

Supporting Information

Difluorocarbene-derived trifluoromethylselenolation of benzyl halides

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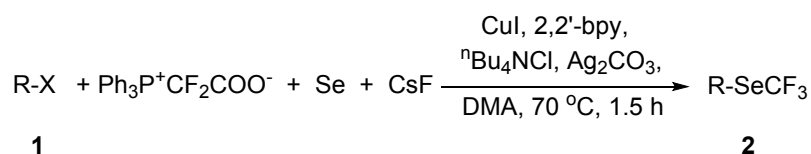
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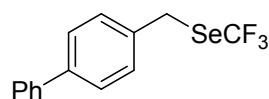
1. General information

Solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. ^1H , ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400MHz or 300 MHz NMR spectrometer. Data for ^1H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (J) in Hz). Mass spectra were obtained on a GC-MS or LC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI mode.

2. Procedure for the preparation of 2

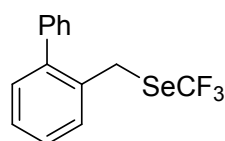


Into a 10 mL sealed tube were added **1a** (0.2 mmol, 49.4mg), $\text{Ph}_3\text{P}^+\text{CF}_2\text{COO}^-$ (0.4 mmol, 142.4 mg), Se (1.2 mmol, 94.8 mg), CsF (0.6 mmol, 91.2 mg), CuI (0.6 mmol, 114.3 mg), 2,2'-bpy (0.4 mmol, 62.4 mg), $^n\text{Bu}_4\text{NCl}$ (0.4 mmol, 111 mg), Ag_2CO_3 (0.04 mmol, 11.1 mg) and DMA (3 mL) under a N_2 atmosphere. The tube was sealed and the mixture was stirred at 70 $^\circ\text{C}$ for 1.5 h. After being cooled to room temperature, the mixture was filtrated. The solid was washed by DCM, and the combined organic phase was washed with water (20 mL \times 3) to remove DMA. The organic phase was dried over Na_2SO_4 . After the solvent was removed by concentration, the residue was subjected to flash column chromatography to afford the final product **2a**.



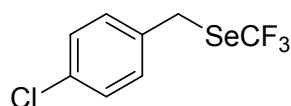
2a

([1,1'-biphenyl]-4-ylmethyl) (trifluoromethyl) selenane; 71%; white solid; M. P.: 65 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.58-7.54 (m, 4H), 7.45-7.39 (m, 4H), 7.34 (t, J = 6.8Hz, 1H), 4.28 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.41 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8 (s), 140.5 (s), 135.1 (s), 130.6 (s), 129.5 (s), 128.8(s), 127.6 (s), 127.1 (s), 122.9 (q, J = 331.0 Hz), 28.9 (q, J = 1.3 Hz). IR (neat) ν = 1488, 1407, 1191, 1103, 842, 765, 738, 728, 662 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3^{74}\text{Se}[\text{M}]^+$: 310.0038, Found: 310.0051.



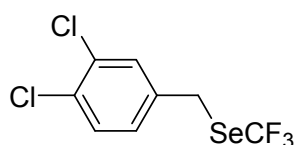
2b

([1,1'-biphenyl]-2-ylmethyl) (trifluoromethyl) selane; 41%; yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.38 (m, 4H), 7.34-7.31 (m, 4H), 7.24 (t, $J = 4.4$ Hz, 1H), 4.20 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.75 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 142.4 (s), 140.3 (s), 133.4 (s), 130.6 (s), 130.3 (s), 129.0 (s), 128.4 (s), 127.93 (s), 127.90 (s), 127.6 (s), 122.9 (q, $J = 331.0$ Hz), 27.3 (q, $J = 1.7$ Hz). IR (neat) $\nu = 3062, 1478, 1451, 1438, 1099, 762, 744, 702\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3^{74}\text{Se}[\text{M}]^+$: 310.0038, Found: 310.0045.



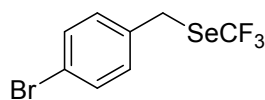
2c

(4-chlorobenzyl) (trifluoromethyl) selane; 57%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.24 (m, 4H), 4.18 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.37 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 134.8 (s), 133.7 (s), 130.3 (s), 129.1 (s), 122.7 (q, $J = 331.4$ Hz), 28.3 (q, $J = 1.8$ Hz). IR (neat) $\nu = 2962, 1492, 1408, 1261, 1095, 864, 800, 739, 704\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_8\text{H}_6\text{ClF}_3^{74}\text{Se}[\text{M}]^+$: 267.9335, Found: 267.9330.



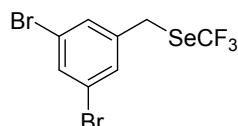
2d

(3,4-dichlorobenzyl) (trifluoromethyl) selane; 55%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 2.1$ Hz, 1H), 7.38 (d, $J = 8.3$ Hz, 1H), 7.16 (dd, $J = 8.2, 2.1$ Hz, 1H), 4.14 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.29 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 136.7 (s), 132.9 (s), 132.0 (s), 130.9 (s), 130.8 (s), 128.3 (s), 122.6 (q, $J = 331.5$ Hz), 27.7 (q, $J = 1.8$ Hz). IR (neat) $\nu = 1593, 1470, 1396, 1201, 1096, 1073, 1034, 891, 738\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_8\text{H}_5\text{Cl}_2\text{F}_3^{74}\text{Se}[\text{M}]^+$: 301.8945, Found: 301.8957.



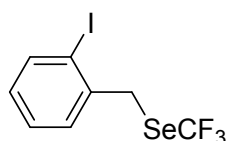
2e

(4-bromobenzyl) (trifluoromethyl) selane; 71%; white liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 4.16 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.36 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 135.3 (s), 132.0 (s), 130.7 (s), 122.5 (q, $J = 331.0$ Hz), 121.8 (s), 28.4 (q, $J = 1.7$ Hz). IR (neat) $\nu = 2960, 2925, 2853, 1590, 1488, 1420, 1403, 1261, 1097, 1012, 801, 477\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_8\text{H}_6^{79}\text{BrF}_3^{74}\text{Se}[\text{M}]^+$: 311.8830, Found: 311.8844.



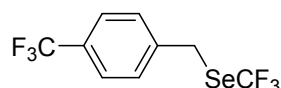
2f

(3,5-dibromobenzyl) (trifluoromethyl) selane; 81%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (s, 1H), 7.42 (s, 2H), 4.12 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.29 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 140.3 (s), 133.5 (s), 130.8 (s), 123.2 (s), 122.4 (q, $J = 331.0$ Hz), 27.5 (s). IR (neat) $\nu = 1584, 1556, 1425, 1219, 1097, 1074, 858, 742, 684\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_8\text{H}_5^{79}\text{Br}_2\text{F}_3^{74}\text{Se}[\text{M}]^+$: 389.7935, Found: 389.7932.



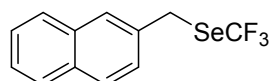
2g

(2-iodobenzyl) (trifluoromethyl) selane; 43%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.8$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 7.4$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 4.29 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.29 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 139.84 (s), 139.75 (s), 130.0 (s), 129.4 (s), 128.8 (s), 122.8 (q, $J = 331.9$ Hz), 100.6 (s), 34.8 (q, $J = 1.6$ Hz). IR (neat) $\nu = 2924, 1563, 1468, 1437, 1199, 1096, 1013, 754, 737, 718, 646\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_8\text{H}_6\text{F}_3\text{I}^{74}\text{Se}[\text{M}]^+$: 359.8691, Found: 359.8695.



2h

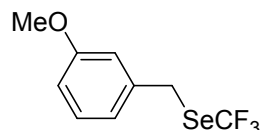
(trifluoromethyl) (4-(trifluoromethyl) benzyl) selane; 50%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 8.2$ Hz, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 4.24 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.39 (s, 3F), -62.73 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 140.6 (s), 130.0 (q, $J = 33.0$ Hz), 129.3 (s), 125.8 (q, $J = 3.8$ Hz), 124.0 (q, $J = 272.1$ Hz), 123.1 (q, $J = 333.0$ Hz), 28.3 (q, $J = 1.6$ Hz). IR (neat) $\nu = 1618, 1558, 1326, 1123, 1097, 1067, 1019, 848, 753, 739\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_9\text{H}_6\text{F}_6^{74}\text{Se}[\text{M}]^+$: 301.9598, Found: 301.9592.



2i

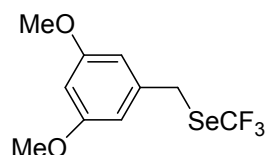
(naphthalen-2-ylmethyl) (trifluoromethyl) selane; 41%; white solid; M. P.: 48 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.83-7.78 (m, 4H), 7.52-7.43 (m, 3H), 4.41 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.35 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 133.43 (s), 133.36 (s), 132.8 (s), 128.8 (s), 127.9 (s), 127.76 (s), 127.75 (s), 126.8(s), 126.5 (s), 126.3 (s), 122.9 (q, $J = 331.4$ Hz), 29.6 (q, $J = 1.7$ Hz). IR (neat) $\nu = 1598, 1507, 1201, 1096, 966, 953, 867, 826, 751, 737, 480\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_9\text{F}_3^{74}\text{Se}[\text{M}]^+$: 283.9881, Found: 283.9884.



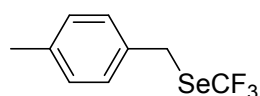
2j

(3-methoxybenzyl) (trifluoromethyl) selane¹; 71%; white liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (t, $J = 7.9$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.85 (t, $J = 1.9$ Hz, 1H), 6.81 (dd, $J = 8.2$ Hz, 2.0 Hz, 1H), 4.21 (s, 2H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.53 (s, 3F).



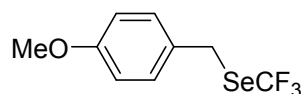
2k

(3,5-dimethoxybenzyl) (trifluoromethyl) selane; 50%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 6.47 (d, $J = 2.2$ Hz, 2H), 6.35 (t, $J = 2.2$ Hz, 1H), 4.16 (s, 2H), 3.77 (s, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.57 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 161.1 (s), 138.2 (s), 122.9 (q, $J = 331.4$ Hz), 107.0 (s), 99.8 (s), 55.3 (s), 29.3 (q, $J = 1.7$ Hz). IR (neat) $\nu = 1608, 1598, 1464, 1430, 1325, 1207, 1158, 1099, 1066, 930, 737\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{11}\text{F}_3\text{O}_2^{74}\text{Se}[\text{M}]^+$: 293.9936, Found: 293.9944.



2l

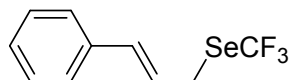
(4-methylbenzyl) (trifluoromethyl) selane²; 58%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 4.22 (s, 2H), 2.33 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.50 (s, 3F).



2m

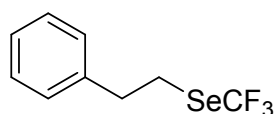
(4-methoxybenzyl)(trifluoromethyl)selane; 45%; slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 8.5$ Hz, 2H), 6.84 (d, $J = 8.5$ Hz, 2H), 4.21 (s, 2H), 3.79

(s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -34.45 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 159.2 (s), 130.2 (s), 127.8 (s), 122.9 (q, $J = 333.2$ Hz), 114.3 (s), 55.3 (s), 28.8 (q, $J = 1.8$ Hz). IR (neat) $\nu = 2956, 1608, 1512, 1464, 1322, 1251, 1096, 1071, 1034, 737, 598\text{cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_9\text{H}_9\text{F}_3\text{O}^{74}\text{Se}[\text{M}]^+$: 263.9830, Found: 263.9819.



2n

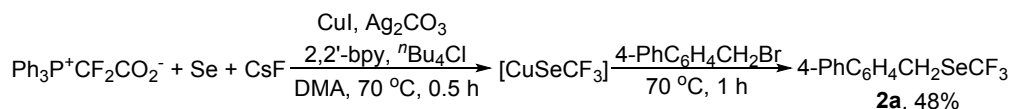
cinnamyl(trifluoromethyl)selane³; The yield determined by ^{19}F NMR spectroscopy was 12%; ^{19}F NMR (376 MHz, CDCl_3) δ -33.86 (s, 3F).



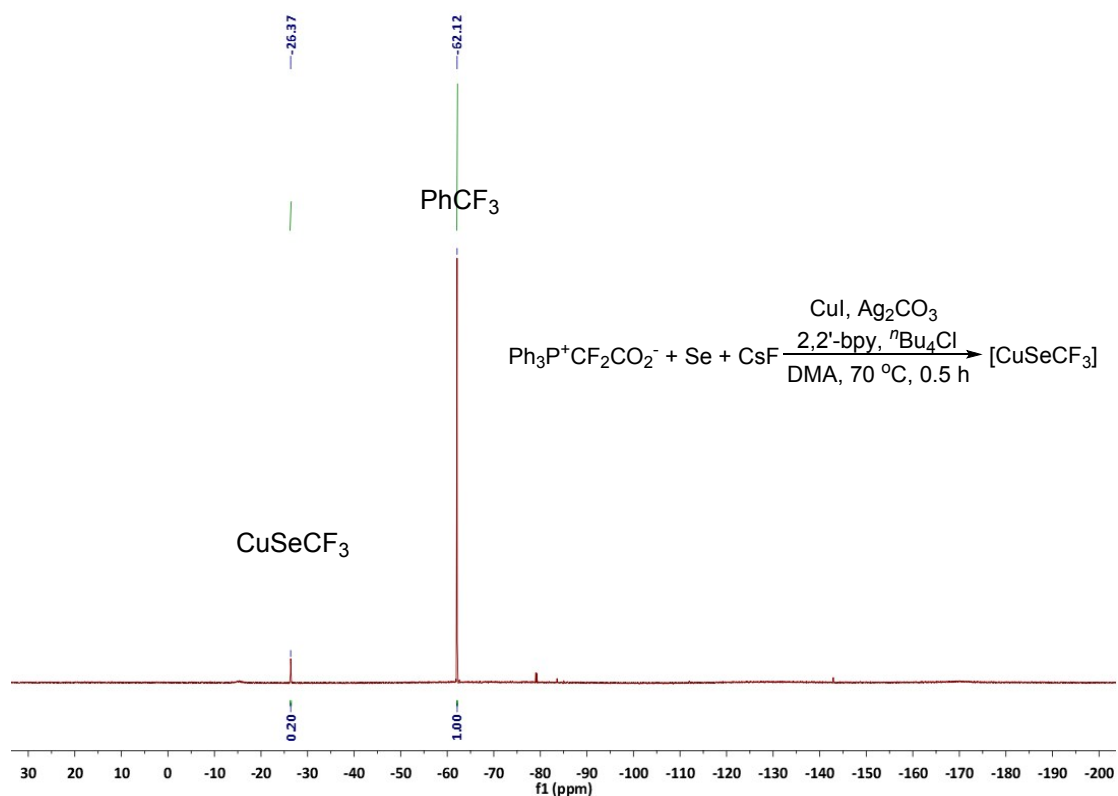
2o

phenethyl(trifluoromethyl)selane^{1, 2}; The yield determined by ^{19}F NMR spectroscopy was 20%; ^{19}F NMR (376 MHz, CDCl_3) δ -34.03 (s, 3F).

