

Supporting Information

Metal-Free Oxidative Trifluoromethylselenolation of Electron-Rich (Hetero)Arenes with the Readily Available [Me₄N][SeCF₃] Reagent

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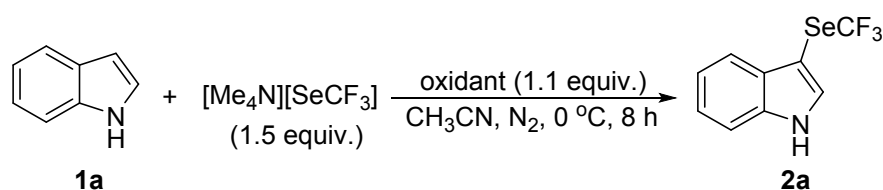
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1. General information

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, the NMR spectra were recorded in CDCl₃ or acetone-d₆ on a 500 MHz (for ¹H), 471 MHz (for ¹⁹F), and 126 MHz (for ¹³C) spectrometer. All chemical shifts were reported in ppm relative to TMS for ¹H NMR (0 ppm) and PhOCF₃ for ¹⁹F NMR (-58.56 ppm) 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, brs = broad singlet. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the yields of the product were determined by using the corresponding pure compound as the external standard. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI or EI instrument. [Me₄N][SeCF₃] was prepared according to the literature.¹ The starting materials (**1s**,² **1w**,³ **1x**,⁴ **1y-1aa**,⁵ and **1af**)⁶ were synthesized according to the literatures. Solvents were dried before use according to the literature.⁷ Other reagents used in the reactions were all purchased from the commercial sources and used without further purification.

2. Screening of the optimal reaction conditions for trifluoromethylselenolation of indole (1a) by [Me₄N][SeCF₃]

Table S1 Trifluoromethylselenolation of **1a** by [Me₄N][SeCF₃] in the presence of different oxidants.

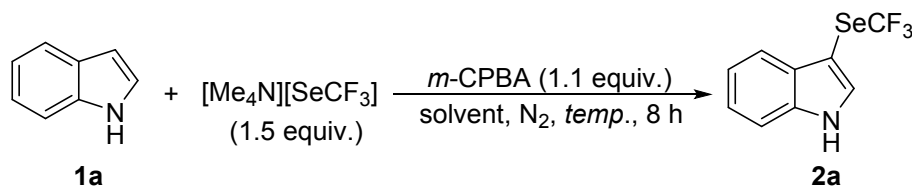


Entry ^a	Oxidant	Yield (2a , %) ^b
1	m-CPBA	96 (93)
2 ^c	TBHP (70% aq.)	62
3 ^c	H ₂ O ₂ (30% aq.)	50
4	DMP	20
5	PhI(OAc) ₂	89
6	DDQ	95

7	TEMPO	2
8	K ₂ S ₂ O ₈	3
9 ^c	KMnO ₄	18
10 ^c	AgNO ₃	<1
11 ^c	AgBF ₄	<1
12 ^c	NIS	96
13 ^c	NBS	73
14 ^c	NCS	>99
15 ^c	I ₂	8
16 ^{c,d}	O ₂	12
17	Selectfluor	69
18 ^c	NFSI	64

^a Reaction conditions: To a mixture of oxidant (0.22 mmol) and [Me₄N][SeCF₃] (0.3 mmol) in CH₃CN (1.0 mL) was added slowly a solution of **1a** (0.2 mmol) in CH₃CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N₂ for 8 hours. ^b Yields were determined by HPLC using **2a** as an external standard (t_R = 4.50 min, λ_{max} = 268 nm, methanol/water = 90:10 (v/v)). Isolated yield was depicted in the parentheses. ^c Reaction conditions: A solution of oxidant (0.22 mmol) in CH₃CN (1 mL) was added slowly to a mixture of [Me₄N][SeCF₃] (0.3 mmol) and **1a** (0.2 mmol) in CH₃CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N₂ for 8 hours. ^d An O₂ balloon was used.

Table S2 The solvent effects on the trifluoromethylselenolation of **1a** by [Me₄N][SeCF₃] in the presence of *m*-CPBA

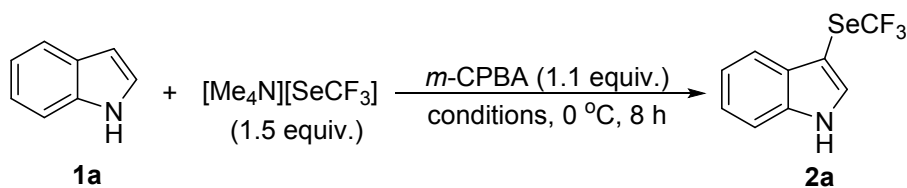


Entry ^a	Solvent	Temperature (°C)	Yield (2a , %) ^b
1	CH₃CN	0	96 (93)
2	DMF	0	85
3	NMP	0	49
4	DCM	0	95

5	DCE	0	86
6	THF	0	78
7	1,4-dioxane	25	41
8	DMSO	25	0
9	toluene	0	41

^a Reaction conditions: To a mixture of *m*-CPBA (0.22 mmol) and [Me₄N][SeCF₃] (0.3 mmol) in solvent (1 mL) was added slowly a solution of **1a** (0.2 mmol) in solvent (1 mL) at 0 °C or 25 °C. The reaction was maintained at 0 °C or 25 °C under N₂ for 8 hours. ^b Yields were determined by HPLC using **2a** as an external standard (*t*_R = 4.50 min, λ_{max} = 268 nm, methanol/water = 90:10 (v/v)). Isolated yield was depicted in the parentheses.

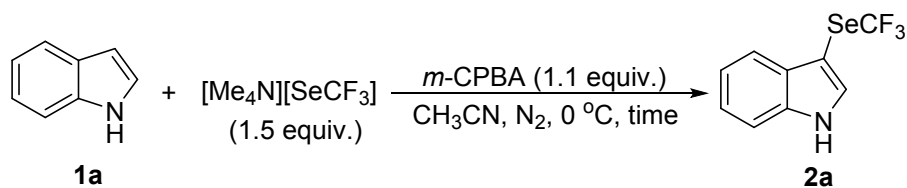
Table S3 The effects of moisture or water on the trifluoromethylselenolation of **1a** by [Me₄N][SeCF₃] in the presence of *m*-CPBA



Entry ^a	Conditions	Yield (2a , %) ^b
1	anhydrous CH₃CN, N₂	96 (93)
2	anhydrous CH ₃ CN + 0.1 mL H ₂ O, N ₂	86
3	undried CH ₃ CN, N ₂	89
4	undried CH ₃ CN, air	89

^a Reaction conditions: To a mixture of *m*-CPBA (0.22 mmol) and [Me₄N][SeCF₃] (0.3 mmol) in solvent (1.0 mL) was added slowly a solution of **1a** (0.2 mmol) in solvent (1 mL) at 0 °C. The reaction was maintained at 0 °C under N₂ for 8 hours. ^b Yields were determined by HPLC using **2a** as an external standard (*t*_R = 4.50 min, λ = 268 nm, methanol/water = 90:10 (v/v)). Isolated yield was depicted in the parentheses.

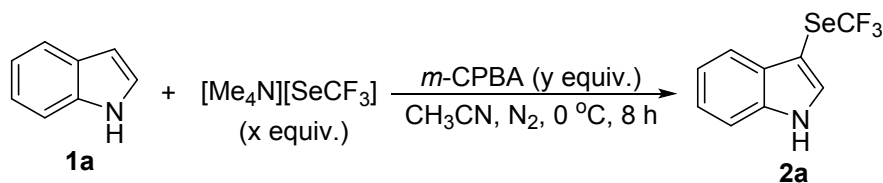
Table S4 Trifluoromethylselenolation of **1a** by [Me₄N][SeCF₃] in the presence of *m*-CPBA at different reaction times.



Entry ^a	Time (h)	Yield (2a , %) ^b
1	10	87
2 ^c	10	87
3	8	96 (93)
4	6	91
5	4	78

^a Reaction conditions: To a mixture of *m*-CPBA (0.22 mmol) and $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (0.3 mmol) in CH_3CN (1 mL) was added slowly a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under a nitrogen atmosphere for 4–10 hours. ^b Yields were determined by HPLC using **2a** as an external standard ($t_{\text{R}} = 4.50$ min, $\lambda_{\text{max}} = 268$ nm, methanol/water = 90:10 (v/v)). Isolated yield was depicted in the parentheses. ^c Reaction conditions: A solution of *m*-CPBA (0.22 mmol) in CH_3CN (1 mL) was added slowly to a mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (0.3 mmol) and **1a** (0.2 mmol) in CH_3CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under a nitrogen atmosphere for 8 hours.

Table S5 Trifluoromethylselenolation of **1a** with different equivalents of $[\text{NMe}_4][\text{SeCF}_3]$ in the presence of *m*-CPBA.

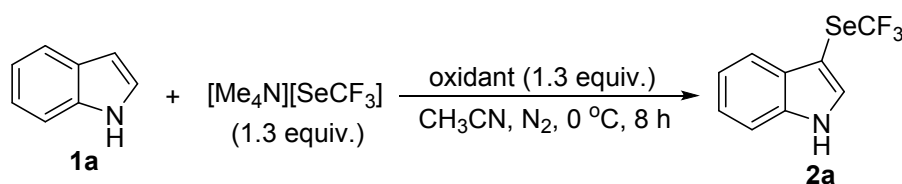


Entry ^a	x	y	Yield (2a , %) ^b
1	1.0	1.1	75
2	1.1	1.1	84
3	1.1	1.5	67
4	1.3	1.1	91
5	1.3	1.3	>99 (97)
6	1.3	1.5	>99

7	1.5	1.1	96 (93)
8	1.8	1.1	93

^a Reaction conditions: To a mixture of *m*-CPBA (0.22 or 0.3 mmol) and [Me₄N][SeCF₃] (0.2, 0.22, 0.26, 0.3, or 0.36 mmol) in CH₃CN (1 mL) was added slowly a solution of **1a** (0.2 mmol) in CH₃CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N₂ for 8 hours. ^b Yields were determined by HPLC using **2a** as an external standard (*t_R* = 4.50 min, λ_{max} = 268 nm, methanol/water = 90:10 (v/v)). Isolated yield was depicted in the parentheses.

Table S6 Trifluoromethylselenolation of **1a** by [Me₄N][SeCF₃] and an oxidant with different charging sequence.

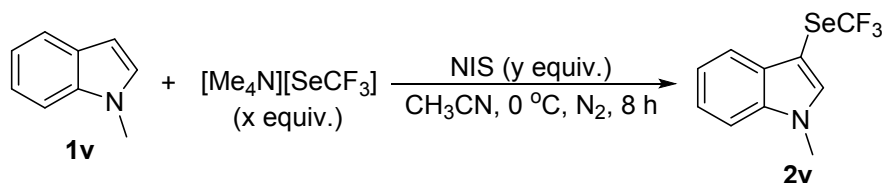


Entry	Oxidant	Yield (2a , %) ^a	Yield (2a , %) ^b
1	<i>m</i> -CPBA	> 99 (97)	> 99
2	NIS	99	97
3	NCS	85	>99
4	NBS	99	91
5	DDQ	9	53
6	PhI(OAc) ₂	> 99	> 99

^a Reaction conditions: To a mixture of oxidant (0.26 mmol) and [Me₄N][SeCF₃] (0.26 mmol) in CH₃CN (1 mL) was added slowly a solution of **1a** (0.2 mmol) in CH₃CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N₂ for 8 hours. Yields were determined by HPLC using **2a** as an external standard (*t_R* = 4.50 min, λ_{max} = 268 nm, methanol/water = 90:10 (v/v)). Isolated yield was depicted in the parentheses. ^b

Reaction conditions: A solution of oxidant (0.26 mmol) in CH₃CN (1 mL) was added slowly to a mixture of [Me₄N][SeCF₃] (0.26 mmol) and **1a** (0.2 mmol) in CH₃CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N₂ for 8 hours. Yields were determined by HPLC using **2a** as an external standard (*t_R* = 4.50 min, λ_{max} = 268 nm, methanol/water = 90:10 (v/v)).

Table S7 Trifluoromethylselenolation of **1v** by [Me₄N][SeCF₃] in the presence of NIS with different reactant ratios.



Entry ^a	x : y	Recovery (1v , %)	Yield (2v , %) ^b
1	1.0 : 1.0	21	62
2	1.1 : 1.1	20	78
3	1.1 : 1.3	<1	83
4	1.2 : 1.2	2	87
5	1.3 : 1.3	<1	90 (90)
6	1.3 : 1.5	<1	85
7	1.4 : 1.4	<1	89
8	1.5 : 1.5	<1	91
9	1.5 : 1.1	88	0

^a Reaction conditions: To a mixture of NIS (0.20, 0.22, 0.24, 0.26, 0.30 mmol) and [Me₄N][SeCF₃] (0.20, 0.22, 0.24, 0.28, 0.3 mmol) in CH₃CN (1 mL) was added slowly a solution of **1v** (0.2 mmol) in CH₃CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N₂ for 8 hours. ^b Yields were determined by HPLC using **2v** as an external standard (*t_R* = 5.71 min, λ = 268 nm, methanol/water = 90:10 (v/v)). Isolated yield was depicted in the parentheses.

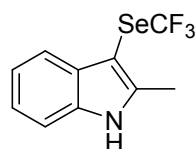
3. General procedures for the trifluoromethylselenolation of (hetero)arenes (**1**) by [Me₄N][SeCF₃] in the presence of an oxidant.

Procedure A: Under a nitrogen atmosphere, a sealed tube was charged with [Me₄N][SeCF₃] (57.7 mg, 0.26 mmol), CH₃CN (1 mL), and *m*-CPBA (52.5 mg, 85%, 0.26 mmol) at room temperature and cooled to 0 °C with stirring. Then, a solution of **1** (0.2 mmol) in CH₃CN (1 mL) was added slowly. The mixture was reacted at 0 °C for 8 hours and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoromethylselenolated products (**2**).

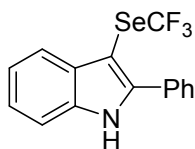
Procedure B: Under a nitrogen atmosphere, a sealed tube was charged with $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (57.7 mg, 0.26 mmol), CH_3CN (1 mL), and NIS (58.5 mg, 0.26 mmol) at room temperature and cooled to 0 °C with stirring. Then, a solution of **1** (0.2 mmol) in CH_3CN (1 mL) was added slowly. The mixture was reacted at 0 °C for 8 hours and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the trifluoromethylselenolated products (**2**).



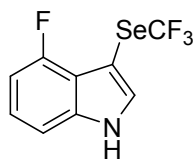
3-((Trifluoromethyl)selenanyl)-1*H*-indole (**2a**).⁸ Light yellow solid (51.3 mg, 97% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 64-66 °C. ¹H NMR (500 MHz, CDCl_3) δ 8.49 (brs, 1H), 7.80 (dm, $J = 5.9$ Hz, 1H), 7.51 (d, $J = 2.7$ Hz, 1H), 7.44 (m, 1H), 7.34-7.29 (m, 2H); ¹⁹F NMR (471 MHz, CDCl_3) δ -35.9 (s, 3F); ¹³C NMR (126 MHz, CDCl_3) δ 136.1, 132.9, 130.0, 123.4, 122.3 (q, $J = 335.1$ Hz), 121.5, 120.1, 111.5, 93.3 (q, $J = 1.6$ Hz).



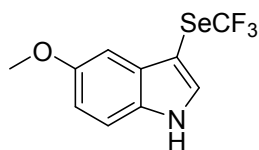
2-Methyl-3-((trifluoromethyl)selenanyl)-1*H*-indole (**2b**). White solid (47.3 mg, 85% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 98-100 °C. ¹H NMR (500 MHz, CDCl_3) δ 8.30 (brs, 1H), 7.70 (m, 1H), 7.32 (m, 1H), 7.25-7.22 (m, 2H), 2.60 (s, 3H); ¹⁹F NMR (471 MHz, CDCl_3) δ -37.4 (s, 3F); ¹³C NMR (126 MHz, CDCl_3) δ 142.8, 135.5, 131.3, 122.7 (q, $J = 336.1$ Hz), 122.6, 121.2, 119.5, 110.7, 91.7 (q, $J = 1.1$ Hz), 13.0. IR (KBr): 3382, 1541, 1455, 1402, 1386, 1291, 1233, 1223, 1131, 1118, 1108, 1098, 1059, 1006, 994, 931, 756, 749, 733 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{10}\text{H}_9\text{F}_3\text{NSe}$ ($[\text{M}+\text{H}]^+$): 279.9847; found: 279.9844.



2-Phenyl-3-((trifluoromethyl)selanyl)-1*H*-indole (**2c**). Brown solid (64.6 mg, 95% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 95-97 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.64 (brs, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 6.9 Hz, 1H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.34-7.29 (m, 2H); ¹⁹F NMR (471 MHz, CDCl₃) δ -36.6 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 144.1, 135.8, 132.1, 131.4, 129.2, 129.1, 128.7, 123.6, 122.5 (q, *J* = 337.1 Hz), 121.7, 120.7, 111.1, 91.3 (q, *J* = 1.3 Hz). IR (KBr): 3364, 3070, 1602, 1579, 1538, 1484, 1445, 1396, 1347, 1324, 1297, 1276, 1224, 1118, 1096, 1009, 990, 852, 819, 769, 751, 735, 696, 635 cm⁻¹. HRMS-ESI (*m/z*) calcd. for C₁₅H₉F₃NSe ([*M*-H]⁻): 339.9858; found: 339.9867.

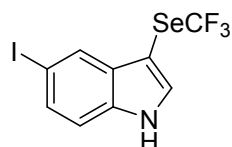


4-Fluoro-3-((trifluoromethyl)selanyl)-1*H*-indole (**2d**). White solid (53.6 mg, 94% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 101-103 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.67 (brs, 1H), 7.47 (s, 1H), 7.24-7.21 (m, 2H), 6.91 (t, *J* = 8.7 Hz, 1H); ¹⁹F NMR (471 MHz, CDCl₃) δ -38.5 (d, *J* = 3.2 Hz, 3F), -124.7 (m, 1F); ¹³C NMR (126 MHz, CDCl₃) δ 156.8 (d, *J* = 250.9 Hz), 139.0 (d, *J* = 9.4 Hz), 133.7, 123.9 (d, *J* = 7.9 Hz), 122.1 (q, *J* = 335.3 Hz), 118.5 (d, *J* = 17.8 Hz), 107.8 (d, *J* = 3.9 Hz), 106.9 (d, *J* = 19.0 Hz), 89.3. IR (KBr): 3457, 3130, 1660, 1634, 1578, 1510, 1444, 1413, 1347, 1317, 1229, 1161, 1132, 1114, 1089, 1029, 987, 948, 839, 833, 779, 731, 678, 614 cm⁻¹. HRMS-ESI (*m/z*) calcd. for C₉H₄F₄NSe ([*M*-H]⁻): 281.9451; found: 281.9460.

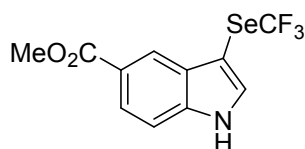


5-Methoxy-3-((trifluoromethyl)selanyl)-1*H*-indole (**2e**).⁹ Pink solid (58.2 mg, 99% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column

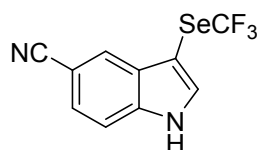
chromatography. M.p.: 102-104 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.51 (brs, 1H), 7.48 (s, 1H), 7.31 (d, $J = 8.8$ Hz, 1H), 7.20 (s, 1H), 6.95 (d, $J = 8.8$ Hz, 1H), 3.91 (s, 3H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.6 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 155.6, 133.3, 131.0, 130.8, 122.3 (q, $J = 336.2$ Hz), 113.9, 112.4, 101.4, 92.8, 55.9.



5-Iodo-3-((trifluoromethyl)selanyl)-1*H*-indole (**2f**). Light yellow solid (76.7 mg, 98% yield), hexane/diethyl ether = 3:1 (v/v) as eluents for column chromatography. M.p.: 75-77 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.60 (brs, 1H), 8.10 (s, 1H), 7.55 (dd, $J = 8.6$, 1.6 Hz, 1H), 7.49 (d, $J = 2.7$ Hz, 1H), 7.22 (d, $J = 8.6$ Hz, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.5 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 135.2, 133.5, 132.5, 131.9, 129.1, 122.1 (q, $J = 335.1$ Hz), 113.4, 92.6 (q, $J = 1.7$ Hz), 85.3. IR (KBr): 3473, 3120, 1698, 1670, 1498, 1442, 1418, 1401, 1304, 1292, 1263, 1236, 1144, 1121, 1076, 1013, 984, 875, 838, 796, 771, 747, 733, 720, 670 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_9\text{H}_4\text{F}_3\text{INSe}$ ($[\text{M}-\text{H}]^-$): 389.8511; found: 389.8506.

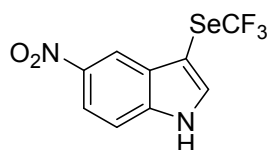


Methyl 3-((trifluoromethyl)selanyl)-1*H*-indole-5-carboxylate (**2g**).⁸ White solid (63.7 mg, >99% yield), hexane/diethyl ether = 1:1 (v/v) as eluents for column chromatography. M.p.: 172-174 °C. ^1H NMR (500 MHz, acetone- d_6) δ 11.34 (brs, 1H), 8.42 (s, 1H), 7.94-7.93 (m, 2H), 7.64 (d, $J = 8.6$ Hz, 1H), 3.91 (s, 3H); ^{19}F NMR (471 MHz, acetone- d_6) δ -38.9 (s, 3F); ^{13}C NMR (126 MHz, acetone- d_6) δ 166.9, 139.4, 136.2, 129.8, 123.8, 123.4, 122.5 (q, $J = 333.9$ Hz), 121.8, 112.2, 92.7 (q, $J = 1.7$ Hz), 51.2.

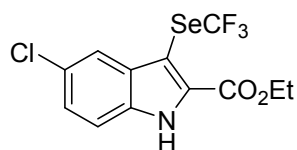


3-((Trifluoromethyl)selanyl)-1*H*-indole-5-carbonitrile (**2h**). Light yellow solid (56.6

mg, 98% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 212-214 °C. ¹H NMR (500 MHz, acetone-d₆) δ 11.60 (brs, 1H), 8.06 (s, 1H), 8.02 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.56 (dd, *J* = 8.5, 1.5 Hz, 1H); ¹⁹F NMR (471 MHz, acetone-d₆) δ -38.9 (s, 3F); ¹³C NMR (126 MHz, acetone-d₆) δ 138.7, 137.1, 130.1, 125.5, 124.6, 122.4 (q, *J* = 333.9 Hz), 119.6, 113.7, 104.3, 92.2. IR (KBr): 3229, 3028, 2993, 2237, 1621, 1470, 1458, 1425, 1340, 1306, 1300, 1244, 1153, 1138, 1130, 1099, 992, 919, 888, 846, 808, 793, 757, 734 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₀H₆F₃N₂Se ([M+H]⁺): 288.9651; found: 288.9644.

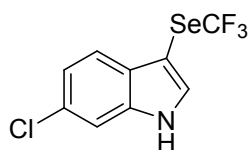


5-Nitro-3-((trifluoromethyl)selanyl)-1*H*-indole (**2i**). Light yellow solid (62.4 mg, >99% yield), petroleum ether/ethyl acetate = 2:1 (v/v) as eluents for column chromatography. M.p.: 193-195 °C. ¹H NMR (500 MHz, acetone-d₆) δ 11.64 (brs, 1H), 8.59 (s, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 8.09 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 1H); ¹⁹F NMR (471 MHz, acetone-d₆) δ -38.8 (s, 3F); ¹³C NMR (126 MHz, acetone-d₆) δ 143.0, 139.9, 138.1, 129.8, 122.4 (q, *J* = 334.8 Hz), 118.0, 115.9, 113.0, 93.7. IR (KBr): 3260, 3107, 3032, 1713, 1618, 1583, 1516, 1501, 1474, 1456, 1419, 1325, 1319, 1301, 1244, 1235, 1205, 1163, 1123, 1091, 1075, 989, 947, 901, 861, 831, 816, 783, 739, 696 cm⁻¹. HRMS-ESI (m/z) calcd. for C₉H₄F₃N₂O₂Se ([M-H]⁻): 308.9396; found: 308.9404.

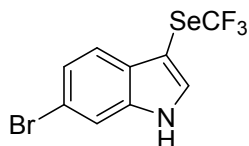


Ethyl 5-chloro-3-((trifluoromethyl)selanyl)-1*H*-indole-2-carboxylate (**2j**). White solid (73.5 mg, 99% yield), hexane/diethyl ether = 1:1 (v/v) as eluents for column chromatography. M.p.: 205-207 °C. ¹H NMR (500 MHz, acetone-d₆) δ 11.87 (brs, 1H), 7.75 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ¹⁹F NMR (471 MHz, acetone-d₆) δ -37.4 (s, 3F); ¹³C NMR (126 MHz, acetone-d₆) δ 159.8, 134.8, 132.8, 132.3, 127.6, 126.1, 122.6 (q, *J* = 334.9 Hz), 120.3, 114.7, 96.7 (q, *J* = 1.6 Hz), 61.4, 13.6. IR (KBr): 3291, 3069, 2994, 1686, 1618, 1509, 1476, 1453, 1439, 1408, 1383, 1355, 1330, 1265, 1246, 1228, 1205,

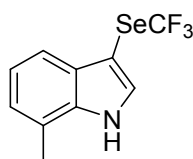
1144, 1128, 1100, 1066, 1032, 1014, 941, 917, 882, 872, 805, 780, 748, 736, 714 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{12}\text{H}_8\text{ClF}_3\text{NO}_2\text{Se}$ ($[\text{M}-\text{H}]^-$): 369.9366; found: 369.9376.



