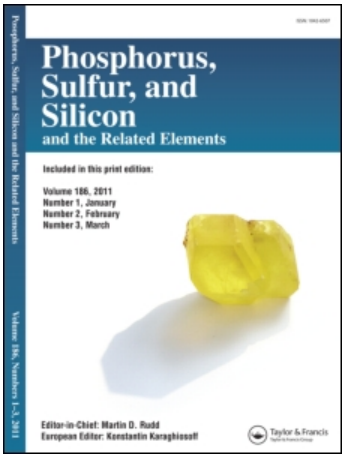

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REACTIONS OF PERFLUOROALKANE-SULFONYL CHLORIDES WITH SILYL ENOL ETHERS CATALYZED BY A RUTHENIUM(II) PHOSPHINE COMPLEX

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REACTIONS OF PERFLUOROALKANE-SULFONYL CHLORIDES WITH SILYL ENOL ETHERS CATALYZED BY A RUTHENIUM(II) PHOSPHINE COMPLEX

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Reactions of trifluoromethane- and tridecafluorohexanesulfonyl chlorides with silyl enol ethers have been investigated in the presence of a ruthenium(II) phosphine complex. Perfluoroalkylation and chlorination occurred depending on the substituent of silyl enol ether; i.e. perfluoroalkylated compound was selectively obtained in the reactions with silyl enol ether possessing an electron-withdrawing group, on the other hand, chlorinated compounds selectively formed in the reaction with a silyl enol ether possessing electron-donating group.

Keywords: Perfluoroalkanesulfonyl chloride; perfluoroalkylation; ruthenium(II) phosphine complex

INTRODUCTION

Recently, we reported that the reaction of alkane- and arenesulfonyl chlorides with alkene in the presence of a ruthenium(II) phosphine complex gave corresponding 1:1 adduct in high yield.[1] On the other hand, the reaction of perfluoroalkanesulfonyl chloride with alkene under similar conditions afforded 1:1 adduct with extrusion of sulfur dioxide in high yield, and therefore the reaction was found to be a convenient and an excellent method for the introduction of perfluoroalkyl group into an alkene.[2] In the course of our studies on the ruthenium(II) catalyzed reactions of various sulfonyl chlorides with alkenes, we found that the reaction of alkane- and arenesulfonyl chlorides with silyl enol ethers in the presence of a ruthenium(II) complex gave β-keto sulfones in high yields.[3]

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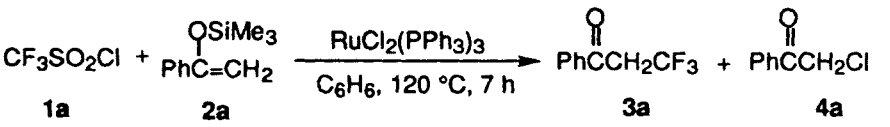


1a **2a** **3a** **4a**

Now, we found the reactions of perfluoroalkanesulfonyl chloride with silyl enol ethers catalyzed by the ruthenium(II) complex gave perfluoroalkylated compounds at the α-position of the precursor, carbonyl compound, of corresponding silyl enol ether in the case where the aromatic ring possesses an electron-withdrawing group, and the results are described herein.

RESULTS AND DISCUSSION

When a solution of trifluoromethanesulfonyl chloride (**1a**) (2.0 mmol), 1-trimethylsiloxy-1-phenylethene (**2a**) (4.0 mmol), and dichlorotris-(triphenylphosphine)ruthenium(II) (0.02 mmol) in benzene (4.0 cm^3) was degassed and heated at 120 °C for 7 h, the reaction proceeded smoothly, afforded 1-phenyl-3,3,3-trifluoro-1-propanone (**3a**) in 58% yield together with chlorinated compound, phenacyl chloride (**4a**) in 13% yield. No such 1:1 adduct as 1-chloro-2-trifluoromethanesulfonyl-1-trimethylsiloxy-1-phenylethane or 1-chloro-3,3,3-trifluoro-1-trimethylsiloxy-1-phenylpropane was found in the reaction products.

Product **3a** can be regarded as the substituted compound of an α-hydrogen of acetophenone, which is a precursor of silyl enol ether **2a**, by a trifluoromethyl group, and the reaction will be an excellent method for the introduction of trifluoromethyl group at an α-position of various carbonyl compounds. Recently, much attention has been paid to a method of introducing a perfluoroalkyl group into a carbonyl compound. Several papers have reported, however, the methods have some drawbacks and there is still a subject of much research for an efficient new synthetic method preparing perfluoroalkylated compounds from carbonyl compounds such as aldehydes, ketones, and esters.[4] Then, further reactions of trifluoromethanesulfonyl chloride with several silyl enol ethers in the presence of a ruthenium(II) phosphine complex were carried out to investigate the scope and limitation of this perfluoroalkylation reaction toward the synthetic application. The results are summarized in Table I.

