluene



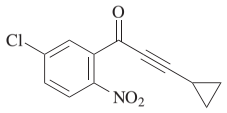
I (—)



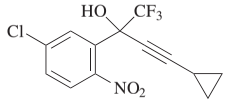
II (—)

I/II = 56:44

507

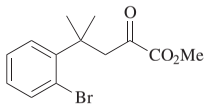


$TMSCF_3$ (2 eq), Me_4NF (20 mol %), catalyst (10 mol %), toluene/CH_2Cl_2 (2:1)

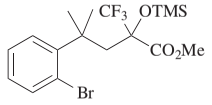


977

Catalyst	Temp (°)	Time (h)		er
45e	–40	2	(88)	75:25
49a	–60 to –30	48	(72)	52:48
49b	–60	2	(86)	50:50
54a	–60	6	(94)	61.5:38.5
54b	–60 to –30	30	(60)	66.5:23.5
54c	–60	8	(74)	52.5:47.5
54d	–60 to –30	17	(32)	50:50

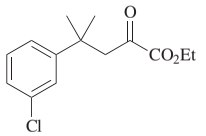


$TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0–5°, 1.5 h

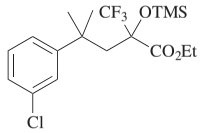


(73)

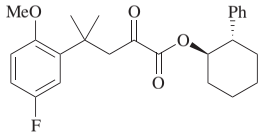
493



1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, rt, o/n
2. TBAF, rt, 2 h

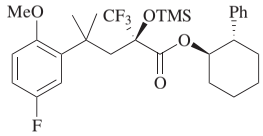


(66) 493



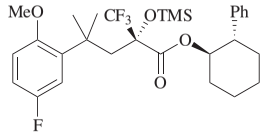
$TMSCF_3$ (1.5 eq), initiator (*x* mol %), THF, cosolvent, –20°

Initiator	*x*	Cosolvent	Time (min)	**I/II**
TBAF	0.5	toluene	20	77:23
TBAF	5	—	20	73:27
TBAF	5	DMF	20	47:53
TBAF	5	CH_2Cl_2	20	58:42
TBAF	5	*t*-BuOMe	20	79:21
TBAF	5	*n*-C_6H_{14}	20	75:25
TBAF	5	toluene	20	84:16
TBAT	5	toluene	30	86:14



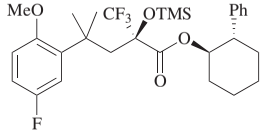
I (—) 506

\+



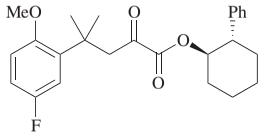
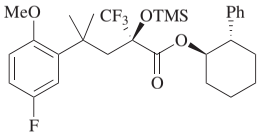
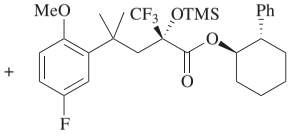
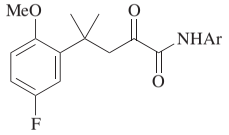
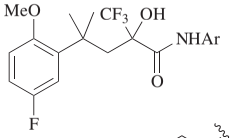
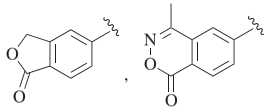
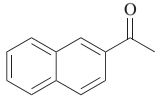
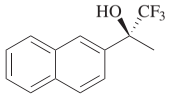
II (—)

1. $TMSCF_3$ (1.5 eq), TBAF (5 mol %), toluene, THF, –20 to –15°, 5 min; rt, 30 min
2. Crystallization (MeOH)

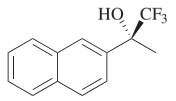


(50) 506

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{12} 	$TMSCF_3$ (1.5 eq), TBAF (5 mol %), toluene, –20°, 5 min; rt, 30 min	 **I** (50)  **II** (—) **I/II** = 5:1	507
	CF_3MgX^g, 0° to rt	 (60) Ar = 	978
	1. $TMSCF_3$ (2 eq), **45e** (0.1 eq), TMAF (0.1 eq), toluene/CH_2Cl_2 (2:1), –60°, 3 h 2. TBAF, H_2O, THF, rt, 1 h	 (70) er 88.5:11.5	458

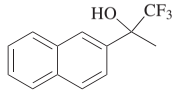
1. $TMSCF_3$ (2 eq), catalyst (0.1 eq), additive (*x* eq), solvent
2. TBAF, H_2O, THF, rt, 1 h



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Catalyst	Additive	*x*	Solvent (s)	Temp (°)	Time (h)		er
46q	AcOLi	0.1	toluene/CH_2Cl_2 (2:1)	–40	2	(99)	59.5:40.5
46q	TMAF	0.1	CH_2Cl_2	–80	3	(56)	85.5:14.5
46q	TMAF	0.1	toluene	–80	24	(30)	86.0:14.0
46q	TMAF	0.1	toluene/CH_2Cl_2 (2:1)	–80	2	(53)	90.0:10.0
46q	TMAF	0.1	toluene/CH_2Cl_2 (1:2)	–60	8	(48)	89.5:10.5
46q	TMAF	0.1	toluene/CH_2Cl_2 (1:1)	–60	8	(70)	91.0:9.0
46q	TMAF	0.1	toluene/CH_2Cl_2 (2:1)	–60	2	(65)	90.5:9.5
46q	TMAF	0.1	toluene/CH_2Cl_2 (2:1)	–40	8	(65)	85.0:15.0
46q	TMAF	0.2	toluene/CH_2Cl_2 (2:1)	–80	12	(98)	93.5:6.5
46q	TMAF•xH_2O	0.1	toluene/CH_2Cl_2 (2:1)	–40	2	(38)	83.0:17.0
46q	TBAF•xH_2O	0.1	toluene/CH_2Cl_2 (2:1)	–40	2	(94)	61.0:39.0
46q	*n*-$Bu_4NH_2F_3$	0.1	toluene/CH_2Cl_2 (2:1)	–40	2	(83)	62.5:37.5
46q	TBAT	0.1	toluene/CH_2Cl_2 (2:1)	–40	2	(89)	59.0:41.0
49a	TMAF	0.1	toluene/CH_2Cl_2 (2:1)	–60	6	(87)	92.5:7.5

1. $TMSCF_3$, TBAF (cat.), 0° to rt, 2 h
2. TBAF



(92)

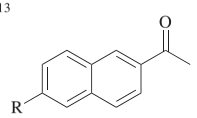
641

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

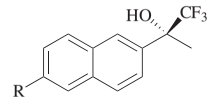
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{12-13}

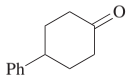


1. $TMSCF_3$ (2 eq), catalyst (0.1 eq), TMAF (*x* eq), toluene/CH_2Cl_2 (2:1)
2. TBAF, H_2O, THF, rt, 1 h

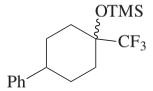


458

R	Catalyst	*x*	Temp (°)	Time (h)		er
H	**49a**	0.1	–60 to –50	6	(87)	92.5:7.5
MeO	**46q**	0.1	–60 to –50	24	(59)	89.0:11.0
MeO	**49a**	0.1	–60 to –50	8	(74)	93.5:6.5
Me	**46q**	0.2	–80 to –70	30	(72)	95.5:4.5
Me	**49a**	0.1	–60 to –50	30	(74)	94.0:6.0



$TMSCF_3$ (1.2 eq), catalyst (5 mol %), solvent, 0° to rt, 1 h

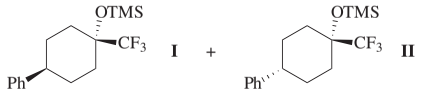


(—)

Catalyst	Solvent	Conv (%)
AcOLi	DMF	80
n-Bu_4NOAc	THF	96

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$TMSCF_3$ (1.2 eq), 4 Å MS (0.5 g/mmol), DMSO, rt, 6 h

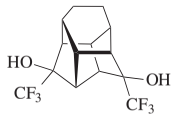


I + **II** (90), **I**/**II** or **II**/**I** = 84:16

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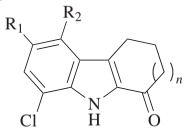
1. $TMSCF_3$ (4 eq), TBAF (cat.), THF, 0°, 4 h
2. HCl, H_2O, o/n



(72)

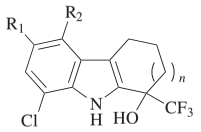
481

C_{12-13}



n = 1 or 2; R^1 = F or Cl; R^2 = H or Cl

$TMSCF_3$,[*h*] CsF, THF



(—)

979

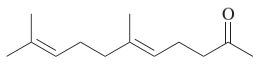
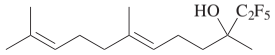
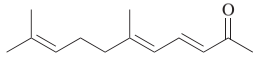
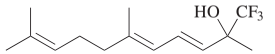
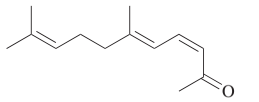
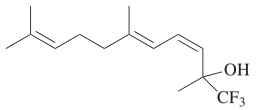
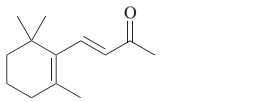
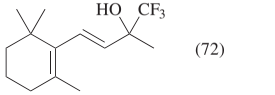
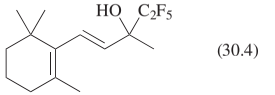
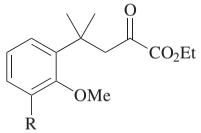
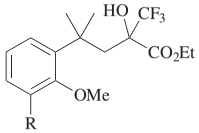
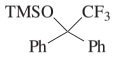
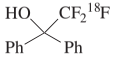
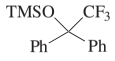
C_{13}		1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h 2. HCl, H_2O, rt, 12 h		(42.1)	398
		1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O		(83)	398
		1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O		(58)	398
		1. $TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 24 h 2. HCl, H_2O		(72)	398
		1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h 2. HCl, H_2O, rt, 12 h		(30.4)	398
C_{13-15}		1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, rt, o/n 2. TBAF (1 eq), rt, 3 h		R Me (65.2) *i*-Pr (76)	980
C_{13}		CHF_3 (5.7 eq), $(TMS)_3N$ (1.5 eq), TBAT (0.2 eq), DMF, THF, –10°, 1 h; rt, 24 h		(87) 71% conv (10) 21% conv	75

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

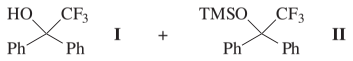
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{13} 	CF_3H (4.3 eq), $(TMS)_3N$ (1.5 eq), TBAT (0.2 eq), *N*-methylmorpholine (1 eq), THF, –10°, 1 h; rt, 24 h	 (—) 20% conv	75
	CF_3H (5.7 eq), $(TMS)_3N$ (1.5 eq), base (*x* eq), DMF, THF, temp, 1 h; rt	 (—)	75

Base	*x*	Temp (°)	Conv (%)
MeONa	0.2	–78	30
MeONa	0.2	–10	39
t-BuOK	0.2	–10	23
t-BuOK	1.5	–10	87

	$[^{18}F]CF_3H$ (0.2 eq), *t*-BuOK (2 eq) DMF, 20°, 10 min	 (100)[i]	79
	1. CF_3H (1.4–8.6 eq), base (*x* eq), DMF, –10°, 1 h; rt, 5 h 2. HCl, H_2O	 **I** +  **II** (—)	

Base	*x*	Conv **I** (%)	**I**	Refs.
NaH	1.1	85	(—)	73
MeONa	1.5	29	(—)	73, 75
EtONa	1.5	23	(—)	73, 75
i-PrONa	1.5	20	(—)	73, 75
t-BuOK	1.1	100	(76)	73, 75
TMS_2NNa	1.1	49	(—)	73

1. CF_3H (1.4–8.6 eq),
base 1 (x eq), base 2 (y eq),
solvent, –10°, 1 h; rt, 5 h
2. HCl, H_2O



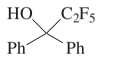
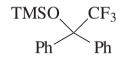
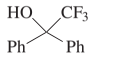
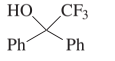
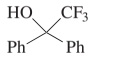
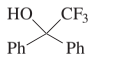
I +



II

Base 1	x	Base 2	y	Solvent (s)	Conv **I** (%)	**I**	Conv **II** (%)	**II**	
TMS_2NLi	1.1	TMS_2NH	0.2	THF	19	(—)	—	(—)	75
TMS_2NK	1.1	TMS_2NH	0.2	DMF	79	(—)	—	(—)	73
TMS_3N	1.5	CsF	0.2	DMF	37	(—)	62	(—)	73
TMS_3N	1.5	CsF	0.2	DMF	37	(18)	66	(68)	75
TMS_3N	1.5	MeONa	1.5	DMF	80	(—)	—	(—)	73, 75
TMS_3N	1.5	EtONa	1.5	DMF	96	(—)	—	(—)	73, 75
TMS_3N	1.5	CF_3CH_2ONa	1.5	DMF	25	(—)	—	(—)	73, 75
TMS_3N	1.5	*i*-PrONa	1.5	DMF	81	(—)	—	(—)	73, 75
TMS_3N	0.2	TMAF	0.2	THF	6	(—)	—	(—)	75
TMS_3N	1.5	TMAF	0.2	DMF	28	(33)	57	(47)	73, 75
TMS_3N	1.5	TMAF	0.2	DMF	80	(—)	10	(—)	75
TMS_3N	1.5	TMAF	1.5	DMF	72	(50)	—	(—)	73, 75
TMS_3N	1.5	TMAF	0.2	THF, DMF (0.3 eq)	52	(7)	38	(60)	73, 75
TMS_3N	1.5	TMAF	0.2	DMEU	41	(—)	34	(—)	73, 75
TMS_3N	1.5	TMAF	0.2	DMPU	51	(—)	16	(—)	73, 75
TMS_3N	1.5	TBAF	0.2	DMF	5	(—)	—	(—)	75
TMS_3N	1.5	TBAT	0.2	DMF	20	(—)	69	(—)	73
TMS_3N	1.5	TBAT	0.2	DMF	69	(69)	40	(30)	75
TMS_3N	1.5	TBAT	0.2	THF, DMF (0.3 eq)	91	(36)	3	(55)	73, 75
TMS_3N	1.5	TBAT	0.2	THF, *N*-formylmorpholine (0.3 eq)	60	(46)	40	(47)	73

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{13} 	C_2F_5I (2.2 eq), TDAE (2.2 eq), DMF, –15° to rt; *h*ν, 1 h; rt, 12 h	 (55)	386
	$TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt	 (88)	122
	1. **79** (2 eq), CsF (0.1 eq), THF, reflux, 20 h 2. HCl, H_2O, rt, 3 h	 (92)	116, 117
	1. Catalyst (1 eq), *t*-BuOK (1 eq), THF/DMF (1:1), rt, 24 h 2. HCl, H_2O, o/n	 (—) Catalyst / Conv (%): **80a** 53; **80b** 90; **80c** 92; **80d** 60; **80e** 77; **80f** 50	119
	1. **81** (2 eq), *t*-BuOK (2 eq), THF/DMF (1:1), rt, 24 h 2. HCl, H_2O, o/n	 (—) 61% conv	119
	1. **62a** (*x* eq), base (*x* eq), solvent, rt, 24 h 2. HCl, H_2O	 (—) *x* / Base / Solvent / Conv (%): — NaH DMF 90; — *t*-BuONa DMF 90; — *t*-BuOK DMF 91; 1 *t*-BuOK THF 50; 2 KH THF 95; 2 TMS_2NK THF 90	110

1. **62c** (*x* eq), additive (1 eq), solvent
2. HCl, H_2O



(—) 110

x	Additive	Solvent (s)	Conv (%)
1	—	DMF	93
1	—	DME/THF (1:1)	68
1	—	THF/DMF (1:1)	91
1	DMF	THF	68
1	18-crown-6	THF	85
2	—	THF	90

1. $CF_3S(O)R$ (1 eq), *t*-BuOK (1 eq), THF, 0°, 1 h
2. HCl, H_2O, o/n



(—) 181

R	Conv (%)
BuO	63
Ph(Me)N	77
Bu_2N	42

1. **73** (1 eq), *t*-BuOK (1 eq), THF, 1 h
2. HCl, H_2O, o/n



(—) 181

Temp	Conv (%)
0°	72
rt	69

1. **74** (1 eq), *t*-BuOK (1 eq), THF, 1 h
2. HCl, H_2O, o/n



(—) 181

Temp	Conv (%)
0°	73
rt	29

1. $PhS(O)CF_3$ (2 eq), *t*-BuOK (2.5 eq), DMF, –50° to rt
2. H_2O



(83) 179

C_{13-15}



CF_3I (2.2 eq), TDAE (2.2 eq), DMF, *h*ν, –20° to rt, 12 h



R	Conv (%)	
Ph	68	(—)
PhCH=CH	65	(53)

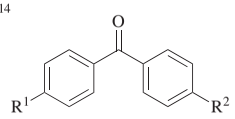
385

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

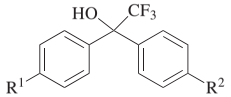
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{13-14}

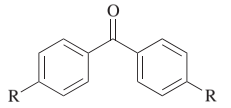


1. $PhSO_2CF_3$ (2 eq), *t*-BuOK (2.5 eq), DMF, –50° to rt
2. H_2O

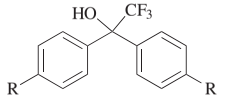


R^1	R^2		
H	H	(86)	179
Cl	Cl	(74)	
O_2N	H	(83)	
MeO	H	(73)	
Me	H	(85)	

C_{13}

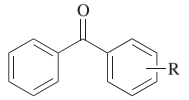


1. **76** (1.2 eq), *t*-BuOK (4.4 eq), *n*-BuNCl (4.4 eq), –30°, 0.5 h
2. Substrate (1 eq), –30°, 1.5 h; to rt

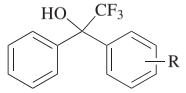


R		
H	(94)	107
MeO	(94)	

C_{13-14}

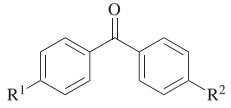


1. CF_3H (1 eq), (inverse addition), Et_2O, –50°; –40°, 10 min
2. KHMDS (1 eq), –40°, 1 h; rt, 10 h

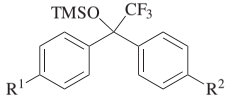


R		
H	(71)	77
4-F	(81)	
3-O_2N	(78)	
4-MeO	(54)	
4-Me	(53)	

C_{13-19}



$TMSCF_3$ (*x* eq), catalyst (*y* eq), DMF, rt



65

R^1	R^2	*x*	Catalyst	*y*	Time (h)	
H	H	3	K_2CO_3	0.2	10	(80)
H	H	2.5	**28**	0.1	16	(65)
Cl	H	1.5	K_2CO_3	0.1	3	(80)
Cl	Cl	1.5	**28**	0.1	1	(81)
Br	H	1.5	K_2CO_3	0.1	1.5	(75)

Br	H	1.5	**28**	0.05	1	(94)
Br	Br	1.5	K_2CO_3	0.1	1	(67)
O_2N	H	1.5	K_2CO_3	0.1	1.5	(85)
O_2N	H	1.5	**28**	0.05	1	(87)
MeO	H	3	K_2CO_3	0.2	24	(67)
MeO	H	2.5	**28**	0.2	24	(55)
Me	H	3	K_2CO_3	0.2	24	(76)
Me	H	2.5	**28**	0.2	24	(65)
Ph	H	2	K_2CO_3	0.1	8	(90)
Ph	H	2	**28**	0.1	12	(74)

C_{13-15}



CF_3H (excess), **57** (1.5 eq), THF, 2 h



Ar	R	Temp (°)		
Ph	Ph	–20	(92)	
4-ClC_6H_4	4-ClC_6H_4	–20	(82)	82
Ph	(*E*)-PhCH=CH	–30	(72)	
Ph	PhC≡C	–30	(92)	

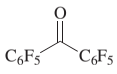
C_{13}



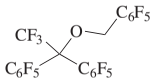
1. $(EtO)_2P(O)CF_3$ (1.2 eq), PhOK (2 eq), DMF, –40°; to rt, 1 h
2. HCl



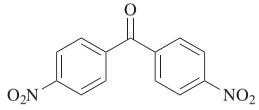
Ar		
Ph	(91)[b]	167
4-ClC_6H_4	(99)[b]	



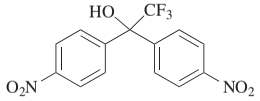
1. $TMSCF_3$ (1 eq), CsF (1 eq), MeCN, –30°, 0.5 h; rt, 5 h
2. $C_6F_5CH_2Br$ (0.52 eq), 90°, 48 h



(53) 466



$TMSCF_3$ (2.8 eq), KF (5 eq), DMA, 50°, few min



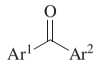
(—) 306

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

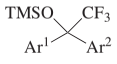
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{13-15}



$TMSCF_3$ (3 eq), Me_3NO (0.15 eq), DMF, rt, 24 h



(—) 65

Ar^1	Ar^2	Conv (%)
4-FC_6H_4	4-FC_6H_4	80
4-ClC_6H_4	4-ClC_6H_4	96
4-BrC_6H_4	Ph	80
3-$O_2NC_6H_4$	Ph	74
4-$O_2NC_6H_4$	Ph	100
3,4-$Cl_2C_6H_3$	Ph	83
4-$CF_3C_6H_4$	Ph	75
3-$CF_3C_6H_4$	3-$CF_3C_6H_4$	100

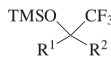
C_{13-17}



1. CF_3H (1.4–8.6 eq), TMS_3N (1.5 eq), catalyst (0.2 eq), solvent, –10°, 1 h; rt, 5 h
2. HCl, H_2O



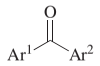
I +



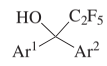
II

R^1	R^2	Catalyst	Solvent (s)	Conv **I** (%)	**I**	Conv **II** (%)	**II**	Refs.
4-FC_6H_4	4-FC_6H_4	CsF	DMF	43	(—)	44	(64)	73, 75
(*E*)-PhCH=CH	Ph	TMAF	DMF	—	(26)	68	(42)	73, 75
(*E*)-PhCH=CH	Ph	TMAF	THF, DMF (0.3 eq)	17	(—)	2	(—)	75
(*E*)-PhCH=CH	(*E*)-PhCH=CH	TMAF	DMF	40	(—)	22	(45)	73, 75

C_{13}

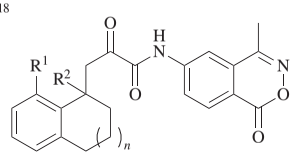


1. $PhSO_2C_2F_5$ (1.5 eq), *t*-BuOK (4.6 eq), THF, –75°; –75 to –70°, 1.5 h
2. HCl, –75 to –70°

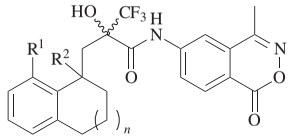


Ar^1	Ar^2		Refs.
Ph	3-$O_2NC_6H_4$	(67)	180
4-ClC_6H_4	4-ClC_6H_4	(93)	
4-$MeOC_6H_4$	4-$MeOC_6H_4$	(99)	

C_{13-18}

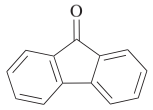


1. $TMSCF_3$ (*x* eq),
additive (*y* eq), DMF
2. TBAF (6 eq), THF, 0.5 h

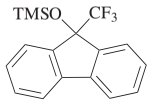


n	R^1	R^2	*x*	Additive	*y*	Temp	Time	Step 2	Diastereomers	
1	H	H	5.25	Cs_2CO_3	1.2	rt	o/n	yes	(26) + (21)	419, 981
1	O_2N	H	5.25	Cs_2CO_3	1.2	rt	o/n	yes	(31) + (10)	419
1	H	Me	5.0	Cs_2CO_3	1.2	rt	3 h	yes	(1.1) + (1.3) + (2.4) + (1.45)	419
1	H	Et	6.9	Cs_2CO_3	1.2	rt	o/n	no	(16.4) + (15.9)	419
1	H	*n*-Pr	7.0	Cs_2CO_3	2.1	0° to rt	—	yes	(7) + (5)	419
1	H	Et_2CH	10.7	CsF	5	rt	o/n	no	(39) + (38)	419
1	H	*c*-C_5H_9	11.6	CsF	5.4	rt	o/n	no	(28) + (28)	419
2	H	Et	5.5	Cs_2CO_3	1.9	rt	26 h	no	(5.7) + (4.3)	419

C_{13}



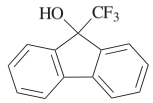
1. CF_3H (1.4–8.6 eq),
TMS_3N (1.5 eq), catalyst (0.2 eq),
solvent, –10°, 1 h; rt, 5 h
2. HCl, H_2O



73
75

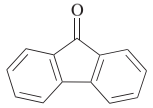
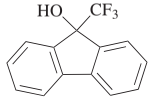
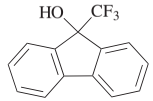
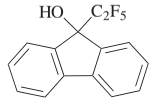
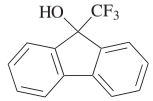
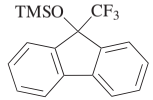
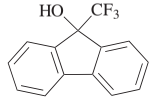
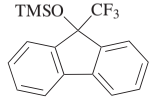
Catalyst	Solvent (s)	Conv (%)	
CsF	DMF	72	(57)
TMAF	THF, DMF (0.3 eq)	83	(75)

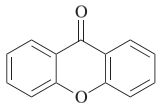
CF_3Br (1 atm), e^-, Zn (anode),
Ni (cathode), Bu_4NBr (0.5 eq),
DMF, –10°, 4–12 h



(30) 868

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{13} 	CF_3Br, e^-, Zn anode, Bu_4NBr, DMF		(30) 234
	CF_3I (2.2 eq), TDAE (2.2 eq), DMF, *h*ν, –20° to rt, 12 h		(65) 73% conv 385
	C_2F_5I (2.2 eq), TDAE (2.2 eq), DMF, –15° to rt; *h*ν, 1 h; rt, 12 h		(95) 386
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 2 h 2. HCl, H_2O		(90) 289
	$TMSCF_3$ (2 eq), KF (0.1 eq), *n*-Bu_4NBr (0.1 eq), toluene, rt, 0.5 h		(90) 457
	1. **62a** (2 eq), *t*-BuOK (2 eq), THF, rt, 24 h 2. HCl, H_2O		(64) 63% conv 110
	63 (2 eq), CsF (0.1 eq), DME, 80°, 5 h		(90) 100% conv 74



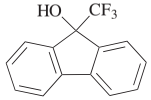
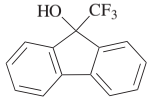
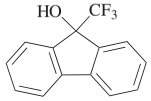
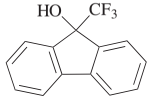
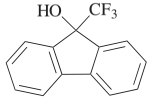
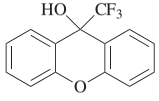
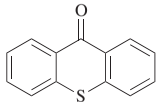
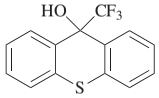
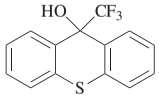
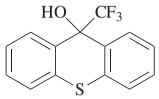
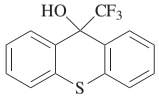
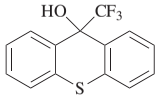
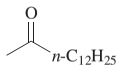
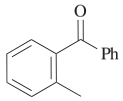
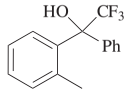
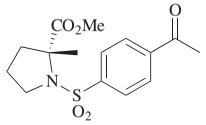
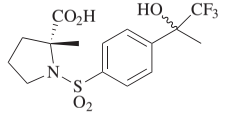
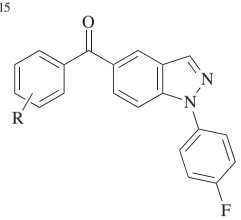
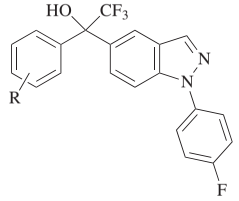
1. **76** (1.2 eq), *t*-BuOK (4.4 eq), *n*-Bu_4NCl (4.4 eq), –30°, 0.5 h 2. Substrate (1 eq), –30°, 1.5 h; to rt		(88)	107
1. $PhCOCF_3$(2 eq), *t*-BuOK (2 eq), THF/DMF (2:1), rt, 20 min 2. HCl, H_2O, o/n		(50) 55% conv	115
1. **85** (1 eq), *t*-BuOK (1 eq), THF/DMF (1:1), rt, 24 h 2. HCl, H_2O, o/n		(95) 100% conv	119
1. CF_3CO_2Me (2 eq), *t*-BuOK (2 eq), THF/DMF (1:1), rt, 24 h 2. HCl, H_2O, o/n		(20) 22% conv	119
1. $(EtO)_2P(O)CF_3$ (1.2 eq), PhOK (2 eq), DMF, –40°; to rt, 1 h 2. HCl		(89)[b]	167
1. $(EtO)_2P(O)CF_3$ (1.2 eq), PhOK (2 eq), DMF, –40°; to rt, 1 h 2. HCl		(83)	167

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{13}			
	1. **62a** (2 eq), *t*-BuOK (2 eq), THF, rt, 24 h 2. HCl, H_2O		(71) 76% conv	110
	1. **76** (1.2 eq), *t*-BuOK (4.4 eq), *n*-BuNCl (4.4 eq), –30°, 0.5 h 2. Substrate (1 eq), –30°, 1.5 h; to rt		(78)	107
	1. $PhCOCF_3$ (2 eq), *t*-BuOK (2 eq), THF/DMF (2:1), rt, 20 min 2. HCl, H_2O, o/n		(90) 100% conv	115
	1. **85** (1 eq), *t*-BuOK (1 eq), THF/DMF (1:1), rt, 24 h 2. HCl, H_2O, o/n		(60) 60% conv	119
	1. CF_3CO_2Me (2 eq), *t*-BuOK (2 eq), THF/DMF (1:1), rt, 24 h 2. HCl, H_2O, o/n		(20) 25% conv	119

C_{14} 	1. $TMSC_2F_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h 2. HCl, H_2O, rt, 12 h		(33.8)	398
	CF_3H (4.3 eq), TMS_3N (1.5 eq), TMAF (1.5 eq), DMF, –10°, 1 h		(11)	75
	1. $TMSCF_3$, TBAF, THF, 0°; rt, 2 h 2. NaOH, MeOH, THF, rt, o/n 3. HCl		(50)	982
$C_{14–15}$ 	1. $TMSCF_3$, THF, rt, 3 h 2. TBAF, rt, 1 h		(35–77)	983

R= 2-F; 4-F; 2-Cl; 3-Cl; 3-Cl-4-F; 2,3-Cl_2; 3,4-Cl_2; 2-Me; 3-Me; 4-Me; 3–CN; 3–CN-4-F

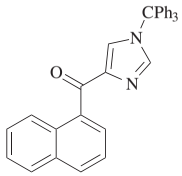
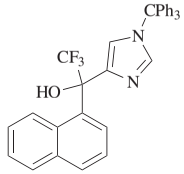
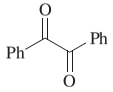
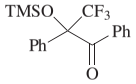
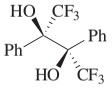
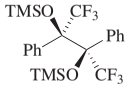
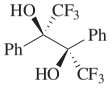
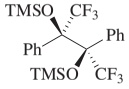
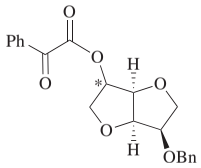
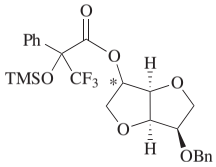
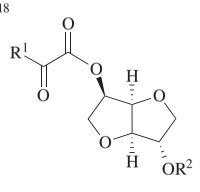
C_{14} 	1. $TMSCF_3$ (2.8 eq), TBAF (7.7 eq), THF, 0°; rt, o/n 2. H_2O, 0.5 h		(75)	984

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

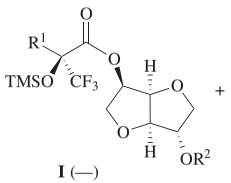
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{14} 	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 2 h 2. HCl, H_2O	 (85)	289
	1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 5 h 2. TMAF, H_2O, 4 h	 **I** (—) +  **II** (—) **I** + **II** (98)	482
	1. $TMSCF_3$ (8.5 eq), TMAF (0.34 eq), THF, 0°, 0.5 h; rt, 24 h 2. TMAF (1.13 eq), THF, rt, 24 h	 **I** (—) +  **II** (—) **I** + **II** (98)	483
	$TMSCF_3$ (1.2 eq), additive (5 mol %), DMF, 0.5 h		417

*Config.	Additive	Temp (°)	Conv (%)	dr
(3*R*)	AcOLi	0 to rt	88	79:21
(3*R*)	*n*-Bu_4NOAc	0	75	79:21
(3*S*)	AcOLi	0 to rt	82	56:44
(3*S*)	*n*-Bu_4NOAc	0	77	55:45

$C_{14–18}$

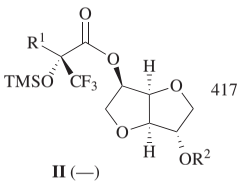


$TMSCF_3$ (x eq), catalyst (y mol %)



I (—)

+



II (—)

417

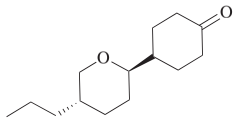
R^1	R^2	x	Catalyst	y	Solvent	Temp (°)	Time (h)	Conv **I** + **II** (%)	**I/II**
Ph	Me	1.4	PhOLi	10	DMF	–45	3	85	89:11
Ph	*t*-Bu	1.4	PhOLi	10	DMF	–45	3	80	88:12
Ph	Bn	1.2	CsF	5	DME	0	0.5	84	49:51
Ph	Bn	1.2	AcOLi	5	DMF	0 to rt	0.5	84	83:17
Ph	Bn	1.2	*n*-Bu_4NOAc	5	DMF	0	0.5	81	83:17
Ph	Bn	1.4	PhOLi	10	DMF	0	3	72	82:18
Ph	Bn	1.4	PhOLi	10	DMF	–20	3	83	85:15
Ph	Bn	1.4	PhOLi	10	DMF	–45	3	82	90:10
Ph	Bn	1.4	PhONa	10	DMF	–45	3	77	90:10
Ph	Bn	1.4	PhOK	10	DMF	–45	3	65	90:10
Ph	4-$ClC_6H_4CH_2$	1.4	PhOLi	10	DMF	–45	3	81	90:10
Ph	1-$C_{10}H_7CH_2$	1.4	PhOLi	10	DMF	–45	3	82	90:10
4-ClC_6H_4	Bn	1.4	PhOLi	10	DMF	–45	3	80	88:12
4-$MeOC_6H_4$	Bn	1.4	PhOLi	10	DMF	–45	5	81	92:8
2-$C_{10}H_7$	Bn	1.4	PhOLi	10	DMF	–45	3	73	89:11

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

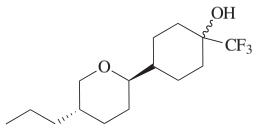
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

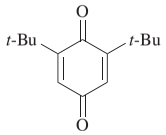
C_{14}



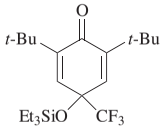
1. $TMSCF_3$, TBAF (cat.), THF, 0° to rt
2. KF, MeOH, reflux, 3 h



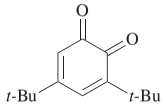
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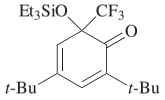
Et_3SiCF_3 (*x* eq), additive (*y* eq), MeCN, rt



x	Additive	*y*	Time (h)		Refs.
1	K_2CO_3	0.2	22	(41)	489
1.17	*n*-Bu_4NHF_2	0.1	0.5	(—)	489a
1.18	KHF_2	1.18	2	(—)	489a
1.53	KF	1.94	1	(70)	489

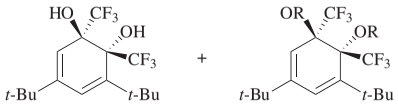


Et_3SiCF_3 (*x* eq), additive (*y* eq), MeCN, rt



x	Additive	*y*	Time (h)		Refs.
1	K_2CO_3	0.2	22	(83)	489
1.17	*n*-Bu_4NHF_2	0.1	0.5	(—)	489a
1.18	KHF_2	1.18	2	(—)	489a
1.53	KF	1.94	1	(90)	489

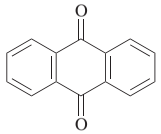
1. $TMSCF_3$ (8.9 eq), TMAF (0.35 eq), THF, 0°, 0.5 h; rt, 24 h
2. TMAF (1.2 eq), THF, rt, 24 h



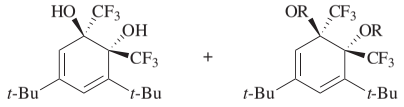
I (—) **I** + **II** (89) **II** (—)

R = H, TMS

483



1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 4 h
2. TMAF, H_2O, 5 h

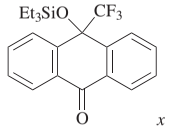


I (—) **I + II** (89) **II** (—)

R = H, TMS

482

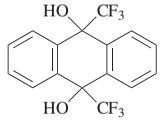
Et_3SiCF_3 (*x* eq), initiator (*y* eq), DMF, rt



489

x	Initiator	*y*	Time (h)	
1	K_2CO_3	0.2	5	(82)
1.53	KF	1.94	1	(86)

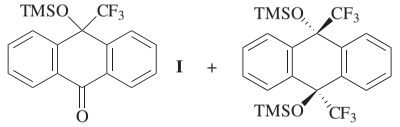
1. $TMSCF_3$ (2.05 eq), TBAF (2 mol %), THF, 10°, 10 min; to rt, 24 h
2. HCl (concd), THF, rt, 3 h



(88)

487

$TMSCF_3$ (1.2 eq), additive (*x* eq), solvent, rt



I + **II**

486

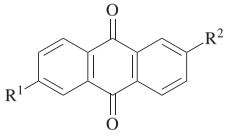
Additive	*x*	Solvent	Time (h)	**I**	**II**
K_2CO_3	0.2	DMF	4	(43)[b]	(27)[b]
CsF	0.1	THF	3	(90)	(0)

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

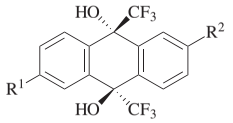
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

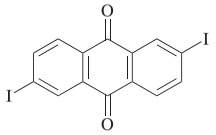
C_{14}



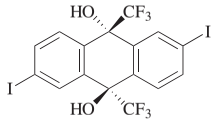
1. $TMSCF_3$ (3 eq), K_2CO_3 (0.4 eq), DMF, 0°; rt, 15 h
2. HCl (concd), EtOH, reflux, 3 h



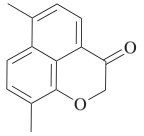
R^1	R^2		Refs.
H	H	(71)	486
H	Br	(100)	
H	I	(100)	
Br	Br	(85)	



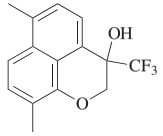
1. $TMSCF_3$ (3 eq), K_2CO_3 (0.4 eq), DMF, 0°; rt, 15 h
2. TBAF



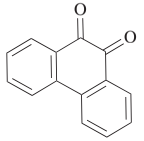
(74) 486



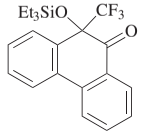
1. $TMSCF_3$, TBAF, THF, rt
2. TBAF, THF, rt



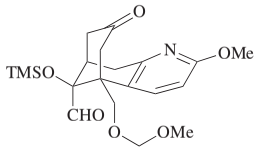
(93) 986



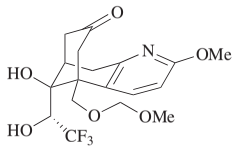
Et_3SiCF_3 (*x* eq), additive (*y* eq), solvent, rt



x	Additive	*y*	Solvent	Time (h)		Refs.
1	K_2CO_3	0.2	DMF	4	(83)	489
1.17	*n*-Bu_4NHF_2	0.1	MeCN	0.5	(—)	489a
1.18	KHF_2	1.18	MeCN	2	(—)	489a
1.53	KF	1.94	DMF	1	(86)	489



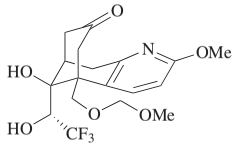
1. $TMSCF_3$, TBAF, THF
2. TBAF



(81)

410

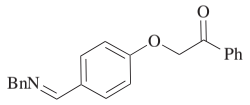
1. $TMSCF_3$ (2 eq), TBAF (1 mol %), THF, rt, 50 min
2. TBAF (2 eq), THF, rt, 15 min



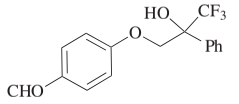
(81)

505

C_{15}

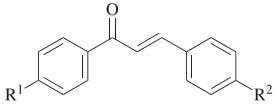


1. $TMSCF_3$, TBAF, THF, 4°, 18 h
2. NH_4F, H_2O
3. HCl, H_2O

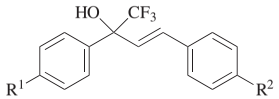


(45)

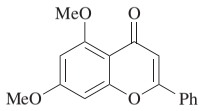
490



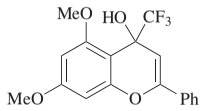
1. CF_3H (1 eq), (inverse addition), Et_2O, –50°; –40°, 10 min
2. KHMDS (1 eq), –40°, 1 h; rt, 10 h



R^1	R^3		
H	H	(67)	77
F	F	(38)	
Cl	H	(60)	
O_2N	H	(0)	
MeO	H	(63)	



1. $TMSCF_3$, TMAF (cat.), 0°, 24 h
2. HCl, H_2O



(—)

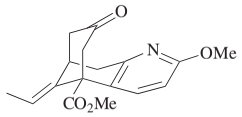
258

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

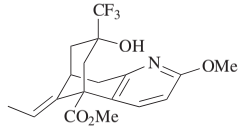
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

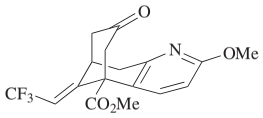
C_{15}



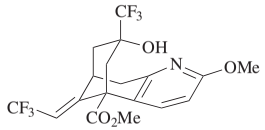
1. $TMSCF_3$ (2.03 eq), TBAF (0.1 eq), THF, rt, 0.5 h
2. TBAF (2.03 eq), THF, rt, 0.25 h



(50) 505, 410

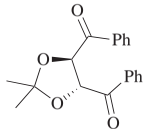


1. $TMSCF_3$ (4.9 eq), TBAF (0.2 mol %), THF, rt, 3 h
2. TBAF (1 eq), THF, rt, 0.25 h

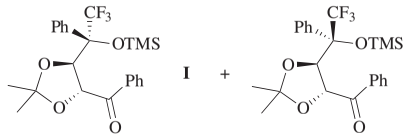


(43) 505, 410

C_{16}



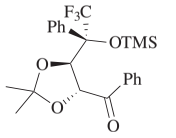
$TMSCF_3$ (x eq), initiator (8 mol %), solvent



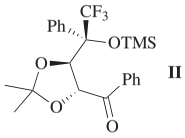
I + **II** 484

x	Initiator	Solvent	Temp (°)	Time (min)	**I + II**	**I/II**
1.05	TMAF	CH_2Cl_2	0	15	(95)	95:5
1.05	TBAF	CH_2Cl_2	0	15	(95)	95:5
1.05	TBAF	THF	0	20	(90)	98:2
1.05	TBAF	THF	–40	60	(90)	99:1
1.1	CsF	DME	–40	180	(90)	70:30
1.5	TBAF	CH_2Cl_2	0	1–2	(99)	96:4
3	TBAF	CH_2Cl_2	0	30	(99)	98:2
3	$Bu_4N^+ Ph_3SnF_2^-$	CH_2Cl_2	0	30	(75)	90:10

TMSCF$_3$ (3 eq), CsF, DME, rt, 12 h

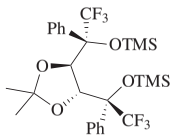


I +

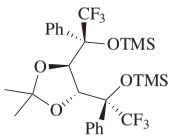


II 484

\+



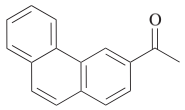
III +



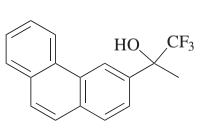
IV

I + **II** (9), **I**/**II** = 1:1

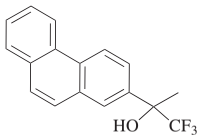
III + **IV** (54), **III**/**IV** or **IV**/**III** = 84:16



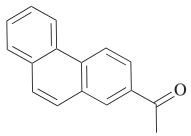
1. TMSCF$_3$ (1.65 eq), TBAF (cat.), THF, 0°; rt, 2 h
2. TBAF, 0.25 h



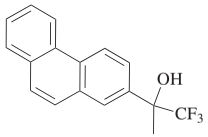
(66) +



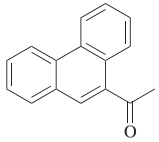
(25) 987



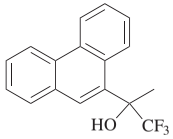
1. TMSCF$_3$ (1.65 eq), TBAF (cat.), THF, 0°; rt, 2 h
2. TBAF, 0.25 h



(61) 987

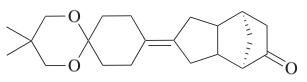
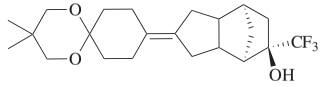
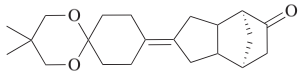
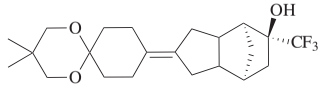
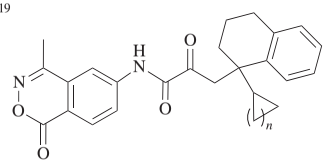
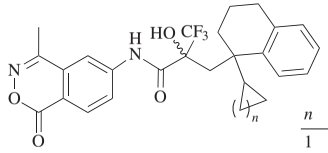
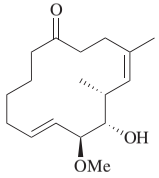
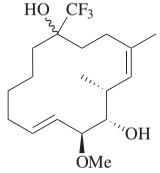
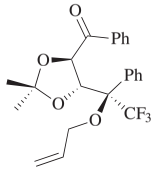
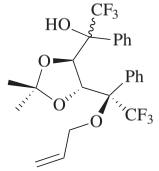


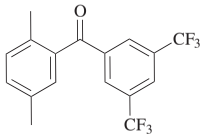
1. TMSCF$_3$ (1.65 eq), TBAF (cat.), THF, 0°; rt, 2 h
2. TBAF, 0.25 h



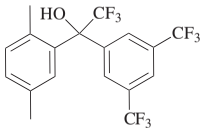
(68) 987

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

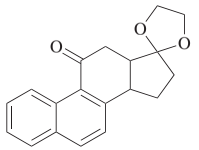
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{16} 	1. $TMSCF_3$ (0.98 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 1 h 2. HF, H_2O, MeCN, 0.5 h	 (60)	988
	1. $TMSCF_3$ (0.98 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 1 h 2. HF, H_2O, MeCN, 0.5 h	 (62)	988
C_{16-19} 	$TMSCF_3$ (5 eq), CsF (2 eq), DMF, o/n	 *n* Temp 1 0° (—) 2 rt (—) 4 rt (—)	420
C_{16} 	1. $TMSCF_3$ (5 eq), TBAF (cat.), THF, rt, 1 h 2. TBAF (excess), 5 h	 (80)	989
C_{17} 	$TMSCF_3$ (2.1 eq), CsF (0.2 eq), DME, rt, 2 h	 (87) dr 69:31	503



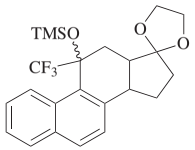
TMSCF$_3$ (2.5 eq), TBAF (5 eq), THF, rt, 1 h



(92) 990

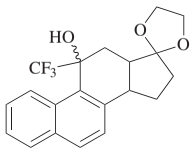


TMSCF$_3$, TBAF (cat.), THF, rt



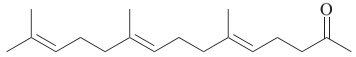
(66) 519

1. TMSCF$_3$ (1.46 eq), TBAF (1.3 mol %), THF, 0°; rt, o/n
2. TMSCF$_3$, TBAF, THF, 0°; rt, o/n
3. HCl, H$_2$O, THF, rt, 48 h

