A New α-Seleno- or Nonselenoperfluoroacyl Olefination of Aldehydes and Ketones Using *β*-Ethoxy-*β*-perfluoroalkyl Vinylic Selenides

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β-Alkoxy vinylic chalcogenides can be easily lithiated by treatment with strong base, and subsequent reactions with aldehydes and ketones afford the 2-chalcogeno allylic alcohols, which are potentially versatile precursors for the 2-chalcogene-substituted allylic cations[1] or their hydrolysis allows the α-chalcogeno formyl olefination of aldehydes and ketones.[2,3]

To explore the α-chalcogene-substituted olefination, we planned to investigate the perfluoroacyl olefination of the aldehydes and ketones using the α-lithio-*β*-perfluoroalkyl vinylic chalcogenides. α-(Methylthio)- or α-(phenylthio)-perfluoroacyl olefinations of the nonenolizable aldehydes have already reported to afford α-(thio)-α,*β*-unsaturated ketones in high yields;[4] however, the α-seleno perfluoroacyl olefination could not be examined because *β*-alkoxy-*β*-perfluoroalkyl vinylic selenides were difficult to prepare by the same method as the sulfur analogues. It is a more efficient route than that of the α-thio-substituted olefination because a new perfluoroalkyl vinylic selenide could provide two kinds of vinyllithiums by deprotonation or transmetalation (Scheme 1).[5] The reactions of each vinyllithium with aldehydes and ketones and the following process would accomplish the α-seleno or nonseleno perfluoroacyl olefination,[6−8] respectively. Here we report a novel α-seleno- or nonseleno perfluoroacyl olefination of the aldehydes and ketones using *β*-ethoxy-*β*-perfluoroalkyl vinylic selenides.

Preparations of the *β*-ethoxy-*β*-perfluoroalkyl vinylic selenides **2**−**5** were performed by our original method. The vinylic selenides were obtained from the reactions between the lithiated[5] bis(phenylseleno)methane (**1**) generated by the treatment with lithium 2,2,6,6-tetramethylpiperidide (LTMP) and $RfCO_2Et$ at −50 °C followed by the elimination of the phenylselenenyl group using methanesulfonyl chloride (Scheme 2).[9] We first examined the deprotonation of the vinylic selenides by a few amide bases (method A).[10] LTMP was found to be effective in their deprotonation of **2** and the reaction with benzaldehyde afforded the *(E)*-2-(phenylseleno)allylic alcohol **6a** in 72% yield. The isomerization of **6a** by *p*-toluenesulfonic acid (1.1 equiv) gave *(Z)*-1,1,1-trifluoro-4-phenyl-3-(phenylseleno)but-3-en-2-one (**14a**) in 53% yield. Spectroscopic data, by showing the carbonyl absorption at *ν* 1710 cm^{-1} in the IR spectrum, exhibiting the olefinic proton at *δ* 8.14 ppm in the ^1H NMR spectrum, and also showing the trifluoromethyl carbon at *δ* 116.3 (J_{C-F} = 293 Hz) and the 2-C at *δ* 180.1 (J_{C-F} = 26 Hz) in the ^{13}C NMR spectrum, indicated that the product was α,*β*-unsaturated trifluoromethyl ketone. We also examined the α-seleno trifluoroacetyl olefination of the other aldehydes and the results are shown in Table 1. *(E)*-Cinnamaldehyde and phenylpropargyl aldehyde gave the trifluoromethyl ketones **14b,c** (Entries 2 and 3); however, the reaction of **2** with ketones such as cyclopentanone did not afford the allylic alcohols.