As shown in Table I, the reactions of **1a** with 1-(4′-chlorophenyl)-1-trimethylsiloxyethene (**2e**) and 1-(4′-nitrophenyl)-1-trimethylsiloxyethene (**2f**) under similar conditions afforded corresponding fluoroalkylated compounds **3c** and **3d**, respectively, in moderate yield. On the other hand, the reactions of **1a** with 1-

TABLE I Reactions of trifluoromethanesulfonyl chloride (**1a**) with silyl enol ethers (**2**) in the presence of a Ru(II) catalyst

Ar in 2		*Products*		*Yields*[a]*/%*	
2a	Ph	**3a**	58 (78)	**4a**	13
2b	*p*-$MeOC_6H_4$	—	0	**4b**	85
2c	*p*-MeC_6H_4	—	0	**4c**	93
2d	*p*-FC_6H_4	**3b**	24 (33)	**4d**	19
2e	*p*-ClC_6H_4	**3c**	51	**4e**	15
2f	*p*-$NO_2C_6H_4$	**3d**	55	—	0

[a]Isolated yields. In parentheses are GC yields.

(4′-methoxyphenyl)-1-trimethylsiloxyethene (**2b**) and 1-(4′-tolyl)-1-trimethylsiloxyethene (**2c**) under similar conditions afforded 4-methoxyphenacyl chloride (**4b**) and 4-methylphenacyl chloride (**4c**) in 85% and 93% yields, respectively, and no expected trifluoromethylated compound was found.

The ruthenium(II) catalyzed reactions of **1a** with several silyl enol ethers possessing carbon-carbon double bond at inner position were also investigated under similar conditions. The reactions of **1a** with 1-phenyl-1-trimethylsiloxy-1-propene (**5a**), 1-trimethylsiloxy-3-phenyl-1-propene (**5b**), and 4-*tert*-butyl-1-trimethylsiloxy-1-cyclohexene (**5c**) under similar conditions afforded trifluoromethylated compounds 2-benzoyl-1,1,1-trifluoropropane (**6a**), 2-trifluoromethyl-3-phenylpropanal (**6b**), and 4-*tert*-butyl-2-trifluoromethylcyclohexanone (**6c**) although the yields were not well. On the other hand, the reactions of **1a** with 1-trimethylsiloxy-1-indene (**5d**), *E*-1-phenyl-3-trimethylsiloxy-1,3-butadiene (**5e**), and 1-methoxy-1-trimethylsiloxy-2-phenylethene (**5f**) under similar conditions afforded corresponding chlorinated compounds **7c**, **7d**, and **7e**, respectively, and no expected trifluoromethylated compound was found. The results are shown in Table II.

The reactions of tridecafluorohexanesulfonyl chloride (**1b**) with silyl enol ethers were also investigated in the presence of the ruthenium(II) complex under similar conditions. The results are summarized in Table III. The reaction of **1b** with 1-trimethylsiloxy-1-phenylethene (**2a**) formed 1-phenyl-3,4,4,5,5,6,6,-7,7,8,8,8-dodecafluorooct-2-en-1-one (**8a**) and phenacyl chloride (**4a**) in 11% and 62% yields, respectively. In this case, chlorination occurred preferentially to the perfluoroalkylation. On the other hand, perfluoroalkylation occurred selectively in the reaction of **1b** with 1-(4′-chlorophenyl)-1-trimethylsiloxyethene

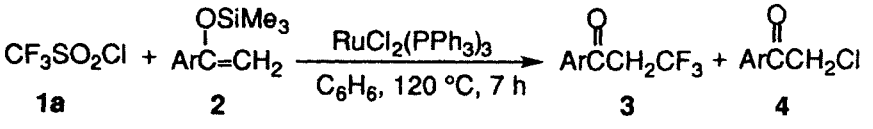
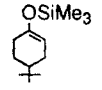
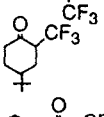
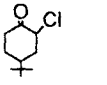
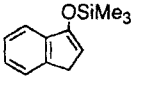
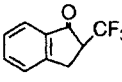
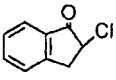


TABLE II Reactions of trifluoromethanesulfonyl chloride (**1a**) with silyl enol ethers (**5**) in the presence of a Ru(II) catalyst

	Substrates	Products	Yields[a] / %		
5a	$PhC(OSiMe_3)=CHCH_3$	$PhCOCH(CF_3)CH_3$	**6a** 28	$PhCOCHClCH_3$	**7a** 19
5b	$PhCH_2CH=CH(OSiMe_3)$	$PhCH_2CH(CF_3)CHO$	**6b** 35	$PhCH_2CHClCHO$	— 0
5c			**6c** 43[b]		**7b** Trace
5d			— 0		**7c** 83
5e	$PhCH=CHC(OSiMe_3)=CH_2$	$PhCH=CHCOCH_2CF_3$	— 0	$PhCH=CHCOCH_2Cl$	**7d** 69
5f	$PhCH=C(OSiMe_3)OCH_3$	$PhCH(CF_3)COCH_3$	— 0	$PhCH(Cl)COCH_3$	**7e** 62

a) Isolated yields. b) GC yield.

