Triethylborane Induced Perfluoroalkylation of Silyl Enol Ethers and Ketene Silyl Acetals with Perfluoroalkyl Iodides

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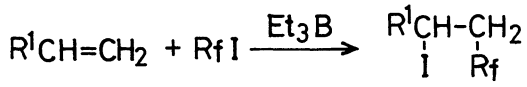
Reaction of perfluoroalkyl iodides with silyl enol ethers mediated by Et_3B in the presence of base such as 2,6-dimethylpyridine provides mixtures of perfluoroalkylated trialkylsilyl enol ethers and α-perfluoroalkylated ketones. The yield and distribution of the products heavily depend on the nature of base employed. Treatment of a reaction mixture consisting of perfluoroalkylated silyl enol ether and α-perfluoroalkylated ketone with concd HCl in THF gives α-perfluoroalkylated ketone as a single product. Reaction of ketene silyl acetals with perfluoroalkyl iodides in the absence of base affords α-perfluoroalkylated esters in excellent yields.

Recently, much attention has been paid to a method of introducing a perfluoroalkyl chain to a carbonyl compound and several reports have appeared in the literature.[1] The methods, however, have some drawbacks and there is still a need for a new method preparing perfluoroalkylated compounds from carbonyl compounds such as aldehydes, ketones, and esters. Previously we have reported that Et_3B induced the successful addition of perfluoroalkyl iodides to acetylenes and olefins (Scheme 1).[2] Here we report further exploitation of this method to (1) the reaction of perfluoroalkyl iodides with trialkylsilyl enol ethers providing perfluoroalkylated silyl enol ethers[3] and (2) the reaction of perfluoroalkyl iodides with ketene silyl acetals affording perfluoroalkylated esters.

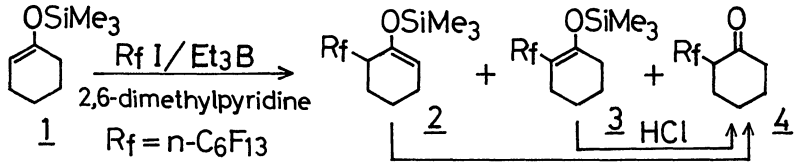


Scheme 1.

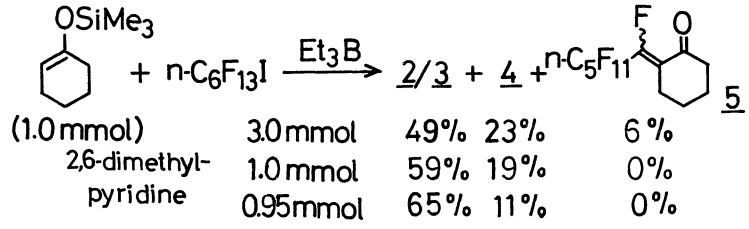
(1) The Reaction of Perfluoroalkyl Iodides with Trialkylsilyl Enol Ethers. Treatment of a hexane solution of 1-trimethylsiloxy-1-cyclohexene (**1**) and perfluorohexyl iodide with a catalytic amount of triethylborane[4] in the presence of base such as 2,6-dimethylpyridine gave a mixture of perfluoroalkylated silyl enol ether (**2** and **3**) and 2-(perfluorohexyl)cyclohexanone (**4**)[1d] in 76% combined yield (**2**+**3**/**4**=86/14, Scheme 2).

The distribution of the products heavily depends on the nature of base employed. The base and the yields of **2**+**3** (ratio of **2**/**3**) and **4** in the reaction between 1-trimethylsiloxy-1-cyclohexene (**1**) and perfluorohexyl iodide are given below: Et_3N, 47 (59/41), 26; 2,2,6,6-tetramethylpiperidine, 63 (68/32), 11; hexamethyldisilazane, 24 (0/100), 44; pyridine, 0, 20; diisopropylethylamine, 12 (65/35), 29. The amount of base also affected the distribution of the products (Scheme 3). The presence of excess base (2,6-dimethylpyridine, 3.0 mmol per 1.0 mmol of silyl enol ether) caused the formation of 2-(perfluorohexylidene)cyclohexanone **5** in 6% yield along with **2**+**3** (49%) and **4** (23%). The use of slightly deficient amount of 2,6-dimethylpyridine suppressed the formation of **5**. The representative results using 2,6-dimethylpyridine (0.95 mmol per 1.0 mmol of silyl enol ether) as a base are summarized in Table 1.

The use of triisopropylsilyl enol ether **6** instead of trimethylsilyl enol ether **1** gave better yields of perfluoroalkylated silyl enol ethers **7** and **8** with less contamination by 2-(perfluoroalkyl)cyclohexanones **4** (Runs 3 and

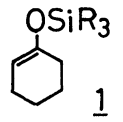
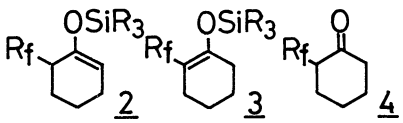
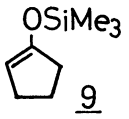
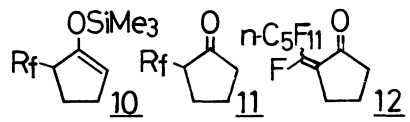
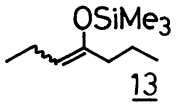
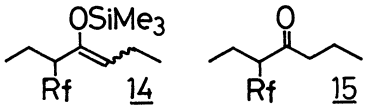
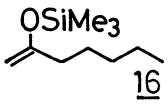
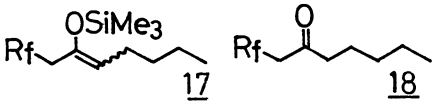
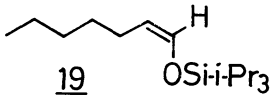
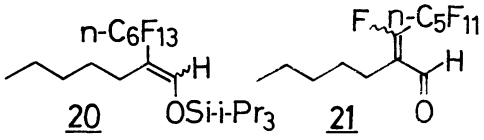


Scheme 2.



Scheme 3.

Table 1. Reaction of Silyl Enol Ether with Perfluoroalkyl Iodide[a)]

Run	Silyl enol ether		R_fI	Product (%)		
						
1		R=Me	n-$C_6F_{13}I$	44	21	11
2		R=Me	i-C_3F_7I	41	11	9
3		**6**:R=*i*-Pr	n-$C_6F_{13}I$	57 (**7**)	14 (**8**)	<5
4		R=*i*-Pr	i-C_3F_7I	47	25	<2
						
5			n-$C_6F_{13}I$	35	26	3
						
6			n-$C_6F_{13}I$	71 (E/Z=60/40)		16
7			i-C_3F_7I	66 (E/Z=70/30)		<2
						
8			n-$C_6F_{13}I$	54 (E/Z=28/72)		24
9			i-C_3F_7I	56 (E/Z=33/67)		15
						
10			n-$C_6F_{13}I$	38 (88/12)[b)]		46 (71/29)[b)]

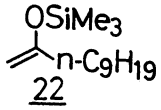
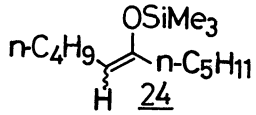
a) Silyl enol ether (2.0 mmol), perfluoroalkyl iodide (2.6 mmol), 2,6-dimethylpyridine (1.90 mmol), and triethylborane (0.4 mmol) were employed. b) Stereochemistry could not be determined.

4). Treatment of 1-trimethylsiloxy-1-cyclopentene **9** with perfluorohexyl iodide gave a mixture of 5-(perfluorohexyl)-1-trimethylsiloxy-1-cyclopentene **10**, 2-(perfluorohexyl)cyclopentanone **11**, and 2-(perfluorohexylidene)cyclopentanone **12** in 35, 26, and 3% yields, respectively. 2-(Perfluorohexyl)-1-trimethylsiloxy-1-cyclopentene was not detected in the reaction mixture. The reaction proceeded with acyclic silyl enol ether as well as cyclic silyl enol ether. In the case of silyl enol ether **13** or **16**, derived from acyclic ketone such as 4-heptanone or 2-heptanone, 5-(perfluoroalkyl)-4-trimethylsiloxy-3-heptenes **14** or 1-(perfluoroalkyl)-2-trimethylsiloxy-2-heptenes **17** was obtained as a single regioisomer as the reaction of 1-trimethylsiloxy-1-cyclopentene **9**. The other isomeric silyl enol ether (3-(perfluoroalkyl)-4-trimethylsiloxy-3-heptene or 1-(perfluoroalkyl)-2-trimethylsiloxy-1-heptene) was not observed in the reaction mixture. Reaction of silyl enol ether **19** derived from heptanal afforded a mixture of 2-(perfluoroalkyl)-1-triisopropylsiloxy-1-heptene **20** and 2-(perfluorohexylidene)heptanal **21**.

Treatment of the reaction mixture consisting of **2**, **3**, and **4** with concd hydrochloric acid in THF at 25 °C for 10 min afforded 2-(perfluoroalkyl)cyclohexanone **4** as a single product in 74% overall yield. The yields of perfluoroalkylated carbonyl compounds after acidic work-up were 78, 73, and 56% for the reaction described in Runs 6, 8, and 9.

Trifluoromethylated organic compounds are of importance from the biological point of view.[5)] Thus, we focussed our attention on trifluoromethylation of carbonyl compounds and examined the reactions of silyl

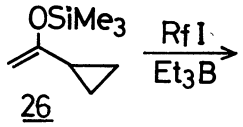
Table 2. Reaction of Silyl Enol Ether with CF_3I or CF_3CH_2I

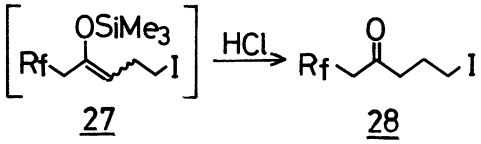
Silyl enol ether (1.0 mmol)	R–X (mmol)	Reaction time/h	Product	Y/%
 22	CF_3I (10)	40	CF_3CH_2CO–*n*-C_9H_{19} **23a**	64
	CF_3CH_2I (2)	15	$CF_3(CH_2)_2CO$–*n*-C_9H_{19} **23b**	79
 24	CF_3I (10)	48	*n*-$C_4H_9CH(CF_3)CO$–*n*-C_5H_{11} **25a**	32
	CF_3CH_2I (2)	20	*n*-$C_4H_9CH(CH_2CF_3)CO$–*n*-C_5H_{11} **25b**	4

enol ether with trifluoromethyl iodide or 2,2,2-trifluoroethyl iodide (Table 2). Treatment of terminal silyl enol ether **22** with excess trifluoromethyl iodide or 2,2,2-trifluoroethyl iodide gave 1,1,1-trifluoro-3-dodecanone **23a** or 1,1,1-trifluoro-4-tridecanone **23b** in 64 or 79% yield, respectively after quenching the reaction mixture by concd HCl. Meanwhile, the reaction of internal silyl enol ether such as **24** with CF_3I or CF_3CH_2I gave the corresponding trifluoro ketone **25a** or **25b** in poor yield.

Reaction of **26** prepared from cyclopropyl methyl ketone with perfluoroalkyl iodides followed by treatment with concd HCl provided the corresponding 5-iodo-1-(perfluoroalkyl)-2-pentanones under cleavage of cyclopropane ring.[6] The reaction proceeded without base such as 2,6-dimethylpyridine. The intermediary silyl enol ether **27b** was isolated in the reaction of **26** with *i*-C_3F_7I in 85% yield (Scheme 4).

Thus, a new method provided us with a synthetic tool



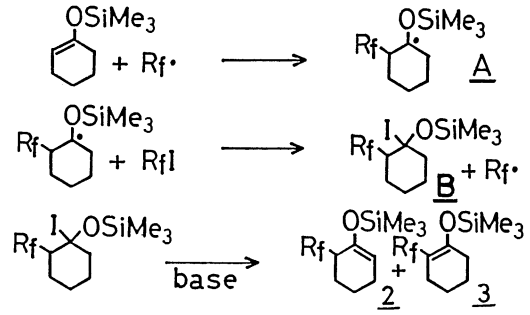


R_f a: *n*-C_6F_{13} 25°C 20 min 88%
b: *i*-C_3F_7 25°C 20 min 83%
c: CF_3 −78°C—5°C 3 h 67%

Scheme 4.