Next, we performed the lithiation of **2** by transmetalation (method B) and examined the reaction with mesityl aldehyde. The allylic alcohol **7a** was obtained in moderate yield, accompanied by *n*-butyl phenyl selenide. The isomerization of **7a** under the same condition afforded the α,*β*-unsaturated trifluoromethyl ketone **15a** (entry 4). The trifluoroacetyl olefinations of the ketones, such as acetophenone and cyclododecanone, proceeded in good yields (entries 5 and 7). Furthermore, we performed the α-seleno olefination using *β*-pentafluoroethyl vinylic selenide **3** with aldehydes to afford the corresponding pentafluoroethyl ketones **17a**,**b** (entries 8 and 9). Nonselenium-type olefinations of the aldehyde and ketone exclusively gave the ketones **18a**,**b** (entries 10 and 11). The α-thio perfluoroacyl olefinations, which have previously been reported, are quite limited for the pentafluoropropionyl olefinations because the *β*-pentafluoroethyl vinylic sulfide could be obtained only in low yields.[4] This perfluoroacyl olefinations reported here are versatile and suitable for the preparations of the α,*β*-unsaturated perfluoroalkyl ketones bearing the long perfluoroalkyl groups. The heptafluoropropionyl or the nonafluorovaleryl olefinations using the vinylic selenide **4**,**5** gave the α,*β*-unsaturated ketones **19**−**22** (entries 12−15).

We also examined the tandem olefination of the α,*β*-unsaturated perfluoroalkyl ketones as shown in Scheme 3. It is noteworthy that the treatment of the dienyl alcohols **23** and **24** with acid afforded the 4,6-bis-(perfluoroalkyl)-*2H*-pyrans **25** and **26**, accompanied by the 1,3-butadienyl perfluoroalkyl ketone acetals **27** and **28**, not the dienyl ketone **29**. Much attention has been paid to the fluorinated heterocycles;[11] so that, they

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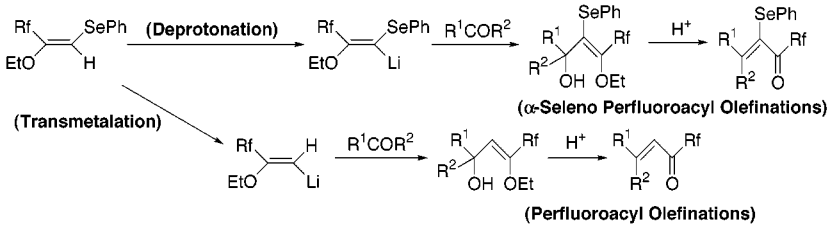
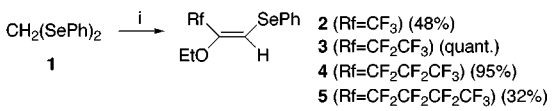
Scheme 1



Scheme 2[a]



[a] Reagent: (i) lithium 2,2,6,6-tetramethylpiperidide (LTMP)/ $RfCO_2Et$/MsCl/−50 °C.

would be expected to show the interesting biological activities.[12] Now we are examining the further investigation of the uneque 4,6-bis(perfluoroalkyl)pyran formations. These results will be reported elsewhere.

Experimental Section[4]

Preparation of (*E*)-2-Ethoxy-1,1,1-trifluoro-3-(phenylseleno)prop-2-ene (2). Typical Procedure. A THF (8.00 mL) solution of bis(phenylseleno)methane (**1**) (6.00 g, 18.4 mmol) was added dropwise to a THF (30.0 mL) solution of lithium 2,2,6,6-tetramethylpiperidide [prepared from 2,2,6,6-tetramethylpiperidine (3.90 g, 27.6 mmol) and *n*-BuLi (16.0 mL of 1.50 M *n*-BuLi in *n*-hexane solution, 23.9 mmol)] under an Ar atmosphere at −50 °C. The mixture was stirred for 10 min, ethyl trifluoroacetate (6.60 mL, 55.2 mmol) and then methanesulfonyl chloride (3.16 g, 27.6 mmol) was added dropwise to it. The whole was stirred for 10 min and poured into water (150 mL). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane to give the title compound **2** (2.31 g, 43%) as a pale yellow oil.

(*E*)-2-Ethoxy-1,1,1-trifluoro-3-(phenylseleno)prop-2-ene (2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (3H, t, J = 7 Hz), 3.82 (2H, q, J = 7 Hz), 5.80 (1H, s), 7.30−7.31 (3H, m), 7.52−7.54 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (q), 65.3 (t), 97.7 (d), 120.9 (s, q, J = 275 Hz), 128.1 (d), 129.7 (d × 2), 131.0 (s), 132.7 (d × 2), 143.5 (s, q, J = 34 Hz); ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −10.98 (3F, s); MS m/z 139 (M^+ − PhSe). Anal. Calcd for $C_{11}H_{11}F_3OSe$: C, 44.76; H, 3.76. Found: C, 44.81; H, 3.74.