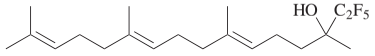


(99) 518

C_{18}

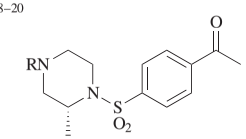


1. TMSC$_2$F$_5$ (1.2 eq), TBAF (1 eq), THF, 0°, 1 h; rt, 12 h
2. HCl, H$_2$O, rt, 12 h

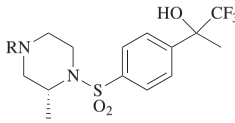


(30.8) 398

C_{18-20}



TMSCF$_3$, TBAF, THF



991

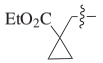
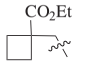
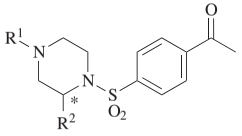
R^j	
2-(4-pyridylethyl)	(63)
	(78)
	(78)

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

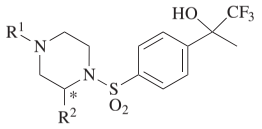
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

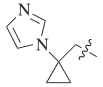
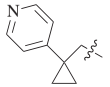
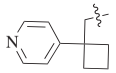
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{18-23}

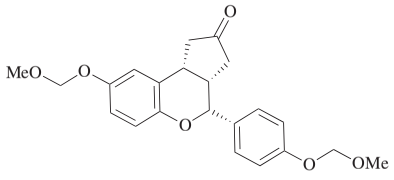


$TMSCF_3$ (x eq), TBAF (y eq), THF

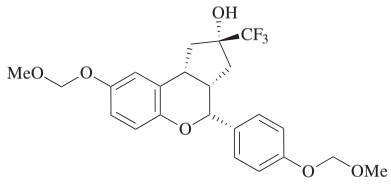


R^1	R^2	x	y	Temp (°)	Time (h)		Refs.
	Me (*R*)	1.5	1.5	0, rt	—, 3.5	(84)	400, 992
	Me (*R*)	3.1	3.1	—	20	(63)	992
	H	1	1	0	2	(20)	992
"	Me (*R*)	1	1	0	2	(—)	992
"	$HOCH_2CH_2$ (*R,S*)	1	1	0	2	(36)	992
	Me (*R*)	3.7	7.4	—	1	(78)	992
	H	3.9	7.8	—	1	(57)	992
"	Me (*R*)	3.9	7.8	—	1	(—)	992

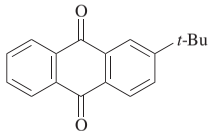
C_{18}



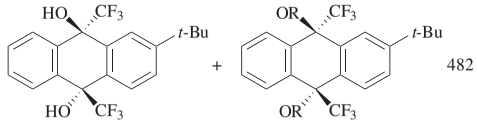
$TMSCF_3$, TBAF, THF



(—) 993



1. $TMSCF_3$ (1.5 eq), TMAF (cat.), THF, 0°, 0.5 h; rt, 8 h
2. TMAF, H_2O, 6 h

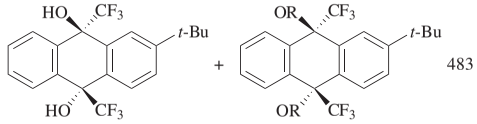


R = H, TMS

I (—) **I** + **II** (94) **II** (—)

482

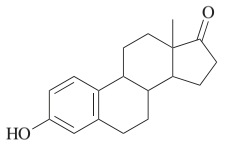
1. $TMSCF_3$ (10.7 eq), TMAF (0.43 eq), THF, 0°, 0.5 h; rt, 24 h
2. TMAF (1.42 eq), THF, rt, 24 h



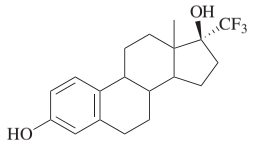
R = H, TMS

I (—) **I** + **II** (94) **II** (—)

483

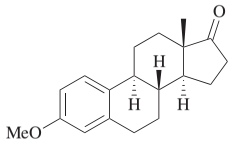


1. $TMSCF_3$ (4.6 eq), TMAF (0.24 eq), THF, 0°, 0.5 h; rt, 4 h
2. HF, H_2O, MeCN, rt, 0.5 h



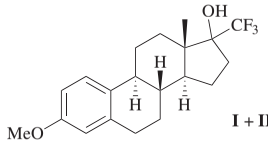
(88)

520



I

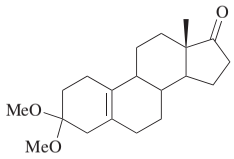
1. $TMSCF_3$, (2.4 eq), TBAF (2 eq), THF, 0° to rt, 24 h
2. HCl, H_2O, rt, 15 h



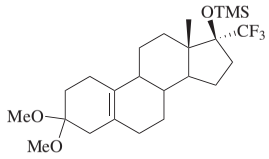
II

I + **II** (62), **I**/**II** = 1:9

122



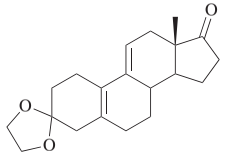
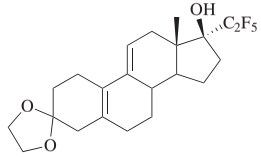
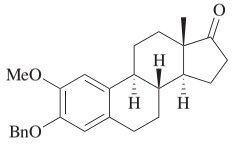
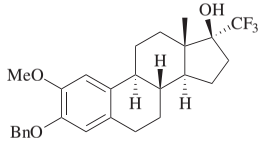
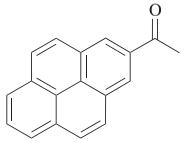
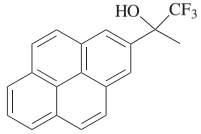
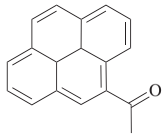
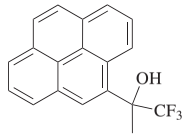
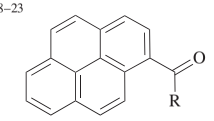
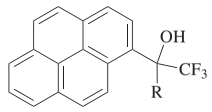
$TMSCF_3$ (4.6 eq), TMAF (0.24 eq), THF, 0°, 0.5 h; rt, 4 h



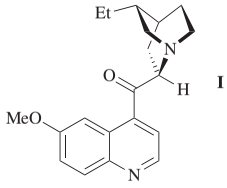
(90)

523

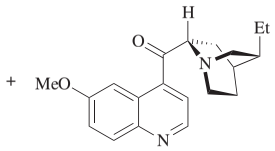
TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{18} 	C_2F_5I (2 eq), MeLi/LiBr (1.8 eq), toluene, –78°, 1 h; 0°, 1 h	 (85)	994
	$TMSCF_3$ (1.5 eq), TBAF (cat.), THF, rt, 10 h	 (70)	525
	$TMSCF_3$ (2 eq), TBAF (0.77 eq), THF, 0°; rt, 3 h	 (48)	987
	$TMSCF_3$ (2 eq), TBAF (0.77 eq), THF, 0°; rt, 3 h	 (57)	987
C_{18-23} 	$TMSCF_3$ (2 eq), TBAF (0.77 eq), THF, 0°; rt, 3 h	 R: Me (85); Ph (90)	987

C_{19}

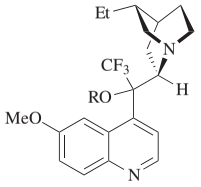


I **I/II** = 10:1



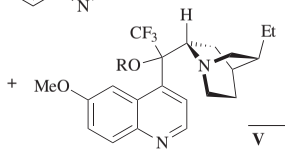
II

TMSCF$_3$ (1.2 eq), TBAF (cat.), DME, THF, rt

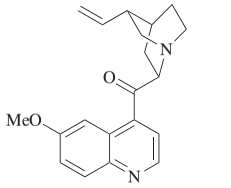


	R		
III	TMS	(—)	455
IV	H	(—)	

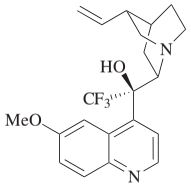
III/IV dr 100:8:16:2



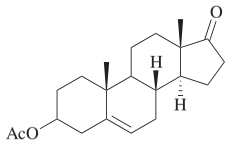
	R		
V	TMS	(—)	
VI	H	(—)	



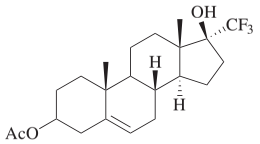
TMSCF$_3$ (2.5 eq), Bu_4N^+ $Ph_3SiF_2^-$ (0.25 eq), THF, 0°; rt, 2 h



(71) 995

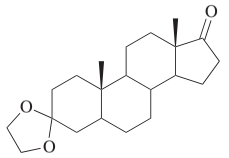
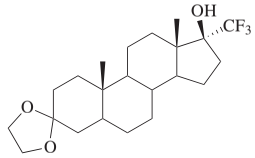
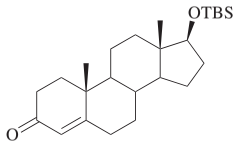
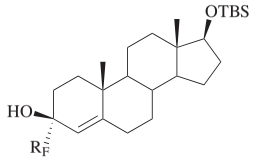
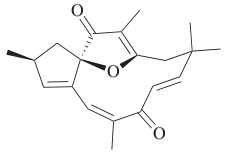
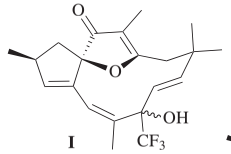
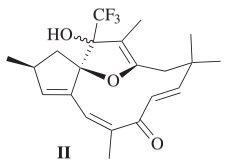
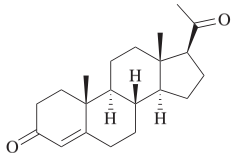
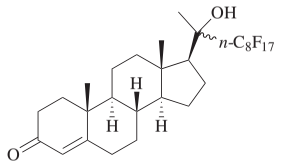


1. TMSCF$_3$ (4.6 eq), TMAF (0.24 eq), THF, 0°, 0.5 h; rt, 4 h
2. HF, H_2O, MeCN, rt, 0.5 h



(83) 520

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{19} 	$TMSCF_3$, TBAF, THF	 (77)	469
	R_FI (2 eq), MeLi (1.8 eq), Et_2O, –78° to rt, 1 h	 R_F: C_2F_5 (85); *n*-C_3F_7 (82); *n*-C_4F_9 (80)	996
C_{20} 	$TMSCF_3$ (4 eq), CsF (1 eq), 0°, 12 h	 **I** +  **II**; **I + II** (89), **I/II** = 40:60	997
C_{21} 	*n*-$C_8F_{17}MgBr$, Et_2O, –78° to rt, 45 h	 (11)	998

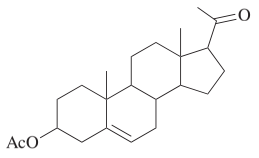
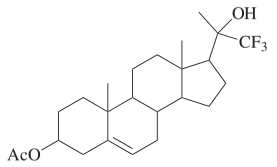
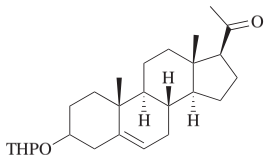
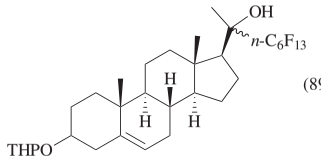
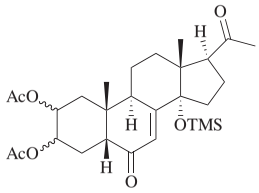
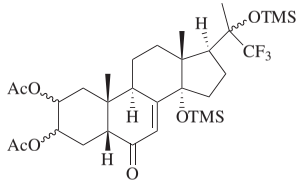
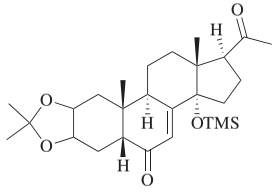
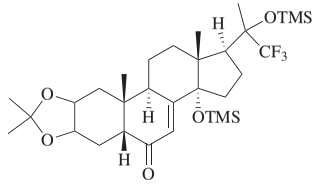
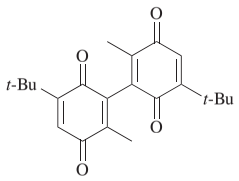
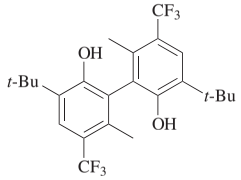
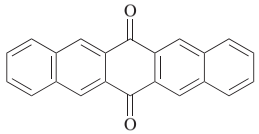
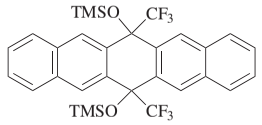
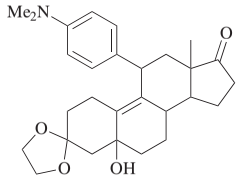
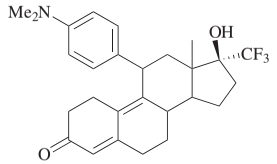
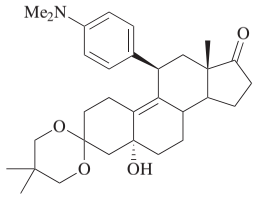
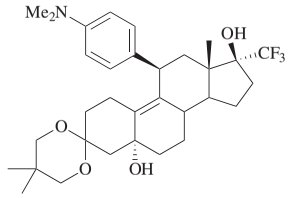
	1. $TMSCF_3$ (4.6 eq), TMAF (0.24 eq), THF, 0°, 0.5 h; rt, 4 h 2. HF, H_2O, MeCN, rt, 0.5 h		(88)	520
	*n*-$C_6F_{13}MgBr$, Et_2O, –78° to rt, 6 h		(89.8)	998
	$TMSCF_3$ (2.96 eq), TBAF (cat.), THF, 0°, 3 min		(94)	521
	$TMSCF_3$ (2.96 eq), TBAF (cat.), THF, 0°, 3 min		(31)	521

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{22} 	1. $TMSCF_3$ (3 eq), K_2CO_3 (0.26 eq), DMF, rt, 12 h 2. Al/Hg (1 eq), THF, reflux, 2 h	 (70)	999
	$TMSCF_3$ (2.2 eq), CsF (1 mol %), THF, 0°, 10 min; rt, 3 h	 (90)	488
C_{24} 	1. $TMSCF_3$ (4.6 eq), TMAF (0.24 eq), THF, 0°, 0.5 h; rt, 4 h 2. HF, H_2O, MeCN, rt, 0.5 h	 (96)	520
	$TMSCF_3$ (4.12 eq), TBAF (2.06 eq), THF, 0°; rt, 2 h	 (97)	526

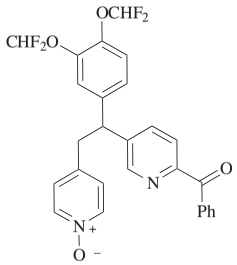
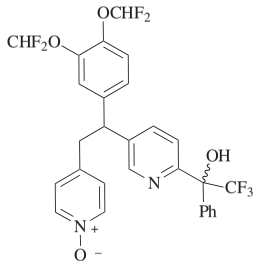
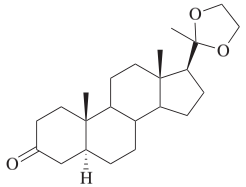
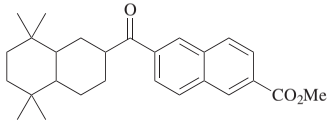
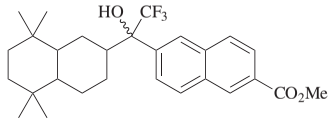
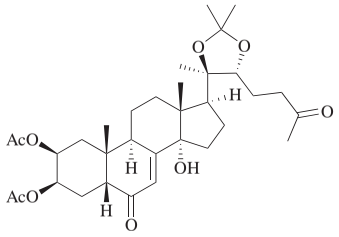
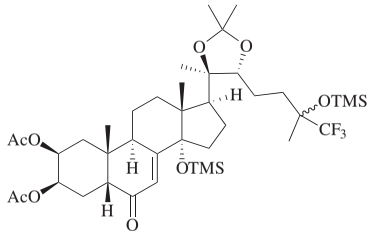
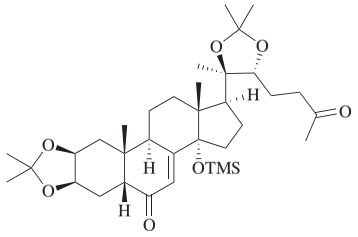
C_{25} 	$TMSCF_3$, TBAF, THF, 0°		(71)		1000
	1. $TMSCF_3$ (1.19 eq), TBAF (0.8 mol %), THF, 0°; rt, 5 h 2. $TMSCF_3$ (0.12 eq), TBAF (0.25 mol %), o/n 3. HCl, H_2O, 5 h		(55)	+ (5)	524
C_{26} 	1. $TMSCF_3$ (1.2 eq), TBAF (2 mol %), THF, 0°; rt, 4 h 2. TBAF (3.02 eq), 16 h		(67)		1001
	$TMSCF_3$ (3 eq), TBAF (0.8 mol %), THF, 0°, 3 min		(87)		522

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

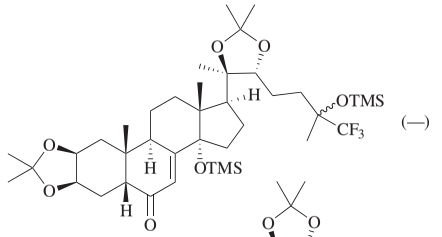
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

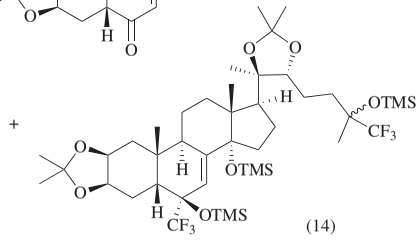
C_{26}



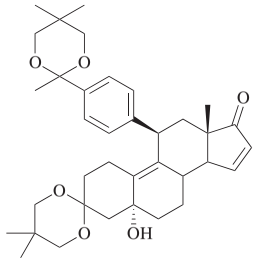
$TMSCF_3$ (6.1 eq), TBAF (0.8 mol %), THF, 0°, 3 min



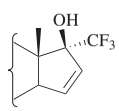
(—) 522



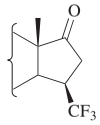
(14)



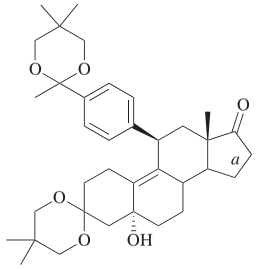
$TMSCF_3$ (4 eq), TBAF (2 eq), THF, 0°; rt, 3 h



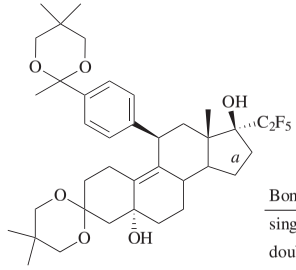
(14) +



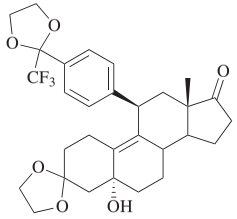
(33) 526



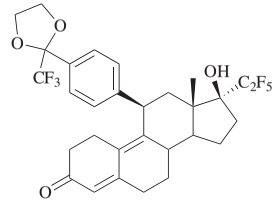
C_2F_5I (8.5 eq), MeLi/LiBr (7 eq),
Et_2O, THF, –78°, 2 h



Bond *a*		
single	(49)	526, 1002
double	(83)	526

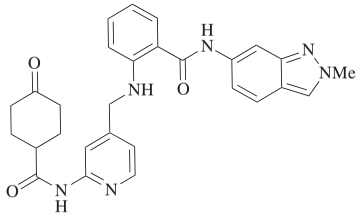


1. C_2F_5I (1.1 eq), MeLi/LiBr (1 eq),
toluene, –78°, 1 h; 0°, 1 h
2. H_2SO_4 (50%), MeOH, 0°; rt, 1 h

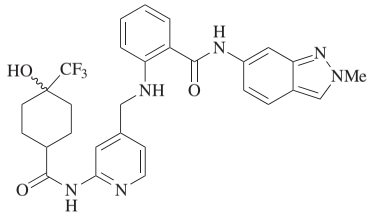


(70) 994

C_{27}



$TMSCF_3$ (1.5 eq), TBAF (1 eq),
THF, rt, o/n



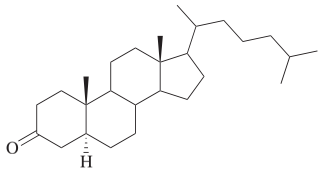
(9) 1003

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

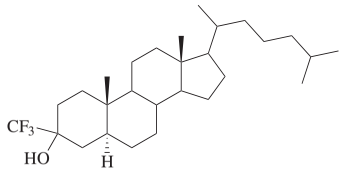
Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

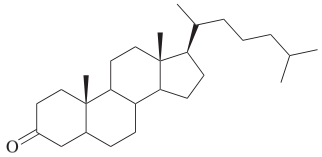
C_{27}



1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 2 h
2. HCl, H_2O, rt, 26 h



(83) 288

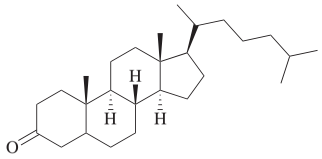


$TMSCF_3$, TBAF, THF

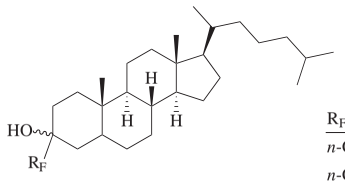


I + **II** 469

I + **II** (52), **I**/**II** = 96:4

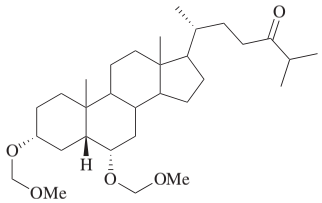


R_FMgBr, Et_2O, –78° to rt, 5 h

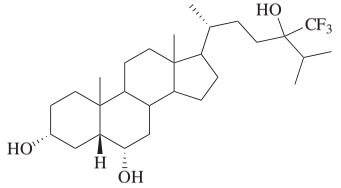


R_F	
n-C_6F_{13}	(30)
n-C_8F_{17}	(40)

998



1. $TMSCF_3$ (4.6 eq), TMAF (0.24 eq), THF, 0°, 0.5 h; rt, 4 h
2. HF, H_2O, MeCN, rt, 0.5 h



(96) 520

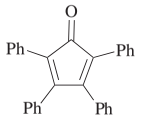
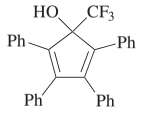
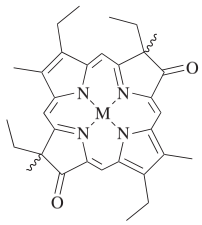
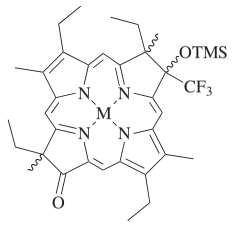
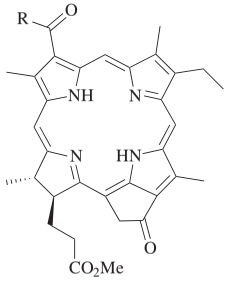
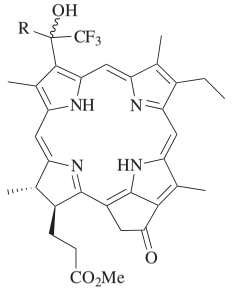
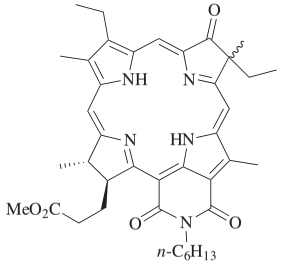
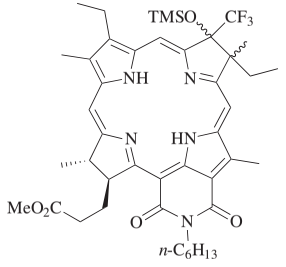
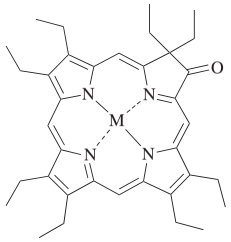
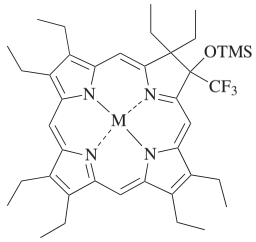
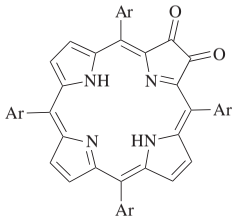
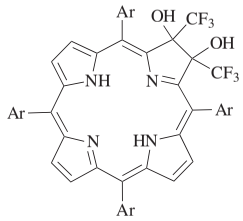
C_{29}		1. $TMSCF_3$ (1.05 eq), TBAF (2 mol %), THF, 10°, 10 min; to rt, 24 h 2. HCl (concd), THF, 70°, 20 h		(89)	487
C_{32}	 M = Zn, 2H	$TMSCF_3$, TBAF (cat.)		(—)	425
C_{33}		1. $TMSCF_3$ (*x* eq), $TBAF•3H_2O$ (*y* mol %), THF, rt, 5 min 2. HCl, H_2O, rt, 1 h		R x y Me 8.3 39 (2) CF_3 10.5 20 (29)	431
		$TMSCF_3$, TBAF (cat.)		(92)	425

TABLE 10. PERFLUOROALKYL ADDITION TO KETONES (*Continued*)

Ketone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{36} 	$TMSCF_3$, TBAF (cat.)	 M: Ni (74), 2H (82)	425
C_{44} 	$TMSCF_3$, TBAF, THF, –40°, 8 h	 (78); Ar = 3-$MeOC_6H_4$	1004

[a] The er was determined after desilylation of the product.

[b] The yield was determined by ^{19}F NMR spectroscopy.

[c] The dr was determined by ^{19}F NMR spectroscopy of the initial adduct.

[d] The product was contaminated with a substantial amount of the less polar isomer.

[e] Use of two equivalents of $TMSCF_3$ gave the same product.

[f] In this paper, the product was reported to crystallize with one molecule of methanol.

[g] X was not specified.

[h] The reaction was also carried out with $TMSC_2F_5$, but no details were given.

[i] The yield is based on [^{18}F]CF_3H and was determined by HPLC.

[j] See the original publication for compounds with other substituents R for which no yields were given other than the range of 20–57%.

TABLE 11. PERFLUOROALKYL ADDITION TO THIOKETONES

Thioketone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{13}



TMSCF$_3$ (2 eq), TBAF (2 eq), THF, syringe pump, 0°; rt, 2 h



I + **II**

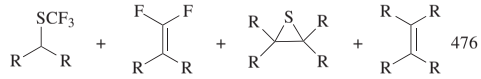
533

R	**I**	**II**
Ph	(30)	(10)
4-MeOC$_6$H$_4$	(35)	(—)

$C_{13–15}$



TMSCF$_3$ (1.25 eq), TBAF (2.5 mol%), 4 Å MS, THF, rt, 3–4 h



I **II** **III** **IV**

476

R	**I**	**II**	**III**	**IV**
Ph	(22)	(6)	(45)	(3)
4-FC$_6$H$_4$	(20)	(—)	(—)	(—)
4-MeOC$_6$H$_4$	(21)	(5)	(—)	(—)
4-MeC$_6$H$_4$	(21)	(9)	(—)	(—)

TABLE 12. PERFLUOROALKYL ADDITION TO ACYLSILANES

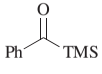
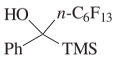
Acylsilane	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_7 	1. *n*-$C_6F_{13}MgBr$, Et_2O, –45°, 15 h 2. HCl, H_2O	 (78)	534

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS

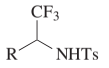
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{2-11}



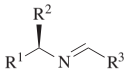
1. $TMSCF_3$ (1.3 eq), TBAT (1.2 eq), THF, 0–5°, 0.75–1 h
2. NH_4Cl, H_2O, 0° to rt



R	
Me	(45)
n-Pr	(50)
c-C_6H_{11}	(80)
Ph	(90)
4-ClC_6H_4	(87)
4-$MeOC_6H_4$	(85)
(*E*)-PhCH=CH	(83)
2-$C_{10}H_7$	(95)

547

C_{2-7}



n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, solvent, –78°



I + **II**

197

R^1	R^2	R^3	Solvent	**I + II**	**I/II**
Me	Ph	*n*-BuO_2C	Et_2O	(53)	77:23
Me	Ph	*i*-Pr	Et_2O	(90)	84:16
Me	Ph	*i*-Pr	toluene	(81)	84:16
Bn	EtO_2C	*n*-Pr	Et_2O	(78)	88:12
Bn	EtO_2C	CH_2=$CHCH_2$	Et_2O	(43)	96:4
i-Pr	MeO_2C	Ph	Et_2O	(54)	98:2
i-Pr	MeO_2C	Ph	toluene	(58)	92:8
i-Bu	EtO_2C	Ph	Et_2O	(73)	94:6
i-Bu	EtO_2C	Ph	toluene	(87)	77:23
Me	Ph	Ph	Et_2O	(63)	77:23
Bn	EtO_2C	Ph	Et_2O	(57)	97:3
Bn	EtO_2C	Ph	toluene	(75)	96:4
Bn	EtO_2C	Ph	toluene	(25)[a]	52:48

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-9}

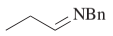


1. R_FI (1.2 eq), $BF_3{\bullet}OEt_2$ (1 eq), Et_2O, –78°
2. MeLi/LiBr (1.2 eq), –78°, 1h

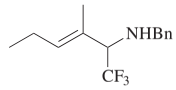


R^1	R^2	R_F		Refs.
Me(MeO)CH	*n*-Pr	n-C_6F_{13}	(46)	313
i-Pr	*i*-Bu	n-C_6F_{13}	(84)	
Ph	Et	C_2F_5	(91)	
Ph	Et	i-C_3F_7	(0)	
Ph	Et	n-C_4F_9	(80)	
Ph	Et	n-C_6F_{13}	(88)	
Ph	Et	n-C_8F_{17}	(79)	
Ph	*t*-Bu	n-C_6F_{13}	(35)	
Ph	*t*-Bu	n-C_6F_{13}	(68)[b]	
Ph	c-C_6H_{11}	n-C_6F_{13}	(69)	
Ph(Me)CH	*n*-Pr	n-C_6F_{13}	(81)	

C_3



$TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, 15 h

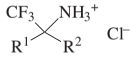


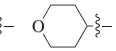
(38) — Refs. 490

C_{3-13}

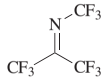


1. $BnNH_2$ (1.05 eq), $MgSO_4$ (5 eq), CH_2Cl_2, rt, 96 h; remove solvent
2. TFA (1.23 eq), $NaHF_2$ (0.8 eq), MeCN/DMF, 0°, 5 min
3. $TMSCF_3$ (1.5 eq) 0°; rt, 12 h
4. Na_2CO_3, rt, 5 min
5. HCl
6. H_2, Pd/C, MeOH, 50 bar

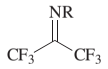


R^1	R^2		Refs.
Me	$MeOCH_2$	(55)	562
Me	Et	(72)	
H	*t*-Bu	(91)	
Me	c-C_3H_7	(41)	
Et	Et	(56)	
H	c-C_5H_9	(93)	
H	c-C_6H_{11}	(50)	
c-C_4H_7	c-C_4H_7	(42)[c]	
		(76)[c]	
c-C_6H_{11}	c-C_6H_{11}	(81)[c]	

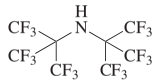
C_3



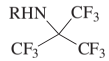
$TMSCF_3$ (4 eq), CsF (1.1 eq), THF, 10° to rt, 2–3 h



1. $TMSCF_3$ (1.1 eq), CsF (*x* eq), solvent, 15° to rt
2. HCl, H_2O



(75) 545



545

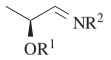
R	*x*	Solvent	Time (h)	
Ph	0.1	THF	12	(10–15)
Ph	1.2	MeCN	2–3	(20–25)
Ph	1.2	THF or DME	2–3	(77)
2-FC_6H_4	1.2	THF	2–3	(67)
3-FC_6H_4	1.2	THF	2–3	(67)
4-FC_6H_4	1.2	THF	2–3	(73)
2,4-$F_2C_6H_3$	1.2	THF	2–3	(75)
3-ClC_6H_4	1.2	THF	2–3	(71)
4-BrC_6H_4	1.2	THF	2–3	(81)
4-$O_2NC_6H_4$	1.2	THF	2–3	(79)
4-$MeOC_6H_4$	1.2	THF	12–16	(48)
2-MeC_6H_4	1.2	THF	12–16	(49)
4-MeC_6H_4	1.2	THF	2–3	(62)
2-$CF_3C_6H_4$	1.2	THF	2–3	(78)
3-$CF_3C_6H_4$	1.2	THF	2–3	(74)
4-$CF_3C_6F_4$	1.2	THF	2–3	(67–84)
3,5-$(CF_3)_2C_6H_3$	1.2	THF	2–3	(69)

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

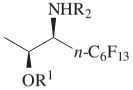
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

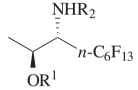
*Please refer the charts preceding the tables for structures indicated by the **bold** numbers.*

C_3



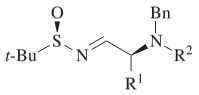
n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2 (x eq), solvent, –78°



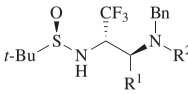
I +  **II** 197

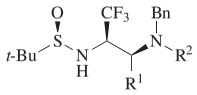
R^1	R^2	x	Solvent	**I** + **II**	**I**/**II**
Me	n-Pr	1.2	Et_2O	(46)	37:63
Me	n-Pr	1.2	toluene	(47)	19:81
Me	n-Pr	2	toluene	(40)	25:75
MOM	n-Pr	1.2	Et_2O	(52)	19:81
MOM	n-Pr	1.2	toluene	(42)	3:97
MOM	CH_2=$CHCH_2$	1.2	Et_2O	(40)	19:81
TBS	CH_2=$CHCH_2$	1.2	Et_2O	(81)	85:15

$C_{3–9}$



$TMSCF_3$ (1.5 eq), TMAF (1.2 eq), THF, –35°, 1–2 h



I +  **II** 555

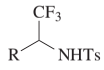
R^1	R^2	**I** + **II**
Me	Bn	(86)
n-Pr	Bn	(85)
i-Pr	Bn	(66)
i-Bu	Bn	(71)
–$(CH_2)_3$–		(79)
Bn	Bn	(81)

I/**II** >99:1

C_{4-8}



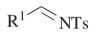
$CF_3B(OMe)_3K$ (1.2 eq), DMF, 70°, 1 h



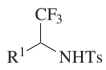
R	
i-Pr	trace[d]
t-Bu	(98)
2-furyl	(87)
Ph	(97)
4-$MeOC_6H_4$	(85)
4-$MeO_2CC_6H_4$	(78)

102

C_{4-11}



1. $TMSCF_3$ (*x* eq), R^2OLi (*y* eq), DMF
2. NH_4Cl, H_2O



(—)

R^1	*x*	R^2	*y*	Temp (°)	Time (h)	Conv (%)	
i-Pr	1.4	Ph	1	0	1	65	549
t-Bu	1.4	Ac	0.1	–20	40	90	549, 131
2-furyl	1.4	Ac	0.1	–20	16	86	549, 131
4-pyridyl	1.4	Ac	0.1	–20	16	89	549, 131
c-C_6H_{11}	1.4	Ac	0.1	–20	40	trace	549, 131
c-C_6H_{11}	1.4	Ph	1	0	1	80	549, 131
4-ClC_6H_4	1.4	Ac	0.1	–20	16	93	549, 131
4-BrC_6H_4	1.4	Ac	0.1	–20	16	80	549, 131
4-$O_2NC_6H_4$	1.4	Ac	0.1	–20	16	92	549, 131
4-$MeOC_6H_4$	1.4	Ac	0.1	–20	40	83	549, 131
4-MeC_6H_4	1.4	Ac	0.1	–20	40	82	549, 131
$Ph(CH_2)_2$	1.4	Ph	1	0	1	35	549, 131
(*E*)-PhCH=CH	2	Ac	0.1	–20	16	78	549, 131
2-$C_{10}H_7$	1.4	Ac	0.1	–20	16	92	549, 131

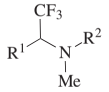
TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{4-11}

1. MeOTf (1.2 eq), CH_2Cl_2, –20° to rt, time 1
2. $TMSCF_3$ (1.5 eq), initiator (*x* eq), DMF, rt, time 2



R^1	R^2	Time 1 (h)	Initiator	*x*	Time 2 (h)	
i-Pr	Bn	0.5	KF	1.5	1	(77)
t-Bu	Bn	0.5	KF	1.5	2	(81)
t-Bu	Bn	0.5	AcONa	2	2	(67)
2-C_4H_3S	4-$MeOC_6H_4$	0.25	AcONa	2	2	(64)
c-C_5H_9	Bn	0.5	KF	1.5	1	(62)
c-C_5H_9	Bn	0.5	AcONa	2	1	(34)
Ph	$CH_2CH{=}CH_2$	0.5	KF	1.5	1	(58)
Ph	$CH_2CH{=}CH_2$	0.5	AcONa	2	1	(51)
(*E*)-PhCH=CH	Me	0.25	AcONa	2	1	(89)
1-$C_{10}H_7$	4-$MeOC_6H_4$	18	KF	1.5	2	(67)

560

C_{4-9}



$TMSCF_3$ (1.5 eq), TFA (1.25 eq), KHF_2 (0.75 eq), DMF (3 eq), MeCN, rt, 3 h



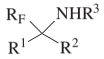
R^1	R^2	**I**	**II**
i-Pr	Bn	(82)	(—)
t-Bu	Bn	(90)	(—)
2-C_4H_3O	*c*-C_6H_{11}	(75)	(—)
2-C_4H_3O	Ph_2CH	(63)	(—)
2-C_4H_3S	*c*-C_3H_5	(50)	(—)
2-C_4H_3S	*c*-C_6H_{11}	(82)	(—)
Ph	Bn	(90)	(—)
2-$MeOC_6H_4$	Bn	(80)	(—)
4-$MeOC_6H_4$	$(MeO)_2CHCH_2$	(75)	(—)
3,4,5-$(MeO)_3C_6H_2$	*n*-Pr	(90)	(—)
3,4,5-$(MeO)_3C_6H_2$	$CH_2CH{=}CH_2$	(81)	(—)
(*E*)-PhCH=CH	Me	(65)	(20)

490

$C_{4–8}$

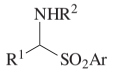


R_FX (1.2 eq), MeLi/LiBr, $BF_3{\bullet}OEt_2$ (1 eq), Et_2O, –78°, 1 h

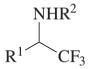


R^1	R^2	R^3	R_F	X		
i-Pr	H	*i*-Bu	*n*-C_6F_{13}	I	(84)	197
Ph	H	Et	C_2F_5	I	(91)	
Ph	H	Et	*n*-C_4F_9	I	(80)	
Ph	H	Et	*n*-C_6F_{13}	I	(88)	
Ph	H	Et	*n*-C_8F_{17}	I	(78)	
Ph	H	Et	*n*-C_8F_{17}	Br	(86)	
Ph	H	*t*-Bu	*n*-C_6F_{13}	I	(35)	
Ph	H	*c*-C_6H_{11}	*n*-C_6F_{13}	I	(69)	
Ph	Me	*n*-C_8H_{17}	*n*-C_6F_{13}	I	(82)	

$C_{4–9}$

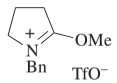


1. $TMSCF_3$ (4 eq). TBAB (5 mol %), 5 Å MS, THF, toluene
2. PhONa (2.2 eq), temp, 16–20 h

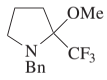


R^1	R^2	Ar	Temp (°)		
n-Pr	Ts	4-MeC_6H_4	–55	(78)	548
i-Pr	Ts	4-MeC_6H_4	–55	(76)	
c-C_6H_{11}	Cbz	Ph	0	(53)	
c-C_6H_{11}	$MesSO_2$	Ph	–30	(75)	
c-C_6H_{11}	Ts	4-MeC_6H_4	–55	(91)	
c-C_6H_{11}	$PMPSO_2$	Ph	–30	(39)	
c-C_6H_{11}	Ph_2PO	4-MeC_6H_4	–30	(51)	
Ph	Cbz	Ph	rt	(75)	
$Ph(CH_2)_2$	Ts	4-MeC_6H_4	–55	(59)	

C_4



$TMSCF_3$ (1.5 eq), KF (1.25 eq), DMF, 50°, 1 h



(80) 635

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{4-14}

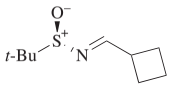


$TMSCF_3$ (1.25 eq), TFA (1.25 eq), KHF_2 (0.75 eq), 0°; rt, 12 h

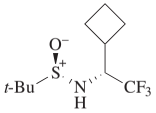


R		Refs.
H	(47)[e]	563
Me	(49)	
$MeSCH_2$	(75)	
n-Bu	(57)	
t-Bu	(71)	
2-furyl	(60)	
2-thienyl	(71)	
5-Me-2-thienyl	(52)	
3-pyridyl	(68)	
c-C_6H_{11}	(68)	
4-FC_6H_4	(53)	
4-BrC_6H_4	(61)	
4-$MeOC_6H_4$	(49)	
4-MeC_6H_4	(48)	
4-$CF_3C_6H_4$	(64)	
3,4-$Me_2C_6H_3$	(62)	
3.5-$Me_2C_6H_3$	(65)	
1-adamantyl	(79)	

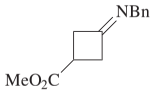
C_5



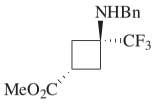
$TMSCF_3$ (3 eq), TMAF (1.2 eq), THF, –55°; to –10°



(70) — 1005



1. TFA (1.3 eq), $NaHF_2$ (0.8 eq), DMF (3 eq), MeCN, 0°, 5 min
2. $TMSCF_3$ (1.5 eq), 0°; rt, 12 h



(23), *trans*/*cis* = 3:1 — 1006

C_{5-11}



$TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 15 h



I

+



II

R^1	R^2	**I**	**II**	
2-furyl	Ph_2CH	(65)	(—)	490
2-thienyl	c-C_3H_5	(63)	(—)	
Ph	MeO_2CCH_2	(50)	(—)	
4-ClC_6H_4	Ph_2CH	(67)	(—)	
2,4-$Cl_2C_6H_3$	t-Bu	(96)	(—)	
2-HOC_6H_4	Bn	(63)	(—)	
(*E*)-PhCH=CH	Me	(62)	(20)	
1-$C_{10}H_7$	c-C_3H_5	(86)	(—)	

C_{5-7}



$TMSCF_3$ (3 eq), CF_3SO_3H (1.6 eq), KHF_2 (1.5 eq), DMF (3 eq), MeCN, rt, 18 h



R^1	R^2		
2-furyl	Ph_2CH	(70)	490
2-thienyl	c-C_3H_5	(66)	
Ph	MeO_2CCH_2	(60)	
Ph	Ph	(70)	
4-$MeOC_6H_4$	$(OMe)_2CHCH_2$	(86)	
2-HOC_6H_4	Bn	(74)	

C_{5-8}



1. $TMSCF_3$ (1.5 eq), TBAT (x eq), THF, rt, 1 h
2. HCl, H_2O, rt



R^1	R^2	x		
t-Bu	Ph	0.05	(trace)	539
c-C_6H_{11}	Ph	0.05	(47)	
Ph	Ph	0.15	(75)	
Ph	4-$MeOC_6H_4$	0.15	(72)	
2-FC_6H_4	Ph	0.05	(74)	
4-FC_6H_4	Ph	0.05	(67)	
4-ClC_6H_4	Ph	0.05	(54)	
2,4-$Cl_2C_6H_3$	Ph	0.05	(77)	
2-BrC_6H_4	Ph	0.05	(83)	
4-BrC_6H_4	Ph	0.05	(50)	
4-$MeOC_6H_4$	Ph	0.15	(38)	
4-MeC_6H_4	Ph	0.15	(46)	

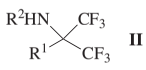
TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-11}

1. $TMSCF_3$ (3.57 eq), **8** (2.69 eq), CsF (3.07 eq), THF, air, 24 h
2. SiO_2, HCl, H_2O, 4 h


I +

II

R^1	R^2	**I**	**II**
2-C_4H_3O	Ph	(54)	(2)
Ph	Ph	(55)	(2)
Ph	3-$CF_3C_6H_4$	(26)	(4)
3-$MeOC_6H_4$	Ph	(42)	(4)
PhCH=CH	Ph	(—)	(19)
2-$C_{10}H_7$	Ph	(57)	(10)

541

C_{5-12}

$PhSCF_3$ (1.4 eq), Et_3GeNa (1.1 eq), THF, HMPA, –60°, 0.5 h



R^1	R^2	
2-C_4H_3O	Ph	(98)
n-C_6H_{13}	Ph	(94)
c-C_6H_{11}	Ph	(95)
Ph	Ph	(96)
Ph	2-ClC_6H_4	(96)
Ph	4-ClC_6H_4	(97)
Ph	2-$MeOC_6H_4$	(96)
Ph	3-$MeOC_6H_4$	(96)
Ph	4-$MeOC_6H_4$	(97)
Ph	2-MeC_6H_4	(96)
Ph	3-MeC_6H_4	(96)
Ph	4-MeC_6H_4	(96)
4-ClC_6H_4	Ph	(97)
4-$MeOC_6H_4$	Ph	(95)
n-C_7H_{15}	Ph	(95)
2-$C_{10}H_7$	Ph	(95)
n-$C_{11}H_{23}$	Ph	(94)

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C_{5-11}



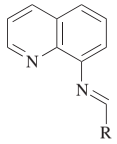
1.$TMSCF_3$ (1.5 eq). TBAB (10 mol %), 5 Å MS, THF, toluene
2. PhONa (1.1 eq), 0°; rt 16–20 h



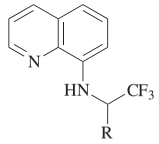
R^1	R^2	
2-thienyl	Ts	(85)
Ph	Ts	(97)
Ph	$MesSO_2$	(81)
Ph	$PMPSO_2$	(90)
Ph	Ph_2PO	(71)
4-ClC_6H_4	Ts	(98)
2-BrC_6H_4	Ts	(85)
4-$MeOC_6H_4$	Ts	(80)
1-$C_{10}H_7$	Ts	(68)
2-$C_{10}H_7$	Ts	(85)

548

C_{5-9}



1. Quinolin-8-amine + RCHO (1.2 eq), 4 Å MS, toluene, rt 1–12 h
2. $Cu(OAc)_2$ (20 mol %), rt, 10 min
3. $TMSCF_3$ (2 eq), 40°, 4–8 h



R	
i-Bu	(47)
2-furyl	(61)
2-pyridyl	(61)
3-pyridyl	(72)
c-C_6H_{11}	(62)
Ph	(81)
4-FC_6H_4	(71)
3-ClC_6H_4	(70)
4-ClC_6H_4	(78)
4-BrC_6H_4	(71)
4-$O_2NC_6H_4$	(72)
4-$MeOC_6H_4$	(69)
4-MeC_6H_4	(67)
3,4-$Me_2C_6H_3$	(63)
(*E*)-PhCH=CH	(53)

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TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-8}



1. R_FI (2.2 eq), TDAE (2.2 eq), DMF, –30°, 0.5 h; rt, o/n
2. HCl or H_2SO_4, H_2O



R	R_F		Refs.
2-furyl	C_2F_5	(60)	386
2-furyl	*n*-C_4F_9	(40)	
2-thienyl	C_2F_5	(55)	
2-thienyl	*n*-C_4F_9	(45)	
Ph	C_2F_5	(50)	
4-FC_6H_4	C_2F_5	(72)	
4-FC_6H_4	*n*-C_4F_9	(70)	
4-ClC_6H_4	C_2F_5	(70)	
4-ClC_6H_4	*n*-C_4F_9	(70)	
4-MeC_6H_4	C_2F_5	(70)	
4-MeC_6H_4	*n*-C_4F_9	(50)	
4-$CF_3C_6H_4$	C_2F_5	(68)	
4-$CF_3C_6H_4$	*n*-C_4F_9	(75)	

C_{5-8}

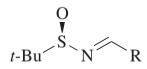


1. $PhSO_2R_F$ (1.5 eq), *t*-BuOK (4.6 eq), THF, –75°; –75 to –70°, 1.5 h
2. HCl, –75 to –70°

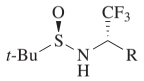


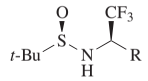
R	R_F		Refs.
t-Bu	C_2F_5	(50)	180
c-C_6H_{11}	C_2F_5	(57)	
2-FC_6H_4	C_2F_5	(88)	
4-FC_6H_4	CF_3	(59)	
4-FC_6H_4	C_2F_5	(96)	
4-ClC_6H_4	C_2F_5	(99)	
2,4-$Cl_2C_6H_3$	CF_3	(91)	
2,4-$Cl_2C_6H_3$	C_2F_5	(96)	
4-BrC_6H_4	CF_3	(72)	
4-BrC_6H_4	C_2F_5	(99)	
4-$MeOC_6H_4$	C_2F_5	(82)	
4-MeC_6H_4	C_2F_5	(88)	