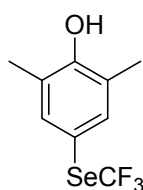
6-Chloro-3-((trifluoromethyl)selanyl)-1*H*-indole (**2k**). White solid (57.3 mg, 96% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. M.p.: 42-44 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.57 (brs, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.52 (s, 1H), 7.45 (s, 1H), 7.27 (d, $J = 8.5$ Hz, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.5 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 136.4, 133.5, 129.4, 128.7, 122.3, 122.2 (q, $J = 335.7$ Hz), 121.1, 111.5, 93.6 (q, $J = 1.5$ Hz). IR (KBr): 3469, 3443, 3115, 1664, 1621, 1614, 1611, 1566, 1501, 1478, 1447, 1385, 1330, 1301, 1272, 1227, 1197, 1153, 1135, 1108, 1085, 1059, 982, 941, 903, 853, 835 780, 732, 708 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_9\text{H}_4\text{ClF}_3\text{NSe}$ ($[\text{M}-\text{H}]^-$): 297.9155; found: 297.9149.



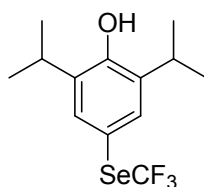
6-Bromo-3-((trifluoromethyl)selanyl)-1*H*-indole (**2l**). White solid (63.1 mg, 92% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 65-67 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.57 (brs, 1H), 7.62 (d, $J = 8.5$ Hz, 1H), 7.58 (s, 1H), 7.49 (s, 1H), 7.38 (d, $J = 8.5$ Hz, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.5 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 136.8, 133.4, 129.0, 124.9, 122.2 (q, $J = 335.8$ Hz), 121.5, 117.0, 114.5, 93.6 (q, $J = 1.6$ Hz). IR (KBr): 3474, 3457, 3129, 3118, 3105, 1662, 1608, 1499, 1446, 1383, 1328, 1302, 1270, 1228, 1198, 1159, 1134, 1101, 1080, 1054, 979, 941, 892, 841, 836, 804, 777, 744, 732 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_9\text{H}_4\text{BrF}_3\text{NSe}$ ($[\text{M}-\text{H}]^-$): 343.8629; found: 343.8623.



7-Methyl-3-((trifluoromethyl)selanyl)-1*H*-indole (**2m**). Light yellow solid (53.2 mg, 96% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 87-89 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.47 (brs, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 2.7 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 2.52 (s, 3H); ¹⁹F NMR (471 MHz, CDCl₃) δ -37.6 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 135.7, 132.5, 129.7, 123.9, 122.3 (q, *J* = 335.9 Hz), 121.7, 120.7, 117.8, 93.7 (q, *J* = 1.6 Hz), 16.4. IR (KBr): 3382, 3146, 2944, 2919, 1676, 1505, 1494, 1453, 1431, 1413, 1383, 1345, 1313, 1282, 1251, 1163, 1136, 1126, 1096, 1070, 1048, 981, 919, 841, 779, 747, 734 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₀H₇F₃NSe ([M-H]⁻): 277.9701; found: 277.9694.

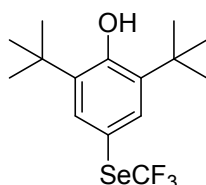


2,6-Dimethyl-4-((trifluoromethyl)selanyl)phenol (**2n**). Light yellow solid (40.9 mg, 76% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 43-45 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (s, 2H), 4.88 (s, 1H), 2.26 (s, 6H); ¹⁹F NMR (471 MHz, CDCl₃) δ -37.1 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 154.4, 137.7, 124.5, 122.5 (q, *J* = 333.8 Hz), 112.2 (q, *J* = 1.3 Hz), 15.7. IR (KBr): 3436, 3048, 2983, 2954, 2927, 2862, 1669, 1600, 1582, 1559, 1477, 1456, 1426, 1405, 1335, 1313, 1277, 1258, 1208, 1158, 1092, 1060, 1032, 998, 940, 874, 737, 728, 719 cm⁻¹. HRMS-ESI (m/z) calcd. for C₉H₈F₃OSe ([M-H]⁻): 268.9698; found: 268.9690.

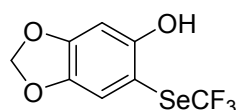


2,6-Diisopropyl-4-((trifluoromethyl)selanyl)phenol (**2o**). Light yellow solid (60.2 mg, 93% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 52-54 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.41 (s, 2H), 5.05 (s, 1H), 3.15 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 12H); ¹⁹F NMR (471 MHz, CDCl₃) δ -37.1 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 152.1, 135.1, 133.0, 122.6 (q, *J* = 333.8 Hz),

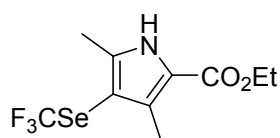
113.3 (q, $J = 1.2$ Hz), 27.2, 22.5. IR (KBr): 3608, 3585, 2967, 2936, 2874, 1576, 1466, 1450, 1436, 1417, 1385, 1363, 1344, 1311, 1262, 1251, 1205, 1136, 1098, 1062, 959, 933, 923, 878, 840, 810, 766, 736, 726 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{13}\text{H}_{16}\text{F}_3\text{OSe}$ ($[\text{M}-\text{H}]^-$): 325.0324; found: 325.0325.



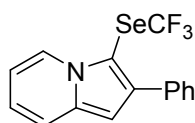
2,6-Di-tert-butyl-4-((trifluoromethyl)selanyl)phenol (**2p**). Light yellow solid (64.3 mg, 91% yield), petroleum ether as eluent for column chromatography. M.p.: 45-47 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 7.53 (s, 2H), 5.49 (s, 1H), 1.46 (s, 18H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.1 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 155.9, 137.3, 134.4, 122.7 (q, $J = 333.9$ Hz), 112.6, 34.4, 30.1. IR (KBr): 3637, 3612, 3089, 2955, 2917, 2874, 1781, 1655, 1573, 1471, 1426, 1393, 1362, 1316, 1231, 1202, 1131, 1094, 930, 886, 808, 772, 752, 736, 693 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{15}\text{H}_{20}\text{F}_3\text{OSe}$ ($[\text{M}-\text{H}]^-$): 353.0637; found: 353.0639.



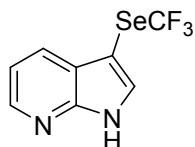
6-((Trifluoromethyl)selanyl)benzo[d][1,3]dioxol-5-ol (**2q**). Light yellow solid (54.2 mg, 95% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 91-93 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 7.05 (s, 1H), 6.64 (s, 1H), 6.07 (s, 1H), 5.98 (s, 2H); ^{19}F NMR (471 MHz, CDCl_3) δ -36.7 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 153.9, 152.5, 142.0, 121.7 (q, $J = 336.9$ Hz), 115.9, 101.9, 97.8, 97.4. IR (KBr): 3422, 3104, 3056, 3002, 2975, 2919, 2852, 1622, 1612, 1591, 1496, 1471, 1439, 1399, 1374, 1278, 1228, 1185, 1156, 1131, 1116, 1092, 1070, 1031, 987, 931, 875, 869, 846, 832, 818, 769, 736, 710 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_8\text{H}_4\text{F}_3\text{O}_3\text{Se}$ ($[\text{M}-\text{H}]^-$): 284.9283; found: 284.9282.



Ethyl 3,5-dimethyl-4-((trifluoromethyl)selanyl)-1*H*-pyrrole-2-carboxylate (**2r**). White solid (47.7 mg, 76% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 173-175 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.54 (brs, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 2.41 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ¹⁹F NMR (471 MHz, CDCl₃) δ -37.9 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 160.6, 138.5, 132.0, 121.4 (q, *J* = 335.5 Hz), 117.7, 101.2, 59.4, 13.5, 11.8, 11.4. IR (KBr): 3384, 3284, 2985, 2925, 1673, 1632, 1564, 1512, 1481, 1440, 1395, 1381, 1322, 1282, 1215, 1119, 1103, 1067, 1044, 1020, 877, 850, 774, 749, 734 cm⁻¹. HRMS-ESI (*m/z*) calcd. for C₁₀H₁₁F₃NO₂Se ([*M*-H]⁻): 313.9913; found: 313.9911.

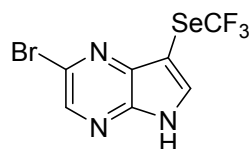


2-Phenyl-3-((trifluoromethyl)selanyl)indolizine (**2s**). White solid (46.9 mg, 69% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. M.p.: 90-92 °C. ¹H NMR (500 MHz, acetone-d₆) δ 8.62 (d, *J* = 7.1 Hz, 1H), 7.67 (dm, *J* = 7.6 Hz, 2H), 7.58 (dm, *J* = 9.0 Hz, 1H), 7.46 (tm, *J* = 7.4 Hz, 2H), 7.38 (tm, *J* = 7.4 Hz, 1H), 7.04 (m, 1H), 6.87 (td, *J* = 6.9, 1.3 Hz, 1H), 6.84 (d, *J* = 0.4 Hz, 1H); ¹⁹F NMR (471 MHz, acetone-d₆) δ -38.3 (s, 3F); ¹³C NMR (126 MHz, acetone-d₆) δ 139.8, 137.7, 135.3, 129.5, 128.2, 127.4, 125.3, 122.1 (q, *J* = 340.3 Hz), 121.2, 118.9, 112.1, 101.8, 97.3 (q, *J* = 1.1 Hz). IR (KBr): 3108, 3061, 3030, 1680, 1662, 1641, 1632, 1602, 1578, 1538, 1505, 1489, 1462, 1449, 1367, 1352, 1332, 1269, 1242, 1190, 1181, 1135, 1093, 1072, 1030, 1011, 974, 918, 834, 830, 789, 761, 734, 720, 698 cm⁻¹. HRMS-ESI (*m/z*) calcd. for C₁₅H₁₁F₃NSe ([*M*+H]⁺): 342.0003; found: 342.0003.

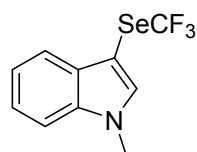


3-((Trifluoromethyl)selanyl)-1*H*-pyrrolo[2,3-*b*]pyridine (**2t**). White solid (47.7 mg, 90% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 194-196 °C. ¹H NMR (500 MHz, DMSO-d₆) δ 12.51 (brs, 1H), 8.34 (d, *J* = 4.3 Hz, 1H), 8.02 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 7.4, 4.3 Hz, 1H); ¹⁹F NMR (471 MHz, DMSO-d₆) δ -37.5 (s, 3F); ¹³C NMR (126 MHz, DMSO-d₆) δ 149.0,

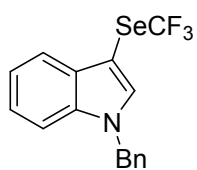
144.5, 135.9, 127.7, 122.9 (q, $J = 336.2$ Hz), 122.6, 117.7, 89.5 (q, $J = 1.5$ Hz). IR (KBr): 3430, 3126, 3075, 3015, 2989, 1608, 1587, 1489, 1445, 1410, 1360, 1340, 1315, 1282, 1244, 1144, 1116, 1092, 1042, 991, 935, 893, 853, 828, 797, 772, 733 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_8\text{H}_4\text{F}_3\text{N}_2\text{Se}$ ($[\text{M}-\text{H}]^-$): 262.9505; found: 262.9509.



2-Bromo-7-((trifluoromethyl)selanyl)-5H-pyrrolo[2,3-b]pyrazine (**2u**). Pink solid (51.8 mg, 75% yield), petroleum ether/ethyl acetate = 3:1 (v/v) as eluents for column chromatography. M.p.: 194-196 °C. ^1H NMR (500 MHz, (acetone- d_6) δ 12.06 (brs, 1H), 8.46 (s, 1H), 8.38 (s, 1H); ^{19}F NMR (471 MHz, acetone- d_6) δ -38.6 (s, 3F); ^{13}C NMR (126 MHz, acetone- d_6) δ 140.5, 140.3, 140.2, 139.9, 134.5, 122.3 (q, $J = 334.4$ Hz), 90.9 (q, $J = 1.7$ Hz). IR (KBr): 3435, 3174, 3107, 3048, 2995, 1780, 1731, 1586, 1543, 1479, 1450, 1434, 1395, 1375, 1343, 1322, 1287, 1245, 1229, 1205, 1150, 1134, 1112, 1092, 1066, 1004, 918, 892, 868, 837, 772, 736, 696 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_7\text{H}_4\text{BrF}_3\text{N}_3\text{Se}$ ($[\text{M}+\text{H}]^+$): 345.8700; found: 345.8700.

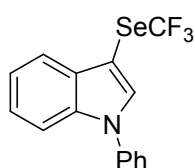


1-Methyl-3-((trifluoromethyl)selanyl)-1H-indole (**2v**).¹⁰ Light yellow solid (50.1 mg, 90% yield), petroleum ether/ethyl acetate = 20:1 (v/v) as eluents for column chromatography. M.p.: 63-65 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 7.8$ Hz, 1H), 7.40-7.38 (m, 2H), 7.35 (m, 1H), 7.30 (m, 1H), 3.84 (s, 3H); ^{19}F NMR (471 MHz, CDCl_3) δ -38.0 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 137.3, 137.1, 130.8, 122.9, 122.3 (q, $J = 335.7$ Hz), 121.1, 120.2, 109.8, 90.9 (q, $J = 1.6$ Hz), 33.2.

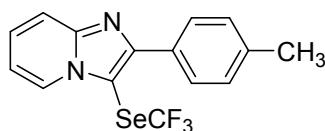


1-Benzyl-3-((trifluoromethyl)selanyl)-1H-indole (**2w**). White solid (59.5 mg, 84% yield), petroleum ether/ethyl acetate = 40:1 (v/v) as eluents for column

chromatography. M.p.: 86-88 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.80 (m, 1H), 7.45 (s, 1H), 7.36-7.31 (m, 4H), 7.30-7.28 (m, 2H), 7.16 (d, $J = 7.1$ Hz, 2H), 5.36 (s, 2H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.8 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 136.9, 136.5, 136.3, 131.0, 129.0, 128.1, 127.0, 123.0, 122.3 (q, $J = 336.2$ Hz), 121.3, 120.3, 110.2, 91.9 (q, $J = 1.6$ Hz), 50.6. IR (KBr): 3107, 3059, 3030, 2926, 1663, 1612, 1605, 1572, 1504, 1480, 1458, 1452, 1439, 1386, 1354, 1338, 1329, 1313, 1297, 1200, 1185, 1176, 1159, 1139, 1100, 1089, 1074, 1029, 969, 954, 927, 893, 833, 841, 809, 775, 760, 739, 724 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{NNaSe}$ ($[\text{M}+\text{Na}]^+$): 377.9979; found: 377.9987.

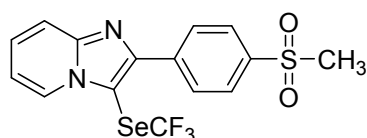


1-Phenyl-3-((trifluoromethyl)selanyl)-1*H*-indole (**2x**). White solid (21.1 mg, 31% yield), petroleum ether as eluent for column chromatography. M.p.: 65-67 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.83 (m, 1H), 7.66 (s, 1H), 7.58-7.55 (m, 3H), 7.54-7.52 (m, 2H), 7.44 (tm, $J = 7.2$ Hz, 1H), 7.33 (m, 2H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.4 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 138.6, 136.6, 136.0, 131.2, 129.8, 127.6, 124.7, 123.6, 122.3 (q, $J = 336.0$ Hz), 121.9, 120.5, 111.0, 94.0 (q, $J = 1.6$ Hz). IR (KBr): 3115, 3058, 1642, 1597, 1511, 1496, 1477, 1453, 1429, 1397, 1367, 1318, 1298, 1281, 1262, 1227, 1205, 1196, 1177, 1158, 1115, 1097, 1073, 1037, 1029, 1012, 995, 979, 966, 935, 926, 910, 851, 827, 822, 803, 775, 746, 720, 695 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{NSe}$ ($[\text{M}+\text{H}]^+$): 342.0003; found: 342.0020.

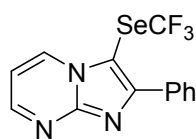


2-(*p*-Tolyl)-3-((trifluoromethyl)selanyl)imidazo[1,2-*a*]pyridine (**2y**). Yellow solid (59.0 mg, 83% yield), petroleum ether/ethyl acetate = 2:1 (v/v) as eluents for column chromatography. M.p.: 146-148 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.52 (d, $J = 6.8$ Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 9.0$ Hz, 1H), 7.38 (tm, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 6.99 (td, $J = 6.9, 1.0$ Hz, 1H), 2.43 (s, 3H); ^{19}F NMR (471 MHz, CDCl_3) δ -36.0 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 154.3, 148.5, 138.9, 130.2,

129.1, 128.9, 127.4, 125.5, 122.2 (q, $J = 340.2$ Hz), 117.7, 113.4, 97.6, 21.4. IR (KBr): 3078, 3056, 3033, 2985, 2922, 2861, 1635, 1613, 1501, 1467, 1411, 1343, 1318, 1267, 1231, 1187, 1155, 1138, 1130, 1098, 1036, 1020, 993, 985, 967, 916, 851, 839, 822, 757, 747, 734, 725, 695 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{15}\text{H}_{12}\text{F}_3\text{N}_2\text{Se}$ ($[\text{M}+\text{H}]^+$): 357.0112; found: 357.0114.

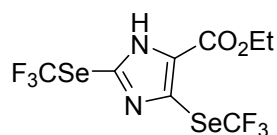


2-(4-(Methylsulfonyl)phenyl)-3-((trifluoromethyl)selanyl)imidazo[1,2-a]pyridine (**2z**). Light yellow solid (65.4 mg, 78% yield), petroleum ether/ethyl acetate = 1:1 (v/v) as eluents for column chromatography. M.p.: 175-177°C. ^1H NMR (500 MHz, CDCl_3) δ 8.52 (d, $J = 6.8$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 2H), 7.72 (d, $J = 9.0$ Hz, 1H), 7.38 (tm, $J = 9.0$ Hz, 1H), 7.30 (d, $J = 7.9$ Hz, 2H), 6.99 (td, $J = 6.9, 1.1$ Hz, 1H), 2.43 (s, 3H); ^{19}F NMR (471 MHz, CDCl_3) δ -35.7 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 151.8, 148.6, 140.4, 138.5, 129.8, 128.1, 127.4, 125.6, 122.0 (q, $J = 339.4$ Hz), 118.1, 114.2, 99.0 (q, $J = 1.1$ Hz), 44.6. IR (KBr): 3106, 3061, 3032, 3013, 2983, 2962, 2927, 2849, 1775, 1709, 1675, 1655, 1635, 1601, 1529, 1499, 1460, 1403, 1345, 1316, 1303, 1268, 1236, 1163, 1146, 1128, 1093, 1016, 992, 978, 960, 955, 916, 856, 843, 826, 777, 763, 757, 745, 734, 719, 694 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{15}\text{H}_{12}\text{F}_3\text{N}_2\text{O}_2\text{SSe}$ ($[\text{M}+\text{H}]^+$): 420.9731; found: 420.9729.

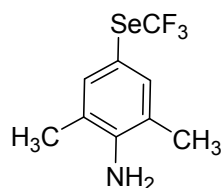


2-Phenyl-3-((trifluoromethyl)selanyl)imidazo[1,2-a]pyrimidine (**2aa**). Light yellow solid (56.1 mg, 82% yield), petroleum ether/ethyl acetate = 1:1 (v/v) as eluents for column chromatography. M.p.: 123-125 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.78 (dd, $J = 6.8, 1.8$ Hz, 1H), 8.70 (dd, $J = 4.1, 2.0$ Hz, 1H), 8.18 (dm, $J = 7.1$ Hz, 2H), 7.51-7.48 (m, 2H), 7.45 (tm, $J = 7.2$ Hz, 1H) 7.07 (dd, $J = 7.0, 4.2$ Hz, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ -35.5 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 155.4, 152.5, 151.4, 133.1, 132.4, 129.5, 129.2, 128.4, 122.1 (q, $J = 339.6$ Hz), 109.9, 96.6. IR (KBr): 3160, 3073, 1773, 1695, 1614, 1525, 1509, 1504, 1489, 1464, 1444, 1430, 1417, 1404, 1396, 1370, 1338, 1295, 1239, 1194, 1159, 1137, 1128, 1099, 1093, 1029, 1003, 989,

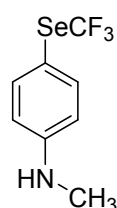
935, 850, 822, 801, 769, 704 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{13}\text{H}_9\text{F}_3\text{N}_3\text{Se}$ ($[\text{M}+\text{H}]^+$): 343.9908; found: 343.9913.



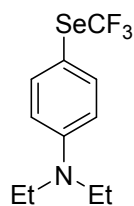
Ethyl 2,4-bis((trifluoromethyl)selanyl)-1*H*-imidazole-5-carboxylate (**2ab**). White solid (29.5 mg, 34% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 98-100 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 11.43 (brs, 1H), 4.44 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H); ^{19}F NMR (471 MHz, CDCl_3) δ -33.4 (s, 3F), -34.4 (s, 3F); ^{13}C NMR (126 MHz, acetone- d_6) δ 159.2, 131.9, 129.8, 129.6, 122.6 (q, $J = 332.6$ Hz), 122.3 (q, $J = 334.3$ Hz), 66.1, 13.6. IR (KBr): 3419, 3395, 3040, 2992, 2971, 2849, 2881, 2825, 1881, 1721, 1647, 1518, 1475, 1450, 1395, 1381, 1325, 1293, 1271, 1223, 1149, 1095, 1049, 1016, 990, 866, 842, 789, 777, 739 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_8\text{H}_7\text{F}_6\text{N}_2\text{O}_2\text{Se}_2$ ($[\text{M}+\text{H}]^+$): 436.8737; found: 436.8736.



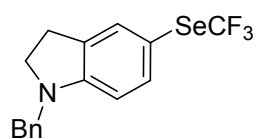
2,6-Dimethyl-4-((trifluoromethyl)selanyl)aniline (**2ac**). Light yellow solid (45.6 mg, 85% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 38-40 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 7.33 (s, 2H), 3.81 (brs, 2H), 2.18 (s, 6H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.6 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 145.1, 137.4, 122.6 (q, $J = 334.2$ Hz), 122.4, 108.9 (q, $J = 1.1$ Hz), 17.3. IR (KBr): 3432, 2922, 2852, 1654, 1591, 1466, 1437, 1379, 1261, 1189, 1166, 1100, 1029, 849, 779, 717, 705 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_9\text{H}_{10}\text{F}_3\text{NNaSe}$ ($[\text{M}+\text{Na}]^+$): 291.9823; found: 291.9820.



N-Methyl-4-((trifluoromethyl)selanyl)aniline (**2ad**). Light brown liquid (42.7 mg, 84% yield), hexane/tetrahydrofuran = 20:1 (v/v) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 8.7 Hz, 2H), 6.59 (dm, *J* = 8.7 Hz, 2H), 4.02 (brs, 1H), 2.88 (s, 3H); ¹⁹F NMR (471 MHz, CDCl₃) δ -37.9 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 150.9, 138.9, 122.6 (q, *J* = 334.2 Hz), 112.9, 108.0, 30.2. IR (KBr): 3431, 3017, 2927, 2902, 2855, 2836, 2820, 1597, 1510, 1481, 1469, 1451, 1434, 1397, 1325, 1296, 1267, 1185, 1102, 1077, 1058, 1001, 817, 736 cm⁻¹. HRMS-ESI (m/z) calcd. for C₈H₉F₃NSe ([M+H]⁺): 255.9847; found: 255.9843.

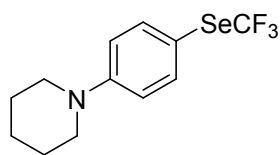


N,N-Diethyl-4-((trifluoromethyl)selanyl)aniline (**2ae**). Colorless liquid (53.3 mg, 90% yield), petroleum ether/ethyl acetate = 40:1 (v/v) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.53 (dm, *J* = 9.0 Hz, 2H), 6.62 (dm, *J* = 9.0 Hz, 2H), 3.38 (q, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H); ¹⁹F NMR (471 MHz, CDCl₃) δ -38.0 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 149.2, 138.9, 122.7 (q, *J* = 334.7 Hz), 112.0, 105.8 (q, *J* = 1.2 Hz), 44.4, 12.4. IR (KBr): 2974, 2933, 2899, 2874, 1589, 1551, 1506, 1469, 1451, 1403, 1378, 1357, 1270, 1197, 1102, 1080, 1013, 808, 735 cm⁻¹. HRMS-ESI (m/z) calcd. for C₁₁H₁₅F₃NSe ([M+H]⁺): 298.0316; found: 298.0319.