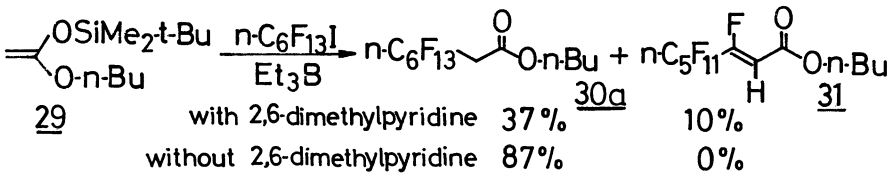
for the preparation of newly functionalized trimethyl silyl enol ethers as well as α-perfluoroalkyl ketones.[7]

We are tempted to assume following reaction mechanism for the formation of perfluoroalkylated silyl enol ethers (Scheme 5): (1) Perfluoroalkyl radical, generated by the action of ethyl radical on perfluoroalkyl iodide, adds to silyl enol ether to give a radical **A**, (2) the radical **A** abstracts iodine from R_fI to give the adduct **B** and regenerates perfluoroalkyl radical, and (3) the coexisting base causes the elimination of HI to give a mixture of two perfluoroalkylated silyl enol ethers (**2** and **3**). The regioselective formation of **B** would be attributed to the electrophilic attack of reactive R_f radical on the electron-rich carbon of silyl enol ether.



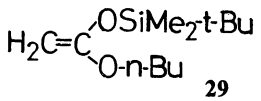
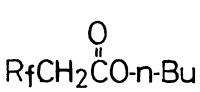
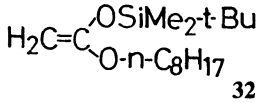
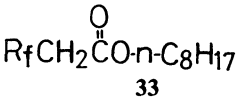
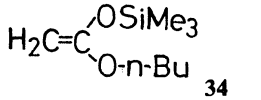
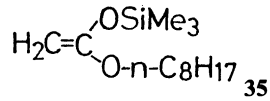
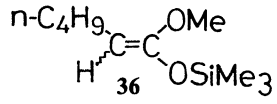
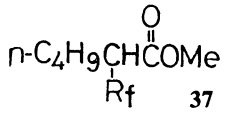
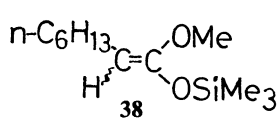
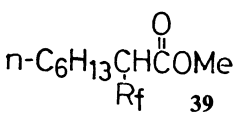
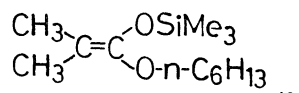
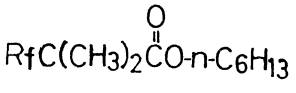
Scheme 5.

(2) The Reaction of Perfluoroalkyl Iodides with Ketene Silyl Acetals. Reaction of ketene silyl acetals with perfluoroalkyl iodides also proceeded easily in the presence of triethylborane catalyst to give α-perfluoroalkylated esters in excellent yields. Exposure of ketene silyl acetal **29** (1.0 mmol) to *n*-$C_6F_{13}I$ (1.3 mmol) in the presence of 2,6-dimethylpyridine (0.95 mmol) provided



Scheme 6.

Table 3. Reaction of Ketene Silyl Acetal with Perfluoroalkyl Iodide

Ketene silyl acetal	R_fI	Reaction time/min	Product	Product %
 **29**	*n*-$C_6F_{13}I$	10	 **30**	87 (**30a**)
	i-C_3F_7I	30		61 (**30b**)
 **32**	CF_3I	120	 **33**	81 (**33b**)
	CF_3CH_2I	30		62 (**33c**)
 **34**	*n*-$C_6F_{13}I$	20[a]	**30**	96 (**30a**)
	i-C_3F_7I	20		49 (**30b**)
 **35**	*i*-C_3F_7I	20	**33**	96 (**33a**)
	CF_3I	120[a]		90 (**33b**)
	CF_3CH_2I	60[a]		77 (**33c**)
 **36**	*n*-$C_6F_{13}I$	20	 **37**	83 (**37a**)
	i-C_3F_7I	20		40 (**37b**)
 **38**	*i*-C_3F_7I	20[a]	 **39**	88 (**39a**)
	CF_3I	120[a]		66 (**39b**)
	CF_3CH_2I	120[a]		32 (**39c**)
 **40**	*n*-$C_6F_{13}I$	4 h	 **41**	63 (**41a**)
	i-C_3F_7I	16 h		27 (**41b**)
	CF_3I	12 h		22 (**41c**)

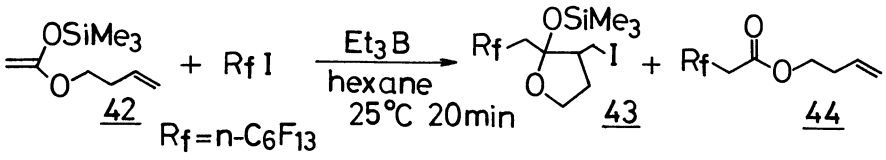
a) TBAF was added prior to work-up. See experimental part.

butyl 2-(perfluorohexyl)acetate (**30a**, 37%) along with butyl 2-(perfluorohexylidene)acetate (**31**, 10%). In contrast, treatment of **29** (2.0 mmol) with *n*-$C_6F_{13}I$ (1.0 mmol) in the absence of 2,6-dimethylpyridine in hexane provided **30a** (87% based on *n*-$C_6F_{13}I$) as a single product (Scheme 6). The yields of **30a** depend on the molar ratio of ketene silyl acetal and perfluoroalkyl iodide employed. The yields of **30a** in the reaction of **34** (x mmol) with *n*-$C_6F_{13}I$ (1.0 mmol) in the presence of catalytic amount of Et_3B (0.2 mmol) are as follows: **34** (2.0 mmol), 96%; **34** (1.5 mmol), 93%; **34** (1.2 mmol), 89%. Slight excess (1.2 equiv) of ketene silyl acetal was enough for the successful reaction. However, the reactions were performed using 2.0 equiv of ketene silyl acetals to obtain better yields and the results are summarized in Table 3.

Not only *n*-$C_6F_{13}I$, *i*-C_3F_7I but also CF_3I[7] or CF_3CH_2I reacted easily to give the corresponding perfluoroalkylated esters in good yields. Perfluoroalkylated ketene silyl acetal could not be detected. Trimethylsilyl acetal (**34** or **35**) reacted equally as dimethyl-*t*-butylsilyl acetal (**29** or **32**) to give the same perfluoroalkylated ester upon treatment with perfluoroalkyl iodides.

Alkyl group substituted ketene silyl acetals (**36**, **38**, and **40**) were prepared and their behavior toward perfluoroalkyl iodides were examined. Whereas the acetals **36** and **38** easily reacted with R_fI to provide the corresponding perfluoroalkylated esters in good yields, the acetal **40** reacted slowly because of its steric hindrance to give ester **41** in poor yields.

Treatment of ketene silyl acetal **42** with *n*-$C_6F_{13}I$ afforded a cyclized product **43** (10%) along with perfluoroalkylated ester **44** (50%) (Scheme 7). The formation of **43** suggests an intermediacy of carbon radical bearing OR and $OSiMe_3$ groups. The result also shows that C–C double bond of ketene silyl acetal is much more reactive than that of simple olefin.



Scheme 7.

Experimental

Distillations of the products were performed by use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Melting point was obtained on a Yanako MP-50929 melting point apparatus and are uncorrected, too. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian XL-200 spectrometer, $CDCl_3$ was used as solvent, and chemical shifts being given in δ with tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded on JEOL JNM-FX 90Q spectrometer and the chemical shifts are given in δ with $CFCl_3$ as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer and the mass spectra on a Hitachi M-80 machine. The analyses were carried out at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl.

Preparation of Silyl Enol Ethers. Trimethylsilyl enol ethers **1**, **9**, **13**, **16**, **22**, and **24** were prepared by the reported procedure.[8-11] Triisopropylsilyl enol ether **6** and **19** were prepared according to the Corey's method.[12] 1-Trimethylsiloxy-1-cyclopropylethylene was obtained following the reported procedure.[13] The physical data are shown below for the silyl enol ethers whose physical data have not been described in the literature.

1-Triisopropylsiloxy-1-cyclohexene (6): Bp 91—96 °C (1 Torr, 1 Torr=133.322 Pa, bath temp); IR(neat) 2936, 2892, 2864, 1670, 1465, 1367, 1195, 885, 826, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02—1.23 (m, 21H), 1.45—1.57 (m, 2H), 1.60—1.72 (m, 2H), 1.95—2.10 (m, 4H), 4.89 (t, J=3.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=12.66, 17.98, 22.38, 23.27, 23.87, 29.92, 103.6, 150.6; MS (70 eV) m/z (rel intensity) 254 (11), 211 (100), 183 (26), 141 (18), 81 (20), 75 (48), 61 (36), 59 (28), 41 (20). Found: C, 70.54; H, 12.02%. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88%.

(Z)-1-Triisopropylsiloxy-1-heptene (19): Bp 81—86 °C (1 Torr, bath temp); IR(neat) 2926, 2864, 1655, 1465, 1256, 1135, 1092, 1069, 882, 683, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.5 Hz, 3H), 1.03—1.20 (m, 21H), 1.22—1.42 (m, 6H), 2.04—2.15 (m, 2H), 4.39 (td, J=7.2, 5.8 Hz, 1H), 6.27 (dt, J=5.8, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=11.98, 14.10, 17.74, 22.57, 23.54, 29.39, 31.63, 110.0, 138.9; MS (70 eV) m/z (rel intensity) 270 (2), 228 (20), 227 (100), 103 (21), 75 (24), 61 (15), 59 (29). Found: C, 70.94; H, 12.85%. Calcd for $C_{16}H_{34}OSi$: C, 71.04; H, 12.67%.

2-Trimethylsiloxy-1-undecene (22). This compound was prepared from 2-undecanone in 79% yield along with 2-trimethylsiloxy-2-undecene (93/7): Bp 85—86 °C (1 Torr); IR (neat) 2954, 2924, 2852, 1654, 1637, 1252, 1013, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.20 (s, 9H), 0.88 (t, J=6.4 Hz, 3H), 1.20—1.53 (m, 14H), 2.01 (t, J=7.3 Hz, 2H), 4.04 (s, 2H); ^{13}C NMR ($CDCl_3$) δ=0.15, 14.11, 22.70, 26.89, 29.15, 29.35, 29.52, 29.60, 31.93, 36.53, 89.75, 159.7; MS (70 eV) m/z (rel intensity) 242 (4), 144 (14), 143 (100), 130 (70), 115 (40), 75 (52), 73 (97), 43 (18), 41 (21). Found: C, 69.57; H, 12.72%. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47%.

(*E*) and (*Z*)-6-Trimethylsiloxy-5-undecene (24, (*E*):(*Z*)= 69:31). The title compound was prepared from 6-undecanone in 82% yield: Bp 75—78 °C (1 Torr); IR(neat) 2956, 2926, 2858, 1664, 1251, 1177, 1100, 888, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 9H), 0.89 (t, J=6.5 Hz, 6H), 1.23—1.52 (m, 10H), 1.87—2.07 (m, 4H), 4.44 (t, J=6.8 Hz, 0.31H), 4.60 (t, J=7.6 Hz, 0.69H); ^{13}C NMR ($CDCl_3$) δ=0.37, 0.62, 14.03, 22.25, 22.58, 25.07, 26.57, 26.78, 31.13, 31.47, 31.56, 32.18, 32.96, 36.63, 107.8 (*E*), 108.4 (*Z*), 150.2 (*Z*), 151.4 (*E*); MS (70 eV) m/z (rel intensity) 242 (14), 227 (9), 200 (18), 199 (100), 171 (9), 143 (14), 130 (23), 73 (15), 69 (10). Found: C, 69.09; H, 12.66%. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47%.

The Reaction of Silyl Enol Ether with Perfluorohexyl or Perfluoroisopropyl Iodide in the Presence of Base (Procedure A). Perfluoroalkylation of cyclohexanone trimethylsilyl enol ether is representative. Et_3B[4] (1.0 M hexane solution, 0.4 ml, 0.4 mmol, M=mol dm^{-3}) was added to a solution of 1-trimethylsiloxy-1-cyclohexene **1** (0.34 g, 2.0 mmol), perfluorohexyl iodide (1.19 g, 2.6 mmol), and 2,6-dimethylpyridine (0.20 g, 1.9 mmol) in hexane (5 ml) at room temperature. After stirring for 8 h at 25 °C, resulting precipitate was filtered through Celite 545. The filtrate was concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give perfluoroalkylated silyl enol ether (**2a** and **3a**, 0.64 g, 65% yield, **2a**/**3a**=68/32) and 2-(perfluorohexyl)cyclohexanone (**4a**,[14] 92 mg, 11% yield). (Procedure A') Treatment of the reaction mixture consisting of **2a**, **3a**, and **4a** with acid afforded 2-(perfluoroalkyl)cyclohexanone (**4a**) as a single product. Thus, the residual oil after concentration of the filtrate was treated with concd aq HCl (35 wt%, 1 ml) in THF (5 ml) for 10 min. Reaction mixture was slowly poured into sat. aq $NaHCO_3$ (40 ml) and extracted with AcOEt (30 ml×2).[15] The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography gave only **4a** in 74% yield.