3. The observation of $[\text{CuSeCF}_3]$ intermediate

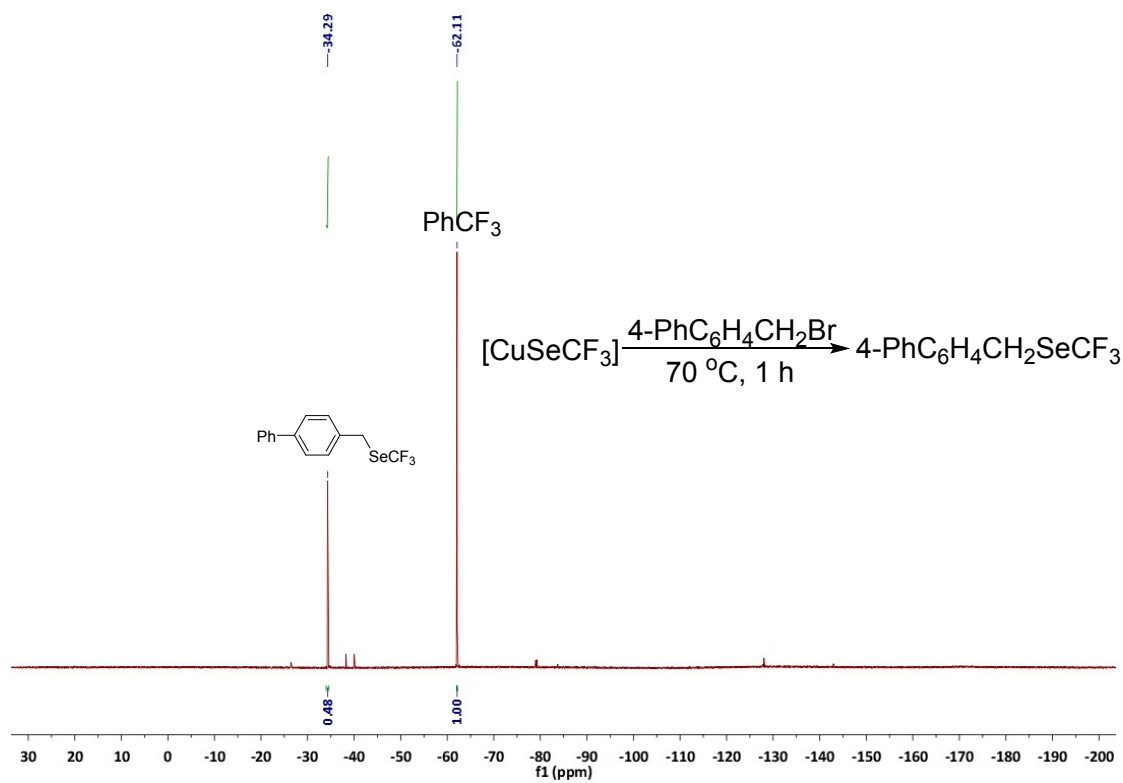


Into a 10 mL sealed tube were added $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$ (0.4 mmol, 142.4 mg), Se (1.2 mmol, 94.8 mg), CsF (0.6 mmol, 91.2 mg), CuI (0.6 mmol, 114.3 mg), 2,2'-bpy (0.4 mmol, 62.4 mg), $^n\text{Bu}_4\text{NCl}$ (0.4 mmol, 111 mg), Ag_2CO_3 (0.04 mmol, 11.1 mg) and DMA (3 mL) under a N_2 atmosphere. The tube was sealed and the mixture was stirred at 70 $^\circ\text{C}$ for 0.5 h. ^{19}F NMR analysis showed that $[\text{CuSeCF}_3]$ complex was generated (0.2 mmol of PhCF_3 was used as an internal standard). The ^{19}F NMR spectrum is shown as follows. The ^{19}F NMR yield was quite low (10% based on $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$), because the complex decomposed during the process of collecting ^{19}F NMR spectrum due to its instability. CuSeCF_3 , ^{19}F NMR (376 MHz, CDCl_3) δ -26.37 (s, 3F)¹.



In order to prove that CuSeCF_3 is the key intermediate, substrate **1a** was added after the complex was generated. The procedure is shown as follows.

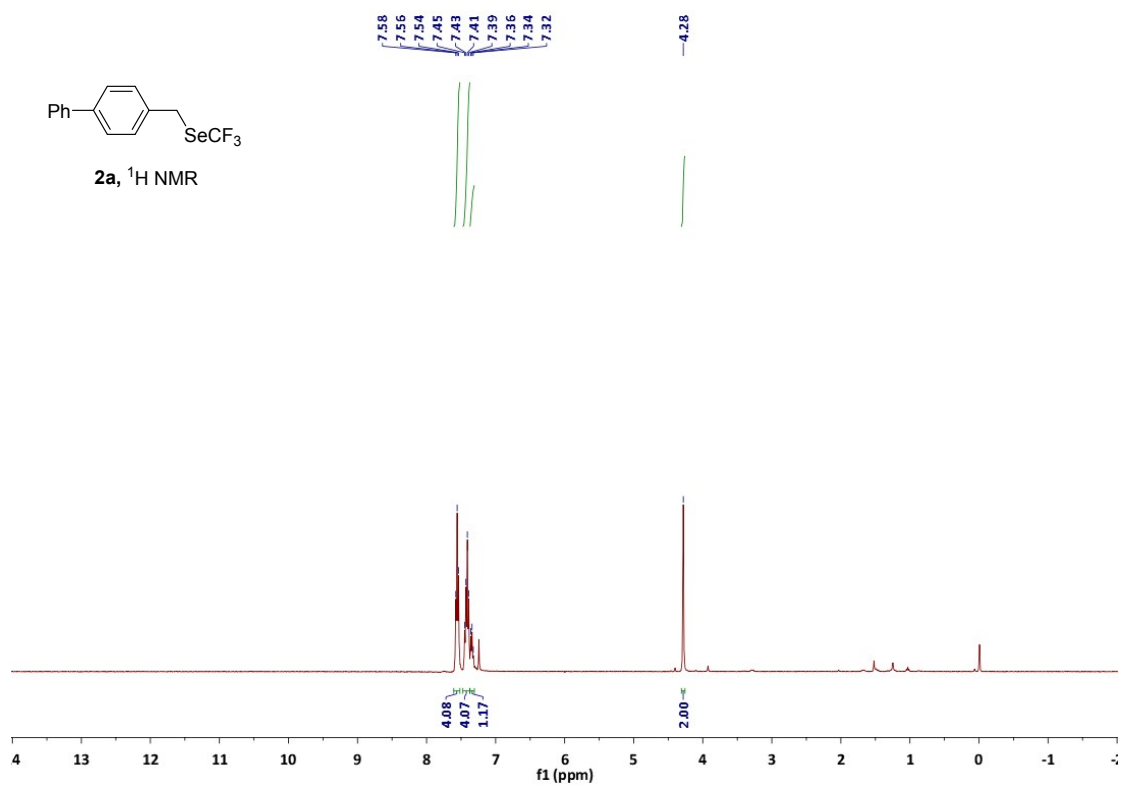
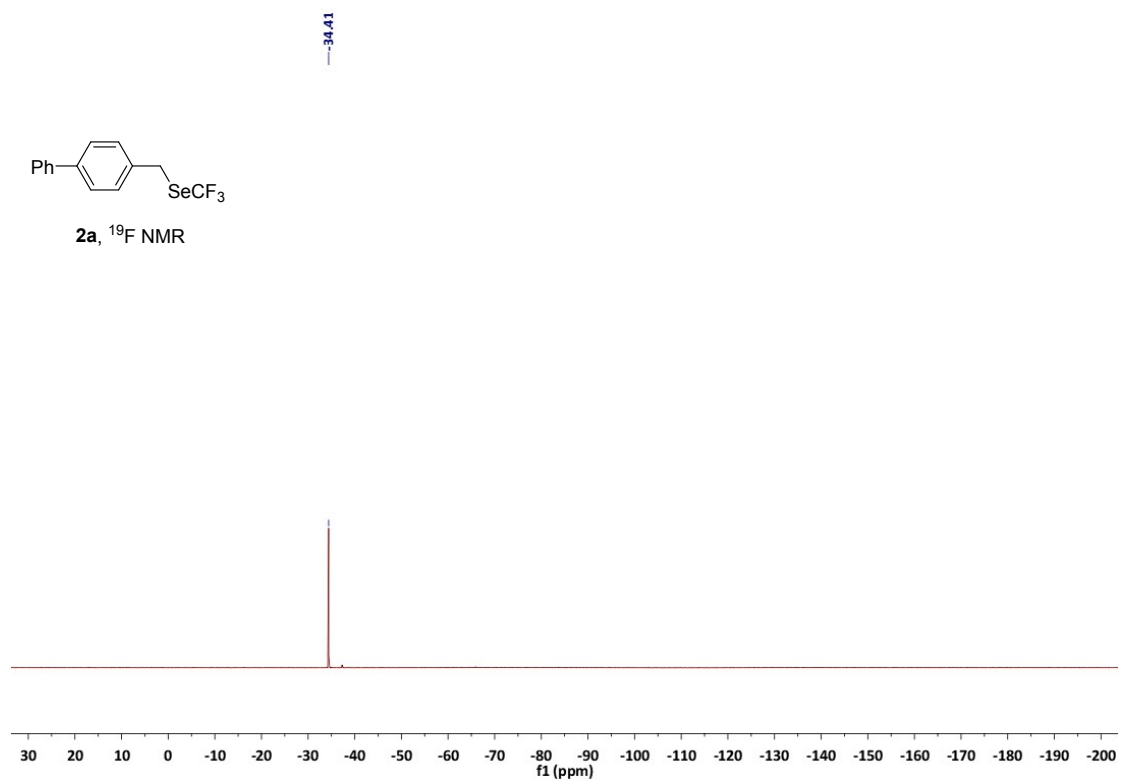
Into a 10 mL sealed tube were added $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$ (0.4 mmol, 142.4 mg), Se (1.2 mmol, 94.8 mg), CsF (0.6 mmol, 91.2 mg), CuI (0.6 mmol, 114.3 mg), 2,2'-bpy (0.4 mmol, 62.4 mg), $^n\text{Bu}_4\text{NCl}$ (0.4 mmol, 111 mg), Ag_2CO_3 (0.04 mmol, 11.1 mg) and DMA (3 mL) under a N_2 atmosphere. The tube was sealed and the mixture was stirred at 70 °C for 0.5 h. Substrate **1a** (0.2 mmol, 49.4 mg) was added and the resulting mixture was stirred at 70 °C for 1 h. The ^{19}F NMR analysis revealed that the desired product was obtained in 48% yield (0.2 mmol of PhCF_3 was used as an internal standard). The ^{19}F NMR spectrum is shown as follows.

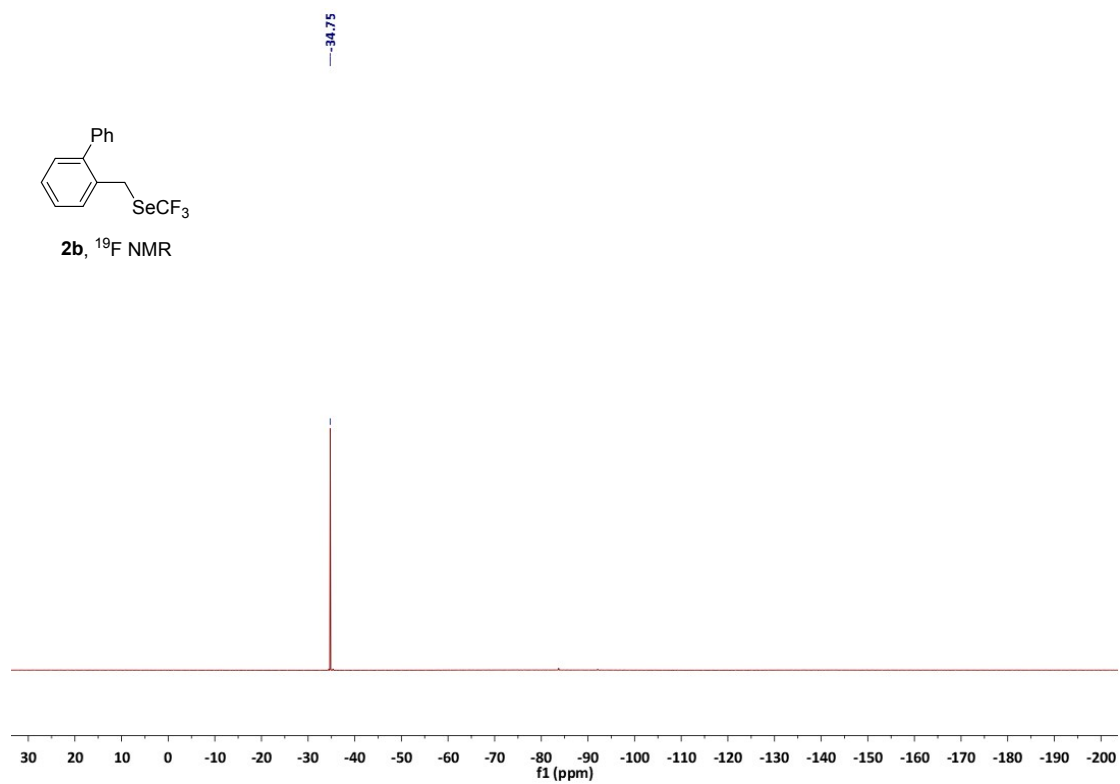
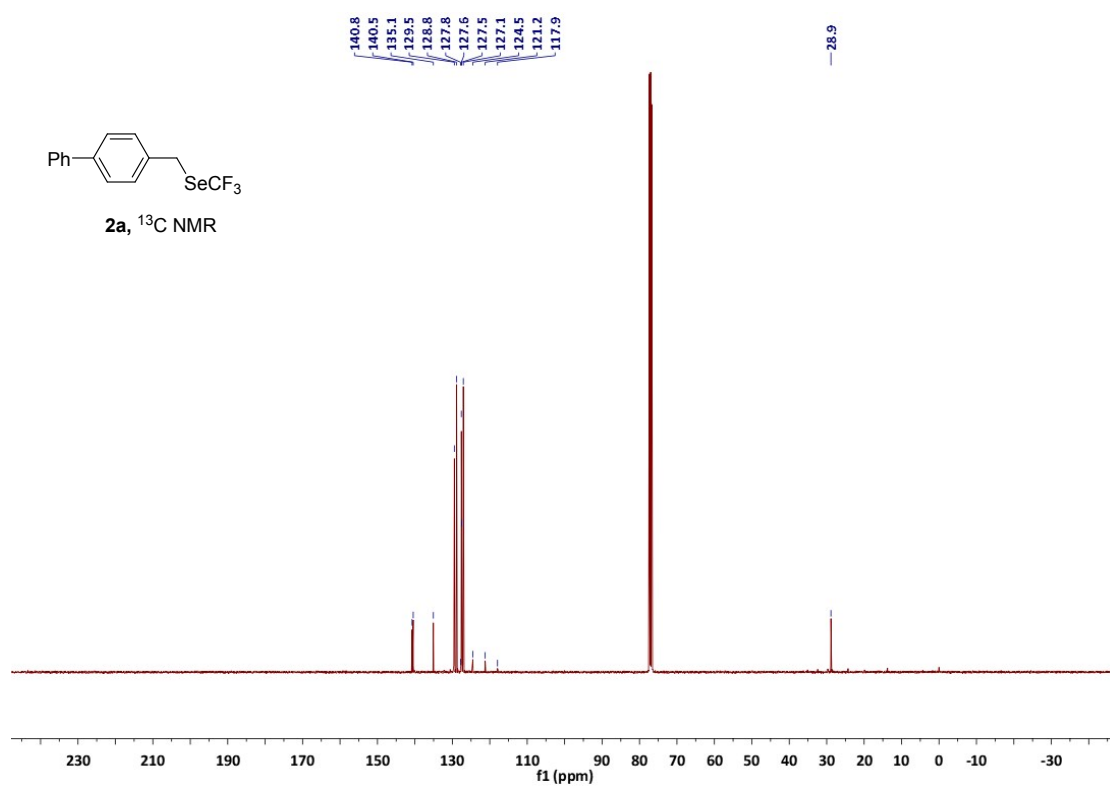