(*E*)-3-Ethoxy-1,1,1,2,2-pentafluoro-4-(phenylseleno)but-3-ene (3): ^{1}H NMR δ 1.32 (3H, t, J = 7 Hz), 3.83 (2H, q, J = 7 Hz), 5.94 (1H, s), 7.30−7.33 (3H, m), 7.53−7.55 (2H, m); ^{13}C NMR δ 14.3 (q), 65.5 (t), 100.9 (d), 111.3 (s, tq, J = 257, 39 Hz), 119.0 (s, qt, J = 288, 39 Hz), 128.2 (d), 129.7 (d × 2), 131.7 (s), 132.9 (d × 2), 142.1 (s, t, J = 26 Hz); ^{19}F NMR δ −37.83 (2F, q, J = 1 Hz), −5.39 (3F, t, J = 3 Hz); MS m/z 189 (M^+ − PhSe). Anal. Calcd for $C_{12}H_{11}F_5OSe$: C, 41.76; H, 3.21. Found: C, 41.72; H, 3.20.

Preparation of (*E*)-2-Ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylseleno)but-2-en-4-ol (6a). Typical Procedure. A THF (1.00 mL) solution of *(E)*-2-ethoxy-1,1,1-trifluoro-3-(phenylseleno)prop-2-ene (**2**) (0.30 g, 1.00 mmol) was added dropwise to a THF (3.0 mL) solution of lithium 2,2,6,6-tetramethylpiperidide (prepared from 2,2,6,6-tetramethylpiperidine (0.28 g, 2.00 mmol) and *n*-BuLi (1.00 mL, 1.50 mmol)) under an Ar atmosphere at −78 °C. The reaction mixture was stirred for 10 min. A THF (1.00 mL) solution of benzaldehyde (0.16 g, 1.50 mmol) was added to the mixture. The workup procedure gave the title compound **6a** (0.29 g, 72%) as a yellow oil: ^{1}H NMR δ 1.17 (3H, t, J = 7 Hz), 2.83 (1H, s), 3.82−3.98 (2H, m), 5.97 (1H, d, J = 7 Hz), 7.13−7.20 (3H, m), 7.21−7.35 (7H, m); ^{13}C NMR δ 15.2 (q), 69.3 (t), 70.1 (d, q, J = 3 Hz), 121.0 (s, q, J = 280 Hz), 125.8 (d × 2), 127.6 (d), 128.4 (d × 2), 129.1 (d × 2), 129.4 (s), 132.7 (d × 2), 134.2 (s), 140.7 (s), 145.0 (s, q, J = 33 Hz); ^{19}F NMR δ −18.13 (3F, s); MS m/z 402 (M^+). Anal. Calcd for $C_{18}H_{17}F_3O_2Se$: C, 53.88; H, 4.27. Found: C, 53.84; H, 4.32.

(*Z*)-2-Ethoxy-1,1,1-trifluoro-4-mesitylbut-2-en-4-ol (7a): ^{1}H NMR δ 1.32 (3H, t, J = 7 Hz), 2.24 (3H, s), 2.40 (6H, s), 3.68−3.83 (2H, m), 5.37 (1H, d, J = 9 Hz), 6.03 (1H, dd, J = 9, 1 Hz), 6.82 (2H, s); ^{13}C NMR δ 14.2 (q), 20.7 (q × 2), 20.9 (q), 64.6 (t), 65.0 (d, q, J = 2 Hz), 108.0 (d), 120.8 (s, q, J = 276 Hz), 130.5 (d × 2), 135.8 (s), 136.3 (s × 2), 137.4 (s), 145.9 (s, q, J = 34 Hz); ^{19}F NMR δ −12.23 (3F, s); MS m/z 273 (M^+ − Me). Anal. Calcd for $C_{15}H_{19}F_3O_2$: C, 62.49; H, 6.64. Found: C, 62.69; H, 6.72.