6-Perfluorohexyl-1-trimethylsiloxy-1-cyclohexene (2a): Bp 68—71 °C (1 Torr, bath temp); IR(neat) 2958, 1669, 1324, 1239, 1203, 1146, 1120, 913, 846, 694, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.20 (s, 9H), 1.48—1.88 (m, 3H), 1.96—2.16 (m, 3H), 2.95 (tm, J=15.6 Hz, 1H), 5.11 (t, J=4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.10, 18.82, 23.18 (two peaks), 41.77 (t, J=20.4 Hz), 108.6, 141.1. ^{13}C-Signals of perfluorohexyl group could not be observed for all perfluorohexyl compounds; ^{19}F NMR ($CDCl_3$) δ=−81.39 (t, J=9.8 Hz, 3F), −108.1 (dm, J=284 Hz, 1F), −113.8 (dm, J=284 Hz, 1F), −121.2 (bs, 2F), −122.2 (bs, 2F), −123.2 (bs, 2F), −126.4—−126.8 (m, 2F); MS (70 eV) m/z (rel intensity) 488 (10), 169 (14), 133 (12), 77 (61), 75 (6), 74 (8), 73 (100), 69 (27), 55 (19), 45 (11), 41 (17). Found: C, 37.17; H, 3.49%. Calcd for $C_{15}H_{17}F_{13}OSi$: C, 36.89; H, 3.51%.

2-Perfluorohexyl-1-trimethylsiloxy-1-cyclohexene (3a): Bp 68—72 °C (1 Torr, bath temp); IR(neat) 2944, 1661, 1375,

1292, 1238, 1204, 1145, 1119, 1074, 1065, 933, 861, 848, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.20 (s, 9H), 1.55—1.75 (m, 4H), 2.14—2.19 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=0.50, 22.10, 22.45, 23.51 (t, J=5.0 Hz), 31.38, 117.1 (t, J=32.7 Hz), 155.8 (t, J=5.5 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.39 (tt, J=9.7, 3.6 Hz, 3F), −108.5 (t, J=14.0 Hz, 2F), −122.1—−123.2 (m, 6F), −126.4—−126.8 (m, 2F); MS (70 eV) m/z (rel intensity) 488 (7), 220 (15), 219 (92), 169 (7), 77 (46), 74 (9), 73 (100), 69 (9), 45 (11), 41 (19). Found: C, 37.15; H, 3.56%. Calcd for $C_{15}H_{17}F_{13}OSi$: C, 36.89; H, 3.51%.

2-(Perfluorohexylidene)cyclohexanone (5): Bp 78—83 °C (7 Torr, bath temp); IR(neat) 1722, 1228, 1204, 1164, 1144, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.81—2.05 (m, 4H), 2.54—2.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=25.01, 25.44, 27.45, 43.35, 129.2 (d, J=6.0 Hz), 198.5; ^{19}F NMR ($CDCl_3$) δ=−81.28 (tt, J=9.8, 3.0 Hz, 3F), −114.1—−114.6 (m, 2F), −121.1 (bs, 1F), −123.3 (bs, 2F), −124.1 (bs, 2F), −126.4—−126.7 (m, 2F); MS (12 eV) m/z (rel intensity) 396 (7), 369 (10), 368 (77), 150 (8), 149 (100), 127 (21), 99 (99), 67 (36), 41 (18). Found: C, 36.51; H, 2.09%. Calcd for $C_{12}H_8F_{12}O$: C, 36.38; H, 2.04%.

6-Perfluoroisopropyl-1-trimethylsiloxy-1-cyclohexene (2b): Bp 50—53 °C (1 Torr, bath temp); IR(neat) 2960, 1664, 1287, 1255, 1219, 1159, 1118, 1099, 985, 964, 936, 902, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 9H), 1.33—1.55 (m, 1H), 1.65—2.10 (m, 5H), 3.03—3.22 (m, 1H), 5.03 (t, J=4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.15. 20.92, 23.34, 23.56 (d, J=10.6 Hz), 41.08 (d, J=18.9 Hz), 93.92 (dm, J=205 Hz), 107.3, 121.2 (qd, J=289, 29.3 Hz), 145.2; ^{19}F NMR ($CDCl_3$) δ=−72.99 (d, J=4.9 Hz, 6F), −173.4—−173.9 (m, 1F); MS (70 eV) m/z (rel intensity) 338 (19), 169 (27), 77 (64), 73 (100), 55 (11), 45 (14), 41 (14). Found: C, 42.76; H, 5.23%. Calcd for $C_{12}H_{17}F_7OSi$: C, 42.60; H, 5.06%.

2-Perfluoroisopropyl-1-trimethylsiloxy-1-cyclohexene (3b): Bp 50—55 °C (1 Torr, bath temp); IR(neat) 2942, 1669, 1369, 1299, 1272, 1259, 1217, 1172, 1144, 1065, 967, 956, 899, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19 (s, 9H), 1.55—1.76 (m, 4H), 2.10—2.21 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=0.89, 22.30 (d, J=3.7 Hz), 22.39, 23.67 (d, J=10.7 Hz), 31.35, 93.21 (dm, J=197 Hz), 101.5 (d, J=22.8 Hz), 121.3 (qd, J=288, 28.7 Hz), 153.1 (d, J=6.0 Hz); ^{19}F NMR ($CDCl_3$) δ=−74.68 (d, J=6.1 Hz, 6F), −177.1 (sep, sep=septet, J=6.1 Hz, 1F); MS (70 eV) m/z (rel intensity) 338 (17), 269 (11), 177 (10), 169 (27), 149 (13), 77 (50), 73 (100), 65 (10), 45 (16), 41 (24). Found: C, 42.49; H, 5.14%. Calcd for $C_{12}H_{17}F_7OSi$: C, 42.60; H, 5.06%.

2-(Perfluoroisopropyl)cyclohexanone (4b): Bp 82—87 °C (36 Torr, bath temp); IR(neat) 1733, 1292, 1274, 1224, 1161, 1134, 1109, 1098, 972 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.60—2.15 (m, 5H), 2.30—2.60 (m, 3H), 3.16—3.30 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=24.61, 27.41, 28.45, 42.74, 51.95 (d, J=20.1 Hz), 92.61 (dm, J=207 Hz), 120.9 (qd, J=288, 27.4 Hz), 202.9 (d, J=4.8 Hz); ^{19}F NMR ($CDCl_3$) δ=−72.85—−73.54 (m, 6F), −178.3—−178.9 (m, 1F); MS (70 eV) m/z (rel intensity) 266 (71), 238 (11), 237 (16), 141 (15), 127 (13), 77 (10), 69 (18), 55 (100), 42 (20), 41 (14). Found: C, 40.90; H, 3.33%. Calcd for $C_9H_9F_7O$: C, 40.61; H, 3.41%.

6-Perfluorohexyl-1-triisopropylsiloxy-1-cyclohexene (7a): Bp 100—105 °C (1 Torr, bath temp); IR(neat) 2946, 2894, 2868, 1668, 1466, 1239, 1200, 1145, 1119, 883, 688, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.01—1.26 (m, 21H), 1.55—1.83 (m, 2H), 2.00—2.18 (m 4H), 2.85—3.10 (m, 1H), 5.08 (t, J=4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=12.75, 17.90 (d, J=3.9 Hz), 18.46, 23.08, 23.31, 41.54 (dd, J=21.0, 18.9 Hz), 107.2, 144.3 (t, J=2.7 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.29 (t, J=9.8 Hz, 3F), −107.6 (d, J=271 Hz, 1F), −113.5 (d, J=271 Hz, 1F), −121.4 (bs, 2F), −122.3 (bs, 2F), −123.2 (bs, 2F), −126.6 (bs, 2F); MS (70 eV) m/z (rel intensity) 572 (2), 529 (30), 349 (17), 105 (50), 77 (100), 63 (13), 59 (13), 43 (34), 41 (17). Found: C, 44.22; H, 5.02%. Calcd for $C_{21}H_{29}F_{13}OSi$: C, 44.06; H, 5.11%.

2-Perfluorohexyl-1-triisopropylsiloxy-1-cyclohexene (8a): Bp 98—103 °C (1 Torr, bath temp); IR(neat) 2950, 2868, 1653, 1375, 1240, 1205, 1145, 1073 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03—1.30 (m, 21H), 1.58—1.80 (m, 4H), 2.10—2.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=13.69, 17.83, 22.14, 22.74, 23.82, 31.67, 102.5 (t, J=21.1 Hz), 156.3 (t, J=4.9 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.32 (t, J=9.8 Hz, 3F), −108.6 (bs, 2F), −122.4 (bs, 4F), −123.3 (bs, 2F), −126.4—−126.8 (m, 2F); MS (70 eV) m/z (rel intensity) 530 (M^+−i-Pr+1, 20), 529 (M^+−i-Pr, 79), 105 (50), 77 (100), 63 (15), 59 (12), 43 (24), 41 (19). Found: C, 43.81; H, 5.21%. Calcd for $C_{21}H_{29}F_{13}OSi$: C, 44.06; H, 5.11%.

6-Perfluoroisopropyl-1-triisopropylsiloxy-1-cyclohexene (7b): Bp 78—83 °C (1 Torr, bath temp); IR(neat) 2944, 2892, 2868, 1664, 1466, 1288, 1268, 1218, 1196, 1159, 1120, 1099, 1064, 965, 897, 882, 832, 677 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95—1.30 (m, 21H), 1.34—1.55 (m, 1H), 1.64—2.08 (m, 5H), 2.99—3.14 (m, 1H), 5.08 (t, J=4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) J=12.90, 17.90 (d, J=6.3 Hz), 20.85, 23.30, 23.72 (d, J=7.8 Hz), 40.94 (d, J=17.1 Hz), 93.86 (dm, J=208 Hz), 107.3, 121.2 (qd, J=288, 28.1 Hz), 146.0; ^{19}F NMR ($CDCl_3$) δ=−72.73 (qd, J=8.6, 6.1 Hz, 3F), −73.65 (qd, J=8.6, 6.1 Hz, 3F), −172.1—−172.7 (m, 1F); MS (70 eV) m/z (rel intensity) 422 (3), 379 (15), 199 (24), 179 (18), 159 (15), 105 (49), 79 (17), 77 (100), 63 (23), 59 (23), 43 (45), 41 (32). Found: C, 51.18; H, 6.99%. Calcd for $C_{18}H_{29}F_7OSi$: C, 51.17; H, 6.92%.

2-Perfluoroisopropyl-1-triisopropylsiloxy-1-cyclohexene (8b): Bp 76—81 °C (1 Torr, bath temp); IR(neat) 2946, 2896, 2870, 1645, 1467, 1371, 1293, 1216, 1180, 1160, 1146, 1067, 984, 968, 959, 898, 884, 844, 771, 723, 686 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.99—1.26 (m, 21H), 1.52—1.74 (m, 4H), 2.07—2.26 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=13.83, 17.90, 22.38, 22.55, 24.03 (d, J=2.2 Hz), 32.26, 93.12 (dm, J=207 Hz), 99.00 (d, J=15.1 Hz), 121.5 (qd, J=289, 28.8 Hz), 155.2; ^{19}F NMR ($CDCl_3$) δ=−74.74 (d, J=6.1 Hz, 6F), −177.2 (sep, J=6.1 Hz, 1F); MS (70 eV) m/z (rel intensity) 422 (0.2), 379 (42), 227 (32), 207 (42), 179 (18), 105 (31), 77 (100), 63 (19), 43 (25), 41 (22). Found: C, 51.03; H, 6.98%. Calcd for $C_{18}H_{29}F_7OSi$: C, 51.17; H, 6.92%.