1-Benzyl-5-((trifluoromethyl)selanyl)indoline (**2af**). Light yellow liquid (46.3 mg, 65% yield), hexane/dichloromethane = 10:1 (v/v) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.43-7.41 (m, 2H), 7.39-7.29 (m, 5H), 6.45 (d, *J* = 8.1 Hz, 1H), 4.32 (s, 2H), 3.46 (t, *J* = 8.5 Hz, 2H), 3.04 (t, *J* = 8.5 Hz, 2H); ¹⁹F NMR (471 MHz, CDCl₃) δ -37.9 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 153.1, 136.8, 136.6, 132.4, 130.2, 127.6, 126.7, 126.3, 121.6 (q, *J* = 334.5 Hz), 107.0, 105.8, 51.9, 51.4, 26.9. IR (KBr): 3086, 3063, 3030, 2958, 2923, 2845, 1597, 1497, 1472, 1454, 1440, 1401, 1386, 1356, 1316, 1272, 1242, 1201, 1111, 1092, 1062, 1029, 1003, 941, 980,

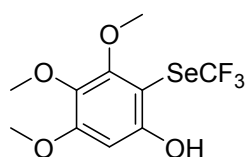
889, 877, 802, 763, 735, 698 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NSe}$ ($[\text{M}+\text{H}]^+$): 358.0316; found: 358.0320.



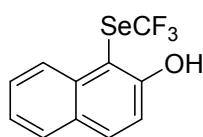
1-(4-((Trifluoromethyl)selanyl)phenyl)piperidine (**2ag**). Colorless liquid (57.3 mg, 93% yield), petroleum ether as eluent for column chromatography. ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 3.26 (t, $J = 5.3$ Hz, 4H), 1.70 (m, 4H), 1.64-1.60 (m, 2H); ^{19}F NMR (471 MHz, CDCl_3) δ -37.5 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 153.1, 138.5, 122.6 (q, $J = 334.0$ Hz), 115.9, 109.4 (q, $J = 1.1$ Hz), 49.2, 25.5, 24.3. IR (KBr): 2937, 2856, 2815, 1647, 1636, 1588, 1558, 1499, 1466, 1452, 1387, 1350, 1308, 1277, 1267, 1241, 1197, 1124, 1101, 1080, 1025, 1001, 919, 858, 814, 736 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{12}\text{H}_{15}\text{F}_3\text{NSe}$ ($[\text{M}+\text{H}]^+$): 310.0316; found: 310.0310.



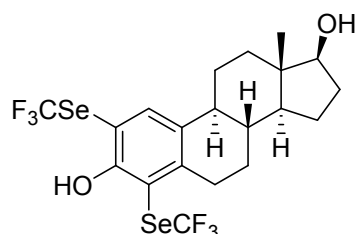
1-((Trifluoromethyl)selanyl)naphthalen-2-amine (**2ah**). Light brown solid (53.4 mg, 92% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 74-76 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 8.33 (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.53 (tm, $J = 7.7$ Hz, 1H), 7.30 (tm, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 8.7$ Hz, 1H), 4.83 (brs, 2H); ^{19}F NMR (471 MHz, CDCl_3) δ -34.6 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 149.4, 137.1, 133.4, 128.4, 128.2, 128.1, 126.1, 122.8, 122.6 (q, $J = 337.7$ Hz), 117.3, 99.9. IR (KBr): 3466, 1614, 1556, 1503, 1469, 1429, 1386, 1348, 1284, 1244, 1213, 1120, 1107, 1046, 1031, 974, 962, 947, 868, 816, 769, 748, 733 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{11}\text{H}_9\text{F}_3\text{NSe}$ ($[\text{M}+\text{H}]^+$): 289.9855; found: 289.9860.



3,4,5-Trimethoxy-2-((trifluoromethyl)selanyl)phenol (**2ai**). Light yellow solid (42.4 mg, 64% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 47-49 °C. ¹H NMR (500 MHz, CDCl₃) δ 6.46 (s, 1H), 6.27 (s, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.80 (s, 3H); ¹⁹F NMR (471 MHz, CDCl₃) δ -34.6 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 158.2, 155.1, 154.7, 136.0, 121.7 (q, *J* = 337.0 Hz), 95.1, 94.5, 61.4, 61.0, 56.0. IR (KBr): 3452, 2944, 2876, 2849, 1596, 1576, 1482, 1461, 1450, 1429, 1404, 1360, 1301, 1232, 1194, 1109, 1093, 1012, 990, 927, 818, 737 cm⁻¹. HRMS-ESI (*m/z*) calcd. for C₁₀H₁₀F₃O₄Se ([M-H]⁻): 330.9702; found: 330.9700.



1-((Trifluoromethyl)selanyl)naphthalen-2-ol (**2aj**). White solid (53.0 mg, 91% yield), petroleum ether/ethyl acetate = 5:1 (v/v) as eluents for column chromatography. M.p.: 81-83 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.31 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.61 (tm, *J* = 7.7 Hz, 1H), 7.42 (tm, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 6.85 (s, 1H); ¹⁹F NMR (471 MHz, CDCl₃) δ -34.6 (s, 3F); ¹³C NMR (126 MHz, CDCl₃) δ 157.2, 135.9, 134.6, 129.4, 128.5, 128.3, 126.5, 124.2, 121.9 (q, *J* = 337.7 Hz), 116.8, 103.7. IR (KBr): 3420, 1617, 1595, 1565, 1508, 1463, 1437, 1396, 1384, 1347, 1253, 1211, 1142, 1123, 1098, 1055, 1029, 982, 966, 951, 928, 866, 824, 769, 752, 737, 728 cm⁻¹. HRMS-ESI (*m/z*) calcd. for C₁₁H₆F₃OSe ([M-H]⁻): 290.9541; found: 290.9555.



(8*R*,9*S*,13*S*,14*S*,17*S*)-13-Methyl-2,4-bis((trifluoromethyl)selanyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (**2ak**). White solid (32.8 mg, 29% yield), petroleum ether/ethyl acetate = 10:1 (v/v) as eluents for column chromatography. M.p.: 72-74 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.76 (s, 1H), 6.81 (s, 1H), 3.75 (t, *J* = 8.5 Hz, 1H), 3.21 (m, 1H), 2.95 (m, 1H), 2.31

(m, 1H), 2.21 (m, 1H), 2.14 (m, 1H), 2.02-1.95 (m, 2H), 1.72 (m, 1H), 1.54-1.49 (m, 2H), 1.41-1.30 (m, 5H), 1.19 (m, 1H), 0.80 (s, 3H); ^{19}F NMR (471 MHz, CDCl_3) δ -34.1 (s, 3F), -35.5 (s, 3F); ^{13}C NMR (126 MHz, CDCl_3) δ 156.3, 147.2, 139.5, 135.5, 122.3 (q, $J = 334.9$ Hz), 122.0 (q, $J = 336.5$ Hz), 111.4 (q, $J = 0.5$ Hz), 106.5 (q, $J = 1.0$ Hz), 81.7, 50.0, 44.0, 43.2, 37.8, 36.5, 32.3, 30.6, 27.1, 26.4, 23.0, 11.0. IR (KBr): 3554, 3420, 2931, 2868, 1575, 1533, 1449, 1421, 1395, 1333, 1279, 1265, 1250, 1131, 1093, 1012, 988, 971, 948, 926, 906, 858, 738 cm^{-1} . HRMS-ESI (m/z) calcd. for $\text{C}_{20}\text{H}_{21}\text{F}_6\text{O}_2\text{Se}_2$ ($[\text{M}-\text{H}]^-$): 566.9782, found: 566.9774.

4. The scale-up synthesis of 2

4.1. Procedure for a large scale synthesis of 2a

Under a nitrogen atmosphere, a round-bottom flask was charged with $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1.155 g, 5.2 mmol), CH_3CN (20 mL), and *m*-CPBA (1.056 g, 85%, 5.2 mmol) at room temperature and cooled to 0 °C with stirring. Then, a solution of **1a** (0.469 g, 4.0 mmol) in CH_3CN (20 mL) was added slowly. The resulting mixture was reacted at 0 °C for 8 hours and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (8:1, v/v) as eluents to give **2a** (1.048 g, 99%) as a light yellow solid.

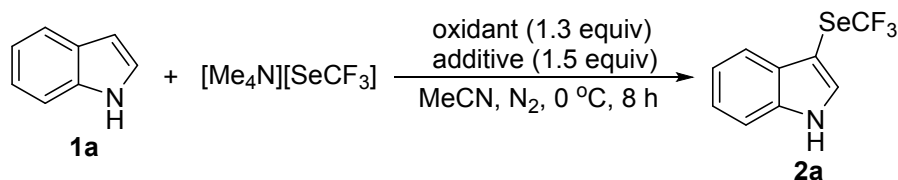
4.2. Procedure for a large scale synthesis of 2v

Under a nitrogen atmosphere, a round-bottom flask was charged with $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (0.577 g, 2.6 mmol), CH_3CN (7.5 mL), and NIS (0.585 g, 2.6 mmol) at room temperature and cooled to 0 °C with stirring. Then, a solution of **1v** (0.262 g, 2.0 mmol) in CH_3CN (7.5 mL) was added slowly. The mixture was reacted at 0 °C for 8 hours and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (8:1, v/v) as eluents to give **2v** (0.529 g, 95%) as a light yellow solid.

5. The control experiments for mechanistic insights

5.1. The standard reactions of 1a, $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and oxidant in the presence of different radical inhibitors.

Table S8



Entry ^a	Oxidant	Additive	Yield (%) ^b
1	<i>m</i> -CPBA	none	>99
2	<i>m</i> -CPBA	TEMPO	98
3	<i>m</i> -CPBA	BHT	>99
4	<i>m</i> -CPBA	1,1-Diphenylethylene	98
5	<i>m</i> -CPBA	Diallyl-PTSA	>99
6	<i>m</i> -CPBA	1,3-dinitrobenzene	93
7	<i>m</i> -CPBA	1,4-dinitrobenzene	95
8 ^c	<i>m</i> -CPBA	none	95
9 ^{c,d}	<i>m</i> -CPBA	none	99
10	NIS	none	99
11	NIS	TEMPO	92
12	NIS	BHT	36
13	NIS	1,1-Diphenylethylene	95
14	NIS	Diallyl-PTSA	84
15	NIS	1,3-dinitrobenzene	94
16	NIS	1,4-dinitrobenzene	89
17 ^c	NIS	none	72
18 ^{c,d}	NIS	none	>99

^a Reaction conditions: To a mixture of oxidant (0.26 mmol), $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (0.26 mmol), and additive (0.3 mmol) in CH_3CN (1 mL) was added slowly a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N_2 for 8 hours. Diallyl-PTSA: *N,N*-diallyl-4-methylbenzenesulfonamide. ^b Yields were determined by HPLC using **2a** as an external standard ($t_{\text{R}} = 4.50$ min, $\lambda = 268$ nm, methanol/water = 90:10 (v/v)). ^c The reaction was run in the darkness. ^d

Reaction conditions: A solution of oxidant (0.26 mmol) in CH_3CN (1 mL) was added slowly to a mixture of **1a** (0.2 mmol), $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (0.26 mmol), and additive (0.3 mmol) in CH_3CN (1 mL) at 0 °C. The reaction was maintained at 0 °C under N_2 for 8 hours.

Figure 1. The ^{19}F NMR analysis of the reaction mixture (entry 1, Table S8, PhOCF_3 (32.0 mg, 0.198 mmol) was used as an internal standard)

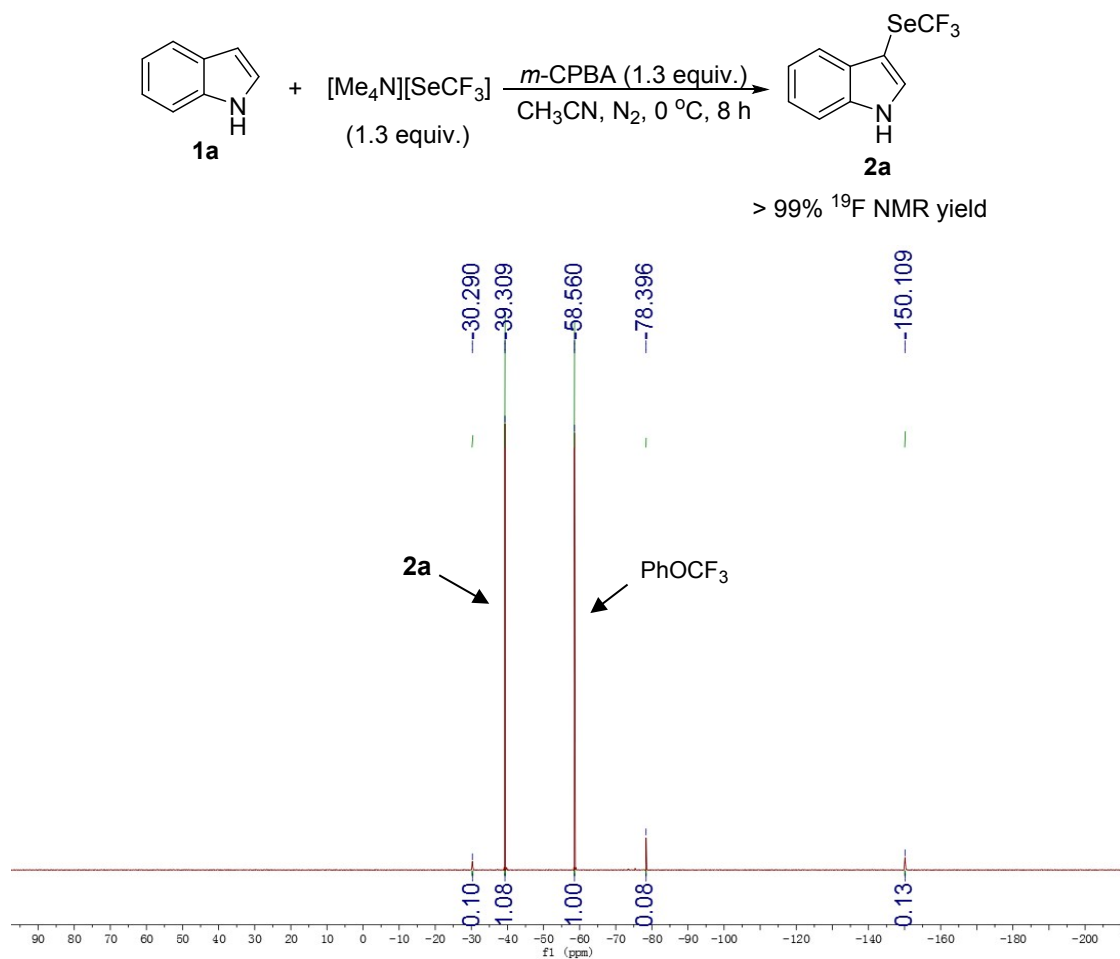
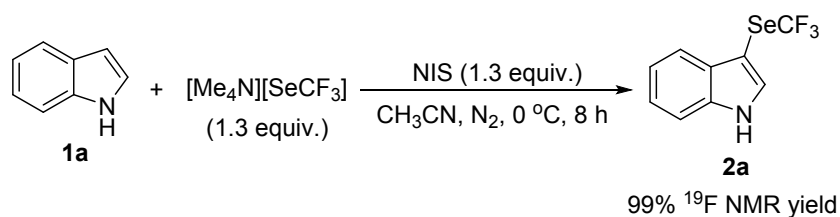


Figure 2. The ^{19}F NMR analysis of the reaction mixture (entry 10, Table S8, PhOCF_3 (33.1 mg, 0.204 mmol) was used as an internal standard)



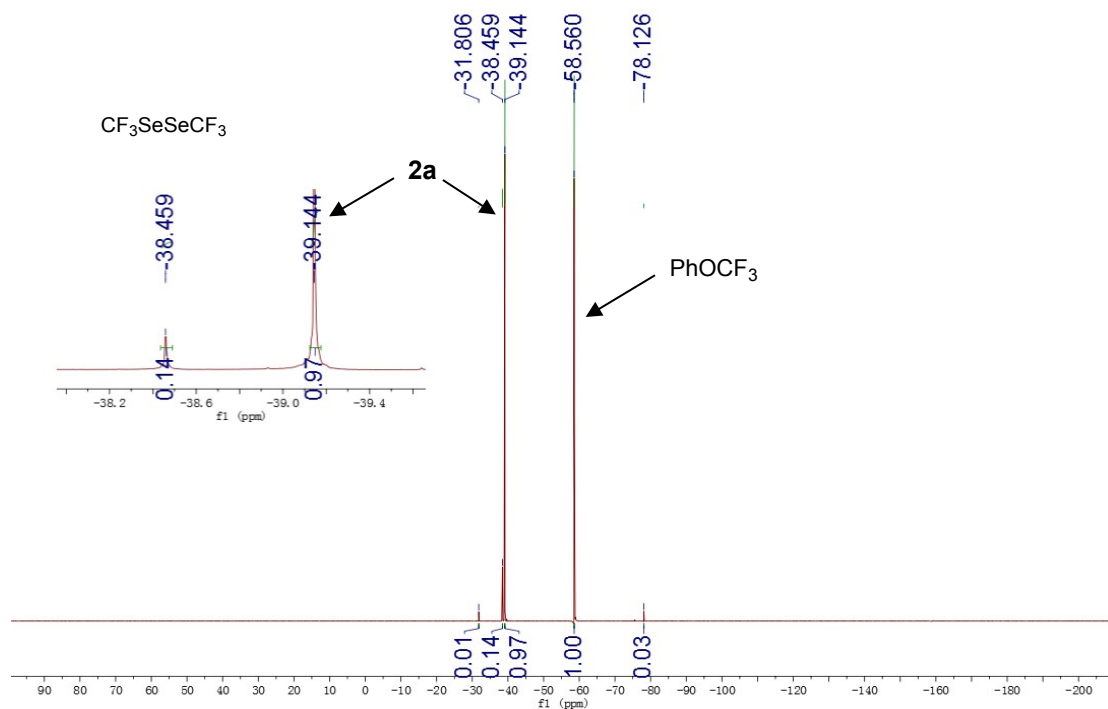
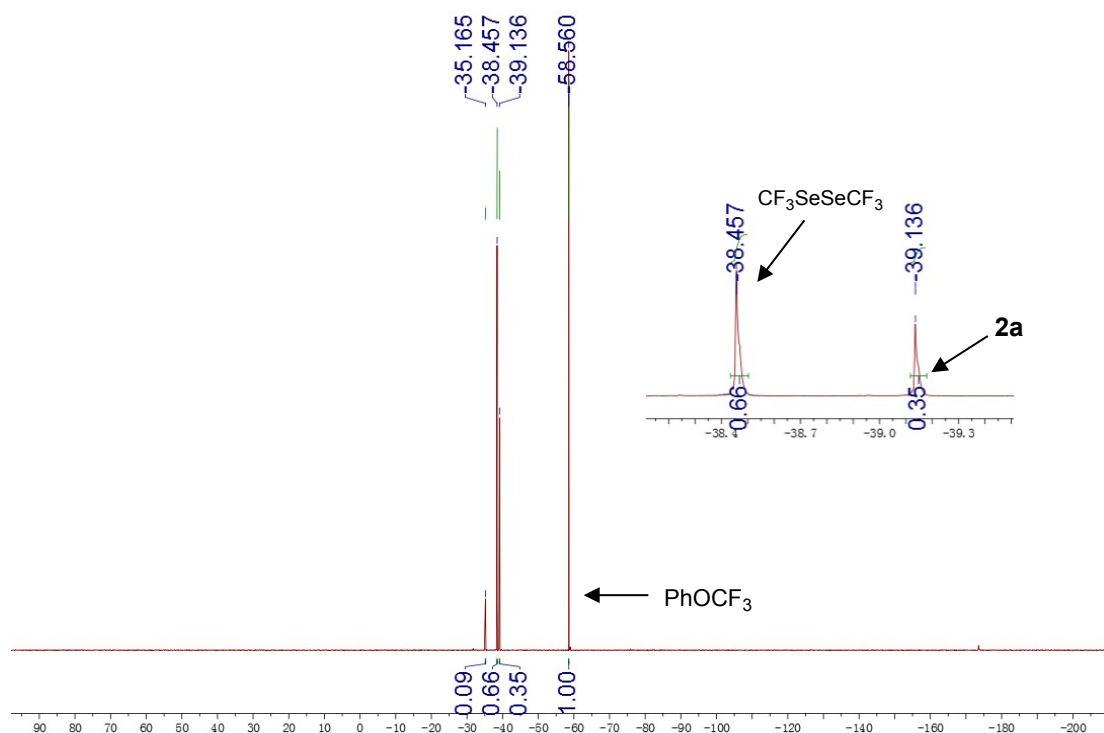
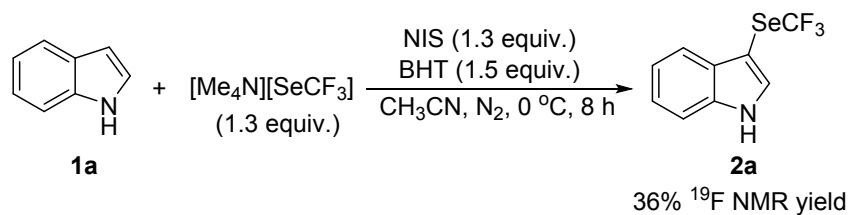
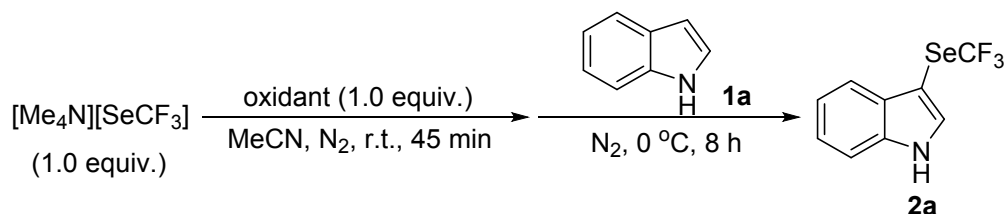


Figure 3. The ^{19}F NMR analysis of the reaction mixture (entry 12, Table S8, PhOCF_3 (33.2 mg, 0.205 mmol) was used as an internal standard)



5.2. Trifluoromethylselenolation of 1a by a mixture of [Me₄N][SeCF₃] and an oxidant which was already reacted at room temperature for 45 minutes.

Table S9



Entry ^a	oxidant	Yield (2a , %) ^b
1	<i>m</i> -CPBA	75%
2	NIS	92%

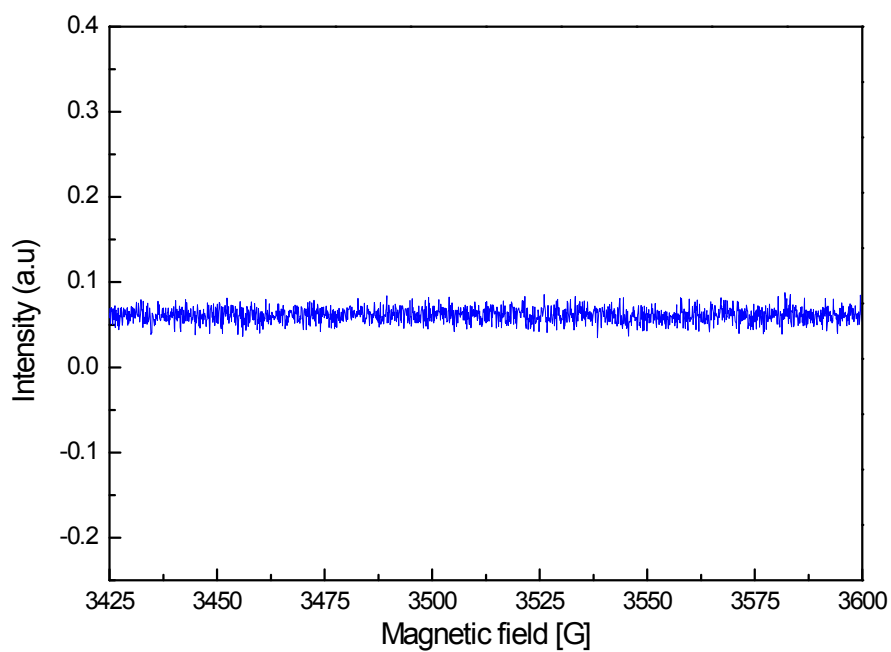
^a Reaction conditions: Oxidant (0.20 mmol) was added to a solution of [Me₄N][SeCF₃] (0.20 mmol) in CH₃CN (1 mL) and kept stirring at room temperature for 45 minutes. Then, a solution of **1a** (0.2 mmol) in CH₃CN (1 mL) was added slowly at 0 °C. The mixture was reacted at 0 °C under N₂ for 8 hours. ^b Yields were determined by HPLC using **2a** as an external standard (*t_R* = 4.50 min, λ_{max} = 268 nm, methanol/water = 90:10 (v/v)).