C_{5-15}



1. $TMSCF_3$ (1.2 eq), initiator (1.1 eq), THF, –55°, 0.5–1 h
2. NH_4Cl, H_2O



I +  **II**

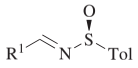
R	Initiator	**I + II**	**I/II**
t-Bu	TBAT	(75)	99:1
2-furyl	CsF	(55)	80:20
2-furyl	TBAT	(85)	97:3
2-pyridyl	CsF	(60)	90:10
2-pyridyl	TBAT	(95)	99:1
3-pyridyl	CsF	(60)	85:15
3-pyridyl	TBAT	(92)	99:1
c-C_6H_{11}	TBAT	(88)	99:1
Ph	CsF	(65)	75:25
Ph	TBAT	(80)	97:3
4-ClC_6H_4	CsF	(53)	85:15
4-ClC_6H_4	TBAT	(95)	>99:1
4-BrC_6H_4	CsF	(50)	80:20
4-BrC_6H_4	TBAT	(90)	>99:1
4-$CF_3C_6H_4$	CsF	(57)	85:15
4-$CF_3C_6H_4$	TBAT	(84)	95:5
$Ph(CH_2)_2$	TBAT	(84)	90:10
2-$C_{10}H_7$	TBAT	(83)	96:4
9-anthryl	TBAT	(90)	99:1

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

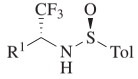
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{5–11}$

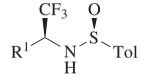


1. $TMSCF_3$ (*x* eq),
   n-Bu_4NOR^2 (1 eq), DMF, 1 h
2. NH_4Cl, H_2O



I

+

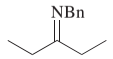


II

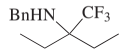
553

R^1	*x*	R^2	Temp (°)	**I** + **II**	**I/II**
t-Bu	1.4	Ac	–40	(91)	96:4
2-furyl	1.4	Ac	–40	(93)	95:5
3-pyridyl	1.4	Ac	–40	(85)	94:6
c-C_6H_{11}	1.4	Ph	–40	(75)	95:5
Ph	1.4	Ac	–40	(91)	96:4
2-ClC_6H_4	1.4	Ac	–40	(92)	96:4
3-ClC_6H_4	1.4	Ac	–40	(93)	95:5
4-ClC_6H_4	1.4	Ac	–40	(94)	95:5
4-BrC_6H_4	1.4	Ac	–40	(94)	94:6
4-$MeOC_6H_4$	2	Ac	–20	(81)	92:8
4-MeC_6H_4	1.4	Ac	–40	(90)	95:5
$Ph(CH_2)_2$	1.4	Ph	–40	(53)	92:8
1-$C_{10}H_7$	1.4	Ac	–40	(92)	96:4

C_5

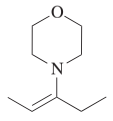


$TMSCF_3$ (1.5 eq), TFA (1.25 eq),
KHF_2 (0.75 eq), DMF (3 eq),
MeCN, rt, 3 h

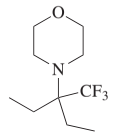


(75)

490

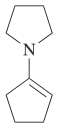


1. $TMSCF_3$ (1.5 eq),
   3-$NCC_6H_4CO_2H$ (1 eq), DMF, rt, 18 h
2. Na_2CO_3, H_2O, rt, 5 min

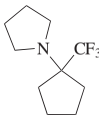


(51)

565



1. $TMSCF_3$ (1.5 eq),
3-$NCC_6H_4CO_2H$ (1 eq), DMF, rt, 18 h
2. Na_2CO_3, H_2O, rt, 5 min



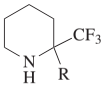
(60)

565

$C_{5–11}$



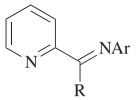
$TMSCF_3$ (1.25 eq), TFA (1.25 eq),
KHF_2 (0.75 eq), 0°; rt, 12 h



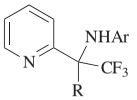
R	
H	(55)[e]
t-Bu	(56)
2-furyl	(65)
3-pyridyl	(67)
c-C_6H_{11}	(53)
Ph	(49)

563

$C_{6–12}$



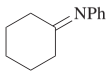
$TMSCF_3$ (2 eq), $Cu(OAc)_2$ (20 mol %)
toluene, 40°, 2 h



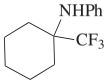
R	Ar	
H	Ph	(74)
Ph	4-MeC_6H_4	(53)

559

C_6

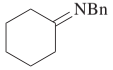


1. $TMSCF_3$ (3.57 eq), **8** (2.69 eq),
CsF (3.07 eq), THF, 24 h
2. SiO_2, HCl, H_2O, 4 h

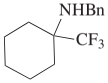


(2)

541



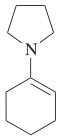
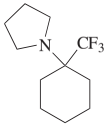
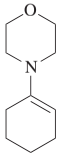
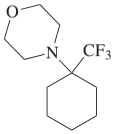
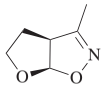
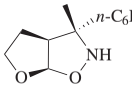
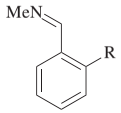
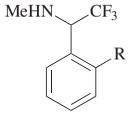
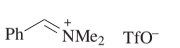
$TMSCF_3$ (1.5 eq), TFA (1.25 eq),
KHF_2 (0.75 eq), DMF (3 eq), MeCN



Temp	Time	
rt	3 h	(62)
0° to rt	o/n	(70)

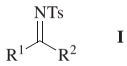
490
1007

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6			
	1. $TMSCF_3$ (1.5 eq), 3-$NCC_6H_4CO_2H$ (1 eq), DMF, rt, 18 h 2. Na_2CO_3, H_2O, rt, 5 min	 (66)	565
	1. $TMSCF_3$ (1.5 eq), 3-$NCC_6H_4CO_2H$ (1 eq), DMF, rt, 18 h 2. Na_2CO_3, H_2O, rt, 5 min	 (50)	565
	*n*-$C_6F_{13}Li$ (1.2 eq), BF_3•OEt_2 (1.2 eq), toluene, –78°, 1 h	 (76)	558, 557
C_7			
	$TMSCF_3$ (2.5 eq), BF_3•OEt_2 (1.2 eq), AcONa (4 eq), DMF, rt, 1 h	 R: H trace; OH (21)	572
	$CF_3B(OMe)_3K$ (1.2 eq), DMF,1 h	 (75)	102
$C_{7–11}$			
	$TMSCF_3$ (2 eq), *t*-Bu_3P (*x* eq), DMF, rt		140

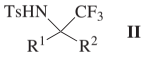
R	*x*	Time (h)	
Ph	0.1	24	trace
Ph	1	19	(63)
4-ClC_6H_4	1	22	(75)
4-BrC_6H_4	1	19	(80)
4-$O_2NC_6H_4$	1	4	(41)
2-$C_{10}H_7$	1	22	(73)

C_{7-13}



I

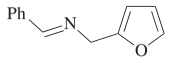
1. CF_3I (2.2 eq), TDAE (2.2 eq), DMF, –30°, 0.5 h; rt, o/n
2. HCl, H_2O



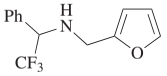
II

R^1	R^2	**I**	**II**	
Ph	H	(—)	(86)	550, 386
4-FC_6H_4	H	(—)	(81)	550, 386
4-ClC_6H_4	H	(—)	(78)	550
4-$O_2NC_6H_4$	H	(—)	(76)	550
4-$MeOC_6H_4$	H	(—)	(84)	550
4-MeC_6H_4	H	(—)	(84)	550, 386
PhCH=CH	H	(—)	(62)	550
Ph	Ph	(50)	(54)	550

C_7



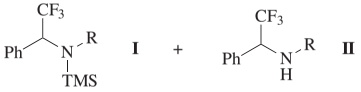
$TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 15 h



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1. $TMSCF_3$ (1.5 eq), initiator (0.15 eq), solvent, rt, 1 h
2. HCl, H_2O, rt



I + **II** 539

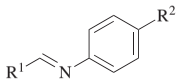
R	Initiator (s)	Solvent	Conv **I** (%)	**I**	Conv **II** (%)	**II**
Ph	TBAT	THF	92	(—)	—	(—)
Ph	TBAT	DMF	75	(—)	—	(—)
Ph	TMAF	THF	72	(—)	12	(—)
Ph	CsF	THF	25	(—)	—	(—)
Ph	CsF, Ph_3SiF	THF	25	(—)	11	(—)
4-$MeOC_6H_4$	TBAT	THF	86	(59)[f]	—	(—)
4-$MeOC_6H_4$	TBAF	THF	—	(21)	—	(19)

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

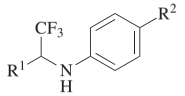
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{7-11}



1. **79** (2.56 eq), CsF (0.1 eq), additive (3 eq), THF, reflux, 20 h
2. HCl, H_2O, SiO_2, 3 h

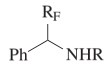


R^1	R^2	Additive	Conv (%)		Refs.
Ph	H	**8**	25	(—)	117
Ph	H	**9**	—	(60)	
4-$MeOC_6H_4$	H	**9**	—	(33)	
4-MeC_6H_4	MeO	**9**	—	(54)	
(*E*)-PhCH=CH	H	**9**	—	(16)	
2-$C_{10}H_7$	H	**9**	—	(44)	

C_7



1. $TMSR_F$ (*x* eq), catalyst (0.1 eq), DMF
2. NH_4Cl, H_2O

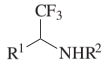


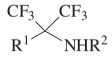
R	R_F	*x*	Catalyst	Temp (°)	Time (h)	Conv (%)		Refs.
4-$ClC_6H_4SO_2$	CF_3	1.4	AcOLi	–20	16	82	(—)	549, 131
2-$O_2NC_6H_4SO_2$	CF_3	1.4	AcOLi	–20	16	87	(—)	131
4-$O_2NC_6H_4SO_2$	CF_3	1.4	AcOLi	–20	16	93	(—)	549, 131
4-$MeC_6H_4SO_2$	CF_3	1.4	$PhCO_2Li$	–20	16	94	(—)	549
4-$MeC_6H_4SO_2$	CF_3	1.4	*t*-$BuCO_2Li$	–20	40	87	(—)	549
4-$MeC_6H_4SO_2$	CF_3	1.4	AcOLi	–20	16	93	(91)	549, 131
4-$MeC_6H_4SO_2$	CF_3	1.4	AcOLi	–20	40	95	(—)	549
4-$MeC_6H_4SO_2$	CF_3	1.4	AcONa	–20	16	86	(—)	549
4-$MeC_6H_4SO_2$	CF_3	1.4	AcOK	–20	16	67	(—)	549
4-$MeC_6H_4SO_2$	CF_3	1.4	*n*-Bu_4NOAc	–20	16	79	(—)	549
4-$MeC_6H_4SO_2$	CF_3	1.4	BnOLi	–20	40	37	(—)	549
4-$MeC_6H_4SO_2$	CF_3	1.4	CsF	–20	40	30	(—)	549
4-$MeC_6H_4SO_2$	C_2F_5	1.4	AcOLi	–20	16	91	(—)	131
4-$MeC_6H_4SO_2$	*n*-C_3F_7	1.4	AcOLi	–20	16	87	(—)	131
Ph_2PO	CF_3	2	AcOLi	rt	16	75	(—)	549, 131

C_{7-8}



1. $TMSCF_3$ (1.5 eq), TMAF (1.35 eq), THF, –60°, 1.5 h; –55° to –45°, 2 h
2. H_2O, –50° to –40°

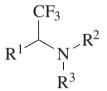


I +  **II**

R^1	R^2	**I**	**II**
Ph	Ph	(89)	(—)
Ph	3-FC_6H_4	(83)	(—)
4-MeC_6H_4	4-FC_6H_4	(72)	(—)
4-$Me_2NC_6H_4$	4-FC_6H_4	(65)	(25)

540

1. $TMSCF_3$ (1.5 eq), TMAF (1.35 eq), THF, –60°, 1.5 h; –55 to –45°, 2 h
2. R^3X (1.12 eq), –45° to rt



R^1	R^2	R^3	X	
Ph	Ph	Me	I	(91)
Ph	Ph	TMS	Cl	(76)
4-MeC_6H_4	4-FC_6H_4	Me	I	(79)
4-MeC_6H_4	4-FC_6H_4	TMS	Cl	(84)

540

$TMSCF_3$ (2 eq), $(R^3)_3P$ (0.2 eq), solvent, rt, 22 h



R^1	R^2	R^3	Solvent	
Ph	Ph	2,4,6-$(MeO)_3C_6H_2$	DMF	(74)
4-ClC_6H_4	Ph	2,4,6-$(MeO)_3C_6H_2$	DMF	(58)
Ph	4-$MeC_6H_4SO_2$	2,4,6-$(MeO)_3C_6H_2$	DMPU	(71)
Ph	4-$MeC_6H_4SO_2$	2,4,6-$(MeO)_3C_6H_2$	DMF	(45)
Ph	4-$MeC_6H_4SO_2$	*t*-Bu	DMPU	trace
Ph	Bn	2,4,6-$(MeO)_3C_6H_2$	DMPU	trace
4-ClC_6H_4	4-$MeC_6H_4SO_2$	2,4,6-$(MeO)_3C_6H_2$	DMPU	(77)
4-BrC_6H_4	4-$MeC_6H_4SO_2$	2,4,6-$(MeO)_3C_6H_2$	DMPU	(70)
4-$O_2NC_6H_4$	4-$MeC_6H_4SO_2$	2,4,6-$(MeO)_3C_6H_2$	DMPU	(60)
4-$MeOC_6H_4$	4-$MeC_6H_4SO_2$	2,4,6-$(MeO)_3C_6H_2$	DMPU	(48)
4-MeC_6H_4	Ph	2,4,6-$(MeO)_3C_6H_2$	DMF	(35)

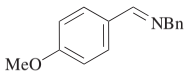
141

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

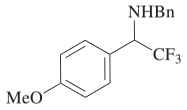
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7

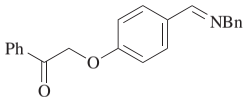


TMSCF$_3$ (x eq), TFA (y eq), initiator (z eq), solvent

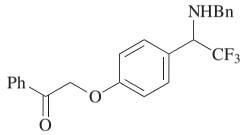


490

x	y	Initiator	z	Solvent	Temp	Time (h)	
—	—	KHF_2	—	MeCN	0°	0.5	(90)
1.5	1.25	KHF_2	0.75	DMF	rt	1	(86–88)
1.5	2	KF	1.5	DMF	rt	1	(86–88)

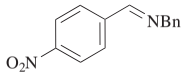


TMSCF$_3$, TFA, KHF_2, MeCN, rt, 3 h

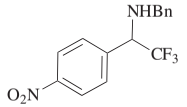


(73)

490



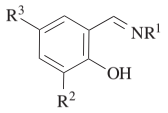
TMSCF$_3$ (x eq), acid (y eq), KHF_2 (z eq), solvent, rt



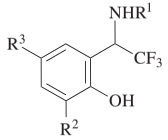
490

x	Acid	y	z	Solvent (s)	Time (h)	
1.5	TFA	1.25	0.75	MeCN	15	(69)
1.5	TFA	1.25	0.75	MeCN, DMF (3 eq)	3	(48)
1.5	CF_3SO_3H	1.25	0.75	DMF	24	(53)
2	TFA	1.5	1	MeCN	15	(71)
3	CF_3SO_3H	1.6	1.5	MeCN	24	(63)
3	CF_3SO_3H	1.6	1.5	MeCN, DMF (3 eq)	24	(83)

C_{7-10}



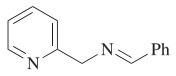
1. Base (1.2 eq), $BF_3{\bullet}OEt_2$ (2.5 eq), solvent, 0°; rt, time 1
2. $TMSCF_3$ (2.5 eq), AcONa (4 eq), rt, time 2
3. Na_2CO_3, H_2O, rt



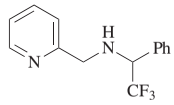
572

R^1	R^2	R^3	Base	Solvent	Time 1 (h)	Time 2 (h)	
Me	H	H	*t*-BuOK	DMF	1	1	(58)
Me	H	H	*t*-BuOK	THF	1	1	(79)
Me	H	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(86)
Me	H	H	*i*-Pr_2NEt	DMF	1	1	(70)
$(MeO)_2CHCH_2$	H	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(90)
n-Pr	H	O_2N	*i*-Pr_2NEt	CH_2Cl_2	2	3	(80)
$CH_2{=}CHCH_2$	H	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(87)
c-C_3H_5	H	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(82)
t-Bu	H	Br	*i*-Pr_2NEt	CH_2Cl_2	2	3	(85)
(2-furyl)CH_2	MeO	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(92)
Ph	H	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(90)
4-MeC_6H_4	H	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(89)
Bn	H	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(96)
Ph	$CH_2{=}CHCH_2$	H	*i*-Pr_2NEt	CH_2Cl_2	2	3	(88)

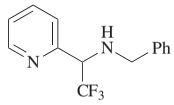
C_7



$TMSCF_3$ (2 eq), $Cu(OAc)_2$ (20 mol %) toluene, 40°, 2 h



(5) +



(5)

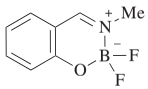
559

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

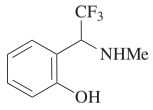
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

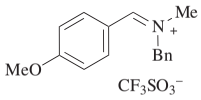
C_7



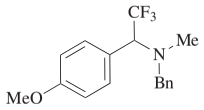
1. $TMSCF_3$ (2.5 eq), AcONa (*x* eq), solvent, rt, time
2. Na_2CO_3, H_2O, rt



x	Solvent	Time (h)	Conv (%)		Refs.
—	DMF	6	11	(—)	572
0.1	DMF	6	—	(73)	
4	MeCN	0.25	<5	(—)	
4	DMF	0.25	—	(85)	
4	DMF	1	—	(88)	

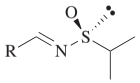


$TMSCF_3$ (1.5 eq), KHF_2 (1 eq), MeCN, rt, 18 h

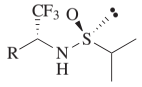


(85) 490

C_{7-11}

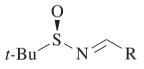


$TMSCF_3$ (4.5 eq), TBAT (1.1 eq), –50°; rt, o/n

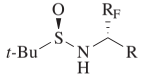


R		dr	Refs.
c-C_6H_{11}	(86)	96:4	1008
Ph	(98)	85:15	
3-$MeOC_6H_4$	(96)	96:4	
2-$C_{10}H_7$	(72)	93:7	

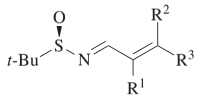
C_{7-15}



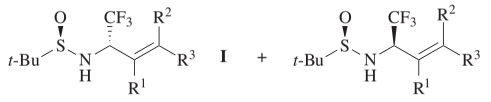
1. $PhSO_2R_F$ (1.5 eq), *t*-BuOK (4.6 eq), THF, –75°; –75 to –70°, 1.5 h
2. HCl, –75 to –70°



R	R_F		dr	Refs.
4-BrC_6H_4	C_2F_5	(57)	97:3	180
	CF_3	(68)	98:2	



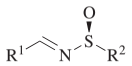
$TMSCF_3$ (1.3 eq), initiator (1.1 eq), THF, –25°, 0.5–1 h



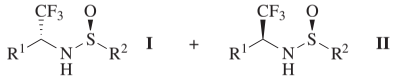
I + **II** 554

R^1	R^2	R^3	Initiator	**I**	**I/II**
H	H	furyl	TBAT	(76)	92:8
Me	H	furyl	TBAT	(50)	98:2
H	H	Ph	TBAT	(55)	90:10
Me	H	Ph	TBAT	(73)	>99:1
n-C_5H_{11}	Ph	H	TBAT	(25)	>99:1
n-C_5H_{11}	Ph	H	TMAF	(82)	90:10
H	Ph	Ph	TBAT	(62)	>99:1
n-C_6H_{13}	Ph	H	TBAT	(20)	>99:1
n-C_6H_{13}	Ph	H	TMAF	(75)	92:8
Ph	Ph	H	TMAF	(62)	93:7

$C_{7–11}$



1. CF_3I (2.2 eq), TDAE (2.2 eq), DMF, –30°, 0.5 h; rt, o/n
2. NH_4Cl, H_2O



I + **II** 550

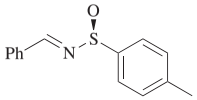
R^1	R^2	**I** + **II**	**I/II**
n-C_6H_{13}	4-MeC_6H_4	(48)	72:28
Ph	4-MeC_6H_4	(66)	87:13
Ph	2,4,6-$Me_3C_6H_2$	(57)	90:10
4-FC_6H_4	4-MeC_6H_4	(69)	85:15
4-ClC_6H_4	4-MeC_6H_4	(67)	88:12
4-$MeOC_6H_4$	4-MeC_6H_4	(71)	82:18
4-MeC_6H_4	4-MeC_6H_4	(73)	86:14
4-$CF_3C_6H_4$	4-MeC_6H_4	(74)	88:12
1-$C_{10}H_7$	4-MeC_6H_4	(42)	94:6

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

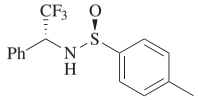
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

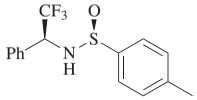
Please refer the charts preceding the tables for structures indicated by the ***bold*** *numbers.*

C_7



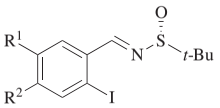
1. $TMSCF_3$ (*x* eq), initiator (1 eq), DMF, 1 h
2. NH_4Cl, H_2O



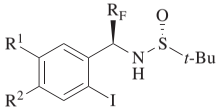
I (—) +  **II** (—) 553

x	Initiator	Temp (°)	Conv **I** + **II** (%)	**I/II**
2	AcOLi	0	56	52:48
2	AcONa	0	68	46:54
2	AcOK	0	77	63:37
2	AcOCs	0	89	75:25
2	*n*-Bu_4NOAc	–40	94	96:4
2	*n*-Bu_4NOAc	–20	97	95:5
2	*n*-Bu_4NOAc	0	92	92:8
1.4	*n*-Bu_4NOAc	–40	93	96:4
2	*n*-Bu_4NOPh	–40	87	94:6
2	*n*-Bu_4NO_2CPh	–40	51	95:5
2	tetrabutylammonium succinimide	–40	6	96:4

C_{7-8}

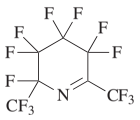


1. $TMSR_F$ (2 eq), Bu_4OAc (1.1 eq), THF, –20°, to completion
2. NH_4Cl

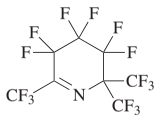


R^1	R^2	R_F		dr[g]	Refs.
H	H	CF_3	(80)	>99:1	1009
H	H	C_2F_5	(83)	99:1	
F	H	CF_3	(70)	97:3	
MeO	H	CF_3	(77)	97:3	
–OCH_2O–		CF_3	(71)	98:2	
CF_3	H	CF_3	(71)	—	

C_7

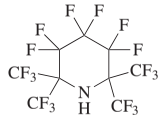


1. $TMSCF_3$ (1 eq), CsF (6.5 mol %), rt, 48 h
2. H_2O



(—) 76% conv

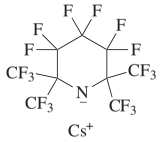
+



(—) 3% conv

1010

$TMSCF_3$ (6 eq), CsF (0.9 eq), rt, 18 h



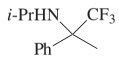
(—) 59% conv

1010

C_8

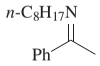


$TMSCF_3$ (1.5 eq), TFA (*x* eq), KHF_2 (*y* eq), DMF (3 eq), MeCN, rt

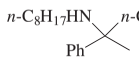


x	*y*	Time (h)	
1.25	0.75	3	(67)
1.6	1.5	18	(68)

490



1. *n*-$C_6F_{13}I$ (1.2 eq), BF_3•OEt_2 (1 eq), Et_2O, –78°
2. MeLi/LiBr (1.2 eq), –78°, 1 h

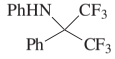


(82)

313

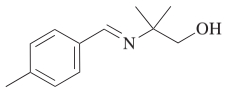


1. $TMSCF_3$ (3.57 eq), **8** (2.69 eq), CsF (3.07 eq), THF, 24 h
2. SiO_2, HCl, H_2O, 4 h

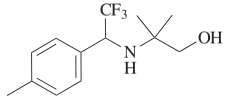


(64)

541



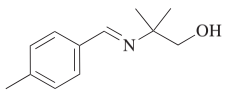
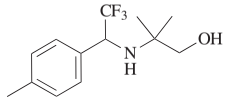
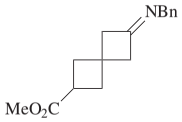
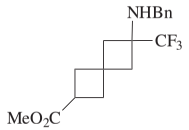
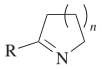
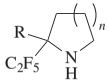
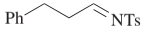
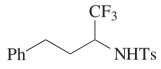
$TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 15 h

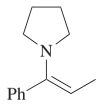


(45)

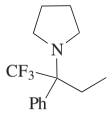
490

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

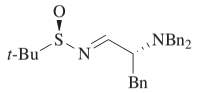
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_8 	$TMSCF_3$ (3 eq), CF_3SO_3H (1.6 eq), KHF_2 (1.5 eq), DMF (3 eq), MeCN, rt, 18 h	 (47)	490
	1. TFA (1.3 eq), $NaHF_2$ (0.8 eq), DMF (3 eq), MeCN, 0°, 5 min 2. $TMSCF_3$ (1.5 eq), 0°; rt, 12 h	 (47)	1006
C_{8-12} 	C_2F_5H (1.5 eq), BuLi (1.2 eq), BF_3•OEt_2, (1.2 eq) THF, –78°, 6 h		196
		n R 1 *n*-Bu (58) 1 *t*-Bu (65) 1 2-furyl (43) 1 Ph (52) 1 4-FC_6H_4 (59) 1 4-$MeOC_6H_4$ (49) 1 3-$CF_3C_6H_4$ (55) 2 *t*-Bu (48) 2 Ph (59) 3 *t*-Bu (55) 3 Ph (43)	
C_9 	$TMSCF_3$ (1.2 eq), TBAT (1.1 eq), THF, 0°, 0.75 h	 (—)	1011



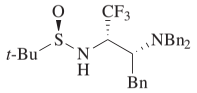
1. $TMSCF_3$ (1.5 eq), RCO_2H (1 eq), DMF, rt
2. Na_2CO_3, H_2O, rt, 5 min

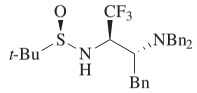


R	Time (h)		
Me	4	(37)	565
Ph	4	(50)	
3,5-$(O_2N)_2C_6H_3$	4	(37)	
3-NCC_6H_4	4	(72)	
3-NCC_6H_4	18	(77)	



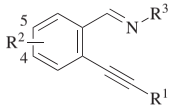
$TMSCF_3$ (1.5 eq), TMAF (1.2 eq), THF, –35°, 1–2 h



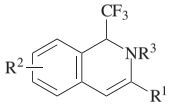
I +  **II** 555

I + **II** (60), **I**/**II** = 4:1

$C_{9–16}$

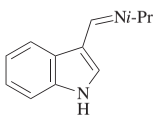
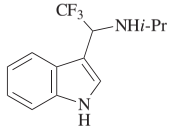
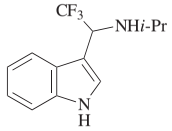
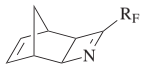
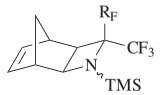
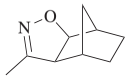
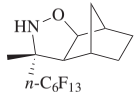
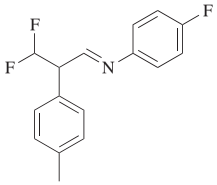
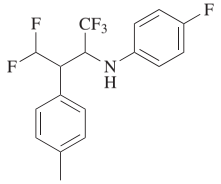


$TMSCF_3$ (4 eq), $AgSbF_6$ (5 mol %), AcOH (1.1 eq), MeCN, rt, 12–24 h

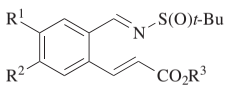


R^1	R^2	R^3		
TMS	4,5-$(MeO)_2$	Ph	(37)[h]	542
c-C_3H_5	H	*t*-Bu	(94)	
n-Bu	H	*t*-Bu	(95)	
Ph	H	*n*-Bu	(40)	
Ph	H	*t*-Bu	(88)	
Ph	H	Ph	(91)	
Ph	H	Bn	(68)	
Ph	4-F	*t*-Bu	(55)	
Ph	5-F	*t*-Bu	(53)	
Ph	5-Cl	*t*-Bu	(48)	
Ph	3-MeO	*t*-Bu	(91)	
Ph	4,5-$(MeO)_2$	*t*-Bu	(90)	
4-FC_6H_4	H	*t*-Bu	(70)	
4-$MeOC_6H_4$	H	*t*-Bu	(78)	
Ph	5-Me	*t*-Bu	(93)	
4-MeC_6H_4	H	*t*-Bu	(77)	

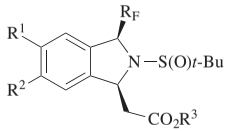
TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_9 	$TMSCF_3$ (2 eq), TFA (1.5 eq), KHF_2 (1 eq), MeCN, rt, 15 h	 (23)	490
	$TMSCF_3$ (3 eq), CF_3SO_3H (1.6 eq), KHF_2 (1.5 eq), DMF (3 eq), MeCN, rt, 18 h	 (20)	490
C_{9-11} 	$TMSCF_3$ (1.05 eq), CsF (3.75 mol %), 0–10°, 70 min	 R_F / (%): CF_3 (85); C_2F_5 (73); n-C_3F_7 (68)	546
C_9 	n-$C_6F_{13}Li$ (1.2 eq), BF_3•OEt_2 (1.2 eq), Et_2O, –78°, 1 h	 (91)	558, 557
C_{10} 	1. $TMSCF_3$ (1.3 eq), TMAF (1.3 eq), THF, –60 to –50°, 1 h; –55 to –45°, 2 h 2. H_2O	 (78)	540

C_{10-11}

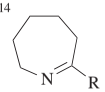


1. $TMSR_F$ (2 eq), TBAT (2 eq), THF, –55°; to –10°, 0.5–1.5 h
2. SiO_2, 1 N HCl (2 drops), –10°, 1 h

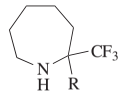


R^1	R^2	R^3	R_F		dr	
H	H	Et	CF_3	(94)	99:1	556
H	H	*i*-Pr	CF_3	(70)	99:1	
H	H	*t*-Bu	CF_3	(88)	99:1	
H	H	Et	C_2F_5	(45)	99:1	
H	H	*t*-Bu	C_2F_5	(71)	99:1	
H	H	*t*-Bu	*n*-C_3F_7	(37)	99:1	
F	H	Et	CF_3	(80)	24:1	
O_2N	H	Et	CF_3	(52)	89:1	
MeO	H	Et	CF_3	(74)	20:1	
–OCH_2O–		Et	CF_3	(77)	99:1	
Me	H	Et	CF_3	(84)	35:1	
CF_3	H	Et	CF_3	(62)	60:1	

C_{10-14}

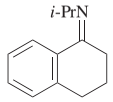


$TMSCF_3$ (1.25 eq), TFA (1.25 eq), KHF_2 (0.75 eq), 0°; rt, 12 h

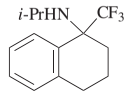


R		
t-Bu	(56)	563
2-furyl	(56)	
3-pyridyl	(56)	
Ph	(44)	
4-$MeC_6H_4CH_2$	(71)	

C_{10}



$TMSCF_3$ (1.5 eq), TFA (1.25 eq), KHF_2 (0.75 eq), DMF (3 eq), MeCN, rt, 3 h



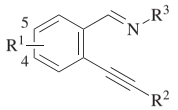
(68) 490

TABLE 13. PERFLUOROALKYL ADDITION TO IMINES AND IMINIUM SALTS (*Continued*)

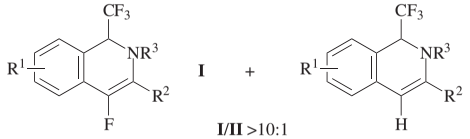
Imine or Iminium Salt	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{12-15}



1. $AgNO_3$ (20 mol %), **59** (20 mol %), $(PhSO_2)_2NF$ (1.5 eq), DMA, rt, 3.5 h
2. $TMSCF_3$ (5 eq), Me_4NF (2 eq), rt, 1 h

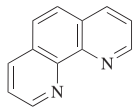


I/II >10:1

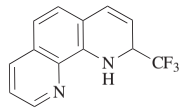
R^1	R^2	R^3		dr
H	*c*-C_3H_5	*i*-Pr	(60)	—
H	*n*-Bu	*i*-Pr	(61)	—
4-F	*n*-Bu	*i*-Pr	(66)	—
4-F	*n*-Bu	*c*-C_3H_5	(67)	—
4-F	*n*-Bu	*c*-C_5H_9	(70)	—
4-F	*n*-Bu	(*S*)-MeO_2C(*i*-Pr)CH	(70)	1.5:1
5-F	*n*-Bu	*n*-Pr	(50)	—
5-F	*n*-Bu	*i*-Pr	(65)	—
5-F	*n*-Bu	Ph	(50)	—
5-F	*n*-Bu	Bn	(60)	—
5-F	*n*-Bu	(*R*)-PhMeCH	(69)	3:1
5-F	*n*-Bu	(*S*)-tetrahydronaphth-2-yl	(69)	1.7:1
5-Cl	*n*-Bu	*i*-Pr	(66)	—
5-MeO	*n*-Bu	*i*-Pr	(65)	—
5-F	Ph	*i*-Pr	(58)[*i*]	—

543

C_{12}

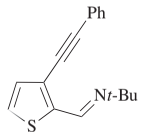
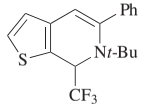
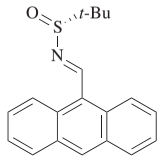
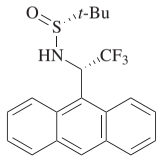


$TMSCF_3$ (2 eq), $Cu(OAc)_2$ (20 mol %) toluene, 40°, 24 h



(8)

559

C_{13} 	$TMSCF_3$ (4 eq), $AgSbF_6$ (5 mol %), AcOH (1.1 eq), MeCN, rt, 12–24 h		(50)	542
C_{15} 	1. $TMSCF_3$ (1.2 eq), TBAT (20 mol %), THF, –50°; –50°, 4 h; –20°, 20 h 2. NH_4Cl, H_2O		(82) dr 99:1	552

[a] The reaction was carried out after the imine and BF_3•OEt_2 were stirred at room temperature for 1 h.

[b] The reaction was carried out in the following ratio: substrate/BF_3•OEt_2/R I/MeLi = 1:2:2.2:2.2.

[c] The combustion analysis of this product did not correspond to the structure shown.

[d] The main product was *N*-tosyl-(2-methylprop-2-enyl)amine.

[e] The reaction was carried out with the trimer, and the mixture was stirred for 20 min before the addition of $TMSCF_3$.

[f] The product was isolated as a mixture with Ph_3SiF.

[g] The er was determined with the NH-Boc derivatives.

[h] The yield given was for R^1 = H.

[i] The **I/II** ratio was 3:1.

TABLE 14. PERFLUOROALKYL ADDITION TO AZIRINES

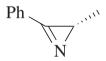
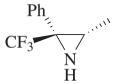
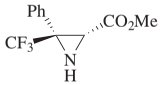
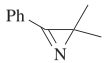
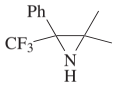
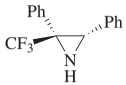
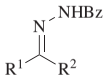
Azirine	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_9			
	$TMSCF_3$, TEAF (cat.)	 (51)	576
	$TMSCF_3$, TBAF (cat.)	 (67)	576
C_{10}			
	$TMSCF_3$, TBAF (1 eq)	 (41)	576
C_{14}			
	$TMSCF_3$ (1.5 eq), TEAF (0.2 eq), THF, –4° to rt, 15 h	 (86)	576

TABLE 15. PERFLUOROALKYL ADDITION TO HYDRAZONES

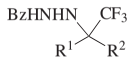
Hydrazone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{3-8}



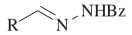
1. BF_3•OEt_2 (1.5 eq), CH_2=$CHCH_2TMS$ (1.5 eq), CH_2Cl_2, reflux, 5 min
2. $TMSCF_3$ (2 eq), AcONa (4 eq), DMF, 50–55°, 3 h



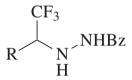
R^1	R^2	
Me	Me	(80)
c-C_3H_5	Me	(27)
–$(CH_2)_4$–		(61)
–$(CH_2)_5$–		(75)
Ph	Me	(46)

577

C_{4-11}



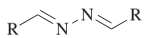
1. BF_3•OEt_2 (1.5 eq), CH_2=$CHCH_2TMS$ (1.5 eq), CH_2Cl_2, reflux, 5 min
2. $TMSCF_3$ (2 eq), AcONa (4 eq), DMF, rt, 2 h



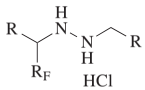
R		Conv (%)
i-Pr	(80)	—
i-Bu	(66)	—
t-Bu	(96)	—
2-furyl	(70)	—
4-$O_2NC_6H_4$	(88)	—
2-$MeOC_6H_4$	(94)	—
4-$MeOC_6H_4$	(79)	—
(*E*)-PhCH=CH	(91)	—
$Ph(CH_2)_2$	(—)	68
1-$C_{10}H_7$	(80)	—

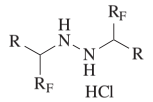
577

C_{4-14}



1. R_FI, MeLi/LiBr, BF_3•OEt_2
2. $LiAlH_4$, BF_3•OEt_2
3. NaOH, H_2O
4. HCl

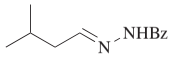
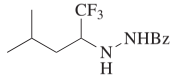
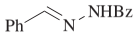
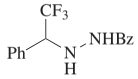
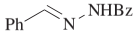
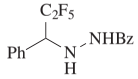
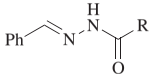
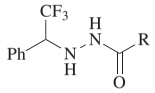
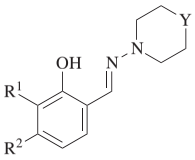
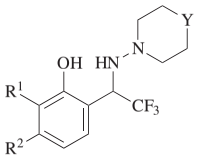


I +  **II**

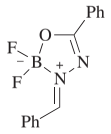
R	R_F	**I**	**II**
Me	*n*-C_8F_{17}	(—)	(31)
i-Pr	*n*-C_8F_{17}	(59)	(—)
Ph	*n*-C_4F_9	(31)	(—)

197

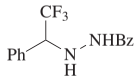
TABLE 15. PERFLUOROALKYL ADDITION TO HYDRAZONES (*Continued*)

Hydrazone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_5 	1. TMSCl (1.2 eq), Et_3N (1.2 eq), $BF_3•OEt_2$ (1.2 eq) 2. $TMSCF_3$ (2 eq), AcONa (4 eq), DMF, rt, 2 h	 (87)	577
C_7 	1. TMSCl, Et_3N, CH_2Cl_2, rt 2. $BF_3•OEt_2$, MeCN, heat 3. $TMSCF_3$ (1.5 eq), AcONa (2 eq), DMF, rt, 1.5 h	 (88)	577
	1. $BF_3•OEt_2$ (1.5 eq), CH_2=$CHCH_2TMS$ (1.5 eq), CH_2Cl_2, rt, 2 h 2. $TMSC_2F_5$ (2 eq), AcONa (4 eq), DMF, rt, 2 h	 (91)	577
	1. $BF_3•OEt_2$, CH_2=$CHCH_2TMS$, CH_2Cl_2, reflux, 5 min 2. $TMSCF_3$, AcONa, DMF, rt, 2 h	 R: H (55); MeO (26); Me (75); Ph (94)	577
$C_{7–11}$ 	1. CH_2=$CHCH_2TMS$ (1.5 eq), $BF_3•Et_2O$ (1.5 eq), CH_2Cl_2, reflux, 10 min; remove solvent 2. $TMSCF_3$ (2 eq), NaOAc (2.5 eq), DMF, 50–52°, 2 h	 R^1 / R^2 / Y: H / H / O (91); H / H / CH_2 (82); MeO / H / O (82); MeO / H / CH_2 (82); –(CH=CH)$_2$– / O (97)	573

C_7

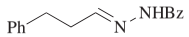


$TMSCF_3$ (1.5 eq), AcONa (2 eq), DMF, rt, 1.5 h

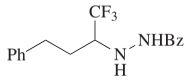


(96) 577

C_9

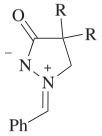


1. TMSCl (1.2 eq), Et_3N (1.2 eq), $BF_3{\bullet}OEt_2$ (1.2 eq)
2. $TMSCF_3$ (2 eq), AcONa (4 eq), DMF, rt, 2 h

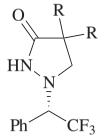


(78) 577

$C_{10–12}$



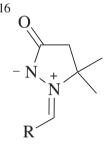
$TMSCF_3$ (*x* eq), **46q** (10 mol %), KOH (6 eq), toluene/CH_2Cl_2 (2:1), 11–27 h



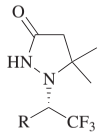
R	*x*	Temp (°)		er
H	10	–40	(67)	88.5:11.5
Me	4	–50	(94)	95.0:5.0

578

$C_{12–16}$



$TMSCF_3$ (*x* eq), catalyst (*y* mol %), KOH (6 eq), solvent



578

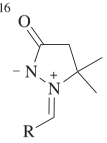
R	*x*	Catalyst	*y*	Solvent (s)	Temp (°)	Time (h)		er
c-C_6H_{11}	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–70 to –60	9	(85)	85.5:14.5
Ph	4	**46q**	10	toluene/CH_2Cl_2 (2:1)	–50	17	(94)	95.0:5.0
4-FC_6H_4	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	12	(89)	94.5:5.5
4-ClC_6H_4	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50 to –40	2, 9[a]	(81)	93.0:7.0
4-BrC_6H_4	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50 to –40	2, 9[a]	(85)	91.5:8.5
3-$MeOC_6H_4$	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	3	(73)	96.0:4.0
4-$MeOC_6H_4$	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	8	(84)	97.5:2.5
2-MeC_6H_4	4	**46q**	10	toluene/CH_2Cl_2 (2:1)	–50 to –40	2, 20[a]	(86)	94.0:6.0
3-Me-C_6H_4	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	6	(72)	97.0:3.0
4-MeC_6H_4	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	8	(87)	95.0:5.0
(*E*)-PhCH=CH	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50 to –40	2, 9[a]	(78)	89.5:10.5

TABLE 15. PERFLUOROALKYL ADDITION TO HYDRAZONES (*Continued*)

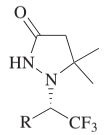
Hydrazone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

$C_{12–16}$

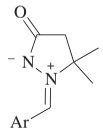


$TMSCF_3$ (x eq), catalyst (y mol %), KOH (6 eq), solvent

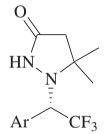


578

R	x	Catalyst	y	Solvent (s)	Temp (°)	Time (h)		er
3,4-$Me_2C_6H_3$	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	9	(89)	94.0:6.0
4-*i*-PrC_6H_4	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	6	(84)	98.0:2.0
4-*t*-BuC_6H_4	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	3	(88)	99.0:1.0
1-$C_{10}H_7$	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50 to –40	2, 18[a]	(74)	96:5:3.5
2-$C_{10}H_7$	4	**46u**	10	toluene/CH_2Cl_2 (2:1)	–50	4	(95)	95.0:5.0
6-MeO-2-$C_{10}H_6$	6	**46q**	30	CH_2Cl_2	–40	8	(90)	95.0:5.0



$TMSCF_3$ (x eq), catalyst (10 mol %), KOH (y eq), $CF_3CH_2CF_2Me$, –20°



579

Ar	x	Catalyst	y	Time (h)		er
Ph	4	**46c**	6	14	(99)	93.0:7.0
4-FC_6H_4	6	**46c**	10	21	(84)	87.0:13.0
3-$MeOC_6H_4$	6	**46c**	10	10	(80)	92.0:8.0
4-$MeOC_6H_4$	6	**46f**	10	18	(65)	94.5:5.5
3-MeC_6H_4	6	**46c**	10	12	(87)	94.5:5.5
4-MeC_6H_4	6	**46c**	10	12	(95)	93.0:7.0
4-*i*-PrC_6H_4	4	**46c**	6	17	(90)	98.0:2.0
4-*t*-BuC_6H_4	6	**46c**	10	21	(94)	98.0:2.0

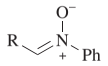
[a] The information regarding the reaction time was not clear. Perhaps what is meant is that the mixture was warmed from –50° to –40° for 2 hours and then stirred at –40° for the period indicated by the second number.

TABLE 16. PERFLUOROALKYL ADDITION TO NITRONES

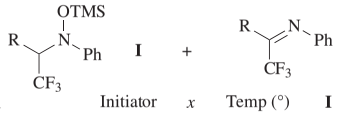
Nitrone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-11}



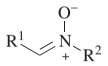
TMSCF$_3$ (2.2 eq), initiator (*x* eq), THF



I + **II**

581

R	Initiator	*x*	Temp (°)	**I**	**II**
2-furyl	*t*-BuOK	—	–78	(54)	(<5)
2-furyl	*t*-BuOK	—	–20	(69)	(—)
2-furyl	*t*-BuOK	—	rt	(<5)	(63)
Ph	*t*-BuOK	—	–20	(89)	(—)
Ph	*t*-BuOK	—	rt	(53)	(14)
Ph	TBAF	0.2	–20	(37)	(10)
Ph	TBAF	0.2	rt	(<5)	(35)
4-ClC$_6$H$_4$	*t*-BuOK	—	–20	(67)	(—)
4-O$_2$NC$_6$H$_4$	*t*-BuOK	—	–20	(54)	(—)
4-MeOC$_6$H$_4$	*t*-BuOK	—	–20	(62)	(—)
1-C$_{10}$H$_7$	*t*-BuOK	—	–20	(83)	(—)



TMSCF$_3$ (*x* eq), *t*-BuOK, THF



I + **II**

580

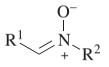
R^1	R^2	*x*	Temp (°)	**I**	**II**
2-furyl	Ph	2	–30 to –20	(18–43)	(—)
2-furyl	Ph	3	–40 to –20	(—)	(78–82)
2-pyridyl	Ph	2	–30 to –20	(<5)	(—)
2-pyridyl	Ph	3	–40 to –20	(—)	(51–76)
4-pyridyl	Ph	2	–30 to –20	(<5)	(—)
4-pyridyl	Ph	3	–40 to –20	(—)	(72–75)
Ph	Ph	2	–30 to –20	(85–93)	(—)
Ph	4-ClC$_6$H$_4$	2	–30 to –20	(52–59)	(—)
Ph	4-MeOC$_6$H$_4$	2	–30 to –20	(62–79)	(—)

TABLE 16. PERFLUOROALKYL ADDITION TO NITRONES (*Continued*)

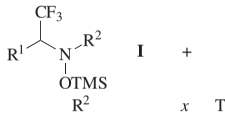
Nitrone	Conditions	Product(s) and Yield(s) (%)	Refs.