(**2e**) to give 1-(4′-chlorophenyl)-3,4,4,5,5,6,6,7,7,8,8,8-dodecafluorooct-2-en-1-one (**8b**) in 56% yield, and the chlorination product, 4-chlorophenacyl chloride (**4e**) formed in low yield (24%). The reaction of **1b** with 1-trimethylsiloxy-1-(4′-nitrophenyl)ethene (**2f**) formed only perfluoroalkylation product, 1-(4′-nitrophenyl)-3,4,4,5,5,6,6,7,7,8,8,8-dodecafluorooct-2-en-1-one (**8c**) in 72% yield, and no chlorination product, 4-nitrophenacyl chloride was found. The results show that perfluoroalkylation selectively occurs when a silyl enol ether possesses a strong electron-withdrawing substituent on the aromatic nucleus. Product **8** may be formed by dehydrofluorination of 1:1 adduct, 1-aryl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-one (**9**) once formed under the reaction conditions. The α-hydrogen of carbonyl compound **8** may be fairly acidic due to the adjacent very strong electron-withdrawing perfluorohexyl group, and hence dehydrofluorination by β-elimination will easily occur under the reaction conditions. Previously, we found that dehydrochlorination of *E*-2-chloro-2-(4′-

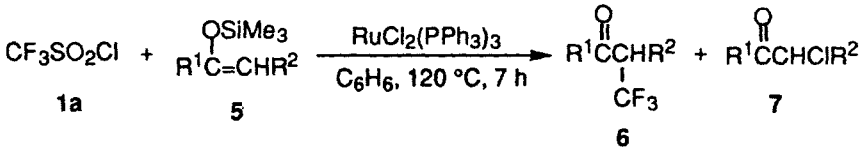


TABLE III Reactions of tridecafluorohexanesulfonyl chloride (**1b**) with silyl enol ethers (**2**) in the presence of a Ru(II) catalyst

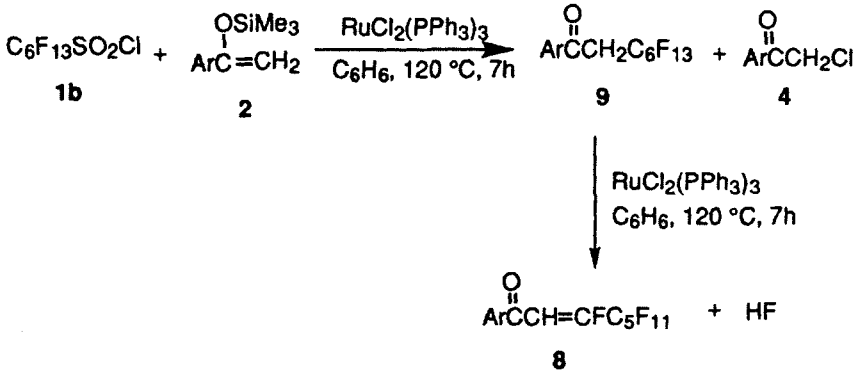
Ar in 2	*Products*	*Yields*[a]*/%*
2a Ph	**8a** 11	**4a** 62
2e *p*-ClC_6H_4	**8b** 56	**4e** 24
2f *p*-$NO_2C_6H_4$	**8c** 72	— 0

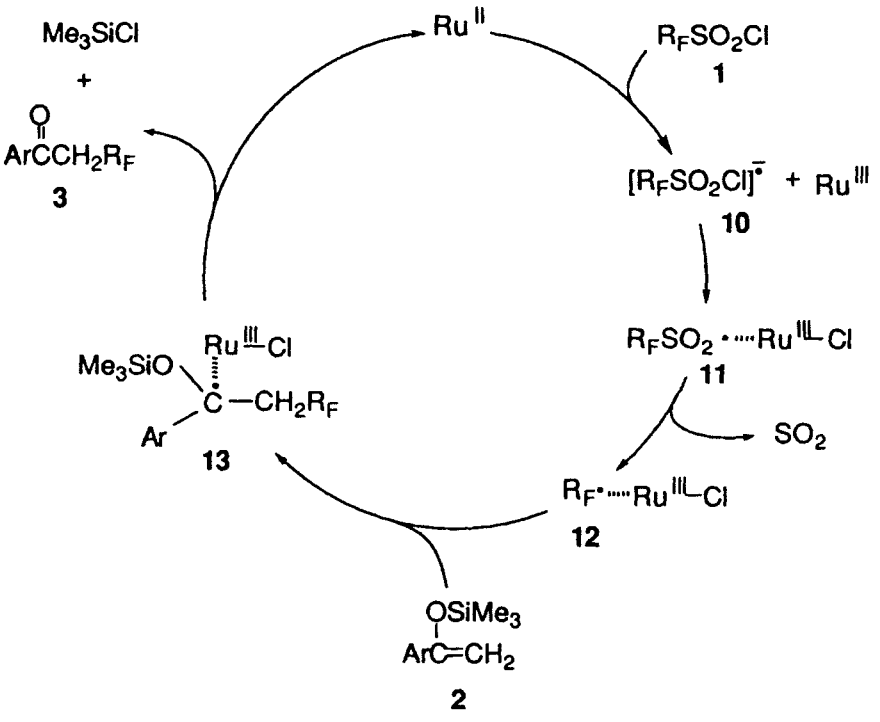
[a]Isolated yields.