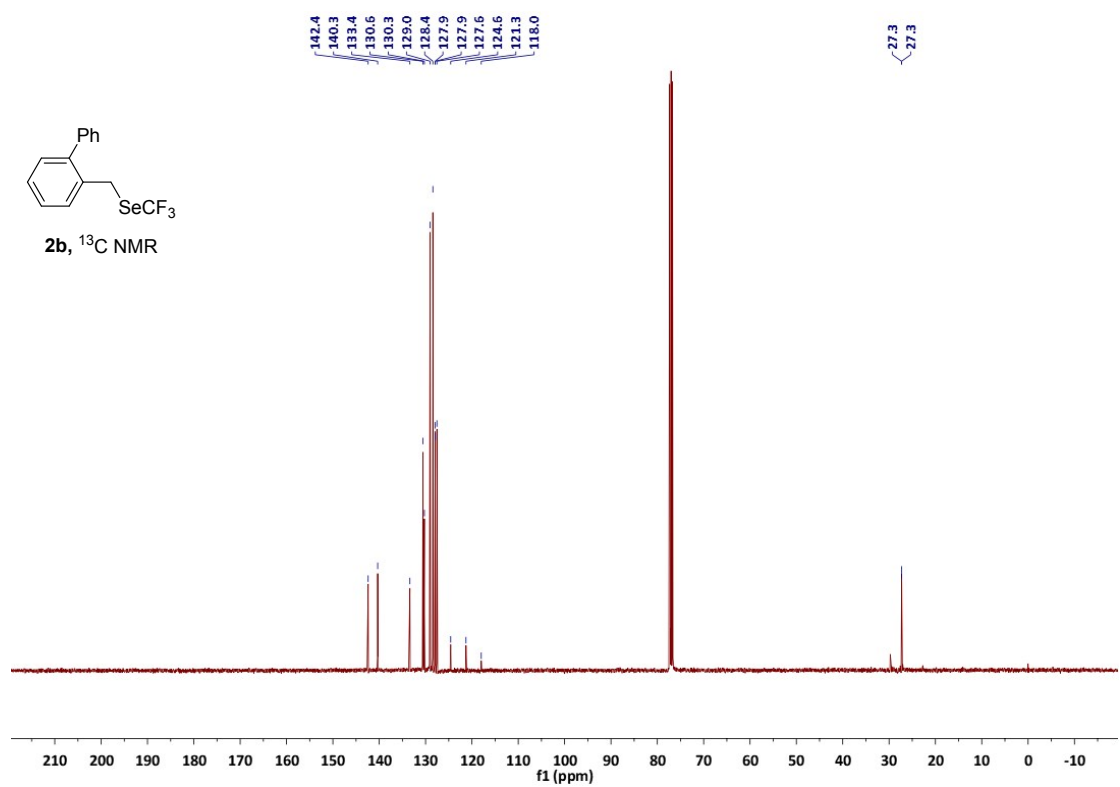
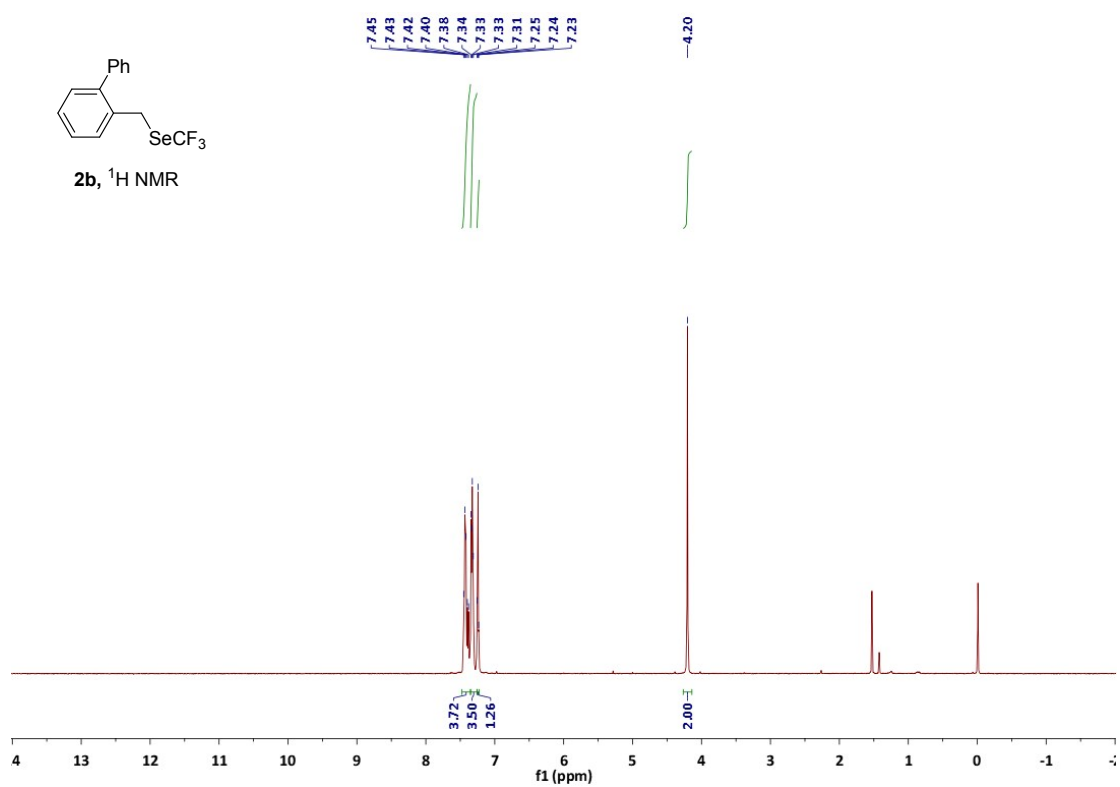
4. References

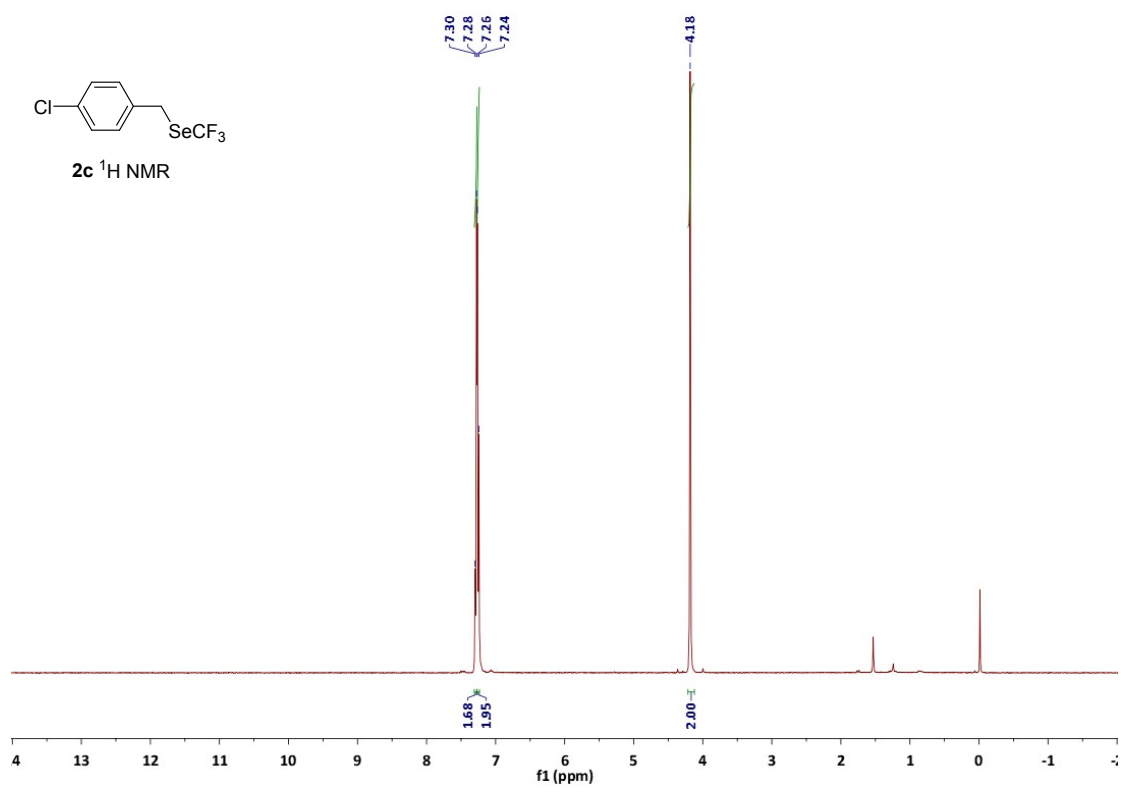
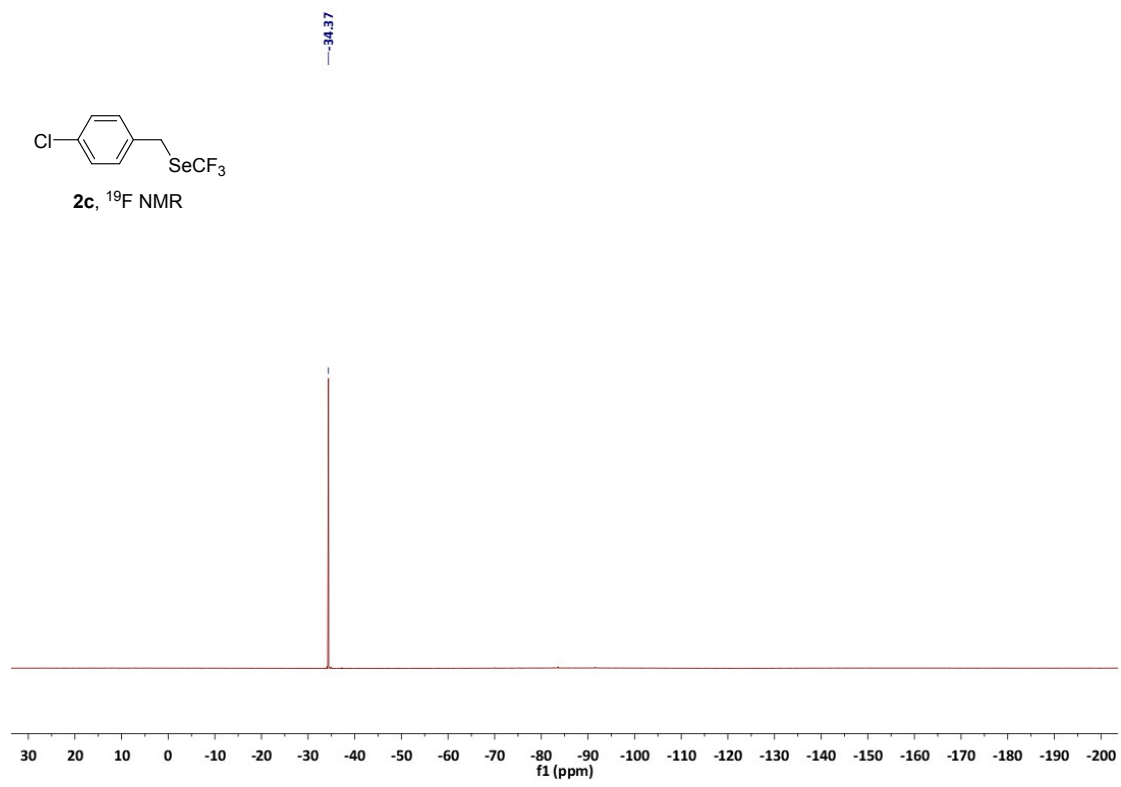
- (1) C. Chen, L. Ouyang, Q. Lin, Y. Liu, C. Hou, Y. Yuan and Z. Weng, *Chem. Eur. J.*, 2014, **20**, 657-661.
- (2) C. Chen, C. Hou, Y. Wang, T. S. A. Hor and Z. Weng, *Org. Lett.*, 2014, **16**, 524-527.
- (3) M. Rong, R. Huang, Y. You and Z. Weng, *Tetrahedron*, 2014, **70**, 8872-8878.