(*E*)-3-Ethoxy-1,1,1,2,2-pentafluoro-6,6-dimethyl-4-(phenylseleno)hept-3-en-5-ol (8a): ^{1}H NMR δ 0.97 (9H, s), 1.13 (3H, t, J = 7 Hz), 2.84 (1H, dd, J = 10, 1 Hz), 3.82−3.90 (1H, m), 4.19−4.26 (1H, m), 4.56 (1H, d, J = 10 Hz), 7.19−7.23 (3H, m), 7.41−7.43 (2H, m); ^{13}C NMR δ 15.3 (q), 26.9 (q × 3), 36.6 (s), 70.2 (t), 74.3 (d, t, J = 13 Hz), 111.7 (s, qt, J = 37, 259 Hz), 118.8 (s, qt, J = 37, 288 Hz), 127.5 (d), 129.2 (d × 2), 131.1 (d × 2), 131.4 (s), 138.1 (s), 144.7 (s, t, J = 24 Hz); ^{19}F NMR δ −33.25 (1F, d, J = 273 Hz), −31.77 (1F, d, J = 273 Hz), −5.62 (3F, t, J = 2 Hz); MS m/z 432 (M^+). Anal. Calcd for $C_{17}H_{21}F_5O_2Se$: C, 47.34; H, 4.91. Found: C, 47.40; H, 4.85.

(*Z*)-3-Ethoxy-1,1,1,2,2-pentafluoro-5-mesitylpent-3-en-5-ol (9a): ^{1}H NMR δ 1.31 (3H, t, J = 7 Hz), 1.95 (1H, brs), 2.25 (3H, s), 2.41 (6H, s), 3.71−3.86 (2H, m), 5.55 (1H, d, J = 9 Hz), 6.06 (1H, dt, J = 9, 2 Hz), 6.83 (2H, s); ^{13}C NMR δ 14.2 (q), 20.8 (q × 2), 20.9 (q), 64.7 (t), 64.8 (d, t, J = 3 Hz), 111.1 (d), 111.3 (s, qt, J = 37, 260 Hz), 118.9 (s, qt, J = 37, 288 Hz), 130.5 (d × 2), 136.0 (s), 136.3 (s × 2), 137.5 (s), 145.2 (s, J = 27 Hz); ^{19}F NMR δ −37.68 (1F, d, J = 282 Hz), −36.46 (1F, d, J = 282 Hz), −5.24 (3F, s); MS m/z 219 (M^+ − mesityl). Anal. Calcd for $C_{16}H_{19}F_5O_2$: C, 56.80; H, 5.66. Found: C, 57.21; H, 5.68.

(*E*)-4-Ethoxy-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-5-(phenylseleno)oct-4-en-6-ol (*E*)-(10): ^{1}H NMR δ 0.96 (9H, s), 1.36 (3H, t, J = 7 Hz), 2.87 (1H, d, J = 12 Hz), 3.89−3.93 (1H, m), 4.05−4.08 (1H, m), 4.53 (1H, d, J = 12 Hz), 7.21−7.27 (3H, m), 7.44−7.46 (2H, m); ^{19}F NMR δ −47.11 (2F, s), −33.98 (1F, dq, J = 278, 9 Hz), −27.98 (1F, dq, J = 278, 9 Hz), −2.56 (3F, t, J = 10 Hz); MS m/z 482 (M^+). Anal. Calcd for $C_{18}H_{21}F_7O_2Se$: C, 44.92; H, 4.40. Found: C, 45.43; H, 4.47.

(*Z*)-4-Ethoxy-1,1,1,2,2,3,3-heptafluoro-6-phenylhex-4-en-6-ol (11): ^{1}H NMR δ 1.30 (3H, t, J = 7 Hz), 2.20 (1H, brs), 3.69−3.81 (2H, m), 5.23 (1H, d, J = 10 Hz), 5.65 (1H, d, J = 10 Hz), 7.23−7.39 (5H, m); ^{19}F NMR δ −49.77 (2F, s), −35.74 (1F, dq, J = 284, 9 Hz), −33.90 (1F, dq, J = 284, 9 Hz), −2.87 (3F, t, J = 9 Hz); MS m/z 346 (M^+). Anal. Calcd for $C_{14}H_{13}F_7O_2$: C, 48.56; H, 3.78. Found: C, 50.98; H, 4.13.

