Markovnikov-Type Hydrotrifluoromethylchalcogenation of Unactivated Alkenes with [Me4N][XCF3] (X = S, Se) and TfOH

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1. General Information

All reactions were carried out under a nitrogen atmosphere unless otherwise specified. The NMR spectra were recorded in CDCl₃ on a 500 MHz (for ¹H), 471 (for ¹⁹F), and 126 (for ¹³C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm) for ¹H NMR and PhOCF₃ (58.0 ppm) or PhCF₃ (63.0 ppm) for ¹⁹F NMR as an internal or external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 µm, 4.6 × 250 mm), and the HPLC yields of the product were determined by using the corresponding pure compound as the external standard. MS experiments were performed on a TOF-Q ESI or EI instrument. Reagents [Me₄N][SeCF₃] (**2a**), [Me₄N][SCF₃] (**2b**), and CsOCF₃ were synthesized according to the literatures.¹ Substrates **1a**-f,² **1g**-**1h**,³ **1i**-**1l**,² **1m**-**1n**,⁴ and **1p**-**1r**⁴ were synthesized according to the literatures. Solvents were dried before use according to the literature.⁵ Other reagents in the reactions were all purchased from the commercial sources and used without further purification.

2. Screening the optimal reaction conditions for hydrotrifluoromethylselenolation of alkenes with [Me₄N][SeCF₃] and TfOH Table S1. Reactions of 1a and 2a in the presence of different acids.^a

Ph 1a	<pre>+ [Me₄N][SeCF₃]acid (1.5 equiv)</pre>	Ph 3a
Entry	Acid	Yield (3a , %) ^b
1	CH ₃ COOH	0, 0 °
2	CF ₃ COOH	0, 0 ^c
3	conc. H ₂ SO ₄	0
4	conc. HCl	0
5	anhydrous HCl in 1,4-dioxane	0 ^d
6	aq. H ₃ PO ₄ (85%)	0, 0 °
7	Et ₃ N·3HF	0, 0 °
8	HBF ₄ (85%) in diethyl ether	0, 0 ^c
9	TsOH•H ₂ O	0, 0 ^c

10	$(CF_3SO_2)_2NH$	0, 0 ^c
11	(1 <i>R</i>)-(-)-10-camphorsulfonic acid	0
12	TfOH	45

^a Reaction conditions: To a solution of **1a** (0.2 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.3 mmol) in CH₂Cl₂ (1 mL) followed by addition of [Me₄N][SeCF₃] (0.3 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 6 h. ^b The yields were determined by HPLC using pure (4-([1,1'-biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)selane (**3a**) as an external standard (t_R = 11.85 min, $\lambda_{max} = 253$ nm, water/methanol (v/v = 10:90)). ^c 40 °C. ^d **1a** (0.2 mmol), acid (0.2 mmol), [Me₄N][SeCF₃] (0.3 mmol), 3 h.

Ph 1a	+ [Me₄N][SeCF₃] <u>TfOH (1.5 equiv)</u> solvent, N₂, r.t., 6 h (1.5 equiv)	Ph 3a
Entry	Solvent	Yield (3a , %) ^b
1	CHCl ₃	0
2	ClCH ₂ CH ₂ Cl	33
3	CH_2Cl_2	45
4	MeCN	0
5	toluene	19
6	PhCl	37
7	(CF ₃) ₂ CH ₂ OH	0
8	CF ₂ ClCFCl ₂	24

Table S2. Reactions of 1a and 2a with TfOH in different solvents.^a

^a Reaction conditions: To a solution of **1a** (0.2 mmol) in solvent (1 mL) was added a solution of TfOH (0.3 mmol) in solvent (1 mL) followed by addition of [Me₄N][SeCF₃] (0.3 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 6 h. ^b The yields were determined by HPLC using pure (4-([1,1'-biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)selane (**3a**) as an external standard (t_R = 11.85 min, $\lambda_{max} = 253$ nm, water/methanol (v/v = 10:90)).

Table S3. Reactions of 1a and 2a with TfOH at different reaction temperatures.^a

Ph 1a	+ [Me ₄ N][SeCF ₃] <u>TfOH (</u> CH ₂ Cl ₂ , N 2a (1.5 equiv)	1.5 equiv) N ₂ , temp., 6 h Ph 3a
Entry	Temp (°C)	Yield (3a , %) ^b
1	0	43
2	r.t.	45
3	40	50
4	60	26

^aReaction conditions: To a solution of **1a** (0.2 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.3 mmol) in CH₂Cl₂ (1 mL) followed by addition of [Me₄N][SeCF₃] (0.3 mmol) within 1 minute. The mixture was reacted under N₂ for 6 b h. The vields were determined by HPLC using pure (4-([1,1'-biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)selane (**3a**) as an external standard (t_R = 11.85 min, λ_{max} = 253 nm, water/methanol (v/v = 10:90)).