5-Perfluorohexyl-1-trimethylsiloxy-1-cyclopentene (10): Bp 65—70 °C (1 Torr, bath temp); IR(neat) 1666, 1654, 1381, 1240, 1205, 1146, 1120, 867, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.21 (s, 9H), 2.05—2.46 (m, 4H), 3.10—3.36 (m, 1H), 4.89 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.43, 22.82, 27.07, 47.52 (dd, J=22.8, 20.3 Hz), 106.9, 148.9; ^{19}F NMR ($CDCl_3$) δ=−81.33 (t, J=9.4 Hz, 3F), −109.5 (t, J=12.8 Hz, 1F), −116.0—−117.1 (m, 1F), −121.6 (bs, 1F), −122.1—−123.5 (m, 5F), −126.3—−126.8 (m, 2F); MS (70 eV) m/z (rel intensity) 475 (M^++1, 11), 474 (M^+, 52), 459 (25), 205 (39), 155 (15), 77 (54), 73 (100), 55 (59). Found: C, 35.50; H, 3.13%. Calcd for $C_{14}H_{15}F_{13}OSi$: C, 35.45; H, 3.19%.

2-(Perfluorohexyl)cyclopentanone (11): Bp 89—94 °C (5 Torr, bath temp); IR(neat) 2890, 2882, 1768, 1350, 1238, 1206, 1147, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.76—2.51 (m, 6H), 2.77—3.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=20.16, 24.51, 38.67, 49.29 (dd, J=24.1, 20.0 Hz), 208.9 (d, J=2.4 Hz); ^{19}F NMR

($CDCl_3$) δ=−81.38 (tt, *J*=10.9, 2.4 Hz, 3F), −115.1—−116.0 (m, 2F), −121.3 (bs, 2F), −122.4 (bs, 2F), −123.2 (bs, 2F), −126.3—−126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 403 (M^++1, 17), 402 (M^+, 100), 383 (11), 382 (46), 354 (12), 343 (8), 340 (10). Found: C, 32.77; H, 1.76%. Calcd for $C_{11}H_7F_{13}O$: C, 32.58; H, 1.75%.

2-(Perfluorohexylidene)cyclopentanone (12): Stereochemistry of alkene could not be determined. Bp 110—115 °C (37 Torr, bath temp); IR(neat) 1747, 1669, 1238, 1194, 1143, 1111, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.95—2.10 (m, 2H), 2.38—2.46 (m, 2H), 2.82—2.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=19.89, 25.83, 38.79, 141.9, (d, *J*=30.3 Hz), 202.6; ^{19}F NMR ($CDCl_3$) δ=−81.34 (t, *J*=8.5 Hz, 3F), −116.6—−117.2 (m, 3F), −123.5 (bs, 4F), −126.6 (bs, 2F); MS (70 eV) *m/z* (rel intensity) 382 (9), 135 (11), 121 (20), 113 (100), 107 (95), 69 (23), 57 (17), 55 (21). Found: C, 34.38; H, 1.51%. Calcd for $C_{11}H_6F_{12}O$: C, 34.57; H, 1.58%.

(*Z*)-5-Ethyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-trimethylsiloxy-3-undecene ((*Z*)-14a): Bp 95—100 °C (35 Torr, bath temp); IR(neat) 2966, 1671, 1362, 1299, 1240, 1195, 1147, 1121, 1087, 847, 733, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.20 (s, 9H), 0.95 (t, *J*=7.4 Hz, 3H), 0.96 (t, *J*=7.5 Hz, 3H), 1.58—1.85 (m, 2H), 1.92—2.15 (m, 2H), 2.60 (tdd, *J*=14.8, 10.3, 4.3 Hz, 1H), 4.59 (t, *J*=7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.83, 11.55, 14.01, 18.07, 19.33, 50.47 (t, *J*=20.5 Hz), 115.5, 141.9; ^{19}F NMR ($CDCl_3$) δ=−81.30 (tt, *J*=9.8, 2.4 Hz, 3F), −113.8—−114.7 (m, 2F), −121.2 (bs, 2F), −122.3 (bs, 2F), −123.3 (bs, 2F), −126.3—−126.7 (m, 2F); MS (70 eV) *m/z* (rel intensity) 504 (23), 489 (10), 448 (9), 207 (14), 143 (14), 77 (34), 73 (100), 70 (14), 69 (9), 55 (30). Found: C, 37.82; H, 4.03%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

(*E*)-5-Ethyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-trimethylsiloxy-3-undecene ((*E*)-14a): Bp 50—55 °C (1 Torr, bath temp); IR(neat) 2966, 1664, 1241, 1146, 962, 886, 848, 659 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19 (s, 9H), 0.90 (t, *J*=7.4 Hz, 3H), 0.96 (t, *J*=7.4 Hz, 3H), 1.60—2.08 (m, 4H), 3.07 (tdd, *J*=15.1, 10.5, 4.1 Hz, 1H), 4.77 (t, *J*=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.00, 11.15, 14.83, 17.24, 20.16, 43.85 (t, *J*=20.7 Hz), 112.9, 143.0; ^{19}F NMR ($CDCl_3$) δ=−81.35 (t, *J*=9.8 Hz, 3F), −113.6 (bs, 2F), −121.8—−122.4 (m, 4F), −123.2 (bs, 2F), −126.4—−126.9 (m, 2F); MS (70 eV) *m/z* (rel intensity) 505 (M^++1, 12), 504 (M^+, 53), 489 (22), 448 (20), 207 (24), 143 (17), 77 (36), 73 (100), 55 (27). Found: C, 38.33; H, 4.04%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

5-Ethyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-undecanone (15a): Bp 97—102 °C (35 Torr, bath temp); IR(neat) 2970, 1731, 1363, 1239, 1207, 1146, 694, 651 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (t, *J*=7.3 Hz, 6H), 1.55—1.73 (m, 2H), 1.78—2.09 (m, 2H), 2.46 (dt, *J*=18.4, 7.2 Hz, 1H), 2.60 (dt, *J*=18.4, 7.3 Hz, 1H), 3.21 (tdd, *J*=15.0, 10.2, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=11.39, 13.31, 16.37, 18.81 (t, *J*=5.1 Hz), 46.19, 54.85 (t, *J*=19.8 Hz), 204.1; ^{19}F NMR ($CDCl_3$) δ=−81.32 (tt, *J*=9.8, 2.4 Hz, 3F), −113.6—−114.1 (m, 2F), −121.1 (bs, 2F), −122.3 (bs, 2F), −123.3 (bs, 2F), −126.3—−126.8 (m, 2F); MS (70 eV) *m/z* (rel intensity) 432 (0.5), 388 (5), 72 (5), 71 (100), 69 (6), 47 (14), 43 (55), 41 (11). Found: C, 35.88; H, 2.98%. Calcd for $C_{13}H_{13}F_{13}O$: C, 36.13; H, 3.03%.

(*Z*)-5-Ethyl-6,7,7,7-tetrafluoro-6-trifluoromethyl-4-trimethylsiloxy-3-heptene ((*Z*)-14b): Bp 82—87 °C (35 Torr, bath temp); IR(neat) 2966, 1670, 1384, 1298, 1256, 1224, 1186, 1160, 1127, 1101, 1088, 1069, 952, 847 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.20 (s, 9H), 0.95 (t, *J*=7.4 Hz, 6H), 1.58—1.85 (m, 2H), 1.97—2.12 (m, 2H), 2.56—2.70 (m, 1H), 4.63 (t, *J*=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) 0.92, 12.50, 13.89, 18.56, 19.54, 50.43 (d, *J*=20.1 Hz), 92.76 (dm, *J*=204 Hz), 115.5, 121.1 (qd, *J*=288, 28.8 Hz), 121.3 (qd, *J*=289, 26.6 Hz), 141.5 (d, *J*=6.5 Hz); ^{19}F NMR ($CDCl_3$) δ=−73.10 (d, *J*=7.3 Hz, 6F), −174.7—−175.7 (m, 1F); MS (70 eV) *m/z* (rel intensity) 355 (M^++1, 12), 354 (M^+, 62), 339 (47), 298 (49), 247 (14), 185 (22), 143 (16), 77 (31), 73 (100). Found: C, 44.14; H, 6.08%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

(*E*)-5-Ethyl-6,7,7,7-tetrafluoro-6-trifluoromethyl-4-trimethylsiloxy-3-heptene ((*E*)-14b): Bp 77—82 °C (35 Torr, bath temp); IR(neat) 2966, 1661, 1297, 1255, 1224, 1159, 1135, 1123, 892, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19 (s, 9H), 0.87 (t, *J*=7.3 Hz, 3H), 0.96 (t, *J*=7.5 Hz, 3H), 1.57—2.06 (m, 4H), 3.04—3.18 (m, 1H), 4.75 (t, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.26, 11.91, 14.82, 17.93, 20.31, 43.79 (d, *J*=20.5 Hz), 92.51 (dm, *J*=203 Hz), 113.3, 121.1 (qd, *J*=290, 27.3 Hz); 121.4 (qd, *J*=290, 27.6 Hz), 142.3 (d, *J*=6.0 Hz); ^{19}F NMR ($CDCl_3$) δ=−72.98—−73.91 (m, 6F), −174.7—−176.1 (m, 1F); MS (70 eV) *m/z* (rel intensity) 354 (11), 339 (9), 298 (12), 185 (9), 143 (9), 77 (33), 73 (100), 55 (10). Found: C, 44.18; H, 6.22%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

5-Ethyl-6,7,7,7-tetrafluoro-6-trifluoromethyl-4-heptanone (15b): Bp 71—76 °C (49 Torr, bath temp); IR(neat) 2968, 2938, 1733, 1299, 1260, 1226, 1163, 1145, 1131, 971 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=7.9 Hz, 3H), 0.93 (t, *J*=7.4 Hz, 3H), 1.55—1.89 (m, 3H), 1.93—2.17 (m, 1H), 2.43 (dtd, *J*=18.3, 7.0, 1.2 Hz, 1H), 2.64 (dtd, *J*=18.3, 7.3, 1.6 Hz, 1H), 3.10—3.25 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=12.31, 13.25, 16.57, 19.00, 48.06, 53.00 (d, *J*=8.6 Hz), 92.19 (dm, *J*=205 Hz), 120.6 (qd, *J*=287, 27.7 Hz), 120.8 (qd, *J*=287, 28.0 Hz), 204.1; ^{19}F NMR ($CDCl_3$) δ=−73.05 (dq, *J*=8.6, 8.5 Hz, 3F), −74.43 (dq, *J*=9.8, 8.5 Hz, 3F), −176.4—−176.9 (m, 1F); MS (70 eV) *m/z* (rel intensity) 239 ($M^+-C_3H_7$, 2), 171 (2), 127 (3), 72 (5), 71 (100), 43 (88), 41 (24). Found: C, 42.30; H, 4.46%. Calcd for $C_{10}H_{13}F_7O$: C, 42.56; H, 4.64%.

(*Z*)-8,8,9,9,10,10,11,11,12,12,13,13,13-Tridecafluoro-6-trimethylsiloxy-5-tridecene ((*Z*)-17a): Bp 94—99 °C (5 Torr, bath temp); IR(neat) 2958, 2930, 1675, 1350, 1240, 1195, 1145, 1121, 1097, 990, 846, 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.20 (s, 9H), 0.90 (t, *J*=6.8 Hz, 3H), 1.25—1.37 (m, 4H), 1.99—2.10 (m, 2H), 2.75 (t, *J*=18.4 Hz, 2H), 4.72 (t, *J*=7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.37, 13.82, 22.41, 25.55, 31.61, 38.32 (t, *J*=22.1 Hz), 116.5, 139.1; ^{19}F NMR ($CDCl_3$) δ=−81.32 (t, *J*=9.8 Hz, 3F), −113.0—−113.5 (m, 2F), −122.1—−122.6 (m,2F), −123.4 (bs, 2F), −123.8 (bs, 2F), −126.3—−126.9 (m, 2F); MS (70 eV) *m/z* (rel intensity) 505 (M^++1, 7), 504 (M^+, 27), 462 (14), 461 (89), 175 (10), 77 (17), 73 (100), 55 (38). Found: C, 37.90; H, 4.15%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

(*E*)-8,8,9,9,10,10,11,11,12,12,13,13,13-Tridecafluoro-6-trimethylsiloxy-5-tridecene ((*E*)-17a): Bp 71—76 °C (1 Torr, bath temp); IR(neat) 2960, 2930, 1670, 1360, 1240, 1195, 1145, 1122, 847, 733, 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.20 (s, 9H), 0.90 (t, *J*=7.0 Hz, 3H), 1.27—1.37 (m, 4H), 1.89—2.00 (m, 2H), 2.86 (t, *J*=18.4 Hz, 2H), 4.91 (t, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.09, 13.87, 22.19, 26.91, 32.31, 33.26 (t, *J*=22.2 Hz), 113.5, 140.6; ^{19}F NMR ($CDCl_3$) δ=−81.32 (t, *J*=9.8 Hz, 3F), −112.3—−112.7 (m, 2F), −122.3 (bs, 2F), −123.4 (bs, 2F), −123.8 (bs, 2F), −126.4—−126.9 (m, 2F); MS (70 eV) *m/z* (rel intensity) 504 (6), 461 (23), 175 (8), 77

(22), 74 (9), 73 (100), 55 (46). Found: C, 38.25; H, 4.17%. Calcd for $C_{16}H_{21}F_{13}OSi$: C, 38.10; H, 4.20%.