(*E*)-5-Ethoxy-1,1,1,2,2,3,3,4,4-nonafluoro-8,8-dimethyl-6-(phenylseleno)non-5-en-7-ol (*E*)-(12): ^{1}H NMR δ 0.96 (9H, s), 1.36 (3H, t, J = 7 Hz), 2.86 (1H, d, J = 12 Hz), 3.88−3.94 (1H, m), 4.04−4.10 (1H, m), 4.52 (1H, d, J = 12 Hz), 7.20−7.30 (3H, m), 7.43−7.46 (2H, m); ^{19}F NMR δ −49.17 to −48.29 (1F, m), −47.77 to −46.91 (1F, m), −44.47 to −43.67 (1F, m), −43.37 to −42.57 (1F, m), −33.04 (1F, brd, J = 280 Hz), −27.84 (1F, brd, J = 280 Hz), −3.16 (3F, t, J = 10 Hz); high-resolution mass calcd for $C_{19}H_{21}F_9O_2Se$: 532.0562, found m/z 532.0554.

(*Z*)-5-Ethoxy-1,1,1,2,2,3,3,4,4-nonafluoro-7-phenylhept-5-en-7-ol (*Z*)-(13): ^{1}H NMR δ 1.32 (3H, t, J = 7 Hz), 1.57 (1H, brs), 3.75−3.83 (2H, m), 5.26 (1H, d, J = 10 Hz), 5.68 (1H, brd, J = 10 Hz), 7.28−7.44 (5H, m); ^{19}F NMR δ −48.42 to −48.35 (2F, m), −46.03 to −45.95 (2F, m), −34.75 (1F, dt, J = 282, 13

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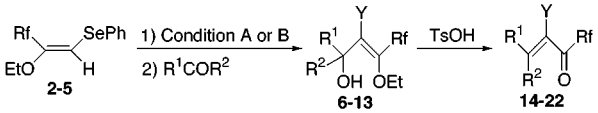
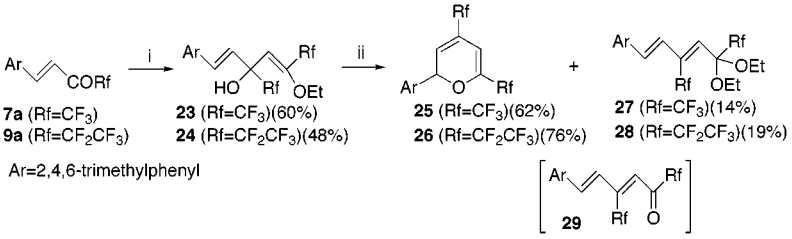
Table 1. α-Seleno or Nonselenoperfluoroacyl Olefinations of Aldehydes and Ketones



	enol ether	carbonyl compound					
entry	(Rf)	R^1	R^2	conditions	Y	alcohol (% yield)	products (% yields)
1	**2** (CF_3)	Ph	H	A[a]	PhSe	(*E*)-**6a** (72)	(*Z*)-**14a** (53)
2	**2**	(*E*)-PhCH=CH	H	A	PhSe	(*E*)-**6b** (74)	(*Z*)-**14b** (70)
3	**2**	phenylethynyl	H	A	PhSe	(*E*)-**6c** (48)	(*E*)- and (*Z*)-**14c** (72)[b]
4	**2**	Mesityl	H	B[c]	H	(*Z*)-**7a** (51)	(*E*)-**15a** (95)
5	**2**	Ph	Me	B	H	(*Z*)-**7b** (48)	(*E*)-**15b** (62)
6	**2**	phenylethynyl	H	B	H	(*Z*)-**7c** (57)	(*E*)-**15c** (71) (*E*)-**16c** (10)[d]
7	**2**	$(CH_2)_{11}$		B	H	**7d** (55)	**15d** (68)
8	**3** (CF_2CF_3)	*t*-Bu	H	A	PhSe	(*E*)-**8a** (64)	(*Z*)-**17a** (94)
9	**3**	(*E*)-PhCH=CH	H	A	PhSe	(*E*)-**8b** (65)	(*Z*)-**17b** (79)
10	**3**	Mesityl	H	B	H	(*Z*)-**9a** (68)	(*E*)-**18a** (96)
11	**3**	(*E*)-PhCH=CH	Me	B	H	(*Z*)-**9b** (47)	(*E*)- and (*Z*)-**18b** (91)[e]
12	**4** ($CF_2CF_2CF_3$)	*t*-Bu	H	A	PhSe	(*E*)- and (*Z*)-**10** (43)[f]	(*Z*)-**19** (90)
13	**4**	Ph	H	B	H	(*Z*)-**11** (61)	(*E*)-**20** (90)
14	**5** ($CF_2CF_2CF_2CF_3$)	*t*-Bu	H	A	PhSe	(*E*)- and (*Z*)-**12** (62)[g]	(*Z*)-**21** (58)
15	**5**	Ph	H	B	H	(*Z*)-**13** (73)	(*E*)-**22** (78)