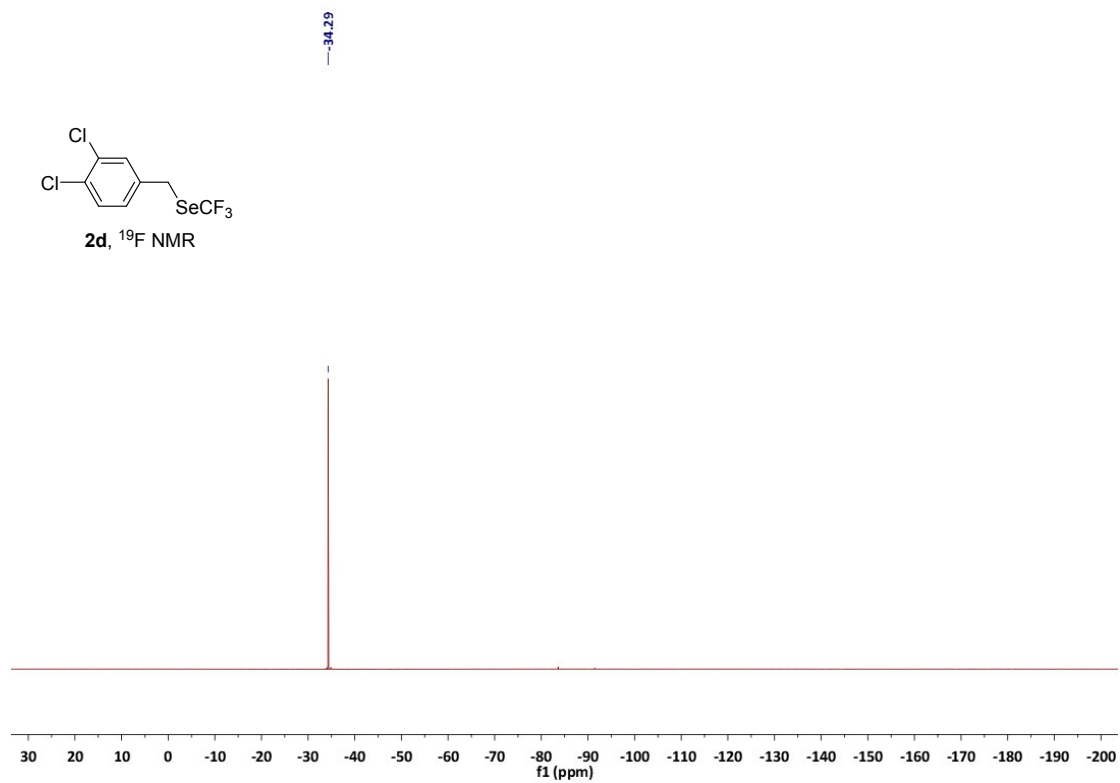
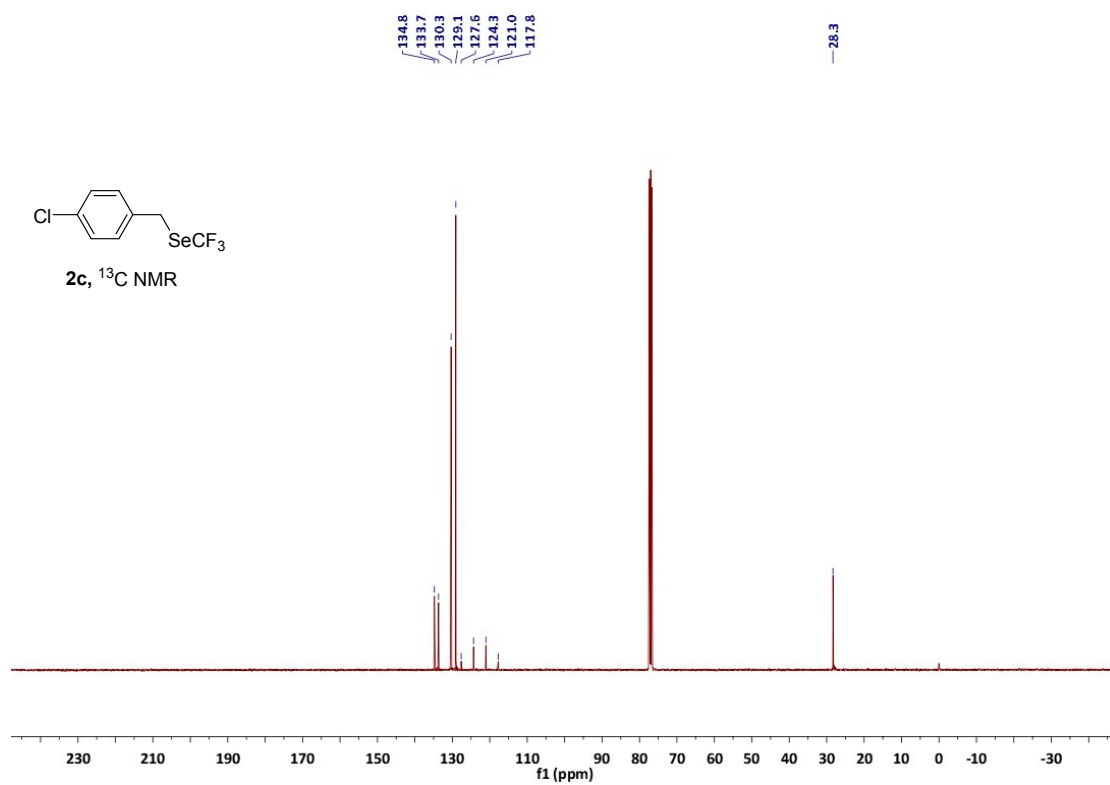
5. Copies of ^{19}F NMR, ^1H NMR, and ^{13}C NMR spectra

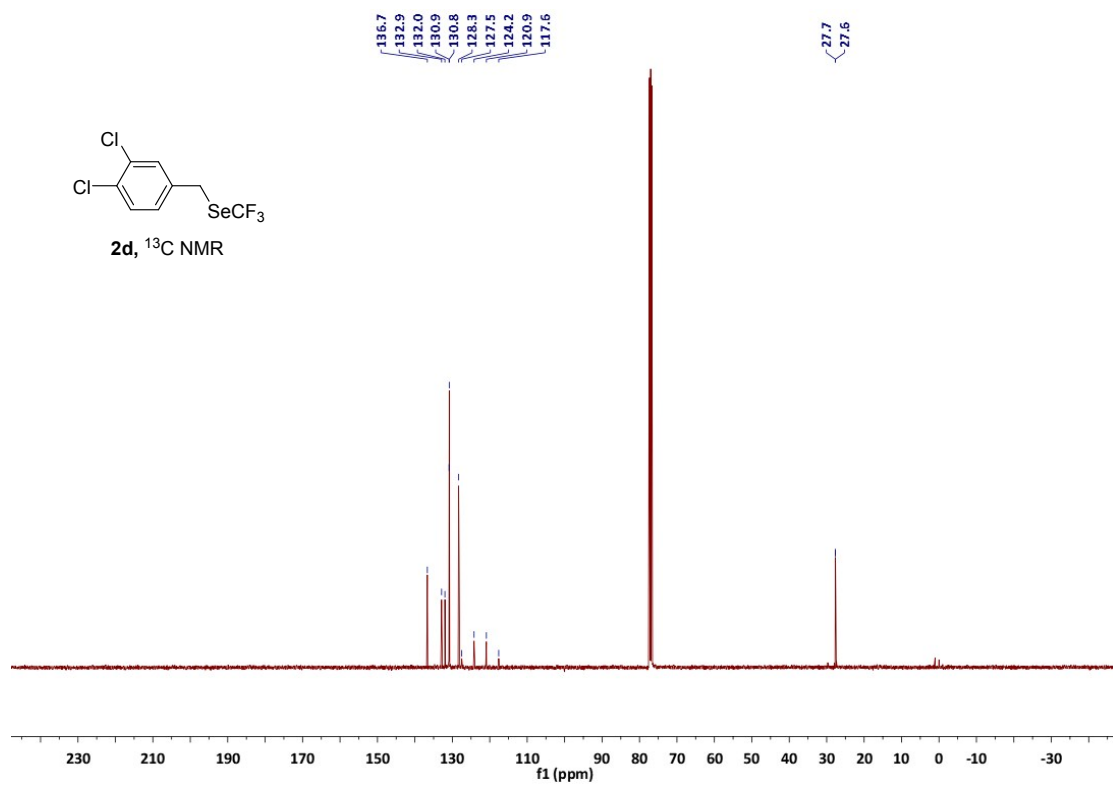
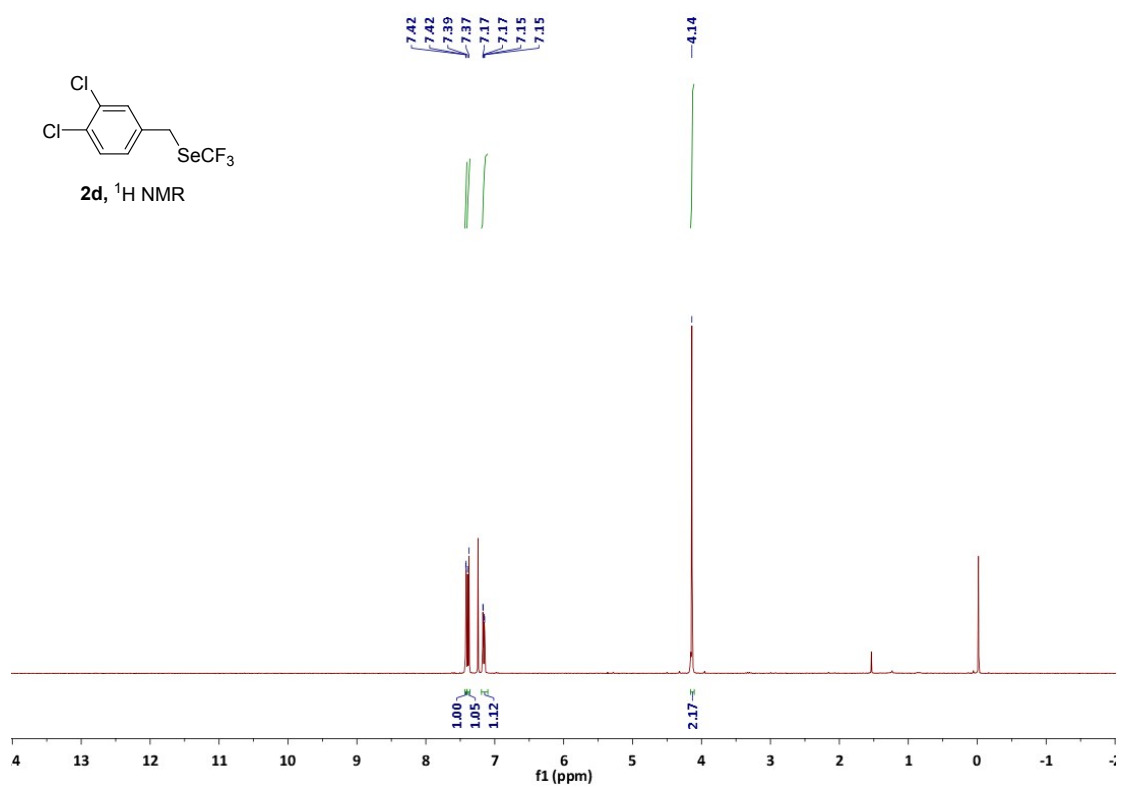


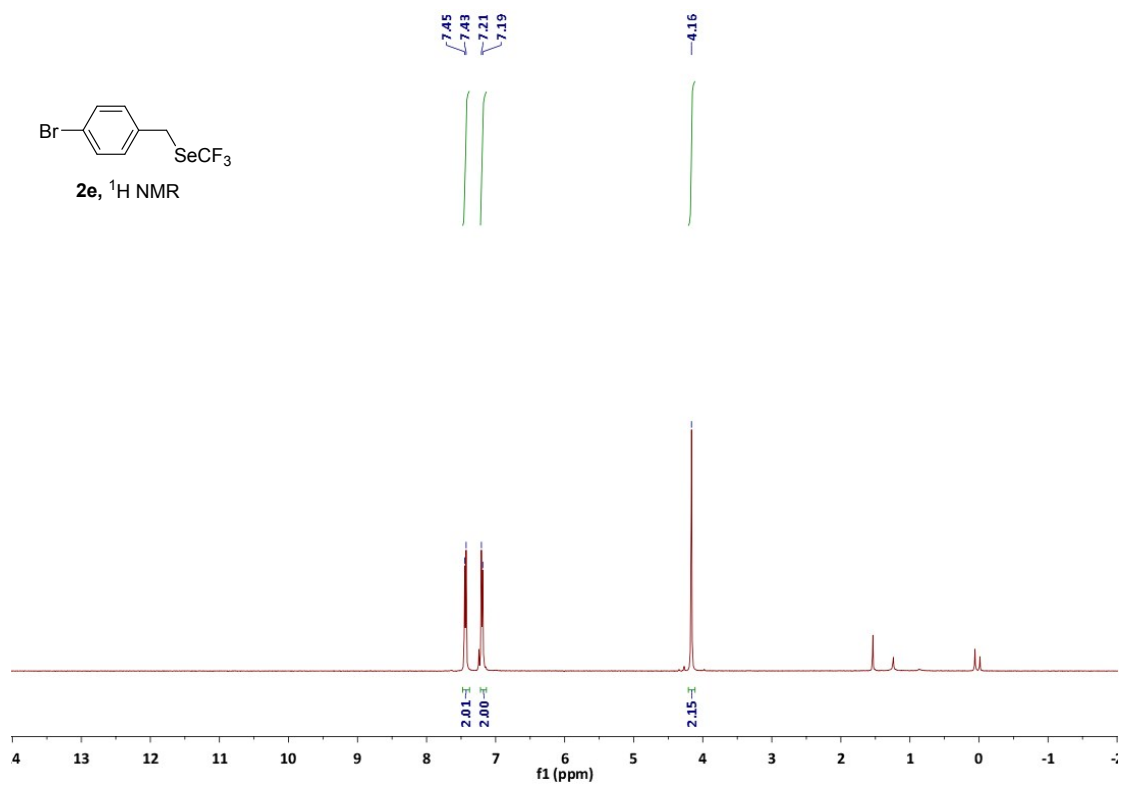
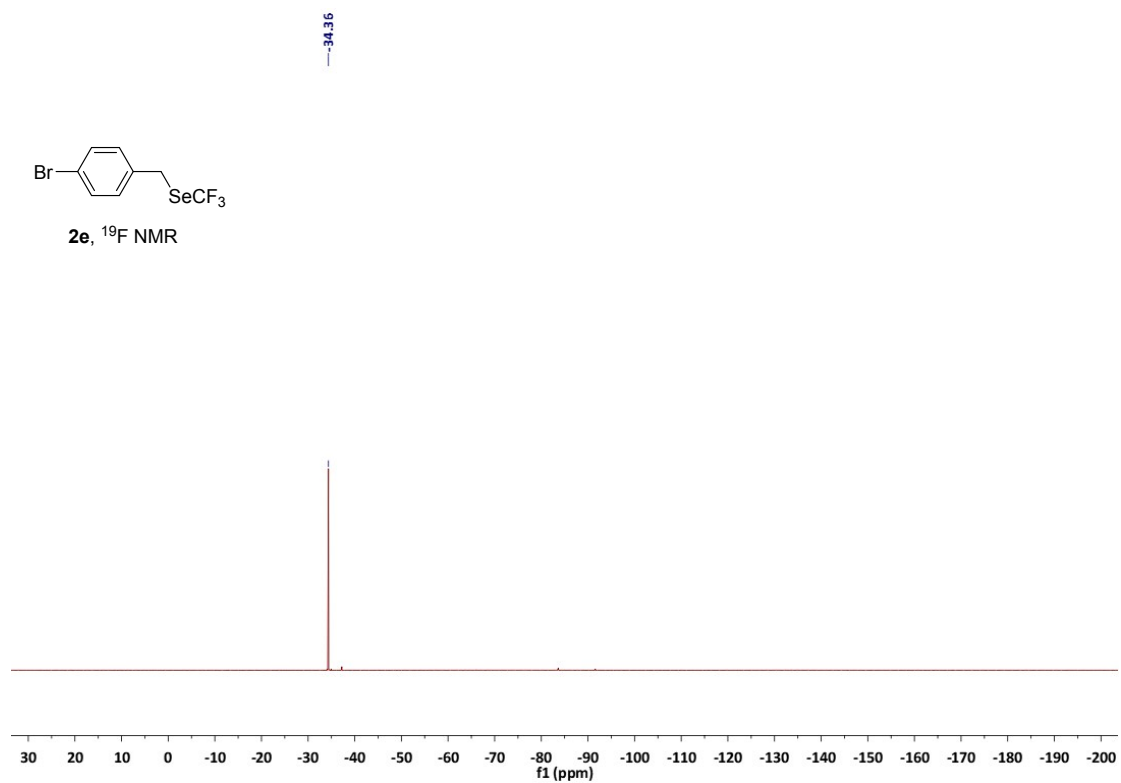