Ph 1a	[≿] + [Me₄N][SeCF₃] <u> </u>	N_2 , r.t., time Ph $3a$
Entry	Time (h)	Yield (3a , %) ^b
1	3	48
2	6	45
3	12	48

Table S4. Reactions of 1a, 2a and TfOH with different reaction times.^a

^a Reaction conditions: To a solution of **1a** (0.2 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.3 mmol) in CH₂Cl₂ (1 mL) followed by addition of [Me₄N][SeCF₃] (0.3 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ atmosphere. ^b The yields were determined by HPLC using pure (4-([1,1'-biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)selane (**3a**) as an external standard (t_R = 11.85 min, $\lambda_{max} = 253$ nm, water/methanol (v/v = 10:90)).

Table S5. Hydrotrifluoromethylselenolation of **1a** by **2a** and TfOH with different reactant ratios.^a

Ph 1a	+ [Me ₄ N][SeCF ₃] <u> </u>	SeCF ₃ Bh Ph 3a
Entry	1a : 2 : TfOH	Yield (3a , %) ^b
1	1:1:1	39
2	1:1.5:1	71 (68)
3	1:2:1	57
4	1:2.5:1	66
5	1:1.5:1.5	48
6	1:1.5:2	15 °
7	1:2:1.5	52
8	1.5 : 1 : 1	42
9	2:1:1	62
10	2:1.5:1	70
11	2:2:1	83 (79)
12	2:2.5:1	81
13	3:1:1	65
14	3:1:1.5	57
15	3:1.5:1	73

^a Reaction conditions: To a solution of **1a** (0.2, 0.3, 0.4 or 0.6 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.2, 0.3 or 0.4 mmol) in CH₂Cl₂ (1 mL) followed by addition of [Me₄N][SeCF₃] (0.2, 0.3, 0.4 or 0.5 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 3 h. ^b The yields were determined by HPLC using pure (4-([1,1'-biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)selane (**3a**) as an external standard ($t_R = 11.85$ min, $\lambda_{max} = 253$ nm, water/methanol (v/v = 10:90)). Isolated yields are depicted in the parentheses. ^c 6 h.

Table S6. Hydrotrifluoromethylselenolation of **1a** by **2a** and TfOH with different metal additives. ^a



1	(Me ₂ S)AuCl	51
2	CuTc	41
3	CuOTf	51
4	CuOAc	29
5	Cu(OAc) ₂	59
6	CuBr ₂	73, 74 °, 38 ^d
7	AgNO ₃	67
8	Ag ₂ CO ₃	30
9	AgTFA	47
10	AgPF ₆	55
11	$AgSbF_6$	51
12	AgOTf	63
13	Ag ₂ O	21

^a Reaction conditions: To a mixture of additive (10 mol%) and **1a** (0.2 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.2 mmol) in CH₂Cl₂ (1 mL) followed by addition of [Me₄N][SeCF₃] (0.3 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 3 h. ^b The yields were determined by HPLC using pure (4-([1,1'-biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)selane (**3a**) as an external standard (t_R = 11.85 min, $\lambda_{max} = 253$ nm, water/methanol (v/v = 10:90)). ^c CuBr₂ (5 mol%). ^d CuBr₂ (20 mol%).

3. General procedure for hydrotrifluoromethylselenolation of alkenes

Under a nitrogen atmosphere, a Schlenk tube was charged with **1** (0.4 or 0.2 mmol) and CH₂Cl₂ (1 mL) with stirring. A solution of TfOH (0.2 mmol) in CH₂Cl₂ was added, followed by addition of [Me₄N][SeCF₃] (**2a**, 0.4 or 0.3 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 3 h and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoromethylselenolated products (**3**).

(4-([1,1'-Biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)selane (3a)



Yellow oil, 59.4 mg (79%, **1a** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 50.8 mg (68%, **1a** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.59 (m, 1H), 2.89-2.79 (m, 2H), 2.19-2.03 (m, 2H), 1.68 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -31.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 141.0, 140.0, 139.2, 128.9, 128.8, 127.3, 127.2, 127.0, 123.2 (q, *J* = 331.1 Hz), 39.5, 39.2, 33.4, 23.1. IR (KBr): 3085, 3057, 3029, 2958, 2926, 2855, 1601, 1564, 1520, 1487, 1450, 1409, 1383, 1260, 1212, 1098, 1008, 838, 761, 738, 697, 598, 550, 507 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₇H₁₈F₃Se ([M + H]⁺): 359.0520; found: 359.0511.