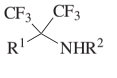
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{5-11}



TMSCF$_3$ (*x* eq), *t*-BuOK, THF

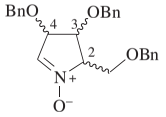


I +  **II**

R^1	R^2	*x*	Temp (°)	**I**	**II**
Ph	3-$CF_3C_6H_4$	2	–30 to –20	(60–72)	(—)
4-ClC_6H_4	Ph	2	–30 to –20	(71–90)	(—)
4-$O_2NC_6H_4$	Ph	2	–30 to –20	(10–22)	(—)
4-$O_2NC_6H_4$	Ph	3	–40 to –20	(—)	(64–77)
2-$MeOC_6H_4$	Ph	2	–30 to –20	(59–74)	(—)
4-$MeOC_6H_4$	Ph	2	–30 to –20	(77–90)	(—)
(*E*)-PhCH=CH	Ph	2	–20	(65–83)	(—)
(*E*)-PhCH=CH	Ph	3	–20	(—)	(58–76)
1-$C_{10}H_7$	Ph	2	–30 to –20	(83–90)	(—)

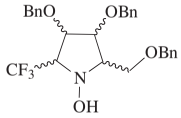
580

C_5



I

TMSCF$_3$ (1 eq), TBAF (1.5 eq), THF, 0°; rt, 0.5 h

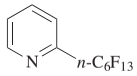


II

Config **I**	Config **II**		Refs.
(2*S*,3*S*,4*S*)	(2*S*,3*S*,4*S*,5*R*)	(60)	582
(2*S*,3*R*,4*S*)	(2*S*,3*R*,4*S*,5*R*)	(69)	
(2*R*,3*R*,4*R*)	(2*R*,3*R*,4*R*,5*R*)	(60)	
(2*S*,3*R*,4*R*)	(2*S*,3*R*,4*R*,5*R*)	(56)	

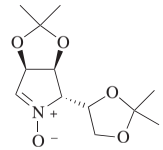
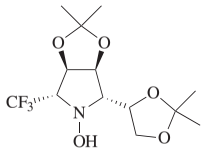
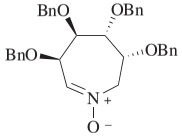
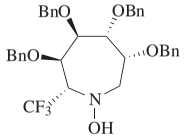
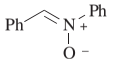
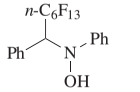
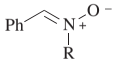
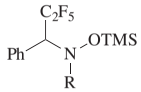


n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, –78°



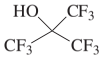
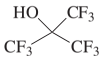
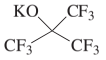
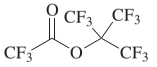
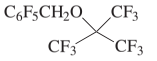
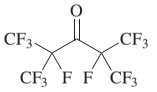
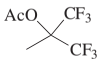
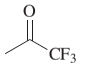
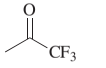
(10)

800, 312

C_6		$TMSCF_3$ (1 eq), TBAF (1.5 eq), THF, 0°; rt, 0.5 h	 (63)	582
		$TMSCF_3$ (3 eq), TBAF (6 eq), THF, 0°; rt, 1 h	 (70) dr >95:5	1012
C_7		n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, Et_2O, –78°	 (66)	197
		1. C_2F_5Li, THF, –78° 2. TMSCl, THF, –78° to rt		581

R	
Me	(62)
c-C_6H_{11}	(59)
Ph	(73)
Bn	(46)

TABLE 17. PERFLUOROALKYL ADDITION TO ACID HALIDES

Acid Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_1 	1. $TMSCF_3$ (3 eq), KF (9 eq), MeCN, rt, 5 h 2. HCl (1.5 eq), rt, 2 h	 (85)	397
	1. $TMSCF_3$ (3.17 eq), KF (3.62 eq), MeCN, –40° to rt, 18 h 2. H_2SO_4, 0.25 h	 (77.1)	465
	$TMSCF_3$ (3.19 eq), KF (3.62 eq), MeCN, –40° to rt, 18 h	 (79)	587
	$TMSCF_3$ (3 eq), KF (cat.), MeCN, rt, 2–5 h	 (>65)	397
	1. $TMSCF_3$ (3.12 eq), CsF (3.12 eq), MeCN, 60°, 20 h 2. $C_6F_5CH_2Br$ (1 eq), 90°, 48 h	 (67)	466
	$(CF_3)_2CFI$ (2 eq), $(Et_2N)_3P$ (1 eq), PhCN, –196°; rt, 24 h	 (61)	596
C_2 	$TMSCF_3$ (1 eq), KF (1 eq), MeCN, –30°, 1 h; rt, 9 h	 (80)	397
	CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 170°, 2 h	 (62.9)	600
	CF_3CO_2Na, CuI, DMF, ~170°	 (62.9)	600

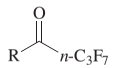
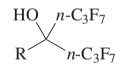
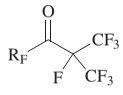
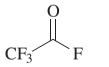
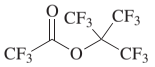
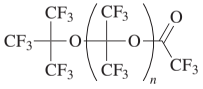
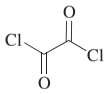
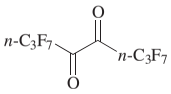
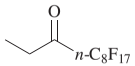
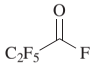
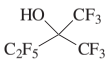
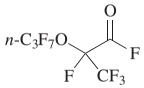
	1. $(Me_2N)_3C^+F^-$, $CF_2{=}C(CF_3)_2$, diglyme, –30°; –20°, 40 min 2. HCl, H_2O	 **I** +  **II** **I + II** (80), **I/II** = 1:1	101
C_{2-5} 	CF_3MgI, *n*-Bu_2O, –30 to 40°, 7 d	 R: Me (59); Et (47); CH_2F (15); CHF_2 (59); CF_3 (49); CF_3CH_2 (37); *n*-Pr (51); *n*-C_4F_9 (43)	199
C_{2-4} 	*n*-C_3F_7MgI, *n*-Bu_2O, –20°, 25 h; –20° to rt, 12–15 h; 50°, 0.5 h	 +  **I** **II** R: Me (15) (22); Et (18) (27); *n*-Pr (21) (23)	204
C_{2-7} 	$(CF_3)_2CFI$ (1 eq), $(Et_2N)_3P$ (1 eq), solvent, –196°; rt, 24 h	 R_F: CF_3 F PhCN (55); CF_3 Cl PhCN (55); C_2F_5 F PhCN (58); C_2F_5 Cl PhCN (58); *n*-C_3F_7 F PhCN (60); *n*-C_3F_7 Cl PhCN (60); C_6F_5 Cl diglyme (69)	596

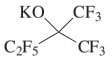
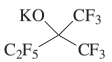
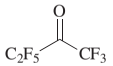
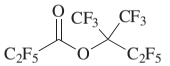
TABLE 17. PERFLUOROALKYL ADDITION TO ACID HALIDES (*Continued*)

Acid Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_2 	$TMSCF_3$ (2 eq), KF (cat.), MeCN, rt	 (>65)	397
	$TMSCF_3$, KF	 (quant)	397
	$TMSCF_3$ (4–4.6 eq), KF (4.0–4.6 eq), MeCN, rt, 8–10 h	 (—) n = 2–4	397
	n-C_3F_7I, Cu, Me_2S, PhCN, rt, 4 h	 (3)	590
C_3 	n-$C_8F_{17}TMS$ (1.23 eq), $(Me_2N)_3SF$ (cat.), DME, –20 to 0°, 0.5 h; rt, 18 h	 (—)	326
C_{3-8} 	$TMSCF_3$ (x eq), KF (y eq), solvent		587

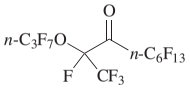
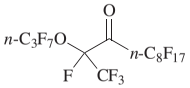
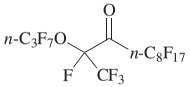
R_F	x	y	Solvent	Temp 1 (°)	Time 1 (h)	Temp 2 (°)	Time 2 (h)	
C_2F_5	2.15	2.25	MeCN	–40	9.5	20	7	(90)
n-C_3F_7	2.35	3	MeCN	–25 to 20	15	—	—	(73.4)
n-C_7F_{15}	2.32	2.87	Me_2CO	–25 to 20	16	—	—	(10.4)

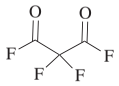
C_3 	1. $TMSCF_3$ (2.15 eq), KF (2.25 eq), MeCN, –40° to rt, 9.5 h; rt, 7 h 2. H_2SO_4	 (85)	465

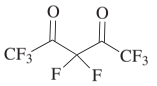
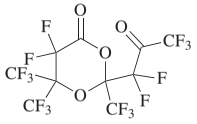


$TMSCF_3$ (2.24 eq), KF (2.55 eq), MeCN, 0–20°, 16 h	 (66.7)		465
$TMSCF_3$ (1 eq), KF (*x* eq), MeCN, –25° to rt, 14 h	 +  + 		465
	I	**II**	**III**

x	I	II	III
0.15	(12.1)	(31.5)	(20)
1	(29.2)	(24.8)	(16.8)

n-$C_6F_{13}TMS$ (1 eq), CsF (8.3 mol %), THF, 0.5 h		(—)	326
n-$C_8F_{17}TMS$ (0.64 eq), $(Me_2N)_3SF$ (cat.), 1,1,2,2-tetrafluorobutane, rt, 2.5 h	 + C_8F_{16}		326
	(—) 83% conv	(—) 9% conv	
n-$C_8F_{17}TMS$ (0.76 eq), $(Me_2N)_3SF$ (cat.), DME, sonication, 0°, 30 min; rt, 20 min		(—) 78% conv	326



1. $TMSCF_3$ (*x* eq), KF (*y* eq), solvent 2. H_2SO_4	 **I** +  **II**		1013

x	*y*	Solvent	Temp 1 (°)	Time 1 (h)	Temp 2 (°)	Time 2 (h)	I	II	III
2	6.35	PhCN	0	16	—	—	(30)	(35)	(—)
5.25	7.3	MeCN	–50	1	20	72	(—)	(—)	(30)

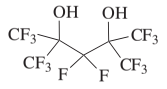
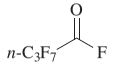
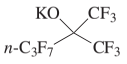
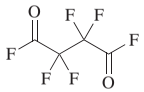
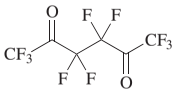
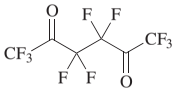
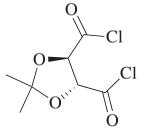
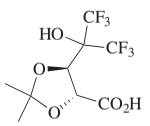
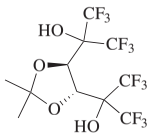
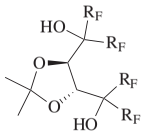
or  **III**

TABLE 17. PERFLUOROALKYL ADDITION TO ACID HALIDES (*Continued*)

Acid Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_4			
	$TMSCF_3$ (2.35 eq), KF (3 eq), MeCN, –25° to rt	 (73.5)	465
	1. $TMSCF_3$ (2.1 eq), KF (4.87 eq), PhCN, 0°, 16 h 2. Vacuum, 120°, 0.5 h	 (71.4)	585
	$TMSCF_3$ (2.1 eq), KF (4.6 eq), PhCN, 0° to rt, 18 h; 70°, 1.5 h	 (52.8)	586
	$TMSCF_3$ (*x* eq), Me_4NF (*x* eq), DME, –50°; –30°, 1 h; to rt, o/n	 or  **I** **II**	594
	R_FI (7.1 eq), MeLi/LiBr (5 eq), Et_2O, –78°, 1 h		594
C_{5-7}			
	$TMSCF_3$, AgF, EtCN, CH_2Cl_2, DMAP, 48–72 h		588

x	**I**	**II**
4	(33)	(—)
7.3	(—)	(20)

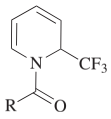
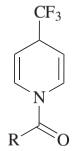
R_F	
C_2F_5	(55)
n-C_3F_7	(25)
n-C_4F_9	(26)
n-C_6F_{13}	(15)

R	
2-furyl	(61)
4-BrC_6H_4	(61)
4-ClC_6H_4	(78)
2-FC_6H_4	(71)
4-$O_2NC_6H_4$	(50)

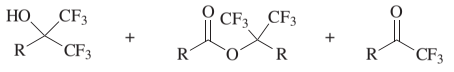
C_{5-8} 

$Cd(CF_3)_2$•DME (*x* eq), DMAP (*y* eq), CH_2Cl_2, rt 

R	*x*	*y*	Time (h)		
2-thienyl	0.5	1.04	24	(81)	589
Ph	0.51	1.01	40	(85)	
4-$O_2NC_6H_4$	0.52	1.07	72	(57)	
4-$MeOC_6H_4$	0.5	1.06	48	(85)	
4-MeC_6H_4	0.51	1.04	48	(78)	

$Cd(CF_3)_2$•DME (*x* eq), pyridine, rt  **I**  **II**  **III** 589

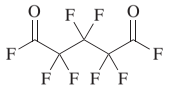
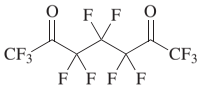
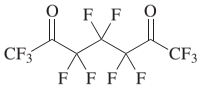
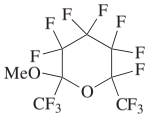
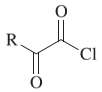
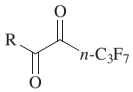
R	*x*	Time (h)	**I**	**II**	**III**
2-furyl	0.52	6	(47)	(48)	(—)
2-thienyl	0.52	6	(47)	(44)	(9)
Ph	0.48	6–8	(44)	(35)	(17)
4-ClC_6H_4	0.37	6	(41)	(34)	(15)
4-$O_2NC_6H_4$	0.52	6	(40)	(34)	(15)
3-$O_2NC_6H_4$	0.55	8	(51)	(27)	(12)
4-$MeOC_6H_4$	0.45	8	(51)	(34)	(10)
4-MeC_6H_4	0.48	6	(41)	(39)	(17)

CF_3I (*x* eq), TDAE (*x* eq), solvent, –20°; rt 

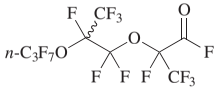
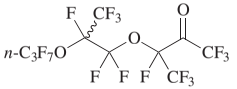
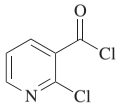
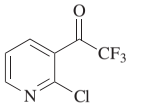
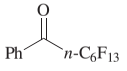
I (—) **II** (—) **III** (—) 599

R	*x*	Solvent	Time (h)	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)
i-Bu	2.2	DME	2	—	34	—
Ph	2.2	DMF	2	5	44	—
Ph	2.2	DME	o/n	—	>98	—
Ph	2.2	DME	2	—	>98	—
Ph	1.1	DME	2	—	22	3
2-FC_6H_4	2.2	DME	2	—	86	—
4-FC_6H_4	2.2	DME	2	—	72	—
4-BrC_6H_4	2.2	DME	2	—	48	—
4-MeC_6H_4	2.2	DME	2	—	>98	—

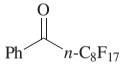
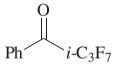
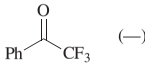
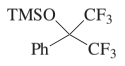
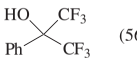
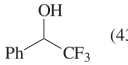
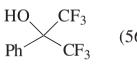
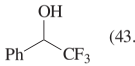
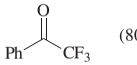
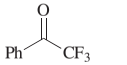
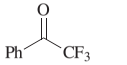
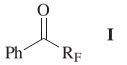
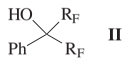
TABLE 17. PERFLUOROALKYL ADDITION TO ACID HALIDES (*Continued*)

Acid Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_5 	1. $TMSCF_3$ (2.1 eq), KF (4.44 eq), PhCN, 0°, 14 h 2. Vacuum, 150°, 1.5 h	 (89.8)	585
	$TMSCF_3$ (2.1 eq), KF (4.4 eq), PhCN, 0° to rt, 17 h; 70°, 2 h	 (80.7)	586
	1. $TMSCF_3$ (2.15 eq), KF (4.47 eq), PhCN, 0°, 18 h 2. Vacuum, Me_2SO_4 (6.44 eq), 110°, 1 h	 (43.1)	585
C_{5-8} 	n-C_3F_7I, Cu, Me_2S, solvent		590

R	Solvent	Temp	Time (h)	
n-C_3F_7	PhCN	rt	8	(3)
t-Bu	PhCN	85°	1	(4.1)
Ph	MeCN	rt	24	(48.8)

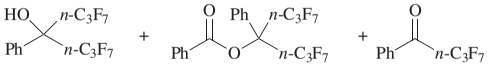
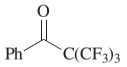
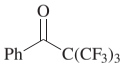
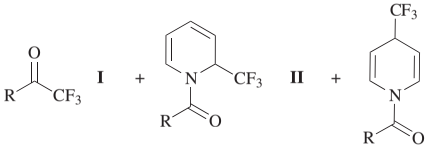
C_6 	Me_3SnCF_3 (0.27 eq), 140°, 20 h	 (49)	160
	$TMSCF_3$, AgF, EtCN, –30°, 15h; rt	 (—)	588
C_7 	n-$C_6F_{13}TMS$ (1 eq), CsF (3.3 mol %), THF-d_8, 60°, 0.25 h	 (—)	326



n-$C_8F_{17}TMS$ (0.91 eq), CsF (2 mol %), DME, 25–30°, 1.5 h		(—)				326
i-C_3F_7ZnI, pyridine, THF, rt, 1 h		(89)				591
$TMSCF_3$ (1.2 eq), TBAF (>1 eq), THF		(—)	+		(—)	122
1. $TMSCF_3$ (2 eq), TMAF (2 eq), DME 2. H_3O^+		(77)				592
1. CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 170°, 2 h 2. HCl, H_2O, 170°, 4 h		(56.5)	+		(43.5)	860, 600
1. CF_3CO_2Na, CuI (1 eq), DMF, ~170° 2. H_2O		(56.5)	+		(43.5)	600
CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 170°, 2 h		(80.3)				600
CF_3CO_2Na, CuI, DMF, ~170°		(80.3)				600
$Bi(CF_3)_3$ (1.5 eq), pyridine, MeCN, rt, 2 h		(69)				168
R_FI (x eq), TDAE (y eq), THF, –40 to –20°, 2 h	 **I**		+	 **II** (—)		127

R_F	x	y	**I**	Conv **II** (%)
C_2F_5	2	1.5	(33)	17
i-C_3F_7	1.1	1	(56)	—

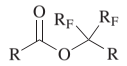
TABLE 17. PERFLUOROALKYL ADDITION TO ACID HALIDES (*Continued*)

Acid Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_7 	n-C_3F_7I (2.2 eq), TDAE (2.2 eq), DME, –20°; rt, 2 h	 (—) 47% conv + (—) 32% conv + (—) 17% conv	599
	$(Me_2N)_3C^+ C(CF_3)_3^-$ (0.75 eq), MeCN	 (42)	101
	1. $(Me_2N)_3C^+ C(CF_3)_3^-$ (0.75 eq), diglyme, –30°; –20°, 40 min 2. HCl, H_2O	 (88)	101
	CF_3H, **57** (2.4 eq), THF, –40°	 **I** +  **II** Time (h) **I** **II** 1 (81) (7) 24 (0) (90)	81
	"$CuCF_3$"[a], HMPA, 45°, 24 h	 (24)[b] +  (22)[b]	53
C_{7-8} 	$Cd(CF_3)_2$•DME (x eq), pyridine (y eq), Et_2O, rt	 **I** + **II** + **III** R x y Time (d) **I** **II** **III** Ph 0.48 1.03 1 (61) (23) (7) 4-$O_2NC_6H_4$ 0.52 1.16 3 (63) (20) (3) 4-MeC_6H_4 0.48 1.03 1 (55) (23) (4)	589

C_{7-9}



R_FX^2 (*x* eq), $(Et_2N)_3P$ (*x* eq),
CH_2Cl_2, temp 1, time 1; rt



598

R	X^1	R_F	X^2	*x*	Temp 1 (°)	Time 1 (h)	
Ph	F	CF_3	Br	1	–70	4	(81)
Ph	Cl	C_2F_5	I	1.2	0	8	(51)
3-FC_6H_4	Cl	CF_3	Br	1.12	–70	7	(48)
3-FC_6H_4	Cl	C_2F_5	I	1.2	0	8	(55)
2-ClC_6H_4	Cl	CF_3	Br	1.12	–70	7	(87)
2-ClC_6H_4	Cl	C_2F_5	I	1.2	0	8	(76)
3-$MeOC_6H_4$	Cl	CF_3	Br	1.12	–70	7	(63)
3-MeC_6H_4	Cl	CF_3	Br	1.12	–70	7	(83)
3-MeC_6H_4	Cl	C_2F_5	I	1.2	0	8	(47)
3,4-$Me_2C_6H_3$	Cl	CF_3	Br	1.12	–70	7	(88)

R_FX^2 (*x* eq), $(Et_2N)_3P$ (*x* eq), solvent



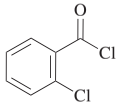
R	X^1	R_F	X^2	*x*	Solvent	Temp 1 (°)	Time 1 (h)	Temp 2 (°)	Time 2 (h)		
Ph	F	*i*-C_3F_7	I	1	CH_2Cl_2	–70	12	—	—	(78)	597
Ph	Cl	CF_3	Br	1.08	CH_2Cl_2	–70	3	rt	—	(52)	597
Ph	Cl	C_2F_5	I	1.08	CH_2Cl_2	–20	—	0	5	(58)	597, 598
3-FC_6H_4	Cl	C_2F_5	I	1.08	MeCN	–20	—	0	5	(56)	597
3-FC_6H_4	F	*i*-C_3F_7	I	1	CH_2Cl_2	–70	12	—	—	(78)	597
4-ClC_6H_4	Cl	C_2F_5	I	1.08	MeCN	–20	—	0	5	(42)	597
2-ClC_6H_4	F	*i*-C_3F_7	I	1	CH_2Cl_2	–70	12	—	—	(83)	597
3-$MeOC_6H_4$	Cl	C_2F_5	I	1.08	CH_2Cl_2	–10	—	0	6	(61)	597
4-$MeOC_6H_4$	Cl	*i*-C_3F_7	I	1.13	CH_2Cl_2	–20	3	–10	5	(76)	597
3,5-$(MeO)_2C_6H_3$	Cl	C_2F_5	I	1.08	MeCN	–20	—	0	5	(44)	597
3-MeC_6H_4	Cl	CF_3	Br	1.08	CH_2Cl_2	–70	3	rt	—	(48)	597
3-MeC_6H_4	Cl	C_2F_5	I	1.08	CH_2Cl_2	–20	—	0	5	(56)	597
3-MeC_6H_4	Cl	C_2F_5	I	1.08	MeCN	–20	—	0	5	(44)	597
4-MeC_6H_4	Cl	C_2F_5	I	1.08	MeCN	–20	—	0	5	(58)	597
4-$CF_3C_6H_4$	Cl	C_2F_5	I	1.08	MeCN	–20	—	0	5	(42)	597
3,4-$Me_2C_6H_3$	Cl	CF_3	Br	1.08	CH_2Cl_2	–70	3	rt	—	(41)	597

TABLE 17. PERFLUOROALKYL ADDITION TO ACID HALIDES (*Continued*)

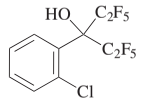
Acid Halide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_7

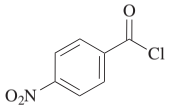


1. C_2F_5I (2 eq), $(Et_2N)_3P$ (2 eq), CH_2Cl_2, –20°; 0°, 8 h
2. HCl (1.83 eq), 0°, 1 h
3. H_2O

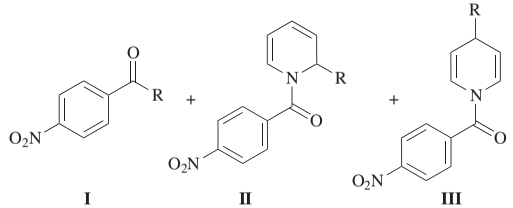


(62)

598



$Cd(R)_2•L$ (*x* eq), pyridine, rt



I **II** **III**

589

$Cd(R)_2•L$	*x*	Time (h)	**I**	**II**	**III**
$Cd(C_2F_5)_2•MeCN$	0.46	8	(22)	(46)	(24)
$Cd(n\text{-}C_3F_7)_2•DME$	0.48	6	(26)	(40)	(27)
$Cd(i\text{-}C_3F_7)_2•MeCN$	0.48	3	(31)	(47)	(16)

C_{7-9}



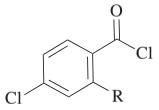
$TMSCF_3$, AgF, EtCN, –30°, 15 h; rt



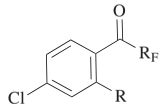
R	
4-$MeOC_6H_4$	(73)
2-$CF_2HOC_6H_4$	(63)
4-MeC_6H_4	(77)
(*E*)-PhCH=CH	(50)

588

C_7

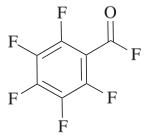


R_FI (2.77 eq), $(Et_2N)_3P$ (1 eq), CH_2Cl_2, 45°, 6 h

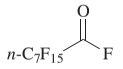


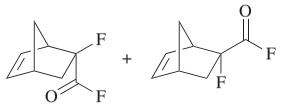
R	R_F	
H	$n\text{-}C_6F_{13}$	(41)
Cl	$n\text{-}C_8F_{17}$	(36)

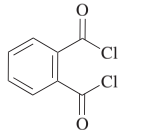
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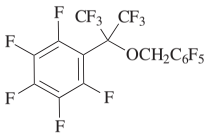
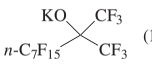
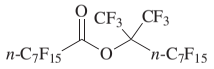
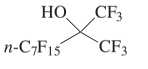
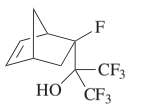
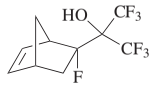


C_8

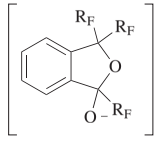




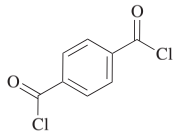


1. $TMSCF_3$ (2 eq), CsF (2.4 eq), MeCN, 60°, 20 h 2. $C_6F_5CH_2Br$ (1 eq), 90°, 48 h		(31)		466
$TMSCF_3$ (2.32 eq), KF (2.87 eq), MeCN, –25° to rt, 16 h		(10.4)	+ 	(—) 465
1. $TMSCF_3$ (2.32 eq), KF (2.87 eq), MeCN, –25° to rt, 16 h 2. H_2SO_4, rt, 1 h		(9.8)		465
1. $TMSCF_3$ (2.2 eq), KF (1.1 eq), CsF (0.1 eq), THF, 10°; rt, o/n 2. HCl, H_2O		**I**	+  **II**	1014

I + **II** (90), **I**/**II** = 3:7

$TMSR_F$ (*x* eq), TMAF (*y* eq), DME, –60°; –50°, 1 h; rt, 24 h	Me_4N^+ 	R_F	*x*	*y*
		CF_3	3.3	3 (85)
		C_2F_5	3.2	2.8 (62)

593



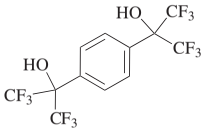
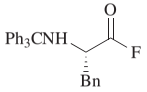
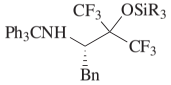
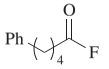
1. $TMSCF_3$ (4.2 eq), TMAF (4 eq), DME, –50°; –30°, 1 h; rt, o/n 2. HCl, H_2O		(82)	592

TABLE 17. PERFLUOROALKYL ADDITION TO ACID HALIDES (*Continued*)

Acid Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_9 	R_3SiCF_3 (2.5 eq), TBAF (cat.), THF, 0°	 R: Me, Time (h): 1 (48); Et, 0.5 (50)	1015
C_{11} 	1. C_2F_5I (5 eq), MeLi/LiBr (5 eq), Et_2O, –78° 2. $KHSO_4$	 **I** + **II** Time (min): 20, **I** (7), **II** (28); 90, **I** (0), **II** (79)	190

[a] "RFCu" is a perfluoroalkylcopper species that contains RFCu, and is sometimes in equilibrium with $[RF_2Cu]-$ and [RFCuX]– (X = halogen).

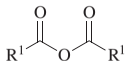
[b] The yield was estimated by gas chromatography.

TABLE 18. PERFLUOROALKYL ADDITION TO ANHYDRIDES

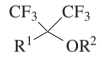
Anhydride	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{1-11}

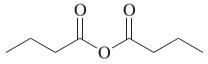


1. $TMSCF_3$ (2.1 eq), TMAF (*x* eq), DME, –50°; –30°, 1 h; rt, o/n
2. Hydrolysis

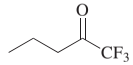


R^1	*x*	Hydrolysis	R^2		Refs.
t-BuO	1	—	TMS	(50)	592
Me	1	—	TMS	(62)	
CF_3	2	HCl, H_2O	H	(87)	
2-furyl	1	—	TMS	(75)	
Ph	1	—	TMS	(82)	
Ph	2	HCl, H_2O	H	(81)	
1-$C_{10}H_7$	1	—	TMS	(88)	

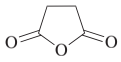
C_4



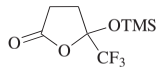
1. CF_3Br, Zn, pyridine, rt, 2.5 h
2. H_3O^+



(20) 601

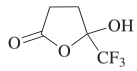


$TMSCF_3$ (1 eq), TBAF (1.5 mol %), THF, 60°, 7 h



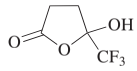
(30) 604

1. $TMSCF_3$ (2 eq), TBAT (10 mol %), THF, 0°; <10°, 4 h
2. H_2O



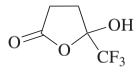
(67) 603

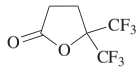
1. CF_3Br, Zn, pyridine, 20°
2. H_3O^+



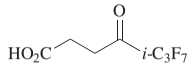
(40) 602

1. CF_3Br, Zn, pyridine, 20°, 1.5 h
2. H_3O^+



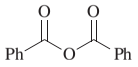
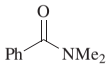
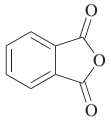
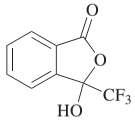
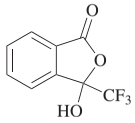
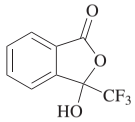
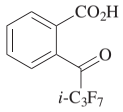
(18) +  (40) 601

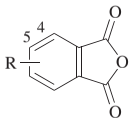
i-C_3F_7ZnI, pyridine, THF



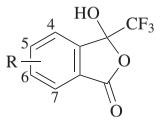
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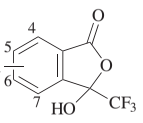
TABLE 18. PERFLUOROALKYL ADDITION TO ANHYDRIDES (*Continued*)

Anhydride	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_7 	CF_3CO_2K (1.72 eq), DMF, 140°, 5.5 h	 (10) +  (20) +  (30)	887
C_8 	1. $TMSCF_3$ (2 eq), TBAT (10 mol %), THF, 0°; <10°, 4 h 2. H_2O	 (91–95)	603
	1. CF_3Br, Zn, pyridine, rt, 1.5 h 2. H_3O^+	 (61)	601, 602
	1. CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 170°, 2 h 2. HCl, H_2O, 170°, 4 h	 (67.4)	600
	i-C_3F_7ZnI, pyridine, THF	 (98)	591



1. CuI (10 mol %), KF (2 eq), phen (10 mol %), THF
2. $TMSCF_3$ (1.2 eq), 50°, 6 h

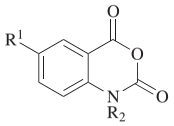


I + 

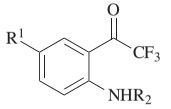
II

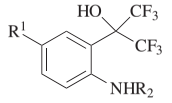
605

R	I + II	I/II
H	(85)	—
4-Cl	(84)	25:75
5-Cl	(90)	50:50
4,5,6,7-Cl_4	(82)	—
5-Br	(85)	62:38
4,5,6,7-Br_4	(79)	—
4-I	(80)	40:60



$TMSCF_3$ (1.3 eq), [KF/TBAB (1:1)] (0.3 eq), DMF, 0°; rt, 5 h

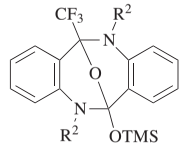


I + 

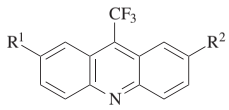
II

607

R^1	R^2	I	II	III	IV
H	H	(0)	(—)	(—)	(—)
H	Me	(87)	(2)	(—)	(—)
H	CH_2=$CHCH_2$	(90)	(<5)	(—)	(—)
H	$NCCH_2$	(0)	(—)	(—)	(—)
H	Ph	(74)	(—)	(6)	(—)
H	4-FC_6H_4	(67)	(—)	(—)	(—)
H	4-$MeOC_6H_4$	(83)	(—)	(—)	(—)
H	Bn	(85)	(<5)	(—)	(—)
H	4-$(Ph_2CH)C_6H_4$	(77)	(7)	(—)	(5)
Br	Me	(80)	(<5)	(—)	(—)

+ 

III

+ 

IV

TABLE 18. PERFLUOROALKYL ADDITION TO ANHYDRIDES (*Continued*)

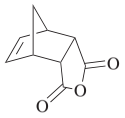
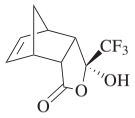
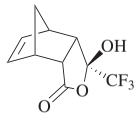
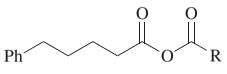
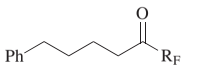
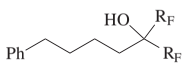
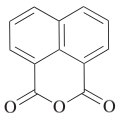
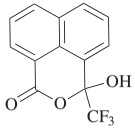
Anhydride	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_9 	$TMSCF_3$ (2 eq), TBAB (10 mol %), THF, 0°; <10°, 4 h	 **I** +  **II** **I** + **II** (90), **I/II** = 97:3	606
C_{11} 	1. R_FI (5 eq), MeLi/LiBr (5 eq), Et_2O, –78° 2. $KHSO_4$	 **I** +  **II** R: *i*-Bu; R_F: C_2F_5; Time (h): 1.5; **I**: (25); **II**: (11) R: $Ph(CH_2)_4$; R_F: C_2F_5; Time (h): 0.5; **I**: (44); **II**: (17) R: $Ph(CH_2)_4$; R_F: C_2F_5; Time (h): 1.5; **I**: (21); **II**: (42) R: $Ph(CH_2)_4$; R_F: *n*-C_3F_7; Time (h): 1; **I**: (12); **II**: (0)	190
C_{12} 	1. CuI (10 mol %), KF (2 eq), phen (10 mol %), THF 2. $TMSCF_3$ (1.2 eq), 50°, 6 h	 (75)	605

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES

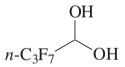
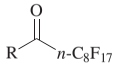
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_1 	1. CF_3H (1 eq, inverse addition), THF, –40°, 20 min 2. KHMDS (1 eq), –40°, 1 h; rt, 10 h	 R: Me, Et Conv (%)[a]: 20, 20	77
	*n*-C_3F_7I, Mg, THF, rt to –80°; –80°, 23 h; –30°, 20 h	 (24)	201
$C_{2–9}$ 	*n*-$C_8F_{17}I$, MeLi/LiBr, Et_2O, –78°, 1 h	 R: $BrCH_2$ (86); *i*-Pr (72); (*E*)-MeCH=CH (58); *t*-Bu (60); (*E*)-MeCH=C(Me) (74); Ph (86); PhC≡C (95); $PhCH_2CH_2$ (86)	625, 624
$C_{2–4}$ 	R_FI, MeLi, Et_2O, –78°, 1 h	 R^1: CF_3, CF_3, CF_2Cl, C_3F_7 R_F: *n*-C_6F_{13} (72), *n*-C_8F_{17} (77), *n*-C_6F_{13} (89), *n*-C_6F_{13} (80)	R^2 = Me, Et	626
C_2 	1. CF_3Br, Zn, pyridine, 20° 2. H_3O^+	 R: CF_3, EtO_2C Acid: —, H_2SO_4 (54)[b], (38)		602
	1. CF_3Br, Zn, pyridine, 20°, 2 h 2. H_3O^+	 R: CF_3 (20), EtO_2C (38)		601

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

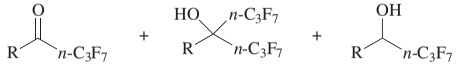
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{2-4}



n-C_3F_7MgI (x eq), n-Bu_2O, –40°, 24 h; –40° to rt, 24 h; rt, 24 h



I **II** **III**

R	x	**I**	**II**	**III**
Me	1	(19)	(21)	(2)
Me	2.5	(11)	(32)	(8)
CF_3	1	(—)	(—)	(—)
CF_3	2.5	(41)	(8)	(8)
Et	1	(16)	(19)	(8)
Et	2.5	(10)	(28)	(9)
C_2F_5	1	(—)	(—)	(—)
C_2F_5	2.5	(39)	(10)	(6)
n-Pr	1	(15)	(13)	(12)
n-Pr	2.5	(14)	(5)	(18)

204

C_{2-9}



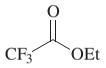
1. $TMSCF_3$ (1.025 eq), CsF (1 mol %), solvent, rt
2. HCl, H_2O, rt, 3 h



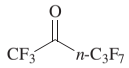
R^1	R^2	Solvent	Time (h)	
Me	Et	PhCN	1	(86)
CH_2=$CHCH_2$	Me	none	3	(84)
Ph	Me	none	1	(90)
(*E*)-PhCH=CH	Me	DME	3	(90)
PhC≡C	Me	none	3	(86)
PhC≡C	Et	none	3	(87)
$Ph(CH_2)_2$	Et	none	4	(90)

470

C_2



n-C_3F_7MgI, Et_2O, –50° to rt



(50)

203

C_{2-3}



R^2I, Al, additive, NMP, 30–33°, 2.5 h



R^1	R^2	Additive		
CF_3	n-C_4F_9	$SnCl_2$	(38)	1016
C_2F_5	C_2F_5	$SnCl_2$	(38)	
C_2F_5	C_2F_5	$HgCl_2$	(33)	

C_{2-8}



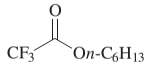
C_2F_5I (x eq), MeLi (y eq)/LiBr, Et_2O, −78°, 0.5 h



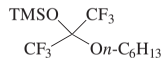
I + **II** 391

R	x	y	**I**	**II**
$MeSCH_2$	6.1	5	(—)	(62)
t-Bu	5.8	5	(93)	(—)
n-C_5H_{11}	6.1	5.8	(66)	(—)
2-pyridyl	4.9	4.7	(—)	(71)
3-pyridyl	6.5	5	(—)	(78)
2-$C_5H_4NCH_2$	7.4	5.1	(—)	(100)[c]
c-C_6H_{11}	6.2	5	(24)	(39)
Ph	5	5	(62)	(—)
Bn	5.3	5.1	(—)	(74)
Bn	7.1	5	(90)	(—)

C_2

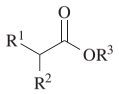


$TMSCF_3$ (1.2 eq), TBAF (1 eq), THF

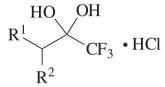


(35) 122

C_{2-9}



1. $TMSCF_3$ (1.05 eq), CsF (2 mol %), DME, rt, 6 h
2. HCl, H_2O, rt, 3 h



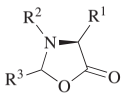
R^1	R^2	R^3		
Me_2N	H	Et	(85)	609
Bn_2N	H	Me	(83)	
Me_2NCH_2	H	Me	(85)	
Bn_2N	Me	Me	(82)	
Me_2N	Bn	Et	(81)	

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

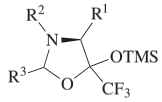
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

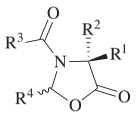
C_{2-9}



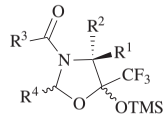
TMSCF$_3$, CsF (cat.), THF, sonication



R^1	R^2	R^3		
H	Boc	H	(60)	612
Me	Boc	H	(85)	
Me	Cbz	H	(85)	
Me	Cbz	4-MeOC$_6$H$_4$	(95)	
BnSCH$_2$	Boc	H	(65)	
MeO$_2$CCH$_2$	Cbz	H	(50)	
i-Pr	Boc	H	(85)	
s-Bu	Boc	H	(95)	
MeO$_2$C(CH$_2$)$_2$	Cbz	H	(70)	
Bn	Boc	H	(80)	
Bn	Cbz	H	(95)	
Bn	Cbz	Ph	(60)	
Bn	Cbz	4-MeOC$_6$H$_4$	(95)	



TMSCF$_3$ (1.2 eq), CsF (cat.), sonication, THF, rt, 20–60 min

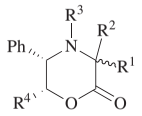


611

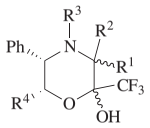
R^1	R^2	R^3	R^4	
H	H	Ph	4-MeOC$_6$H$_4$	(—)
Me	H	*t*-BuO	H	(85)
Me	H	BnO	H	(69)
BnSCH$_2$	H	*t*-BuO	H	(77)
Me	Me	Ph	4-MeOC$_6$H$_4$	(72)
Me	Me	PhOCH$_2$	4-MeOC$_6$H$_4$	(75)
i-Pr	H	*t*-BuO	H	(84)
MeO$_2$C(CH$_2$)$_2$	H	BnO	H	(73)
i-Bu	H	*t*-BuO	H	(95)
Bn	H	*t*-BuO	H	(98)

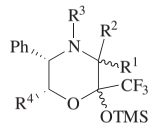
Bn	H	BnO	H	(95)
Bn	H	Ph	*t*-Bu	(71)
Bn	H	BnO	*t*-Bu	(80)
Bn	H	BnO	Ph	(53)

C_{2-9}



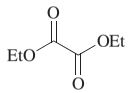
$TMSCF_3$, CsF or TBAF, THF



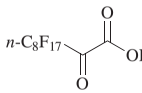
I +  **II** (—) 622

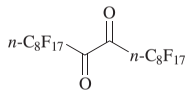
R^1	R^2	R^3	R^4	**I**
H	H	Boc	Ph	(82)
Me	H	Boc	H	(>95)
Me	H	Boc	Ph	(35)
Me	Me	Cbz	H	(60)
n-C_4H_9	H	Boc	H	(76)
Bn	H	Cbz	H	(>95)

C_2



n-$C_8F_{17}Li$, Et_2O, –78°



I +  **II** (—) 650

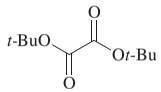
Time (h)	**I**
0.5	(95)[d]
1	(84)

R_FI, Zn/Cu, $ClCO_2Et$ (cat.)