tolyl)ethyl styryl sulfone occurred in the presence of dichlorotris(triphenylphosphine)ruthenium(II) giving *E,E*-2-(4′-tolyl)vinyl styryl sulfone.[5]

A plausible reaction mechanism for the ruthenium(II) catalyzed reactions of sulfonyl chloride **1** with silyl enol ether **2** is given in Scheme 1. The redox-transfer reaction between sulfonyl chloride **1** and the ruthenium(II) catalyst affords anion radical **10** of compound **1**, which cleaves homolytically to give sulfonyl radical **11** and Ru^{III}-Cl. Sulfonyl radical **11** releases sulfur dioxide giving perfluoroalkyl radical **12** which adds to the carbon-carbon double bond of silyl enol ether **2** to give carbon radical **13**. Carbon radical **13** affords perfluoroalkylated compound **3** and trimethylchlorosilane, and the ruthenium(II) catalyst is regenerated. The radicals **11**, **12**, and **13** are considered to be confined in the coordination sphere of the ruthenium catalyst.[6]

Two pathways are plausible for the formation of **3** and trimethylchlorosilane from radical intermediate **13**. One is the chlorine abstraction which bonded with ruthenium by carbon radical in **13a** ($R_F = C_6F_{13}$, Ar = Ph) in the coordination sphere giving 1:1 adduct, 1-chloro-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-trimethylsiloxy-1-phenylocatane (**14a**) and ruthenium(II) complex. The formation of adduct **14** will be plausible since Uchimoto *et al.* reported that the radical reaction of perfluorohexyl iodide with 1-trimethylsiloxy-1-cyclohexene in the

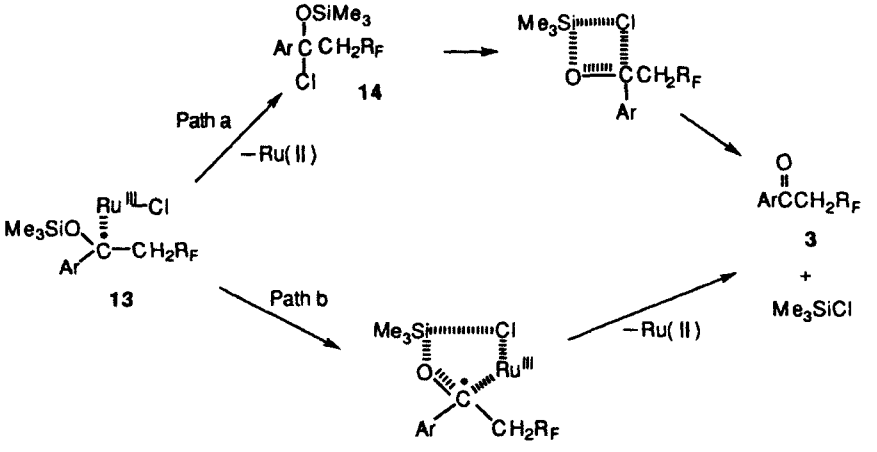




SCHEME 1

presence of triethylborane gave 2-perfluorohexyl-1-iodo-1-trimethylsiloxycyclohexane.[7] Adduct **14** will rapidly degradate to compound **3** and trimethylchlorosilane probably *via* a four-center type reaction since the affinity between silicon and chlorine atoms is strong and the reaction among these atoms may occur very easily (path a in Scheme 2). The other mechanism is a direct reaction between silicon and chlorine atoms in **13** *via* a five-member ring transition state without forming adduct **14** (path b), since radical intermediate **13** is considered to be confined in the coordination sphere of the ruthenium complex, and therefore such a five-membered transition state will easily form. The fact that no adduct **14** (Ar = Ph, $R_F = CF_3$) was found in the reaction mixture in the ruthenium(II) catalyzed reaction of **1a** with **2a** means that either adduct **14** eliminates trimethylchlorosilane very rapidly under the reaction conditions (path a) or **3** is formed directly from **13** *via* the 5-center transition state (path b).