5.3. The EPR analysis of the reaction mixtures of 1a, [Me₄N][SeCF₃] and *m*-CPBA or NIS under the standard conditions.

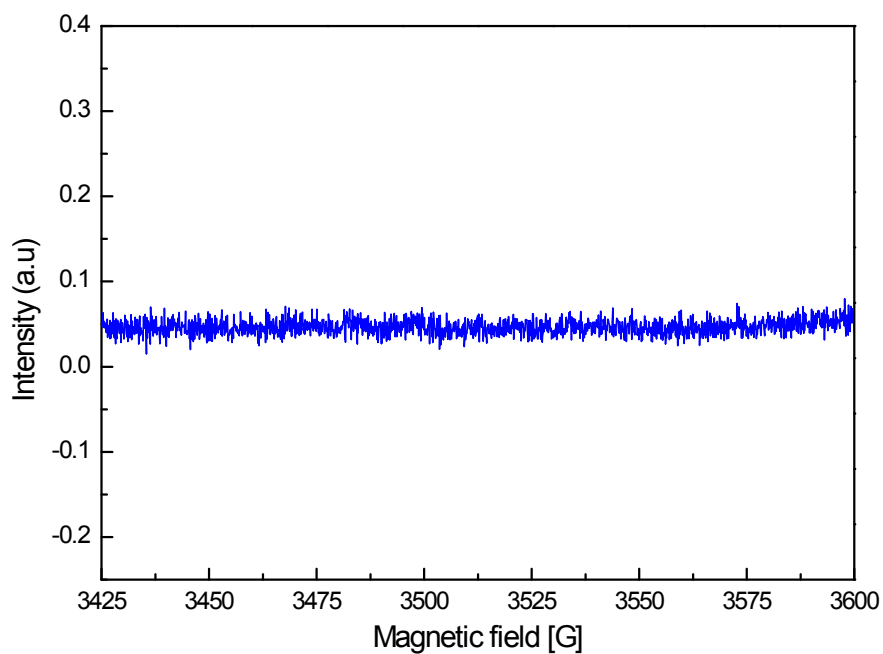
General: EPR experiments were carried out at room temperature using a Bruker EMX spectrometer operating at X-band with 100 kHz modulation frequency. The instrument settings were as follows: microwave power: 0.002 or 2.0 mW; modulation amplitude: 0.6 G; center field set: 3509.85 G; time constant: 0.01 ms; scan time: 30.04 s; number of scans: 5.

Procedure: Under a nitrogen atmosphere, a sealed tube was charged with [Me₄N][SeCF₃] (0.13 mmol, 28.9 mg), **1a** (0.1 mmol, 11.7 mg), PBN (0.2 mmol, 35.4 mg), and CH₃CN (1 mL) at room temperature and cooled to 0 °C with stirring. A solution of oxidant (0.13 mmol) in CH₃CN (0.5 mL) was added slowly. The mixture was reacted at 0 °C for 30 min and then analyzed by EPR spectroscopy.

The EPR spectrum of the reaction mixture of [Me₄N][SeCF₃]/**1a**/PBN and *m*-CPBA:



The EPR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]/\mathbf{1a}/\text{PBN}$ and NIS:



5.4. The ^{19}F NMR analysis of the mixtures of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and an oxidant at room temperature after reacting for 45 minutes.

General procedure: Under a N₂ atmosphere, oxidant (0.1, 0.15 or 0.4 mmol) was added to a solution of [Me₄N][SeCF₃] (0.1, 0.15, 0.2, 0.4 mmol) in CH₃CN (1.0 mL). The mixture was maintained at room temperature for 45 minutes and analyzed by ¹⁹F NMR using PhOCF₃ (24.5 mg, 0.151 mmol) as an internal standard.

Figure 4. The ¹⁹F NMR spectrum of the reaction mixture of [Me₄N][SeCF₃] and *m*-CPBA (4 equiv.):

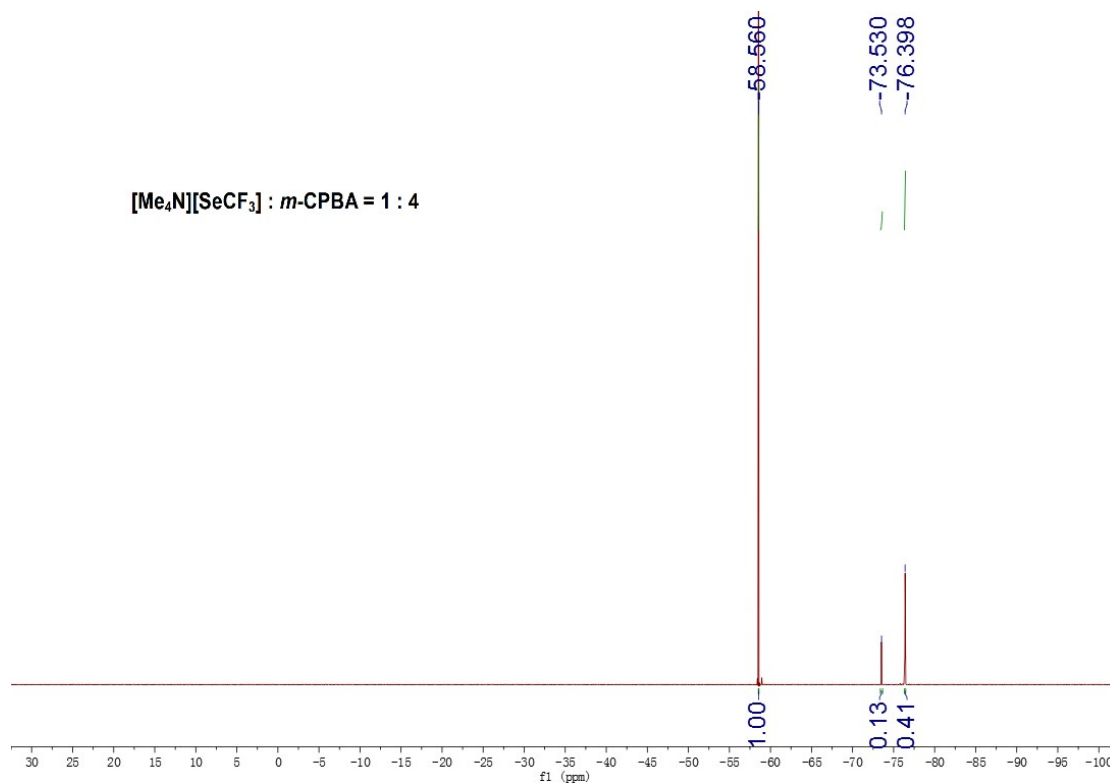


Figure 5. The ¹⁹F NMR spectrum of the reaction mixture of [Me₄N][SeCF₃] and *m*-CPBA (1.5 equiv.):

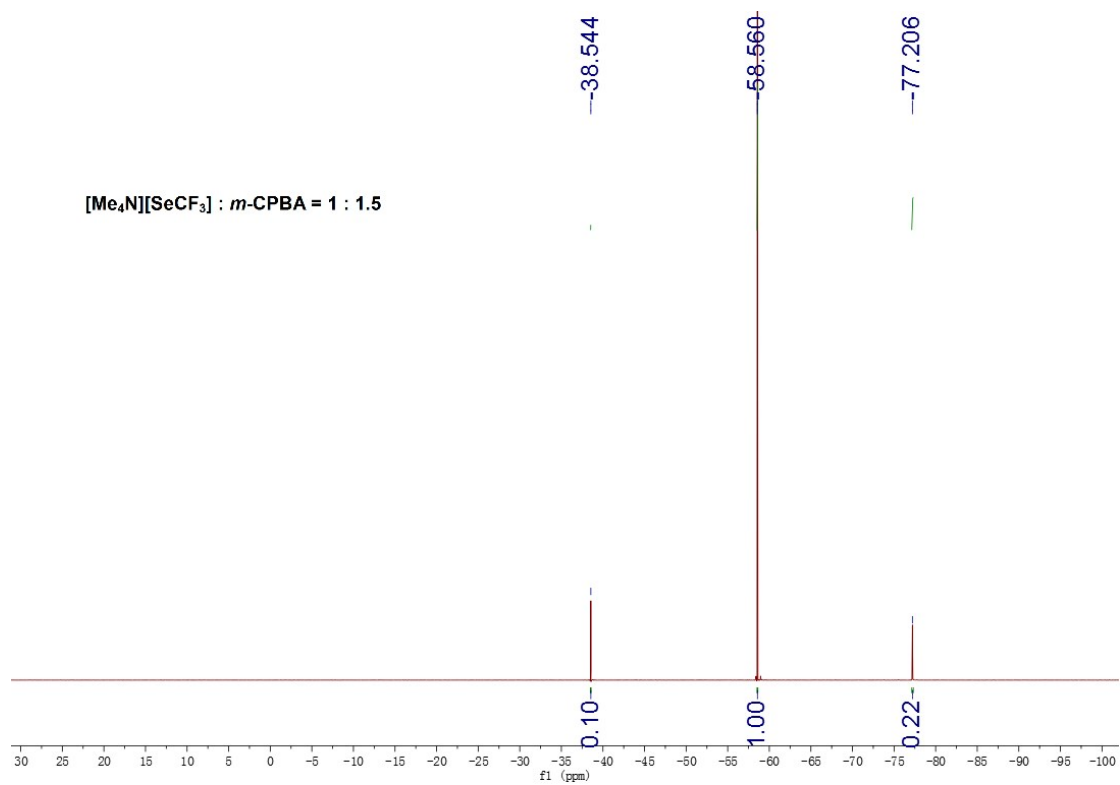


Figure 6. The ¹⁹F NMR spectrum of the reaction mixture of [Me₄N][SeCF₃] and *m*-CPBA (1 equiv.):

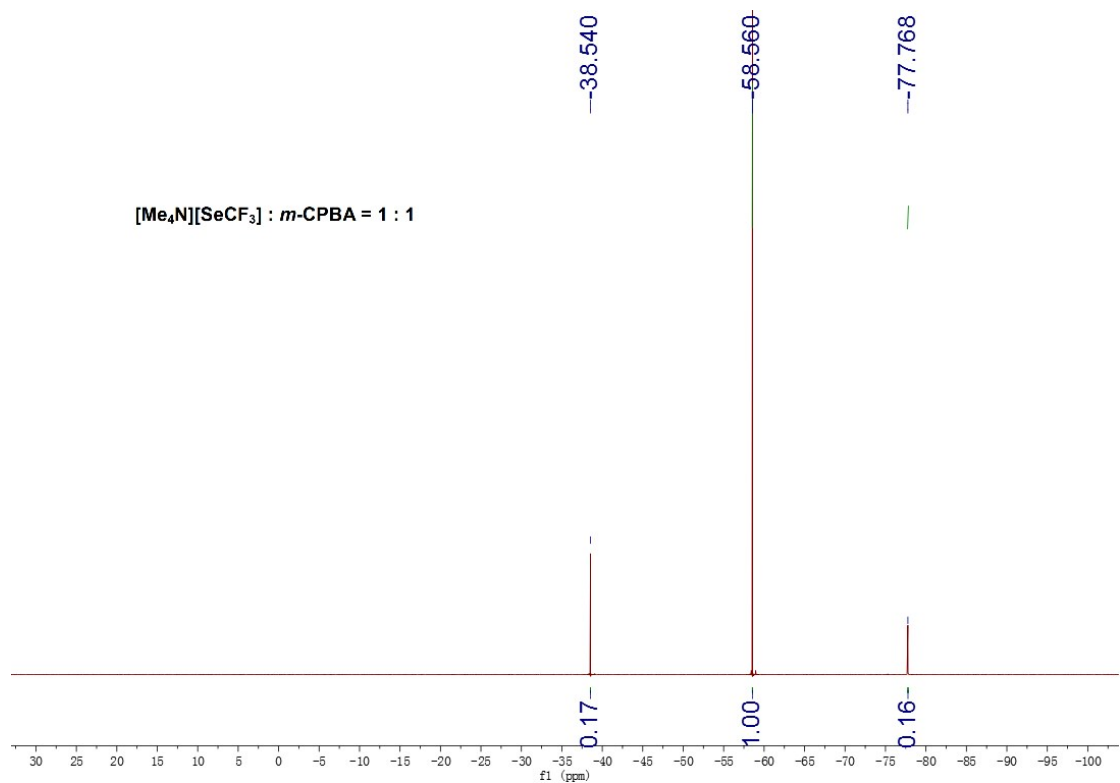


Figure 7. The ¹⁹F NMR spectrum of the reaction mixture of [Me₄N][SeCF₃] (1.5

equiv.) and *m*-CPBA:

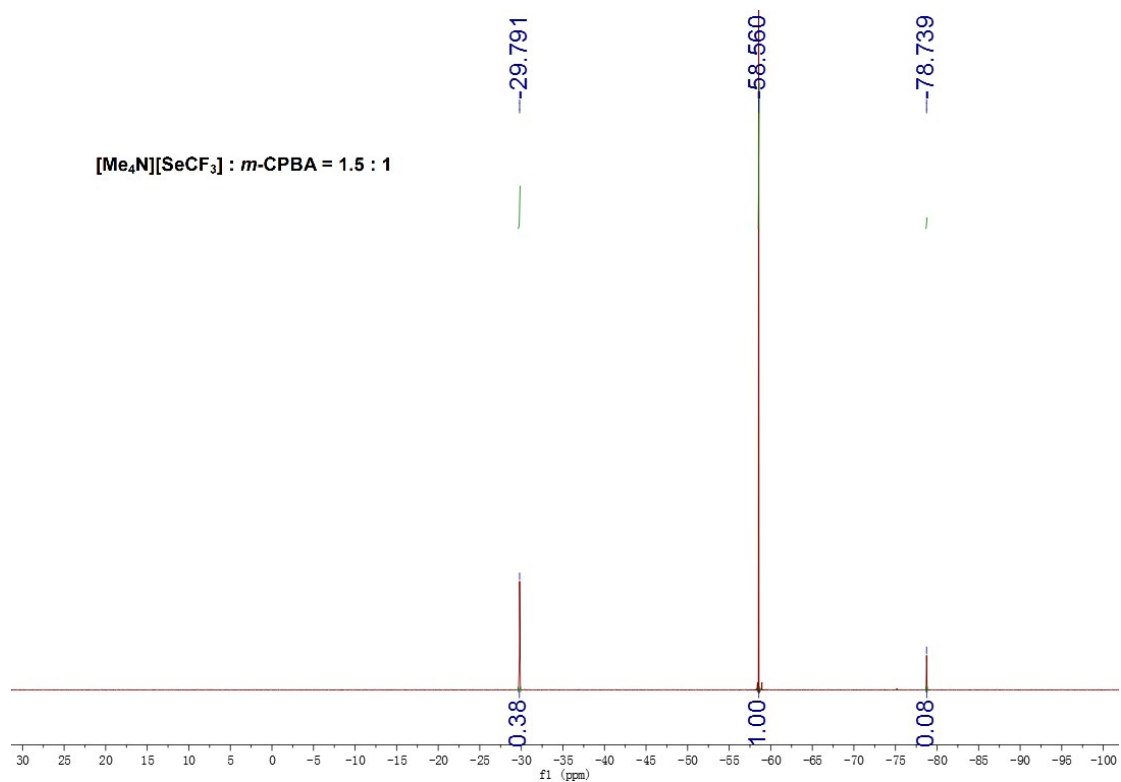


Figure 8. The ¹⁹F NMR spectrum of the reaction mixture of [Me₄N][SeCF₃] (2 equiv.) and *m*-CPBA:

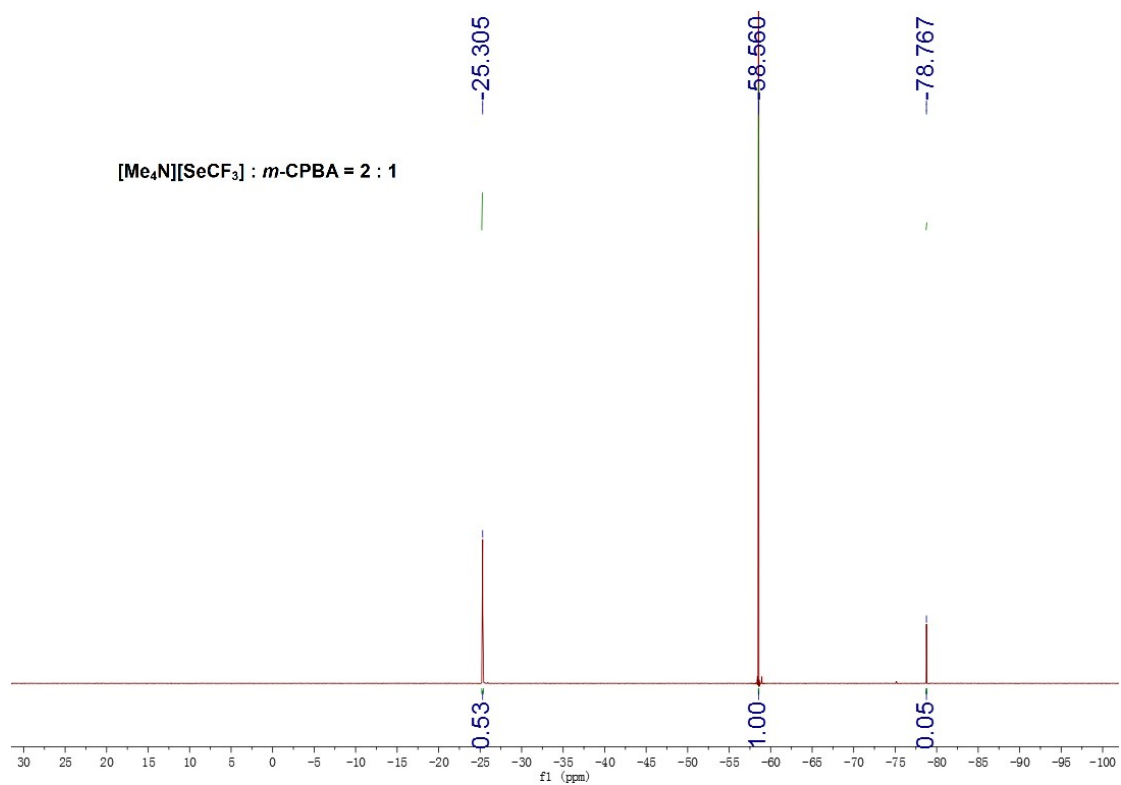
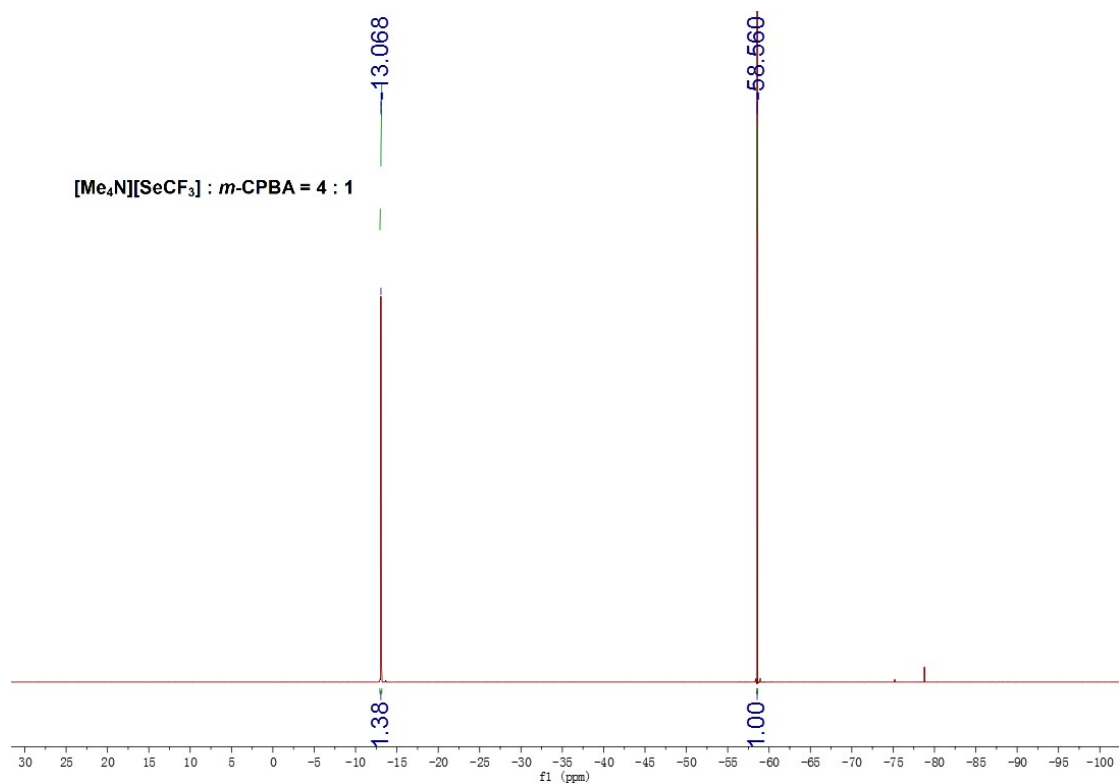


Figure 9. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (4 equiv.) and *m*-CPBA:



The combination of the above spectra (Figures 4-9)

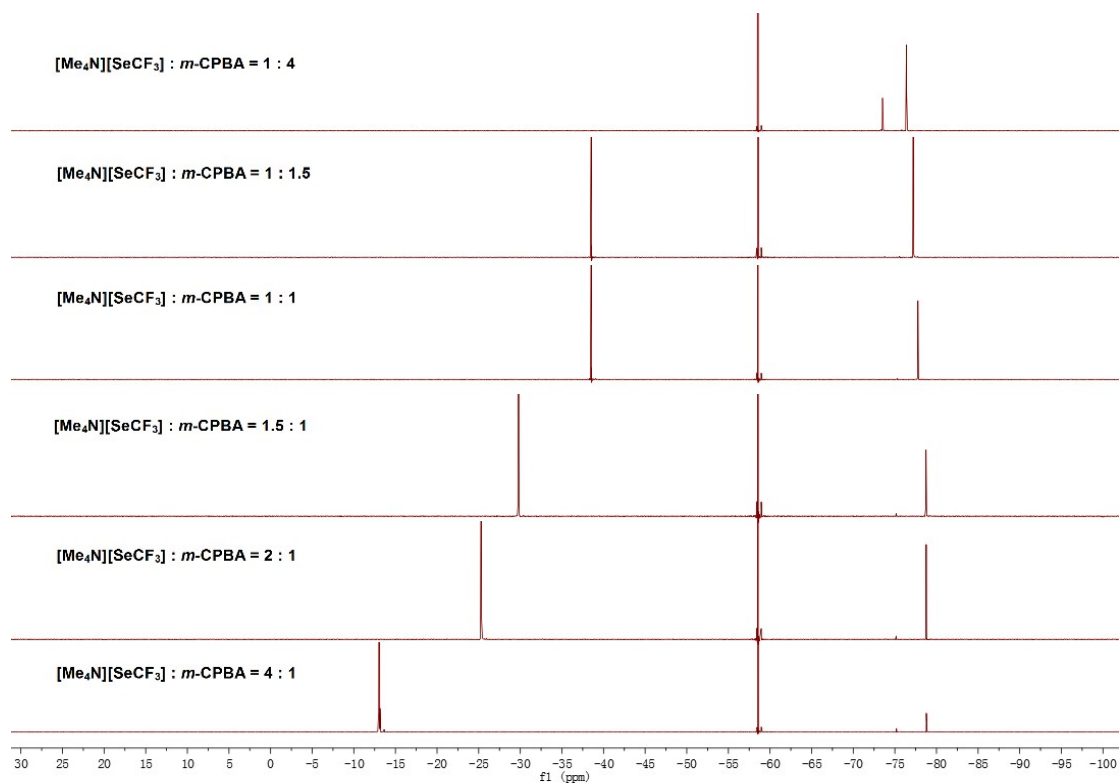


Figure 10. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and NIS (4 equiv.):

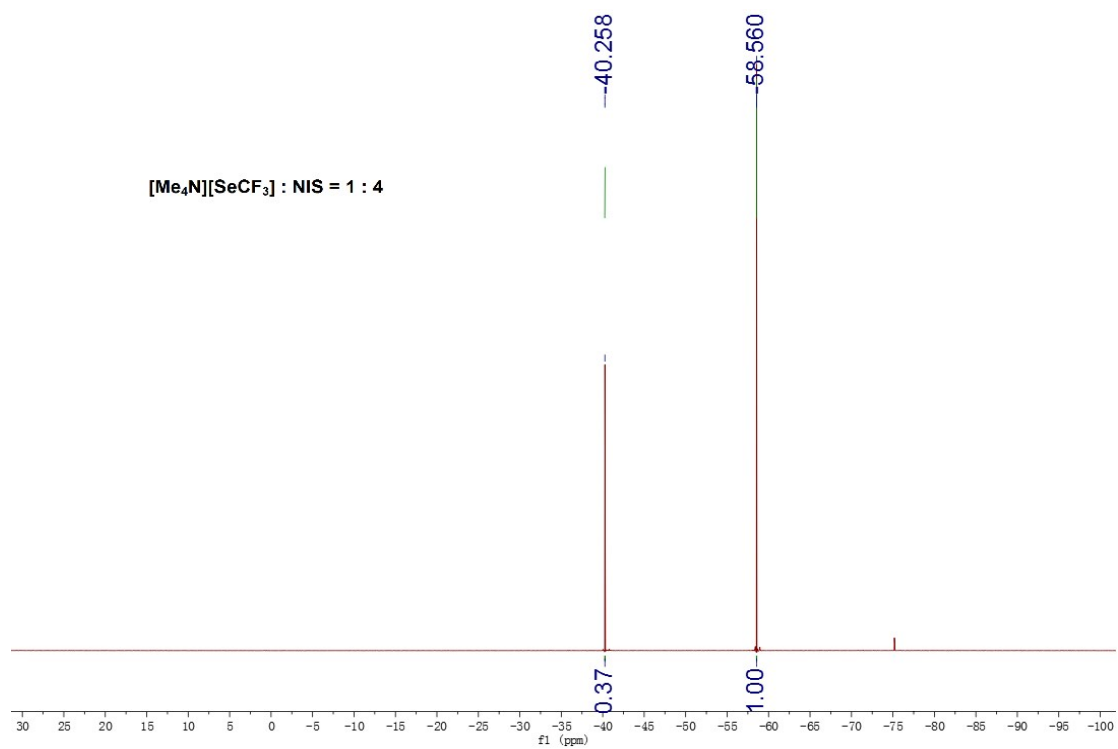


Figure 11. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and NIS (1.5 equiv.):