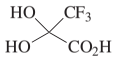


R_F	
n-C_4F_9	(65)
n-C_6F_{13}	(60)
n-C_8F_{17}	(50)

1017



1. $TMSCF_3$, TBAF (cat.), THF
2. HCl, CH_2Cl_2

 (78) 610

$TMSC_2F_5$ (2 eq), TBAF (0.1 eq), THF, reflux, 6 h

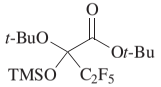
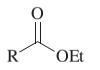
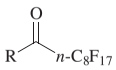
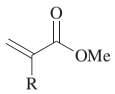
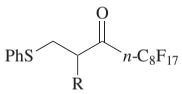
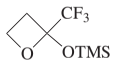
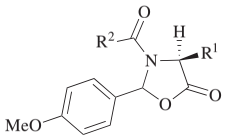
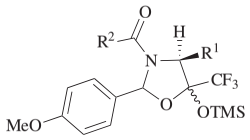
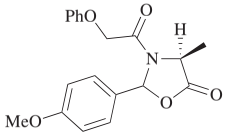
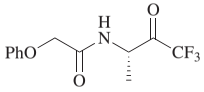
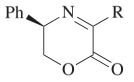
 (89) 1018

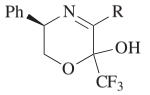
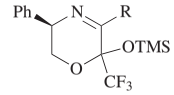
TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{3-9} 	*n*-C_8F_{17}Li (0.97 eq), Et_2O, –78°	 R: $(CF_3)_2CFO(CF_2)_2$, Time (h): 0.75, (96); R: *n*-C_8F_{17}, Time (h): 0.5, (94)	650
C_{3-4} 	1. *n*-$C_8F_{17}I$, MeLi/LiBr, Et_2O, –78°, 1 h 2. PhSH, rt, 1 h	 R: H, (58); Me, (80)	625
C_3 	$TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h	 (—)	122
C_{3-9} 	$TMSCF_3$ (1.2 eq), TBAF (2.5 mol %), THF, rt, 20–60 min	 R^1 R^2: Me BnO (92); Me Ph (94); *i*-Pr BnO (86); Bn BnO (91)	611
C_3 	1. $TMSCF_3$, TBAF (cat.), THF 2. TBAF (1 eq), THF 3. Amberlite, MeCN	 (80)	613, 614

C_{3-10}

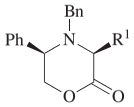


1. $TMSCF_3$ (2 eq), initiator (*x* eq), solvent
2. NH_4Cl, H_2O, rt, 3 h

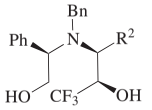
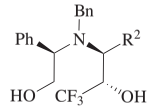

I +

II

621

R	Initiator	*x*	Solvent	Temp (°)	**I**	**II**
Me	CsF	1	THF	0	(55)	(—)
Me	K_2CO_3	0.1	DMF	rt	(65)	(—)
Me	*t*-BuOK	0.5	THF	0	(38)	(12)
Me	TASF	0.5	THF	0	(72)	(—)
Me	TBAF	0.5	THF	0	(56)	(—)
Me	TBAT	0.5	THF	0	(54)	(—)
$MeO_2C(CH_2)_2$	TASF	0.5	THF	0	(74)	(—)
t-Bu	TASF	0.5	THF	0	(65)	(—)
$CH_2{=}CH(CH_2)_3$	TASF	0.5	THF	0	(69)	(—)
Ph	TASF	0.5	THF	0	(32)	(—)
$Ph(CH_2)_2$	TASF	0.5	THF	0	(75)	(—)



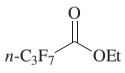
1. $TMSCF_3$ (2 eq), TBAT (1.1 eq), THF, 0°
2. NH_4Cl, H_2O, rt, 3 h
3. $NaBH_4$ (2 eq), MeOH, H_2O, rt, 4 h


I +

II

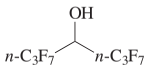
621

R^1	R^2	**I + II**	**I/II**
Me	Me	(54)	88:12
$MeO_2C(CH_2)_2$	$HO(CH_2)_3$	(37)	50:50
$Ph(CH_2)_2$	$Ph(CH_2)_2$	(67)	60:40

C_4

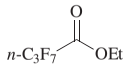
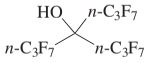
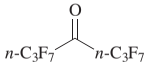
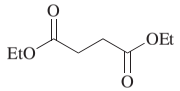
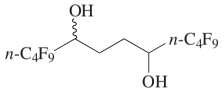
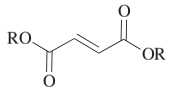
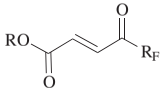
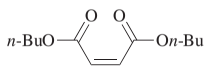
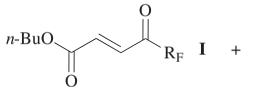
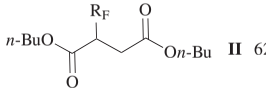
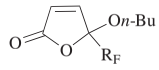
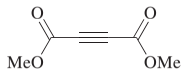
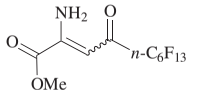


n-C_3F_7Li, Et_2O, –60°, 0.75 h; –50 to –36°, 36 h; rt, 24 h

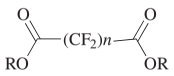

(42)

1019

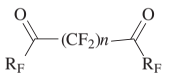
TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_4			
	*n*-C_3F_7I, MeLi, Et_2O, –45°, 0.5 h; –35°, 6 h; –35° to rt, 15 h	 (37)	188
	n-C_3F_7I, Mg, Et_2O, rt to –50°; –50° 18 h; –40°, 24 h; –30°, 12 h	 (20)	201
	1. *n*-C_4F_9Li, E_2O, <–90° 2. $LiAlH_4$	 (60)	956
	R_FI, MeLi/LiBr, Et_2O, –78°, 1 h	 R = Me, R_F = *n*-C_6F_{13} (63); R = *n*-Bu, R_F = *n*-C_8F_{17} (61)	625
	R_FY, MeLi/LiBr, additive (1 eq), Et_2O, –78°, 1 h	 **I** +  **II**	625
	R_F = *n*-C_4F_9, Y = *n*-Bu_4Sn, Additive = —, **I** = (—), **I** (*E*)/(*Z*) = 10:1, **II** = (—), **I**/**II**/**III** = 33:10:0	+  **III** (—)	
	R_F = *n*-C_6F_{13}, Y = I, Additive = BF_3•Et_2O, **I** = (91), **I** (*E*)/(*Z*) = 5:6, **II** = (—), **I**/**II**/**III** = 56:24:5		
	R_F = *n*-C_8F_{17}, Y = I, Additive = —, **I** = (46), **I** (*E*)/(*Z*) = 10:1, **II** = (21), **I**/**II**/**III** = —		
	1. *n*-$C_6F_{13}I$, MeLi/LiBr, Et_2O, –78°, 1 h 2. NH_4Cl, H_2O	 (71)	625

C_{4-5}



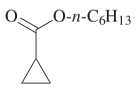
R_FI (2 eq), MeLi, Et_2O, –78°



n	R_F		
2	*n*-C_3F_7	(67)	
3	C_2F_5	(72)	R = Me, Et
3	*n*-C_3F_7	(75)	

626

C_4

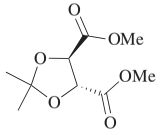


1. $TMSCF_3$ (1.2 eq), CsF (1 mol %), THF, rt, to completion
2. $TBAF•3H_2O$ (2 mol %), rt, 2 h
3. Distillation
4. Cs_2CO_3 (0.5 eq), rt, 3 h

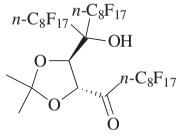


I + **II** **I + II** (67) **I/II** = —

1020

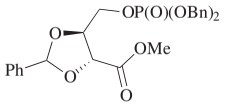


n-$C_8F_{17}MgBr$ (4 eq), Et_2O, –30°, 4 h

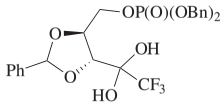


(71)

1021



1. $TMSCF_3$, CsF
2. TBAF, THF

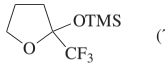


(70)

424



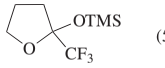
$TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h



(70)

122

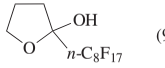
$TMSCF_3$ (1.08 eq), TBAF (1 mol %), THF, 0°; 20°, 2 h



(50)

604

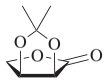
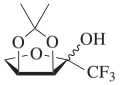
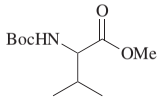
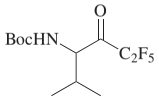
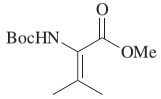
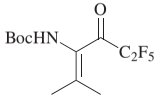
n-$C_8F_{17}I$, MeLi/LiBr, Et_2O, –78°, 1 h



(99)

625, 624

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

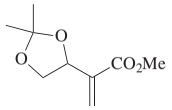
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_4 	1. $TMSCF_3$ (1.1 eq), TEAF (cat.), THF, rt, 0.25 h 2. TEAF (1 eq), THF, rt, 0.25 h	 (91)	617, 618
C_5 	C_2F_5I, MeLi/LiBr, Et_2O, toluene, –70°	 (70)	1022
	C_2F_5I, MeLi/LiBr, Et_2O, –70°	 (25)	1022
C_{5-11} XCF_2CO_2R	KF (1 eq), CuI (1 eq), DMF	RCF_3	245

R	X	Temp (°)	Time (h)	
CH_2=$CHCH_2$	Cl	100	5	(78)
CH_2=$CHCH_2$	Br	70	8	(89)
HC≡CCH_2	Cl	100	4	(78)
Bn	Cl	100	10	(59)
Bn	Br	80	8	(68)
4-$ClC_6H_4CH_2$	Cl	100	10	(62)
4-$ClC_6H_4CH_2$	Br	80	8	(64)
3-$ClC_6H_4CH_2$	Cl	100	10	(53)
3-$ClC_6H_4CH_2$	Br	80	8	(65)
2-$ClC_6H_4CH_2$	Cl	100	12	(48)
2-$ClC_6H_4CH_2$	Br	80	10	(58)
3-$O_2NC_6H_4CH_2$	Cl	110	12	(47)
3-$O_2NC_6H_4CH_2$	Br	85	8	(58)
4-$O_2NC_6H_4CH_2$	Cl	110	12	(51)
4-$O_2NC_6H_4CH_2$	Br	85	9	(53)
4-$MeC_6H_4CH_2$	Cl	100	10	(65)
4-$MeC_6H_4CH_2$	Br	80	7	(71)

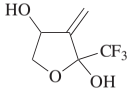
				3-$MeC_6H_4CH_2$	Cl	100	10	(68)	
				3-$MeC_6H_4CH_2$	Br	80	8	(68)	
				$PhCH{=}CHCH_2$	Cl	100	5	(81)	
				$PhCH{=}CHCH_2$	Br	70	4	(87)	

				R	Temp (°)	Time (h)		
$FSO_2CF_2CO_2R$	CuI (1 eq), DMF	RCF_3		$CH_2{=}CHCH_2$	50	4	(85)	245
				Bn	60	7	(71)	
				4-$ClC_6H_4CH_2$	60	8	(75)	
				3-$ClC_6H_4CH_2$	60	8	(69)	
				2-$ClC_6H_4CH_2$	65	9	(63)	
				4-$BrC_6H_4CH_2$	70	8	(72)	
				3-$O_2NC_6H_4CH_2$	70	7	(60)	
				4-$O_2NC_6H_4CH_2$	70	8	(58)	
				4-$MeC_6H_4CH_2$	60	6	(75)	
				3-$MeC_6H_4CH_2$	60	6	(73)	
				$PhCH{=}CHCH_2$	50	4	(90)	

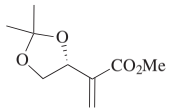
C_5



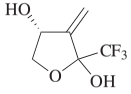
1. $TMSCF_3$ (1.53 eq), CsF (2.9 mol %), rt, 26 h
2. HCl, H_2O, THF, rt, 18 h



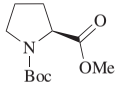
(78) 1023



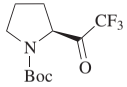
1. $TMSCF_3$ (1.21 eq), CsF (7 mol %), rt, 21 h
2. HCl, H_2O, THF, rt, 24 h



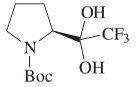
(47) 1023



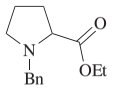
1. $TMSCF_3$ (1.5 eq), TBAF (5 mol %), pentane, THF, –78° to rt, 18 h
2. $NaHCO_3$, H_2O, 0°



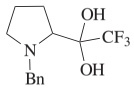
(28) +



(40) 1024

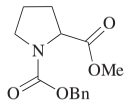
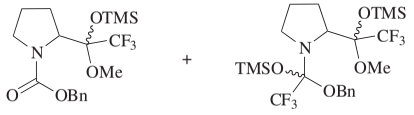
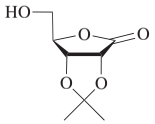
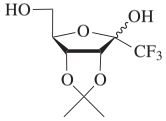
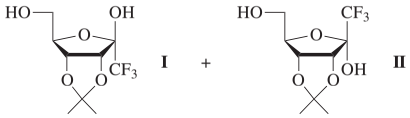
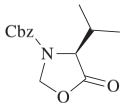
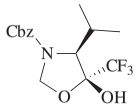
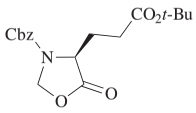
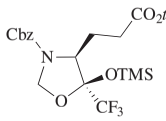


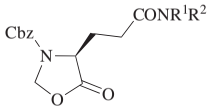
1. $TMSCF_3$ (1.05 eq), CsF (2 mol %), DME, rt, 6 h
2. HCl, H_2O, rt, 3 h



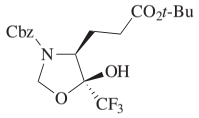
•HCl (82) 609

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_5			
	$TMSCF_3$ (1.05 eq), CsF (2 mol %), DME, rt, 6 h	 (—) 60% conv + (—) 10% conv	609
	1. $TMSCF_3$ (2.1 eq), THF, rt, 10 min 2. TEAF (cat.), THF, rt, 15 min 3. TEAF (2 eq), THF, rt, 15 min	 (92)	617, 618
	1. $TMSCF_3$ (1.1 eq), TEAF (1–5 mol %), THF, 0°, 15 min 2. TEAF (1.1 eq), THF, 15 min	 **I** + **II** **I** + **II** (92), **I**/**II** = 1:3	406
 57.9 kg	1. $TMSCF_3$ (1.2 eq), CsF (20 mol %), THF, 0–10°, 1 h 2. Remove volatiles 3. MeOH, 0–10°, 0.5 h	 (100)	616
	$TMSCF_3$ (1.24 eq), CsF (0.15 eq), THF, sonication, rt, 2 h	 (92)	615



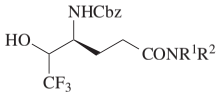
1. $TMSCF_3$ (1.24 eq), CsF (0.15 eq), THF, sonication, rt, 2 h
2. H_2O, sonication, 0.5 h



(72)

615

1. $TMSCF_3$, CsF, THF, sonication, rt, 3 h
2. MeOH, rt, 0.5 h
3. $NaBH_4$, rt, o/n



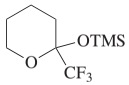
(48–61)

R^1	R^2
Me	Bn
$-(CH_2)_2OCH_2-$	
n-Pr	*n*-Pr

1025

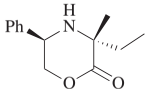


$TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0° to rt, 1 h

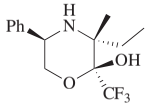


(75)

122



1. $TMSCF_3$ (2 eq), TBAT (1.1 eq), THF, 0°
2. NH_4Cl, H_2O, rt, 3 h



(63)

621

C_{6-13}



$PhSCF_3$ (1.4 eq), Et_3GeNa (1.1 eq), THF, HMPA, –60°, 1.5 h



R	
3-pyridyl	(93)
4-$MeOC_6H_4$	(94)
t-$BuCO_2(CH_2)_7$	(96)
$PhCO_2(CH_2)_7$	(94)
$Ph(CH_2)_2$	(95)
n-C_9H_{19}	(95)
n-$C_{10}H_{21}$	(98)
$CH_2=CH(CH_2)_8$	(96)
1-$C_{10}H_7$	(95)
n-$C_{11}H_{23}$	(96)
4-PhC_6H_4	(96)

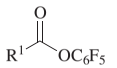
172

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

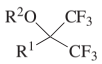
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{6-9}

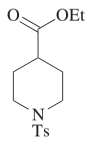


1. $TMSCF_3$ (2.1 eq), TMAF (*x* eq), DME, –50°; –30°, 1 h; rt, o/n
2. Hydrolysis

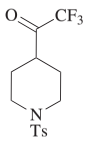


R^1	*x*	Hydrolysis	R^2		
2-pyridyl	1	—	TMS	(52)	592
3-pyridyl	1	—	TMS	(72)	
4-pyridyl	1	—	TMS	(60)	
Ph	1	—	TMS	(92)	
Ph	2	HCl, H_2O	H	(81)	
(*E*)-PhCH=CH	1	—	TMS	(81)	

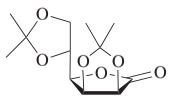
C_6



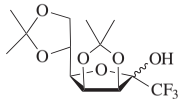
1. $TMSCF_3$ (1.2 eq), *n*-Bu_4NOAc (5 mol %), toluene, 0° to rt, 4 h
2. Hydrolysis



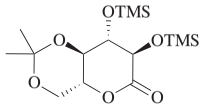
(—) 76% conv — 131



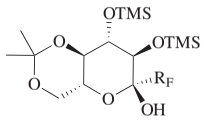
1. $TMSCF_3$ (2.1 eq), THF, rt, 10 min
2. TEAF (cat.), THF, rt, 15 min
3. TEAF (2 eq.), THF, rt, 15 min



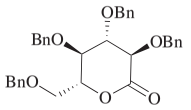
(98) — 618



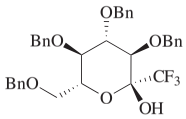
R_FI, EtMgBr, dark, –10°



R_F		
n-C_4F_9	(96)	1026
n-C_6F_{13}	(—)	
n-C_8F_{17}	(—)	

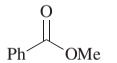


$TMSCF_3$ (1.2 eq), TBAF (0.1 eq), THF, 0°



(72) — 619

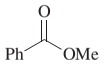
C_7



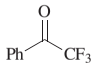
1. CF_3H, **57** (1.2 eq), THF, –40°, 24 h
2. TMSCl



(58) — 81

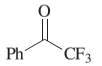


1. CF_3H (4 eq), base (1.5 eq), solvent, –10°, 4 h
2. HCl, H_2O



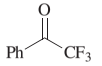
Base	Solvent		
KH	DMF, DMSO	(70)	71
KHMDS	DMF	(60)	71, 76, 75

1. CF_3H (1 eq, inverse addition), THF, –40°, 20 min
2. KHMDS (1 eq), –40°, 1 h; rt, 10 h



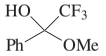
30% conv[a] 77

$PhSO_2CF_3$, *t*-BuOK, –50 to –20°



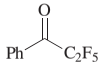
(30) 179

CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 170°, 6 h

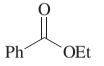


trace 600

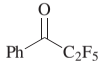
1. $TMSC_2F_5$ (1.1 eq), CsF (6 mol %), rt, 12 h
2. KF (2 eq), MeOH, rt, 4 h



(50) 1027

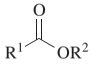


C_2F_5I, MeLi/LiBr, Et_2O, –110°

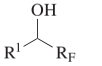


(74) 391

C_{7-11}



1. R_FI (5.4 eq), PhMgBr (*x* eq), Et_2O, –78°, 1 h
2. $Ti(Oi\text{-}Pr)_4$ (*x* eq), –78°; rt, time
3. HCl, H_2O, rt



627

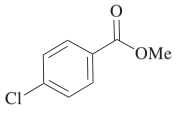
R^1	R^2	R_F	*x*	Time (h)	Conv (%)	
Ph	Me	*n*-C_3F_7	3.6	3	—	(76)
Ph	Me	*n*-C_4F_9	1.2	3	55	(—)
Ph	Me	*n*-C_4F_9	2.4	3	86	(—)
Ph	Me	*n*-C_4F_9	3.6	3	100	(—)
Ph	Me	*n*-C_6F_{13}	3.6	3	—	(87)
Ph	Ph	*n*-C_4F_9	3.6	3	88	(—)
4-$MeOC_6H_4$	Me	*n*-C_4F_9	3.6	3	—	(72)
n-C_7H_{15}	Me	*n*-C_4F_9	6	20	—	(51)
Bn	Me	*n*-C_4F_9	6	20	—	(41)
4-$CF_3C_6H_4$	Me	*n*-C_4F_9	3.6	3	—	(84)
(*E*)-PhCH=CH	Me	*n*-C_4F_9	3.6	3	—	(73)
1-$C_{10}H_7$	Me	*n*-C_4F_9	6	20	—	(94)
2-$C_{10}H_7$	Me	*n*-C_4F_9	3.6	3	—	(99)

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

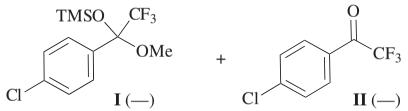
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

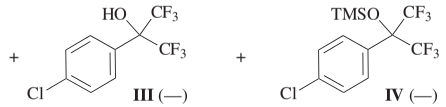
C_7



$TMSCF_3$ (1.2 eq), *n*-Bu_4NOAc (5 mol %), solvent, 0° to rt



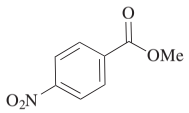
I (—) + **II** (—)



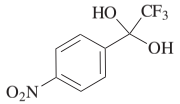
III (—) + **IV** (—)

131

Solvent	Time (h)	Conv **I** (%)	Conv **II** (%)	Conv **III** + **IV** (%)
CH_2Cl_2	3	—	4	—
Et_2O	1	50	34	11
DMF	3	—	20	4
THF	1	—	33	43
C_5H_{12}	1	65	5	26
toluene	1	93	—	1



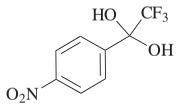
1. $TMSCF_3$ (1.2 eq), *n*-Bu_4NOAc (5 mol %), Et_2O, –78° to rt, 1 h
2. Hydrolysis



(—) 78% conv

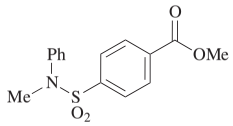
131

1. $TMSCF_3$, TBAF (cat.), CH_2Cl_2, –78° to rt
2. HCl, H_2O, Me_2CO

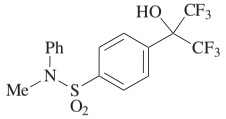


(92)

1028



TMSCF$_3$, TBAF, THF, rt, 24 h



(50)

1029

C$_{7-9}$



1. TMSCF$_3$ (x eq),
n-Bu$_4$NOAc (5 mol %),
toluene, 0° to rt, 1 h
2. Hydrolysis

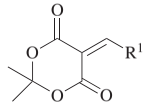


(—)

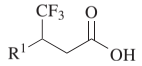
R^1	R^2	x	Conv (%)
4-ClC$_6$H$_4$	Me	1.2	90
4-ClC$_6$H$_4$	i-Pr	1.2	64
4-MeOC$_6$H$_4$	Me	1.5	83
(E)-PhCH=CH	Me	1.5	84
Ph(CH$_2$)$_2$	Et	1.5	82

131

C$_{7-14}$

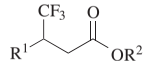


1. TMSCF$_3$ (1.5 eq), NaOAc (1.5 eq),
DMF, 50°, 2 h
2. HCl, H$_2$O, 120–120°, 1 h to give **I**
3a. R^{2}X, K$_2$CO$_3$ to give **II**
3b. NaBH$_4$, BF$_3$•Et$_2$O to give **III**



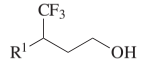
I

or



II

or

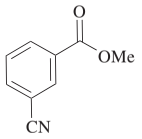
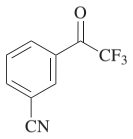
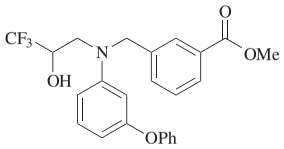
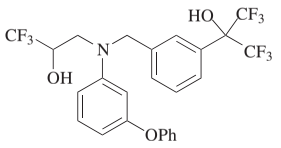
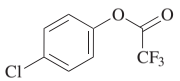
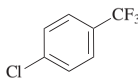
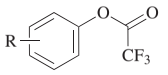
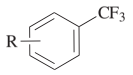
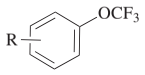


III

286

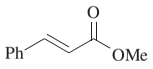
R^1	R^2	X	**I**	**II**	**III**
i-Pr	Bn	Br	—	(62)[e]	—
2-furyl	Me	I	—	(66)	—
2-thienyl	Me	I	—	(75)	—
Ph	Me	I	—	(76)	—
4-ClC$_6$H$_4$	Me	I	—	(88)	—
4-O$_2$NC$_6$H$_4$	Me	I	—	(83)	—
4-Me$_2$NC$_6$H$_4$	—	—	—	—	(88)
2-MeOC$_6$H$_4$	Me	I	—	(81)	—
4-MeOC$_6$H$_4$	—	—	(98)	—	—
4-MeOC$_6$H$_4$	Me	I	—	(88)	—
4-MeOC$_6$H$_4$	—	—	—	—	(90)
3,4,5-(MeO)$_3$C$_6$H$_2$	Me	I	—	(85)	—
(E)-PhCH=CH	Me	I	—	(74)	—
1-C$_{10}$H$_7$	Me	I	—	(75)	—

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

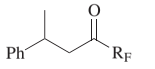
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_8 	1. $TMSCF_3$ (1.25 eq), CsF (5 mol %), CH_2Cl_2, rt, 2 d 2. HCl, H_2O, rt, 5 h	 (50)	1030
	1. $TMSCF_3$ (4 eq), TBAF (0.2 eq), toluene, THF, 40°, 18 h 2. $TMSCF_3$ (4 eq), TBAF (0.2 eq), 50°, 2 h	 (11)	1031
	C (graphite pellets), 650°	 (60) 12% conv	1032
C_{8-9}  **I**	Pt, vacuum	 **II** (—) +  **III** (—) + $PhCF_3$ **IV**	1033

R	Temp (°)	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)	**IV**
H	600	low	71	—	—
H	650	50	15.5	trace	—
H	700	100	11	trace	—
4-F	650	50	2	19.2	—
4-Cl	650	50	10	6.6	—
2-Me	650	—	25.3	10.3	"considerable amounts"
3-Me	650	—	19.5	6	"considerable amounts"
4-Me	650	—	12.9	22	"considerable amounts"

C_9

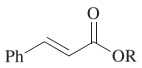


1. R_FI, MeLi/LiBr, Et_2O, –78°, 1 h
2. MeCu (1 eq)

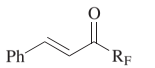


R_F	
n-C_4F_9	(37)
n-C_6F_{13}	(52)
n-C_8F_{17}	(75)

625, 624

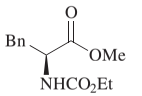


R_FI, MeLi/LiBr, Et_2O, –78°, 1 h

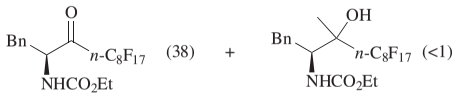


R	R_F	
Me	i-C_3F_7	(—)
Me	n-C_4F_9	(85)
Me	n-C_6F_{13}	(83)
Me	n-C_8F_{17}	(93)
Et	n-C_8F_{17}	(83)

625, 624

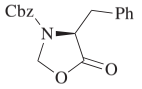


n-$C_8F_{17}I$, MeLi/LiBr, Et_2O, –78°



(38) + (<1)

1034, 1035



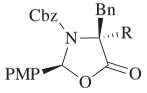
$TMSCF_3$ (4 eq), CsF (0.5 eq), $CF_3CH_2CF_2Me$, rt, 15 h



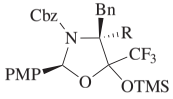
I + **II** (97), **I**/**II** = 49:51

387

$C_{9–10}$



$TMSCF_3$, CsF (cat.), THF



R	
H	(—)
Me	(0–35)

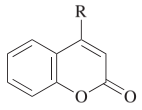
622

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

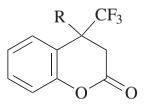
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

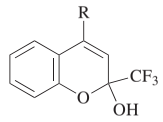
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_{9-10}



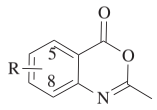
1. $TMSCF_3$ (2 eq), initiator (x eq), Lewis acid (1 eq), solvent
2. HCl, H_2O



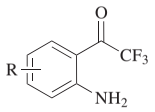
I +  **II** (—) 290

R	Initiator	x	Lewis Acid	Solvent	Temp	Conv **I** (%)	**I**	Conv **II** (%)
H	TMAF	1	—	DME	–30° to rt	8	(—)	53
H	*t*-BuOK	3	**26**	CH_2Cl_2	rt	35	(20)	—
CF_3	TMAF	1	—	DME	–30° to rt	1	(—)	44
CF_3	TMAF	3	**26**	CH_2Cl_2	rt	61	(—)	6

C_{9-11}

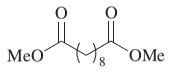


1. $TMSCF_3$ (2 eq), TBAF (10 mol %), DMSO, THF, rt, 15 h
2. HCl

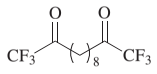


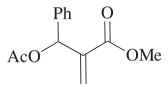
R		
6-Cl	(13)	623
6,8-Cl_2	(17)	
6,7-$(MeO)_2$	(23)	
8-Me	(53)	
6-Cl, 8-Me	(57)	
6-I, 8-Me	(43)	
4-NC, 8-Me	(32)	

C_{10}

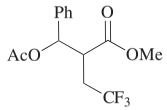
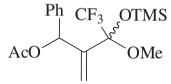


$PhSCF_3$ (2.8 eq), Et_3GeNa (2.2 eq), THF, HMPA, –60°, 1.5 h

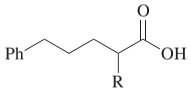
 (97) 172



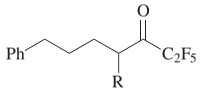
1. $TMSCF_3$ (1.5 eq), Bu_4NOAc (5 mol %), DMF, –20°, 18 h
2. HCl

 (15) +  (15) 295

C_{11}

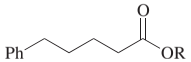


1. C_2F_5I (5 eq), MeLi/LiBr (5 eq), Et_2O, –78°
2. $KHSO_4$

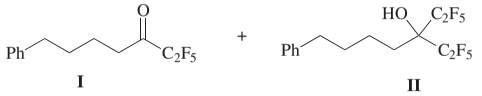


R	Time (h)	
H	1.5	trace
H	20	(45)
F	4	(49)

190



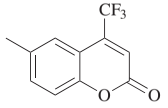
1. C_2F_5I (5 eq), MeLi/LiBr (5 eq), Et_2O, –78°
2. $KHSO_4$



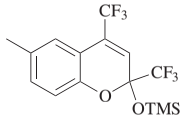
I **II**

R	Time (min)	**I**	**II**
Me	30	(44)	(46)
Me	240	(0)	(99)
C_6F_5	3	(0)	(84)
C_6F_5	90	(0)	(88)

190

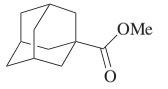


$TMSCF_3$, TMAF (cat.), THF

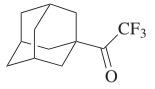


(40)

292



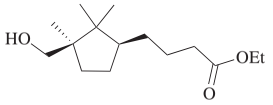
$PhSCF_3$ (1.4 eq), Et_3GeNa (1.1 eq), THF, HMPA, –60°, 1.5 h



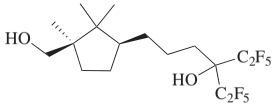
(96)

172

C_{13}



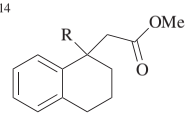
C_2F_5I, MeLi, Et_2O, –78°



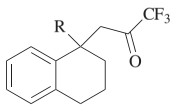
(—)

1036

$C_{13–14}$



CF_3H, TMS_2NK, DMF, –10°, o/n



R	
Me	(—)
Et	(85)

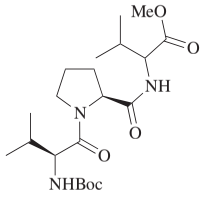
1037, 1038

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

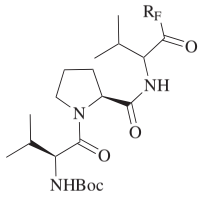
Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{15}



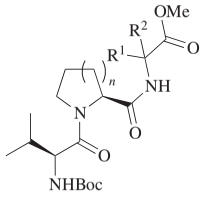
R_FI, MeLi/LiBr, Et_2O, –78°, 1 h



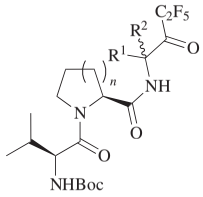
R_F		
n-C_3F_7	(13)	
n-C_4F_9	(9)	

1022

$C_{15–16}$



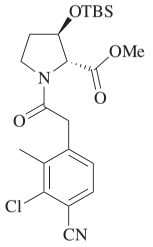
C_2F_5I, MeLi/LiBr, Et_2O, –78°C, 30 min; –50°, 5 min



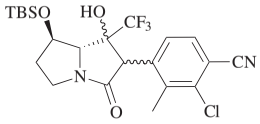
R^1	R^2	*n*	
Me_2C=		1	(57)
H	*i*-Pr	1	(42)
H	*i*-Pr	2	(11)

1022

C_{15}

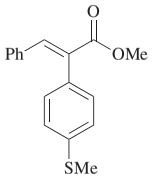


1. $TMSCF_3$ (2.9 eq), CsF (0.18 eq), THF, rt, o/n
2. HCl, H_2O, dioxane, MeOH, rt, 2 h
3. Imidazole (4.8 eq), TBSCl (2.9 eq), CH_2Cl_2, rt, 2 h

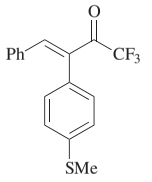


(10)

1039

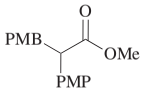


1. $TMSCF_3$ (1.25 eq), CsF (1 mol %), rt, 3 h
2. HCl, H_2O, rt, 3 h

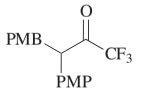


(68)

1040

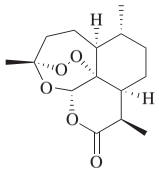


1. $TMSCF_3$ (1.2 eq), CsF (0.1 eq), THF, rt, 3 d
2. HCl, H_2O

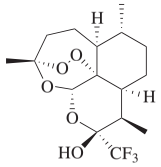


(48)

1041



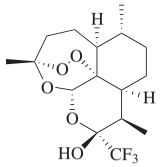
1. $TMSCF_3$ (2 eq), TBAF (0.1 eq), THF, 0°, 2 h
2. H_2O, rt, 0.5 h



(78)

442

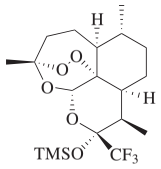
$TMSCF_3$ (1.1 eq), TBAF (1.1 eq), THF, rt, 25 h



(87)

620

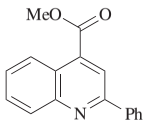
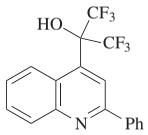
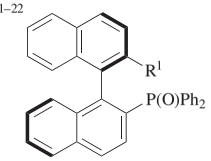
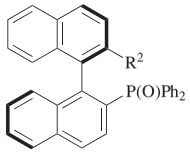
$TMSCF_3$ (2 eq), TBAF (5 mol %), THF, 0°, 2 h



(—)

442

TABLE 19. PERFLUOROALKYL ADDITION TO CARBOXYLIC ACIDS, ESTERS, AND LACTONES (*Continued*)

Acid, Ester, or Lactone	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{16} 	1. $TMSCF_3$ (2.15 eq), CsF (cat.), $MeOCH_2CH_2OMe$, 0°; rt, o/n 2. HCl, rt, 4 h	 (64)	1042
$C_{21–22}$ 	1. $TMSCF_3$ (*x* eq), CsF (0.3 eq), PhCN, 0°, to rt, 4 h 2. $TMSCF_3$ (*x* eq), rt, 8 h 3. $TMSCF_3$ (*x* eq), rt, 12 h 4. 4N HCl, THF, rt, 12 h		1043

R^1	*x*	R^2	
MeO_2C	2.45	CF_3CO	(79)
CF_3CO	3.7	$HO(CF_3)_2C$	(90)

[a] The conversion was determined by ^{19}F NMR spectroscopy.

[b] The product was obtained as a hydrate.

[c] The corresponding enol was formed.

[d] The yield was determined by gas chromatography.

[e] Benzyl 4-methylpent-3-enoate was also formed in 21% yield.

TABLE 20. PERFLUOROALKYL ADDITION TO NITRILES

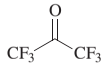
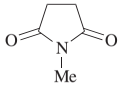
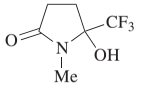
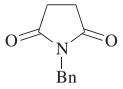
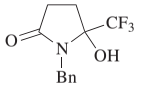
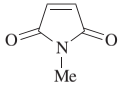
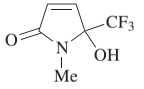
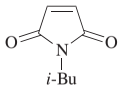
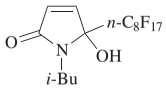
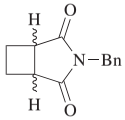
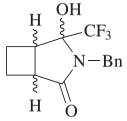
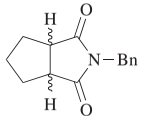
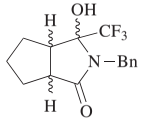
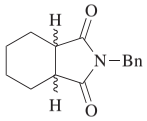
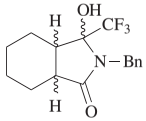
Nitrile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the chart preceding the tables for structures indicated by the **bold** numbers.*			
C_2			
MeCN	CF_3MgI, *n*-Bu_2O, –25 to 50°, 4 h	 (38)	199
CF_3CN	CF_3MgI, *n*-Bu_2O, –20°, 3 d; 30°, 2 d	 (33)	199
$C_{7–13}$			
RCN	$TMSCF_3$ (5 eq), TBAF•HF (2.1 eq), THF, 0°; rt, 2 h	 R: Ph (58); 4-FC_6H_4 (63); 4-ClC_6H_4 (54); 3-BrC_6H_4 (76); 4-BrC_6H_4 (75); 4-$Me_2NC_6H_4$ (78); 4-$MeOC_6H_4$ (52); 3-$(Et_2N)O_2SC_6H_4$ (82); 4-MeC_6H_4 (78); 4-PhC_6H_4 (79)	641

TABLE 21. PERFLUOROALKYL ADDITION TO IMIDES

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_4			
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt 2. HCl, H_2O	 (85)	289
	1. $TMSCF_3$ (2 eq), CsF (0.1 eq), THF, 0° to rt, 5 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O	 (88)	628
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt 2. HCl, H_2O	 (40)	289
	n-$C_8F_{17}I$, MeLi/LiBr, Et_2O, –78°, 0.5 h	 (42)	625
C_6			
	1. $TMSCF_3$ (4 eq), CsF (0.2 eq), THF, rt, 16 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O	 (79)	628
C_7			
	1. $TMSCF_3$ (2 eq), CsF (0.1 eq), THF, rt, 5 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O	 (94)	628
C_8			
	1. $TMSCF_3$ (2 eq), initiator (0.1 eq), THF, 0° to rt, 4 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O	 (86)	628

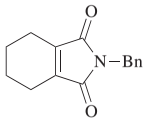
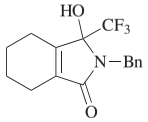
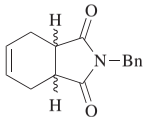
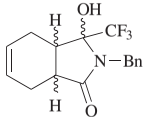
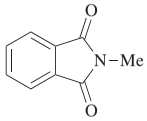
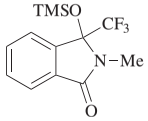
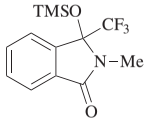
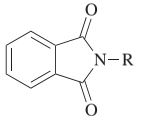
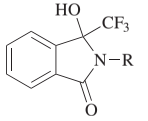
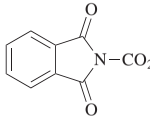
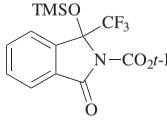
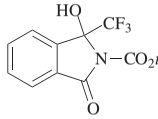
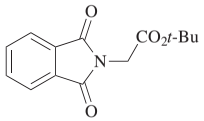
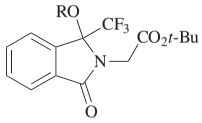
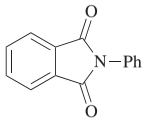
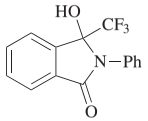
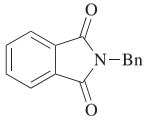
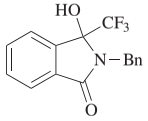
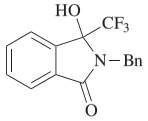
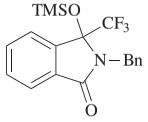
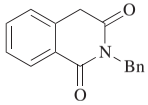
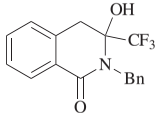
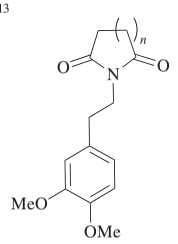
	1. $TMSCF_3$ (2 eq), initiator (0.1 eq), THF, 0° to rt, 5 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O		(91)	628
	1. $TMSCF_3$ (2 eq), CsF (0.1 eq), THF, 0° to rt, 4 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O		(99)	628
	1. **62a** (2 eq), *t*-BuOK (2 eq), THF, rt, 24 h 2. TMSCl		(76) 79% conv	110
	CF_3H (2.9 eq), $(TMS)_3N$ (1.5 eq), TMAF (0.24 eq), DMF, THF, –10°, 1 h; rt		(—) 7% conv	75
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt 2. HCl, H_2O		R: EtO_2C (87); $(EtO)_2CHCH_2$ (78); *n*-Bu (68)	289
	$TMSCF_3$ (2 eq), *t*-Bu_3P (0.1 eq), DMF, rt, 0.5 h	 **I** +  **II**	**I** + **II** (99), **I**/**II** = 35:65	140

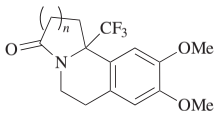
TABLE 21. PERFLUOROALKYL ADDITION TO IMIDES (*Continued*)

Imide	Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_8				
	$TMSCF_3$ (2 eq), KF (0.1 eq), *n*-Bu_4NBr (0.1 eq), toluene, 40°, 24 h		(77) R = H, TMS	457
	$TMSCF_3$ (1.5 eq), TBAF (1–2 mol %), THF, 0°; rt, 1 h		(93)	630
	1. $TMSCF_3$ (2 eq), TBAF (0.1 eq), THF, 0° to rt, 5 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O		(95)	628
	$TMSCF_3$ (2 eq), *t*-Bu_3P (0.1 eq), DMF, rt, 0.5 h		(88)	140
	$TMSCF_3$ (2 eq), KF (0.1 eq), *n*-Bu_4NBr (0.1 eq), toluene, rt, 24 h		(86)	457
C_9				
	1. $TMSCF_3$ (2 eq), CsF (0.2 eq), THF, rt, 4 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O		(trace)	628

$C_{12–13}$



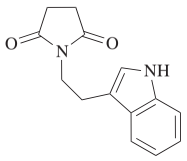
1. $TMSCF_3$ (1.5 eq). TBAF (1–2 mol %), THF, 0°; rt, 1 h; remove solvent
2. $MeSO_3H$ (5 eq), $ClCH_2CH_2Cl$, 55°, to completion
3. $NaHCO_3$



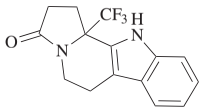
n	
1	(86)
2	(78)

630

C_{14}

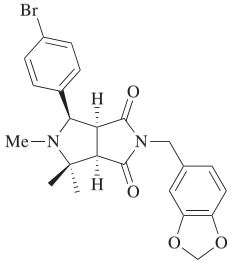


1. $TMSCF_3$ (1.5 eq). TBAF (1–2 mol %), THF, 0°; rt, 1 h; remove solvent
2. $MeSO_3H$ (5 eq), $ClCH_2CH_2Cl$, 55°, to completion
3. $NaHCO_3$

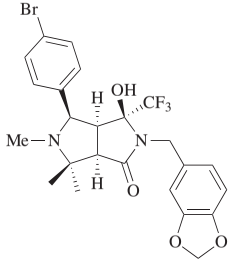


(75)

630



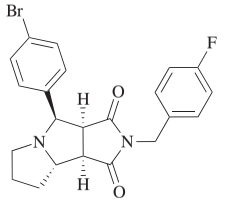
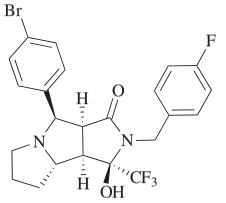
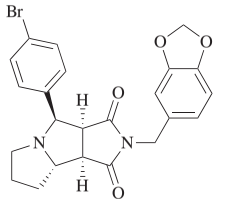
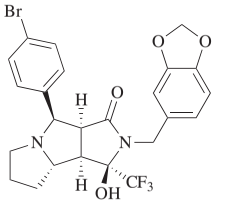
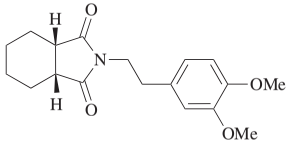
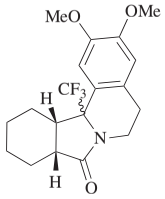
1. $TMSCF_3$ (4 eq), CsF (0.2 eq), THF, –40 to 10°, 4 h
2. HCl, H_2O



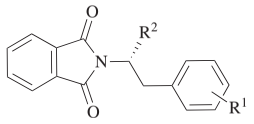
(59)

628

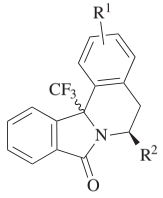
TABLE 21. PERFLUOROALKYL ADDITION TO IMIDES (*Continued*)

Imide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{15}  (±) endo, trans	1. $TMSCF_3$ (4 eq), CsF (0.1 eq), THF, 0–10°, 6 h 2. HCl, H_2O, 0°, 0.5 h	 (±) (64)	629
	1. $TMSCF_3$ (4 eq), CsF (0.2 eq), THF, –10 to 0°, 3 h 2. HCl, H_2O	 (57)	628
C_{16} 	1. $TMSCF_3$ (1.5 eq). TBAF (1–2 mol %), THF, 0°; rt, 1 h; remove solvent 2. $MeSO_2H$ (5 eq), $ClCH_2CH_2Cl$, 55°, to completion 3. $NaHCO_3$	 (83)	630

$C_{16–17}$

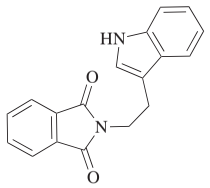


1. $TMSCF_3$ (1.5 eq). TBAF (1–2 mol %), THF, 0°; rt, 1 h; remove solvent
2. $MeSO_2H$ (5 eq), $ClCH_2CH_2Cl$, 55°, to completion
3. $NaHCO_3$

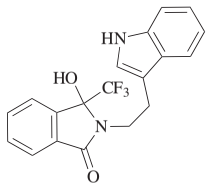


R^1	R^2		
H	H	(76)	
2-Cl	H	(68)	
4-Cl	H	(73)	630
2-Br	H	(64)	
2-I	H	(69)	
3,4-$(MeO)_2$	H	(84)	
3,4-OCH_2O–	H	(86)	
2-Me	H	(70)	
3-Me	H	(75)	
4-Me	H	(73)	
H	$HOCH_2$	(72)	

C_{18}

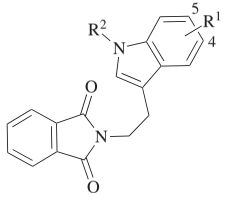


$TMSCF_3$ (1.5 eq), TBAF (1–2 mol %), THF, 0°; rt, 1 h

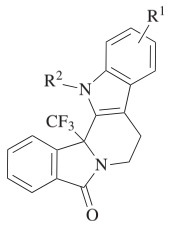


(81) 630

$C_{18–20}$



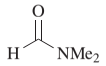
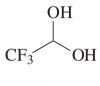
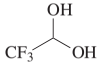
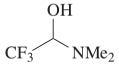
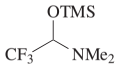
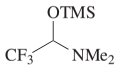
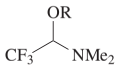
1. $TMSCF_3$ (1.5 eq). TBAF (1–2 mol %), THF, 0°; rt, 1 h; remove solvent
2. $MeSO_2H$ (5 eq), $ClCH_2CH_2Cl$, 55°, to completion
3. $NaHCO_3$



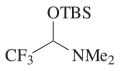
R^1	R^2		
H	H	(80)	
H	Me	(81)	
H	Ts	(0)[a]	630
5-Cl	H	(77)	
5,7-Cl_2	H	(82)	
5-Br	H	(89)	
6-CF_3	H	(73)	
4,6-Me_2	H	(71)	

[a] The detosylated compound was formed in 84% yield.

TABLE 22. PERFLUOROALKYL ADDITION TO AMIDES

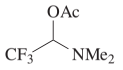
Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_1			
	1. CF_3H (2 eq), KH (2 eq), DMSO, rt, 0.75 h 2. DMF, –45°, 0.5 h 3. HCl, H_2O, –25°	 (—)	72
	1. CF_3H (4.09 eq), base (1 eq), solvent, –10°, 0.5–1.25 h 2. H_2SO_4, H_2O, –10° to rt	 (—) Base / Solvent (s) / Conv (%): $MeSOCH_2Na$ / DMF, DMSO / 85 $MeSOCH_2K$ / DMF, DMSO / 81 *t*-BuOK / DMF / 60 TMS_2NK / DMF / 100	71
	1. CF_3H (8.6 eq), *t*-BuOK (1 eq), DMF, –15°, 0.5 h 2. H_2SO_4	 (—) 60% conv	76, 75
	1. CF_3H (4.09 eq), *t*-BuOK (1 eq), DMF, –10°, 0.75–1.25 h 2. AcOH (1.01 eq), –10° to rt	 (58)	71
	1. CF_3H (6.1 eq), $(TMS)_2NK$ (1 eq), DMF, –10°, 0.5 h; –10° to rt, 0.5 h 2. TMSCl (1.46 eq)	 (—) 79% conv	76, 75
	1. CF_3H (5.7 eq), $(TMS)_3N$ (1.5 eq), TBAT (0.2 eq), DMF, THF, –10°, 1 h; rt 2. TMSCl (1 eq), rt	 (—) 27% conv	75
	1. CF_3H (4 eq), $(TMS)_2NK$ (*x* eq), DMF, –20°, 0.5 h 2. RX (1.1 eq), –10° to rt	 (—) *x* / R / X / Conv (%): 0.1 / TMS / $(TMS)_2N$ / 59 1 / TMS / Cl / 48.5 1 / TMS / $(TMS)_2N$ / 33.5 1 / TBS / Cl / 55	75

1. CF_3H (4.09 eq), $(TMS)_2NK$ (1 eq), DMF, –10°, 0.75–1.25 h
2. TBSCl (1.1 eq), –10° to rt
3. H_2O



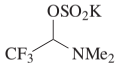
(60) 71

1. CF_3H (7.5 eq), KH (1 eq), DMF, DMSO, –10°, 0.5 h; –10° to rt, 0.5 h
2. HOAc (1.09 eq)



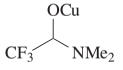
(—) 76% conv 76, 75

1. CF_3H (7.3 eq), KH (1 eq), DMF, DMSO, –10°, 0.5 h; –10° to rt, 0.5 h
2. SO_2 (2.12 eq)



(—) 77% conv 76, 75

1. CF_3H (1 eq), $MeSOCH_2K$ (2 eq), CuI (1 eq), DMF, –20°
2. Amine, –20°; rt, time



I (—) + CF_3Cu **II** (—) 48

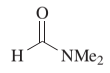
Amine	Time (h)	Conv **I** (%)	Conv **II** (%)
—	—	66	14
—	14	20	38
pyridine	—	65	20
pyridine	14	trace	trace
DMEU	—	88	4
DMEU	14	29	47
DMEU	19	27	47
$[MeO(CH_2)_2O(CH_2)_2]_3N$	—	91	—
$[MeO(CH_2)_2O(CH_2)_2]_3N$	14	27	31

TABLE 22. PERFLUOROALKYL ADDITION TO AMIDES (*Continued*)

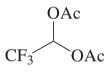
Amide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_1

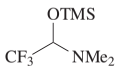


1. CF_3Br, e^-, anode, additive
2. Ac_2O, pyridine



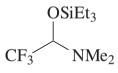
Anode	Additive		Refs.
Zn	—	(23.5)	234
Zn	TMSCl	(25)	
Mg	—	(27)	
Mg	TMSCl	(21)	
Mg	BF_3•OEt_2	(29)	
Mg	$AlCl_3$	(35)	
Al	—	(40)	
Al	TMSCl	(67)	
Al	$AlCl_3$	(74)	
Al	BF_3•OEt_2	(77.5)	

$TMSCF_3$ (2 eq), Et_4NCN (2 mol %), MeCN, DMF, –45° to rt, 2 h; rt, 10 h



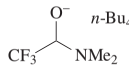
(20) 137

Et_3SiCF_3 (2 eq), TBAF (0.2 eq), DMF, THF, 0°, 0.5 h; rt



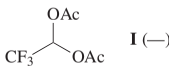
(—) 60% conv

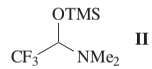
+



(—) 75

1. CF_3Br, Bu_4NBr (1 eq), additive (x eq), e^-, metal anode, Ni cathode, DMF, 0°
2. Ac_2O, HCl, H_2O, pyridine, 0.5 h

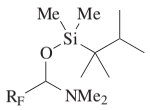


I (—) + 

II (—) 93

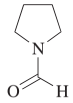
Metal	Additive	x	Conv **I** (%)	Conv **II** (%)
Mg	—	—	27	—
Mg	$AlCl_3$	8	35	—
Mg	TMSCl	8	21	—
Mg	$BF_3{\bullet}OEt_2$	8	29	—
Al	—	—	40	—
Al	$AlCl_3$	8	74	—
Al	TMSCl	4	65	—
Al	TMSCl	8	67	—
Al	TMSCl	24	31	15
Al	$BF_3{\bullet}OEt_2$	8	77.5	—
Zn	—	—	23.5	—[a]
Zn	TMSCl	8	25	—[a]

R_FI, Zn, **20**, 0° to rt, 2 h

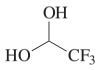


R_F	
CF_3	(74)
C_2F_5	(62)
n-C_7F_{15}	(80)

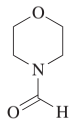
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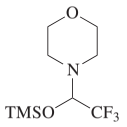
1. CF_3H (8.6 eq), t-BuOK (1 eq), –15°, 0.5 h
2. H_2SO_4



(—) 56% conv 76, 75

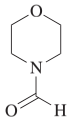
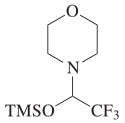
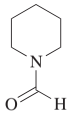
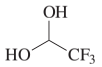
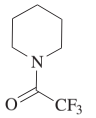
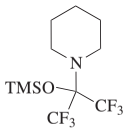
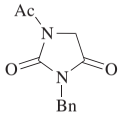
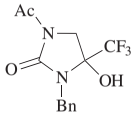
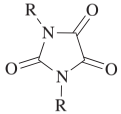
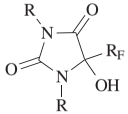


CF_3H, $(TMS)_3N$, TBAF, THF



(78) 74

TABLE 22. PERFLUOROALKYL ADDITION TO AMIDES (*Continued*)

Amide	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_1 	1. CF_3H (5.7 eq), $(TMS)_3N$ (1.5 eq), TBAT (0.2 eq), THF, –10°, 1 h; rt 2. TMSCl (1 eq), rt, 1 h	 (60)	75
	1. CF_3H (8.6 eq), *t*-BuOK (1 eq), –15°, 0.5 h 2. H_2SO_4	 (—) 52% conv	76, 75
C_2 	CF_3Br, e^-, Al anode	 (12)[b], Faradaic yield (63)	234
	1. $TMSCF_3$ (1.2 eq), TBAF (cat.), THF, 0°, 1 h; rt 2. HCl, H_2O	 (88)	289
C_3 	1. $TMSCF_3$ (2 eq), TMAF (0.2 eq), THF, rt, 12 h 2. TBAF (2 eq), THF, rt, 0.5 h 3. HCl, H_2O	 (28)	628
	1. $TMSR_F$ (2 eq), TBAF (0.1 eq), THF, rt 2. HCl, H_2O, rt		636

R	R_F	
Me	CF_3	(50)
Me	C_2F_5	(48)
c-C_6H_{11}	CF_3	(58)
c-C_6H_{11}	C_2F_5	(31)
Ph	CF_3	(35)
Ph	C_2F_5	(25)

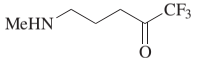
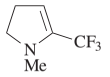
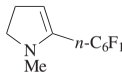
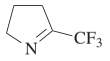
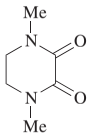
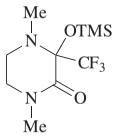
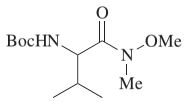
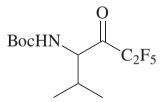
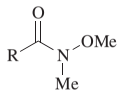
C_4		CF_3Br, e^-, Al anode		(70)	234
		CF_3Br (0.1 eq), Al (8 mol %), autoclave, 80°, 3 h		(44)[c]	123
		n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, Et_2O, –78°		(55)	197
		1. Substrate (1 eq) + EtO_2CCF_3 (1 eq) added to NaH (1.33 eq), THF at reflux; reflux, 1 h 2. AcOH, rt 3. 6 N HCl, reflux, 60 h 4. Distill hemiaminal at 760 Torr		(79)	1044
		$TMSCF_3$, TBAF (cat.), THF		(—)	289
C_5		C_2F_5I, MeLi/LiBr, Et_2O, toluene, –70°		(62–70)	1022

TABLE 22. PERFLUOROALKYL ADDITION TO AMIDES (*Continued*)

Amide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{5-11}

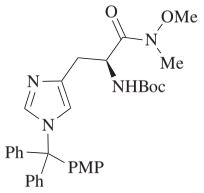


1. $TMSCF_3$ (2 eq), CsF (0.2 eq), toluene, rt, 24 h
2. TBAF (1 eq), THF, H_2O, 50°, 2 h

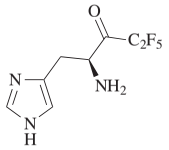


R		Refs.
4-Br-2-furyl	(66)	637
4-Br-2-thienyl	(63)	
4-pyridyl	(90)[d]	
2-furyl$(CH_2)_2$	(51)	
3-BrC_6H_4	(72)	
2-$O_2NC_6H_4$	(0)	
3-$O_2NC_6H_4$	(78)	
2-MeOC_6H_4	(25)[e]	
4-MeOC_6H_4	(88)	
3,5-$(MeO)_2C_6H_3$	(99)	
n-C_7H_{15}	(59)	
n-BuCHEt	(0)	
c-$C_6H_{11}CH_2$	(61)	
Bn	(—)[f]	
2-MeC_6H_4	(0)	
BnCH_2	(76)	
4-F$C_6H_4(CH_2)_2$	(61)	
2-MeO$C_6H_4(CH_2)_2$	(75)	
3-MeO$C_6H_4(CH_2)_2$	(81)	
4-MeO$C_6H_4(CH_2)_2$	(73)	
$Me_2C{=}CH(CH_2)_2CHMeCH_2$	(48)	
PhCMe_2	(0)	
2-Me$C_6H_4(CH_2)_2$	(66)	
4-Me$C_6H_4(CH_2)_2$	(78)	
4-*t*-BuC_6H_4	(81)	
1-$C_{10}H_7$	(84)	

C_6



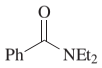
1. C_2F_5Li (3 eq), THF, –78° to rt, 4 h
2. TFA, H_2O, rt, 1 h
3. HCl, H_2O



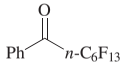
(—)

1045

C_7



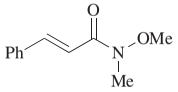
n-$C_6F_{13}I$, MeLi/LiBr, BF_3•OEt_2, Et_2O, –78°



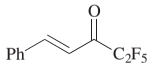
(66)

197

C_9



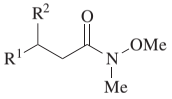
1. C_2F_5I (5 eq), MeLi/LiBr (5 eq), Et_2O, –78°, 1 h
2. $KHSO_4$



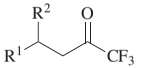
(74)

190

$C_{9–13}$



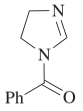
1. $TMSCF_3$ (2 eq), CsF (0.2 eq), toluene, 0°, 20 min
2. TBAF (1 eq), hexanes, H_2O, 50°, 2 h



R^1	R^2	
Ph	H	(76)
Ph	Me	(69)
2-FC_6H_4	H	(69)
3-FC_6H_4	H	(61)
2-i-$PrOC_6H_4$	H	(50)
3-MeC_6H_4	H	(61)
1-$C_{10}H_7$	H	(45)

882

C_{10}



1. $TMSCF_3$ (2.1 eq), TMAF (x eq), DME, –50°; –30°, 1 h; rt, o/n
2. Hydrolysis



x	Hydrolysis	R	
1	—	TMS	(94)
2	HCl, H_2O	H	(87)

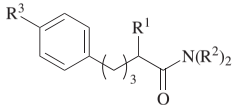
592

TABLE 22. PERFLUOROALKYL ADDITION TO AMIDES (*Continued*)

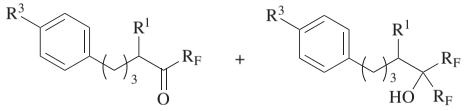
Amide	Conditions	Product(s) and Yield(s) (%)	Refs.