If we assume that **14** is formed, when the reaction of sulfonyl chloride **1b** with silyl enol ether **2a** is carried out in the presence of a base, the resulting 1:1 adduct, 1-chloro-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-trimethylsiloxy-1-



SCHEME 2

phenyloctane (**14a**) is expected to be dehydrochlorinated giving 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-trimethylsiloxy-1-phenyl-1-octene together with dehydrofluorinated compound **8a**. However, no such product was found when the ruthenium(II) catalyzed reaction of **1b** with **2a** was carried out in the presence of 2,6-di-*tert*-butylpyridine, and **8a** was obtained as the sole product. Therefore, path b is more reasonable in the ruthenium(II) catalyzed reaction.

The chlorinated compound **4** is considered to be formed by a non catalytic reaction as follows. The chlorine atom and sulfonyl moiety of trifluoromethanesulfonyl chloride (**1a**) are polarized to $\delta+$ and $\delta-$, respectively, in contrast to ordinary alkane- and arenesulfonyl chlorides since the trifluoromethyl group is very strong electron-withdrawing group. Therefore, a nucleophilic attack may occur on the chlorine atom of trifluoromethanesulfonyl chloride (**1a**) by the π-electron of the carbon-carbon double bond in the silyl enol ether possessing an electron-donating group giving phenacyl chloride derivatives (**4**). However, such a reaction does not occur when the aromatic nucleus of the silyl enol ether possesses a strong electron-withdrawing group; i.e. in this case the π-electrons of carbon-carbon double bond in the silyl enol ether has insufficient nucleophilic ability to attack the chlorine atom of **1a**.

In fact, it is reported that trifluoromethanesulfonyl chloride (**1a**) acts as an electrophilic chlorinating reagent; i.e. Hakimelahi and Just reported that 2-ethoxycarbonyl-γ-butyrolactone was chlorinated by trifluoromethanesulfonyl chloride (**1a**) in the presence of triethylamine.[8] Moreover, nucleophilic attack by π-electrons of the silyl enol ether on the chlorine atom of sulfuryl chloride giving α-chloro ketones is reported by Olah *et al.*[9]. These findings support that chlorinated compound **4** is obtained by a nucleophilic attack with silyl enol ethers on the chlorine atom of trifluoromethanesulfonyl chloride.

EXPERIMENTAL

Melting points were determined on a Yamato MP21 apparatus and are uncorrected. IR spectra were determined on a JASCO A-100 IR spectrophotometer with samples either neat liquid or KBr disks. ^{1}H and ^{13}C NMR spectra were determined on a JEOL JNM-EX 400 FT NMR spectrometer at 400 and 100 MHz, respectively, using Me_4 Si as an internal standard. ^{19}F NMR spectra were taken on a JEOL JNM-EX 400 FT NMR spectrometer at 376 MHz using $CFCl_3$ as an external standard. Mass spectra were measured on a JEOL JMS-AX 500 spectrometer by electron impact (EI) at 70 eV. Gas-liquid chromatography (GLC) were performed using a Hitachi G-3000 gas chromatograph with OV-1 (10%) 25 m capillary column. Gel-permeation chromatography (GPC) was performed using a JAI-LC-08 and JAI-LC-908 liquid chromatograph with two JAI-GEL-1H columns (20 mm × 600 mm) with chloroform as eluent.

All solvents were distilled and stored under nitrogen. *p*-Methoxyacetophenone and *p*-fluoroacetophenone of Wako Chemicals, *p*-methylacetophenone, *p*-nitroacetophenone, 3-phenylpropionaldehyde, and methyl phenylacetate of Nakarai Chemicals, *p*-chloroacetophenone, propiophenone, 4-*tert*-butylcyclohexane, 1-indanone, and 4-phenyl-3-buten-2-one of Tokyo Kasei Chemicals, and trimethylchlorosilane of Shinetsu Chemical Industry were used without further purification for the preparation of corresponding silyl enol ethers. 1-Trimethylsiloxy-1-phenylethene (**2a**) from Aldrich Chemicals was used without further purification. Trifluoromethanesulfonyl chloride from Aldrich Chemicals, tridecafluorohexanesulfonyl chloride from Hydrus Chemicals were used without further purification. Dichlorotris(triphenylphosphine)ruthenium(II) was prepared by the method described in the literature, mp 123 °C.[10]

General procedure for the preparation of silyl enol ethers[11]