(4-(4-Fluorophenyl)butan-2-yl)(trifluoromethyl)selane (3b)



Yellow oil, 25.8 mg (43%, **1b** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 23.4 mg (39%, **1b** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 3.50 (m, 1H), 2.78-2.68 (m, 2H), 2.09-1.93 (m, 2H), 1.62 (d, *J* = 7.0 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F), -117.2 (m, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 161.5 (d, *J* = 244.5 Hz), 136.4 (d, *J* = 3.3 Hz), 129.7 (d, *J* = 7.8 Hz), 123.1 (q, *J* = 330.8 Hz), 115.3 (d, *J* = 21.1 Hz), 39.3, 39.2, 32.9, 23.0. IR (KBr): 3041, 2927, 2856, 1602, 1511, 1455, 1383, 1259, 1224, 1157, 1098, 1016, 827, 760, 738, 543 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₄⁷⁴Se: 294.0100; found: 294.0109.

(4-(4-Chlorophenyl)butan-2-yl)(trifluoromethyl)selane (3c)



Yellow oil, 49.3 mg (78%, 1c : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 36.0 mg (57%,

1c : $[Me_4N][SeCF_3]$: TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.50 (m, 1H), 2.79-2.69 (m, 2H), 2.09-1.94 (m, 2H), 1.62 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 139.3, 132.0, 129.7, 128.7, 123.1 (q, *J* = 331.3 Hz), 39.2, 39.1, 33.0, 23.0. IR (KBr): 3084, 3028, 2927, 2856, 1895, 1731, 1598, 1493, 1455, 1408, 1383, 1290, 1279, 1260, 1232, 1214, 1096, 1035, 1016, 832, 818, 807, 778, 738, 715, 672, 663, 631, 523 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₀H₁₂Cl ([M – SeCF₃]⁺): 167.0622; found: 167.0624.

(4-(4-Bromophenyl)butan-2-yl)(trifluoromethyl)selane (3d)



Yellow oil, 58.3 mg (81%, **1d** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 43.2 mg (60%, **1d** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 3.50 (m, 1H), 2.78-2.68 (m, 2H), 2.09-1.93 (m, 2H), 1.62 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 139.8, 131.6, 130.1, 123.1 (q, *J* = 331.0 Hz), 120.0, 39.2, 39.0, 33.1, 23.0. IR (KBr): 3025, 2961, 2926, 2863, 1489, 1454, 1405, 1383, 1278, 1260, 1214, 1097, 1074, 1012, 960, 897, 828, 813, 802, 770, 738, 711, 654, 634, 605, 515 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₃Br⁷⁴Se: 353.9299; found: 353.9307.

(4-(4-Iodophenyl)butan-2-yl)(trifluoromethyl)selane (3e)



Yellow oil, 69.3 mg (85%, **1e** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 43.2 mg (53%, **1e** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.49 (m, 1H), 2.76-2.67 (m, 2H), 2.08-1.93 (m, 2H), 1.62 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 140.5, 137.6, 130.5, 123.1 (q, *J* = 331.2 Hz), 91.3, 39.2, 39.0, 33.2, 23.0. IR (KBr): 3019, 2960, 2925, 2854, 1485, 1454, 1401, 1382, 1291, 1275, 1260, 1230, 1213, 1202, 1097, 1063, 1035, 1007, 897, 826, 799, 766, 738, 709, 512 cm⁻¹. HRMS-ESI (m/z) calcd. for $C_9H_{12}ISe$ ([M – CF₃]⁻): 337.9196; found: 337.9198.

(Trifluoromethyl)(4-(4-(trifluoromethyl)phenyl)butan-2-yl)selane (3f)



Yellow oil, 42.0 mg (60%, **1f** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 30.1 mg (43%, **1f** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.51 (m, 1H), 2.89-2.79 (m, 2H), 2.13-1.98 (m, 2H), 1.64 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F), -62.4 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 145.0, 128.7, 128.6 (q, *J* = 32.4 Hz), 125.5 (q, *J* = 3.8 Hz) 124.3 (q, *J* = 271.5 Hz), 123.1 (q, *J* = 330.8 Hz), 39.2, 38.9, 33.5, 23.0. IR (KBr): 2958, 2929, 2858, 1620, 1456, 1419, 1384, 1327, 1165, 1117, 1095, 1068, 1019, 899, 840, 823, 738, 650, 633, 599 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₂F₆⁷⁴Se: 344.0068; found: 344.0061.