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

C_{11}



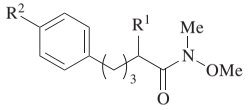
1. R_FI (5 eq), MeLi/LiBr (5 eq), Et_2O, –78°
2. $KHSO_4$



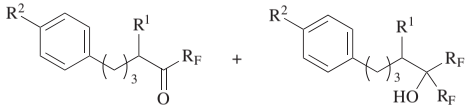
I **II**

190

R^1	$N(R^2)_2$	R^3	R_F	Time (h)	**I**	**II**
H	NH_2	H	C_2F_5	1.5	(0)	(0)
H	4-morpholinyl	H	C_2F_5	1	(88)	(0)
H	4-morpholinyl	H	C_2F_5	2	(84)	(14)
H	4-morpholinyl	H	n-C_3F_7	1.5	(54)	(0)
H	4-morpholinyl	n-$C_6H_{13}O$	C_2F_5	2.5	(34)	(0)
F	4-morpholinyl	H	C_2F_5	0.5	(68)	(0)



1. R_FI (5 eq), MeLi/LiBr (5 eq), Et_2O, –78°
2. $KHSO_4$

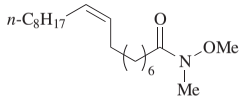


I **II**

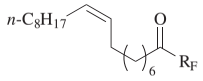
190

R^1	R^2	R_F	Time (h)	**I**	**II**
H	H	C_2F_5	1	(99)	(0)
H	H	C_2F_5	1.5	(98)	(0)
H	H	n-C_3F_7	1.5	(99)	(0)
H	n-$C_6H_{13}O$	C_2F_5	2	(44)	(0)
F	H	C_2F_5	1	(91)	(0)
F	H	n-C_3F_7	1.5	(71)	(0)

C_{18}

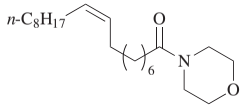


1. R_FI (5 eq), MeLi/LiBr (5 eq), Et_2O, –78°
2. $KHSO_4$

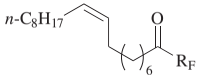


R_F	Time (h)	
C_2F_5	1	(86)
n-C_3F_7	1.5	(84)

190



1. R_FI (5 eq), MeLi/LiBr (5 eq), Et_2O, –78°
2. $KHSO_4$



R_F	Time (h)		
C_2F_5	1	(99)	190
n-C_3F_7	1.5	(68)	

[a] Other products such as CF_3ZnBr and $(CF_3)_2Zn$ were formed.

[b] The ketone is in equilibrium with the hydrate.

[c] The yield was based on CF_3Br.

[d] The product was isolated as the hydrate.

[e] The conversion was determined by ^1H NMR spectroscopy.

[f] Decomposition occurred.

TABLE 23. PERFLUOROALKYL ADDITION TO OTHER CARBOXYLIC ACID DERIVATIVES

Acid Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_1			
CO_2	CF_3H, **57** (1 eq), THF, –40°, 24 h	$CF_3CO_2^-$[**57**]$^+$ (78)	81
	$TMSCF_3$ (1 eq), CsF (0.67 eq), DME, –196°; rt, 24 h	$CF_3CO_2^-Cs^+$ (95)	644
CO_2 excess	*i*-Pr_3SiCF_3 (0.45 eq), 18-crown-6 (1 eq), *t*-BuOK (1 eq), THF, –78°, 1 h; to rt	CF_3CO_2K (76)[a]	80
CO_2	$TMSC_2F_5$ (1 eq), CsF (0.67 eq), DME, –196°; rt, 24 h	$C_2F_5CO_2^-Cs^+$ (95)	644
	$TMSCF_3$ (1.05 eq), TMAF (1 eq), DME, –196°; –40°, 1 h; rt, 1 h	$CF_3CO_2^-NMe_4^+$ (97)	645
	C_2F_5Br, Zn, DMF, ultrasound	$C_2F_5CO_2H$ (35.2)	1046
	1. *i*-C_3F_7Ag, MeCN, 3 h 2. BnCl (1.2 eq), 4 h.	*i*-$C_3F_7CO_2Bn$ (60)	647
	n-C_3F_7MgI, Et_2O, –80°	*n*-$C_3F_7CO_2H$ (45)	200
	n-C_3F_7MgI, solvent, –80°	*n*-$C_3F_7CO_2H$ Solvent / Time (h) Et_2O 24 (41) THF 48 (51)	201
	n-C_3F_7MgI, *n*-Bu_2O	*n*-$C_3F_7CO_2H$ **I** Temp (°) / **I**[b] / **I**[c] –40 (57) (50) –20 (65) (59) 0 (56) (46) 20 (43) (23)	202
	R_FI, *n*-BuLi, Et_2O, –90°, 0.5 h; –90° to rt	R_FCO_2H R_F *n*-C_3F_7 (8) *i*-C_3F_7 (3) *n*-C_7F_{15} (38)	189

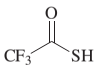
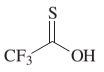
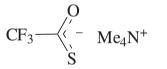
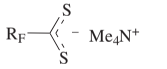
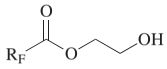
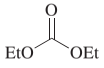
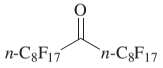
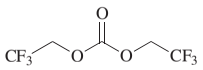
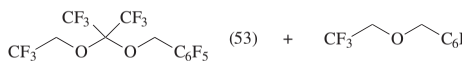
	R_FI, *n*-BuLi (1.5 eq), Et_2O, –100 to –90°; 0°	R_FCO_2H	R_F: *n*-C_3F_7 (54); *i*-C_3F_7 (3); *n*-C_7F_{15} (38)	189
	R_FI, Zn, DMF, ultrasound, 1 h	R_FCO_2H	R_F: *i*-C_3F_7 (48); *n*-C_4F_9 (61); *n*-C_6F_{13} (77); *n*-C_8F_{17} (72)	648
	R_FX, $MnCl_2$/Na, DMF, ultrasound	R_FCO_2H	R_F X: *i*-C_3F_7 I (41); *n*-C_4F_9 I (52); *n*-C_4F_9 Br (39); *n*-C_6F_{13} I (62); *n*-C_8F_{17} I (61); *n*-C_8F_{17} Br (46)	316
	R_FI, Zn/Cu (1.5:1), DMSO, 25–30°, 1.5–3 h	R_FCO_2H	R_F: *n*-C_4F_9 (40–42); *n*-C_6F_{13} (45–63); *n*-C_8F_{17} (47)	646
$^{14}CO_2$	*n*-$C_7F_{15}Li$, Et_2O, –196 to –75°, 20 min; –75° to rt	*n*-$C_7F_{15}{}^{14}CO_2H$	(48) 4.93 mCi/mmol	1047
	1. *n*-$C_8F_{17}MgBr$, Et_2O, THF, –70° to rt, 20 h 2. EtOH, H_2SO_4 (cat.), reflux, 4 h	*n*-$C_8F_{17}CO_2Et$	(70)	130
COS	1. $TMSCF_3$ (1 eq), CsF (0.67 eq), $MeO(CH_2)_2OH$, –196°; rt, 24 h 2. HCl	 (—) +  (—)		644

TABLE 23. PERFLUOROALKYL ADDITION TO OTHER CARBOXYLIC ACID DERIVATIVES (*Continued*)

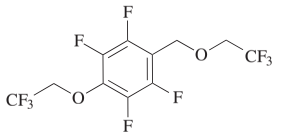
Acid Derivative	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_1			
COS	$TMSCF_3$ (1.05 eq), TMAF (1 eq), DME, –196°; –40°, 1 h; rt, 1 h	 (95)	645
CS_2	$TMSR_F$ (1.05 eq), TMAF (1 eq), DME, –60°; –40°, 1 h; rt, 1 h	 R_F: CF_3 (98); C_2F_5 (95)	645
	1. $TMSC_2F_5$ (1 eq), TMAF (1 eq), DME, –60°; –40°, 1 h 2. RBr (1.05 eq), –40° to rt	$C_2F_5CS_2R$: R = CH_2=$CHCH_2$ (84); n-C_4H_9 (72)	649
	R_FI, Zn/Cu, $ClCO_2Et$ (cat.), 80–90°	 R_F: C_4F_9 (80); C_6F_{13} (70); C_8F_{17} (60)	1017
	R_FI, Zn/Cu, $ClCO_2Et$ (cat.), >50°	R_FCO_2H: C_4F_9 (85); C_6F_{13} (70); C_8F_{17} (60)	1017
	n-$C_8F_{17}M$ (x eq), Et_2O	n-$C_8F_{17}CO_2Et$ **I** +  **II**	650
		M: MgBr, x 1.05, Temp (°) –78, Time (h) 0.25, **I** (2), **II** (—) MgBr, 1.05, –78, 4.5, (63), (—) MgBr, 1.05, –60, 20, (94), (2) Li, 2.3, –78, 0.5, (16), (55)	
	R_FI, Zn/Cu, $ClCO_2Et$ (cat.), 80°	R_FCO_2Et: C_4F_9 (70); C_6F_{13} (60); C_8F_{17} (50)	1017



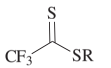
1. $TMSCF_3$ (1 eq), CsF (1 eq), MeCN, 60°, 12 h
2. $C_6F_5CH_2Br$ (1 eq), 90°, 48 h



(53) + (14) 466

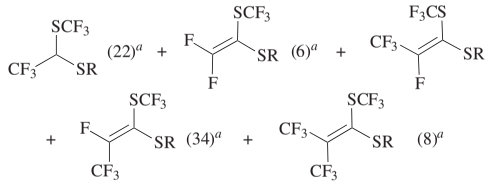
+  (15)

C_2



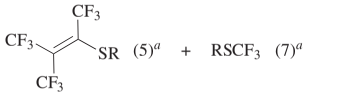
R = $BnCH_2$

$TMSCF_3$ (1.5 eq), CsF (0.1 eq), DME, rt, 3 h

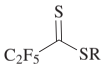


(22)[a] + (6)[a] + (10)[a] 1048

+ (34)[a] + (8)[a]

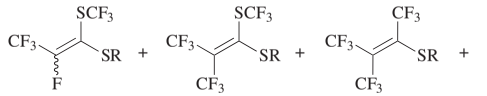
+  (5)[a] + $RSCF_3$ (7)[a]

C_3



R = $BnCH_2$

$TMSCF_3$ (*x* eq), initiator (*y* eq), DME, rt



+ + + $RSCF_3$ 1048

I **II** **III** **IV**

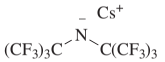
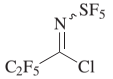
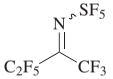
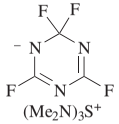
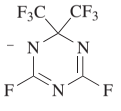
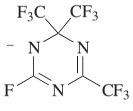
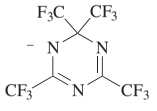
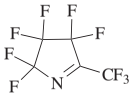
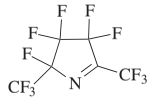
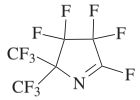
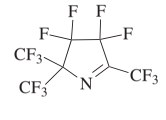
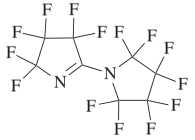
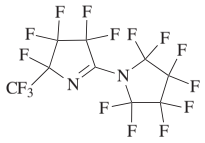
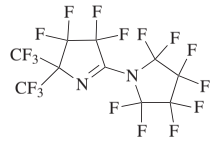
x	Initiator	*y*	Time (min)	**I**[a]	**I** (*E*)/(*Z*)	**II**[a]	**III**[a]	**IV**[a]
1.1	CsF	0.1	60	(36)	—	(17)	(10)	(4)
1.1	K_2CO_3	0.1	240	(60)	—	(13)	(9)	(5)
1.5	CsF	0.1	240	(59)	65:35	(15)	(12)	(7)
1.5	K_2CO_3	0.1	240	(59)	—	(15)	(12)	(7)
4	CsF	0.1	5	(—)	—	(—)	(—)	(60)
4	K_2CO_3	6	30	(50)	—	(10)	(15)	(10)

[a] The yield was determined by ^{19}F NMR spectroscopy.

[b] CO_2 was added during the formation of *n*-C_3F_7MgI.

[c] CO_2 was added after the formation of *n*-C_3F_7MgI.

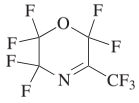
TABLE 24. PERFLUOROALKYL ADDITION TO IMIDOYL HALIDES

Imidoyl Halide	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_2 	$TMSCF_3$ (excess), CsF, THF	 (95)	545
C_3 	$TMSCF_3$, CsF, MeCN	 (55)	639
	$TMSCF_3$ (4.8 eq), MeCN, –196°; –40°, 0.75 h	 (—) +  (—) +  (—)	640
C_4 	$TMSCF_3$ (*x* eq), KF (0.2 eq), solvent, 0°, 1 h; rt, 20 h	 **I** (—) +  **II** (—) +  **III** (—) +  **IV** (—) +  **V** (—) +  **VI** (—) +  **VII** (—)	803

x	Solvent	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)	Conv **IV** (%)	Conv **V** (%)	Conv **VI** (%)	Conv **VII** (%)
1	tetraglyme	8	9	—	20	9	9	4
1.01	PhCN	6	2	11	16	3	6	—
3.02	PhCN	6	3	7	18	5	3	—
3.02	tetraglyme	3	4	—	15	5	7	2

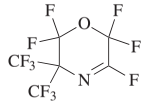


TMSCF$_3$ (*x* eq), KF (0.2 eq),
solvent, 0°, 1 h; rt, 20 h



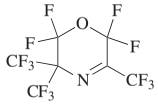
I (—)

+



II (—)

+

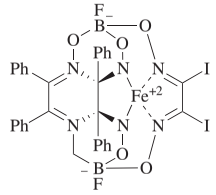


III (—)

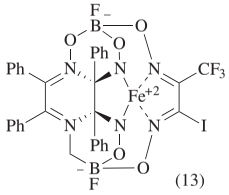
803

x	Solvent	Conv **I** (%)	Conv **II** (%)	Conv **III** (%)
1.01	tetraglyme	25	12	11
1.02	PhCN	24	12	5
3.01	tetraglyme	10	14	17
3.03	PhCN	—	26	20

C_{31}

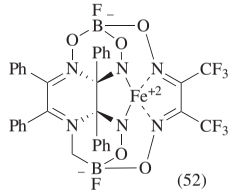


1. [Cu(MeCN)$_4$]BF$_4$ (5.3 eq), KF (22 eq),
MeSCH$_2$CH$_2$SMe (5.3 eq),
benzene, THF, rt, 0.25 h
2. TMSCF$_3$ (5.3 eq), rt; 40°, 0.25 h
3. Substrate (1 eq), rt; 40°, 4 h



(13)

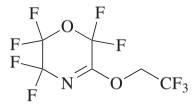
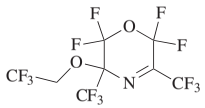
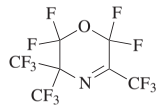
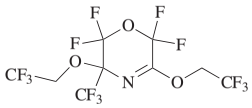
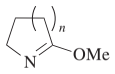
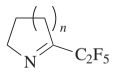
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(52)

1049

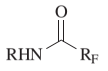
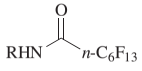
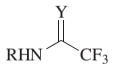
TABLE 25. PERFLUOROALKYL ADDITION TO IMINO ESTERS

Imino Ester	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_4 	$TMSCF_3$ (1.05 eq), KF (0.2 eq), 0°, 1 h; rt, 20 h	 +  (—) 9% conv (—) 5% conv +  (—) 3% conv	803
$C_{4–6}$ 	C_2F_5H (1.5 eq), BuLi (1.2 eq), $BF_3•OEt_2$ (1.2 eq), THF, –78°, 6 h	 **I**	196

n	**I**[a]	**I**
1	(65)	(34)
2	(83)	(62)
3	(52)	(—)

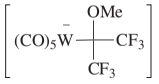
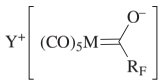
[a] The yield was determined by ^{19}F NMR spectroscopy.

TABLE 26. PERFLUOROALKYL ADDITION TO CYANATES, THIOCYANATES, AND THEIR ISOFORMS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_1			
RN=C=O	R_FX, Zn, DMF, 3–24 h	 R: Me, R_F: C_4F_9, X: I (40); Ph, CF_3, Br (17); Ph, C_2F_5, I (33); Ph, C_4F_9, I (53)	642
	MeLi (1.1 eq), *n*-$C_6F_{13}I$, Et_2O, 0°, microreactor	 R: *n*-Bu (86)[a]; Ph (79)[a]	198
R–N=C=Y	1. $TMSCF_3$ (1.05 eq), TBAF or CsF (1 eq), DME or THF, –60°; –40°, 1 h; rt, 1 h 2. HCl, H_2O	 R: Me, Y: S (95); Et, S (92); *c*-C_6H_{11}, O (91); Ph, S (90); 4-FC_6H_4, O (89); 4-FC_6H_4, S (90); 4-$O_2NC_6H_4$, S (88); 1-adamantyl, O (94)	643
ROCN	R_FMgBr, –15° to rt, 2 h	R_FCN **I** + R_FCO_2Et **II**: R: Et, R_F: C_4F_9, Solvent: Et_2O, **I**: (—), **II**: (49); Ph, C_4F_9, Et_2O, (60), (—); Ph, C_4F_9, Bu_2O, (25), (—); Ph, C_6F_{13}, Et_2O, (50), (—); Ph, C_6F_5, Et_2O, (45), (—); Ph, C_8F_{17}, Et_2O, (65), (—)	394

[a] The yield was determined by gas chromatography.

TABLE 27. PERFLUOROALKYL ADDITION TO OTHER CARBON ELECTROPHILES

Carbon Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			
	1. Substrate (1 eq), Me_4NF (1.25 eq) DME, –30° 2. $TMSCF_3$ (1.38 eq, dropwise), –30°, 0.5 h; –30°, 1 h; rt, 2 h	 (77)	651
C_6			
$M(CO)_6$	1. Substrate (1 eq), YF (2.4 eq), DME, –30° 2. $TMSR_F$ (1.43 eq) dropwise, –30°, 0.5 h; rt, 1 h		651

M	Y	R_F	
Cr	Me_4N	CF_3	(—)
Cr	Cs•(15-c-5)$_2$	CF_3	(—)
W	Me_4N	CF_3	(96)
W	Cs•(15-c-5)$_2$	CF_3	(—)
W	Me_4N	C_2F_3	(—)
W	Cs•(15-c-5)$_2$	C_2F_3	(—)
W	Me_4N	C_2F_5	(—)

TABLE 28. PERFLUOROALKYL ADDITION TO BORON ELECTROPHILES

Boron Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
BF_3	1. Me_3SnCF_3 (3 eq), CCl_4, 60°, 12 h 2. KF (3 eq), H_2O	$K^+[(CF_3)BF_3]^-$ (—) + $K^+[(CF_3)_2BF_2]^-$ (60)	158
	Me_3SnCF_3 (0.82 eq), CCl_4, –196 to 20°; 20°, 1 h	$Me_3Sn^+[(CF_3)BF_3]^-$ (—)	1050
	Bu_3SnCF_3 (0.97 eq), CCl_4, –196° to rt, 10 min	$Bu_3Sn^+[(CF_3)BF_3]^-$ (95)	652
BCl_3	1. Me_3SnCF_3 (2.54 eq), 2-methylpentane, –70° 2. Me_3N (6 eq), –40°; rt 3. KF, 2 d	$CF_3BF_2{\bullet}NMe_3$ (20) + $CF_2ClBF_2{\bullet}NMe_3$ (30)	1051
BBr_3	1. Me_3SnCF_3 (2.54 eq), 2-methylpentane, –90° 2. Me_3N (6 eq), –40°; rt 3. KF, 2 d	$CF_3BF_2{\bullet}NMe_3$ (20) + $CF_2BrBF_2{\bullet}NMe_3$ (50)	1051
$B(OMe)_3$	1. $TMSCF_3$, KF (3 eq), THF, 0° to rt, 2 h 2. KHF_2 (4 eq), 18 h	$K^+[CF_3BF_2(OMe)]^-$ (—)	658
	1. $TMSCF_3$ (1.1 eq), KF (1 eq), THF, rt, 18 h 2. HF (6 eq), H_2O, rt, 12–16 h 3. KOH, H_2O	$K^+(CF_3BF_3)^-$ (85)	658
	n-C_3F_7TMS (1.2 eq), KF (1 eq), DME, 0.5 h	$K^+[n\text{-}C_3F_7B(OMe)_3]^-$ (—) 22% conv	657
	C_2F_5H (1.2 eq), *n*-BuLi (1 eq), Et_2O, hexane, –70°, 1 h; rt	$Li^+[C_2F_5B(OMe)_3]^-$ (95)	656

TABLE 28. PERFLUOROALKYL ADDITION TO BORON ELECTROPHILES (*Continued*)

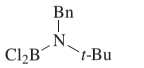
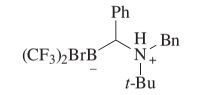
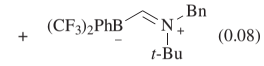
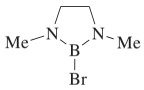
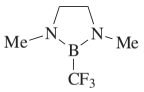
Boron Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
$B(OMe)_3$	1. R_FMgBr, Et_2O, –55°, 0.25 h 2. KHF_2, H_2O 3. HF, H_2O, o/n	$K^+[R_FBF_3]^-$ R_F (%) *n*-C_3F_7 (64) C_6F_{13} (55)	659
	1. R_FMgBr, Et_2O, –78° 2. HF, H_2O, KF	$K^+(R_FBF_3)^-$ R_F (%) C_2F_5 (73) *n*-C_3F_7 (70) *n*-C_4F_9 (70)	660
	1. C_2F_5Br (0.92 eq), PhMgBr (0.88 eq), Et_2O, <–65°, 1 h 2. Substrate (1 eq), –65 to –40°; –78°, 2 h 3. HF, cold; rt, o/n 4. KOH, H_2O, <15°	$K^+(C_2F_5BF_3)^-$ (33)	1079
$B(OR)_3$	R_FTMS (1.05 eq), YF (1 eq), THF or DME	$Y^+[R_FB(OR)_3]^-$	656

R	R_F	Y	Temp 1	Time 1 (h)	Temp 2 (°)	Time 2 (h)	
Me	CF_3	K	rt	24–36	—	—	(98)
Me	CF_3	Me_4N	0°	0.5	rt	3	(98)
Me	C_2F_5	K	rt	4	50	4	(98)
Et	CF_3	K	rt	24–36	—	—	(95)
Et	C_2F_5	K	rt	4	50	4	(96)

1. CF_3H (1 eq, inverse addition), THF, 0–5°, 5 min 2. KHMDS (1 eq), 0°, 1–2 h; rt, 16 h 3. HF (48%), 0°; rt, 12–14 h 4. KOH to pH>7	CF_3BF_3K	R (%) Me (53) *n*-Bu (66)	77

	$TMSCF_3$ (1.1 eq), KF (0.9 eq), THF, rt, 24–48 h	$CF_3B(OR)_3K$	R: Me (99); $MeO(CH_2)_2$ (67);  (43); Bn (38)	103
Cl_2BNMe_2	CF_3Br, $(Et_2N)_3P$ (1.1 eq), sulfolane, 4°; 85°	$(CF_3)ClB{\bullet}NMe_2$ (14) + $(CF_3)_2B{\bullet}NMe_2$ (19)		1052
$Cl_2BNR^1R^2$	1. CF_3Br, $(Et_2N)_3P$ (3.2–3.4 eq), CH_2Cl_2, 0°; rt, 1 h 2. HCl, H_2O	$(CF_3)_3B{\bullet}NHR^1R^2$ **I** + $(CF_3)_3B{\bullet}NH_2R^1$ **II**	R^1 / R^2 / **I** / **II**: Me / Me (35) (—); Et / Et (77) (1); $-(CH_2)_5-$ (15) (—); Me / *t*-Bu (5) (7); Me / Bn (1) (—); *c*-C_6H_{11} / *c*-C_6H_{11} (18) (—)	654
Br_2BNMe_2	CF_3Br (2.46 eq), $(Et_2N)_3P$ (2 eq), CH_2Cl_2, –100°, 1.5 h; –78°, 1 h; rt, 2 h	$(CF_3)_2B{\bullet}NMe_2$ (8)		1053
Cl_2BNEt_2	CF_3Br (5 eq), $(Et_2N)_3P$ (1.2 eq), CH_2Cl_2, –78°, 1.5 h; rt, 6 h	$(CF_3)ClB{\bullet}NEt_2$ (10)		1080

TABLE 28. PERFLUOROALKYL ADDITION TO BORON ELECTROPHILES (*Continued*)

Boron Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
Cl_2BNEt_2	1. CF_3I (3.88 eq), TDAE (3.06 eq), CH_2Cl_2, 0°, 20 min; 20°, 1 h 2. H_2O	$(CF_3)_3B•NHEt_2$ (32)	89
Br_2BNEt_2	1. CF_3Br, $(Et_2N)_3P$ 2. H_2O	$(CF_3)_3B•NHEt_2$ (—)	89
	CF_3Br (5 eq), $(Et_2N)_3P$ (1.2 eq), CH_2Cl_2, –78°, 1.5 h; rt, 6 h	$(CF_3)BrB•NEt_2$ (10)	1080
	CF_3Br (5 eq), $(Et_2N)_3P$ (2.2 eq), CH_2Cl_2, –78°, 1.5 h; rt, 6 h	$(CF_3)_2B•NEt_2$ (20)	1080
Br_2BN*i*-Pr_2	CF_3Br (5 eq), $(Et_2N)_3P$ (2.05 eq), CH_2Cl_2, –78°, 1.5 h; rt, 6 h	$(CF_3)_2B•N$*i*-Pr_2 (35)	1080
$BrB(NMe_2)_2$	CF_3Br (2.89 eq), $(Et_2N)_3P$ (1.25 eq), CH_2Cl_2, –70°, 0.25 h; rt, 3 h	$CF_3B(NMe_2)_2$ (20)	1053
	1. CF_3Br, $(Et_2N)_3P$ (3.3 eq), CH_2Cl_2, 0°; rt, 5 d 2. HCl, H_2O, 0°	$(CF_3)_3B•NH_2Bn$ (9.3) +  (4.3) +  (0.08)	653
	CF_3Br (2.44 eq), $(Et_2N)_3P$ (1 eq), CH_2Cl_2, –70°, 0.25 h; rt, 3 h	 (25)	1053

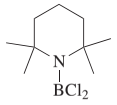
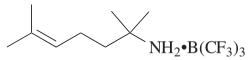
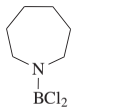
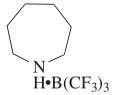
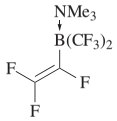
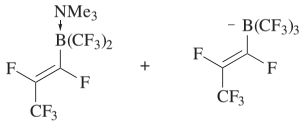
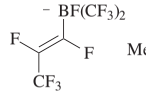
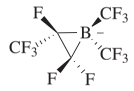
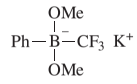
	1. CF_3Br, $(Et_2N)_3P$ (3.5 eq), CH_2Cl_2, 0°; rt, 1 h 2. HCl, H_2O	 (22)		653
	1. CF_3Br, $(Et_2N)_3P$ (3.2 eq), CH_2Cl_2, 0°; rt, 1 h 2. HCl, H_2O	 (19)		653
C_2				
$(CF_3)_2B{\bullet}NMe_2$	1. R_FI, TDAE, CH_2Cl_2, –5° 2. HCl, H_2O	$(CF_3)_2R_FB{\bullet}NHMe_2$	R_F / C_2F_5 (80) / *n*-C_4F_9 (80)	655
C_4				
	$TMSCF_3$ (6.5 eq), TMAF (2.8 eq), THF, –60 to 0°, 7 h	 + Me_4N^+		809
		(—) 45% conv	(—) 40% conv	
		+  Me_4N^+ +  Me_4N^+		
		(—) 10% conv	(—) 5% conv	
C_6				
$PhB(OMe)_2$	$TMSCF_3$ (1.25 eq), KF (1 eq), DME, rt, o/n	 (97)		663

TABLE 29. PERFLUOROALKYL ADDITION TO NON-CARBON GROUP 14 ELECTROPHILES
A. SILICON

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
$SiCl_4$	1. CF_3Br (1 eq), $(Et_2N)_3P$ (1 eq), CH_2Cl_2, –78 to 75° 2. Pyridine (0.32 eq) 3. HCl, –90°	Cl_3SiCF_3 (50)	664
	1. *n*-BuLi (8 eq), C_2F_5H (10 eq), hexane, –85° 2. Substrate (1 eq), to rt, 2.5 h 3. $[PPh_4]Cl$, CH_2Cl_2	$[PPh_4][Si(C_2F_5)_3F_2]$ (88)	1054
$BrSiH_3$	CF_3Br, $(Et_2N)_3P$ (1.02 eq), PhCN	CF_3SiH_3 (—) + CF_3SiF_3 (—) + SiH_4 (—) + SiF_3H (—) + CF_3H (—) + $SiFH_2(NEt_2)$ (—) + $CF_3SiF_2(NEt_2)$ (—) + $CF_3SiH_2(NEt_2)$ (—) + $CF_3Si(NEt_2)_3$ (—)	665
C_{0-6}			
$RSiCl_3$	LiC_2F_5 (*x* eq), Et_2O, cosolvent, –80°; to rt	$RSi(C_2F_5)_3$: R / *x* / Cosolvent — Et_2N 3.6 hexane (82); Me 3.15 pentane (57); Et 3.34 pentane (47); Ph 3.17 hexane (84)	1055
C_{0-9}			
$(R^1)_2R^2SiCl$	1. CF_3H (1 eq), Et_2O, –78°, 10 min 2. KHMDS (1 eq), –78°, 2 h; rt, 1 h	$(R^1)_2R^2SiCF_3$: R^1 / R^2 — TMS TMS (68); Me *n*-Pr (58); Me *t*-Bu (42); Et CF_3 (44); Et Et (71); *i*-Pr *i*-Pr (78)	77

C_{0-6}

$R^1R^2{}_2SiCl$ — R^3CF_3 (*x* eq), Mg (*y* eq), DMF — $R^1R^2{}_2SiCF_3$ **I** + R^3–R^3 **II** (—) — 125, 1056

R^1	R^2	R^3	*x*	*y*	Temp (°)	Time (h)	**I**	Conv **I** (%)
TMS	TMS	$PhSO_2$	0.45	7.8	–40 to rt	0.5	(62)	85
Me	Me	$MeSO_2$	—	—	rt	20	(40)	—
Me	Me	PhS	—	—	rt	4	(—)	45
Me	Me	PhSO	0.22	0.44	0 to rt	0.5–2	(81)	100
Me	Me	$PhSO_2$	—	—	0 to rt	0.5–2	(83)	100
Me	Me	$PhSO_2$	0.33	1	0	—	(95)	100
Et	Et	PhSO	—	—	rt	0.5	(—)	98
Et	Et	$PhSO_2$	0.33	1	0 to rt	1.3	(95)	100
t-Bu	Me	PhSO	—	—	rt	0.5	(—)	73
t-Bu	Me	$PhSO_2$	0.33	1	–30 to rt	3 h	(57)	75

C_0

$(Et_2N)SiCl_3$ — CF_3Br, $(Et_2N)_3P$ (3 eq), PhCN, 0°, 1.5 h — $(Et_2N)_2Si(CF_3)_2$ (—) — 665

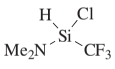
$(Et_2N)SiHCl_2$ — CF_3Br, $(Et_2N)_3P$ (4.17 eq), PhCN, 0°, 5 h — $(Et_2N)SiH(CF_3)_2$ (—) 48% conv + $(Et_2N)Si(CF_3)_3$ (—) 33% conv + $(Et_2N)SiHClCF_3$ (—) 11% conv — 665

$(Me_2N)_2SiHCl$ — CF_3Br, $(Et_2N)_3P$ (1.22 eq), PhCN, 0° to rt, 3.5 h — $(Me_2N)_2SiHCF_3$ (86) — 664

$(i\text{-}Pr_2N)SiHCl_2$ — CF_3Br, $(Et_2N)_3P$ (2 eq), PhCN, rt, 6 h — $(i\text{-}Pr_2N)SiH(CF_3)_2$ (74.7) — 665

C_1

$MeSiCl_3$ — CF_3Br, $(Et_2N)_3P$, PhCN or CH_2Cl_2 — $MeSiCl_2CF_3$ (—) — 90



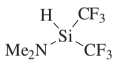
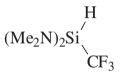
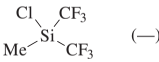
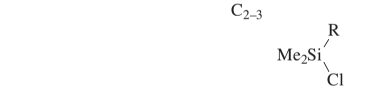
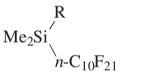
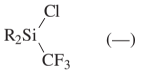
CF_3Br, $(Et_2N)_3P$ (1.06 eq), CH_2Cl_2, –90°, 1 h; –78°, 5 h —  (11.4) +  (20.7) — 665

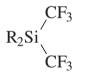
TABLE 29. PERFLUOROALKYL ADDITION TO NON-CARBON GROUP 14 ELECTROPHILES (*Continued*)

A. SILICON (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_2 Me_2SiCl_2	CF_3I (4.3 eq), TDAE (2.9 eq), PhCN, 0°, 20 min; 20°, 1 h	$Me_2Si(CF_3)_2$ (63)	89
C_2 	CF_3Br, $(Et_2N)_3P$, PhCN or CH_2Cl_2	 (—)	90
C_{2-3} 	*n*-$C_{10}F_{21}MgX$, THF, –78°, 6–8 h; –78° to rt	 R: H (57); Me (63)	1057
C_{2-12} R_2SiCl_2	CF_3Br, $(Et_2N)_3P$, PhCN or CH_2Cl_2	 (—) R = Me, Ph	90
C_3 TMSCl	1. KHMDS (1 eq, inverse addition), toluene, –85°; –85°, 20 min 2. CF_3H (1 eq), –85°, 5 h; rt 2 h	$TMSCF_3$ (80)	77
	CF_3Br, $(Et_2N)_3P$	$TMSCF_3$ (—)	667
	CF_3Br, Zn (1 eq), NMP, 3 h	$TMSCF_3$ (—) + $CF_3ZnBr•2NMP$ (—)	124
	CF_3Br, Al, NMP, 50°, few min; rt	$TMSCF_3$ (62)	124
	CF_3Br, $(Et_2N)_3P$, PhCN or CH_2Cl_2	$TMSCF_3$ (95)	90
	R_FX (1.25 eq), $(Et_2N)_3P$ (1.1 eq), PhCN, –78°; 0°, 2–4 h; rt, 2–4 h	$TMSR_F$ R_F X: CF_3 Br (80–90); C_2F_5 I (80–90)	92

TMSCl	CF_3Br (2.98 eq), $(Et_2N)_3P$ (1.02 eq), PhCN, –60°, 3.5 h; –60° to rt, 14 h	$TMSCF_3$	(75)	91
	CF_3Br (2.53 eq), $(Et_2N)_3P$ (1.41 eq), CH_2Cl_2, –78°, 2 h; rt, o/n	$TMSCF_3$	(69)	489, 489a
	CF_3Br, *n*-Bu_4N^+ PF_6^-, PhOMe, HMPA, e^-, Al anode, Ni cathode, –30°	$TMSCF_3$	(73) 100% conv	94
	CF_3Br, *n*-$Bu_4N^+Br^-$, DMF, e^-, Al anode, Ni cathode, –15°	$TMSCF_3$	(90) + $Me_3SiSiMe_3$ (—) 10–15% conv	95
	CF_3X, $Et_4N^+BF_4^-$, DMF, e^-, Zn anode, Fe cathode	$TMSCF_3$	X: Br (—); I (32)	96
	CF_3I (1.94 eq), TDAE (1.31 eq), PhCN, 0°, 20 min; 20°, 1 h	$TMSCF_3$	(94)	89
	$AgCF_3$	$TMSCF_3$	(—)	154
	C_2F_5H, *n*-BuLi, Et_2O, –70 to –60°, 0.5 h	$TMSC_2F_5$	(93)	128
	R_FBr (2.11 eq), $(Et_2N)_3P$ (1.06 eq), PhCN, –60°, 3 h; rt, o/n	R_FTMS **I** + $(TMS)_2O$ **II**	R_F: C_2F_5 **I** (50) **II** (5); *n*-C_3F_7 **I** (68) **II** (40)	122
	C_2F_5I (1.13 eq), $(Et_2N)_3P$ (1 eq), *n*-PrCN, –25 to –20°, 0.75 h; –15 to –10°, 5 h; rt	$TMSC_2F_5$	(87)	126

TABLE 29. PERFLUOROALKYL ADDITION TO NON-CARBON GROUP 14 ELECTROPHILES (*Continued*)
A. SILICON (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_3				
TMSCl	R_FI (1.2 eq), TDAE (1 eq), diglyme, –30°	R_FTMS	R_F Time (h): C_2F_5 2 (81); *n*-C_3F_7 2 (75); *i*-C_3F_7 2.5 (55); *n*-C_4F_9 1.5 (68)	127
	i-C_3F_7Li, Et_2O, –50° to rt, 3 h; reflux, 3 h	*i*-C_3F_7TMS	(17.5)	217
	n-$C_8F_{17}MgBr$, THF, –70° to rt, 4 h	*n*-$C_8F_{17}TMS$	(77)	130
	n-$C_8F_{17}Br$ (0.2 eq), Mg (0.3 eq), –40°, 1 h; –40° to rt, 18 h	*n*-$C_8F_{17}TMS$	(12.7)	326
	n-$C_8F_{17}I$, MeMgBr, THF, Et_2O, –60 to –50°, 5 h	*n*-$C_8F_{17}TMS$	(76)	129
TMSOTf	$C_6F_{13}I$, MeLi (1.1 eq), Et_2O, 0°, (microreactor)	*n*-$C_6F_{13}TMS$	(30)[a]	198
C_{3-13}	CF_3Br, $(Et_2N)_3P$, PhCN or CH_2Cl_2		R: Me (—); Ph (48)	90
C_{3-18}				
$(R^1)_2R^2SiCl$	CF_3Br (1.06 eq), Bu_4NBr (1.06 eq), e^-, DME, electrolytic autoclave	$(R^1)_2R^2SiCF_3$	R^1 R^2: Me Me (80); Me $ClCH_2$ (80)[a]; Me Ph (55); Et Et (75)[a]; CH_2=CH CH_2=CH (70)[a]; Ph Me (20)[a]; Ph Ph (10)[a]	123

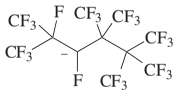
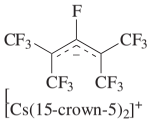
		CF_3Br (1.13 eq in 5 portions), Al (0.67 eq), NMP, autoclave, rt, o/n[b]	$(R^1)_2R^2SiCF_3$	R^1 / R^2 /	123
				Me / Me / (84)	
				Me / $ClCH_2$ / (80)[a]	
				Me / Ph / (50)[a]	
				Et / Et / (75)[a]	
				CH_2=CH / CH_2=CH / (30)[a]	
				Ph / Me / (20)[a]	
				Ph / Ph / (10)[a]	
C_4					
	Et_2SiCl_2	*n*-C_3F_7I, MeLi, Et_2O, –52°, 0.5 h; –52 to 20°	$Et_2SiCl(n\text{-}C_3F_7)$ (17.8) + $Et_2Si(n\text{-}C_3F_7)_2$ (10.2)		188
	$TMSCF_3$	$TMSCF_3$, TMAF (< 1 eq), THF, –90 to –60°	$(Me_4N)^+[Me_3Si(CF_3)_2]^-$ (—)		63
		$TMSCF_3$ (1–13 eq), CsF (1 eq), 15-crown-5 (2 eq), <5°	$[Cs(15\text{-crown-}5)_2]^+$ $[Me_3Si(CF_3)_2]^-$ (—)		145
		$TMSCF_3$ (1–13 eq), CsF (1 eq), 15-crown-5 (2 eq), >5°	$[Cs(15\text{-crown-}5)_2]^+$  (—)		145
		$TMSCF_3$ (11 eq), CsF (1 eq), 15-crown-5 (2 eq), DME, –20° to rt, 3 h; rt, 12 h	 $[Cs(15\text{-crown-}5)_2]^+$ (60.7) + $[(CF_3)_3C^\bullet]$ (—) + $[F^\bullet]$ (—)		145

TABLE 29. PERFLUOROALKYL ADDITION TO NON-CARBON GROUP 14 ELECTROPHILES (*Continued*)

A. SILICON (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_4			
$TMSCF_3$	$TMSCF_3$ (*x* eq), Q^+A^-, DME, –55° or THF, –78°	 (95) *x* Q A 2 Me_4N F 2 $(Me_2N)_3C$ F 2 $(Me_2N)_4P$ F 2 $(Me_2N)_3S$ $TMSF_2$ 3 Me_4N HF_2 3 $(Me_2N)_3C$ HF_2 3 $(Me_2N)_4P$ HF_2	64
$(Me_4N)^+[Me_3Si(CF_3)F]^-$	$TMSCF_3$, THF, –60°	$(Me_4N)^+[Me_3Si(CF_3)_2]^-$ (—)	63
C_{12}			
n-Bu_3SiCl	CF_3Br (3.14 eq), $(Et_2N)_3P$ (1.38 eq), CH_2Cl_2, –59°, 1 h; rt, 1 h	*n*-Bu_3SiCF_3 (64)	489, 489a

[a] The yield was determined by gas chromatography.

[b] These conditions are for R^1,R^2 = Me; conditions for the other substrates were not given.

TABLE 29. PERFLUOROALKYL ADDITION TO NON-CARBON GROUP 14 ELECTROPHILES (*Continued*)
B. GERMANIUM

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
GeI_4	$(CF_3)_2Cd$•DME, solvent	$(CF_3)_4Ge$ **I** + $(CF_3)_3GeI$ **II**	230
		Solvent / Time (h) / **I** / **II** / **I/II**: $Br(CH_2)_2Br$ / 1 / (43) / (4.7) / 9.3:1; $Br(CH_2)_4Br$ / 0.5 / (42.3) / (—) / (—)	
C_3			
Me_3GeCl	CF_3Br, $(Et_2N)_3P$	Me_3GeCF_3 (—)	667
	CF_3Br (1.06 eq), Bu_4NBr (1.06 eq), e^-, DME, electrolytic autoclave	Me_3GeCF_3 (90)[a]	123
C_6			
Et_3GeCl	R_FX (*x* eq), $(Et_2N)_3P$ (*y* eq), CH_2Cl_2, –60°, 1–2 h; rt, 2–3 h	Et_3GeR_F: R_F / X / *x* / *y*: CF_3 / Br / 2.37 / 0.94 / (52); CF_3 / I / 1.71 / 1.12 / (66); n-C_4F_9 / Br / 1.65 / 1.2 / (78)	666

[a] The yield was determined by gas chromatography.