To a solution of ketone (0.5 mol) in DMF (32 mL) was added triethylamine (19.5 g, 192 mmol) and then trimethylchlorosilane (10.4 g, 96 mmol) under nitrogen, and the solution was refluxed with stirring for 48 h. The organic com-

ponent was extracted with pentane (80 mL), and the extract was washed with a saturated potassium bicarbonate solution (80 mL) 3 times, with water (80 mL) 3 times, with 1.5 N hydrochloric acid (80 mL) 2 times, with water (80 mL), with saturated potassium bicarbonate solution (80 mL) 2 times, with water (80 mL) 2 times, and with brime (80 mL). The solvent was removed under reduced pressure, and the residual oil of silyl enol ether was purified by distillation. Yields and boiling points of silyl enol ethers are as follows: 1-(4′-methoxyphenyl)-1-trimethylsiloxyethene (**2b**, yield 50%, bp 88 °C/0.50 mmHg); 1-trimethylsiloxy-1-(4′-tolyl)ethene (**2c**, yield 67%, bp 59–60 °C/0.45 mmHg); 1-(4′-fluorophenyl)-1-trimethylsiloxyethene (**2d**, yield 59%, bp 43–46 °C/0.50 mmHg); 1-(4′-chlorophenyl)-1-trimethylsiloxyethene (**2e**, yield 42%, bp 54–56 °C/0.8 mmHg); 1-trimethylsiloxy-1-(4′-nitrophenyl)ethene (**2f**, yield 34%, bp 95–97 °C/0.45 mmHg); 1-phenyl-1-trimethylsiloxy-1-propene (**5a**, yield 36%, bp 38.5–39.5 °C/0.15 mmHg); 3-phenyl-1-trimethylsiloxy-1-propene (**5b**, yield 65%, bp 59–61 °C/0.45 mmHg); 4-*tert*-butyl-1-trimethylsiloxy-1-cyclohexene (**5c**, yield 41%, bp 73 °C/4.2 mmHg); 1-trimethylsiloxy-1-indene (**5d**, yield 52%, bp 76–77 °C/0.5 mmHg).

E-1-Phenyl-3-trimethylsiloxy-1,3-butadiene[12] (**5e**, yield 77%, bp 66 °C 0.16 mmHg) and 1-methoxy-1-trimethylsiloxy-2-phenylethene[13] (**5f**, yield 41%, bp 63.5–64.5 °C/0.25 mmHg) were prepared according to the procedures in the literatures.

General procedure for the reaction of sulfonyl chloride with silyl enol ethers

A solution containing sulfonyl chloride **1** (2.0 mmol), silyl enol ether **2** (4.0 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in dry benzene (4.0 mL) was degassed by a freeze-pump-thaw cycle, sealed in an ampoule, and heated at 120 °C for 7 h. The reaction mixture was subjected to column chromatography on Merck 7734 silica-gel 60 with hexane-dichloromethane (2:1) or hexane-benzene (1:1) as eluent. The product was further purified by recrystallization from dichloromethane-hexane and identified by IR, NMR, and MS spectroscopy. The physical and spectral data for the compounds obtained are as follows.

3,3,3-Trifluoro-1-phenyl-1-propanone (3a)

colorless needles; mp 35.8–36.4 °C (24 °C[14]); IR (KBr) 3000, 2950, 1700, and 1260 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.80 (2H, q, J = 10.0 Hz), 7.51 (2H, dd, J = 8.3 and 7.3 Hz), 7.64 (1H, t, J = 7.3 Hz), and 7.94 (2H, d, J =

8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 43.2, 124.1, 128.4, 129.0, 134.3, 135.9, and 189.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 63.2 (3F, t, J = 10.0 Hz); MS (EI) *m/z* 188 (M^+), 105, and 69.

3,3,3-Trifluoro-1-(4'-fluorophenyl)-1-propanone (3b)

colorless prisms; mp 31.5–32.4 °C; IR (KBr) 3100, 2950, 1700, 1600, 1520, 1370, and 1230 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.78 (2H, q, J = 10.0 Hz), 7.19 (2H, dd, J = 8.3 and 8.3 Hz), and 7.98 (2H, dd, J = 8.3 and 3.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 41.8, 115.9, 123.5, 130.8, 132.0, 166.0, and 187.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 62.4 (3F, t, J = 10.0 Hz) and 103.3 (1F, m); MS (EI) *m/z* 206 (M^+), 123, and 95; HRMS, Found: *m/z* 206.0372. Calcd for $C_9H_5OF_4$: M, 206.0355.

1-(4'-Chlorophenyl)-3,3,3-trifluoro-1-propanone (3c)

colorless needles; mp 53.8–54.3 °C (39 °C[14]); IR (KBr) 3080, 3000, 1700, 1600, 1430, 1370, 1270, and 1230 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.77 (2H, q, J = 10.0 Hz), 7.49 (2H, d, J = 8.6 Hz), and 7.88 (2H, d, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 42.1, 123.8, 129.3, 129.7, 134.1, 140.9, and 188.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 63.2 (3F, t, J = 10.0 Hz); MS (EI) *m/z* 222 (M^+), 141, 113, and 69.