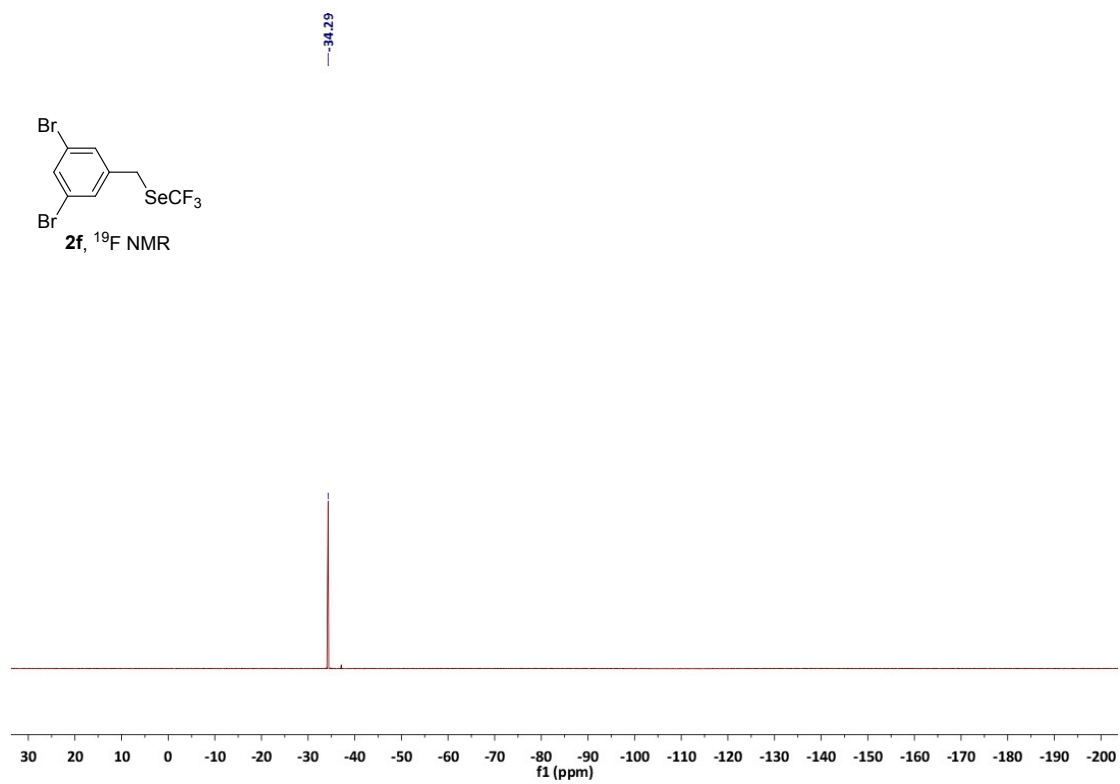
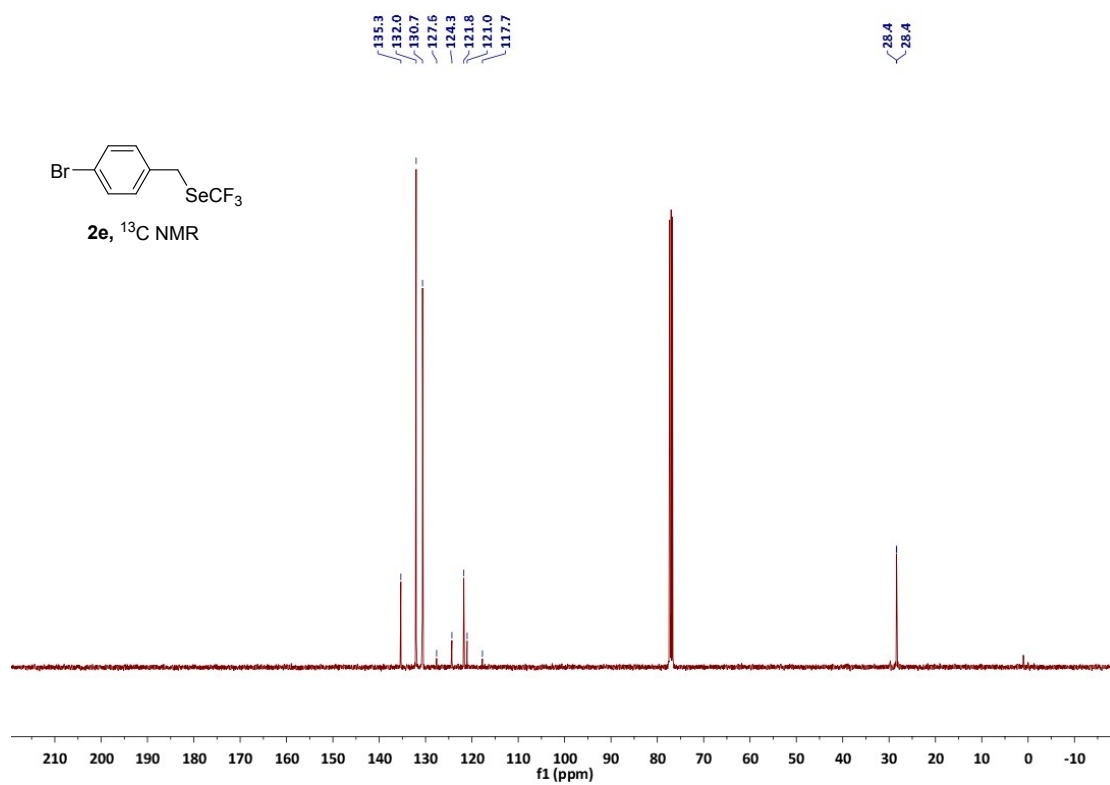


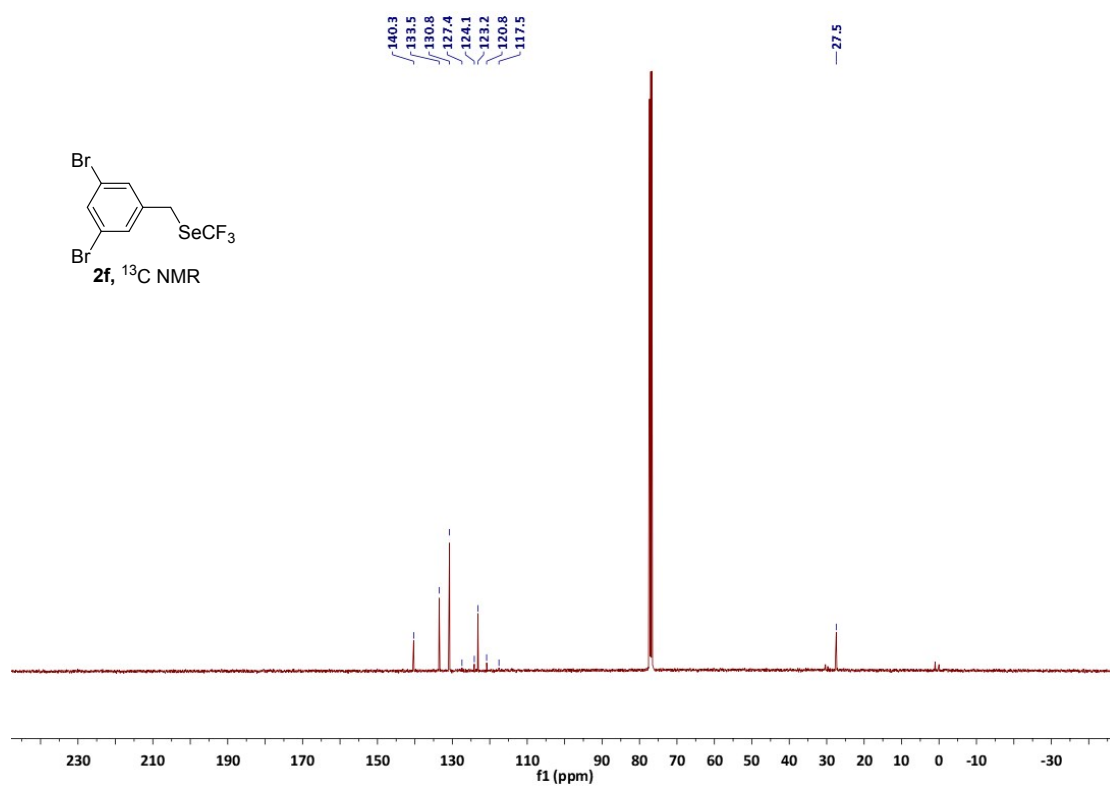
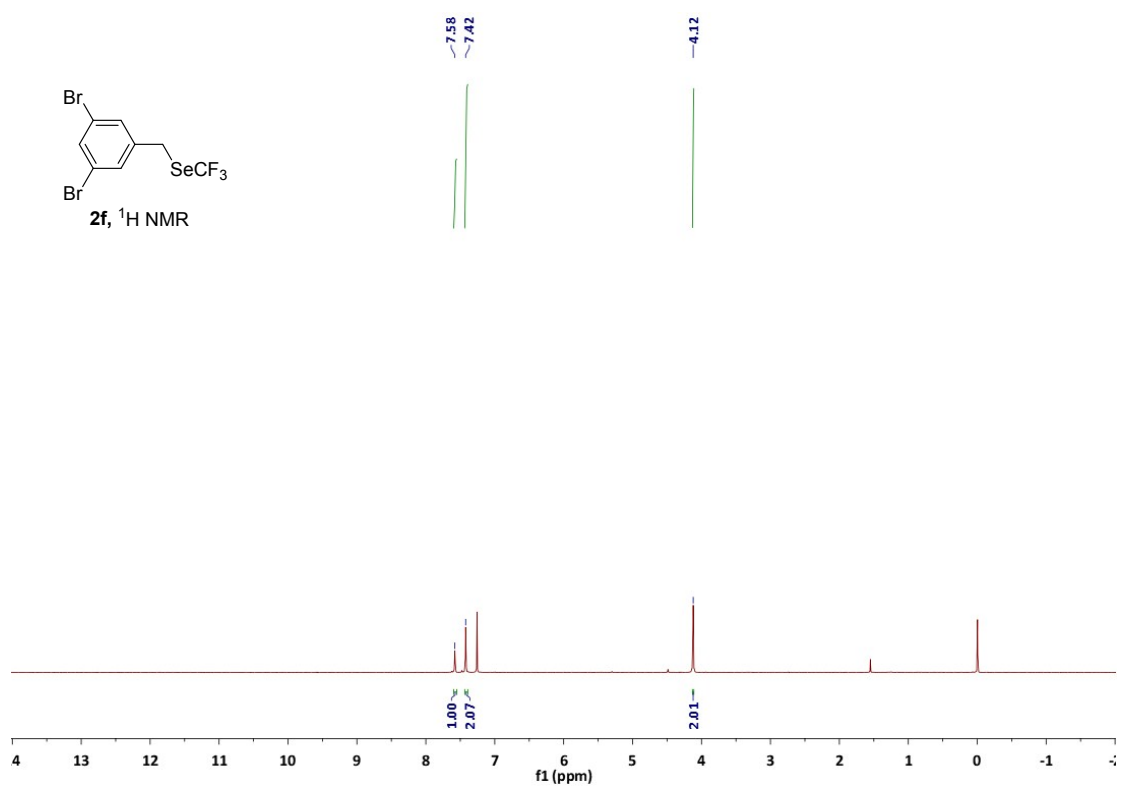


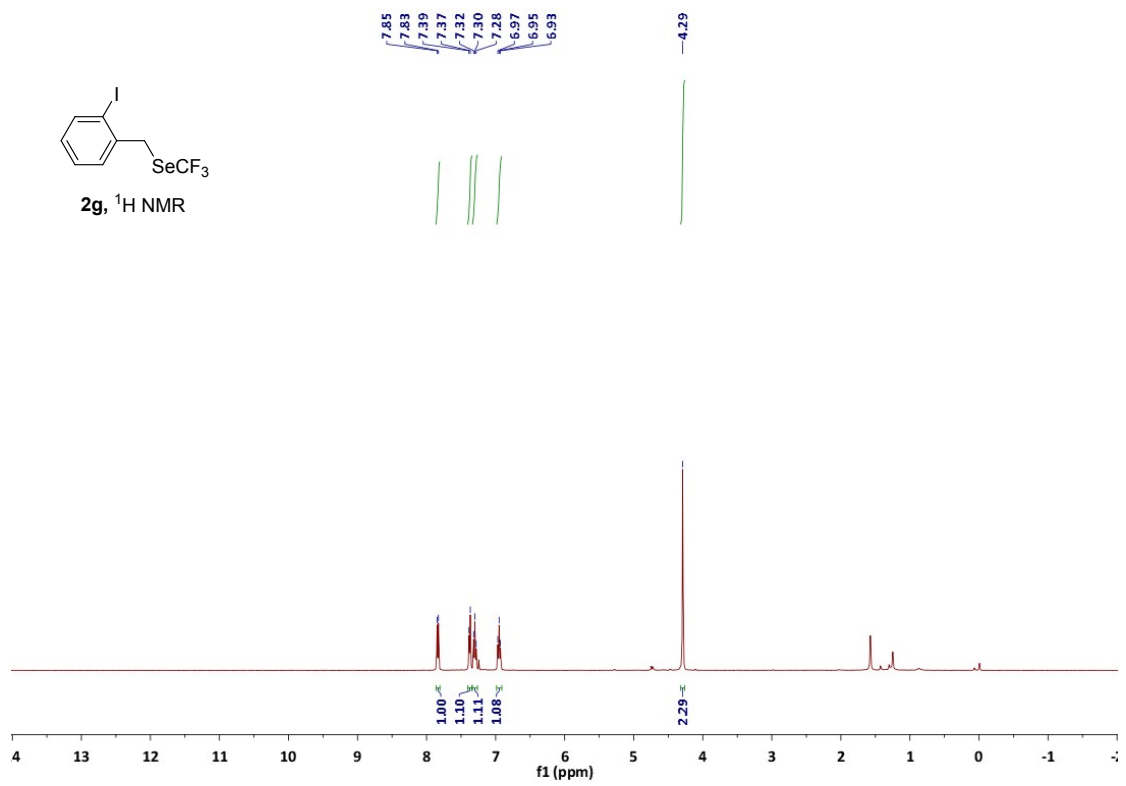
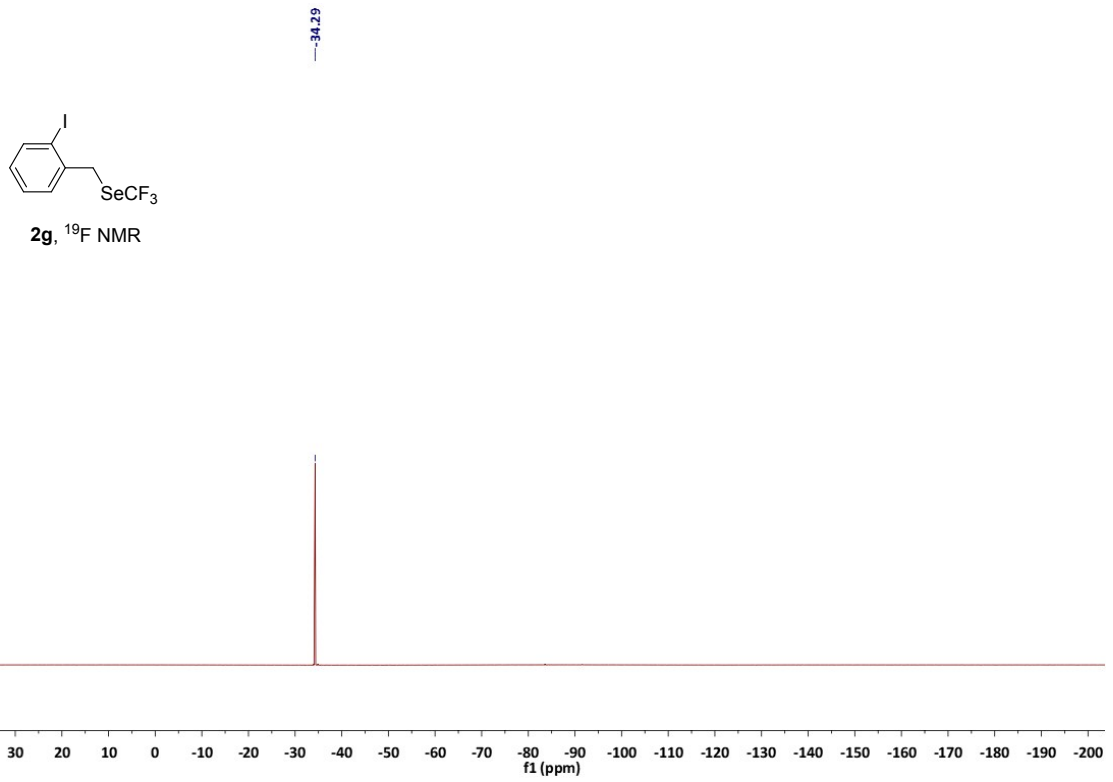