TABLE 29. PERFLUOROALKYL ADDITION TO NON-CARBON GROUP 14 ELECTROPHILES (*Continued*)

C. TIN

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_0			
$SnBr_4$	$(CF_3)_2Cd$•DME, $Br(CH_2)_6Br$	$Sn(CF_3)_4$ **I** (—) + $(CF_3)_3SnBr$ **II** + CF_3SnBr_3 **III** (—)	230
		Time (h) / **II** / **I/II/III**: 3 / (—) / 8.9:1.0:1.5; 5 / trace / 1.0:tr:3.5	
C_3			
Me_3SnCl	CF_3Br, $(Et_2N)_3P$	Me_3SnCF_3 (—)	667
	$Me_4N^+ B(CF_3)_4^-$, –78°	Me_3SnCF_3 (—)	169
	$AgCF_3$	Me_3SnCF_3 (—)	154
	82 (1.15 eq), DME, –45°; rt, 16 h	Me_3SnCF_3 (—) 58% conv	155
Me_3SnONO_2	$(R_F)_2Cd$•DME, MeCN, 75°	Me_3SnR_F (—) ($R_F = C_2F_5$, *i*-C_3F_7)	231
Me_3SnCl	CF_3Br (1.06 eq), Bu_4NBr (1.06 eq), e^-, DME, electrolytic autoclave	Me_3SnCF_3 (70)[a]	123
	$(R_F)_2Cd$•diglyme, solvent, 70°, 24 h	Me_3SnR_F: R_F / Solvent / (80): CF_3 / diglyme; (63.8): C_2F_5 / diglyme; (75): *i*-C_3F_7 / MeCN	153
C_{12}			
Bu_3SnCl	R_FI, Zn, DMF, rt	Bu_3SnR_F: R_F / (65): *n*-C_3F_7; (52): *n*-C_4F_9; (35): *n*-C_6F_{13}	1058

		R_FI, Cd, DMF, rt, 2 h	Bu_3SnR_F	R_F n-C_4F_9 (39) n-C_6F_{13} (21)	1059
		n-$C_6F_{13}I$, MeLi (1.1 eq), Et_2O, 0°, microreactor	$Bu_3Sn(n\text{-}C_6F_{13})$ (2)[a]		198
	(n-$Bu_3Sn)_2O$	$TMSCF_3$ (2.48 eq), TBAF (cat.), THF, rt, 18 h	n-Bu_3SnCF_3 (95) + $(TMS)_2O$ (—)		150
C_{13}	$Bu_3Sn^+(CF_3BF_3)^-$	$Bu_3Sn^+(CF_3BF_3)^-$, LiF (1.5 eq), H_2O, rt, 12 h; reflux, 1 h	$Li^+[(CF_3)_2BF_2]^-$ (19)		652

[a] The yield was determined by gas chromatography.

TABLE 29. PERFLUOROALKYL ADDITION TO NON-CARBON GROUP 14 ELECTROPHILES (*Continued*)

D. LEAD

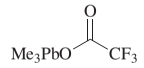
Electrophile	Conditions	Product(s) and Yield(s) (%)		Refs.
Please refer to the chart preceding the tables for structures indicated by the ***bold*** *numbers.*				
C_3				
Me_3PbCl	CF_3Br, $(Et_2N)_3P$	Me_3PbCF_3	(—)	667
	$(R_F)_2Cd$•diglyme, MeCN, 70°, 24 h	Me_3PbR_F	R_F / CF_3 (85.1); C_2F_5 (91.2); *i*-C_3F_7 (70)	153

TABLE 30. PERFLUOROALKYL ADDITION TO GROUP 15 ELECTROPHILES
A. NITROGEN

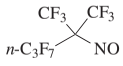
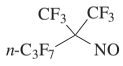
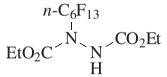
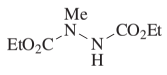
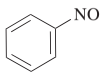
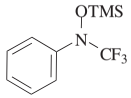
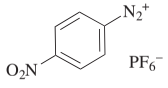
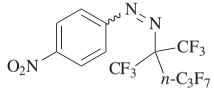
Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
NOF	$C_2F_5CF{=}C(CF_3)_2$ (0.98 eq), TASF (0.9 mol %), PhCN, 0°; rt, 1.5 h	 (55)	68
NOCl	**84** (0.92 eq), MeCN, 0°	 (25)	68
	$TMSR_F$ (1 eq), CsF (1 eq), DME, –196°; rt, 3 h	R_FNO: CF_3 (92); C_2F_5 (85); n-C_6F_{13} (<20); n-C_7F_{15} (<20); n-C_8F_{17} (<20)	644
C_1			
	n-$C_6F_{13}I$, MeLi/LiBr, Et_2O, –78°, 1 h	 (65) +  (18)	625
C_6			
	$TMSCF_3$, TBAF, THF, 0°	 (—) 100% conv	13
	1. **84** (1 eq), MeCN, 0°; rt, 1.5 h 2. H_2O	 (89), (*E*)/(*Z*) = —	68

TABLE 30. PERFLUOROALKYL ADDITION TO GROUP 15 ELECTROPHILES (*Continued*)

B. PHOSPHORUS

	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_0	PCl_3	CF_3Br (3.25 eq), $(Et_2N)_3P$ (5 eq), $(EtO)_2CO$, 12 h	$(Et_2N)_2PCF_3$ (70)	668
	PI_3	$(CF_3)_2Cd$•DME, $Br(CH_2)_6Br$, 0.5 h	$(CF_3)_3P$ (20) + $(CF_3)_2PI$ (30)	230
	PF_5	Me_3SnCF_3 (0.1 eq), rt, 1 h	$(Me_3Sn)^+[(CF_3)PF_5]^-$ (—)	159
		Me_3SnCF_3 (0.8 eq), rt, 1 h	$(Me_3Sn)^+[(CF_3)PF_5]^-$ (—) + $(CF_3)PF_4$ (—)	159
		Me_3SnCF_3 (6.75 eq), rt, 3 h	$(Me_3Sn)^+[(CF_3)PF_5]^-$ (—) + $(CF_3)PF_4$ (—) + $(CF_3)_2PF_3$ (—) + $(CF_3)_3PF_2$ (—)	159
$C_{0\text{-}6}$	R_2PCl	CF_3Br, $(Et_2N)_3P$	R_2PCF_3 (—) R = Me, *i*-Pr, Et_2N	669
C_0	$(Me_2N)_3P$	CF_3I (0.57 eq), 60°, 2 h	$(Me_2N)_3P$ (27) + CF_3I (21) + $(Me_2N)_2PCF_3$ (36) + $(Me_2N)_4P^+I^-$ (35)	1060
		$(CF_3)_2CFI$ (0.45 eq), rt, 72 h	$(Me_2N)_3P$ (29) + $(CF_3)_2CFI$ (14) + $(Me_2N)_2PCF(CF_3)_2$ (24) + $(Me_2N)_4P^+I^-$ (—)	1060
	$(PhO)_3P$	$TMSR_F$ (3 eq), initiator (*x* eq), rt	$(R_F)_3P$	674

R_F	Initiator	*x*	Solvent	Conv (%)	
CF_3	CsF	0.1	Et_2O	90	(—)
CF_3	CsF	3	Et_2O	98	(80)
C_2F_5	CsF	0.1	Et_2O	95	(—)
C_2F_5	CsF	3	Et_2O	98	(85)
C_2F_5	PhONa	0.5	Et_2O	75	(—)
C_2F_5	TBAT	0.5	Et_2O	45	(—)
n-C_3F_7	CsF	0.5	PhCN	35	(—)
n-C_4F_9	CsF	3	Et_2O	20	(—)

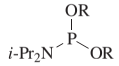
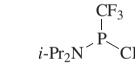
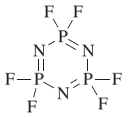
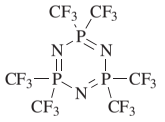
	CF_3Br, $(Et_2N)_3P$	$(CF_3)_3P$	(—)		669
	CF_3Br (4.5 eq), $(Et_2N)_3P$ (4.5 eq), HMPA, –60°, 1 h; 36°, 1 h	$(CF_3)_3P$	(85)		673
	$TMSCF_3$ (2.2 eq), CsF (3 eq), Et_2O, –78° to rt, o/n	$(CF_3)_3P$	(—)		675
	$TMSCF_3$ (2 eq), CsF (2.2 eq), THF, rt, 4 h		(75)	R = 4-$O_2NC_6H_4$	672, 1061
$(4\text{-}NCC_6H_4O)_3P$	$TMSR_F$ (3 eq), CsF (*x* eq), PhCN, Et_2O	$(R_F)_3P$	90% conv	R_F *x* *n*-C_3F_7 0.5 (—) *n*-C_4F_9 3 (40) *n*-C_6F_{13} 3 (—)	674
$(RO)_3PO$	R_FI (3 eq), Cu/Zn	$(R_F)_3PO$	(—)	R R_F Temp (°) Me *n*-C_4F_9 90 Me *n*-C_6F_{13} 90 Bu *n*-C_4F_9 100 Bu *n*-C_6F_{13} 100	682
	R_FI (2 eq), Cu/Zn	$(R_F)_2P(O)OR$	(—)	R R_F Temp (°) Me *n*-C_4F_9 60 Me *n*-C_6F_{13} 60 Et *n*-C_4F_9 60 Et *n*-C_6F_{13} 60 Bu *n*-C_4F_9 80 Bu *n*-C_6F_{13} 80	682
$(EtO)_2P(O)F$	$TMSCF_3$ (2 eq), CsF (cat.), THF, 24 h	$(EtO)_2P(O)CF_3$	(85)		680

TABLE 30. PERFLUOROALKYL ADDITION TO GROUP 15 ELECTROPHILES (*Continued*)
B. PHOSPHORUS (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)				Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*						
C_0						
$(RO)_2P(O)H$	$TMSCF_3$ (4 eq), Cu catalyst (x mol %), phen (x mol %), K_2CO_3 (4 eq), $ClCH_2CH_2Cl$, air, 50°, 36 h	$(RO)_2P(O)CF_3$	R	Catalyst	x	681
			Et	$Cu(OH)_2$	30 (56)	
			Pr	$Cu(OH)_2$	60 (73)	
			n-Bu	$Cu(OEt)_2$	30 (87)	
			i-Bu	$Cu(OEt)_2$	30 (85)	
			$Cl(CH_2)_4$	$Cu(OH)_2$	30 (70)	
			n-C_6H_{13}	$Cu(OH)_2$	60 (90)	
			c-C_6H_{11}	$Cu(OEt)_2$	30 (76)	
$(n\text{-BuO})_2P(O)F$	$TMSCF_3$ (2 eq), KF (6.8 mol %), 60°, 4 h	$(n\text{-BuO})_2P(O)CF_3$	(93)			679
$(PhO)_3PO$	$TMSCF_3$ (1.2 eq), TMAF (4 eq), DME, –40°, 2 h; 0°, 4 h	Me_4N^+ 	(82)			683
	$TMSCF_3$ (2.1 eq), CsF (3 eq), DME, –40°, 2 h; rt, o/n	Cs^+ 	(48)			683
	$TMSCF_3$ (1 eq), CsF (0.1 eq), THF, rt, 4 h		(65)			672
	$TMSCF_3$ (7 eq), CsF (0.25 eq), THF, 70°, 24 h		(90)			684

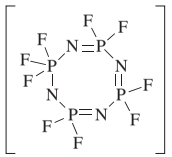
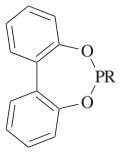

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TABLE 30. PERFLUOROALKYL ADDITION TO GROUP 15 ELECTROPHILES (*Continued*)
B. PHOSPHORUS (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_2			
$(CF_3)_2PF_3$	Me_3SnCF_3 (1.23 eq), rt, 6 h	$(Me_3Sn)^+[(CF_3)_3PF_3]^-$ (—)	159
Cl_2P–PCl_2	CF_3Br (14 eq), $(Et_2N)_3P$ (8 eq), solvent, –60 to –55°, 1 h; rt, o/n	$(CF_3)_2P$–$P(CF_3)_2$ Solvent: CH_2Cl_2 (15); THF (—); toluene (—); PhCN (—)	1063
	C_2F_5Cl (4 eq), BuLi, Et_2O, –95° to rt, 3h	$(C_2F_5)_2P$–$P(C_2F_5)_2$ (68)	670
$(PhO)_2P$–$P(OPh)_2$	$TMSR_F$ (4 eq), CsF (4 eq), Et_2O, rt	$(R_F)_2P$–$P(R_F)_2$ (—) R_F: CF_3 95; C_2F_5 90	674
	$TMSCF_3$ (6.25 eq), CsF (0.3 eq), Et_2O, rt, 24 h	$(CF_3)_2P$–$P(CF_3)_2$ (42)[a]	677
C_{2-3} 	C_2F_5Li (2.15 eq), Et_2O, –78°	$(C_2F_5)_2PR$ (—) R = Et, *i*-Pr	1062
C_3			
$(CF_3)_3P$	$TMSCF_3$, F^-	$[(CF_3)_4P]^-$ (—)	669
	$TMSCF_3$ (2 eq), $(Me_2N)_3S^+[Me_3SiF_2]^-$ (1 eq), THF, –55°	$(Me_2N)_3S^+[(CF_3)_4P]^-$ (—) + $(Me_2N)_3S^+[(CF_3)_3PF]^-$ (5–10)	64

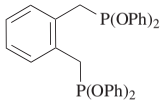
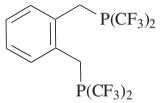
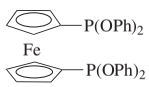
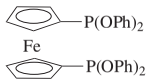
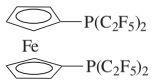
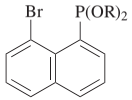
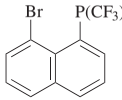
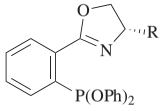
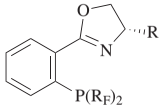
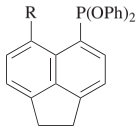
		$TMSCF_3$ (2–2.5 eq), TMAF (1 eq), DME, –60°	$Me_4N^+[(CF_3)_4P]^-$ (—)	64
	$(CF_3)_3PF_2$	Me_3SnCF_3 (1.72 eq), rt, 6 h	$(Me_3Sn)^+[(CF_3)_4PF_2]^-$ (16)	159
		Me_3SnCF_3 (1.72 eq), 65°, 2.5 h	$(Me_3Sn)^+[(CF_3)_4PF_2]^-$ (70) + CF_4 (—) + $CF_2{=}CF_2$ (—) + CF_3H (—)	159
C_6				
	$PhP(OPh)_2$	$TMSR_F$ (2 eq), CsF (0.1 eq), Et_2O, rt	$PhP(R_F)_2$ (—) R_F / Conv (%): CF_3 90; C_2F_5 90	674
C_{6-10}				
	$(4\text{-}NCC_6H_4O)_2PR$	$TMSCF_3$ (2.1 eq), CsF (0.21 eq), Et_2O, MeCN, 0° to rt, 5 h	$RP(CF_3)_2$ R / (%): Ph (61); 1-adamantyl (73)	1064
C_8				
	$PhP(CN)_2$	$TMSCF_3$ (2 eq), Et_4NCN (2 mol %), MeCN, –45° to rt, 2 h; rt, 10 h	$PhP(CF_3)_2$ (75)	137
		$TMSCF_3$ (4.4 eq), CsF (4 eq), Et_2O, rt, 48 h	 (68)	1065
C_{10}		$TMSCF_3$ (5.2 eq), CsF (4.5 eq), Et_2O, rt, o/n	 (66)	1066

TABLE 30. PERFLUOROALKYL ADDITION TO GROUP 15 ELECTROPHILES (*Continued*)
B. PHOSPHORUS (*Continued*)

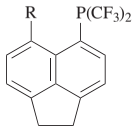
Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_{10} 	$TMSC_2F_5$ (5.3 eq), CsF (4 eq), Et_2O, reflux, 4 h	 (70)	1066
	$TMSCF_3$ (2.5 eq), CsF (*x* eq), solvent, rt, 4 h	 R: Et, *x*: 1, Solvent: Et_2O or THF, (0); R: Ph, *x*: 2.5, Solvent: THF, (66)	675
C_{12} Ph_2PCl	CF_3Br, $(Et_2N)_3P$	Ph_2PCF_3 (—)	667
	C_2F_5Cl, *n*-BuLi, Et_2O, –78° to rt	$Ph_2PC_2F_5$ (89)	671
Ph_2POPh	$TMSR_F$ (1 eq), CsF (0.5 eq), Et_2O, rt	Ph_2PR_F: R_F = CF_3, Conv (%) 90, (—); R_F = C_2F_5, Conv (%) 98, (80)	674
C_{12-16} 	1.$TMSR_F$ (2.1 eq), CsF (2.1 eq), dioxane, o/n 2. After 8 h, if necessary, $TMSR_F$ (3.6 eq)		676

R	R_F	Temp (°)	[b]
i-Pr	CF_3	rt	(65)
i-Pr	C_2F_5	40	(45)
t-Bu	CF_3	rt	(71)
t-Bu	C_2F_5	40	(47)
Ph	CF_3	rt	(61)
Ph	C_2F_5	40	(41)
Bn	CF_3	rt	(57)
Bn	C_2F_5	40	(37)

C_{12}



$TMSCF_3$ (2.5 eq), CsF (*x* eq), solvent, –78° to rt; rt, 3 h



R	*x*	Solvent		
Br	3	THF	(60)	675
i-Pr_2P	2.5	Et_2O or THF	(0)	

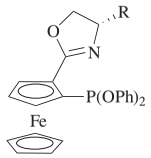
C_{13}

Ph_2PCN

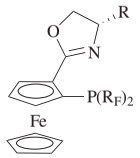
$TMSCF_3$ (1.06 eq), [18-crown-6-K]CN (10 mol %), CH_2Cl_2, –78° to rt, 2 h

Ph_2PCF_3 (70) 137

$C_{16–20}$

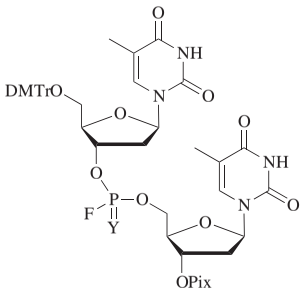


1.$TMSR_F$ (2.2 eq), CsF (2.2 eq), Et_2O, o/n
2. After 8 h, if necessary, $TMSR_F$ (2.8 eq)

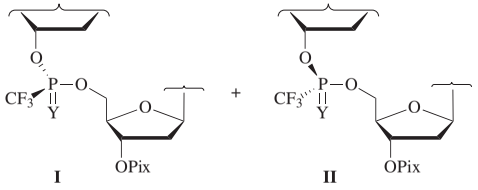


R	R_F	Temp (°)	[b]	
i-Pr	CF_3	rt	(51)	
i-Pr	C_2F_5	40	(40)	676
t-Bu	CF_3	rt	(32)	
t-Bu	C_2F_5	40	(40)	
Ph	CF_3	rt	(39)	
Ph	C_2F_5	40	(38)	
Bn	CF_3	rt	(40)	
Bn	C_2F_5	40	(30)	

C_{20}



$TMSCF_3$ (1 eq), CsF (0.1 eq), THF, rt, 4 h



I **II** 672

Y	**I + II**	**I/II**
—	(82)	1:1
O	(90)	1:1

[a] The yield was determined by NMR spectroscopy.

[b] The yield includes preparation of the substrate.

TABLE 30. PERFLUOROALKYL ADDITION TO GROUP 15 ELECTROPHILES (*Continued*)
C. ARSENIC, ANTIMONY, AND BISMUTH

	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
	Arsenic			
C_{12}	Ph_2AsCl	CF_3Br, $(Et_2N)_3P$	Ph_2AsCF_3 (—)	667
	Antimony			
C_0	SbX_3	$Cd(CF_3)_2$•2MeCN (1.5 eq), MeCN, –40°, 8 h	$Sb(CF_3)_3$ X: Cl (82), Br (75), I (83)	686
C_2	Me_2SbCl	CF_3Br, $(Et_2N)_3P$	Me_2SbCF_3 (—)	667
	Bismuth			
C_0	$BiCl_3$	CF_3ZnBr•2MeCN (9 eq), CH_2Cl_2, 0–30°, 14 d	$Bi(CF_3)_3$ (70)	687
	$BiBr_3$	$AgCF_3$	$Bi(CF_3)_3$ (—)	154
C_3	$Bi(CF_3)_3$	$TMSCF_3$ (3 eq), TMAF (1 eq), Et_2O, –70 to –60°, 1 h	$Me_4N^+[Bi(CF_3)_4]^-$ (quant)	169

C_{6-7}

$RBiBr_2$ $Cd(CF_3)_2$•2MeCN (2.2 eq), MeCN, rt

$Bi(CF_3)_3$ **I** + R_2BiCF_3 **II** + $RBi(CF_3)_2$ **III** 168

R	Time (d)	**I + II + III**	**I/II/III**
3-FC_6H_4	3	(87)	13:21:66
4-FC_6H_4	3	(85)	3:29:68
4-MeC_6H_4	2	(78)	25:33:42
4-$CF_3C_6H_4$	5	(92)	2:8:90

C_{12-14}

R_2BiCl $Cd(CF_3)_2$•2MeCN (1.1 eq), MeCN, rt

$Bi(CF_3)_3$ **I** + R_2BiCF_3 **II** + $RBi(CF_3)_2$ **III** 168

R	Time (d)	**I + II + III**	**I/II/III**
3-FC_6H_4	8	(79)	3:71:26
4-FC_6H_4	8	(84)	0:90:10
4-MeC_6H_4	5	(90)	0:98:2
4-$CF_3C_6H_4$	8	(94)	4:93:3

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES
A. SULFUR

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
S	1. CF_3H (4 eq), *t*-BuOK (0.5 eq), ZnO (0.25 eq), DMF, 46° 2. HCl, H_2O, H_2O_2	CF_3SO_3H (—) 1.5% conv	700
S_8	$TMSCF_3$ (1.2 eq), TMAF (1 eq), DME or THF, –60°, 0.5 h; –60° to rt, o/n	Me_4NSCF_3 (88) + CF_3SCF_3 trace + CF_3H trace	688
	$TMSCF_3$ (1.2 eq), CsF (1 eq), DME or THF, –60°, 0.5 h; –60° to rt, o/n	$CsSCF_3$ (—)	688
	$TMSCF_3$ (1.2 eq), CsF (1 eq), L (2 eq), DME, –30° to rt, 2.5 h	L_2CsSCF_3 (quant) L = benzo-15-crown-5	688
	t-C_4F_9Ag, MeCN, 50°, 1 h	$AgSC(CF_3)_3$ (32)	724
S_8 4 eq	1. CF_3H (1 eq), THF, –78°, few min 2. KHMDS (4 eq), –78°, 1 h; rt, 10 h 3. H_2O_2 (30%, 6 eq), H_2SO_4 (1 eq), rt, 1 h	CF_3SO_3H 100% conv[a]	77

S_8	3 eq	$RB(OH)_2$, $TMSCF_3$ (5 eq), CuSCN (10 mol %), phen (2 mol %), K_3PO_4 (3 eq), 4 Å MS, DMF, Ar, rt, 24 h	$RSCF_3$	R Ph 4-BrC_6H_4 4-$MeOC_6H_4$ 4-$PhOC_6H_4$ 4-$BnOC_6H_4$ 3,4,5-$(MeO)_3C_6H_2$ 4-$MeSO_2C_6H_4$ 3-$H_2NCOC_6H_4$ 4-NCC_6H_4 4-$MeO_2CC_6H_4$ 4-CH_2=CHC_6H_4 4-*t*-BuC_6H_4 1-$C_{10}H_7$ 6-MeO-2-$C_{10}H_6$ 3-PhC_6H_4 4-PhC_6H_4 4-BzC_6H_4	(95) (84) (59)[b] (91) (86) (90) (61) (66) (70) (67) (78) (84) (71) (89) (82) (64) (58)	690
SO_2		CF_3Br, M, DMF	$(CF_3SO_2)_nM$	n = 2, 3	M Zn Cd Mn Al	(44) (—) (—) (—)	1067
		1. C_2F_5I, MeLi, Et_2O, –78°, 5 min 2. SO_2, –78°, 2 h; –78° to rt 3. H_2O_2, AcOH, H_2O, 100°, 2 h; reflux, 1 h 4. H_2SO_4	$C_2F_5SO_3H$	(80)			703

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

A. SULFUR (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
SO_2	1. R_FI, PhMgBr, Et_2O, –45° 2. H_2O 3. Cl_2, HCl	R_FSO_2Cl (—) $R_F = n\text{-}C_4F_9, n\text{-}C_5F_{11}, n\text{-}C_8F_{17}$	703
	1. R_FI, Zn/Cu (3:2), DMSO, rt to 45°, 2–4 h 2. Cl_2, MeOH	R_FSO_2Cl R_F: $n\text{-}C_4F_9$ (40–55); $n\text{-}C_6F_{13}$ (45–80); $n\text{-}C_8F_{17}$ (52–75)	646
	$TMSR_F$ (1 eq), CsF (0.67 eq), DME, –196°; rt, 24 h	$R_FSO_2^-Cs^+$ (95) $R_F = CF_3, C_2F_5$	644
	$CF_3(CF_2)_nMgX$, Et_2O, –45°	$[CF_3(CF_2)_nSO_2]_2Mg$ (—) $n = 3, 5, 7$	1068
SO_3	$TMSCF_3$ (0.77 eq), Cl_2FCCF_2Cl, –196°; rt, 0.25–0.5 h	CF_3SO_3TMS (83)	710
SO_2Cl_2	**82** (2.85 eq), DME, –60 to 10°	CF_3SO_2Cl (—) 91% conv	155
	$Me_4N^+B(CF_3)_4^-$, –78°	CF_3SO_2Cl (—)	169
$(MeO)_2SO$	1. $TMSCF_3$ (1 eq), CsF (1 mol %), PhCN, 50°, 0.5 h 2. HCl, H_2O, rt, 3 h	$(CF_3)_2SO$ (77)	470
C_{0-1}			
	$TMSCF_3$ (x eq), KF (cat.), MeCN, rt, 1–8 h	 R^1 / R^2 / x / R^3: F F 1 F (>75); F F 2 CF_3 (—); Cl Cl 1 F (>75); CF_3 F 1 CF_3 (>75); CF_3 Cl 1 CF_3 (>75)	397

C_0

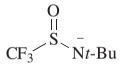
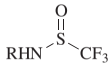
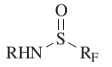
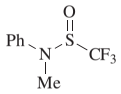
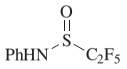
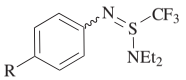
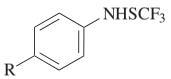
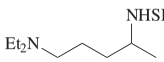
t-BuNSO	$TMSCF_3$ (1.1 eq), TMAF (1 eq), THF, –80°; –45°, 2 h; rt, 1 h	 Me_4N^+	(93)	707
RNSO	1. $TMSCF_3$ (1.1 eq), TMAF (1 eq), DME or THF, –60°; –50°, 2 h; rt, 1 h 2. NH_4Cl, H_2O		R: *t*-Bu (85); *c*-C_6H_{11} (75); Ph (85); 3-FC_6H_4 (75); 3-$CF_3C_6H_4$ (80); PhCHMe (78)	707
	1. R_FMgCl, *n*-Bu_2O, –35° 2. NH_4Cl, H_2O		R / R_F: *n*-C_4H_9 / C_6F_{13} (55); *c*-C_6H_{11} / C_6F_{13} (76); Ph / C_2F_5 (71); Ph / C_4F_9 (78); Ph / C_6F_{13} (68); Ph / C_8F_{17} (57); 4-ClC_6H_4 / C_2F_5 (54); $PhSO_2$ / C_6F_{13} (24)	709
PhNSO	1. $TMSCF_3$ (1.1 eq), TMAF (1 eq), DME or THF, –60°; –50°, 2 h; rt, 1 h 2. MeI		(87)	707

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)
A. SULFUR (*Continued*)

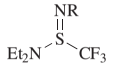
Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
PhNSO	1. $TMSC_2F_5$ (1.1 eq), TMAF (1 eq), THF, –80°; –60°, 2 h 2. NH_4Cl, H_2O, –30°	 (80)	707
Et_2NSF_3	1. $TMSCF_3$ (1.1 eq), *i*-Pr_2NEt (1 eq), CH_2Cl_2, –20°, 1 h 2. 4-$RC_6H_4NH_2$ (1 eq), 0°; rt	 **I** (—) +  **II** (—)	706

R	Time (h)	Conv **I** (%)	Conv **II** (%)
H	4	65	30
H	24	10	85
O_2N	4	85	—
O_2N	24	80	4

Et_2NSF_3	1. $TMSR_F$ (1 eq), *i*-Pr_2NEt (1 eq), CH_2Cl_2, –20°, 1 h 2. RNH_2 (1 eq), 0°; rt, o/n	$RHNSR_F$	R_F	R	Conv (%)		706
			CF_3	Ph	81	(95)	
			CF_3	4-FC_6H_4	60	(75)	
			CF_3	4-ClC_6H_4	66	(80)	
			CF_3	4-$MeOC_6H_4$	43	(75)	
			CF_3	4-MeC_6H_4	68	(90)	
			CF_3	Bn	64	(75)	
			C_2F_5	Ph	—	(56)	
			C_2F_5	Bn	—	(66)	

	1. $TMSR_F$ (1 eq), *i*-Pr_2NEt (1 eq), CH_2Cl_2, –20°, 1 h 2. $Et_2N(CH_2)_3CHMeNH_2$ (1 eq), 0°; rt, o/n		R_F	Conv (%)		706
			CF_3	50	(74)	
			C_2F_5	—	(20)	

1. $TMSCF_3$ (0.91 eq),
   i-Pr_2NEt (1.82 eq),
   CH_2Cl_2, –20°, 1 h
2. RNH_2 (1 eq), 0°; rt, 4 h



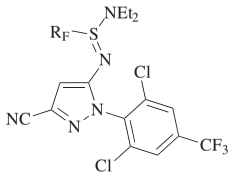
R	Conv (%)		
CF_3SO_2	99	(94)	706
BnO_2C	73	(69)	
2-$O_2NC_6H_4$	23	(36)	
3-$O_2NC_6H_4$	57	(76)	
4-$O_2NC_6H_4$	85	(80)	
2-MeC_6H_4	99	(95)	
2-$CF_3C_6H_4$	21	(40)	

1. $TMSCF_3$ (1 eq), *i*-Pr_2NEt (1 eq),
   CH_2Cl_2, –20°, 1 h
2. $PhCHMeNH_2$ (1 eq), 0°; rt, o/n

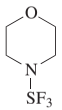


(75) 41% conv 706

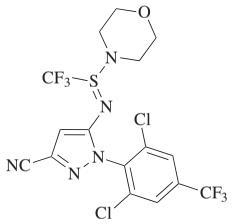
1. $TMSR_F$ (0.91 eq),
   i-Pr_2NEt (1.82 eq),
   CH_2Cl_2, –20°, 1 h
2. **29** (1 eq), 0°; rt, 4 h



R_F	Conv (%)		
CF_3	51	(49)	706
C_2F_5	10	(22)	



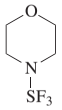
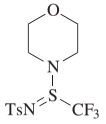
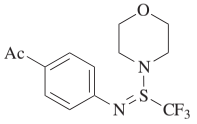
1. $TMSCF_3$ (0.91 eq),
   i-Pr_2NEt (1.82 eq),
   CH_2Cl_2, –20°, 1 h
2. **29** (1 eq), 0°; rt, 4 h



(49) 24% conv 706

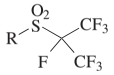
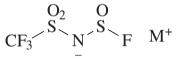
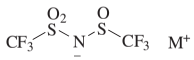
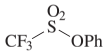
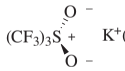
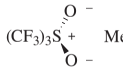
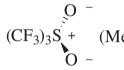
TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

A. SULFUR (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0 	1. $TMSCF_3$ (0.91 eq), *i*-Pr_2NEt (1.82 eq), CH_2Cl_2, –20°, 1 h 2. $TsNH_2$ (1 eq), 0°; rt, 4 h	 (49)	706
	1. $TMSCF_3$ (0.91 eq), *i*-Pr_2NEt (1.82 eq), CH_2Cl_2, –20°, 1 h 2. 4-$AcC_6H_4NH_2$ (1 eq), 0°; rt, 4 h	 (90) 70% conv	706
C_1 $CF_3N{=}SF_2$	$TMSCF_3$ (2 eq), CsF (2 eq), MeCN, –196°; rt, 8–10 h	$CF_3N{=}S(CF_3)_2$ (68)	639
C_{1-8} RSSR	$TMSCF_3$ (*x* eq), TBAF (*y* eq), THF, 1 h	$RSCF_3$ **I** + RSTMS **II** (—)	695

R	*x*	*y*	Temp (°)	Conv **I** (%)	**I**
Me	2	2[c]	0 to rt	47	(—)
t-Bu	2	2[c]	0 to rt	4	(—)
c-C_6H_{11}	2	2[c]	0 to rt	51	(46)
Ph	2	2[c]	0 to rt	32	(25)
Bn	2	2[c]	0 to rt	79	(70)
n-C_8H_{17}	1	1	0	36	(—)
n-C_8H_{17}	1	1[c]	0	60	(—)
n-C_8H_{17}	1	1	rt	18	(—)
n-C_8H_{17}	1	2	0	50	(—)
n-C_8H_{17}	2	0.5[c]	0	75	(—)
n-C_8H_{17}	2	1[c]	0	90	(—)
n-C_8H_{17}	2	2	0	70	(—)
n-C_8H_{17}	2	2[c]	0 to rt	96	(80)

C_1

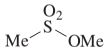
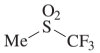
RSO_2X	$(CF_3)_2CFI$ (1 eq), $(Et_2N)_3P$ (1 eq), PhCN, –196°; rt, 24 h		R	X		596
			Me	Cl	(66)	
			CF_3	F	(90)	
	1. MF (2 eq), THF, rt, 0.5 h 2. $TMSCF_3$ (1.13 eq), rt, 2 h		(quant)		M = K, Cs	708
	$TMSCF_3$ (3 eq), KF (1.1 eq), 18-crown-6 (1 eq), DMF, –40°; 0°, 20 h		K^+(18-crown-6)	(50)		155
	$TMSCF_3$ (3 eq), TMAF (1.1 eq), THF, –30°, 3 h		Me_4N^+	(79)		155
	$TMSCF_3$ (2.9 eq), TASF (1.1 eq), THF, –30°, 0.5 h		$(Me_2N)_3S^+$	(65)		155

$C_{1–10}$

	$TMSCF_3$ (2 eq), TBAF (0.5 eq), THF, 0°, 0.5 h; 21°, 12 h		R^1	R^2		712
			Me	Ts	(0)	
			Ph	Bz	(79)	
			Ph	Ts	(72)	
			Ph	Ns	(52)	
			4-FC_6H_4	Bz	(54)	
			2-ClC_6H_4	Bz	(59)	
			4-ClC_6H_4	Bz	(74)	
			2-MeC_6H_4	Bz	(69)	
			4-MeC_6H_4	Boc	(75)	
			4-MeC_6H_4	Bz	(76)	
			4-MeC_6H_4	Ts	(70)	
			4-MeC_6H_4	Ns	(55)	
			4-*t*-BuC_6H_4	Bz	(51)	
			4-*t*-BuC_6H_4	Ts	(67)	

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

A. SULFUR (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_1			
	1. $TMSCF_3$ (1 eq), CsF (1 mol %), PhCN, 100°, 6 h 2. HCl, H_2O, rt, 3 h	 (88)	470
C_{2-7}			
RSCN	R_FX, Zn, pyridine, 5–20°, 1–3 h	RSR_F R R_F X Me CF_3 Br (16) Me n-C_8F_{17} I (54) Ph CF_3 Br (22) Ph n-C_4F_9 I (73)	642
C_{2-8}			
RSCN	R_FM, solvent	RSR_F R R_F M Solvent Temp (°) Me i-C_3F_7 K sulfolane 100 (51) Ph i-C_3F_7 K sulfolane 100 (56) 4-ClC_6H_4 i-C_3F_7 K sulfolane 100 (57) 4-$O_2NC_6H_4$ n-C_4F_9 MgI Et_2O –15 (45) Bn n-C_4F_9 MgI Et_2O –15 (50) Bn n-C_4F_9 Cu DMSO 100 (25) Bn i-C_3F_7 K sulfolane 100 (37)	1069

C_{2-6}

RSSR

CF_3I (*x* eq), TDAE (2.2 eq), DMF, –5 to 0°, 0.5 h; rt

$RSCF_3$

R	*x*	Time (h)	Conv[b] (%)	[b]	
Et	2.2	12	>98	(—)	1070
Et	4.2	2	180	(—)	1070, 386
Bu	2.2	2	>98	(—)	1070
Bu	2.2	4	>98	(—)	1070
Bu	2.2	12	>98	(—)	1070
Bu	3.2	4	130	(—)	1070
Bu	4.2	2	170	(—)	1070, 386
Bu	4.2	4	175	(—)	1070
Bu	5	4	170	(—)	1070
Bu	5	12	170	(—)	1070, 386
2-pyridyl	4.2	2	180	(—)	1070, 386
4-pyridyl	5	12	200	(—)	1070, 386
Ph	2.2	12	80	(—)	1070
Ph	5	12	186	(178)	1070, 386

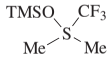
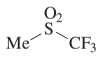
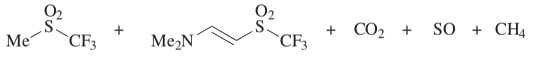
R_FI (*x* eq), TDAE (2.2 eq), DMF, 0°, 0.5 h; rt

RSR_F

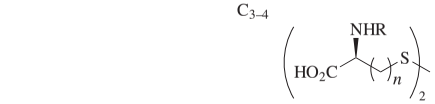
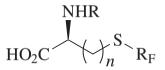
R	R_F	*x*	Time (h)	[b]	
Et	C_2F_5	4.2	2	(136)	386
Et	C_2F_5	4.2	4	(170)	
Et	C_2F_5	4.2	12	(176)	
Et	*n*-C_4F_9	2.2	12	(40)	
n-Bu	C_2F_5	4.2	12	(180)	
n-Bu	*n*-C_4F_9	2.2	12	(40)	
n-Bu	*n*-C_4F_9	4.2	12	(40)	
2-pyridyl	C_2F_5	4.2	2	(198)	
2-pyridyl	*n*-C_4F_9	2.2	12	(100)	
2-pyridyl	*n*-C_4F_9	4.2	12	(196)	
4-pyridyl	C_2F_5	4.2	2	(190)	
4-pyridyl	*n*-C_4F_9	2.2	12	(196)	
Ph	C_2F_5	4.2	2	(198)	
Ph	*n*-C_4F_9	2.2	12	(70)	
Ph	*n*-C_4F_9	4.2	12	(140)	

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

A. SULFUR (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_2			
Me_2SO	$TMSCF_3$ (1 eq), TBAF (1 eq), THF, –30°, 2 h; rt, 12 h	 (—)	397
	CuI (0.1 eq), DMF, 100–110°, 6 h	 (20–30)	252
	Cu (x eq), DMF, 100–110°	 + CO_2 + SO + CH_4 (95.5) (46) (42)	252
		I **II**	

x	Time (h)	Conv **I** (%)	**I**	Conv **II** (%)	**II**
0.16	0.75–1	—	(25)	—	(—)
0.16	1	—	(30)	—	(10)
0.16	2	24	(—)	18	(—)
0.16	4	12	(—)	32	(—)
0.16	6	5	(—)	35	(—)
0.2[d]	1	16	(—)	—	(—)

C_{3-4}							
	1. Na (4.2 eq), NH_3 (liq.), –78° 2. R_FI (2.5 eq, –78°, 20 min; to rt		R	n	R_F		1071
			H	1	CF_3	(65)	
			H	2	CF_3	(93)	
			H	2	C_2F_5	(67)	
			Boc	2	CF_3	(70)	

C_{4-8} RSSR

CF_3H (1.4–8.6 eq), base (x eq), additive (y eq), solvent, –15°, 5.5 h

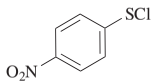
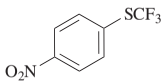
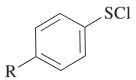
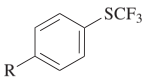
RSCF$_3$ **I** + RSCHF$_2$ **II** (—) + RSN(TMS)$_2$ **III** (—)

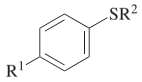
R	Base	x	Additive	y	Solvent	Conv **I** (%)	**I**	Conv **II** (%)	Conv **III** (%)	
t-Bu	$(TMS)_3N$	1.5	TMAF	1.5	DMF	23	(—)	—	—	73, 75
c-C_6H_{11}	*t*-BuOK	1.1	—	—	DMF	45	(—)	—	—	73, 75
c-C_6H_{11}	$(TMS)_3N$	1.5	TMAF	1.5	DMF	54	(50)	—	—	73, 75
c-C_6H_{11}	$(TMS)_2NLi$	1.1	$(TMS)_2NH$	0.2	DMF	2	(—)	1	—	73, 75
Ph	*t*-BuOK	1.1	—	—	DMF	82	(75)	—	—	73, 75
Ph	$(TMS)_3N$	1.5	TMAF	1.5	DMF	6	(—)	—	trace	73, 75
Ph	$(TMS)_2NLi$	1.1	$(TMS)_2NH$	0.2	DMF	4	(—)	23	46	73, 75
n-C_8H_{17}	*t*-BuOK	1.1	—	—	DMF	54	(34)	—	—	73, 75
n-C_8H_{17}	$(TMS)_3N$	1.5	TMAF	1.5	THF	66	(—)	—	—	73, 75
n-C_8H_{17}	$(TMS)_3N$	1.5	TMAF	1.5	DMF	73	(65)	—	—	73, 75
n-C_8H_{17}	$(TMS)_3N$	1.5	TBAT	1.5	DMF	60	(50)	—	—	73
n-C_8H_{17}	$(TMS)_2NLi$	1.1	$(TMS)_2NH$	0.2	DMF	51	(45)	—	—	73, 75

Catalyst (x eq), initiator (x eq), solvent RSCF$_3$ 111

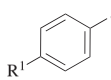
R	Catalyst	x	Initiator	Solvent	Temp (°)	Time (h)	Conv (%)	
t-Bu	**62b**	2	TBAT	DME	80	5	5	(—)
c-C_6H_{11}	**62b**	1	TBAT	DME	60	5	54	(—)
c-C_6H_{11}	**62b**	2	TBAT	DME	60	5	75	(70)
c-C_6H_{11}	**63**	2	TBAT	DME	80	5	90	(82)
Ph	**62a**	2	*t*-BuOK	THF	rt	24	87	(70)
Ph	**62b**	1	TBAT	DME	60	5	43	(—)
Ph	**62b**	2	TBAT	DME	60	5	78	(69)
Ph	**62b**	2	TBAT	DME	80	5	95	(—)
Ph	**63**	2	CsF	DME	80	5	50	(—)
Ph	**63**	2	TBAT	DME	80	5	90	(70)
4-ClC_6H_4	**62b**	2	TBAT	DME	80	5	95	(86)
n-C_8H_{17}	**62a**	2	*t*-BuOK	THF	rt	24	5	(—)
n-C_8H_{17}	**62b**	2	TBAT	DME	80	5	97	(87)

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)
A. SULFUR (*Continued*)

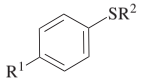
Electrophile	Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_{5-9}				
RSCN	$TMSCF_3$ (2 eq), TBAF (*x* eq), THF, 0°, time 1, rt, time 2	$RSCF_3$	R: 1-methyl-2-pyrrolyl; *x* 0.2; Time 1 (min) 5; Time 2 (h) 2.5; (32) *c*-C_6H_{11}; 0.2; 5; 2.5; (33) Ph; 0.2; 5; 2.5; (70) 4-$O_2NC_6H_4$; 0.2; 5; 2.5; (58) 2,4-$(MeO)_2C_6H_3$; 0.2; 5; 2.5; (30) Bn; 2[c]; 120; 0.5; (47) Bn; 0.2; 5; 2.5; (87) *n*-C_8H_{17}; 2[c]; 120; 0.5; (58) *n*-C_8H_{17}; 0.2; 5; 2.5; (76)	696
C_{5-7}				
RSSR	CF_3CO_2K (1.97 eq), sulfolane, 180–230°, 10 min	$RSCF_3$	R: 2-pyridyl (32) Ph (56) 4-FC_6H_4 (82) 4-ClC_6H_4 (56) 2-BrC_6H_4 (48) 4-$MeOC_6H_4$ (50) 4-MeC_6H_4 (51)	1072
C_6				
	$TMSCF_3$ (2 eq), TBAF (2 eq), THF, 0°		(14)	695
	$TMSCF_3$, TASF (1.1 eq), solvent, 0–20°, 2 h		R: Solvent H: pentane (59) Cl: pentane (72) O_2N: THF (69)	694



CF_3H (4 eq), *t*-BuOK (1.1 eq), DMF, –30°, 40 min

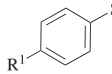


R^1	R^2		
O_2N	Cl	(60)	71
H	PhS	(80)	
H	$PhSO_2$	(90)	



I

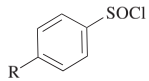
1. CF_3H (10.7 eq), *t*-BuOK (1.25 eq), DMF, –30°, 30–40 min
2. AcOH



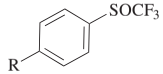
II

R^1	R^2	Conv **I** (%)	Conv **II** (%)	
H	PhS	56.5	77	76
H	$PhSO_2$	100	90	
O_2N	Cl	100	22	

$C_{6–7}$



$TMSCF_3$ (2 eq), TASF (1.1 eq), THF, –30 to 10°



R	Time (h)		
H	1.5	(52)	694
Cl	1.5	(58)	
O_2N	1	(56)	
Me	1	(61)	

$PhSO_2Cl$

CF_3CO_2Na (4 eq), CuI (1 eq), DMF, 170°, 2 h — $PhSO_2CF_3$ (83.5) — 600

n-C_4F_9I (1.2 eq), TDAE (1 eq), DME, –15 to –10°, 2 h — $PhSO_2C_4F_9$ (30) — 127

RSO_2F

Me_3SnCF_3 (*x* eq), initiator (0.1 eq), rt — RSO_2CF_3 — 161

R	*x*	Initiator	Solvent	Time (h)	
Ph	2	TASF	petrol ether	1	(92)
Ph	2	TASF	petrol ether	1.5	(96)
Ph	5	$(Et_2N)_3P^+NHMe{\bullet}HF_2^-$	THF	1	(20)
4-ClC_6H_4	2	TASF	petrol ether	1.5	(95)
3-$O_2NC_6H_4$	2	TASF	petrol ether	1.5	(70)
4-MeC_6H_4	2	TASF	petrol ether	1.5	(96)

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

A. SULFUR (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.

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

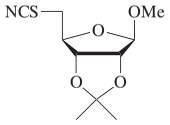
C_{6-7}

RSO_2F — $TMSCF_3$ (x eq), initiator (y eq), rt — RSO_2CF_3 — 161

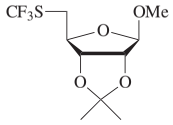
R	x	Initiator	y	Solvent	Time (h)	
Ph	1.3	TASF	0.1	petrol ether	1	(81)
Ph	2	TASF	0.1	THF	1	(98)
Ph	2	TASF	0.1	petrol ether	0.5	(100)
Ph	2	TASF	0.1	THF	1.5	(96)
Ph	2	$(Et_2N)_3P^+NHMe{\bullet}HF_2^-$	0.1	DMF	1	(10)
Ph	2	$(Et_2N)_3P^+NHMe{\bullet}HF_2^-$	0.1	THF	1	(17)
Ph	2	$(Et_2N)_3P^+NHMe{\bullet}PhO^-$	0.1	THF	1	(75)
Ph	2	$(Et_2N)_3P^+NHMe{\bullet}PhO^-$	0.1	THF	2	(93)
Ph	2	TBAF	1	THF	1	(15)
Ph	5	TBAF	1	THF	1	(90)
Ph	10	$(Et_2N)_3P^+NHMe{\bullet}HF_2^-$	0.1	THF	1	(60)
4-ClC_6H_4	2	TASF	0.1	petrol ether	1	(96)
3-$O_2NC_6H_4$	2	TASF	0.1	petrol ether	1	(73)
4-MeC_6H_4	2	TASF	0.1	petrol ether	0.5	(99)
4-MeC_6H_4	2	TASF	0.1	THF	1	(96)