3,3,3-Trifluoro-1-(4'-nitrophenyl)-1-propanone (3d)

pale yellow needles; mp 99.0–99.8 °C (103 °C[14]); IR (KBr) 2950, 1700, 1600, 1520, 1420, 1370, 1350, 1320, 1270, and 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.86 (2H, q, J = 10.6 Hz), 8.12 (2H, d, J = 8.6 Hz), and 8.37 (2H, d, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 42.7, 123.5, 124.2, 129.5, 139.9, 150.9, and 188.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 63.2 (3F, t, J = 10.6 Hz); MS (EI) *m/z* 233 (M^+), 217, 187, 151, and 69.

Phenacyl chloride (4a)

mp 51.0–51.8 °C (54 °C[15]); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.67 (2H, s), 7.50 (2H, dd, J = 7.3 and 7.3 Hz), 7.62 (1H, t, J = 7.3 Hz), and 7.96 (2H, d, J = 7.3 Hz); MS (EI) *m/z* 154 (M^+), 105, and 77.

4-Methoxyphenacyl chloride (4b)

colorless needles; mp 97.9–98.5 °C (56–57 °C[15]); IR (KBr) 3020, 3000, 2950, 1700, and 1600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.88 (3H, s), 4.65 (2H, s), 6.96 (2H, d, J = 5.3 Hz), and 7.94 (2H, d, J = 5.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 45.3, 55.5, 113.7, 113.8, 126.9, 130.6, and 189.3; MS (EI) *m/z* 184 (M^+), 135, and 77.

4-Methylphenacyl chloride (4c)

mp 53.1–53.8 °C (56–57 °C[16]); ^1H NMR (400 MHz, $CDCl_3$) δ = 2.43 (3H, s), 4.69 (2H, s), 7.30 (2H, d, J = 8.0 Hz), and 7.86 (2H, d, J = 8.0 Hz); MS (EI) *m/z* 168 (M^+), 119, 105, and 91.

4-Fluorophenacyl chloride (4d)

mp 42.7–43.6 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.67 (2H, s), 7.18 (2H, dd, J = 8.8 and 8.8 Hz), and 8.01 (2H, dd, J = 8.8 and 5.1 Hz); MS (EI) *m/z* 172 (M^+), 137, 124, and 96; HRMS, Found: *m/z* 172.0075. Calcd for C_8H_6OFCl: M, 172.0091.

4-Chlorophenacyl chloride (4e)

mp 96.8–97.6 °C (102–103 °C[16]); ^1H NMR (400 MHz, $CDCl_3$) δ = 4.66 (2H, s), 7.48 (2H, d, J = 8.6 Hz), and 7.91 (2H, d, J = 8.6 Hz); MS (EI) *m/z* 188 (M^+, ^{35}Cl), 141, and 111.

2-Benzoyl-1,1,1-trifluoropropane[17] (6a)

colorless oil; IR (KBr) 2900, 1690, 1600, 1460, 1450, 1380, 1260, 1220, 1160, and 1130 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.48 (3H, d, J = 7.8 Hz), 4.26 (2H, qq, J = 9.1 and 7.8 Hz), and 7.36–7.97 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.7, 44.2, 125.3, 128.6, 128.9, 134.0, 135.6, and 194.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 68.71 (3F, d, J = 9.1 Hz); MS (EI) *m/z* 202 (M^+), 105, 77 and 69.

2-Trifluoromethyl-3-phenylpropanal (6b)

colorless oil; IR (neat) 3027, 2924, 1734, 1602, 1496, 1454, 1256, 1122, and 844 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.07 (1H, dd, J = 14.2 and 4.6 Hz), 3.25 (1H, dd, J = 14.2 and 9.0 Hz), 3.35–3.40 (1H, m), 7.19 (5H, m),

and 9.71 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 29.1, 57.6, 127.2, 128.2, 128.8, 128.9, 136.4, and 193.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 66.8 (3F, d, J = 9.0 Hz); MS (EI) *m/z* 202 (M^+), 132, 90, and 68; HRMS, Found: *m/z* 202.0623. Calcd for $C_{10}H_9OF_3$: M, 202.0605.

4-tert-Butyl-2-trifluoromethylcyclohexanone[18] (6c)

colorless oil; IR (neat) 2980, 1730, 1270, 1160, 1110, and 960 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.95 (9H, s), 1.50–1.62 (3H, m), 2.13–2.51 (4H, m), and 3.08 (1H, m); ^{19}F NMR (376 MHz, $CDCl_3$) δ = 70.4 (3F, s); MS (EI) *m/z* 222 (M^+), 151, and 69; HRMS, Found: *m/z* 222.1220. Calcd for $C_{11}H_{17}OF_3$: M, 222.1231.