[a] Condition A: lithium 2,2,6,6-tetramethylpiperidide/THF/−78 °C/aldehydes. [b] *E*/*Z* = 31:69. [c] Condition B: BuLi/THF/−78 °C/aldehydes or ketones. [d] **16c:** (*E*)-2,2-diethoxy-1,1,1-trifluoro-6-phenylhex-3-en-5-yne. [e] *E*/*Z* = 65:35. [f] *E*:*Z* = 98:2. [g] *E*/*Z* = 37:63.

Scheme 3[a]



[a] Reagents: (i) BuLi/Rf(EtO)C=CHSePh/−78 °C; (ii) TsOH/83 °C.

Hz), −32.87 (1F, dt, *J* = 282, 13 Hz), −3.11 (3F, t, *J* = 10 Hz); high-resolution mass calcd for $C_{15}H_{13}F_9O_2$ 396.0771, found *m*/*z* 396.0758.

(2*Z*,5*E*)-2-Ethoxy-1,1,1-trifluoro-6-mesityl-4-(trifluoromethyl)hex-2,5-dien-4-ol (23): ^{1}H NMR δ 1.40 (3H, t, *J* = 7 Hz), 2.21 (6H, s), 2.25 (3H, s), 2.71 (1H, s), 3.17 (2H, q, *J* = 7 Hz), 5.25 (1H, s), 5.75 (1H, d, *J* = 16 Hz), 6.78 (1H, d, *J* = 16 Hz), 6.85 (2H, s); ^{13}C NMR δ 14.1 (q), 20.6 (q × 2), 21.2 (q), 65.2 (t), 75.4 (s, q, *J* = 28 Hz), 102.9 (d), 119.8 (s, q, *J* = 276 Hz), 125.2 (s, *J* = 286 Hz), 128.9 (d × 2), 129.7 (d), 132.6 (s), 133.1 (d), 136.2 (s × 2), 137.2 (s), 149.4 (s, q, *J* = 37 Hz); ^{19}F NMR δ −16.06 (3F, s), 1.45 (3F, s); MS *m*/*z* 382 (M^+). Anal. Calcd for $C_{18}H_{20}F_6O_2$: C, 56.55; H, 5.27. Found: C, 56.54; H, 5.34.

Preparation of (*Z*)-1,1,1-Trifluoro-4-phenyl-3-(phenylseleno)but-3-en-2-one (14a). Typical Procedure. A $ClCH_2CH_2Cl$ (3.00 mL) solution of **6a** (0.26 g, 0.65 mmol) and *p*-toluenesulfonic acid (0.16 g, 0.84 mmol) was heated at 83 °C for 10 min. The mixture was poured into a saturated $NaHCO_3$ (50.0 mL). The workup procedure afforded the title compound (0.12 g, 53%) as a yellow oil: ^{1}H NMR δ 7.19−7.23 (3H, m), 7.35−7.45 (5H, m), 7.76−7.78 (2H, m), 8.14 (1H, s); ^{13}C NMR δ 116.3 (s, q, *J* = 293 Hz), 127.3 (s), 127.9 (d), 128.7 (d × 2), 129.4 (s), 129.6 (d × 2), 131.3 (d × 2), 131.41 (d), 132.3 (d × 2), 134.4 (s), 150.4 (d, q, *J* = 3 Hz), 180.1 (s, q, *J* = 26 Hz); ^{19}F NMR δ −13.63 (3F, s); MS *m*/*z* 356 (M^+). Anal. Calcd for $C_{16}H_{11}F_3OSe$: C, 54.10; H, 3.12. Found: C, 54.04; H, 3.22.