8,8,9,9,10,10,11,11,12,12,13,13,13-Tridecafluoro-6-tridecanone (18a): Bp 100—105 °C (43 Torr, bath temp); IR(neat) 2960, 2934, 1732, 1363, 1240, 1204, 1145, 1124, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, J=6.7 Hz, 3H), 1.23—1.40 (m, 4H), 1.55—1.70 (m, 2H), 2.58 (t, J=7.3 Hz, 2H), 3.16 (t, J=18.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.84, 22.37, 22.88, 31.03, 43.10 (t, J=22.1 Hz), 44.48, 200.0; ^{19}F NMR ($CDCl_3$) δ=−81.29 (bs, 3F), −111.2—−112.0 (m, 2F), −122.2 (bs, 2F), −123.4 (bs, 4F), −126.3—−126.8 (m, 2F); MS (70 eV) m/z (rel intensity) 432 (5), 376 (100), 361 (45), 356 (95), 341 (47), 99 (45), 56 (36), 43 (61). Found: C, 36.06; H, 2.94%. Calcd for $C_{13}H_{13}F_{13}O$: C, 36.13; H, 3.03%.

(*Z*)-1,1,1,2-Tetrafluoro-2-trifluoromethyl-4-trimethylsiloxy-4-nonene ((*Z*)-17b): Bp 50—55 °C (1 Torr, bath temp); IR(neat) 2958, 2930, 1675, 1378, 1332, 1286, 1221, 1187, 1163, 1151, 1117, 1069, 999, 978, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.19 (s, 9H), 0.89 (t, J=6.5 Hz, 3H), 1.26—1.36 (m, 4H), 1.94—2.06 (m, 2H), 2.73 (d, J=21.5 Hz, 2H), 4.71 (t, J=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.46, 13.88, 22.29, 25.39, 31.39, 36.08 (d, J=19.7 Hz), 91.39 (dm, J=206 Hz), 116.3, 120.8 (qd, J=288, 27.9 Hz), 139.9 (d, J=2.8 Hz); ^{19}F NMR ($CDCl_3$) δ=−76.60 (d, J=7.3 Hz, 6F), −183.0 (tsep, tsep=triplet, septet, J=22.0, 7.3 Hz, 1F); MS (70 eV) m/z (rel intensity) 354 (4), 311 (22), 219 (10), 77 (15), 74 (9), 73 (100). Found: C, 43.95; H, 6.02%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

(*E*)-1,1,1,2-Tetrafluoro-2-trifluoromethyl-4-trimethylsiloxy-4-nonene ((*E*)-17b): Bp 49—54 °C (1 Torr, bath temp); IR(neat) 2958, 2932, 1671, 1332, 1286, 1224, 1187, 1163, 1118, 998, 918, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (s, 9H), 0.90 (t, J=7.0 Hz, 3H), 1.25—1.37 (m, 4H), 1.89—2.02 (m, 2H), 2.86 (d, J=20.8 Hz, 2H), 4.80 (t, J=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.08, 13.90, 22.25, 26.87, 30.89 (d, J=20.9 Hz), 32.28, 91.21 (dm, J=206 Hz), 112.5, 120.8 (qd, J=286, 24.5 Hz), 141.0; ^{19}F NMR ($CDCl_3$) δ=−76.82 (d, J=6.1 Hz, 6F), −182.3 (tsep, J=20.8, 6.1 Hz, 1F); MS (70 eV) m/z (rel intensity) 354 (22), 312 (18), 311 (100), 298 (15), 219 (32), 77 (16), 73 (68), 57 (24), 56 (11), 43 (22), 41 (22). Found: C, 44.14; H, 6.07%. Calcd for $C_{13}H_{21}F_7OSi$: C, 44.06; H, 5.97%.

1,1,1,2-Tetrafluoro-2-trifluoromethyl-4-nonanone (18b): Bp 82—87 °C (45 Torr, bath temp); IR(neat) 2958, 2934, 1729, 1340, 1288, 1227, 1164, 1131, 1108, 996 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, J=6.7 Hz, 3H), 1.20—1.40 (m, 4H), 1.53—1.68 (m, 2H), 2.56 (t, J=7.1 Hz, 2H), 3.07 (d, J=21.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.66, 22.35, 22.94, 30.97, 40.33 (d, J=19.1 Hz), 44.44, 90.69 (dm, J=208 Hz), 120.4 (qd, J=287, 27.8 Hz), 200.6; ^{19}F NMR ($CDCl_3$) δ=−77.01 (d, J=7.3 Hz, 6F), −183.0 (tsep, J=22.0, 7.3 Hz, 1F); MS (70 eV) m/z (rel intensity) 282 (7), 253 (5), 239 (15), 227 (21), 226 (100), 211 (36), 206 (6), 186 (3), 99 (5). Found: C, 42.83; H, 4.65%. Calcd for $C_{10}H_{13}F_7O$: C, 42.56; H, 4.64%.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2-pentyl-1-triisopropylsiloxy-1-octene (20, Major, Stereochemistry (*E* or *Z*) could not be determined): Bp 92—97 °C (1 Torr, bath temp); IR(neat) 2948, 2868, 1659, 1466, 1240, 1145, 1112, 882, 708, 686, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=6.7 Hz, 3H), 1.03—1.56 (m, 27H), 2.12—2.20 (m, 2H), 6.83 (t, J=2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=11.79, 13.97, 17.44, 22.49, 23.99, 28.53, 32.04, 111.1 (t, J=20.4 Hz), 146.4 (t, J=12.5 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.35 (t, J=9.8 Hz, 3F), −109.2—−109.6 (m, 2F), −122.1—−122.5 (m, 4F), −123.2 (bs, 2F), −126.4—−126.7 (m, 2F); MS (12 eV) m/z (rel intensity) 546 (M^+−^{i}Pr+1, 26), 545 (M^+−^{i}Pr, 100), 489 (4), 395 (3), 139 (2), 133 (3), 121 (2), 105 (2). Found: C, 45.18; H, 5.89%. Calcd for $C_{22}H_{33}F_{13}OSi$: C, 44.90; H, 5.65%.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2-pentyl-1-triisopropylsiloxy-1-octene (20, Minor): Bp 105—110 °C (4 Torr, bath temp); IR(neat) 2950, 2868, 1656, 1466, 1281, 1240, 1202, 1146, 1130, 882, 808, 710, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.7 Hz, 3H), 1.00—1.50 (m, 27H), 1.98—2.05 (m, 2H), 6.59 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=11.67, 14.01, 17.37, 22.39, 27.78, 30.01, 31.27, 107.3 (t, J=20.3 Hz), 146.8 (t, J=5.7 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.32 (t, J=9.8 Hz, 3F), −108.9—−109.3 (m, 2F); −122.2—−122.7 (m, 4F), −123.3 (bs, 2F), −126.3—−126.8 (m, 2F); MS (12 eV) m/z (rel intensity) 546 (M^+−i-Pr+1, 26), 545 (M^+−i-Pr, 100), 489 (10), 395 (15), 157 (14), 133 (12), 121 (11), 105 (43), 77 (67), 43 (12). Found: C, 44.83; H, 5.54%. Calcd for $C_{22}H_{33}F_{13}OSi$: C, 44.90; H, 5.65%.

3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluoro-2-pentyl-2-octenal (21, Major, Stereochemistry (*E* or *Z*) could not be determined): Bp 91—96 °C (27 Torr, bath temp); IR(neat) 2960, 2932, 2866, 1697, 1658, 1361, 1301, 1237, 1201, 1166, 1145, 1113, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.7 Hz, 3H), 1.24—1.50 (m, 6H), 2.41—2.51 (m, 2H), 10.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=13.75, 22.23, 23.32 (d, J=3.8 Hz), 27.73, 31.46, 132.3 (d, J=9.1 Hz), 187.5 (d, J=8.3 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.25 (t, J=9.8 Hz, 3F), −107.1 (bs, 1F), −111.6 (bs, 2F), −123.3 (bs, 4F), −126.5 (bs, 2F); MS (12 eV) m/z (rel intensity) 412 (7), 384 (23), 364 (19), 357 (34), 356 (53), 335 (50), 143 (100). Found: C, 38.03; H, 2.90%. Calcd for $C_{13}H_{12}F_{12}O$: C, 37.88; H, 2.93%.

3,4,4,5,5,6,6,7,7,8,8,8-Dodecafluoro-2-pentyl-2-octenal (21, Minor): Bp 88—93 °C (24 Torr, bath temp); IR(neat) 2960, 2934, 2874, 1700, 1660, 1362, 1237, 1205, 1144, 1113, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.23—1.46 (m, 6H), 2.26—2.34 (m, 2H), 10.23 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=13.77, 22.17 (two peaks), 29.21, 31.72, 129.3, 187.6 (d, J=18.8 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.26 (t, J=9.8 Hz, 3F), −115.6 (bs, 2F), −123.1 (bs, 4F), −126.2—−126.6 (m, 3F); MS (12 eV) m/z (rel intensity) 412 (0.6), 335 (5), 145 (11), 143 (100), 95 (7), 85 (24), 68 (8), 56 (24). Found: C, 37.58; H, 2.86%. Calcd for $C_{13}H_{12}F_{12}O$: C, 37.88; H, 2.93%.

The Reaction of Silyl Enol Ether with Trifluoromethyl Iodide in the Presence of Base. Typical procedure is as follows. CF_3I (2.88 g, 14.7 mmol) was introduced into the flask pre-cooled to −78 °C, then hexane (7.4 ml), silyl enol ether (**22** (purity: 93%), 354 mg, 1.36 mmol), 2,6-dimethylpyridine (159 mg, 1.47 mmol) and Et_3B (0.96 M hexane solution, 0.30 ml, 0.29 mmol) were slowly added to the flask. After addition of these reagents, the reaction mixture was warmed to room temperature and stirred for 40 h. The resulting precipitate was filtered through Celite 545 and the filtrate was concentrated in vacuo. Treatment of the crude product with concd aq HCl in THF and purification by silica-gel column chromatography gave **23a** in 64% yield. 1,1,1-Trifluoro-3-dodecanone (**23a**): Mp 44.5—45.5 °C; IR($CDCl_3$) 2926, 2854, 1731, 1367, 1341, 1274, 1255, 1160, 1139 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=6.4 Hz, 3H), 1.27 (bs, 12H), 1.53—1.70 (m, 2H), 2.53 (t, J=7.3 Hz, 2H), 3.21 (q, J=10.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.04, 22.63, 23.16, 28.90, 29.21, 29.31, 29.36, 31.83, 43.50, 46.18 (q, J=28.2 Hz), 123.7 (q, J=277 Hz), 200.2; ^{19}F NMR ($CDCl_3$) δ=−62.91 (t,

J=10.3 Hz); MS (12 eV) m/z (rel intensity) 238 (12), 220 (23), 164 (26), 153 (26), 150 (34), 139 (32), 127 (30), 126 (88), 112 (100), 110 (46), 71 (25). Found: C, 60.72; H, 9.10%. Calcd for $C_{12}H_{21}F_3O$: C, 60.49; H, 8.88%.

5-Trifluoromethyl-6-undecanone (25a): Bp 79—84 °C (1 Torr, bath temp); IR(neat) 2958, 2932, 2870, 1729, 1261, 1163, 1123, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=6.8 Hz, 6H), 1.17—1.47 (m, 8H), 1.53—1.99 (m, 4H), 2.47 (dt, J=17.9, 7.1 Hz, 1H), 2.61 (dt, J=17.9, 7.3 Hz, 1H), 3.19 (dqd, J=9.2, 8.9, 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.59, 13.80, 22.39 (two peaks), 22.70, 25.61, 29.02, 31.07, 43.64, 55.56 (q, J=25.0 Hz), 124.9 (q, J=280 Hz), 204.4; ^{19}F NMR ($CDCl_3$) δ=−67.33 (d, J=8.9 Hz); MS (12 eV) m/z (rel intensity) 238 (3), 167 (4), 126 (5), 100 (7), 99 (100), 85 (4), 72 (4), 71 (19), 56 (6), 43 (7). Found: C, 60.20; H, 9.10%. Calcd for $C_{12}H_{21}F_3O$: C, 60.49; H, 8.88%.