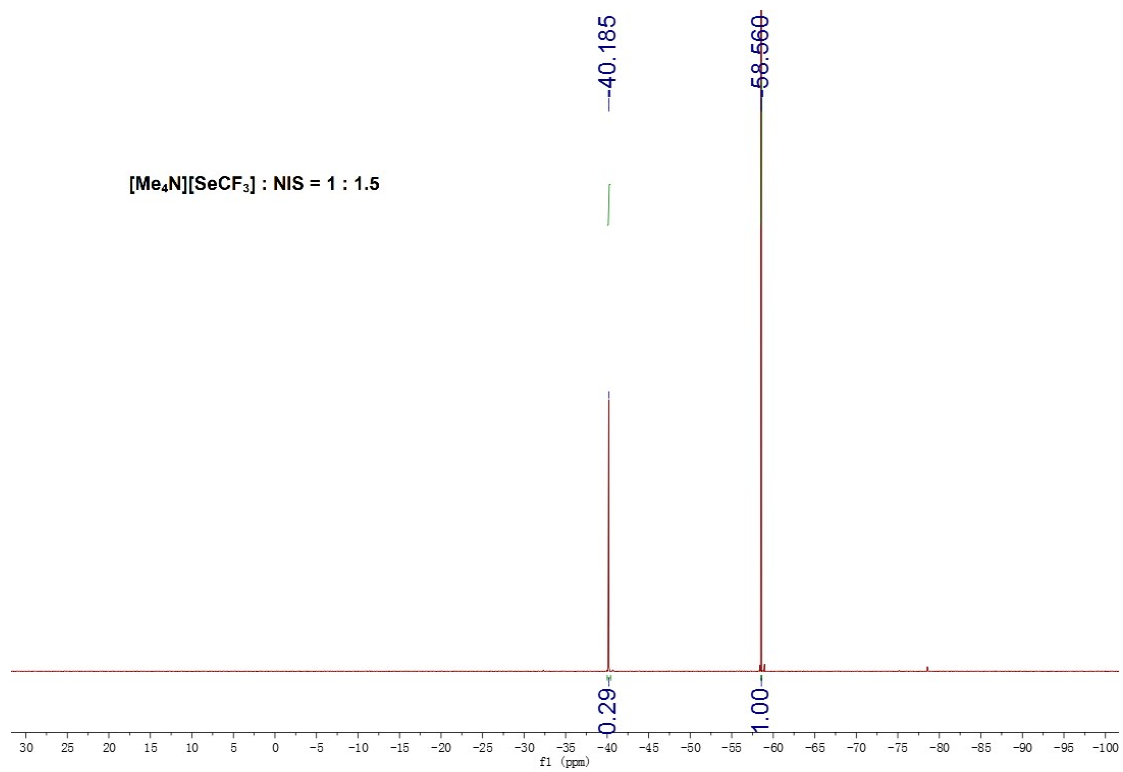


Figure 12. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and NIS (1 equiv.):

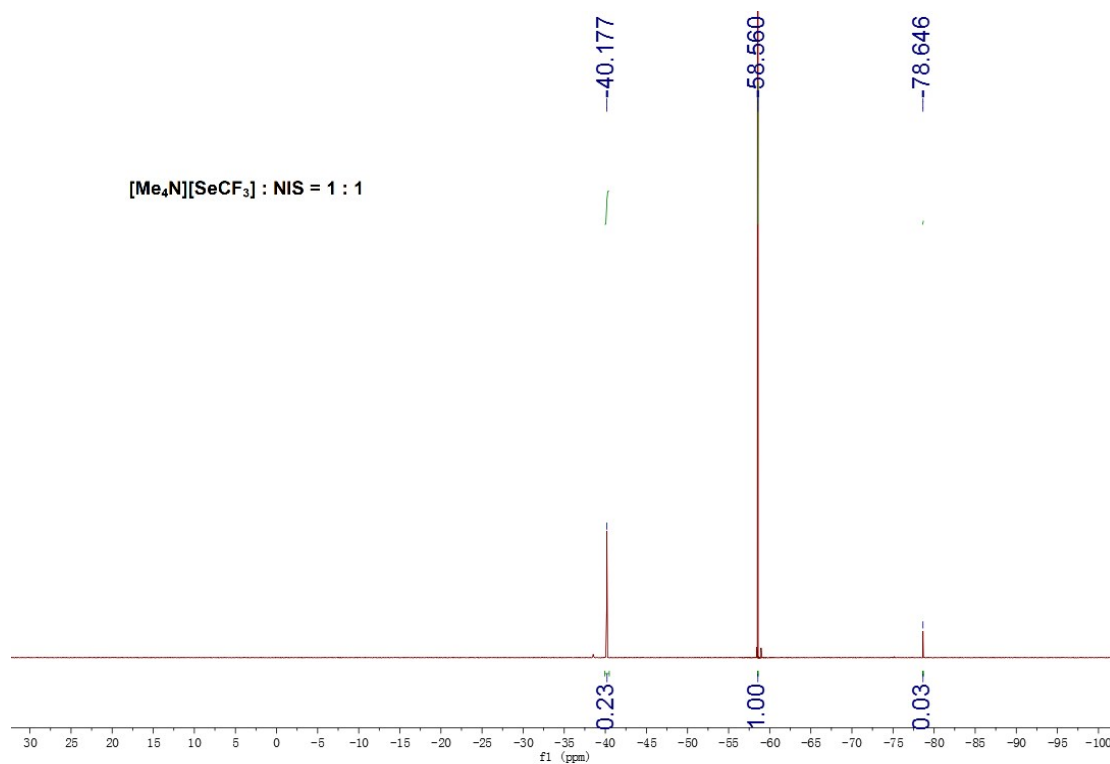


Figure 13. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1.5 equiv.) and NIS:

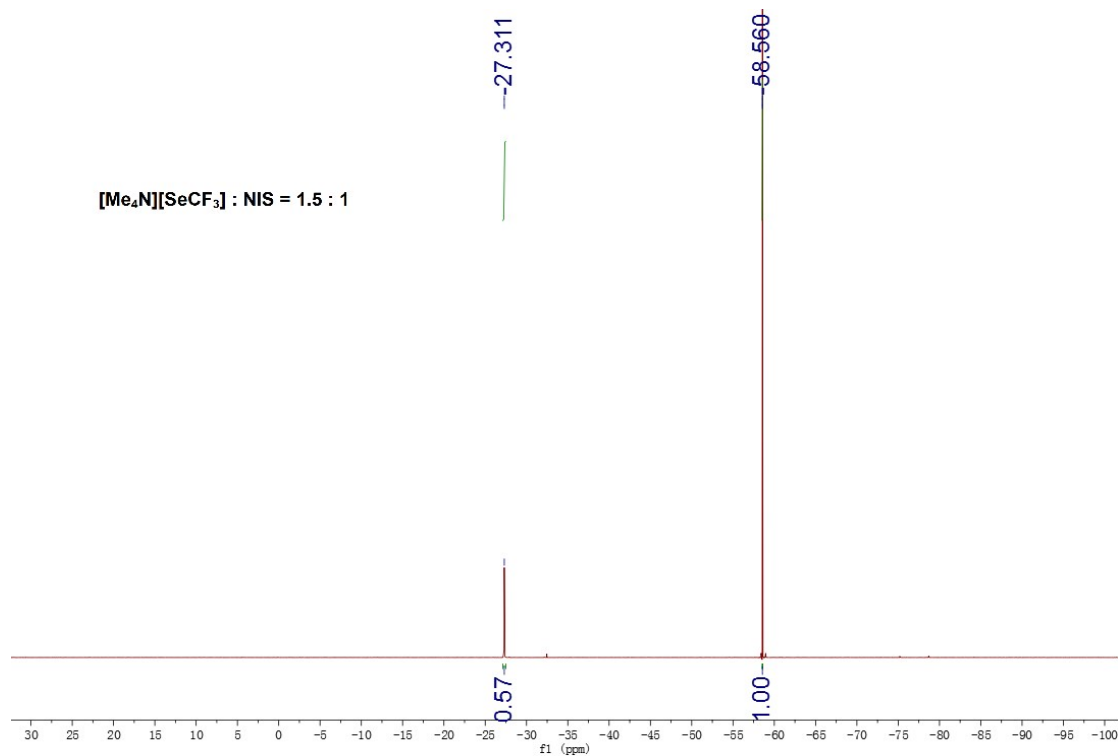


Figure 14. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (2 equiv.) and NIS:

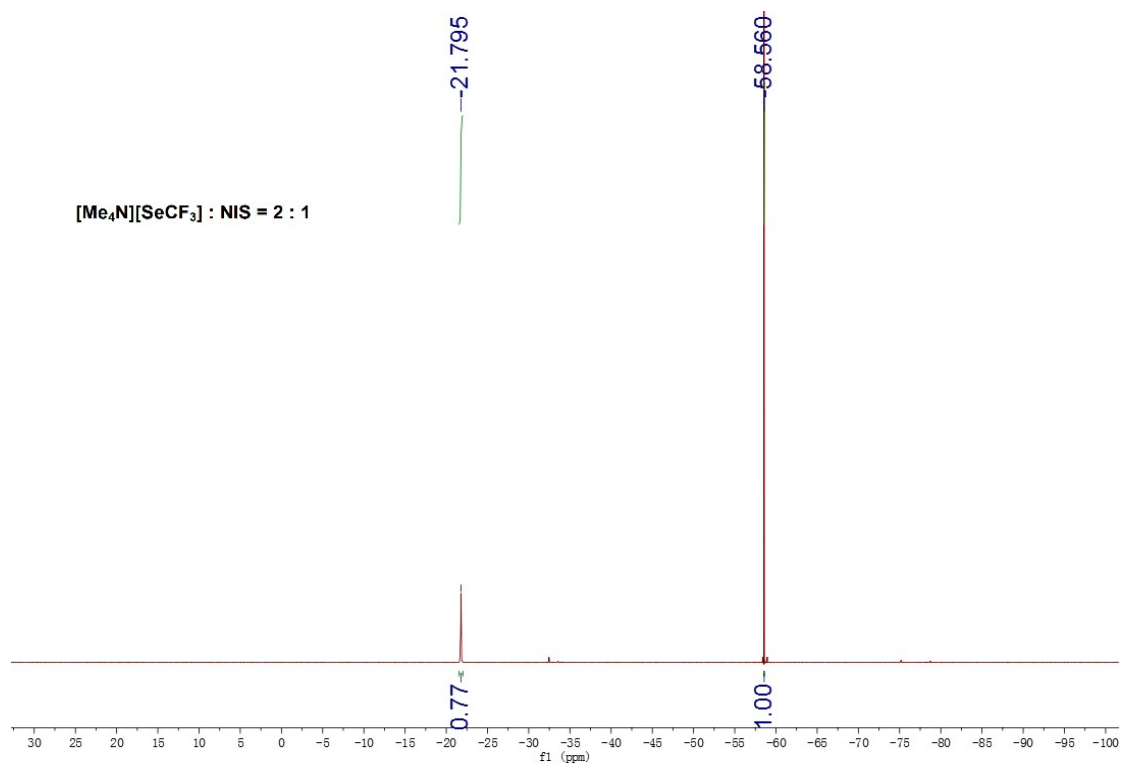
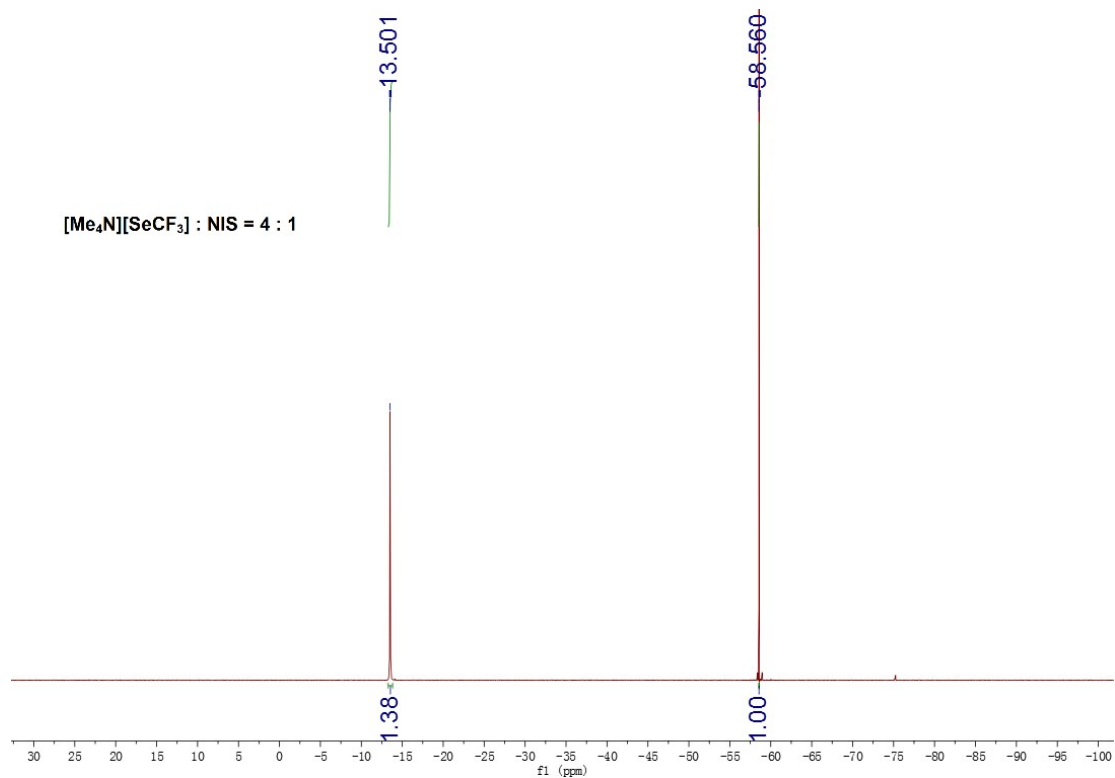


Figure 15. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (4 equiv.) and NIS:



The combination of the above spectra (Figures 10-15)

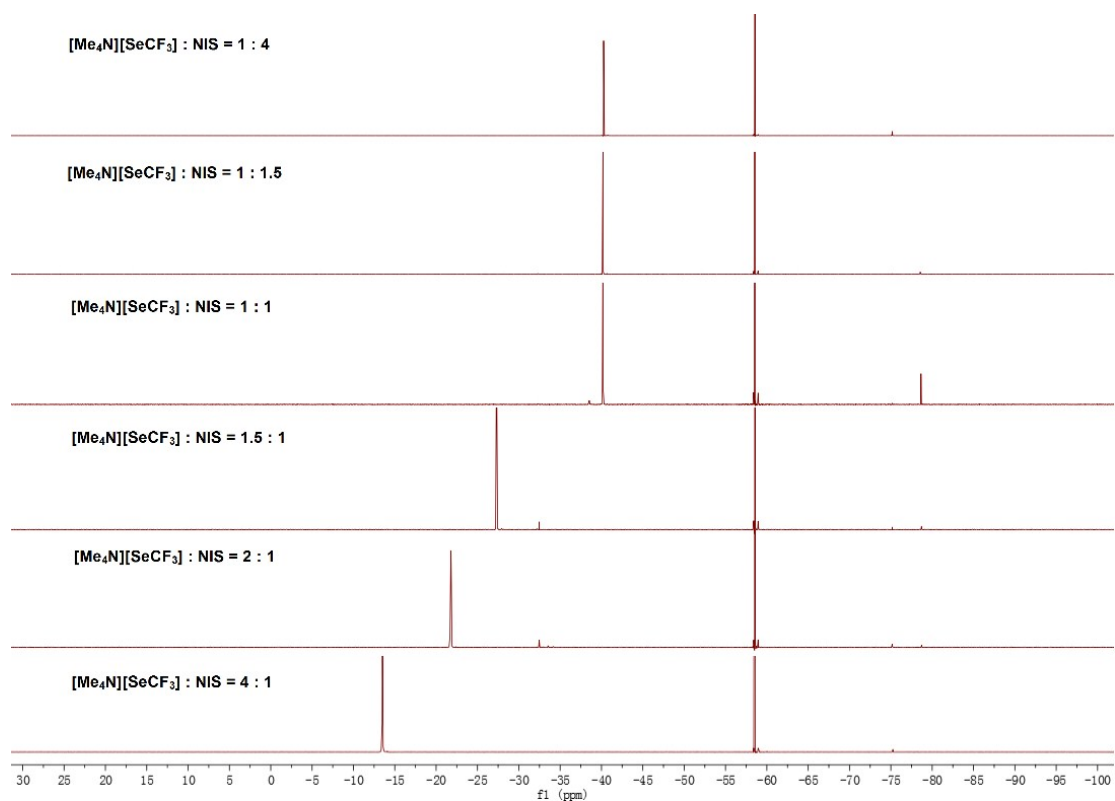


Figure 16. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and DDQ (4 equiv.):

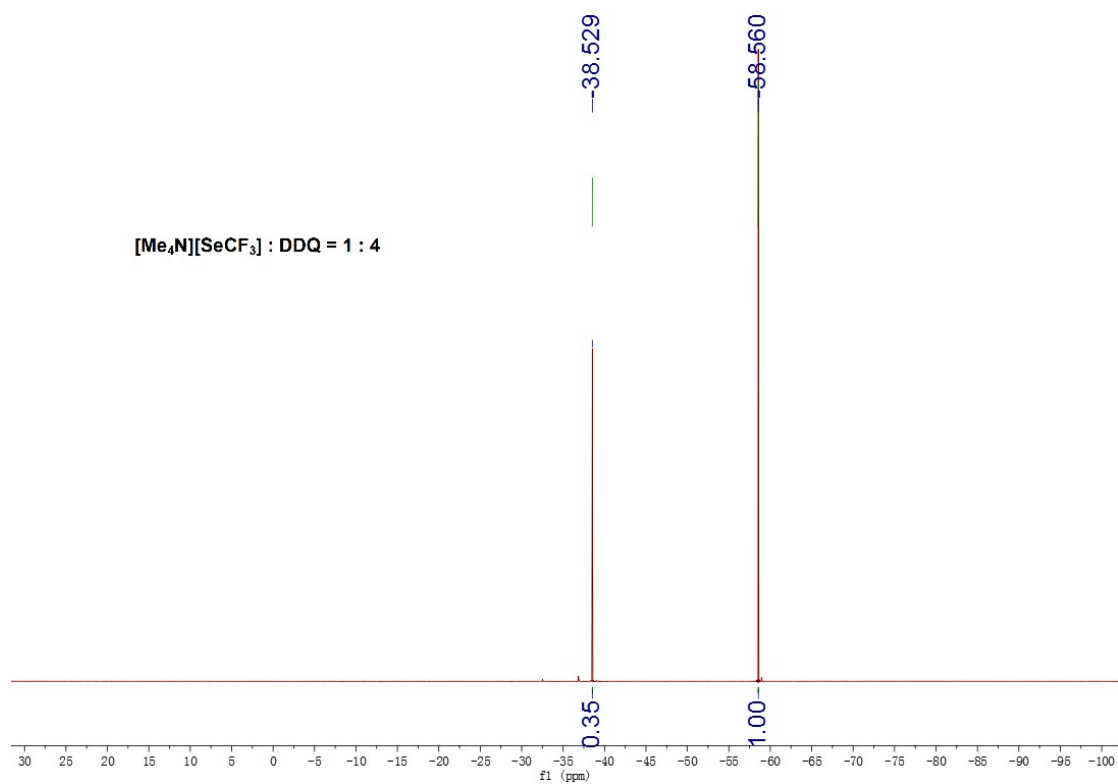


Figure 17. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and DDQ (1.5 equiv.):

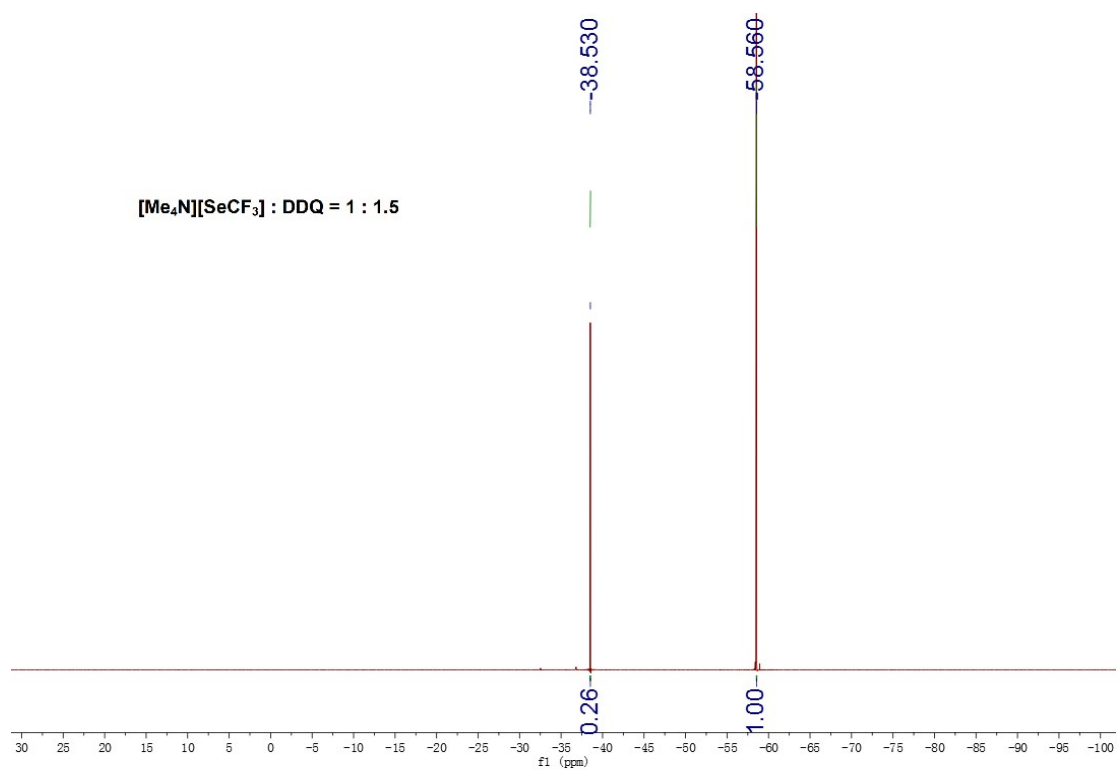


Figure 18. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and DDQ (1 equiv.):

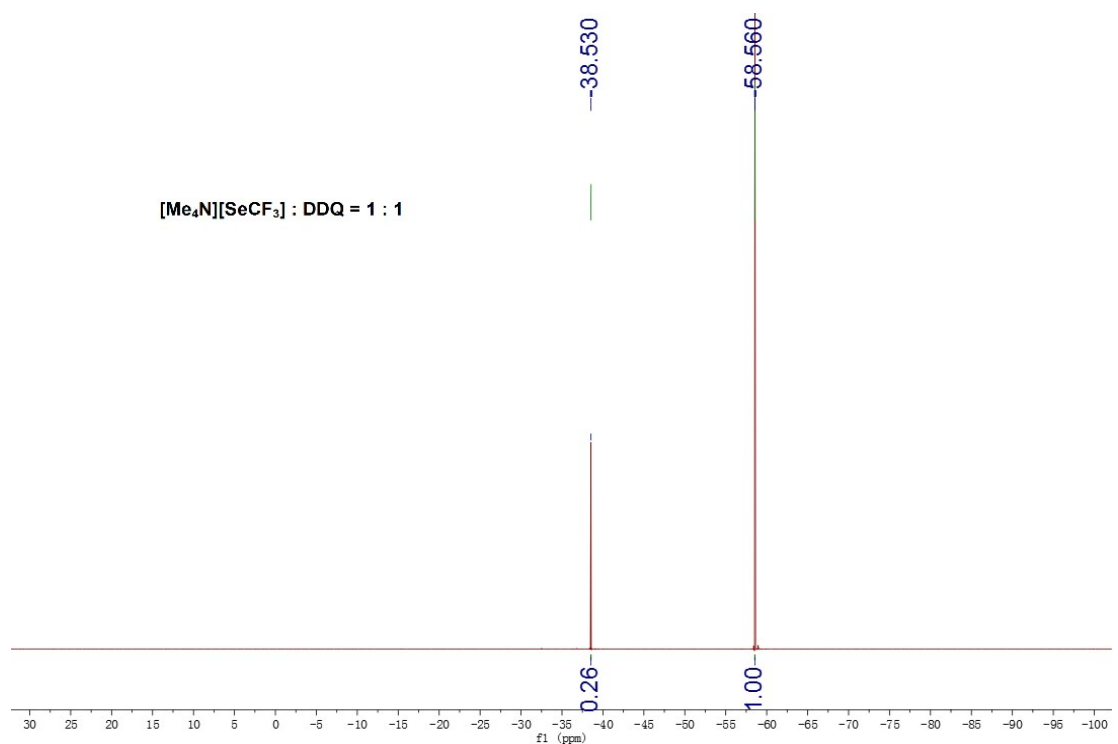


Figure 19. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1.5 equiv.) and DDQ:

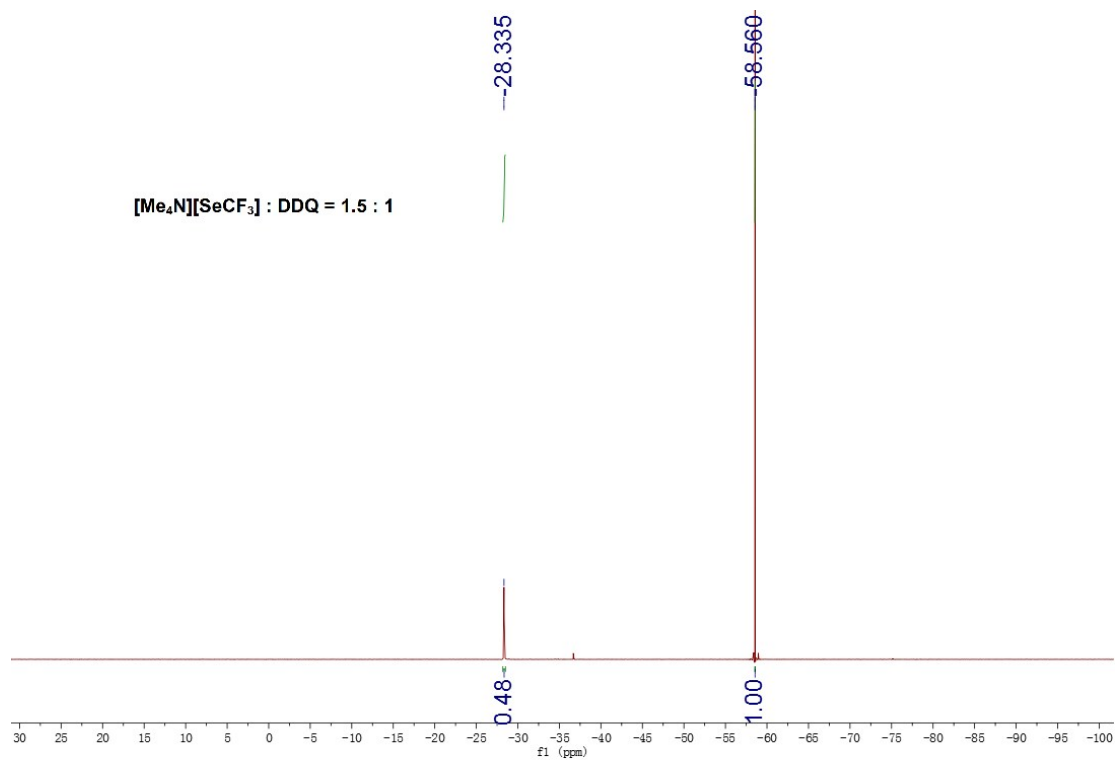


Figure 20. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (2 equiv.) and DDQ:

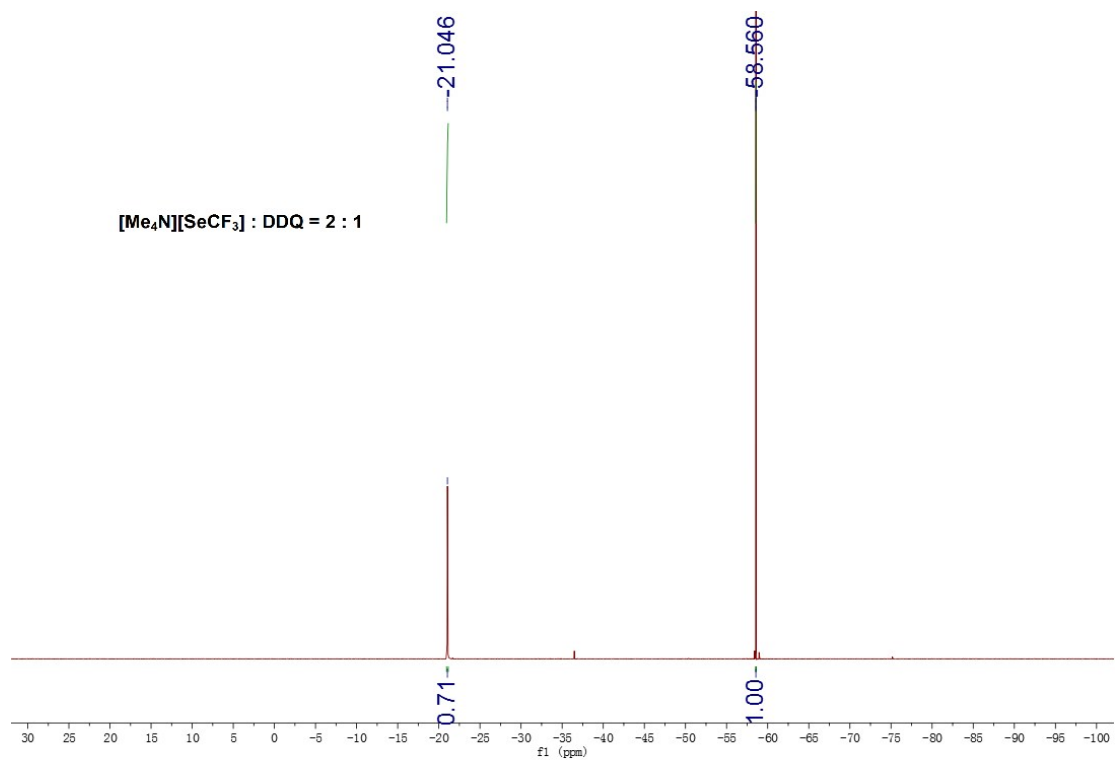
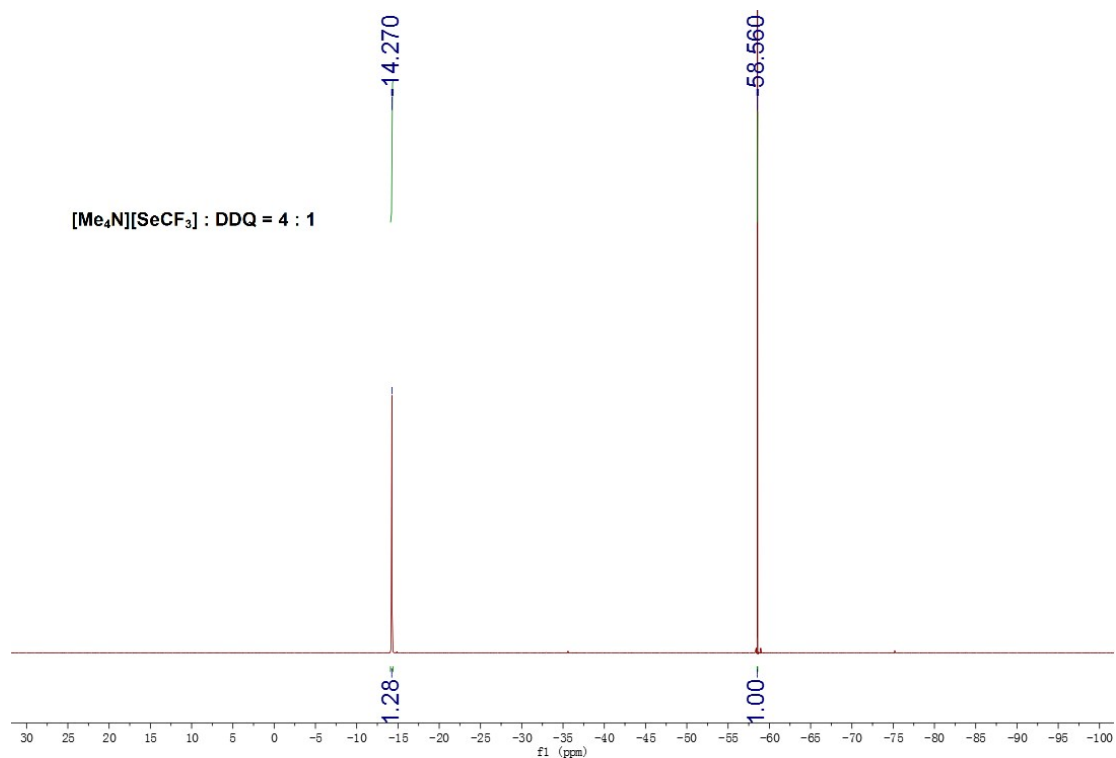


Figure 21. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (4 equiv.) and DDQ:



The combination of the above spectra (**Figures 16-21**)

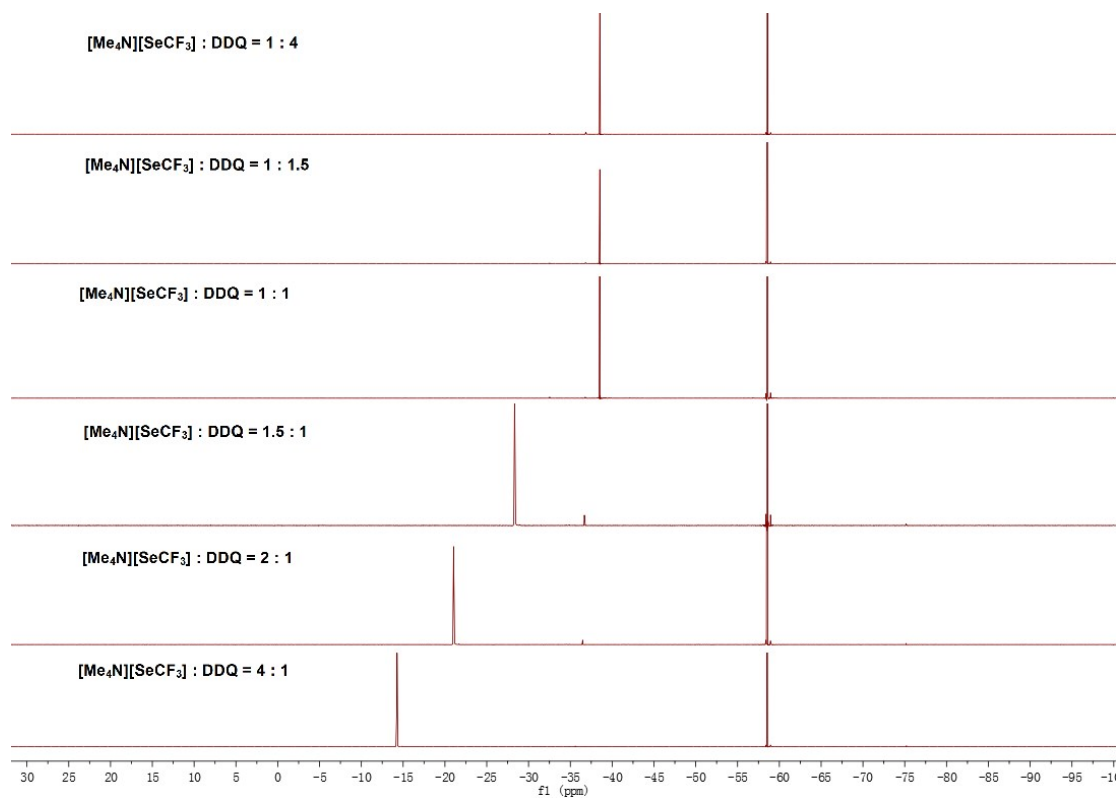


Figure 22. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and $\text{PhI}(\text{OAc})_2$ (4 equiv.):

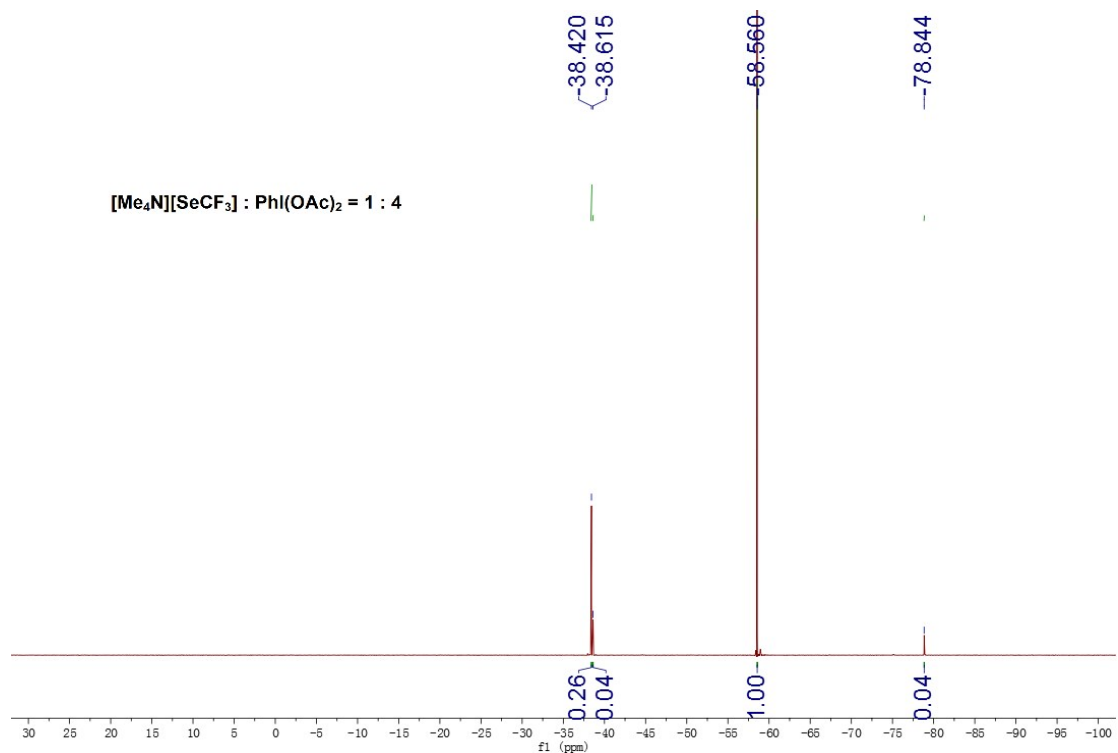


Figure 23. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and $\text{PhI}(\text{OAc})_2$ (1.5 equiv.):

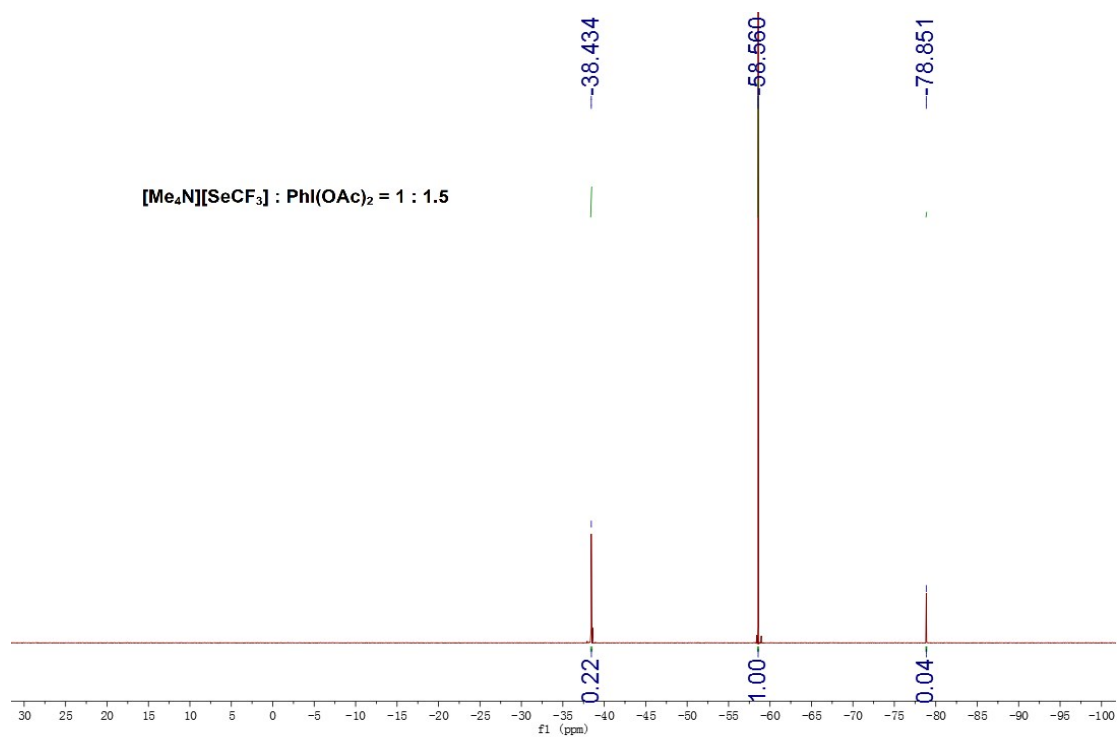


Figure 24. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and $\text{PhI}(\text{OAc})_2$ (1 equiv.):

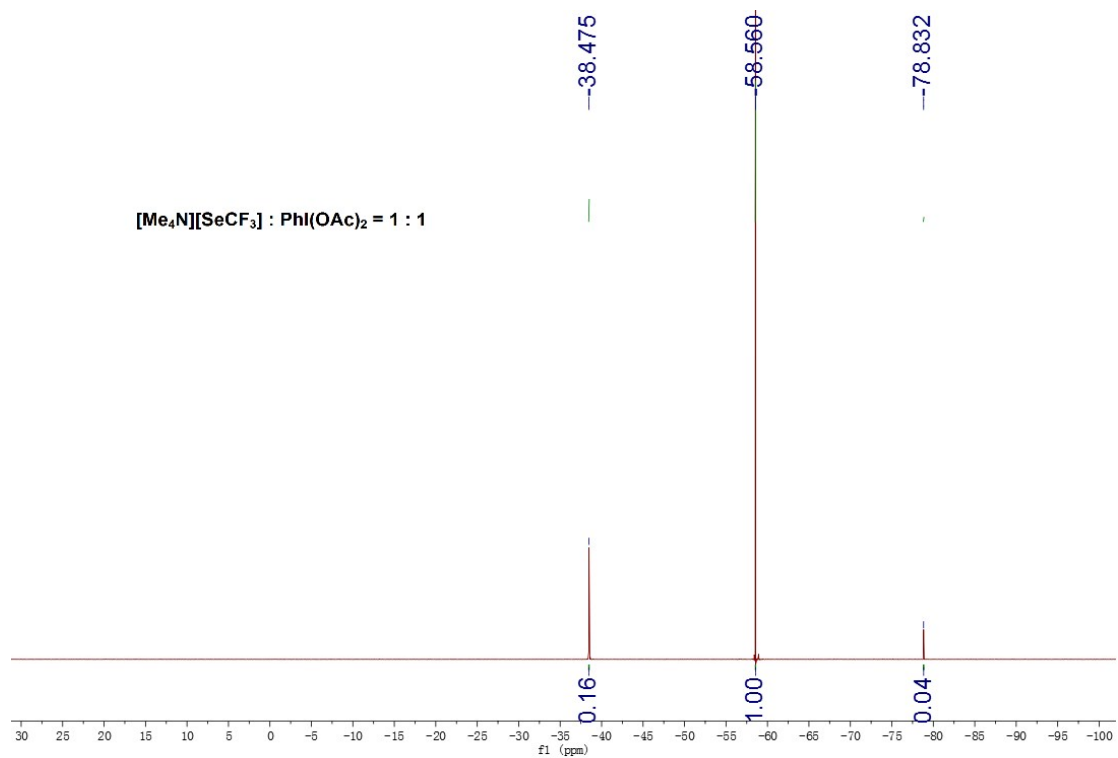


Figure 25. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1.5 equiv.) and $\text{PhI}(\text{OAc})_2$:

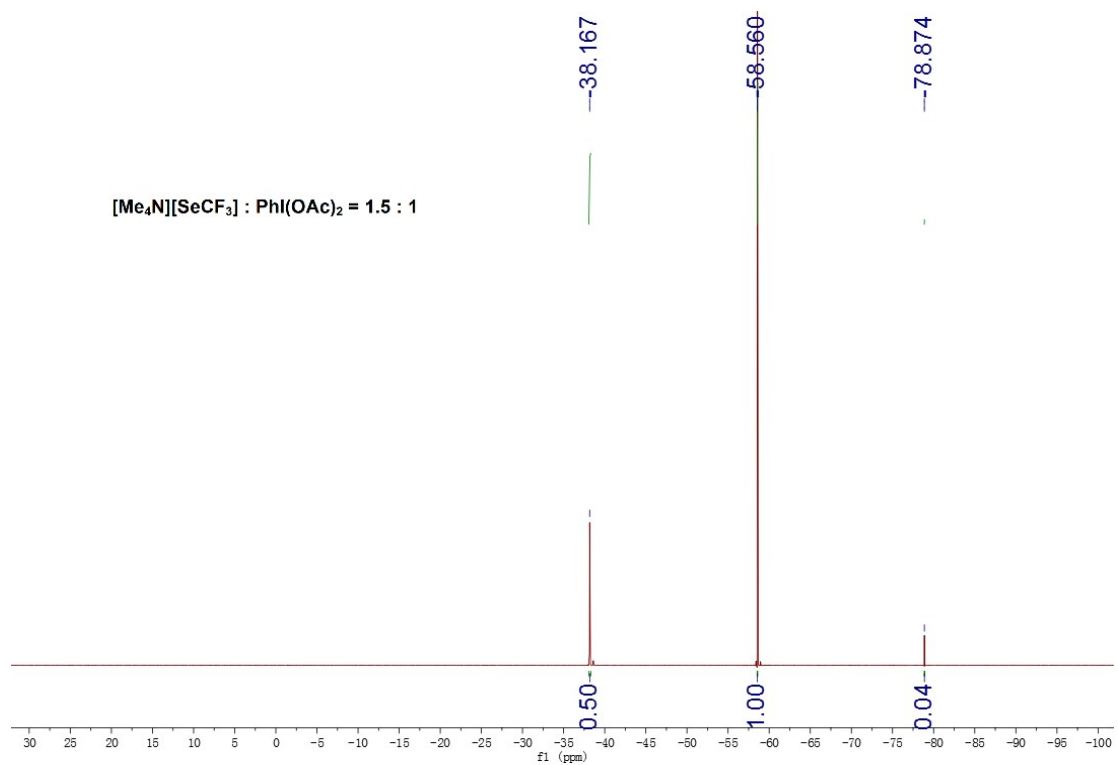


Figure 26. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (2 equiv.) and $\text{PhI}(\text{OAc})_2$:

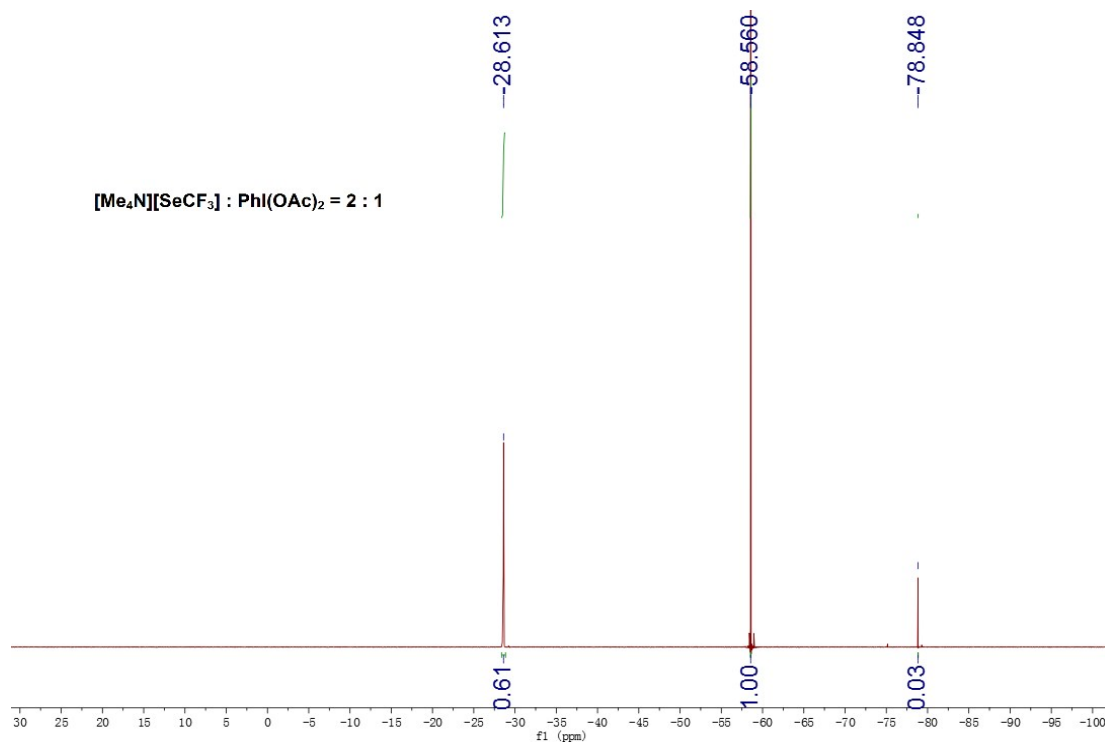
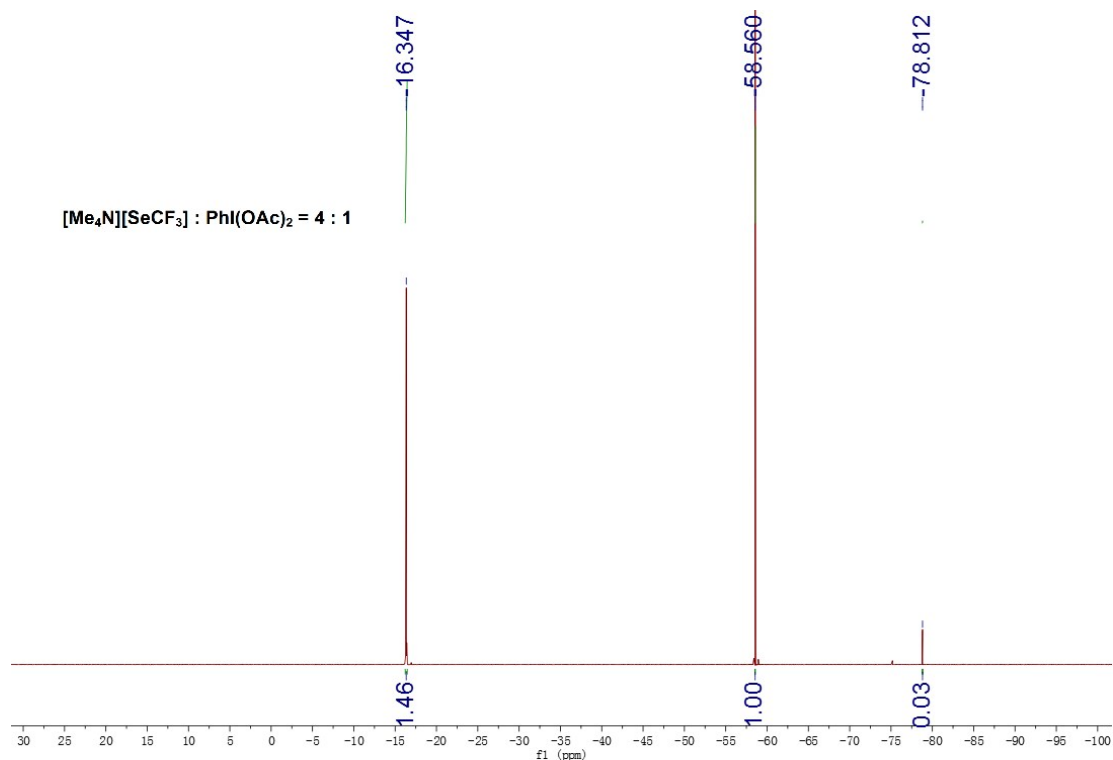
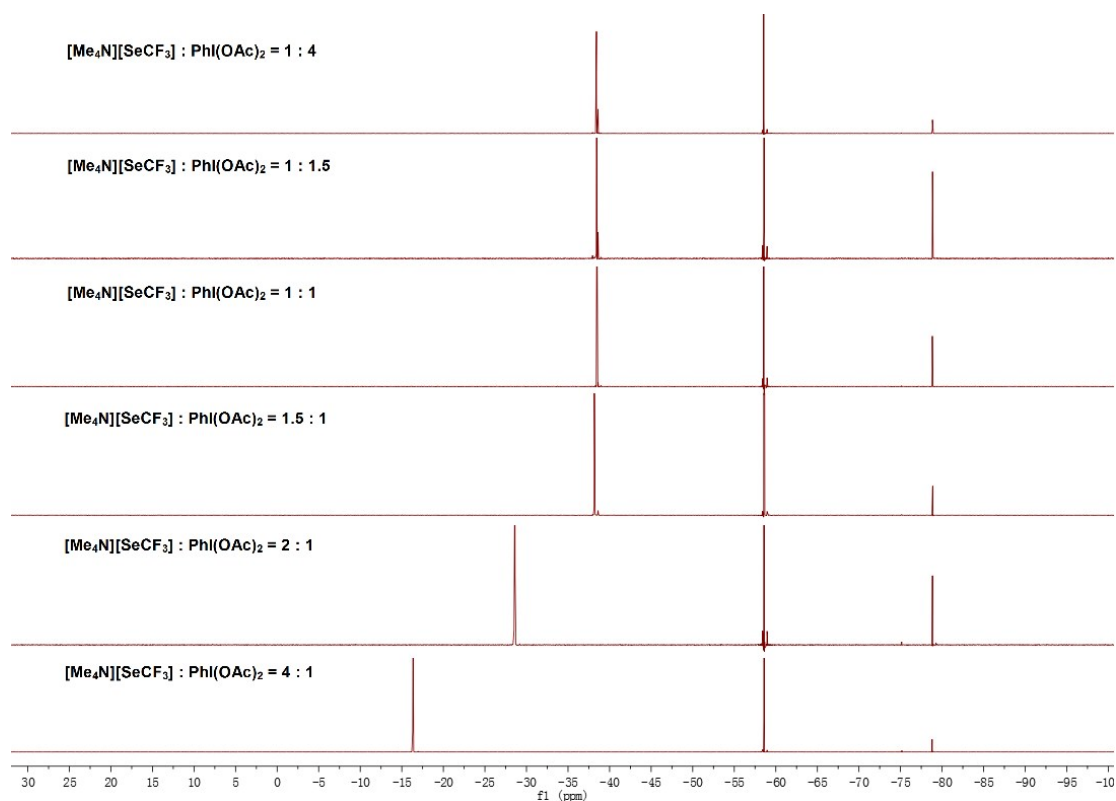


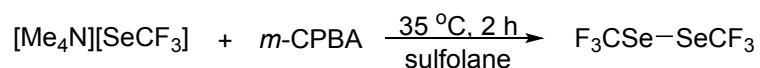
Figure 27. The ^{19}F NMR spectrum of the reaction mixture of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (4 equiv.) and $\text{PhI}(\text{OAc})_2$:



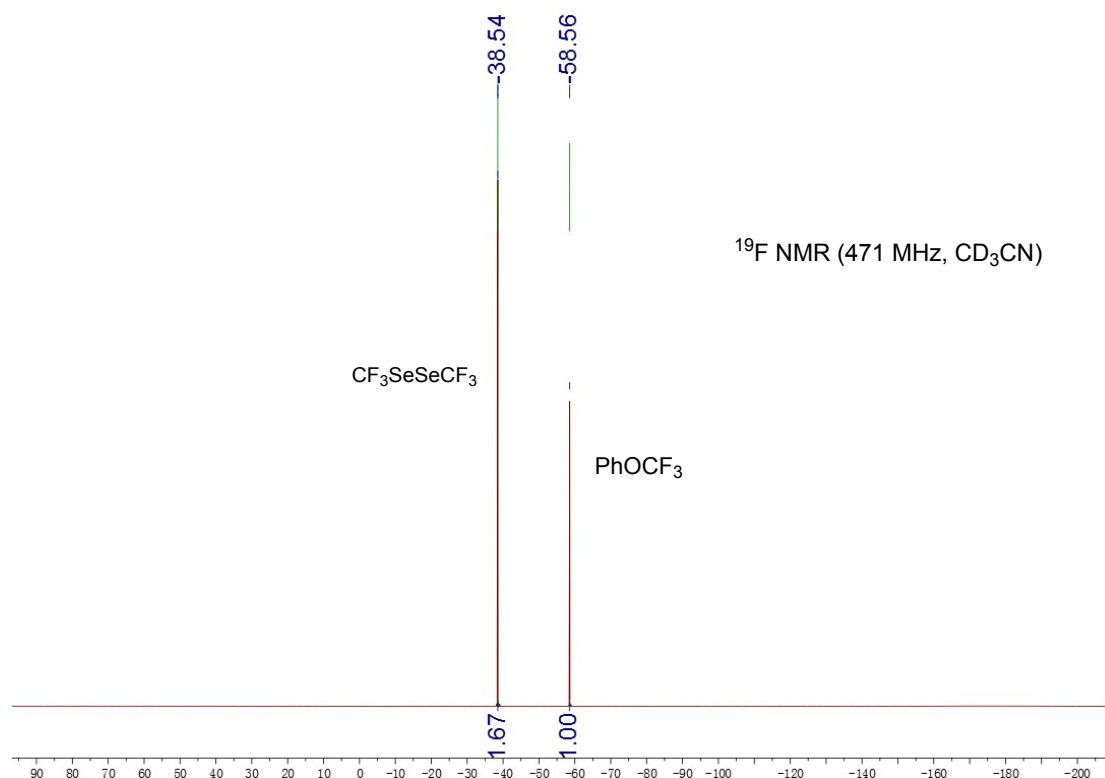
The combination of the above spectra (Figures 22-27)



5.5. Isolation of the possible reactive intermediates



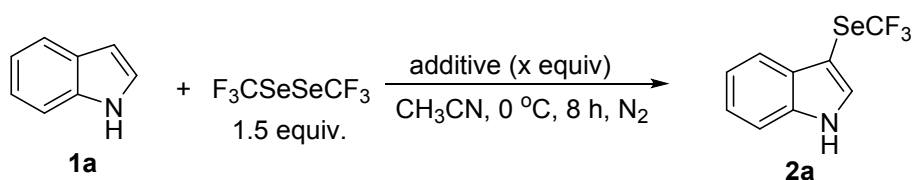
Procedure A: Under a nitrogen atmosphere, a Schlenk tube was charged with $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (2 mmol, 444 mg) and sulfolane (5 mL, degass). Then, *m*-CPBA (2 mmol, 400 mg) was added and the tube was sealed. The mixture was reacted at 35 °C for 2 h and distilled under reduced pressure (4.2 KPa / 60 °C / 2 h). The volatile compounds were captured by cold trap (liquid nitrogen) to give a light yellow liquid (133.3 mg).



$\text{CF}_3\text{SeSeCF}_3$ (88% purity): ^{19}F NMR (471 MHz, CD_3CN) δ -38.5 (s, 6F).¹¹

The purity of $\text{CF}_3\text{SeSeCF}_3$ was calculated according to the ^{19}F NMR spectrum using PhOCF_3 (30.5 mg, 0.188 mmol) as an internal standard.

Table S10 The reactions of **1a** with $\text{CF}_3\text{SeSeCF}_3$ under the standard or similar conditions



Entry ^a	Additive (x equiv.)	Recovery (1a , %) ^b	Yield (2a , %) ^b
1	None	87	< 1
2 ^c	3-chlorobenzoic acid (1.1 equiv.)	87	< 1
3 ^d	<i>m</i> -CPBA (0.5 equiv.)	62	< 1

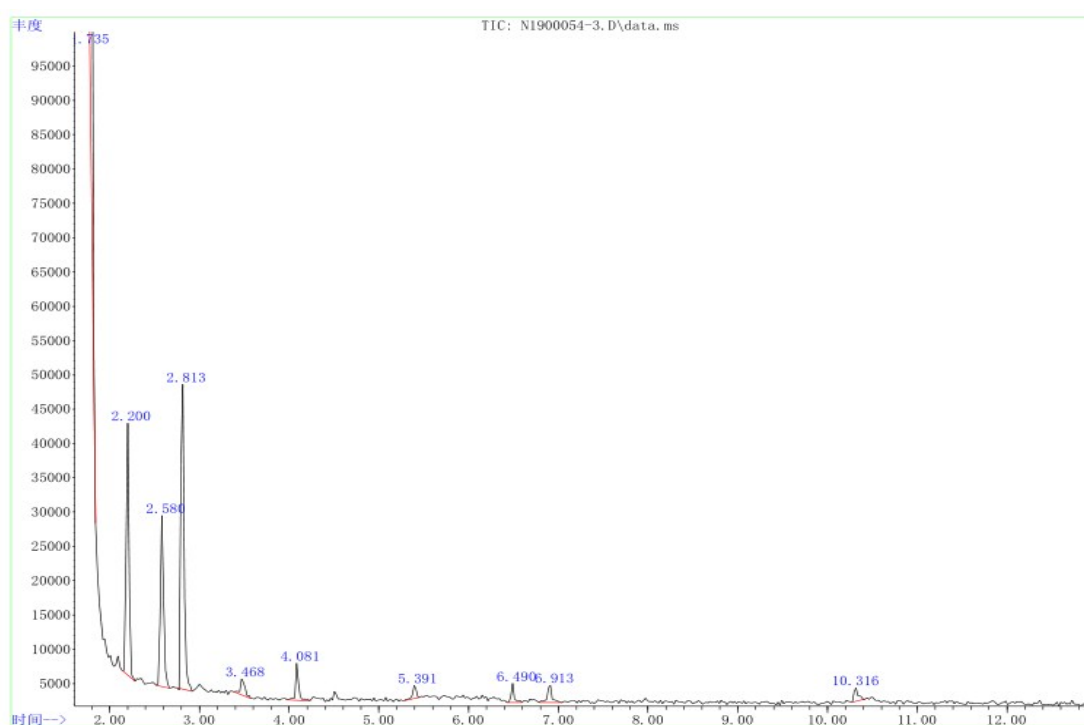
^a Reaction conditions: $\text{F}_3\text{CSeSeCF}_3$ (0.3 mmol) was dissolved in CH_3CN (1 mL) and cooled to 0 °C. Then, a solution of **1a** (0.2 mmol) in CH_3CN (1 mL) was added. The mixture was maintained at 0 °C under N_2 for 8 hours. ^b The conversion of **1a** and the yields of **2a** were determined by HPLC ($\lambda = 268$ nm, water/methanol = 10 : 90 (v / v)) using pure 1*H*-indole (**1a**, $t_{\text{R}} = 3.624$ min) and 3-((trifluoromethyl)selanyl)-1*H*-

indole (**2a**, $t_R = 4.523$ min) as the external standards, respectively. ^c 3-Chlorobenzoic acid (0.22 mmol) ^d *m*-CPBA (0.1 mmol).

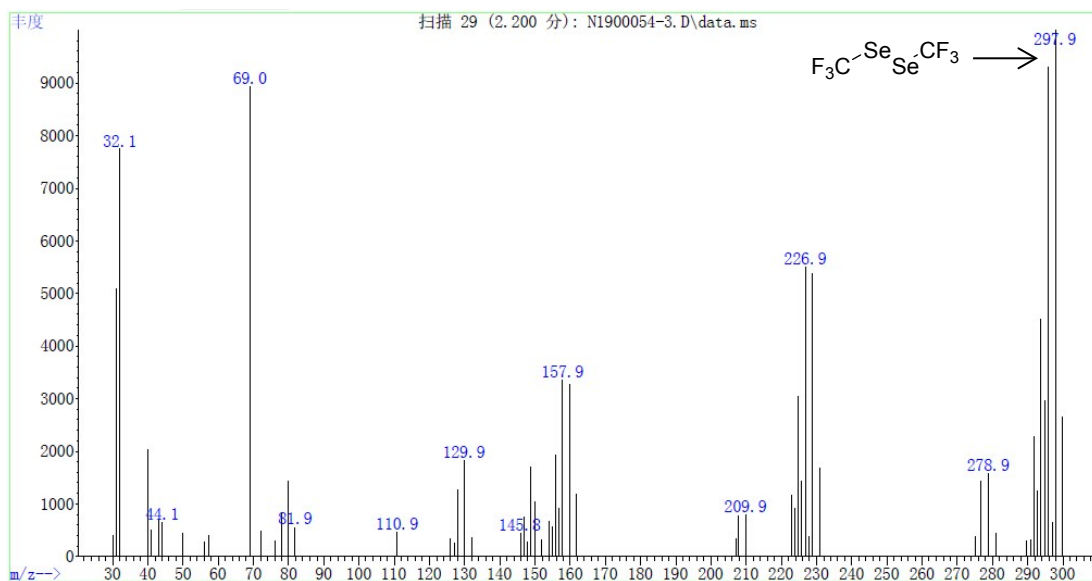
5.6. GC-MS analysis of the reaction mixture of [Me₄N][SeCF₃] and *m*-CPBA

Procedure: *m*-CPBA (0.2 mmol) was added to a solution of [Me₄N][SeCF₃] (0.2 mmol) in CH₃CN (2 mL). The mixture was maintained at room temperature under N₂ for 45 minutes and examined by a GC-MS instrument (Agilent 222-5532LTM DB-5ms).

Figure 28. The GC-MS spectra of the above reaction mixture



Retention time = 2.20 minutes, CF₃SeSeCF₃ (m/z 297.9) was detected (see below):



5.7. The cyclic voltammetry of $[\text{Me}_4\text{N}][\text{SeCF}_3]$

General: The electrochemical studies were performed by using a CHI660E electrochemical workstation with a three-electrode one-compartment cell fitted with a Pt working microelectrode (0.5×37 mm), a Pt wire counter electrode, and a Ag/AgCl reference electrode (Ag wire dipped in saturated KCl aqueous solution). The General Purpose Electrochemical Software (GPES) was utilized to record and process the data. The dry CH_3CN from commercial source was degassed by bubbling nitrogen gas before use. All experiments were performed at ambient temperature with a scan rate of $0.05 \text{ V} \cdot \text{s}^{-1}$ in CH_3CN solutions containing 1.0 or 2.0 mmol/L analyte and 0.1 mol/L $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte. Potentials were referenced to an external ferrocene/ferrocenium reference redox couple ($E_{1/2} = 0.481 \text{ V}$ vs. Ag/AgCl).

Figure 29. Cyclic voltammogram of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (2.0 mmol/L) in CH_3CN containing $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte (0.1 mol/L).

$$E_{\text{pa}} = 0.28 \text{ V}$$

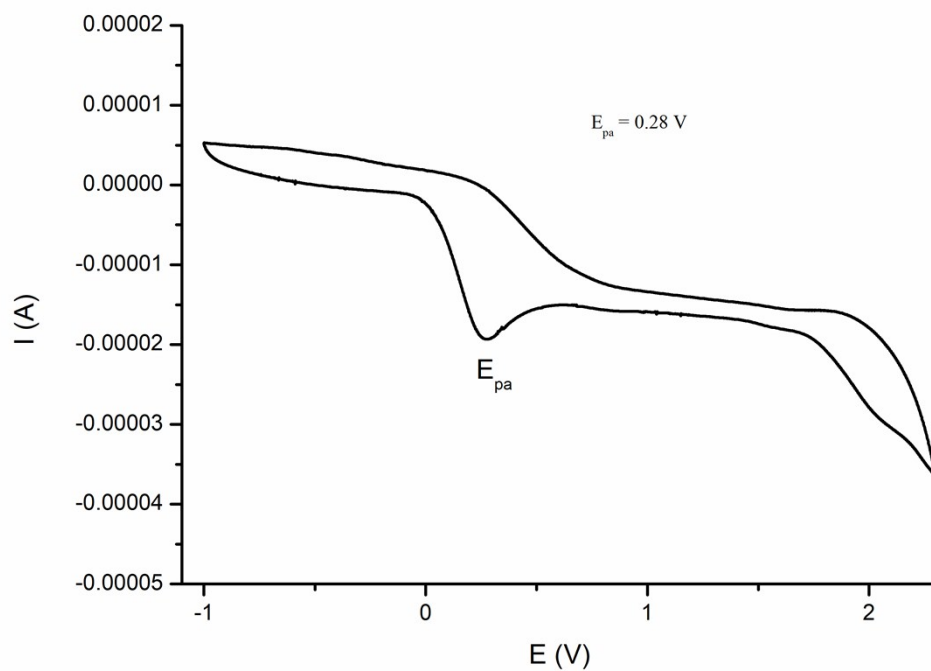


Figure 30. Cyclic voltammogram of $[\text{Me}_4\text{N}][\text{SCF}_3]$ (2.0 mmol/L) in CH_3CN containing $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ supporting electrolyte (0.1 mol/L).

$E_{\text{pa}} = 0.89 \text{ V}$

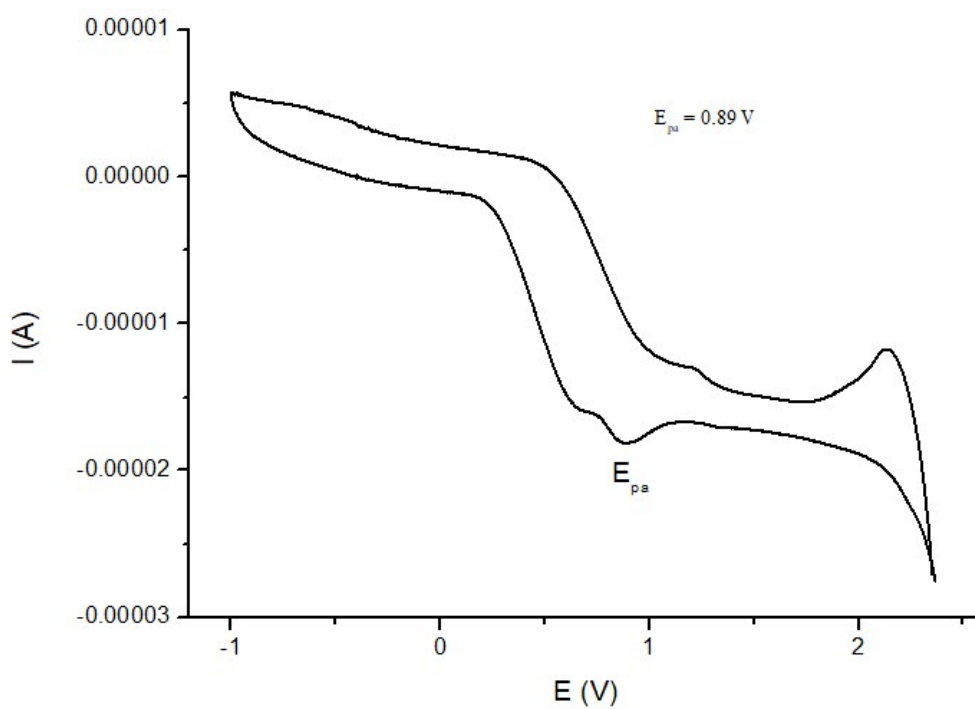
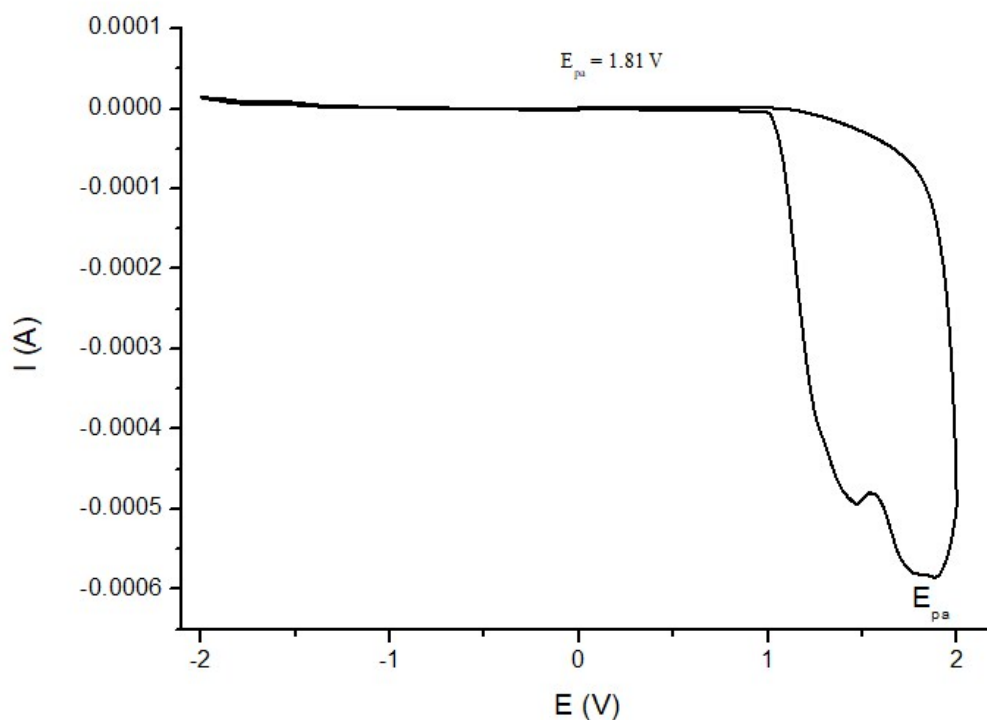


Figure 31. Cyclic voltammogram of indole (1.0 mmol/L) in CH_3CN containing $[n\text{-}$

Bu₄N][PF₆] supporting electrolyte (0.1 mol/L).