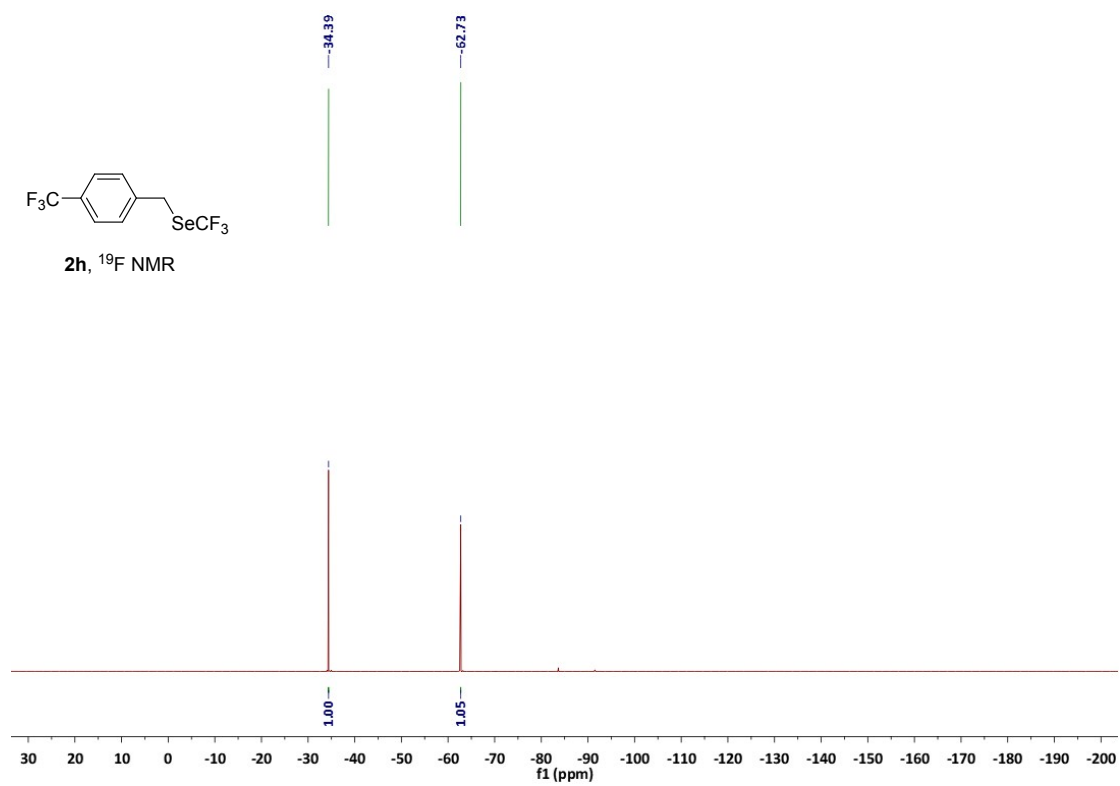
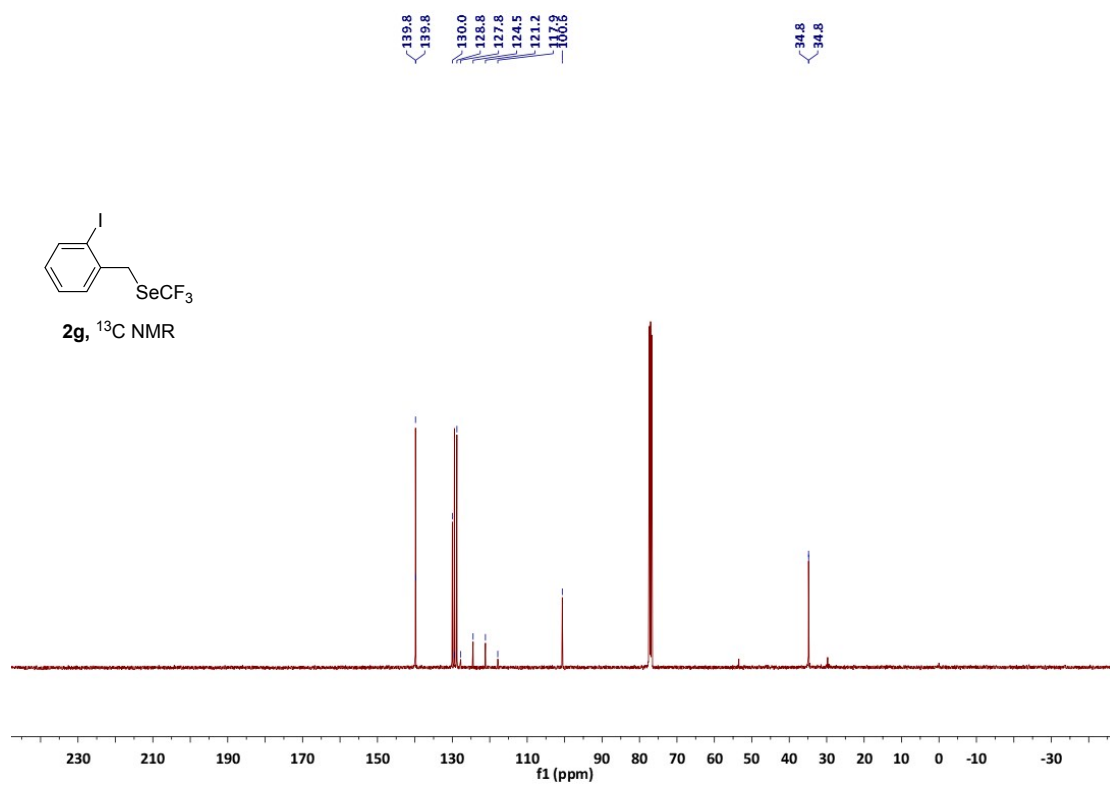


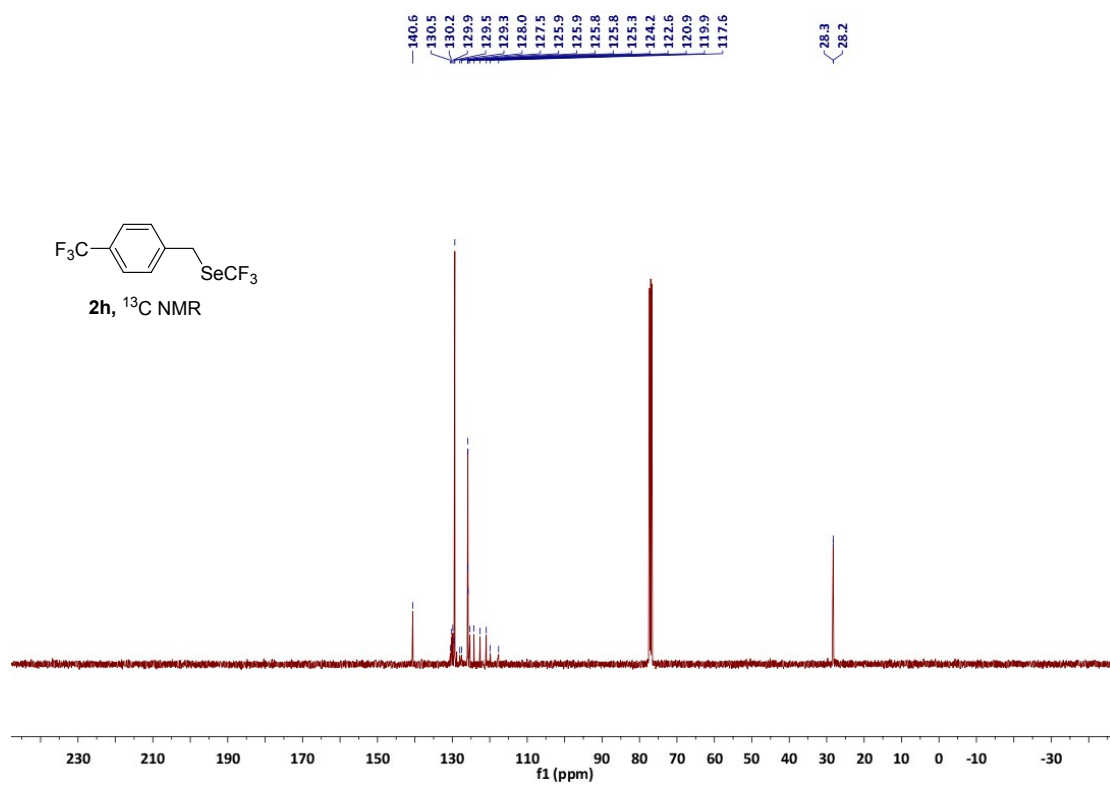
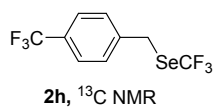
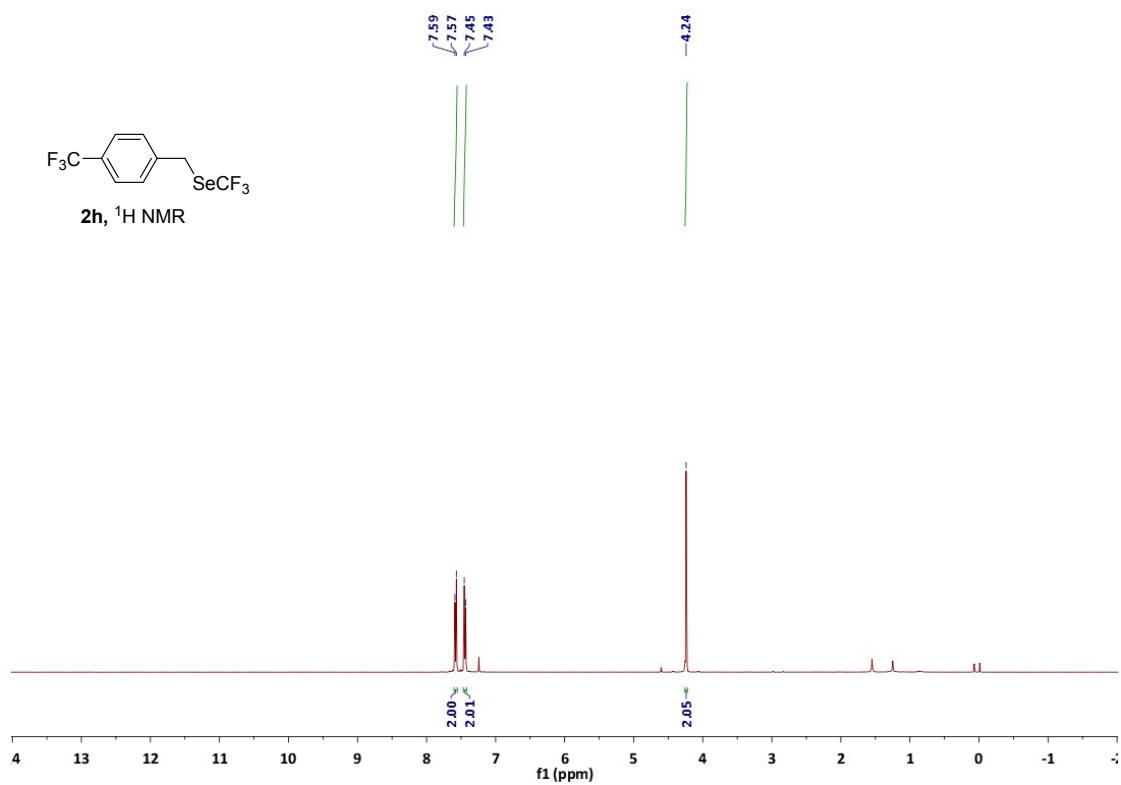
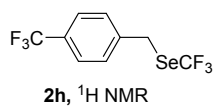


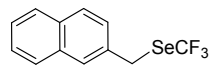




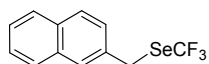
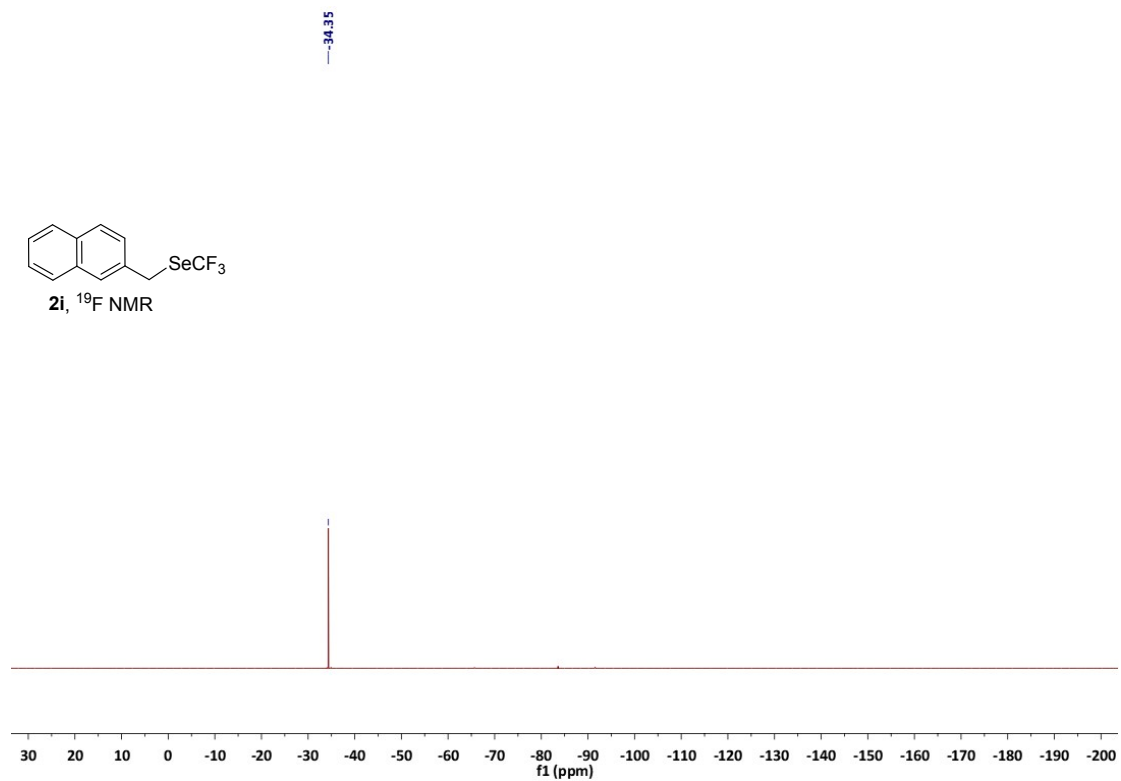