The Reaction of Silyl Enol Ether with 2,2,2-Trifluoroethyl Iodide in the Presence of Base. The reactions were performed according to Procedure A′ described for the reaction of silyl enol ether with R_fI with some variation of the quantity of reagents and reaction time, which are shown below.

1,1,1-Trifluoro-4-tridecanone (23b). Et_3B (0.96 M hexane solution, 0.42 ml, 0.40 mmol) was added to a solution of silyl enol ether (**22** (purity: 93%), 486 mg, 1.86 mmol), CF_3CH_2I (840 mg, 4.00 mmol) and 2,6-dimethylpyridine (205 mg, 1.91 mmol) in hexane (5 ml) at room temperature. The resulting mixture was stirred for 15 h. Acidic work-up followed by purification gave **23b** in 79% yield: Bp 90—95 °C (1 Torr, bath temp); IR(neat) 2926, 2854, 1723, 1442, 1364, 1315, 1256, 1231, 1143, 1091, 612 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.5 Hz, 3H), 1.27 (bs, 12H), 1.52—1.70 (m, 2H), 2.28—2.53 (m, 4H), 2.64—2.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.99, 22.61, 23.73, 27.86 (q, J=29.8 Hz), 29.11, 29.21, 29.32, 29.36, 31.82, 34.76 (q, J=2.7 Hz), 42.76, 127.0 (q, J=277 Hz), 207.1; ^{19}F NMR ($CDCl_3$) δ=−67.17 (t, J=10.3 Hz); MS (12 eV) m/z (rel intensity) 252 (9), 155 (66), 153 (16), 141 (29), 140 (100), 112 (37), 110 (21), 85 (15), 71 (28), 57 (20). Found: C, 62.04; H, 9.48%. Calcd for $C_{13}H_{23}F_3O$: C, 61.88; H, 9.19%.

5-(2,2,2-Trifluoroethyl)-6-undecanone (25b): Bp 65—70 °C (1 Torr, bath temp); IR(neat) 2956, 2930, 2862, 1719, 1467, 1459, 1378, 1257, 1131, 1102, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=6.8 Hz, 6H), 1.15—1.75 (m, 12H), 1.88—2.21 (m, 1H), 2.48 (t, J=7.5 Hz, 2H), 2.57—2.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.77, 13.88, 22.44, 22.54, 23.00, 28.79, 31.25, 31.82, 34.53 (q, J=28.4 Hz), 42.80, 44.93 (q, J=2.7 Hz), 126.6 (q, J=277 Hz), 211.5; ^{19}F NMR ($CDCl_3$) δ=−65.50 (t, J=10.8 Hz); MS (12 eV) m/z (rel intensity) 252 (3), 196 (8), 140 (7), 100 (6), 99 (100), 71 (15), 43 (4). Found: C, 62.04; H, 9.46%. Calcd for $C_{13}H_{23}F_3O$: C, 61.88; H, 9.19%.

The Reaction of 1-Trimethylsiloxy-1-cyclopropylethylene (26) with Perfluorohexyl or Perfluoroisopropyl Iodides. Perfluoroisopropylation of **26** is representative. Et_3B (1.0 M hexane solution, 0.20 ml, 0.20 mmol) was added to a solution of silyl enol ether (0.16 g, 1.0 mmol) and i-C_3F_7I (0.50 g, 1.7 mmol) in hexane (2 ml). After stirring for 20 min, the reaction mixture was concentrated in vacuo. Purification by silica-gel column chromatography gave **27b** in 85% yield. Treatment of crude product with concd aq HCl in THF according to Procedure A′ and purification by distillation gave **28b** in 83% yield.

(*Z*), (*E*)-6,7,7,7,-Tetrafluoro-1-iodo-6-trifluoromethyl-4-trimethylsiloxy-3-heptene (27b, (*Z*):(*E*)=81:19): Bp 92—97 °C (1 Torr, bath temp); IR(neat) 2960, 1671, 1374, 1333, 1286, 1222, 1164, 1149, 1121, 1003, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.22 (s, 9H), 2.53 (dt, J=7.6, 7.0 Hz, 0.38H), 2.60 (td, J=7.4, 7.0 Hz, 1.62H), 2.75 (d, J=21.6 Hz, 1.62H), 2.86 (d, J=21.0 Hz, 0.38H), 3.10 (t, J=7.4 Hz, 1.62H), 3.14 (t, J=7.0 Hz, 0.38H), 4.75 (t, J=7.0 Hz, 0.81H), 4.80 (t, J=7.6 Hz, 0.19H); ^{13}C NMR for (*Z*)-isomer ($CDCl_3$) δ=0.43, 4.00, 30.12, 35.99 (d, J=19.5 Hz), 91.41 (dm, J=207 Hz), 114.5, 120.9 (qd, J=288, 28.8 Hz), 142.4 (d, J=2.6 Hz); ^{13}C NMR for (*E*)-isomer ($CDCl_3$) δ=−0.15, 5.92, 31.21, 31.49 (d, J=19.0 Hz), 111.0, 143.6 (d, J=3.4 Hz), (^{13}C of $^iC_3F_7$ could not be detected); ^{19}F NMR ($CDCl_3$) δ=−76.56 (d, J=6.1 Hz, 4.86F), −76.79 (d, J=7.3 Hz, 1.14F), −182.1 (tsep, J=20.8, 7.3 Hz, 0.19F), −183.0 (tsep, J=22.0, 6.1 Hz, 0.81F); MS (70 eV) m/z (rel intensity) 452 (2), 326 (18), 325 (100), 233 (8), 73 (18). Found: C, 29.16; H, 3.58%. Calcd for $C_{11}H_{16}F_7IOSi$: C, 29.22; H, 3.57%.

6,7,7,7-Tetrafluoro-1-iodo-6-trifluoromethyl-4-heptanone (28b): Bp 73—78 °C (1 Torr, bath temp); IR(neat) 1728, 1338, 1289, 1223, 1165, 1117, 1045, 1002 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.04—2.18 (m, 2H), 2.75 (t, J=7.0 Hz, 2H), 3.11 (d, J=21.9 Hz, 2H), 3.23 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=5.31, 26.60, 40.55 (d, J=19.0 Hz), 44.69, 90.52 (dm, J=209 Hz), 120.3 (qd, J=288, 27.0 Hz), 199.1; ^{19}F NMR ($CDCl_3$) δ=−76.98 (d, J=4.9 Hz, 6F), −182.8 (bs, 1F); MS (70 eV) m/z (rel intensity) 253 (M^+−I, 61), 211 (100), 155 (14), 95 (14), 69 (36), 42 (19), 41 (27). Found: C, 25.51; H, 2.29%. Calcd for $C_8H_8F_7IO$: C, 25.28; H, 2.12%.

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoro-1-iodo-4-undecanone (28a): Bp 100—105 °C (1 Torr, bath temp); IR(neat) 1729, 1345, 1241, 1209, 1146 cm^{-1} δ=^{1}H NMR ($CDCl_3$) δ=2.07—2.20 (m, 2H), 2.78 (t, J=6.9 Hz, 2H), 3.22 (t, J=18.6 Hz, 2H), 3.25 (t, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=5.26, 26.52, 43.20 (t, J=22.1 Hz), 44.66, 198.4; ^{19}F NMR ($CDCl_3$) δ=−81.45 (bs, 3F), −111.5 (bs, 2F), −122.2 (bs, 2F), −123.4 (bs, 4F), −126.7 (bs, 2F); MS (70 eV) m/z (rel intensity) 403 (M^+−I, 67), 362 (9), 361 (100), 341 (9), 197 (11), 169 (8), 155 (7), 69 (13), 41 (8). Found: C, 24.85; H, 1.52%. Calcd for $C_{11}H_8F_{13}IO$: C, 24.93; H, 1.52%.

The Reaction of 1-Trimethylsiloxy-1-cyclopropylethylene with Trifluoromethyl Iodide. CF_3I (0.40 ml, 5.0 mmol) was collected in the flask pre-cooled to −78 °C. Hexane (2 ml), silyl enol ether (0.16 g, 1.0 mmol) and Et_3B (0.20 mmol) were added to CF_3I and the mixture was warmed to 5 °C over 3 h. After evaporation of solvent, the crude product was treated with concd aq HCl in THF. Purification by distillation gave **28c** in 67% yield: Bp 65—70 °C (1 Torr, bath temp); IR(neat) 1733, 1419, 1380, 1270, 1223, 1159, 1142, 1091, 626 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.05—2.18 (m, 2H), 2.72 (t, J=6.9 Hz, 2H), 3.24 (t, J=6.6 Hz, 2H), 3.26 (q, J=10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=5.55, 26.30, 43.59, 46.18 (q, J=28.3 Hz), 123.4 (q, J=277 Hz), 198.6; ^{19}F NMR ($CDCl_3$) δ=−62.85 (t, J=9.8 Hz); MS (70 eV) m/z (rel intensity) 153 (M^+−I, 58), 127 (7), 111 (100), 91 (6), 83 (12), 42 (9), 41 (11), 39 (8). Found: C, 25.57; H, 2.79%. Calcd for $C_6H_8F_3IO$: C, 25.74; H, 2.88%.

Preparation of Ketene Silyl Acetals. The following ketene silyl acetals were prepared by the reported procedure.[9,16] The physical data for 1-hexyloxy-2-methyl-1-trimethylsiloxy-1-propene (**40**) is described in the literature.[17] The physical data for other compounds are shown below.

1-Butoxy-1-(*t*-butyldimethylsiloxy)ethylene (29): Bp 66—68 °C (2 Torr); IR(neat) 2958, 2930, 1653, 1277, 1254, 837,

784 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 6H), 0.93 (s, 9H), 0.94 (t, J=7.3 Hz, 3H), 1.33—1.52 (m, 2H), 1.59—1.72 (m, 2H), 3.06 (d, J=2.3 Hz, 1H), 3.22 (d, J=2.3 Hz, 1H), 3.68 (t, J=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=−4.56, 13.73, 18.09, 19.31, 25.62, 30.95, 60.32, 67.48, 161.5; MS (70 eV) m/z (rel intensity) 230 (9), 174 (14), 159 (13), 131 (78), 117 (91), 75 (100), 73 (67), 57 (15), 43 (14), 41 (23). Found: C, 62.27; H, 11.62%. Calcd for $C_{12}H_{26}O_2Si$: C, 62.55; H, 11.37%.

1-(t-Butyldimethylsiloxy)-1-octyloxyethylene (32): Bp 114—117 °C (2 Torr); IR(neat) 2954, 2928, 2856, 1651, 1276, 1254, 829, 785 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 6H), 0.89 (t, J=6.6 Hz, 3H), 0.93 (s, 9H), 1.28 (bs, 10H), 1.60—1.73 (m, 2H), 3.05 (d, J=2.3 Hz, 1H), 3.22 (d, J=2.3 Hz, 1H), 3.67 (t, J=6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=−4.54, 14.07, 18.13, 22.65, 25.63, 26.11, 28.89, 29.22 (two peaks), 31.80, 60.32, 67.78, 161.5; MS (70 eV) m/z (rel intensity) 286 (2), 187 (28), 175 (18), 119 (17), 117 (100), 75 (67), 73 (44), 43 (23). Found: C, 67.23; H, 12.23%. Calcd for $C_{16}H_{34}O_2Si$: C, 67.07; H, 11.96%.

1-Butoxy-1-(trimethylsiloxy)ethylene (34): Bp 95—101 °C (39 Torr); IR(neat) 2960, 1657, 1278, 1252, 1088, 1023, 849, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.22 (s, 9H), 0.94 (t, J=7.2 Hz, 3H), 1.34—1.52 (m, 2H), 1.60—1.73 (m, 2H), 3.06 (d, J=2.5 Hz, 1H), 3.21 (d, J=2.5 Hz, 1H), 3.70 (t, J=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=0.05, 13.69, 19.26, 30.91, 60.03, 67.54, 161.2; MS (70 eV) m/z (rel intensity) 188 (3), 131 (26), 117 (94), 75 (100), 73 (97), 72 (23), 57 (22), 56 (41), 45 (26), 43 (80), 41 (43). Found: C, 57.20; H, 10.91%. Calcd for $C_9H_{20}O_2Si$: C, 57.40; H, 10.70%.