(*E*)-1,1,1-Trifluoro-4-mesitylbut-3-en-2-one (15a): mp 19−20 °C; ^{1}H NMR δ 2.13 (3H, s), 2.29 (6H, s), 6.68 (1H, dd, *J* = 16, 1 Hz), 6.92 (2H, s), 8.20 (1H, d, *J* = 16 Hz); ^{13}C NMR δ 21.3 (q), 21.5 (q × 2), 116.7 (s, *J* = 291 Hz), 121.3 (d), 129.9 (s), 130.1 (d × 2), 138.6 (s × 2), 140.9 (s), 148.6 (d), 180.2 (s, q, *J* = 35 Hz); ^{19}F NMR δ −1.48 (3F, s); MS *m*/*z* 242 (M^+). Anal. Calcd for $C_{13}H_{13}F_3O$: C, 64.46; H, 5.41. Found: C, 64.33; H, 5.42.

(*Z*)-1,1,1,2,2-Pentafluoro-6,6-dimethyl-4-(phenylseleno)-hept-4-en-3-one (17a): ^{1}H NMR δ 1.37 (9H, s), 7.22−7.25 (3H, m), 7.28 (1H, brs), 7.38−7.40 (2H, m); ^{13}C NMR δ 30.0 (Me × 3), 36.0 (s), 107.6 (s, qt, *J* = 271, 37 Hz), 118.0 (s, qt, *J* = 288, 37 Hz), 127.5 (s), 127.9 (d), 129.2 (s), 129.6 (d × 2), 132.6 (d × 2), 163.2 (d), 182.7 (s, t, *J* = 26 Hz); ^{19}F NMR δ −36.32 (2F, d, *J* = 1 Hz), −3.81 (3F, s); MS *m*/*z* 386 (M^+). Anal. Calcd for $C_{15}H_{15}F_5OSe$: C, 46.69; H, 3.94. Found: C, 46.77; H, 3.92.

(*E*)-1,1,1,2,2-Pentafluoro-5-mesitylpent-4-en-3-one (18a): yellow needles; mp 44−47 °C; ^{1}H NMR δ 2.30 (3H, s), 2.39 (6H, s), 6.81 (1H, d, *J* = 16 Hz), 6.93 (2H, s), 8.24 (1H, d, *J* = 16 Hz); ^{13}C NMR δ 21.3 (q), 21.5 (q × 2), 108.1 (s, qt, *J* = 38, 266 Hz), 118.4 (s, qt, *J* = 35, 287 Hz), 121.4 (d), 129.8 (s), 130.2 (d × 2), 138.9 (s × 2), 141.1 (s), 148.5 (d), 182.5 (s, qt, *J* = 26 Hz); ^{19}F NMR δ −46.29 (2F, s), −4.32 (3F, s); MS *m*/*z* 173 ($M^+ - CF_2CF_3$). Anal. Calcd for $C_{14}H_{13}F_5O$: C, 57.54; H, 4.48. Found: C, 57.44; H, 4.47.

(*Z*)-1,1,1,2,2,3,3,3-Heptafluoro-7,7-dimethyl-5-(phenylseleno)oct-5-en-4-one (19): ^{1}H NMR δ 1.37 (9H, s), 7.21 (1H, s), 7.23−7.26 (3H, m), 7.39−7.42 (2H, m); ^{19}F NMR δ −47.74 (2F, t, *J* = 7 Hz), −34.02 (2F, q, *J* = 9 Hz), −4.08 (3F, s); MS *m*/*z* 436 (M^+). Anal. Calcd for $C_{16}H_{15}F_7OSe$: C, 44.15; H, 3.47. Found: C, 44.24; H, 3.41.