(4-(4-Nitrophenyl)butan-2-yl)(trifluoromethyl)selane (3g)



Yellow oil, 46.4 mg (71%, **1g** : [Me4N][SeCF₃] : TfOH = 2 : 2 : 1) and 28.1 mg (43%, **1g** : [Me4N][SeCF₃] : TfOH = 1 : 1.5 : 1), a mixture of petroleum ether and ethyl acetate (40 : 1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.50 (m, 1H), 2.94-2.84 (m, 2H), 2.14-2.00 (m, 2H), 1.64 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 148.7, 146.7, 129.2, 123.9, 123.0 (q, *J* = 331.1 Hz), 39.0, 38.7, 33.6, 23.0. IR (KBr): 3112, 3080, 2950, 2929, 2856, 2453, 2217, 1927, 1727, 1602, 1520, 1495, 1455, 1384, 1347, 1319, 1289, 1236, 1214, 1180, 1098, 1035, 1016, 973, 891, 858, 848, 806, 768, 747, 738, 698, 660, 647, 632, 619, 513 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₁H₁₃F₃NO₂Se ([M + H]⁺): 328.0058; found: 328.0060.

(4-(2-Nitrophenyl)butan-2-yl)(trifluoromethyl)selane (3h)



Yellow oil, 37.3 mg (57%, **1h** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 21.6 mg (33%, **1h** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), a mixture of petroleum ether and ethyl acetate (40 : 1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.40-7.36 (m, 2H), 3.60 (m, 1H), 3.11-2.98 (m, 2H), 2.14-2.03 (m, 2H), 1.66 (d, *J* = 7.0 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.1 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 149.2, 136.1, 133.2, 132.0, 127.5, 125.0, 123.1 (q, *J* = 330.5 Hz), 39.5, 38.5, 31.3, 22.8. IR (KBr): 3069, 2964, 2928, 2856, 1611, 1579, 1527, 1481, 1457, 1383, 1348, 1281, 1231, 1215, 1099, 959, 861, 813, 787, 739, 702, 667 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₃NO₂⁷⁴Se: 321.0045; found: 321.0039.

(4-(4-(*Tert*-butyl)phenyl)butan-2-yl)(trifluoromethyl)selane (3i)



Yellow oil, 45.3 mg (67%, **1i** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 33.8 mg (50%, **1i** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.55 (m, 1H), 2.79-2.69 (m, 2H), 2.12-1.96 (m, 2H), 1.64 (d, *J* = 6.9 Hz, 3H), 1.32 (s, 9H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 149.0, 137.8, 128.0, 125.4, 123.2 (q, *J* = 331.2 Hz), 39.5, 39.2, 34.4, 33.1, 31.4, 23.0. IR (KBr): 3056, 3024, 2964, 2868, 1517, 1457, 1412, 1394, 1382, 1364, 1269, 1234, 1215, 1203, 1098, 1035, 1019, 829, 815, 738, 569 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₅H₂₁F₃⁷⁴Se: 332.0820; found: 332.0816.

(4-(*p*-Tolyl)butan-2-yl)(trifluoromethyl)selane (**3j**)



Yellow oil, 46.2 mg (78%, 1j: [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 29.6 mg (50%, 1j : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column

chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.12-7.08 (m, 4H), 3.53 (m, 1H), 2.78-2.68 (m, 2H), 2.33 (s, 3H), 2.10-1.94 (m, 2H), 1.63 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 137.7, 135.7, 129.2, 128.3, 123.2 (q, *J* = 330.5 Hz), 39.4, 39.3, 33.2, 23.0, 21.0. IR (KBr): 3048, 3020, 2925, 2859, 1516, 1454, 1381, 1260, 1214, 1097, 1022, 830, 807, 738, 543 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃⁷⁴Se: 290.0351; found: 290.0349.

(4-(o-Tolyl)butan-2-yl)(trifluoromethyl)selane (3k)



Yellow oil, 30.2 mg (51%, **1k** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 34.3 mg (58%, **1k** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.16-7.14 (m, 4H), 3.60 (m, 1H), 2.82-2.70 (m, 2H), 2.32 (s, 3H), 2.06-1.92 (m, 2H), 1.67 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.1 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 139.1, 135.8, 130.4, 128.8, 126.3, 126.1, 123.1 (q, *J* = 330.2 Hz), 39.8, 38.1, 31.2, 23.0, 19.2. IR (KBr): 3066, 3018, 2958, 2928, 2869, 1605, 1493, 1459, 1382, 1265, 1222, 1098, 1012, 754, 739 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃⁷⁴Se: 290.0351; found: 290.0345.