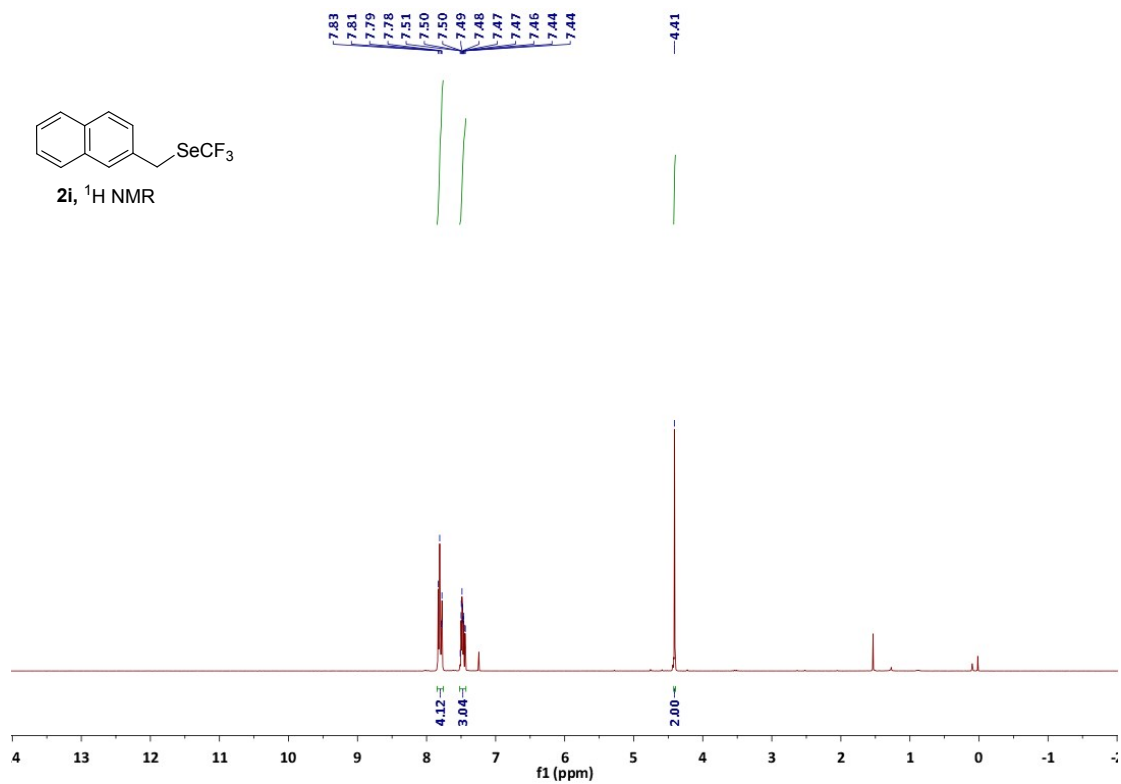


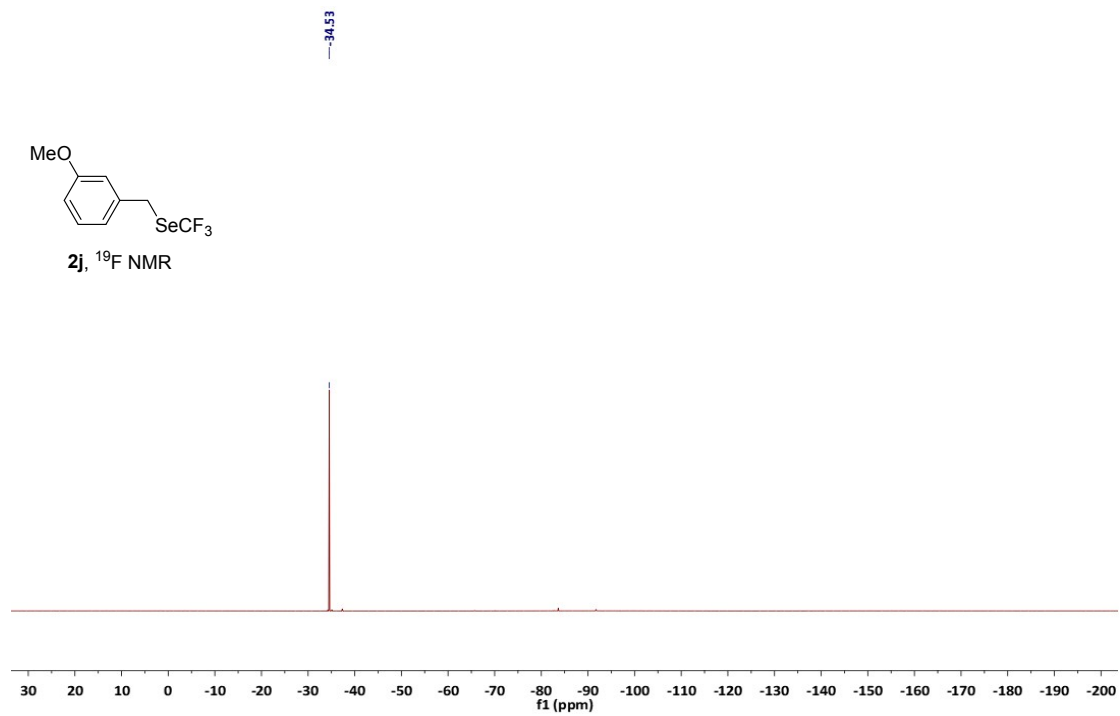
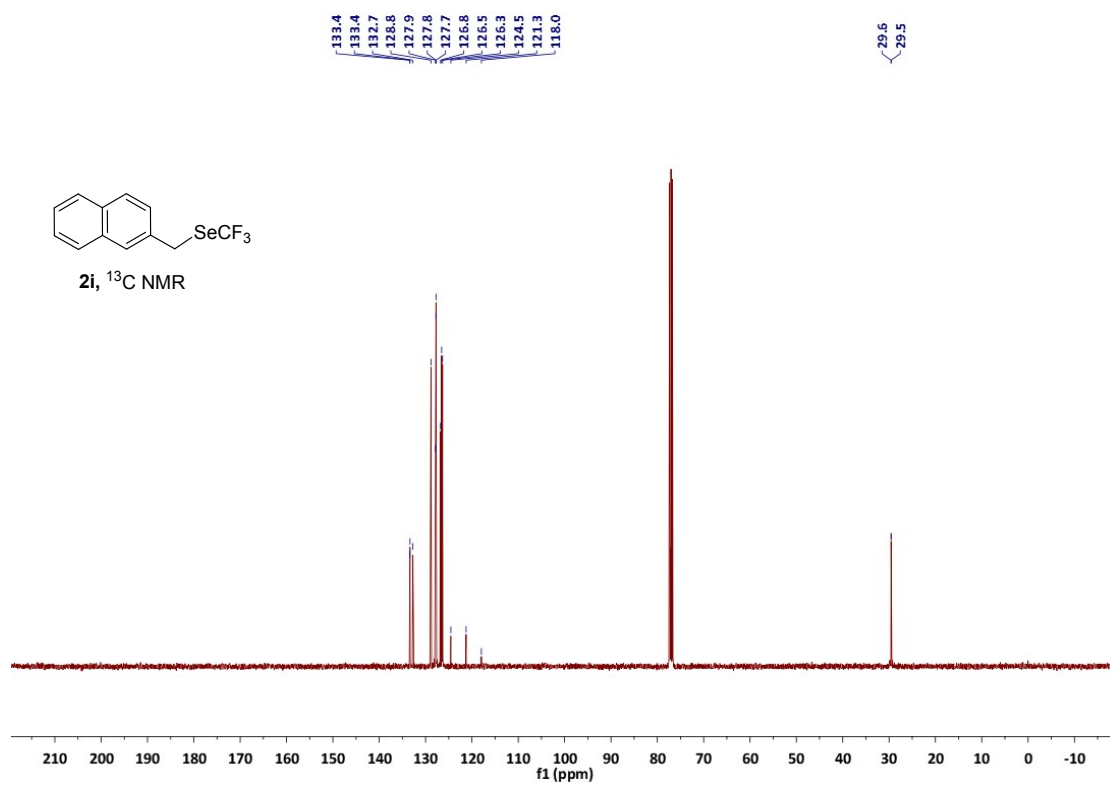


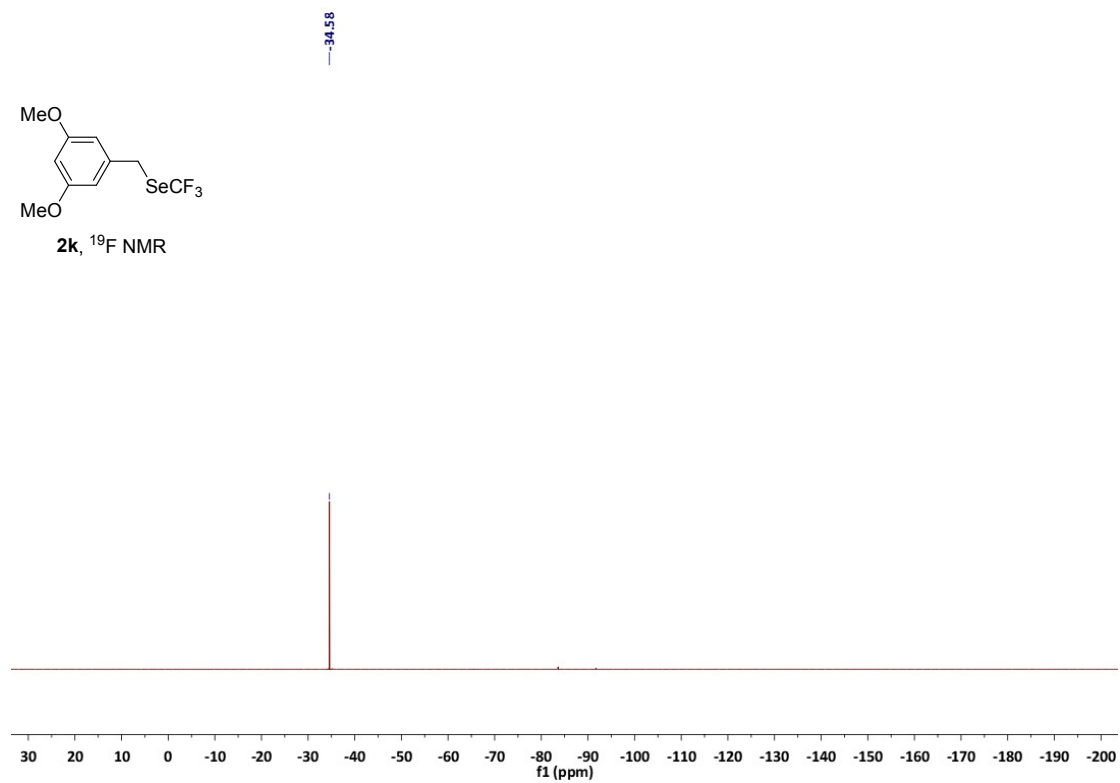
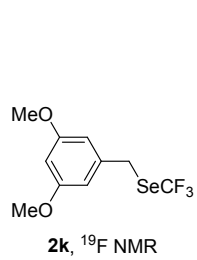
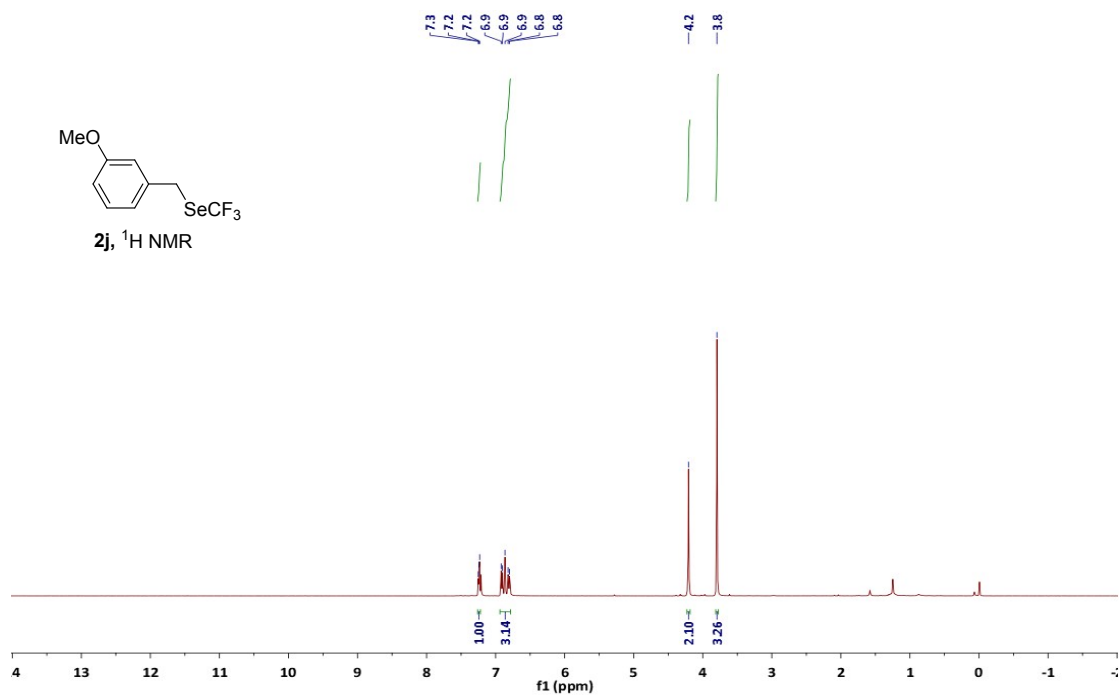
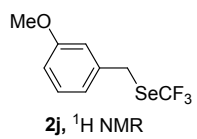
2i, ^{19}F NMR