(*E*)-1,1,1,2,2,3,3-Heptafluoro-6-phenylhex-5-en-4-one (20): ^{1}H NMR δ 7.18 (1H, d, *J* = 16 Hz), 7.40−7.53 (3H, m), 7.64−7.67 (2H, m), 7.98 (1H, d, *J* = 16 Hz); ^{19}F NMR δ −48.93 (2F, s), −44.07 (2F, q, *J* = 9 Hz), −2.80 (3F, t, *J* = 9 Hz); high-resolution mass calcd for $C_{12}H_7F_7O$ 300.0385, found *m*/*z* 300.0378.

(*Z*)-1,1,1,2,2,3,3,4,4-Nonafluoro-8,8-dimethyl-6-(phenylseleno)non-6-en-5-one (21): ^{1}H NMR δ 1.37 (9H, s), 7.20 (1H, s), 7.24−7.27 (3H, m), 7.39−7.42 (2H, m); ^{19}F NMR δ −47.53 to −47.46 (2F, m), −43.95 to −43.88 (2F, m), −33.19 (2F, brt, *J* = 13 Hz), −3.24 (3F, tt, *J* = 10, 3 Hz); MS *m*/*z* 486 (M^+). Anal. Calcd for $C_{17}H_{15}F_9OSe$: C, 42.08; H, 3.12. Found: C, 42.28; H, 3.12.

(*E*)-1,1,1,2,2,3,3,4,4-Nonafluoro-7-phenylhept-6-en-5-one (22): ^{1}H NMR δ 7.12 (1H, d, *J* = 16 Hz), 7.42−7.53 (3H,

m), 7.65−7.68 (2H, m), 7.99 (1H, d, J = 16 Hz); ^{19}F NMR δ −48.28 to −48.15 (2F, m), −45.76 to −45.62 (2F, m), −43.64 (2F, t, J = 12 Hz), −3.24 (3F, tt, J = 9, 3 Hz); MS m/z 350 (M^+). Anal. Calcd for $C_{13}H_7F_9O$: C, 44.59; H, 2.01. Found: C, 44.70; H, 2.26.

***2H*-2-Mesityl-4,6-bis(trifluoromethyl)pyran (25):** ^{1}H NMR δ 2.28 (3H, s), 2.37 (6H, s), 5.92 (2H, brs), 6.51 (1H, brs), 6.90 (2H, s); ^{19}F NMR δ −10.46 (3F, s), −6.62 (3F, s); MS m/z 335 ($M^+ - 1$). Anal. Calcd for $C_{16}H_{14}F_6O$: C, 57.15; H, 4.20. Found: C, 57.09; H, 4.29. (3*E*,5*E*)-1,1,1-Trifluoro-6-mesityl-4-(trifluoromethyl)hex-3,5-dien-2-one was observed by ^{1}H NMR spectroscopy at δ 6.74 (1H, brs), 6.92 (2H, s), 7.60 (1H, d, J = 17 Hz), 7.75 (1H, d, J = 17 Hz) and ^{19}F NMR spectroscopy at δ −16.60 ppm.

(3*E*,5*E*)-2,2-Diethoxy-1,1,1-trifluoro-6-mesityl-4-(trifluoromethyl)hex-3,5-diene (27): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (6H, t, J = 7 Hz), 3.62−3.68 (4H, m), 5.95 (1H, s), 6.88 (2H, s), 6.96 (1H, d, J = 17 Hz), 7.02 (1H, d, J = 17 Hz); ^{19}F NMR δ −4.14 (3F, s), 9.82 (3F, s); MS m/z 410 (M^+). Anal. Calcd for $C_{20}H_{24}F_6O_2$: C, 58.53; H, 5.89. Found: C, 58.43; H, 5.73.

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Supporting Information Available: Characterization data for the products **4**, **5**, **6b**,**c**, **7b**−**d**, **8b**, **9b**, (***Z*)-12**, **14b**,**c**, **15b**−**d**, **16c**, **17b**, and **18b** and ^{1}H and ^{19}F NMR spectra, complete with peak assignments of other products and full lists of IR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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