(4-(*m*-Tolyl)butan-2-yl)(trifluoromethyl)selane (3l)



Yellow oil, 33.7 mg (57%, **1**] : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 26.1 mg (44%, **1**] : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.20 (t, *J* = 7.5 Hz, 1H), 7.04-6.99 (m, 3H), 3.54 (m, 1H), 2.79-2.69 (m, 2H), 2.35 (s, 3H), 2.12-1.96 (m, 2H), 1.64 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 140.8, 138.1, 129.2, 128.4, 126.9, 125.4, 123.2 (q, *J* = 330.4 Hz), 39.5, 39.2, 33.6, 23.1, 21.4. IR (KBr): 3023, 2966, 2925, 2860, 1610, 1591, 1489, 1455, 1382, 1355, 1213, 1098, 882, 783, 738, 719, 699 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃⁷⁴Se: 290.0351; found: 290.0357. (4-(4-Methoxyphenyl)butan-2-yl)(trifluoromethyl)selane (3m)



Yellow oil, 33.7 mg (78%, **1m** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 26.1 mg (57%, **1m** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), a mixture of petroleum ether and ethyl acetate (80 : 1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 3.52 (m, 1H), 2.76-2.66 (m, 2H), 2.09-1.93 (m, 2H), 1.63 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 158.1, 132.9, 129.3, 123.1 (q, *J* = 331.0 Hz), 114.0, 55.3, 39.4, 39.4, 32.7, 23.1. IR (KBr): 3032, 2991, 2954, 2928, 2855, 2837, 1613, 1584, 1513, 1456, 1382, 1301, 1248, 1178, 1098, 1038, 827, 809, 750, 738, 552, 519 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₅H₂₁F₃⁷⁴Se: 332.0820; found: 332.0816.

(4-(Naphthalen-2-yl)butan-2-yl)(trifluoromethyl)selane (3n)



Yellow oil, 49.8 mg (75%, **1n** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 34.5 mg (52%, **1n** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.83-7.79 (m, 3H), 7.64 (s, 1H), 7.49-7.43 (m, 2H), 7.33 (dd, *J* = 8.4 Hz, 1.1 Hz, 1 H), 3.57 (m, 1H), 2.99-2.90 (m, 2H), 2.22-2.06 (m, 2H), 1.66 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -31.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 138.3, 133.6, 132.1, 128.1, 127.6, 127.4, 127.0, 126.6, 126.1, 125.4, 123.2 (q, *J* = 330.9 Hz), 39.4, 39.0, 33.8, 23.1. IR (KBr): 3054, 3015, 2958, 2924, 2853, 1633, 1601, 1509, 1454, 1382, 1261, 1242, 1201, 1097, 1019, 960, 888, 853, 817, 746, 738 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₅H₁₅F₃⁷⁴Se: 326.0351; found: 326.0352.

 $(4-Phenylbutan-2-yl)(trifluoromethyl)selane (30)^6$



Yellow oil, 23.1 mg (41%, **1o** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 11.3 mg (20%, **1o** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.23-7.19 (m, 3H), 3.53 (m, 1H), 2.82-2.73 (m, 2H), 2.13-1.97 (m, 2H), 1.63 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.0 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 140.8, 128.5, 128.4, 126.2, 123.1 (q, *J* = 330.5 Hz), 39.4, 39.2, 33.7, 23.0.

(6-Phenylhexan-2-yl)(trifluoromethyl)selane (3p)



Yellow oil, 33.5 mg (54%, **1p** : [Me₄N][SeCF₃] : TfOH = 2 : 2 : 1) and 21.1 mg (34%, **1p** : [Me₄N][SeCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, *J* = 7.60 Hz, 2H), 7.21-7.18 (m, 3H), 3.55 (m, 1H), 2.64 (t, *J* = 7.7 Hz, 2H), 1.84-1.70 (m, 2H), 1.69-1.63 (m, 2H), 1.58 (d, *J* = 6.9 Hz, 3H), 1.52-1.44 (m, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -32.3 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 142.3, 128.4, 128.3, 125.8, 123.2 (q, *J* = 330.8 Hz), 39.9, 37.4, 35.7, 31.0, 27.1, 22.9. IR (KBr): 3084, 3064, 3028, 2932, 2859, 1604, 1497, 1454, 1382, 1205, 1099, 1030, 909, 747, 738, 699 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₃H₁₇F₃⁷⁴Se: 304.0507; found: 304.0502.

4. General procedure for hydrotrifluoromethylthiolation of alkenes

Under a nitrogen atmosphere, a Schlenk tube was charged with **1** (0.4 or 0.2 mmol) and CH₂Cl₂ (1 mL) with stirring. A solution of TfOH (0.2 mmol) in CH₂Cl₂ was added, followed by addition of [Me₄N][SCF₃] (**2b**, 0.4 or 0.3 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 3 h and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoromethylthiolated products (**4**).