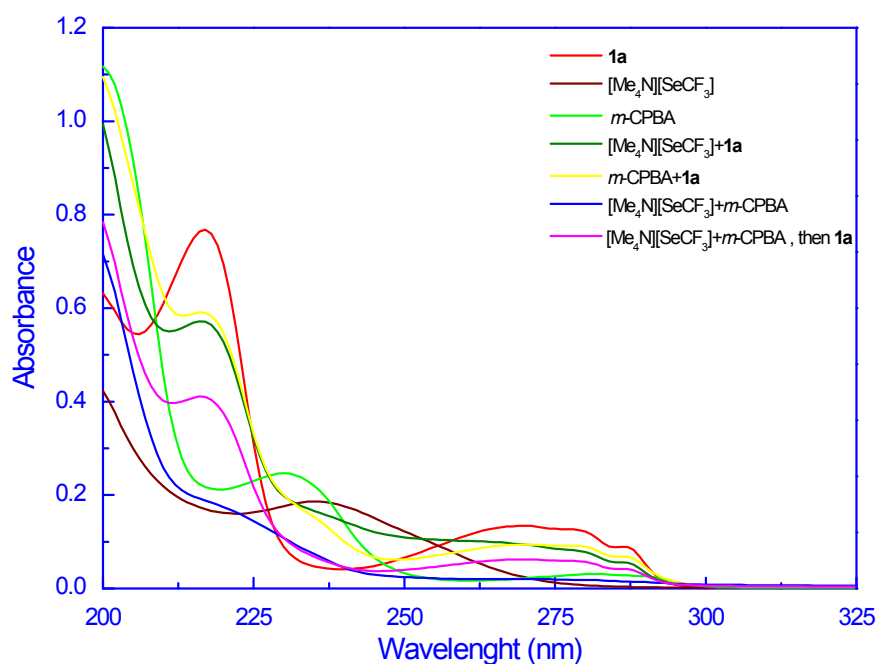
$E_{pa} = 1.81 \text{ V}$



5.8. The UV-vis spectra of the individual reactants and their mixtures

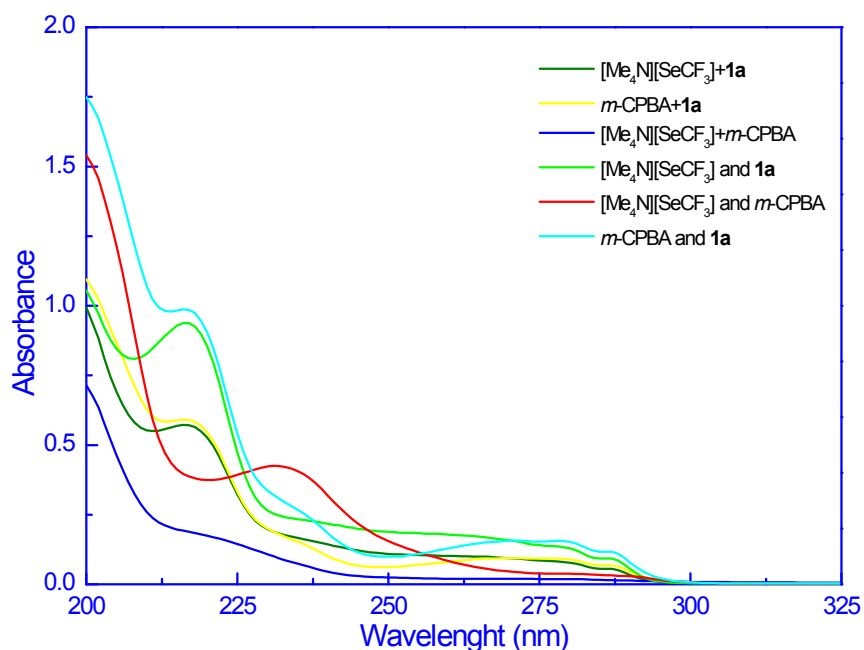
General: The UV-vis absorption spectra of the individual reactants and their mixtures were measured on an AOE 360 spectrophotometer to investigate the formation of possible donor-acceptor complexes and the electron transfer reactions among these compounds. The anhydrous acetonitrile solutions of individual **1a**, [Me₄N][SeCF₃] and oxidant were prepared at the concentration of 0.02 mmol/L and their mixtures were prepared by mixing these individual solutions. The resulting solutions were scanned from 200 to 800 nm by the UV-vis spectrophotometer at room temperature.

Figure 32. The UV-vis absorption spectra of **1a**, [Me₄N][SeCF₃], *m*-CPBA and their mixtures.



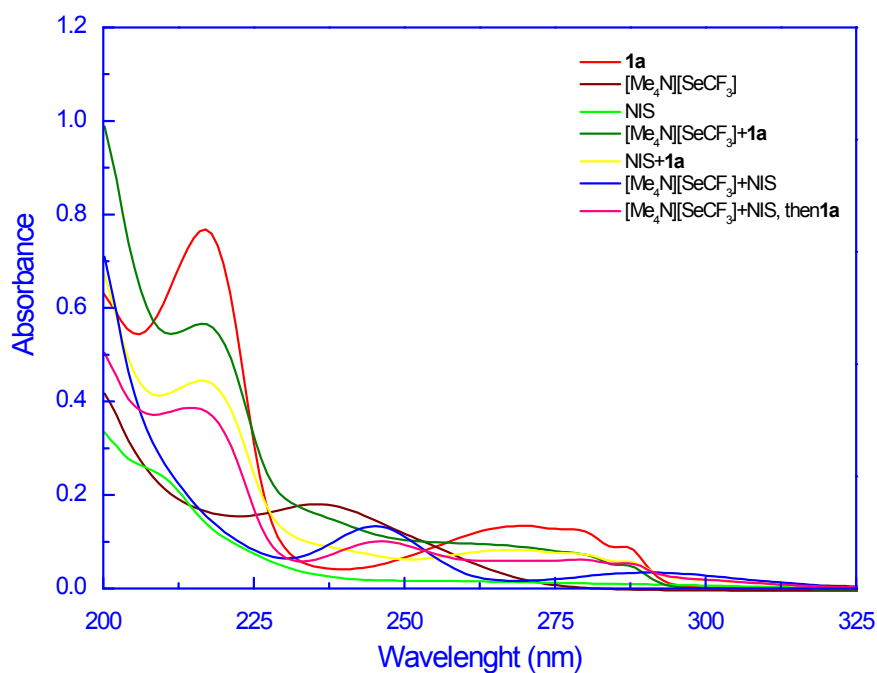
Red: a solution of **1a**; **Wine:** a solution of $[\text{Me}_4\text{N}][\text{SeCF}_3]$; **Green:** a solution of *m*-CPBA; **Olive:** a mixture of the individual solutions of **1a** and $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1:1, v/v); **Yellow:** a mixture of the individual solutions of **1a** and *m*-CPBA (1:1, v/v); **Blue:** a mixture of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and *m*-CPBA (1:1, v/v); **Magenta:** a mixture of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and *m*-CPBA was treated with a solution of **1a** (1:1:1, v/v/v).

Figure 33. Comparison of the UV-vis spectra of the mixtures with the mathematical sum of the UV-vis spectra of the individual compounds.



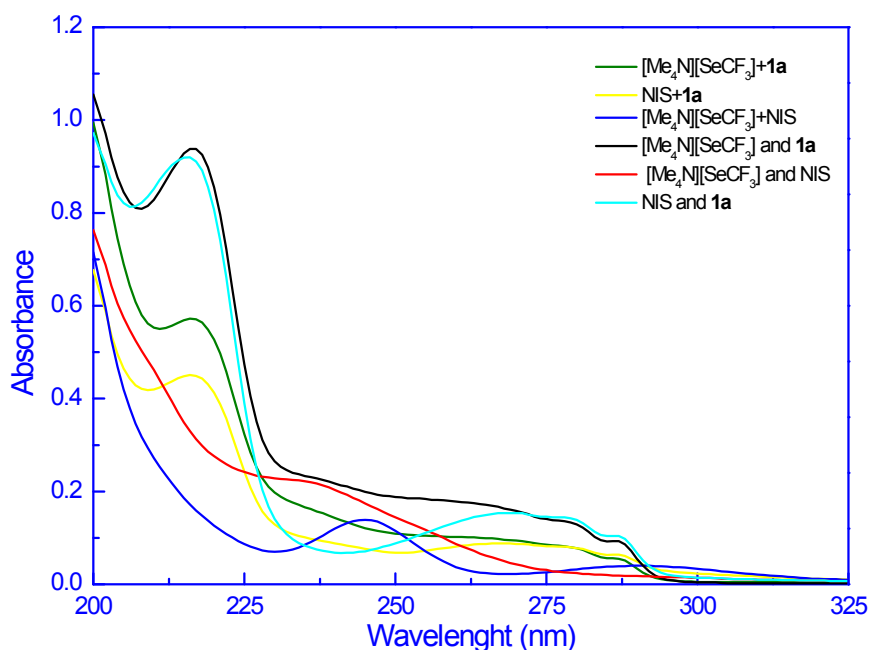
Olive: a mixture of the individual solutions of **1a** and $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1:1, v/v); **Yellow:** a mixture of the individual solutions of **1a** and *m*-CPBA (1:1, v/v); **Blue:** a mixture of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and *m*-CPBA (1:1, v/v); **Green:** a mathematical sum of the UV-vis spectra of the individual solutions of **1a** and $[\text{Me}_4\text{N}][\text{SeCF}_3]$; **Red:** a mathematical sum of the UV-vis spectra of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and *m*-CPBA; **Cyan:** a mathematical sum of the UV-vis spectra of the individual solutions of **1a** and *m*-CPBA.

Figure 34. The UV-vis absorption spectra of **1a**, $[\text{Me}_4\text{N}][\text{SeCF}_3]$, NIS and their mixtures.



Red: a solution of **1a**; **Wine:** a solution of $[\text{Me}_4\text{N}][\text{SeCF}_3]$; **Green:** a solution of NIS; **Olive:** a mixture of the individual solutions of **1a** and $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1:1, v/v); **Yellow:** a mixture of the individual solutions of **1a** and NIS (1:1, v/v); **Blue:** a mixture of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and NIS (1:1, v/v); **Magenta:** a mixture of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and NIS was treated with a solution of **1a** (1:1:1, v/v/v).

Figure 35. Comparison of the UV-vis spectra of the mixtures with the mathematical sum of the UV-vis spectra of the individual compounds.



Olive: a mixture of the individual solutions of **1a** and $[\text{Me}_4\text{N}][\text{SeCF}_3]$ (1:1, v/v); **Yellow:** a mixture of the individual solutions of **1a** and NIS (1:1, v/v); **Blue:** a mixture of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and NIS (1:1, v/v); **Black:** a mathematical sum of the UV-vis spectra of the individual solutions of **1a** and $[\text{Me}_4\text{N}][\text{SeCF}_3]$; **Red:** a mathematical sum of the UV-vis spectra of the individual solutions of $[\text{Me}_4\text{N}][\text{SeCF}_3]$ and NIS; **Cyan:** a mathematical sum of the UV-vis spectra of the individual solutions of **1a** and NIS.

5.9. The reactions of **1a** and $[\text{Me}_4\text{N}][\text{SCF}_3]$ under the standard conditions that were used for $[\text{Me}_4\text{N}][\text{SeCF}_3]$.

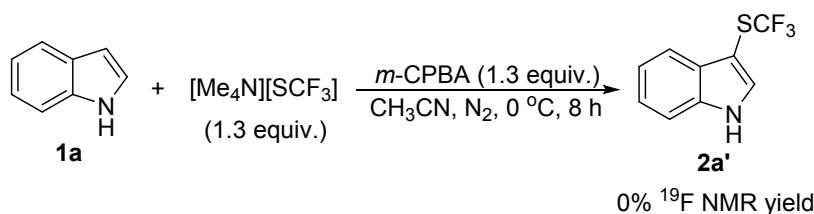


Figure 36. The ^{19}F NMR analysis of the above reaction mixture (no trifluoromethylthiolated product was observed according to the ^{19}F NMR spectrum by using PhOCF_3 (33.7 mg, 0.208 mmol) as an internal standard):^{12a}

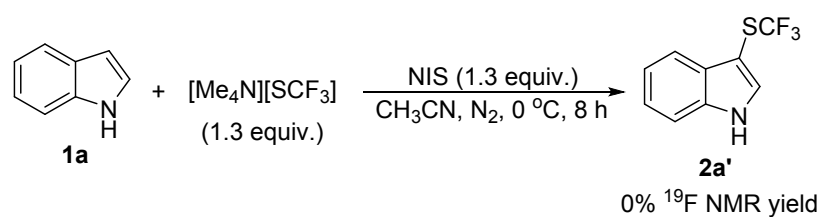
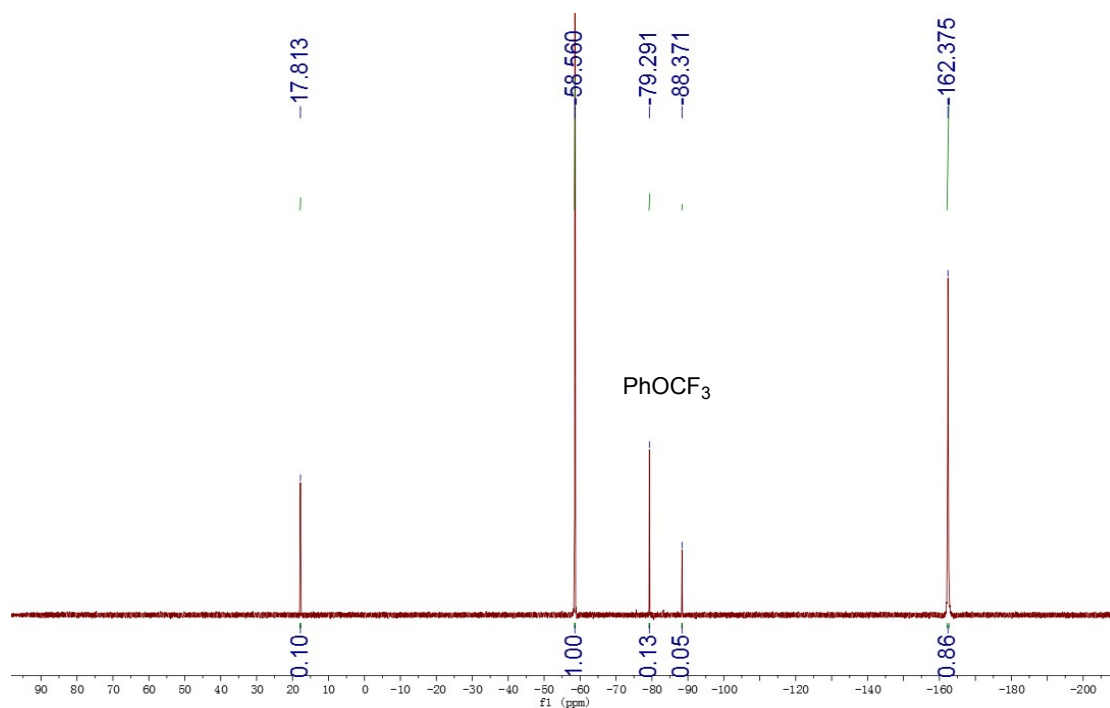
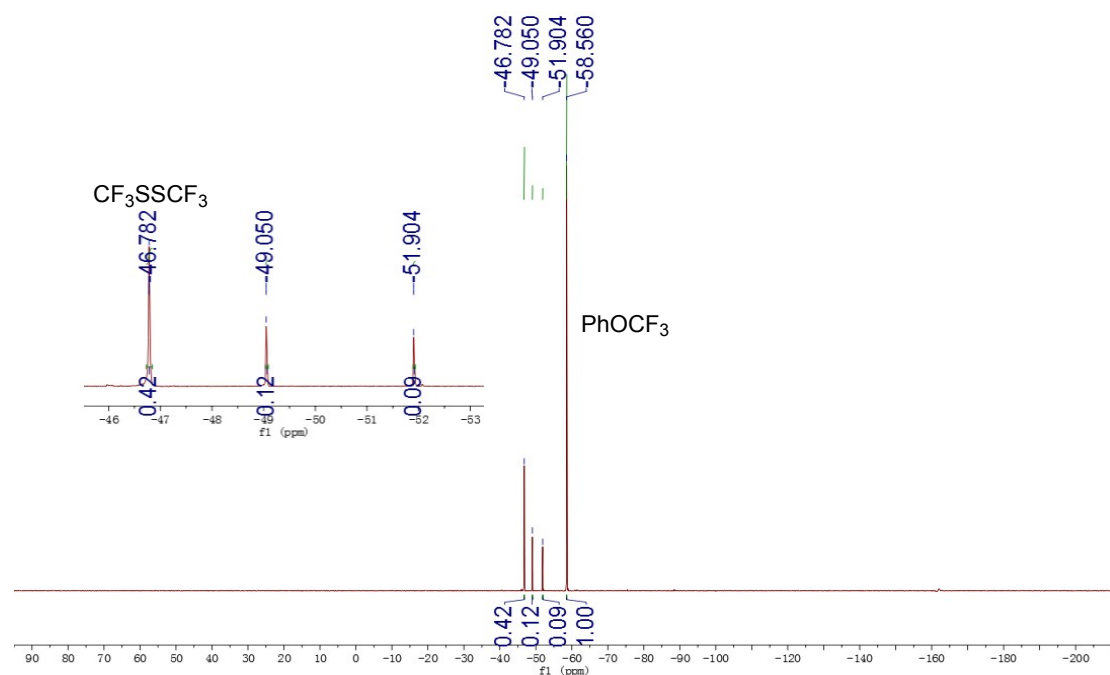


Figure 37. The ^{19}F NMR analysis of the above reaction mixture (no trifluoromethylthiolated product was observed according to the ^{19}F NMR spectrum by using PhOCF_3 (34.4 mg, 0.212 mmol) as an internal standard):^{12a}



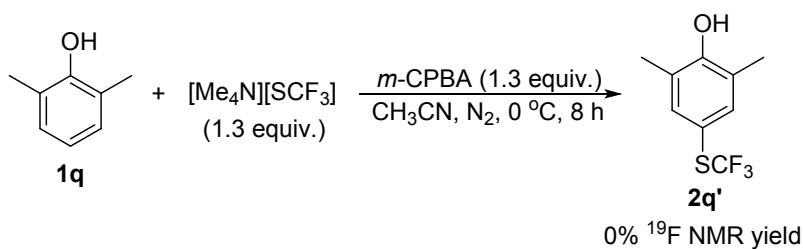


Figure 38. The ^{19}F NMR analysis of the above reaction mixture (no trifluoromethylthiolated product was observed according to the ^{19}F NMR spectrum by using PhOCF_3 (34.2 mg, 0.211 mmol) as an internal standard):^{12b}

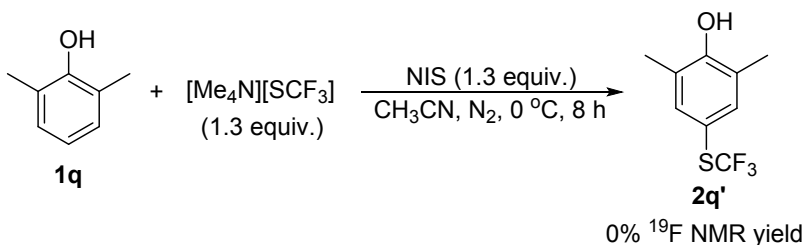
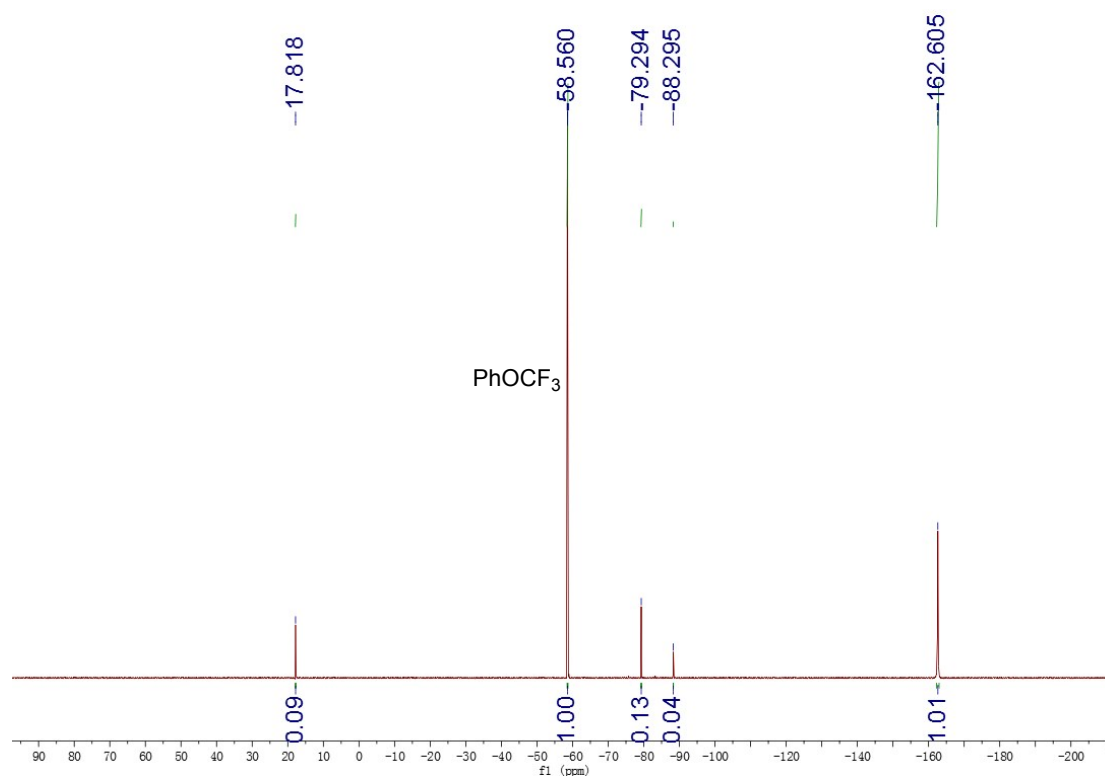
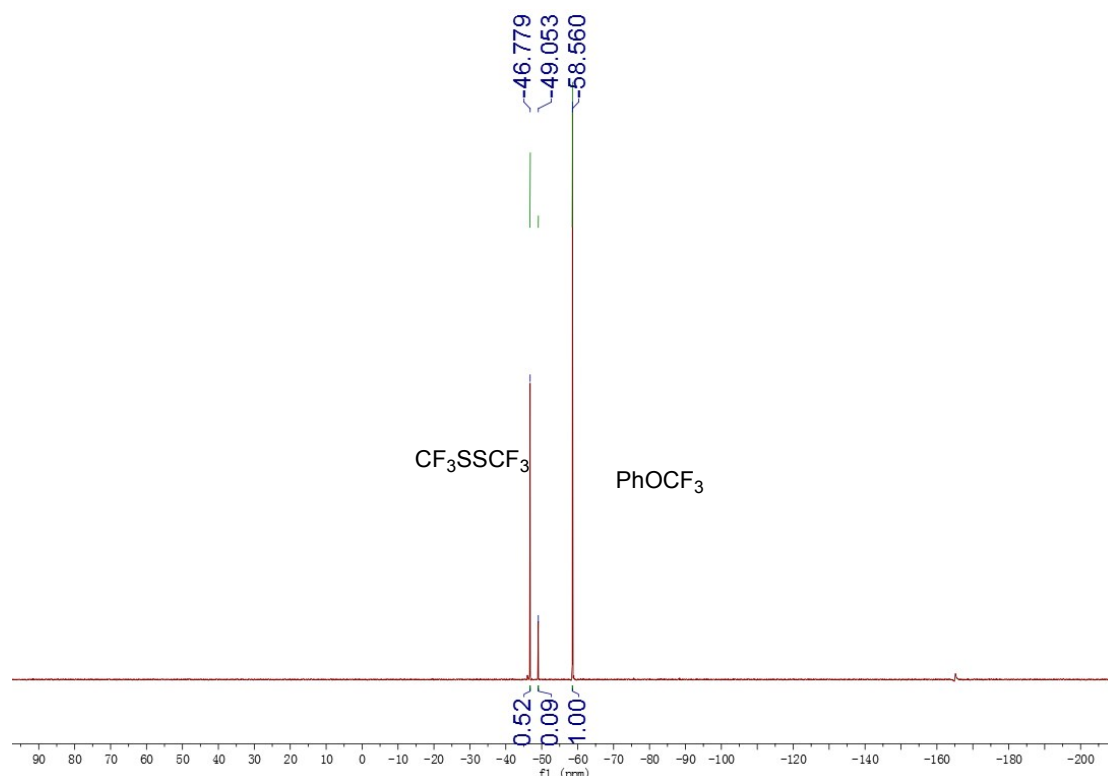


Figure 39. The ^{19}F NMR analysis of the above reaction mixture (no trifluoromethylthiolated product was observed according to the ^{19}F NMR spectrum by using PhOCF_3 (33.9 mg, 0.209 mmol) as an internal standard):^{12b}



Reference:

- [1] (a) W. Tyrra, D. Naumann, Y. L. Yagupolskii, *J. Fluorine Chem.* **2003**, *123*, 183-187. (b) T. Dong, J. He, Z.-H. Li, C.-P. Zhang, *ACS Sustainable Chem. Eng.* **2018**, *6*, 1327-1335.
- [2] B. Li, Z. Chen, H. Cao, H. Zhao, *Org. Lett.* **2018**, *20*, 3291-3295.
- [3] A. Das, K. Watanabe, H. Morimoto, T. Ohshima, *Org. Lett.* **2017**, *19*, 5794-5797.
- [4] C. R. Johnson, M. I. Ansari, A. Coop, *ACS Omega* **2018**, *3*, 10886-10890.
- [5] K. Pericherla, P. Kaswan, P. Khedar, B. Khungar, K. Parangb, A. Kumar, *RSC Adv.* **2013**, *3*, 18923-18930.
- [6] T. Torigoe, T. Ohmura, M. Sugimoto, *Angew. Chem. Int. Ed.* **2017**, *56*, 14272-14276.
- [7] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed; Butterworth Heinemann: Oxford, 2003.
- [8] Q. Glenadel, E. Ismalaj, T. Billard, *J. Org. Chem.* **2016**, *81*, 8268-8275.
- [9] N. Muniraj, J. Dhineshkumar, K. R. Prabhu, *ChemistrySelect* **2016**, *5*, 1033-1038.
- [10] S. Potash, S. Rozen, *J. Org. Chem.* **2014**, *79*, 11205-11208.
- [11] C. J. Marsden, *J. Fluorine Chem.* **1975**, *5*, 401-422.
- [12] (a) K. Lu, Q. Li, X. Xi, Y. Huang, Z. Gong, P. Yu, X. Zhao, *Org. Chem. Front.*

2018, 5, 3088-3092. (b) M. Jereb, K. Gosak, *Org. Biomol. Chem.* **2015**, 13, 3103-3115.

6. The NMR spectra of 2