C_6

$(PhSO_2)_2NF$ — i-Pr_3SiCF_3 (0.45 eq), 18-crown-6 (1 eq), t-BuOK (1 eq), THF, –78°, 1 h; to rt — $PhSO_2CF_3$ (41)[e] — 80



$TMSCF_3$ (2 eq), TBAF (0.22 eq), THF



(56) — 698

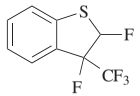
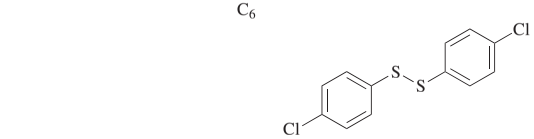
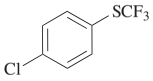
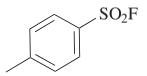
PhSSPh	*i*-Pr_3SiCF_3 (0.45 eq), 18-crown-6 (1 eq), *t*-BuOK (1 eq), THF, –78°, 1 h; to rt	$PhSCF_3$	(70)[e]					80
			x	*y*	Temp (°)	Conv CF_3H (%)	Selectivity **I** (%)[f]	
	CF_3H (*x* eq), *t*-BuOK (*y* eq), DMF, 12 h	$PhSCF_3$	0.53	0.67	46	2	63	700
		I	2.66	0.67	46	9	54	
			3.74	0.2	46	16	53	
			3.74	0.5	46	13	50	
			3.74	0.67	30	16	53	
			3.74	0.67	46	12	53	
			3.74	0.67	55	11	48	
			3.74	1	46	7	42	
			4.81	0.67	46	14	48	
	1. $PhSO_2CF_3$ (1 eq), *t*-BuOK (2 eq), DMF, –30° to rt, 0.5 h 2. H_2O	$PhSCF_3$	(87)					179
	$MeSCF_3$, *t*-BuOK	$PhSCF_3$	(2)					179
	1. **76** (1.25 eq), *t*-BuOK (4.4 eq), *n*-Bu_4NCl (4.4 eq), –30°, 0.5 h 2. Substrate (1 eq), –30°, 1.5 h; to rt	$PhSCF_3$	(73)[e]					107
	n-$C_3F_7CO_2K$ (2 eq), DMF, 130°, 6 h	$PhS(n\text{-}C_3F_7)$ +	$PhS(i\text{-}C_3F_7)$ +					701
		(—) 29% conv	(—) 33% conv	(—) 15% conv				
	1. $(EtO)_2P(O)CF_3$ (1.2 eq), PhOK (2 eq), DMF, –40°; to rt, 1 h 2. HCl	$PhSCF_3$	(26)[e]					167

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

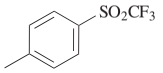
A. SULFUR (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6 	CF_3H (excess), **57** (1.5 eq), THF, –10°, 2 h	 (74)	82
RSSR	CF_3CO_2K (2 eq), DMF or NMP, 140°, 6 h	$RSCF_3$: R = Ph (84); 4-$O_2NC_6H_4$ (—)	887, 701
C_{6-8} RSSR	1. **83** (1 eq), *t*-BuOK (1 eq), THF, 0° to rt, 1 h 2. HCl, H_2O, o/n	$RSCF_3$: R = Ph Conv 67 (50); 4-ClC_6H_4 20 (—); C_8H_{17} 44 (30)	181
C_{6-7} RSSR	$C_2F_5CO_2K$ (1.2 eq), DMF, 145°, 5 h	RSC_2F_5: R = Ph (70); 4-$O_2NC_6H_4$ (42); 4-MeC_6H_4 (50)	701
C_{7-9} RSCN	CF_3H, base (*x* eq), TMAF (*y* eq), solvent, –10°, 2 h	$RSCF_3$: R = *c*-C_6H_{11}, Base *t*-BuOK, *x* 1.1, *y* 0, DMF, Conv 46 (—); R = *c*-C_6H_{11}, Base $(TMS)_3N$, *x* 1.5, *y* 0.2, DMF, Conv 5 (—); R = *c*-C_6H_{11}, Base $(TMS)_3N$, *x* 1.5, *y* 1.5, DMF, Conv 25 (—); R = 2,4-$(MeO)_2C_6H_3$, Base *t*-BuOK, *x* 1.1, *y* 0, DMF, Conv 24 (—); R = 2,4-$(MeO)_2C_6H_3$, Base $(TMS)_3N$, *x* 1.5, *y* 1.5, THF, Conv 23 (28); R = *n*-C_8H_{17}, Base $(TMS)_3N$, *x* 1.5, *y* 1.5, THF, Conv 11 (—); R = *n*-C_8H_{17}, Base $(TMS)_3N$, *x* 1.5, *y* 1.5, DMF, Conv 40 (—)	75

C_7

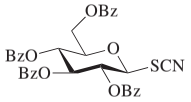


$TMSCF_3$ (2 eq), TASF (0.1 eq), pentane, 0° to rt, 2 h

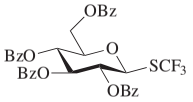


(83)

694

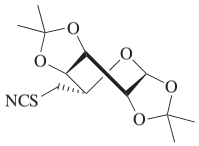


$TMSCF_3$ (2 eq), TBAF (0.22 eq), THF

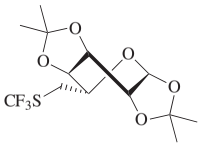


698

Temp 1 (°)	Time 1 (min)	Temp 2	Time 2 (h)	
–78	40	—	—	(76)
–25	60	rt	2	(61)
0	5	—	—	(30)

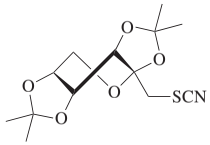


$TMSCF_3$ (2 eq), TBAF (0.22 eq), THF

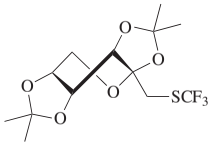


698

Temp 1 (°)	Time 1 (min)	Temp 2	Time 2 (h)	
–25	60	rt	2	(39)
0	5	rt	2	(42)



$TMSCF_3$ (2 eq), TBAF (0.22 eq), THF, 0°

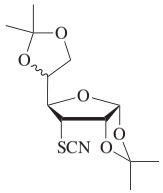
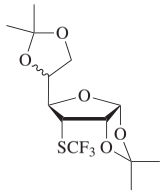
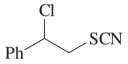
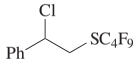
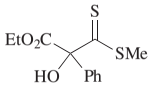
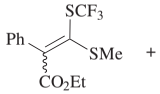
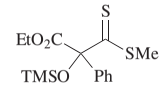
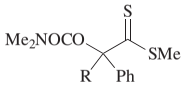
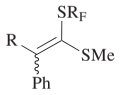


(68)

698

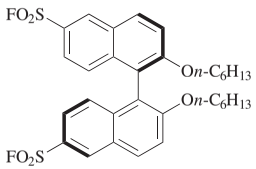
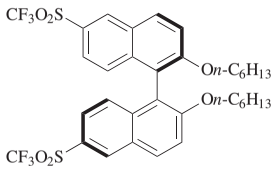
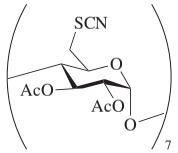
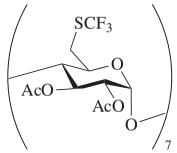
TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

A. SULFUR (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_7 	$TMSCF_3$ (2 eq), TBAF (0.22 eq), THF, 0°	 (60)	698
C_8			
BnSCN	$TMSCF_3$, TBAF, THF, rt, 2.5 h	$BnSCF_3$ (—)	697
	CF_3CO_2K (1.59 eq), DMF or NMP, 140°, 3 h	$BnSCF_3$ (36)	887
C_9 	*n*-C_4F_9MgBr, Et_2O, –15° to rt	 (22)	394
	$TMSCF_3$ (1.1 eq), TMAF (*x* eq), THF, –20° to rt, 18.5 h	 +  **I** **II**	702
		x **I** **II** 0.1 (23) (33) 0.5 (60)[g] (0)	
C_{9-10} 	$TMSR_F$ (*x* eq), CsF (*y* eq), DME, rt, 14 h; $TMSR_F$ (*z* eq), rt, 10 h		702

R	R_F	*x*	*y*	*z*		(*E*)/(*Z*)
Me	CF_3	1.02	0.18	0.47	(79)	82:18
Me	C_2F_5	1.05	0.18	0.45	(83)	86:14
Et	CF_3	1.16	0.1	0.34	(91)	87:13
Et	C_2F_5	1.09	0.18	0.41	(90)	88:12

C_9				
$Ph(CH_2)_3SS(CH_2)_3Ph$	$TMSCF_3$ (2.1 eq), TBAF (2 eq), THF, 0°; rt, 1 h	$Ph(CH_2)_3SCF_3$ (—)		1073

C_{12-14}					
$R^1R^2SF_2$	1. $TMSCF_3$ (1.97 eq), TMAF (1 eq), DME, –60°; –45°, 1 h; –65°, 40 min 2. $BF_3{\bullet}OEt_2$ (2 eq), rt	$R^1R^2\overset{+}{S}CF_3\ \ BF_4^-$	R^1 / R^2 /		704
			Ph / Ph	(75)	
			Ph / 4-$O_2NC_6H_4$	(40)	
			4-FC_6H_4 / 4-FC_6H_4	(61)	
			4-$O_2NC_6H_4$ / 4-$O_2NC_6H_4$	(35)	
			Ph / 3,5-$(CF_3)_2C_6H_3$	(42)	
C_{20}		$TMSCF_3$ (4 eq), TASF (0.2 eq), pentane, THF, 5°, 24 h		(80)	711
C_{49}		$TMSCF_3$ (*x* eq), TBAF (*y* eq), THF, rt			699

x	*y*	Time (h)	
2	cat.	2.5	(35)
2	cat.	24	(42)
4	cat.	3.5	(72)
4	4	3.5	(44)

[a] The conversion was determined by ^{19}F NMR spectroscopy.

[b] Conversions and yields are based on one equivalent of starting disulfide.

[c] The TBAF solution in THF was introduced slowly using a syringe pump.

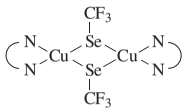
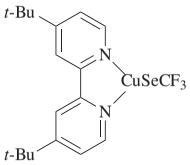
[d] The reaction was carried out in the presence of 1,4-dinitrobenzene (5 mol %).

[e] The yield was determined by ^{19}F NMR spectroscopy.

[f] Percent selectivity refers to the ratio of observed $PhSCF_3$ compared to all other products.

[g] A trifluoromethylated product of unknown structure was formed in 10% yield.

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)
B. SELENIUM

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
Se (red)	$TMSCF_3$ (1.05 eq), TMAF (1 eq), DME, –78°, 1 h; rt, o/n; –30°, 24 h	$Me_4N^+(CF_3Se)^-$ (65–70)	713
Se (red)	$TMSCF_3$ (1.12 eq), CsF (1 eq), L (2 eq), DME, –30°, 0.5 h; rt, o/n	CsL_2SeCF_3 (30) + CF_3H trace + $Se(CF_3)_2$ trace; L = 15-crown-5	714
Se	RI (0.33 eq), Cu, 220–230°, 15 h	RSeR (—) + RSeSeR (—); R = C_2F_5, *i*-C_3F_7, *n*-C_4F_9, *n*-C_6F_{13}	718
Se 1 eq	1. $TMSCF_3$ (1.5 eq), CuI (0.5 eq), KF (1.5 eq), rt, 14 h 2. Ligand (0.5 eq), MeCN, rt; –25°, 48 h		715
		Ligand 2,2'-bipyridine (41) 4,4'-dimethylbipyridine (43) **53** (59)	
	1. $TMSCF_3$ (1.5 eq), CuI (0.5 eq), KF (1.5 eq), rt, 14 h 2. dtbpy (0.5 eq), MeCN, rt; –25°, 48 h	 (46)	715
Se	CuI (10 mol %), phen (10 mol %), RX (0.5 eq), $TMSCF_3$ (1.5 eq), KF(1.5 eq), Ag_2CO_3 (2.5 eq), DMF, 80°, 16 h	$RSeCF_3$ R — X 4-$MeC_6H_4S(CH_2)_3$ — Br (94) $PhO(CH_2)_4$ — Br (91) $AcO(CH_2)_5$ — Br (80) $EtO_2C(CH_2)_5$ — Br (89) $Et_2NCO(CH_2)_5$ — Br (91) $NC(CH_2)_6$ — Br (90) $PhCH_2CH_2$ — Br (91) 4-$MeC_6H_4CH_2$ — Br (64) $Ph(CH_2)_3$ — Br (82) $Ph(CH_2)_2CHMe$ — I (89) 1-indolyl$(CH_2)_3CHMe$ — Br (85) *n*-$C_{12}H_{25}$ — Br (85)	716

		CuI (x mol %), phen (x mol %), ArI (0.5 eq), $TMSCF_3$ (1.5 eq), KF (1.5 eq), Ag_2CO_3 (2.5 eq), DMF, 80°, 16 h	$ArSeCF_3$	Ar	x	716
				2-thienyl	20 (68)	
				2-pyridyl	20 (53)	
				3,4-$Cl_2C_6H_3$	20 (84)	
				4-$O_2NC_6H_4$	30 (73)	
				2-$MeOC_6H_4$	30 (74)	
				4-$MeOC_6H_4$	20 (64)	
				2-CH_2=$CHCH_2OC_6H_4$	10 (80)[a]	
				4-MeC_6H_4	20 (80)	
				4-NCC_6H_4	20 (91)	
				2-$MeO_2CC_6H_4$	20 (80)	
				4-t-BuC_6H_4	20 (83)	
				1-$C_{10}H_7$	20 (75)	
				4-PhC_6H_4	20 (70)	
	$(MeO)_2SeO$	1. $TMSCF_3$ (1.025 eq), CsF (1 mol %), PhCN, 50°, 2 h 2. HCl, H_2O, rt, 3 h	$(CF_3)_2SeO$	(84)		470
C_{1-6}						
	RSeSeR	R_FI (x eq), TDAE (2.2 eq), DMF, 0° to rt; rt, o/n	$RSeR_F$	R / R_F / x / [b]		
				Me / CF_3 / 4.2 / (180)		386
				Me / n-C_4F_9 / 2.2 / (196)		386
				Ph / CF_3 / 2.2 / (100)		386, 1070
				Ph / CF_3 / 4.2 / (198)		386
				Ph / CF_3 / 5 / (198)		386, 1070
				Ph / C_2F_5 / 2.2 / (98)		386
				Ph / C_2F_5 / 4.2 / (198)		386
				Ph / n-C_4F_9 / 2.2 / (198)		386
				4-ClC_6H_4 / C_2F_5 / 4.2 / (198)		386

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)
B. SELENIUM (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6			
PhSeCl	CF_3Br, $(Et_2N)_3P$	$PhSeCF_3$ (—)	667
PhSeSePh	CF_3H (1.4–8.6 eq), base (*x* eq), DMF, –15°, 5.5 h	$PhSeCF_3$ **I** (—) + $PhSeCHF_2$ **II** (—) + $PhSeN(TMS)_2$ **III** (—) Base / *x* / Conv **I** (%) / **I** *t*-BuOK / 1.1 / 77 / (—) $(TMS)_3N$, TMAF / 1.5 / 61 / (47)	73, 75
	$TMSCF_3$ (2 eq), TBAF (2 eq), THF, 0°	$PhSeCF_3$ (43)	717
	$TMSCF_3$ (2 eq), TBAF (2 eq), THF, syringe pump, 0° to rt, 1 h	$PhSeCF_3$ (40)	695
	1. $(EtO)_2P(O)CF_3$ (1.2 eq), PhOK (2 eq), DMF, –40°; to rt, 1 h 2. HCl	$PhSeCF_3$ (34)[a]	167
RSeSeR	Catalyst (2 eq), initiator (2 eq), solvent	$RSeCF_3$ R / Catalyst / Initiator / Solvent / Temp (°) / Time (h) / Conv (%) Ph / **62a** / *t*-BuOK / THF / rt / 24 / 45 (35) Ph / **62b** / TBAT / DME / 80 / 5 / 92 (80) 4-ClC_6H_4 / **62b** / TBAT / DME / 80 / 5 / 75 (80)	111
C_{7-9}			
RSeCN	$TMSCF_3$ (2 eq), TBAF (0.2 eq), THF, 0°, 5 min; rt, 2.5 h	$RSeCF_3$ R Ph (58) Bn (70) *n*-C_8H_{17} (75)	696, 717

[a] The yield was determined by ^{19}F NMR spectroscopy.

[b] The yield was based on one equivalent of starting diselenide.

TABLE 31. PERFLUOROALKYL ADDITION TO GROUP 16 ELECTROPHILES (*Continued*)

C. TELLURIUM

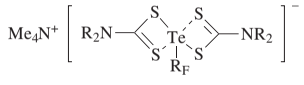
Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_0			
Te	*n*-$C_6F_{13}I$ (0.33 eq), Cu, 180°, 12 h	(*n*-$C_6F_{13})_2Te$ (41)	718
	$TMSCF_3$ (0.67 eq), TMAF (0.67 eq), DME, –60° to rt, 3 h	$Me_4N^+(CF_3Te)^-$ (60)	720
$[R_2NC(S)S]_2Te$	$TMSR_F$ (1.2 eq), TMAF (1 eq), DME, –60° to rt, 1.5 h	 (quant)	719
		R = Et, Bn; $R_F = CF_3$, C_2F_5	
C_2			
$(CF_3)_2Te$	$TMSCF_3$ (1 eq), TMAF (0.8 eq), DME or THF, –100°; –60°, 2 h	$Me_4N^+(CF_3Te)^-$ (quant)	721
$(CF_3)_2TeF_2$	1. $TMSCF_3$ (3 eq), TMAF 2. Pyridinium tetrafluoroborate	$(CF_3)_4Te$ (—)	185
$(CF_3)_2TeCl_2$	$(CF_3)_2Cd$•DME, MeCN, –10°	$(CF_3)_4Te$ (70)	722

TABLE 32. PERFLUOROALKYL ADDITION TO GROUP 17 ELECTROPHILES
A. CHLORINE

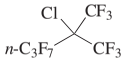
Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0 Cl_2	$Zn(CF_3)_2$•2pyridine	CF_3Cl (—)	723
	n-C_3F_7ZnI, dioxane, reflux	*n*-C_3F_7Cl (11.6)	213
	84, PhCN, 0°	 (77)	68

TABLE 32. PERFLUOROALKYL ADDITION TO GROUP 17 ELECTROPHILES (*Continued*)

B. BROMINE

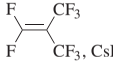
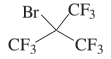
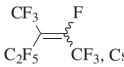
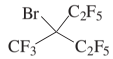
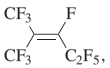
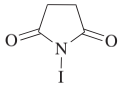
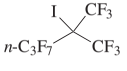
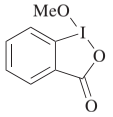
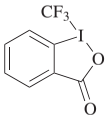
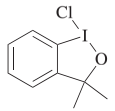
Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
Br_2	*n*-C_3F_7ZnI, dioxane, reflux	*n*-C_3F_7Br (44)	213
	 CF_3, CsF, tetraglyme, rt	 (—)	1074
	 CF_3, CsF, tetraglyme, rt	 (—)	1074
	 C_2F_5, CsF, tetraglyme, rt	 (—)	1074
	84 (1.04 eq), PhCN, 10–15°; rt, 0.5 h	 (99)	68

TABLE 32. PERFLUOROALKYL ADDITION TO GROUP 17 ELECTROPHILES (*Continued*)

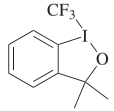
C. IODINE

Electrophile	Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_0				
I_2	*i*-Pr_3SiCF_3 (0.45 eq), 18-crown-6 (1 eq), *t*-BuOK (1 eq), THF, –78°, 1 h; to rt	CF_3I (48)[a]		80
	$(CF_3CO_2^-)_nM^{n+}$, heat	CF_3I (—)	$M^{n+} = Na^+, K^+, Ag^+, Pb^{2+}$	1075
	n-C_3F_7ZnI, dioxane, reflux	*n*-C_3F_7I (77)		213
	i-C_3F_7Ag, DMF, 1 h	*i*-C_3F_7I (42)		724
ICl	CF_3MX, DMF, rt to 40°	CF_3I (92)	M = Mg, Zn; X = Br, I	232
	$Li[Ag(CF_3)_4]$, MeCN, 20°, 2 h; 60°, 4–5 h	CF_3I (—)		1076
	**84**, THF, –30°		(—) 50% conv	68
C_1				
CF_3I	$TMSCF_3$ (1 eq), TMAF (0.9 eq), DME or THF, –100°; –60°, 2 h	$Me_4N^+[(CF_3)_2I]^-$	(quant)	721
C_7				
	$TMSCF_3$ (1.5 eq), CsF (3 mol %), MeCN, rt, 15 h		(55)	727

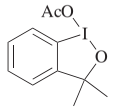
C_9



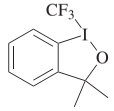
1. AcOK (1.68 eq), MeCN, rt, 1 h
2. $TMSCF_3$ (1.54 eq), TBAT (0.3 mol %), MeCN, –17°, 16 h; –12°,
3. $TMSCF_3$ (0.22 eq), –12° to rt, 3 h; rt, 3 h



(89) 725

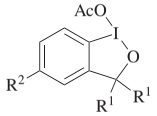


CsF (0.025 eq), $TMSCF_3$ (1.4 eq), MeCN, rt, 24 h

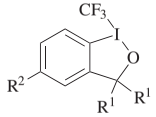


(56) 770

$C_{9–10}$



$TMSCF_3$ (*x* eq), initiator (*y* mol %), MeCN, rt



R^1	R^2	*x*	Initiator	*y*	Time (h)		
Me	H	1.56	CsF	1	16	(46)	727
CF_3	H	1.5	CsF	2	18	(50)	
CF_3	Me	1.5	TBAT	1	15	(39)	

[a] The yield was determined by ^{19}F NMR spectroscopy.

TABLE 33. PERFLUOROALKYL ADDITION TO XENON ELECTROPHILES

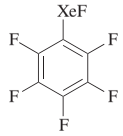
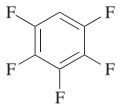
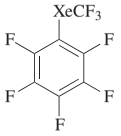
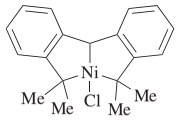
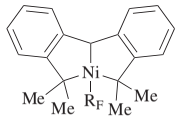
Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$Cd(CF_3)_2$ (0.18 eq), CH_2Cl_2, –78°; –40°, 10 min; –20°, 10 min; –10°, 10 min	 (27) +  (5.5) + CF_3H (5.5) + CF_3Cl (3.6)	730

TABLE 34. PERFLUOROALKYL ADDITION TO TRANSITION-METAL ELECTROPHILES

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
CuCl	1. *t*-BuOK (2.1 eq), DMF, rt, 0.5 h 2. HCF_3 (50 psi initial pressure), rt, 0.25 h 3. $Et_3N•3HF$ (0.33 eq)	$3CuCF_3•Et_3N•3HF$ (98)[a]	56
	1. *t*-BuOK (2.04 eq), DMF, rt, 0.5 h 2. HC_2F_5 (1.1 eq, added over 1 h), rt; rt, 1 h 3. $Et_3N•3HF$ (0.33 eq)	$3CuC_2F_5•Et_3N•3HF$ (>95)[a]	279
CuI	*i*-Pr_3SiCF_3 (0.09 eq), 18-crown-6 (0.2 eq), *t*-BuOK (0.2 eq), THF, –78°, 1 h; to rt	$CuCF_3$ (66)[a]	80
[K(DMF)]*t*-BuO_2Cu	1. CF_3H (excess), DMF, rt 2. 18-crown-6 (1.1 eq)	[K(18-crown-6)]*t*-BuO$CuCF_3$ (63)	57
$(Ph_3P)_3CuOR$	$TMSCF_3$ (*x* eq), THF, 50°, 13 h	$(Ph_3P)_3CuCF_3$ R: $(CF_3)_2CH$, *x*: 1, (92) R: Ph, *x*: 1.5, (30)	751
AgF	$TMSCF_3$, MeCN, EtCN, *n*-PrCN, *n*-BuCN, DMF, pyridine, or *N*-methylimidazole	$AgCF_3$ (—) 100% conv	154
	$TMSCF_3$, EtCN, rt, 5 min	$AgCF_3$ (—)	282
	1. Pyridine, rt, 0.25 h 2. $TMSC_2F_5$ (1.5 eq), rt, o/n	$AgC_2F_5•py$ (96)	752
AuCl	1. $TMSCF_3$ (2.25 eq), Me_4NF (2 eq), DME, –60°; to –30° 2. Substrate (1 eq), –30° to rt, o/n	$[Au(CF_3)_2]NMe_4$ (60)	754

TABLE 34. PERFLUOROALKYL ADDITION TO TRANSITION-METAL ELECTROPHILES (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_0			
$AuCl_3$	1. $TMSCF_3$ (6.6 eq), CsF (6 eq), THF, –78°, 1 h 2. Substrate (1 eq), Ph_4PBr (1 eq), –60°, 1 h; to rt, o/n	$[Au(CF_3)_2]PPh_4$ (49) + $[Au(CF_3)_4]PPh_4$ (22)	753
[AuCl(tetrahydrothiophene)]	1. $TMSCF_3$ (3.3 eq), CsF (3 eq), THF, –78°, 1 h 2. Substrate (1 eq), Ph_4PBr (1 eq), –60°, 1 h; to rt, o/n	$[Au(CF_3)_2]PPh_4$ (87)	753
$[(Ph_3P)_3RhF]$	$TMSCF_3$ (1.1 eq), benzene, 3.5 h	$[(Ph_3P)_2Rh(CF_3)(F)]$ (85)	736
	1. $TMSCF_3$ (1.06 eq), benzene, 2 h 2. Ph_3P (5.8 eq), hexanes, 2 d	$[(Ph_3P)_3Rh(CF_3)]$ (84)	736
$NiBr_2$•DME	1. $TMSCR_F$ (2.5 eq), AgF_2 (2 eq), MeCN, rt, 2 h 2. Substrate (1 eq), rt, 2 d	$[(MeCN)_2Ni(R_F)_2]$ R_F: CF_3 (90); C_2F_5 (89)	737
	1. dtbpy (1.1 eq), THF, rt, 10 min 2. CsF (4.5 eq), DMF, 5 min 3. $TMSR_F$ (*x* eq), rt, o/n	 R_F *x*: CF_3 4.6 (11); C_2F_5 4.0 (20)	738
	$TMSR_F$ (3 eq), CsF (9 eq), THF, rt, 16 h	 R_F: CF_3 (—); C_2F_5 (25)	740

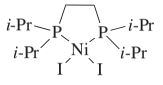
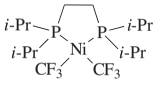
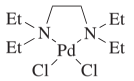
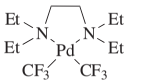
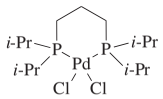
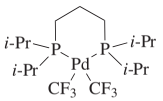
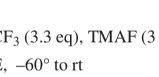
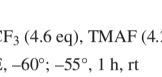
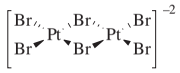
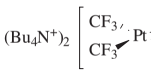
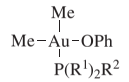
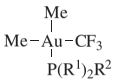
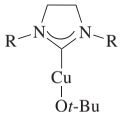
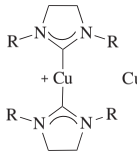
	$TMSCF_3$ (10 eq), CsF (10 eq), THF, rt, 58 h		(26)		739
	$TMSCF_3$ (5.9 eq), CsF (10 eq), CH_2Cl_2, rt, 68 h		(59)		742
	$TMSCF_3$ (7.7 eq), CsF (11 eq), CH_2Cl_2, rt, 40 h		(85)		742
	$TMSCF_3$ (3.3 eq), TMAF (3 eq), DME, –60° to rt	Me_4N^+ 		M Pd (85) Pt (92)	749
	$TMSCF_3$ (4.6 eq), TMAF (4.2 eq), DME, –60°; –55°, 1 h, rt	$(Me_4N^+)_2$ 		M Pd (82) Pt (79)	749
$(Bu_4N^+)_2$ 	1. $TMSCF_3$ (9.2 eq), CsF (8.8 eq), THF, –78°, 1 h 2. Substrate (1 eq), Bu_4NBr (2 eq), –78° to rt, o/n	$(Bu_4N^+)_2$ 	(68)		750
C_1					
$AgCF_3$	$AgCF_3$, $[Ph_3P{=}N{-}PPh_3]^+Cl^-$ (0.5 eq), EtCN, rt	$[Ph_3P{=}N{-}PPh_3]^+[Ag(CF_3)_2]^-$	(—)		282
C_2					
Me_2M	$MeTeCF_3$ (1 eq), DME (1 eq), $CFCl_3$, 24 h	$MeMCF_3$•DME (quant) +	Me_2Te (quant)	M = Cd, Zn	222

TABLE 34. PERFLUOROALKYL ADDITION TO TRANSITION-METAL ELECTROPHILES (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_2			
Me_2M	$(CF_3)_2Te$ (0.5 eq), DME (1 eq), 24 h	$MeMCF_3$•DME (quant) + Me_2Te (quant); M = Cd, Zn	222
	$(CF_3)_2Te$ (1 eq), DME (1 eq), $CFCl_3$, 0°, 24 h	$(CF_3)_2M$•DME (quant) + Me_2Te (—); M = Cd, Zn	222
	$(CF_3)_2Te$ (2 eq), DME (1 eq), 24 h	$(CF_3)_2M$•DME (quant) + $MeTeCF_3$ (78); M = Cd, Zn	222
$MeMCF_3$•DME	$MeTeCF_3$ (1.6 eq), 0°, 2 h; rt, 24 h	$(CF_3)_2M$•DME (—) + Me_2Te (—); M = Cd, Zn	222
	TMSCF$_3$ (*x* eq), THF, rt, 3 h		751
$C_{3–18}$			
$(R^1)_2R^2PAuOR^3$	TMSCF$_3$ (*x* eq), THF, –40°, 1 h; rt, 3 h	$(R^1)_2R^2PAuCF_3$	751
C_3			
	TMSCF$_3$ (2 eq), THF, rt, 21 h	 $Cu(CF_3)_2^-$ (67); R = 2,4,6-$Me_3C_6H_2$	278

R^1	R^2	*x*	Conv (%)	
Me	Me	3	—	(78)
Et	Et	3	100	(—)
Me	Ph	3	—	(91)
Ph	Me	1	100	(—)

R^1	R^2	R^3	*x*	
Me	Me	$(CF_3)_2CH$	1	(87)
Me	Ph	$(CF_3)_2CH$	1	(21)
c-C_6H_{11}	*c*-C_6H_{11}	$(CF_3)_2CH$	1	(23)
c-C_6H_{11}	*c*-C_6H_{11}	Ph	2	(32)
Ph	Ph	$(CF_3)_2CH$	2	(21)
Ph	Ph	Ph	2	(23)

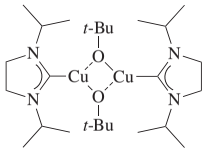
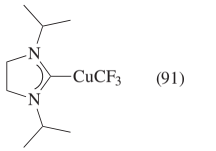
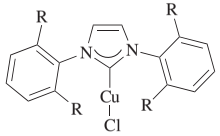
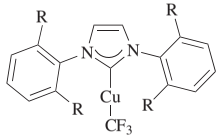
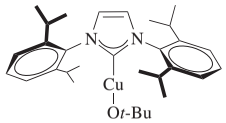
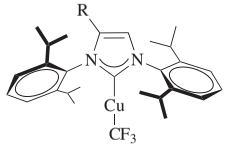
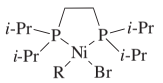
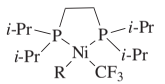
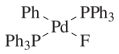
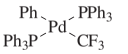
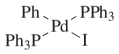
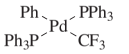
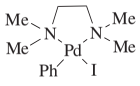
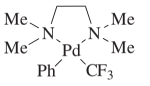
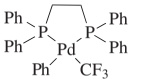
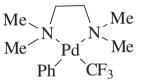
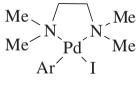
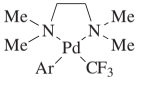
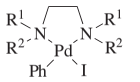
		$TMSCF_3$ (1.5 eq), THF, rt, 20 h		(91)		277
		1. *t*-BuOK (1 eq), DMF, rt, 2 h 2. $TMSCF_3$ (2 eq), rt, 16 h		(94)	R = *i*-Pr	741
		$TMSCF_3$ (2 eq), THF, rt, 24 h			**I** R= TMS; **II** R= H **I** + **II** (—), 100% conv, **I**/**II** = 82:18	277
C_4	Et_2M	$(CF_3)_2Te$ (1 eq), DME, 24 h	$(CF_3)_2M$•DME (quant)	+ Et_2Te (—)	M = Cd, Zn	222
C_6	PhHgCl	$AgCF_3$	$PhHgCF_3$	(—)		154
		$TMSCF_3$ (2 eq), CsF (2 eq), THF, rt, 14 h		R Ph (57) 4-$MeOC_6H_4$ (68) 3-MeC_6H_4 (54) 2-$C_{10}H_7$ (70)		739

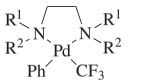
TABLE 34. PERFLUOROALKYL ADDITION TO TRANSITION-METAL ELECTROPHILES (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6 	$TMSCF_3$, benzene		(—)	743
	1. AgF (2.96 eq), benzene, sonication, rt, 5.5 h 2. $TMSCF_3$ (8.3 eq), benzene, CH_2Cl_2		(82)	743
	$TMSCF_3$ (1.9 eq), CsF (3 eq), THF, rt, 2.5 h		(91)	742
	1. $TMSCF_3$ (1.7 eq), $Ph_2P(CH_2)_2PPh_2$ (1 eq), CsF (2.95 eq), THF, rt, 1.5 h 2. $TMSCF_3$ (1.7 eq), 80 min		(71)	742
	$3CuCF_3•Et_3N•3HF$ (Table 34, C_0, 1.5 eq), DMF, NMR tube, 50°		(100)[a]	56
C_{6-7} 	$TMSCF_3$ (2 eq), CsF (3 eq), 22°, 3 h		Ar 4-FC_6H_4 (76) 2-$MeOC_6H_4$ (10) 4-$MeOC_6H_4$ (34) 2-MeC_6H_4 (59) 3-MeC_6H_4 (42) 4-MeC_6H_4 (57) 4-$CF_3C_6H_4$ (42) 4-NCC_6H_4 (51)	744 746 746 746 746 746 746 746

C_6

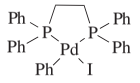


$TMSCF_3$ (2 eq), CsF (3 eq), rt

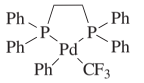


R^1	R^2	Time (h)	
Et	Et	20	(56)
–$(CH_2)_5$–		6	(67)

746

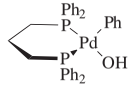


$TMSCF_3$ (1.9 eq), CsF (3 eq), THF, rt, 70 min



(69)

742



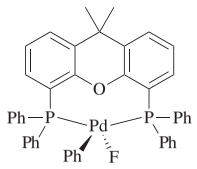
CHF_3 (10 eq), Lewis base (x eq), DMF, rt



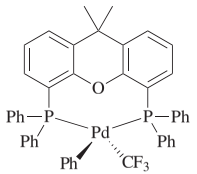
I + **II**

748

Lewis Base	x	Time (h)	**I**	**II**
none	—	24	trace	—
n-Bu_3P	1	0.5	(83)	(16)
n-Bu_3P	1	24	(49.5)	(49.5)
t-Bu_3P	1	24	(4)	—
$(c\text{-}C_6H_{11})_3P$	1	24	(41)	—
Ph_3P	1	24	(10)	—
$(4\text{-}MeC_6H_4)_3P$	1	24	(18)	—
dppp	1	24	(76)	—
pyridine	5	18	(17)	—
Et_3N	10	5	(0)	—
$Ph_3P{=}N{=}PPh_3$	1	18	(7)	—
KI	1	18	(13)	—



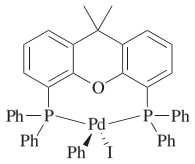
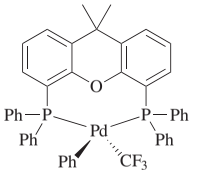
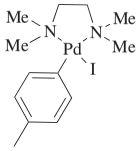
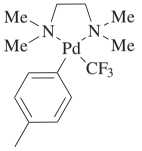
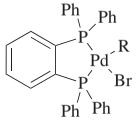
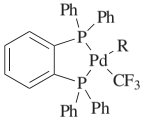
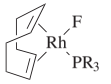
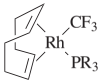
$TMSCF_3$, benzene



(—)

743

TABLE 34. PERFLUOROALKYL ADDITION TO TRANSITION-METAL ELECTROPHILES (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_6			
	1. AgF (2.35 eq), benzene, sonication, rt, 5 h 10 min 2. $TMSCF_3$ (6.7 eq), benzene	 (88)	743
$[Pd(\mu\text{-}OH)(Ph)(PPh_3)]_2$	CF_3H (10 eq), ligand L (x eq), DMF, rt, 12 h	$[(L)Pd(Ph)CF_3]$ L x dppe 2 (15) dppp 2 (81) tmeda 1.5 (1)	748
C_7			
	$TMSCF_3$ (2 eq), CsF (2.7 eq), THF, rt, 1.5 h	 (90)	742
	1. $TMSCF_3$ (2 eq), TBAT (1.05 eq), THF, rt, 5 min 2. $TMSCF_3$ (1.01 eq)	 (52.2) R = 2-MeC_6H_4	1077
C_8			
 **I**	$TMSCF_3$, rt, 24 h	 **II** (—) R **II/I** *i*-Pr 2:1 *c*-C_6H_{11} 1.5:1	733

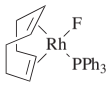
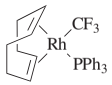
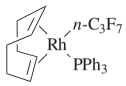
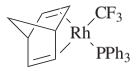
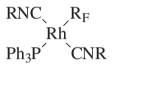
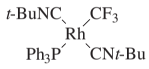
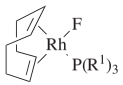
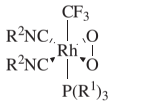
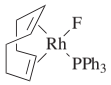
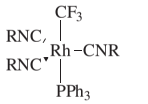
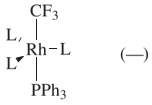
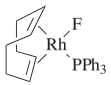
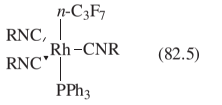
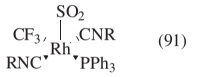
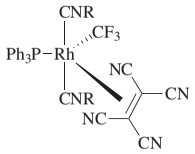
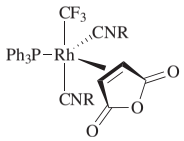
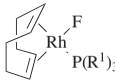
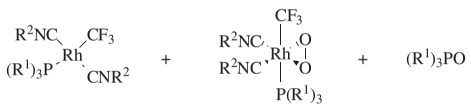
	$TMSCF_3$ (1.08 eq), THF, rt, 10–30 min		(76)	732, 733
	n-C_3F_7TMS (0.87 eq), THF, rt, 0.25 h		(93.1)	733
	1. $TMSCF_3$ (2 eq), THF, rt, 5 min 2. Norbornadiene (8.15 eq), Et_2O, 1 h		(84.5)	733
	1. $TMSR_F$ (x eq), THF 2. RNC (2 eq), rt, 1 h; Et_2O		R_F = CF_3, x = 1.76, R = 2,6-$Me_2C_6H_3$ (65.6) R_F = n-C_3F_7, x = 2, R = 2,6-$Me_2C_6H_3$ (55.7)	733
	1. $TMSCF_3$ (2 eq), THF 2. t-BuNC (2.06 eq), rt, 1 h; 0°, 0.5 h		(96.8)	733
	1. $TMSCF_3$ (x eq), THF 2. R^2NC (2 eq), rt, 1 h 3. Air, 0.5 h		R^1 = Ph, x = 2, R^2 = 2,6-$Me_2C_6H_3$ (54.5) R^1 = 4-$MeOC_6H_4$, x = 2.1, R^2 = 2,6-$Me_2C_6H_3$ (55.5)	733
	1. $TMSCF_3$ (1.5 eq), THF 2. RNC (3.08 eq), rt, 1 h; n-C_6H_{14}		(85)	R = 2,6-$Me_2C_6H_3$	733
	1. $TMSCF_3$ (2 eq), $C_6D_5CD_3$, THF 2. L, –196°		(—)	L = CO, ^{13}CO	733

TABLE 34. PERFLUOROALKYL ADDITION TO TRANSITION-METAL ELECTROPHILES (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*			
C_8			
	1. *n*-C_3F_7TMS (2 eq), THF 2. RNC (3 eq), rt, 1 h; *n*-C_5H_{12}, 0°, 10 min	 (82.5) R = 2,6-$Me_2C_6H_3$	733
	1. $TMSCF_3$ (1.82 eq), THF, rt, 5 min 2. RNC (1.95 eq), rt, 1 h 3. SO_2, THF, 0.5 h; *n*-C_5H_{12}	 (91) R = 2,6-$Me_2C_6H_3$	734
	1. $TMSCF_3$ (2 eq), RNC (2.06 eq), THF 2. TCNE (1 eq), 35 min; Et_2O	 (94) R = 2,6-$Me_2C_6H_3$	734
	1. $TMSCF_3$ (2.1 eq), RNC (2.1 eq), THF 2. Maleic anhydride (1.16 eq), rt, 1 h; Et_2O, 0°, 0.25 h	 (51) R = 2,6-$Me_2C_6H_3$	734
	1. $TMSCF_3$ (2 eq), THF, rt, 5 min 2. RNC (3.1 eq), rt, 0.75 h 3. H_2O_2 (1 eq), H_2O, rt, 0.5 h; EtOH	$CF_3Rh(CNR)_3$ (55) R = 2,6-$Me_2C_6H_3$	734
	1. $TMSCF_3$ (2 eq), THF 2. R^2NC (1.97 eq), 0°, 1 h; *n*-C_5H_{12}	 **I** (—) **I/II** = 8:1 **II** (—) **III** (—) R^1 = 4-$MeOC_6H_4$; R^2 = 2,6-$Me_2C_6H_3$	733

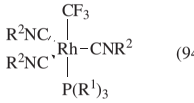
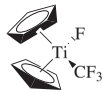
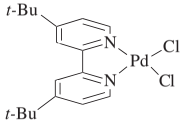
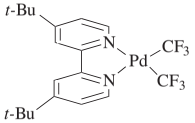
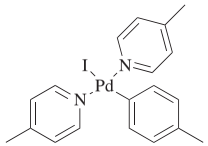
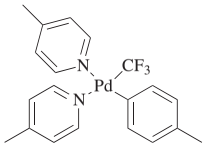
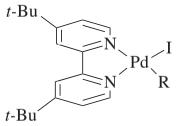
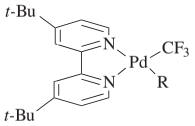
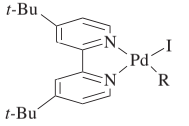
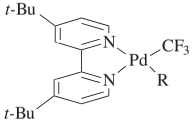
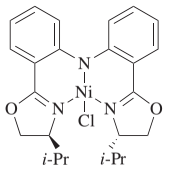
C_{10} 	1. $TMSCF_3$ (2 eq), THF 2. R^2NC (3 eq), rt, 1 h; n-C_5H_{12}		(94.5)	R^1 = 4-$MeOC_6H_4$; R^2 = 2,6-$Me_2C_6H_3$	733
	$TMSCF_3$ (10 eq), CsF (1 eq), Et_2O, THF, rt, 15 h		(60)		731, 1078
C_{16} $[Rh(\mu\text{-}OH)(cod)]_2$	$TMSCF_3$ (6.3 eq), RNC (6.18 eq), THF, 18 min; Et_2O, –30°, o/n	$CF_3Rh(CNR)_3$	(56)	R = 2,6-$Me_2C_6H_3$	734
	$TMSR_F$ (4 eq), L (6 eq), THF, rt, 2 h	$[R_FRhL_3]$	(—)[b]	R_F = CF_3, n-C_3F_7; L = $PhPMe_2$•Ph_2PMe	735
	1. $TMSR_F$ (4 eq), Ph_2PMe (6 eq), THF, rt, 2 h 2. Addend L 3. rt, 0.5–0.75 h	$[RhR_F(L)(Ph_2PMe)_3]$	R_F / Addend L / (89)	CF_3 / CO gas	735
			CF_3 / O_2 (air)	(38)	
			CF_3 / MeC_6H_4NC (2 eq)	(91)	
			n-C_3F_7 / CO gas	(73)	
	1. $TMSCF_3$ (4 eq), Ph_2PMe (6 eq), THF, rt, 2 h 2. MeI (6 eq), rt, 3.5 h	$[CF_3RhI_2(Ph_2PMe)_2Me]^-Ph_2PMe_2^+$	(47)		735
	1. $TMSCF_3$ (4 eq), Ph_2PMe (6 eq), THF, rt, 2 h 2. MeI (4 eq), rt, 0.5 h 3. Tl(acac) (2 eq), rt, 1 h	$[CF_3Rh(acac)(Ph_2PMe)_2Me]$	(52)		735
	1. $TMSR_F$ (4 eq), $PhPMe_2$ (6 eq), THF, rt, 2 h 2. MeC_6H_4CN (2 eq), rt, 1 h	$[R_FRh(MeC_6H_4CN)(PhPMe_2)_3]$	R_F / (64)	CF_3	735
			R_F / (58)	n-C_3F_7	

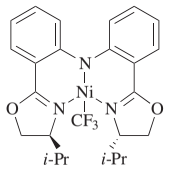
TABLE 34. PERFLUOROALKYL ADDITION TO TRANSITION-METAL ELECTROPHILES (*Continued*)

Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
Please refer to the charts preceding the tables for structures indicated by the ***bold*** *numbers.*			
C_{16}			
$[Rh(\mu\text{-}OH)(cod)]_2$	1. $TMSCF_3$ (4 eq), $PhPMe_2$ (6 eq), THF, rt, 2 h 2. MeI (4.3 eq), rt, 40 min	$[CF_3Rh(Me)(I)(PhPMe_2)_3]$ (81)	735
C_{18}			
	$TMSCF_3$ (8 eq), CsF (1 eq), CH_2Cl_2, rt, 3 d	 (61)	744
C_{19}			
	$TMSCF_3$ (4.1 eq), CsF (4.1 eq), THF, rt, 0.25 h	 (54)	745
C_{24-30}			
	$TMSCF_3$ (2 eq), CsF (3 eq), THF, 22°, 3 h		
		R: Ph (47) — 746 4-FC_6H_4 (70) — 744 2-MeC_6H_4 (45) — 746 3-MeC_6H_4 (54) — 746 4-$CF_3C_6H_4$ (63) — 744 4-NCC_6H_4 (54) — 746 4-PhC_6H_4 (58) — 744	
C_{24-25}			
	1. $TMSCF_3$ (2 eq), CsF (3 eq), THF, 22°, time 1 2. $TMSCF_3$ (2 eq), CsF (3 eq), 22°, time 2		
		R: 4-$MeOC_6H_4$ — Time 1 (h): 24 — Time 2 (h): 48 — (32) — 744 4-MeC_6H_4 — 3 — 24 — (49)	

C_{24}



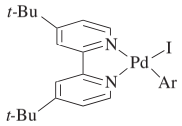
TMSCF$_3$ (6 eq), CsF (6 eq), DMF, rt, 15 h



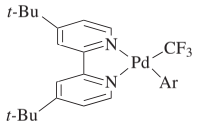
(82)

741

C_{30-32}



TMSCF$_3$ (2 eq), CsF (3 eq), THF, 3 h



Ar	Temp (°)		
2-PhC$_6$H$_4$	0	(58)	786
2-BzC$_6$H$_4$	0	(96)	786
4-BzC$_6$H$_4$	22	(51)	746
2-(3'-MeC$_6$H$_4$)(4-Me)C$_6$H$_3$	0	(39)	786

[a] The yield was determined by ^{19}F NMR spctroscopy.

[b] The complexes were not isolated but characterized by NMR spectroscopy.

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