2-Chloro-1-phenyl-1-propanone[19] (7a)

colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.75 (3H, d, J = 6.5 Hz), 5.26 (1H, q, J = 6.5 Hz), 7.50 (2H, t, J = 7.5 Hz), 7.61 (1H, t, J = 7.5 Hz), and 8.02 (2H, d, J = 7.5 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.9, 52.8, 128.7, 129.0, 133.7, 134.0, and 193.6; MS (EI) *m/z* 168 (M^+), 105, and 77.

2-Chloro-1-indanone[20] (7c)

^1H NMR (400 MHz, $CDCl_3$) δ = 3.28 (1H, dd, J = 17.6 and 3.9 Hz), 3.77 (1H, dd, J = 17.6 and 7.8 Hz), 4.55 (1H, dd, J = 7.8 and 3.9 Hz), 7.40–7.45 (2H, m), 7.64 (1H, d, J = 7.3 Hz), and 7.79 (1H, d, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 37.4, 55.6, 124.9, 126.3, 128.3, 133.7, 136.0, 150.7, and 199.2; MS (EI) *m/z* 166 (M^+), 132, and 77.

E-*1-Chloro-4-phenylbut-3-en-2-one[21] (7d)*

^1H NMR (400 MHz, $CDCl_3$) δ = 4.31 (2H, s), 6.98 (1H, d, J = 16.1 Hz), 7.43–7.60 (5H, m), and 7.71 (1H, d, J = 16.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 41.5, 121.6, 128.6, 129.0, 131.1, 133.9, 145.2, and 191.2; MS (EI) *m/z* 180 (M^+), 131, and 103.

Methyl chlorophenylacetate[22] (7e)

^1H NMR (400 MHz, $CDCl_3$) δ = 3.76 (3H, s), 5.36 (1H, s), and 7.36–7.50 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 53.2, 59.2, 128.2, 129.2, 129.6, 134.0, and 169.1; MS (EI) *m/z* 184 (M^+) and 125.

3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluoro-1-phenyloct-2-en-1-one (8a)

colorless oil; IR (neat) 3080, 1710, 1670, 1600, 1460, 1360, 1240, 1200, 1150, and 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.75 (1H, d, J = 31.7 Hz), 7.53 (2H, dd, J = 7.5 and 7.5 Hz), 7.65 (1H, t, J = 7.5 Hz), and 7.92 (2H, d, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 110.7, 128.8, 129.1, 134.5, 136.3, and 186.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 81.9, (3F, m), 113.1 (1F, m), 119.4 (2F, m), 123.8–123.9 (4F, m), and 127.3 (2F, m); MS (EI) *m/z* 418 (M^+), 399, 171, 105, and 77; HRMS, Found: *m/z* 418.0190. Calcd for $C_{14}H_6OF_{12}$: M, 418.0227.

1-(4'-Chlorophenyl)-3,4,4,5,5,6,6,7,7,8,8,8-dodecafluorooct-2-en-1-one (8b)

colorless needles, mp 32.5–33.2 °C; IR (neat) 3100, 1700, 1590, 1410, 1360, 1240, 1140, 1120, 1100, and 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.70 (1H, d, J = 31.5 Hz), 7.51 (2H, d, J = 8.5 Hz), and 7.86 (2H, d, J = 8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 110.3, 129.4, 130.9, 134.7, 141.1, and 185.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 82.0 (3F, m), 112.1 (1F, m), 119.5 (2F, m), 123.9–124.4 (4F, m), and 127.4 (2F, m); MS (EI) *m/z* 452 (M^+) and 139. Found: C, 37.21; H, 0.97%. Calcd for $C_{14}H_5OF_{12}Cl$: C, 37.15; H, 1.11%.

3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluoro-1-(4'-nitrophenyl)oct-2-en-1-one (8c)

pale yellow plates; mp 56.2–56.9 °C; IR (neat) 3120, 1710, 1660, 1620, 1550, 1360, 1260, 1240, 1210, 1150, and 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.70 (1H, d, J = 30.7 Hz), 8.08 (2H, d, J = 9.0 Hz), and 8.39 (2H, d, J = 9.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 109.4, 124.2, 129.7, 140.5, 150.8, and 184.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ = 82.0 (3F, m), 109.4 (1F, m), 119.6 (2F, q, J = 11.3 Hz), 123.6–123.8 (4F, m), and 127.3 (2F, m); MS (EI) *m/z* 463 (M^+), 417, 341, and 150. Found: C, 36.24; H, 0.94; N, 2.71%. Calcd for $C_{14}H_5O_3NF_{12}$: C, 36.23; H, 1.30; N, 3.02%.

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