(4-([1,1'-Biphenyl]-4-yl)butan-2-yl)(trifluoromethyl)sulfane (4a)



Yellow oil, 29.8 mg (48%, **1a** : [Me₄N][SCF₃] : TfOH = 2 : 2 : 1) and 20.5 mg (33%, **1a** : [Me₄N][SCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 3.35 (m, 1H), 2.86-2.77 (m, 2H), 2.05-1.93 (m, 2H), 1.50 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -38.8 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 140.9, 140.0, 139.2, 131.2 (q, *J* = 305.9 Hz), 128.8, 128.8, 127.3, 127.1, 127.0, 40.7, 38.5, 32.5, 22.5. IR (KBr): 3081, 3057, 3029, 2966, 2928, 2859, 1602, 1520, 1487, 1451, 1409, 1383, 1298, 1264, 1247, 1146, 1116, 1040, 1008, 965, 912, 838, 761, 732, 697, 642, 586, 553, 510 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₇H₁₇F₃S: 310.1003; found: 310.1006.

(4-(4-Bromophenyl)butan-2-yl)(trifluoromethyl)sulfane (4b)



Yellow oil, 23.7 mg (38%, **1d** : [Me₄N][SCF₃] : TfOH = 2 : 2 : 1) and 25.0 mg (40%, **1d** : [Me₄N][SCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 3.29 (m, 1H), 2.77-2.68 (m, 2H), 1.98-1.86 (m, 2H), 1.46 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 139.8, 131.6, 131.1 (q, *J* = 305.9 Hz), 130.1, 120.0, 40.5, 38.3, 32.2, 22.5. IR (KBr): 3026, 2966, 2929, 2856, 1897, 1732, 1646, 1592, 1489, 1456, 1405, 1383, 1296, 1246, 1156, 1116, 1073, 1042, 1012, 898, 829, 803, 771, 756, 711, 639, 521 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₃BrS: 311.9795; found: 311.9796.

(4-(4-Iodophenyl)butan-2-yl)(trifluoromethyl)sulfane (4c)



Yellow oil, 34.6 mg (48%, **1e** : [Me₄N][SCF₃] : TfOH = 2 : 2 : 1) and 33.8 mg (47%, **1e** : [Me₄N][SCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 3.29 (m, 1H), 2.76-2.67 (m, 1H), 1.98-1.86 (m, 2H), 1.46 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 140.5, 137.6, 131.1 (q, *J* = 306.0 Hz), 130.5, 91.2, 40.5, 38.3, 32.3, 22.5. IR (KBr): 3068, 3021, 2965, 2928, 2857, 1898, 1640, 1588, 1486, 1455, 1402, 1383, 1354, 1297, 1280, 1235, 1148, 1115, 1062, 1041, 1007, 961, 898, 826, 801, 756, 710, 631, 519 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₃IS: 359.9656; found: 359.9660.

(4-(4-Nitrophenyl)butan-2-yl)(trifluoromethyl)sulfane (4d)



Yellow oil, (26.8 mg (**1g** : [Me₄N][SCF₃] : TfOH = 2 : 2 : 1), 48%; 23.4 mg (**1g** : [Me₄N][SCF₃] : TfOH = 1 : 1.5 : 1), 42%), a mixture of petroleum ether and ethyl acetate (40 : 1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 3.30 (m, 1H), 2.94-2.83 (m, 2H), 2.01-1.94 (m, 2H), 1.49 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 148.6, 146.7, 131.0 (q, *J* = 306.5 Hz), 129.2, 123.9, 40.5, 37.9, 32.8, 22.5. IR (KBr): 3080, 2928, 2855, 2447, 1916, 1687, 1601, 1520, 1495, 1456, 1384, 1347, 1295, 1112, 1041, 1016, 901, 858, 848, 806, 756, 748, 698, 633, 519 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₁H₁₂F₃NO₂S: 279.0541; found: 279.0538.

(4-(4-(*Tert*-butyl)phenyl)butan-2-yl)(trifluoromethyl)sulfane (4e)



Yellow oil, 12.2 mg (21%, **1i** : [Me₄N][SCF₃] : TfOH = 2 : 2 : 1) and 9.3 mg (16%, **1i** : [Me₄N][SCF₃] : TfOH = 1 : 1.5 : 1), petroleum ether as eluent for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.33 (m, 1H), 2.78-2.69 (m, 2H), 1.99-1.88 (m, 2H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.32 (s, 9H). ¹⁹F NMR (471 MHz, CDCl₃) δ -38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 149.0, 137.8, 131.2 (q, *J* = 306.3 Hz), 128.0, 125.4, 40.8, 38.5, 34.4, 32.3, 31.4, 22.4. IR (KBr): 3057, 3025, 2965, 2929, 2858, 1645, 1512, 1461, 1415, 1395, 1382, 1364, 1269, 1150, 1116, 1043, 1020, 900, 829, 814, 756, 645, 570 cm⁻¹.