1-(Trimethylsiloxy)-1-octyloxyethylene (35): Bp 91—96 °C (1 Torr); IR(neat) 2956, 2926, 2854, 1656, 1277, 1252, 1019, 848 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.22 (s, 9H), 0.88 (t, J=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60—1.73 (m, 2H), 3.05 (d, J=2.5 Hz, 1H), 3.20 (d, J=2.5 Hz, 1H), 3.68 (t, J=6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=0.08, 14.03, 22.62, 26.09, 28.87, 29.22 (two peaks), 31.78, 60.03, 67.85, 161.2; MS (70 eV) m/z (rel intensity) 244 (2), 187 (20), 133 (42), 117 (100), 75 (43), 73 (48), 56 (21), 43 (51), 41 (23). Found: C, 63.62; H, 11.51%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%.

1-Methoxy-1-(trimethylsiloxy)-1-hexene (36, (*E*):(*Z*)=83:17): Bp 102—105 °C (36 Torr); IR(neat) 2956, 1682, 1254, 1227, 1174, 1089, 906, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.19 (s, 1.53H), 0.23 (s, 7.47H), 0.89 (t, J=6.8 Hz, 3H), 1.25—1.40 (m, 4H), 1.90—2.01 (m, 2H), 3.47 (t, J=6.8 Hz, 0.17H), 3.48 (s, 0.51H), 3.52 (s, 2.49H), 3.67 (t, J=7.1 Hz, 0.83H); ^{13}C NMR for (*E*)-isomer ($CDCl_3$) δ=−0.32, 13.92, 22.20, 24.10, 32.91, 54.76, 85.33, 153.5; MS (70 eV) m/z (rel intensity) 202 (8), 159 (47), 89 (19), 73 (58), 59 (11), 55 (100), 45 (11). Found: C, 59.47; H, 11.22%. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96%.

1-Methoxy-1-(trimethylsiloxy)-1-octene (38, (*E*):(*Z*)=88:12): Bp 68—70 °C (1 Torr); IR(neat) 2956, 2922, 2852, 1682, 1253, 1227, 1170, 1091, 902, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.19 (s, 1.08H), 0.23 (s, 7.92H), 0.88 (t, J=6.5 Hz, 3H), 1.28 (bs, 8H), 1.89—2.03 (m, 2H), 3.47 (t, J=6.8 Hz, 0.12H), 3.48 (s, 0.36H), 3.51 (s, 2.64H), 3.67 (t, J=7.3 Hz, 0.88H); ^{13}C NMR for (*E*)-isomer ($CDCl_3$) δ=−0.30, 14.07, 22.68, 24.43, 28.85, 30.67, 31.78, 54.78, 85.42, 153.5; MS (70 eV) m/z (rel intensity) 230 (10), 160 (11), 159 (75), 89 (16), 73 (52), 59 (11), 55 (100), 41 (11). Found: C, 62.68; H, 11.63%. Calcd for $C_{12}H_{26}O_2Si$: C, 62.55; H, 11.37%.

1-(3-Butenyloxy)-1-(trimethylsiloxy)ethylene (42): Bp 90—91 °C (39 Torr); IR(neat) 2958, 1653, 1277, 1253, 1088, 1018, 990, 911, 847, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.22 (s, 9H), 2.43 (qt, J=6.7, 1.3 Hz, 2H), 3.07 (d, J=2.6 Hz, 1H), 3.23 (d, J=2.6 Hz, 1H), 3.75 (t, J=6.7 Hz, 2H), 5.08 (ddt, J=10.2, 1.8, 1.3 Hz, 1H), 5.13 (ddt, J=17.0, 1.8, 1.3 Hz, 1H), 5.84 (ddd, J=17.0, 10.2, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.09, 33.28, 60.26, 67.00, 117.0, 134.4, 161.0; MS (70 eV) m/z (rel intensity) 186 (3), 101 (21), 75 (61), 73 (100), 55 (73), 54 (85), 43 (45). Found: C, 57.74; H, 9.82%. Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74%.

The Reaction of 1-Butoxy-1-(*t*-butyldimethylsiloxy)ethylene with Perfluorohexyl Iodide in the Presence of 2,6-Dimethylpyridine (Procedure A). This reaction gave a mixture of **30a** and **31** in 37 and 10% yields respectively. Butyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoate (**30a**): Bp 76—81 °C (7 Torr, bath temp); IR(neat) 2964, 1754, 1396, 1353, 1241, 1208, 1146, 1122, 1064, 709, 628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.94 (t, J=7.2 Hz, 3H), 1.31—1.49 (m, 2H), 1.57—1.73 (m, 2H), 3.14 (t, J=17.7 Hz, 2H), 4.20 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.53, 18.94, 30.37, 37.02 (t, J=22.5 Hz), 65.91, 163.9; ^{19}F NMR ($CDCl_3$) δ=−81.34 (tt, J=7.4, 3.0 Hz, 3F), −111.6—−112.6 (m, 2F), −112.1 (bs, 2F), −123.4 (bs, 4F), −126.3—−126.8 (m, 2F); MS (70 eV) m/z (rel intensity) 434 (0.2), 361 (26), 69 (18), 57 (42), 56 (100), 55 (12), 41 (35). Found: C, 33.45; H, 2.46%. Calcd for $C_{12}H_{11}F_{13}O_2$: C, 33.20; H, 2.55%. (*E*)-Butyl 3,4,4,5,5,6,6,7,7,8,8,8-dodecafluoro-2-octenoate (**31**): Bp 83—88 °C (13 Torr, bath temp); IR(neat) 2964, 1736, 1702, 1350, 1275, 1239, 1206, 1143, 1114, 723, 644 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.96 (t, J=7.3 Hz, 3H), 1.33—1.51 (m, 2H), 1.60—1.76 (m, 2H), 4.24 (t, J=6.6 Hz, 2H), 6.00 (d, J=29.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.45, 19.02, 30.44, 65.64, 107.2 (t, J=4.0 Hz), 161.6 (d, J=2.7 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.14—−81.43 (m, 3F), −107.7—−108.7 (m, 1F), −118.9—−119.4 (m, 2F), −123.2 (bs, 4F), −126.6 (bs, 2F); MS (12 eV) m/z (rel intensity) 359 (M^+−C_4H_7, 6), 341 (5), 57 (5), 56 (100), 55 (2). Found: C, 35.02; H, 2.49%. Calcd for $C_{12}H_{10}F_{12}O_2$: C, 34.80; H, 2.43%.

The Reactions of Ketene Silyl Acetals with Perfluorohexyl Iodide without Base (Procedure B). Following procedure for the reaction of ketene *t*-butyldimethylsilyl acetal derived from butyl acetate with perfluorohexyl iodide is typical. Under argon atmosphere, Et_3B was added to a solution of ketene silyl acetal (**29**, 456 mg, 1.98 mmol) and perfluorohexyl iodide (440 mg, 0.99 mmol) in hexane (4.9 ml). After stirring for 10 min, sat. aq $NaHCO_3$ (5 ml) was added to the reaction mixture. The mixture was vigorously stirred for 40 min, then poured into water (30 ml) and extracted with hexane (30 m×2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was purified by silica-gel column chromatography to give **30a** in 87% yield.

Methyl 2-Butyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoate (37a): Bp 98—103 °C (20 Torr, bath temp); IR(neat) 2964, 2936, 2870, 1757, 1458, 1437, 1350, 1239, 1194, 1145, 1116, 712, 695, 652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (t, J=6.8 Hz, 3H), 1.21—1.47 (m, 4H), 1.74—2.07 (m, 2H), 3.06—3.29 (m, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.42, 22.19, 24.87, 28.98, 48.15 (dd, J=22.6, 20.6 Hz), 52.28, 168.1 (d, J=7.8 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.32 (t, J=9.8 Hz, 3F), −113.7 (dm, J=266 Hz, 1F), −116.4 (dm, J=266 Hz, 1F), −121.8—−122.4 (m, 4F), −123.3 (bs, 2F), −126.3—−126.9 (m, 2F); MS (70 eV) m/z (rel intensity) 448 (0.1), 392 (11), 129 (16), 123 (100), 91 (13), 88 (14), 87 (12), 69 (14), 59 (68), 57 (11), 55

(24), 43 (13), 42 (14), 41 (21). Found: C, 34.82; H, 2.84%. Calcd for $C_{13}H_{13}F_{13}O_2$: C, 34.84; H, 2.92%.

Hexyl 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-2,2-dimethyloctanoate (41a): Bp 69—74 °C (2 Torr, bath temp); IR(neat) 2960, 2932, 2862, 1746, 1477, 1277, 1241, 1195, 1177, 1147, 1112, 1063, 697, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.23—1.42 (m, 6H), 1.46 (s, 6H), 1.57—1.71 (m, 2H), 4.14 (t, J=6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.74, 19.99, 22.48, 25.46, 28.29, 31.34, 48.48 (t, J=20.8 Hz), 66.02, 170.6 (t, J=3.1 Hz); ^{19}F NMR ($CDCl_3$) δ=−81.33, (tt, J=9.9, 2.5 Hz, 3F), −112.4 (bs, 2F), −114.7 (bs, 2F), −118.1 (bs, 2F), −123.1 (bs, 2F), −126.3—−126.8 (m, 2F); MS (12 eV) m/z (rel intensity) 407 ($M^+-C_6H_{11}$, 15), 85 (49), 84 (100), 69 (9), 57 (11), 56 (37), 43 (51). Found: C, 39.22; H, 3.89%. Calcd for $C_{16}H_{19}F_{13}O_2$: C, 39.20; H, 3.91%.

The Reaction of Ketene Silyl Acetals with Perfluoroisopropyl Iodide. Et_3B (0.2 mmol) was added to a solution of ketene silyl acetal (2.0 mmol) and perfluoroisopropyl iodide (1.0 mmol) in hexane (5 ml) at 0 °C. After an addition of Et_3B, the reaction mixture was immediately warmed up to room temperature and stirred for appropriate time given in Table 3. Work-up and purification were performed according to Procedure B. In the case of ketene trimethylsilyl acetals **34** or **35**, butyl or octyl 2-(trimethylsilyl)acetate was obtained as by-product. These trimethylsilyacetates could be produced by isomerization of starting ketene acetals **34** and **35** under the reaction conditions. Tetrabutylammonium fluoride (TBAF, 1.0 mmol per 1.0 mmol of ketene silyl acetal) was added to the reaction mixture prior to work-up to remove these by-products from perfluoroalkylated esters **30** and **33**. Thus, TBAF was added and the resulting mixture was stirred for 10 min at room temperature. The resulting mixture was poured into dil aq NH_4Cl (sat. aq NH_4Cl:water=1:10). Extraction and purification by silica-gel column chromatography provided the desired perfluoroalkylated esters.

Butyl 3,4,4,4-Tetrafluoro-3-trifluoromethylbutanoate (30b): Bp 68—73 °C (36 Torr, bath temp); IR(neat) 2962, 1753, 1346, 1296, 1229, 1202, 1168, 1129, 1060, 1004, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (t, J=7.1 Hz, 3H), 1.30—1.48 (m, 2H), 1.57—1.71 (m, 2H), 3.07 (d, J=20.4 Hz, 2H), 4.17 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.46, 18.91, 30.26, 34.21 (d, J=19.8 Hz), 65.96, 89.98 (dm, J=211 Hz), 120.4 (qd, J=288, 27.9 Hz), 164.4 (d, J=2.5 Hz); ^{19}F NMR ($CDCl_3$) δ=−77.25 (d, J=7.3 Hz, 6F), −182.9 (tsep, J=20.1, 7.3 Hz, 1F); MS (70 eV) m/z (rel intensity) 284 (0.6), 255 (3), 229 (5), 212 (6), 211 (100), 191 (2), 163 (2), 56 (3). Found: C, 38.26; H, 3.94%. Calcd for $C_9H_{11}F_7O_2$: C, 38.04; H, 3.90%.

Octyl 3,4,4,4-Tetrafluoro-3-trifluoromethylbutanoate (33a): Bp 69—74 °C (1 Torr, bath temp); IR(neat) 2958, 2930, 2860, 1754, 1347, 1296, 1230, 1202, 1169, 1061, 1006, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59—1.73 (m, 2H), 3.06 (d, J=20.4 Hz, 2H), 4.16 (t, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.94, 22.60, 25.69, 28.26, 29.11 (two peaks), 31.75, 34.22 (d, J=19.9 Hz), 66.24, 89.99 (dm, J=211 Hz), 120.4 (qd, J=288, 28.2 Hz), 164.4; ^{19}F NMR ($CDCl_3$) δ=−77.23 (d, J=6.9 Hz, 6F), −182.9 (tsep, J=20.2, 6.9 Hz, 1F); MS (12 eV) m/z (rel intensity) 229 ($M^+-C_8H_{15}$, 12), 112 (55), 84 (100), 83 (81), 82 (30), 70 (84), 69 (34), 68 (29), 56 (52). Found: C, 46.06; H, 5.81%. Calcd for $C_{13}H_{19}F_7O_2$: C, 45.89; H, 5.63%.

