Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper Catalyzed Oxidative Coupling Reactions for Trifluoromethylselenolations - Synthesis of R-$SeCF_3$ Compounds with Air Stable Tetramethylammonium trifluoromethylselenate

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1. General Information

Pentane was distilled. Other solvents were used as purchased unless otherwise stated. Commercial reagents were used as purchased without further purification. Me_4NSeCF_3 was prepared according to the reported procedure.[1] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was carried out using Merck Kieselgel 60 silica gel (230-400 mesh). Thin-layer chromatography was carried out using Merck Kieselgel 60 F_{254} (230-400 mesh) fluorescent treated silica and were visualized under UV light (250 and 354 nm) or by staining with aqueous potassium permanganate solution.

^{1}H NMR spectra were recorded in deuterated solvents on Varian spectrometers at 300, 400 or 600 MHz, with residual protic solvent as the internal standard. ^{13}C NMR spectra were recorded in deuterated solvents on Bruker or Varian spectrometers at 75, 100 or 125 MHz, with the central peak of the deuterated solvent as the internal standard. ^{19}F NMR spectra were recorded in deuterated solvents on Bruker or Varian spectrometers at 376 or 564 MHz. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (*J*) are given in Hertz (Hz). The ^{1}H NMR spectra are reported as δ/ppm downfield from tetramethylsilane (multiplicity, number of protons, assignment, coupling constant *J*/Hz). The ^{13}C and ^{19}F NMR spectra are reported as δ/ppm, with multiplicity and coupling constant (*J*/Hz) where relevant. IR spectra were recorded on a Perkin Elmer 1760 FTIR spectrometer, only diagnostic absorbances (λ_{max}) are reported. Low resolution mass spectra were recorded on a Thermo Finnigan SSQ 7000 mass spectrometer (CI, Methane). Melting points were recorded on a Büchi Melting Point M-565 apparatus, at ambient pressure and are uncorrected.

Alkynes **1a**, **1b**, **1c**, **1e**, **1f**, **1g**, **1i**, **1j**, **1k**, **1l** and boronic acids **3a**, **3b**, **3c**, **3d**, **3f**, **3k**, **3l** were purchased from commercial sources. Boronic acids and esters **5e**[2], **3g**[3], **5h**[4], **3i**[5], **5j**[6], **5m**[7], **5n**[8] and alkynes **1d**[9], **1h**[10] were prepared according to reported procedures. All analytical data match previously reported values.

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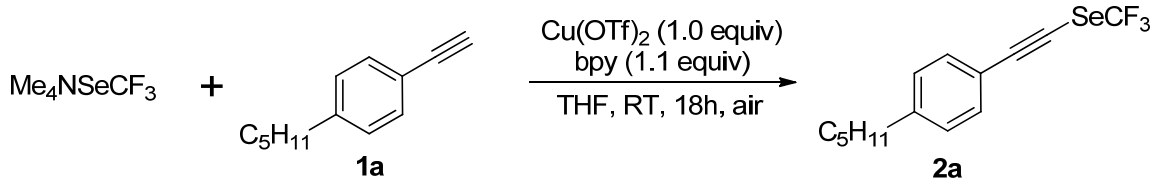
[1] Naumann, D.; Tyrra, W.; Yagupolskii, Y. L. *J. Fluorine Chem.* **2003**, 123, 183-187.
[2] Fürstner, A.; Seidel, G.; *Org. Lett.* **2002**, 4, 541 – 543.
[3] Diemer, V.; Chaumeil, H.; Defoin, A.; Fort, A.; Boeglin, A.; Carre, C.; *Eur. J Org. Chem.* **2008**, 10, 1767 – 1776.
[4] Xie, F.; Zhao, H.; Li, D.; Chen, H.; Quan, H.; Shi, X.; Lou, L.; Hu, Y.; *J. Med. Chem.* **2011**, 54, 3200 – 3205.
[5] Hoffmann, M.; Bischoff, D.; Dahmann, G.; Klicic, J.; Schaenzle, G.; Wollin, S. L. M.; Convers-Reignier, S. G.; East, S. P.; Marlin, F. J.; McCarthy, C.; Scott, J.; *WO2013/14060*, **2013.**
[6] Nakagawa, H.; Kawai, S.; Nakashima, T.; Kawai, T.; *Org. Lett.* **2009**, 1475 – 1478.
[7] Yuan, W.; Ma, S.; *Org. Biomol. Chem.* **2012**, 10, 7266 – 7268.
[8] Brown, J. M.; Lloyd-Jones, G. C.; *J. Am. Chem. Soc.* **1994**, 116, 866 – 878.
[9] Takalo, H.; Kankare, J.; Haenninen, E.; *Acta Chem. Scand. B* **1988**, 42, 448 – 454.
[10] Ames, D. E.; Bull, D.; Takundwa, C.; *Synthesis* **1981**, 5, 364 – 365.