HRMS-ESI (m/z) calcd. for $C_{15}H_{22}F_{3}S$ ([M + H]⁺): 291.1380; found: 291.1389.

(4-(*p*-Tolyl)butan-2-yl)(trifluoromethyl)sulfane (4f)



Yellow oil, (9.4 mg (**1j** : [Me₄N][SCF₃] : TfOH = 2 : 2 : 1), 19%; 7.9 mg (**1j** : [Me₄N][SCF₃] : TfOH = 1 : 1.5 : 1), 16%), petroleum ether as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.31 (m, 1H), 2.77-2.68 (m, 2H), 2.33 (s, 3H), 1.99-1.86 (m, 2H), 1.46 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -38.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 137.7, 135.7, 131.2 (q, *J* = 306.5 Hz), 129.2, 128.3, 40.6, 38.6, 32.4, 22.5, 21.0. IR (KBr): 3191, 2961, 2924, 2853, 1739, 1660, 1632, 1516, 1464, 1411, 1378, 1261, 1100, 1020, 865, 800, 756, 703 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃S: 248.0847; found: 248.0841.

(4-(Naphthalen-2-yl)butan-2-yl)(trifluoromethyl)sulfane (4g)



Yellow oil, 26.1 mg (46%, **1n** : [Me₄N][SCF₃] : TfOH = 2 : 2 : 1) and 22.7 mg (40%, **1n** : [Me₄N][SCF₃] : TfOH = 1 : 1.5 : 1) , petroleum ether as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.83-7.79 (m, 3H), 7.64 (s, 1H), 7.49-7.43 (m, 2H), 7.34 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.35 (m, 1H), 2.99-2.89 (m, 2H), 2.11-1.98 (m, 2H), 1.50 (d, *J* = 6.9 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -38.8 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 138.3, 133.6, 132.1, 131.2 (q, *J* = 306.5 Hz), 128.2, 127.7, 127.5, 127.0, 126.6, 126.1, 125.4, 40.7, 38.4, 33.0, 22.5. IR (KBr): 3055, 3021, 2927, 2855, 1635, 1601, 1509, 1455, 1382, 1351, 1298, 1271, 1247, 1146, 1117, 1044, 1019, 961, 910, 889, 853, 817, 747 cm⁻¹. HRMS-EI (m/z) calcd. for C₁₂H₁₅F₃S: 284.0847; found: 284.0841.

5. Hydrotrifluoromethoxylation of alkenes with CsOCF₃/TfOH

Procedure: Under a nitrogen atmosphere, a Schlenk tube was charged with **1a** (0.4 mmol) and CH_2Cl_2 (1 mL) with stirring. A solution of TfOH (0.2 mmol) in CH_2Cl_2

was added, followed by addition of $CsOCF_3$ (0.4 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 3 h.

Ph 1a	+ CsOCF ₃ <u> </u>	OCF ₃
Entry ^a	Temp. (°C)	Yield (6 a , %)
1	r.t.	0, 0 ^b
2	40	0, 0 ^b
3	60	0, 0 ^b

^a Reaction conditions: To a solution of **1a** (0.4 mmol) in CH₂Cl₂ (1 mL) was added a solution of TfOH (0.2 mmol) in CH₂Cl₂ (1 mL), followed by addition of CsOCF₃ (0.4 mmol) within 1 minute. The mixture was reacted at room temperature under N₂ for 3 h. The yields were determined by ¹⁹F NMR using PhCF₃ as an internal standard. ^b The same reaction was run with **1a** (0.2 mmol), TfOH (0.2 mmol) and CsOCF₃ (0.3 mmol).

6. The control experiments for mechanistic insights

		CD ₃ CN
		r.t., 2 min
Experiment 1:	(i equiv)	

Under a nitrogen atmosphere, a sealed tube was charged with [Me₄N][SeCF₃] (11.1 mg, 0.05 mmol) and a solution of TfOH (0.05 mmol) in CD₃CN (1 mL) with stirring. The mixture was maintained at room temperature for 2 minutes and analyzed by ¹⁹F and ¹H NMR using PhOCF₃ (31.9 mg, 0.2 mmol) as an internal standard.

Figure S1. ¹⁹F NMR spectrum of the above reaction mixture.



Figure S2. ¹H NMR spectrum of the above reaction mixture.