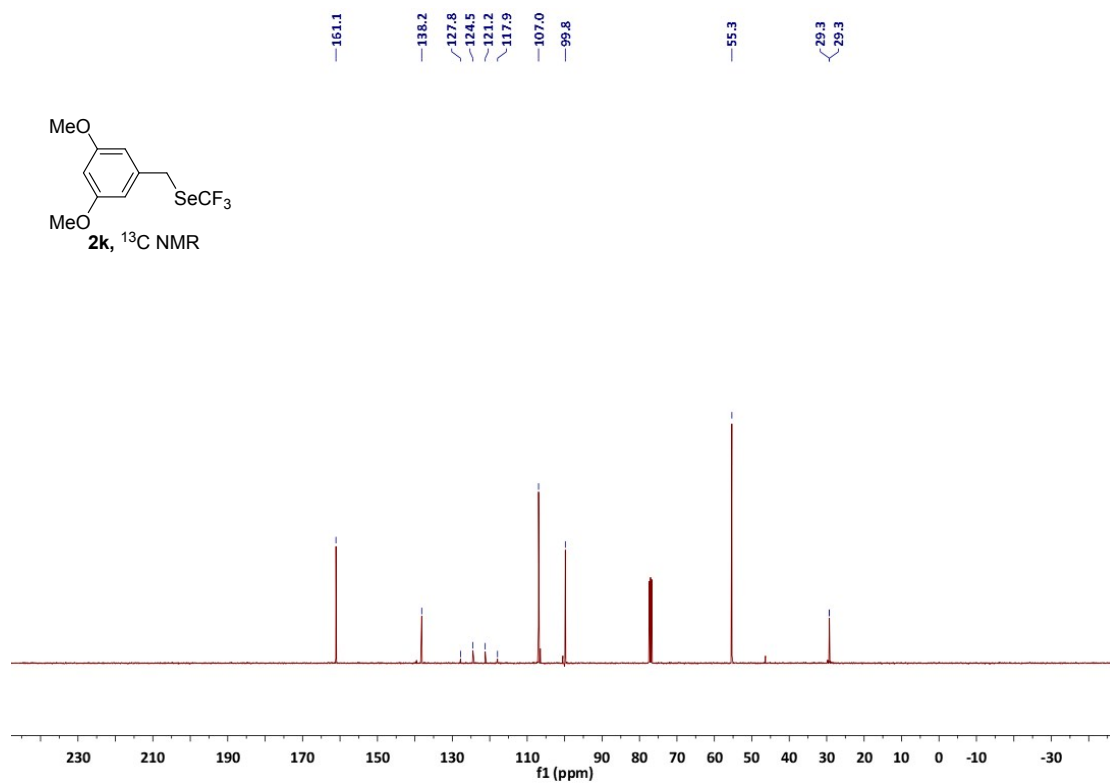
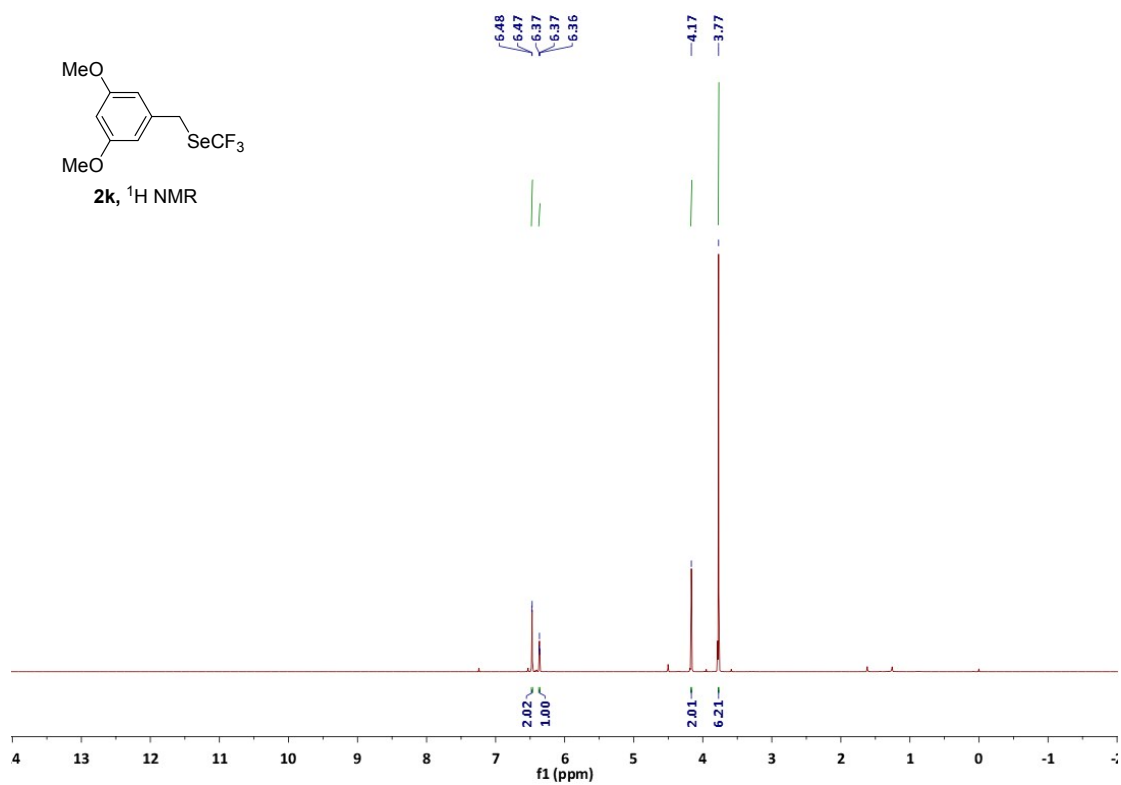


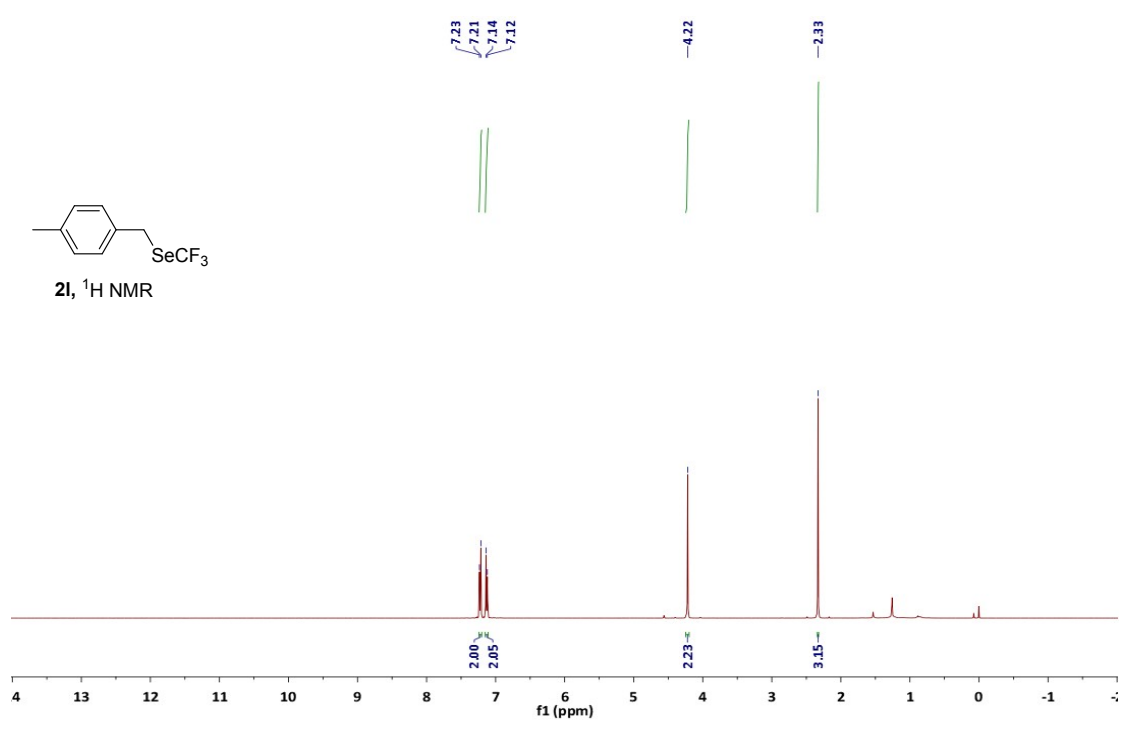
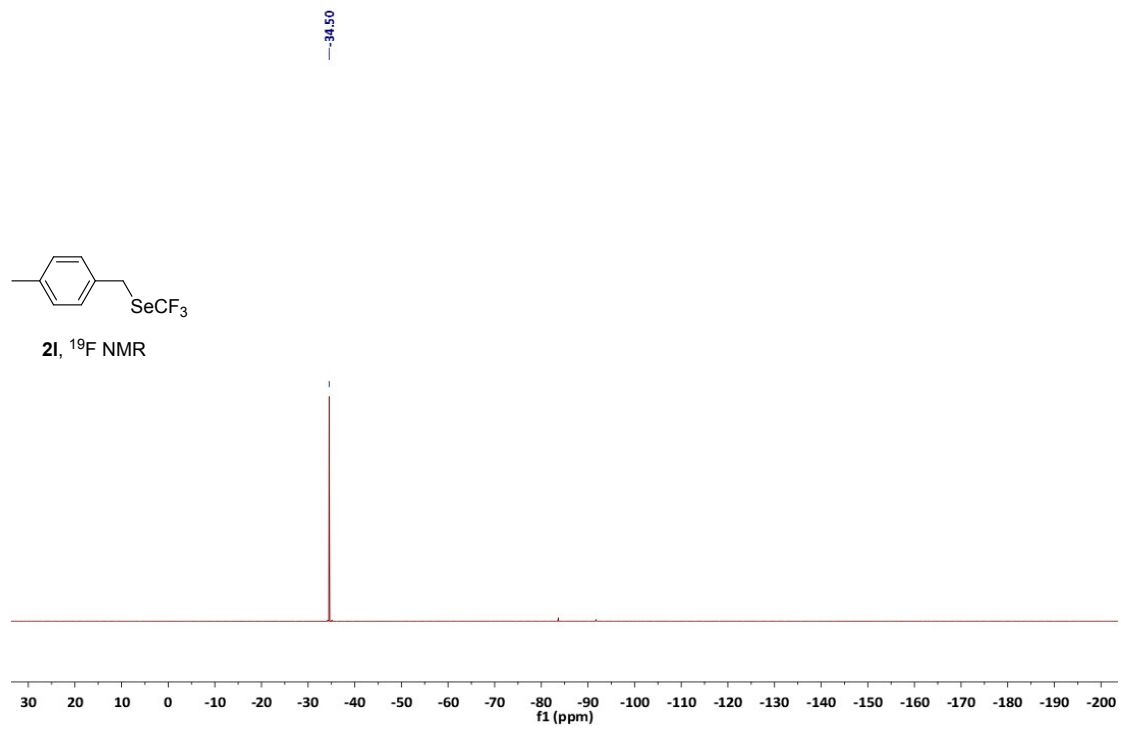
2i, ^1H NMR

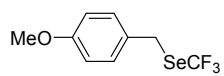




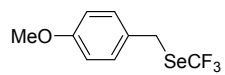
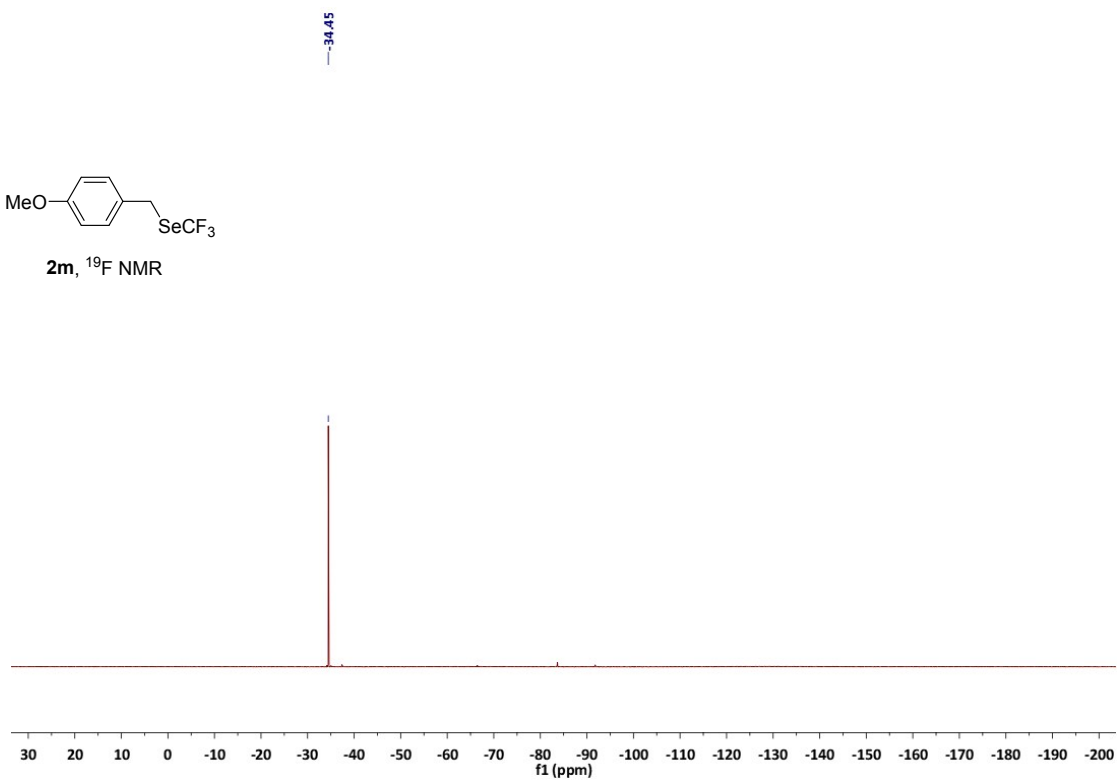




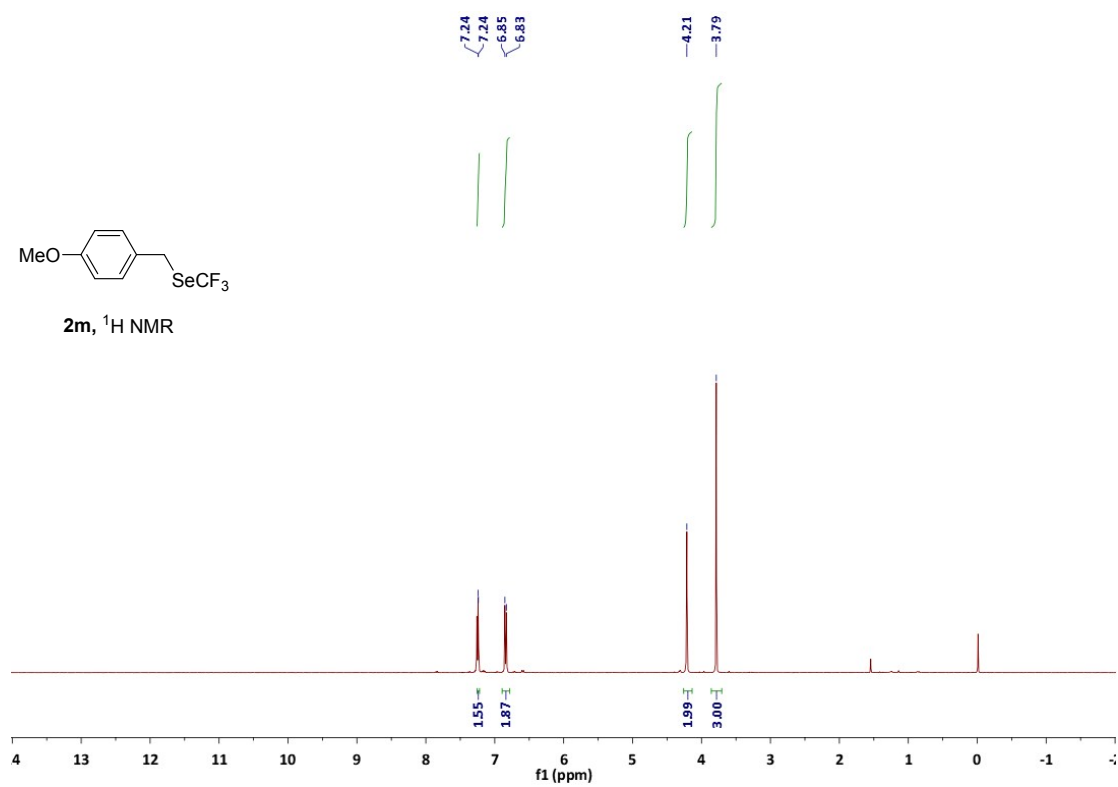


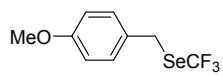


2m, ^{19}F NMR



2m, ^1H NMR





2m, ^{13}C NMR