Methyl 2-(Perfluoroisopropyl)hexanoate (37b): Bp 78—83 °C (50 Torr, bath temp); IR(neat) 2962, 2934, 2878, 1757, 1460, 1439, 1282, 1222, 1169, 1135, 1111, 1092, 984, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (t, J=7.0 Hz, 3H), 1.15—1.50 (m, 4H), 1.69—1.86 (m, 1H), 1.91—2.12 (m, 1H), 3.10—3.24 (m, 1H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.56, 22.12, 25.44, 29.84, 46.90 (d, J=20.1 Hz), 52.51, 91.53 (dm, J=208 Hz), 120.7 (qd, J=289, 29.9 Hz), 168.3 (d, J=6.0 Hz); ^{19}F NMR ($CDCl_3$) δ=−74.04 (d, J=7.3 Hz, 6F), −178.6 (dsep, J=12.2, 6.1 Hz, 1F); MS (70 eV) m/z (rel intensity) 298 (0.2), 267 (23), 255 (21), 242 (80), 173 (100), 141 (11), 129 (18), 59 (13). Found: C, 40.25; H, 4.54%. Calcd for $C_{10}H_{13}F_7O_2$: C, 40.28; H, 4.39%.

Methyl 2-(Perfluoroisopropyl)octanoate (39a): Bp 85—90 °C (24 Torr, bath temp); IR(neat) 2958, 2930, 2860, 1757, 1459, 1439, 1302, 1229, 1168, 1134, 1114, 1093, 976, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.28 (bs, 8H), 1.67—1.89 (m, 1H), 1.92—2.13 (m, 1H), 3.09—3.23 (m, 1H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.77, 22.41, 25.69, 27.67, 28.64, 31.38, 46.90 (d, J=20.2 Hz), 52.39, 91.48 (dm, J=209 Hz), 120.6 (qd, J=287, 27.0 Hz), 168.0—168.2 (m); ^{19}F NMR ($CDCl_3$) δ=−74.03 (d, J=6.1 Hz, 6F), −178.7 (dsep, J=13.4, 6.1 Hz, 1F); MS (70 eV) m/z (rel intensity) 326 (2), 297 (25), 295 (13), 255 (58), 242 (100), 173 (91), 59 (17), 55 (14), 43 (17), 41 (16). Found: C, 43.96; H, 5.27%. Calcd for $C_{12}H_{17}F_7O_2$: C, 44.18; H, 5.25%.

Hexyl 3,4,4,4-Tetrafluoro-3-trifluoromethylbutanoate (41b): Bp 72—77 °C (3 Torr, bath temp); IR(neat) 2958, 2932, 2860, 1743, 1472, 1287, 1228, 1190, 1166, 1149, 1116, 1033, 995, 726 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, J=6.6 Hz, 3H), 1.26—1.45 (m, 6H), 1.50 (s, 6H), 1.58—1.74 (m, 2H), 4.12 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.84, 21.23, 22.46, 25.44, 28.15, 31.29, 46.54 (d, J=19.0 Hz), 66.23, 93.87 (dm, J=216 Hz), 121.2 (qd, J=289, 28.7 Hz), 171.4; ^{19}F NMR ($CDCl_3$) δ=−70.76 (d, J=4.9 Hz, 6F), −178.0 (bs, 1F); MS (12 eV) m/z (rel intensity) 257 ($M^+-C_6H_{11}$, 27), 85 (65), 84 (62), 69 (11), 57 (24), 56 (32), 43 (100). Found: C, 45.93; H, 5.81%. Calcd for $C_{13}H_{19}F_7O_2$: C, 45.89; H, 5.63%.

The Reaction of Ketene Silyl Acetals with Trifluoromethyl Iodide. CF_3I (1.0 mmol) was introduced into the flask precooled to −78 °C, then hexane (5.0 ml) and ketene silyl acetal (2.0 mmol) were added to the flask. Et_3B (0.2 mmol) was added and the reaction mixture was immediately warmed up to room temperature. After stirring for several hours (Table 3), extractive work-up followed by purification gave the corresponding trifluoromethylated ester.

Octyl 3,3,3-Trifluoropropanoate (33b): Bp 56—61 °C (1 Torr, bath temp); IR(neat) 2956, 2926, 2856, 1754, 1418, 1399, 1364, 1269, 1221, 1119 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59—1.74 (m, 2H), 3.17 (q, J=10.1 Hz, 2H), 4.18 (t, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.01, 22.60, 25.69, 28.34, 29.09 (two peaks), 31.72, 39.66 (q, J=30.9 Hz), 65.95, 123.4 (q, J=277 Hz), 164.1 (q, J=4.2 Hz); ^{19}F NMR ($CDCl_3$) δ=−64.02 (t, J=10.4 Hz); MS (70 eV) m/z (rel intensity) 129 ($M^+-C_8H_{15}$, 6), 112 (23), 84 (94), 83 (73), 70 (100), 69 (45), 68 (30), 56 (73). Found: C, 55.21; H, 8.13%. Calcd for $C_{11}H_{19}F_3O_2$: C, 54.99; H, 7.97%.

Methyl 2-Trifluoromethyloctanoate (39b): Bp 78—83 °C (24 Torr, bath temp); IR(neat) 2956, 2928, 2860, 1755, 1459, 1439, 1354, 1272, 1209, 1165, 1107 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.4 Hz, 3H), 1.21—1.41 (m, 8H), 1.67—2.01 (m, 2H), 3.11 (dqd, J=9.9, 8.4, 4.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.87, 22.44, 26.11, 26.70, 28.74, 31.37, 50.28 (q, J=27.4 Hz), 52.44, 124.7 (q, J=280 Hz), 168.2 (q,

J=2.7 Hz); ^{19}F NMR ($CDCl_3$) δ=−68.86 (d, J=8.5 Hz); MS (12 eV) m/z (rel intensity) 226 (0.3), 155 (23), 143 (13), 142 (100), 116 (27), 115 (18), 85 (27), 84 (16). Found: C, 53.05; H, 7.82%. Calcd for $C_{10}H_{17}F_3O_2$: C, 53.09; H, 7.57%.

Hexyl 3,3,3-Trifluoro-2,2-dimethylpropanoate (41c): Bp 58—63 °C (5 Torr, bath temp); IR(neat) 2956, 2932, 2860, 1745, 1476, 1401, 1282, 1206, 1152, 1119 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.6 Hz, 3H), 1.24—1.39 (m, 6H), 1.42 (s, 6H), 1.58—1.73 (m, 2H), 4.16 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.87, 19.67, 22.46, 25.36, 28.32, 31.28, 48.45 (q, J=25.5 Hz), 65.84, 126.4 (q, J=282 Hz), 170.5; ^{19}F NMR ($CDCl_3$) δ=−75.42 (s); MS (12 eV) m/z (rel intensity) 157 ($M^+-C_6H_{11}$, 31), 139 (8), 85 (32), 84 (100), 69 (24), 57 (13), 56 (68), 43 (50), 42 (9). Found: C, 55.09; H, 8.18%. Calcd for $C_{11}H_{19}F_3O_2$: C, 54.99; H, 7.97%.

The Reaction of Ketene Silyl Acetals with 2,2,2-Trifluoroethyl Iodide. The reactions were performed according to Procedure B.

Octyl 4,4,4-Trifluorobutanoate (33c): Bp 72—77 °C (1 Torr, bath temp); IR(neat) 2958, 2928, 2858, 1744, 1332, 1265, 1230, 1192, 1145, 1112, 985 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.30 (bs, 10H), 1.57—1.71 (m, 2H), 2.33—2.63 (m, 4H), 4.11 (t, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.99, 22.60, 25.83, 27.09 (q, J=3.3 Hz), 28.50, 29.14 (two peaks), 29.35 (q, J=29.6 Hz), 31.74, 65.26, 126.5 (q, J=277 Hz), 170.9; ^{19}F NMR ($CDCl_3$) δ=−67.56 (t, J=10.4 Hz); MS (12 eV) m/z (rel intensity) 143 ($M^+-C_8H_{15}$, 27), 112 (44), 84 (96), 83 (83), 82 (24), 70 (100), 69 (36), 68 (23), 56 (59). Found: C, 56.84; H, 8.61%. Calcd for $C_{12}H_{21}F_3O_2$: C, 56.68; H, 8.32%.

Methyl 2-(2,2,2-Trifluoroethyl)octanoate (39c): Bp 88—93 °C (24 Torr, bath temp); IR(neat) 2954, 2928, 2858, 1744, 1438, 1381, 1260, 1203, 1153, 1126, 1096 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.5 Hz, 3H), 1.27 (bs, 8H), 1.45—1.77 (m, 2H), 2.05—2.33 (m, 1H), 2.47—2.77 (m, 2H), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.97, 22.49, 26.68, 28.86, 31.51, 32.52, 35.87 (q, J=29.1 Hz), 39.34, 51.96, 126.2 (q, J=277 Hz), 174.6; ^{19}F NMR ($CDCl_3$) δ=−65.93 (t, J=10.4 Hz); MS (70 eV) m/z (rel intensity) 240 (0.9), 169 (18), 156 (100), 87 (42), 59 (22), 57 (11), 55 (18), 43 (18), 41 (21). Found: C, 54.70; H, 8.18%. Calcd for $C_{11}H_{19}F_3O_2$: C, 54.99; 7.97%.

The Reaction of 42 with Perfluorohexyl Iodide. Following the procedure B, treatment of ketene silyl acetal **42** with perfluorohexyl iodide provided a cyclized product **43** (10%) and perfluoroalkylated ester **44** (50%). 3-Iodomethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-2-(trimethylsiloxy)-oxolane (**43**): Bp 93—98 °C (1 Torr, bath temp); IR(neat) 2956, 2894, 1363, 1234, 1146, 1123, 1018, 908, 845, 719, 709, 634 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.14 (s, 9H), 1.73—1.94 (m, 1H), 2.28—2.76 (m, 4H), 3.04 (dd, J=10.2, 9.9 Hz, 1H), 3.38 (dd, J=9.9, 4.2 Hz, 1H), 3.81 (ddd, J=10.6, 8.6, 6.2 Hz, 1H), 4.01 (ddd, J=8.6, 8.3, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.06, 3.54, 32.86, 39.10 (t, J=20.0 Hz), 51.10, 65.81, 103.7; ^{19}F NMR ($CDCl_3$) δ=−81.31 (tt, J=9.8, 3.0 Hz, 3F), −112.7—−114.1 (m, 2F), −122.1 (bs, 2F), −123.4 (bs, 2F), −124.0 (bs, 2F), −126.3—−126.8 (m, 2F); MS (12 eV) m/z (rel intensity) 632 (0.1), 618 (12), 506 (21), 505 (100), 489 (8), 304 (6), 303 (49), 299 (15), 55 (54). Found: C, 28.72; H, 2.96%. Calcd for $C_{15}H_{18}F_{13}IO_2Si$: C, 28.49; H, 2.87%.

3-Butenyl 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctanoate (44): Bp 91—96 °C (27 Torr, bath temp); IR(neat) 1755, 1352, 1241, 1207, 1145, 1122, 709, 628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.43 (qt, J=6.7, 1.3 Hz, 2H), 3.14 (t, J=17.5 Hz, 2H), 4.26 (t, J=6.7 Hz, 2H), 5.11 (ddt, J=10.2, 1.7, 1.3 Hz, 1H), 5.13 (ddt, J=17.1, 1.7, 1.3 Hz, 1H), 5.78 (ddt, J=17.1, 10.2, 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=32.81, 36.92 (t, J=22.5 Hz), 64.99, 117.5, 133.3, 163.8; ^{19}F NMR ($CDCl_3$) δ=−81.31 (tt, J=6.9, 3.0 Hz, 3F), −111.6—−112.5 (m, 2F), −122.2 (bs, 2F), −123.3 (bs, 4F), −126.3—−126.8 (m, 2F); MS (12 eV) m/z (rel intensity) 432 (2), 362 (9), 361 (100), 341 (16), 55 (5), 54 (93). Found: C, 33.49; H, 2.23%. Calcd for $C_{12}H_9F_{13}O_2$; C, 33.35; H, 2.10%.

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