Under a nitrogen atmosphere, a sealed tube was charged with [Me₄N][SeCF₃] (11.1 mg, 0.05 mmol) and a solution of TfOH (0.05 mmol) in CD₃CN (1 mL) with stirring.

The mixture was maintained at room temperature for 1 hour and analyzed by ¹⁹F and ¹H NMR using PhOCF₃ (31.9 mg, 0.2 mmol) as an internal standard.



Figure S3. ¹⁹F NMR spectrum of the above reaction mixture.





Figure S5. The combination of Figures 1 and 3



Figure S6. The combination of Figures 2 and 4



Under a nitrogen atmosphere, a sealed tube was charged with [Me₄N][SeCF₃] (11.1

mg, 0.05 mmol) and a solution of TfOH (7.5 mg, 0.05 mmol) in CD_2Cl_2 (1 mL) with stirring. The mixture was maintained at room temperature for 2 minutes and analyzed by ¹⁹F and ¹H NMR using PhOCF₃ (28.2 mg, 0.18 mmol) as an internal standard.



Figure S7. ¹⁹F NMR spectrum of the above reaction mixture.

Figure S8. ¹H NMR spectrum of the above reaction mixture



Experiment 4:
$$[Me_4N][SeCF_3] + TfOH \xrightarrow{CD_2Cl_2}{r.t., 1 h}$$

Under a nitrogen atmosphere, a sealed tube was charged with [Me₄N][SeCF₃] (11.1 mg, 0.05 mmol) and a solution of TfOH (7.5 mg, 0.05 mmol) in CD₂Cl₂ (1 mL) with stirring. The mixture was maintained at room temperature for 1 hour and analyzed by ¹⁹F and ¹H NMR using PhOCF₃ (28.2 mg, 0.18 mmol) as an internal standard.

Figure S9. ¹⁹F NMR spectrum of the above reaction mixture.



Figure S10. ¹H NMR spectrum of the above reaction mixture.







Figure S12. The combination of Figures 8 and 10



Under a nitrogen atmosphere, a sealed tube was charged with **1a** (10.4 mg, 0.05 mmol) and a solution of TfOH (7.5 mg, 0.05 mmol) in CD_2Cl_2 (1 mL) with stirring. The mixture was maintained at room temperature for 2 minutes and analyzed by ¹⁹F and ¹H NMR using PhOCF₃ (28.0 mg, 0.18 mmol) as an internal standard.

Figure S13. ¹⁹F NMR spectrum of the above reaction mixture.



Figure S14. ¹H NMR spectrum of the above reaction mixture.



Under a nitrogen atmosphere, a sealed tube was charged with 1a (10.4 mg, 0.05 mmol) and a solution of TfOH (7.5 mg, 0.05 mmol) in CD₂Cl₂ (1 mL) with stirring. The

mixture was maintained at room temperature for 1 hour and analyzed by ¹⁹F and ¹H NMR using PhOCF₃ (28.0 mg, 0.18 mmol) as an internal standard.



Figure S15. ¹⁹F NMR spectrum of the above reaction mixture.

Figure S16. ¹H NMR spectrum of the above reaction mixture.





Figure S17. The combination of Figures 13 and 15

Figure S18. The combination of Figures 14 and 16





Experiment 7:

Under a nitrogen atmosphere, a sealed tube was charged with **1a** (20.8 mg, 0.10 mmol) and a solution of TfOH (7.5 mg, 0.05 mmol) in CD_2Cl_2 (1 mL) with stirring. The mixture was maintained at room temperature for 2 minutes and analyzed by ¹⁹F and ¹H NMR using PhOCF₃ (26.5 mg, 0.17 mmol) as an internal standard.

Figure S19. ¹⁹F NMR spectrum of the above reaction mixture.



Figure S20. ¹H NMR spectrum of the above reaction mixture.



Experiment 8:

Under a nitrogen atmosphere, a sealed tube was charged with **1a** (20.8 mg, 0.10 mmol) and a solution of TfOH (7.5 mg, 0.05 mmol) in CD₂Cl₂ (1 mL) with stirring. The mixture was maintained at room temperature for 1 hour and analyzed by $^{19}\mathrm{F}$ and $^{1}\mathrm{H}$ NMR using PhOCF₃ (26.5 mg, 0.17 mmol) as an internal standard.

Figure S21. ¹⁹F NMR spectrum of the above reaction mixture.



Figure S22. ¹H NMR spectrum of the above reaction mixture.



Figure S23. The combination of Figures 19 and 21



Figure S24. The combination of Figures 20 and 22



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7. NMR spectra of the products.









90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 fl (ppm)



S38

S48

S65