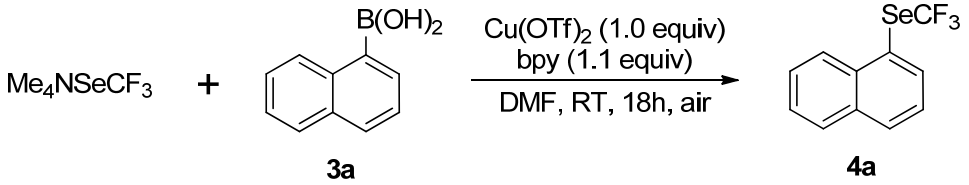
2. *Optimization of the conditions for terminal alkynes*



Entry [a]	solvent	Cu source	ligand	additive	Yield (%) [b]
1	**THF**	**$Cu(OTf)_2$ (1 equiv)**	**bpy**	**-**	**93**
2[c]	THF	$Cu(OTf)_2$ (1 equiv)	bpy	-	<2
3[d]	THF	$Cu(OTf)_2$ (1 equiv)	bpy	-	94
4	THF	$Cu(OTf)_2$ (10 mol%)	bpy	-	<5
5	THF	-	bpy	-	0
6	THF	$Cu(OTf)_2$ (1 equiv)	-	-	9
7	THF	$Cu(OTf)_2$ (1 equiv)	bpy	KF (2 equiv)	53
8	THF	$Cu(OTf)_2$ (1 equiv)	bpy	Cs_2CO_3 (2 equiv)	33
9	THF	$Cu(OTf)_2$ (1 equiv)	bpy	K_3PO_4 (2 equiv)	55
10	DMF	$Cu(OTf)_2$ (1 equiv)	bpy	-	77
11	DMSO	$Cu(OTf)_2$ (1 equiv)	bpy	-	87
12	**MeCN**	**$Cu(OTf)_2$ (1 equiv)**	**bpy**	**-**	**93**
13	MeOH	$Cu(OTf)_2$ (1 equiv)	bpy	-	86
14	MeOH/H_2O 9:1	$Cu(OTf)_2$ (1 equiv)	bpy	-	83
15	DCE	$Cu(OTf)_2$ (1 equiv)	bpy	-	65
16	toluene	$Cu(OTf)_2$ (1 equiv)	bpy	-	16
17	hexane	$Cu(OTf)_2$ (1 equiv)	bpy	-	<5
18	THF	$CuSO_4$ (1 equiv)	bpy	-	<5
19	THF	$Cu(acac)_2$ (1 equiv)	bpy	-	<5
20	THF	$Cu(OAc)_2$ (1 equiv)	bpy	-	25
21	THF	CuI (1 equiv)	bpy	-	38
22[c]	THF	CuI (1 equiv)	bpy	-	0
23	THF	CuTC (1 equiv)	bpy	-	16
24	THF	$Cu(MeCN)_4PF_6$ (1 equiv)	bpy	-	40
25	THF	$Cu(OTf)_2$ (1 equiv)	bpy-OMe	-	86
26	THF	$Cu(OTf)_2$ (1 equiv)	dtbpy	-	88
27	THF	$Cu(OTf)_2$ (1 equiv)	phen	-	74
28	THF	$Cu(OTf)_2$ (1 equiv)	TMEDA	-	81

[a] Reaction conditions: Alkyne **1a** (0.10 mmol), Me_4NSeCF_3 (0.11 mmol), $Cu(OTf)_2$ (0.10 mmol) and bipyridine (0.11 mmol) in THF (1 mL) were stirred at RT for 18h; [b] Yields were determined by ^{19}F NMR analysis with $PhCF_3$ as internal standard; [c] Reaction under argon atmosphere; [d] reaction under oxygen atmosphere;

3. Optimization of the conditions for boronic acids

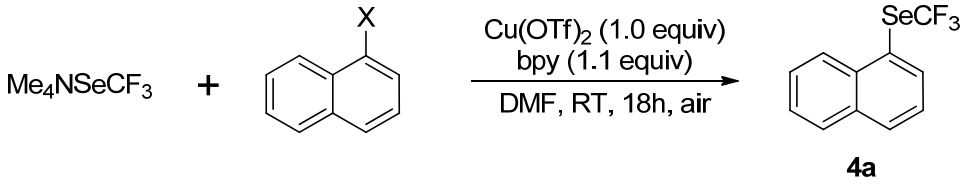


3a **4a**

Entry[a]	solvent	Cu source	ligand	additive	Yield (%) [b]
1	**DMF**	**$Cu(OTf)_2$ (1 equiv)**	**bpy**	**-**	**88**
2[c]	DMF	$Cu(OTf)_2$ (1 equiv)	bpy	-	20
3[d]	DMF	$Cu(OTf)_2$ (1 equiv)	bpy	-	90
4	DMF	$Cu(OTf)_2$ (10 mol%)	bpy	-	7
5	DMF	-	bpy	-	0
6	DMF	$Cu(OTf)_2$ (1 equiv)	-	-	26
7	DMF	$Cu(OTf)_2$ (1 equiv)	bpy	KF (2 equiv)	78
8	DMF	$Cu(OTf)_2$ (1 equiv)	bpy	Cs_2CO_3 (2 equiv)	67
9	DMF	$Cu(OTf)_2$ (1 equiv)	bpy	K_3PO_4 (2 equiv)	77
10	DMF	$Cu(OTf)_2$ (1 equiv)	bpy	MS 4Å	81
11	DMSO	$Cu(OTf)_2$ (1 equiv)	bpy	-	82
12	MeCN	$Cu(OTf)_2$ (1 equiv)	bpy	-	73
13	MeOH	$Cu(OTf)_2$ (1 equiv)	bpy	-	77
14	MeOH/H_2O 9:1	$Cu(OTf)_2$ (1 equiv)	bpy	-	82
15	DCE	$Cu(OTf)_2$ (1 equiv)	bpy	-	37
16	THF	$Cu(OTf)_2$ (1 equiv)	bpy	-	57
17	toluene	$Cu(OTf)_2$ (1 equiv)	bpy	-	50
18	hexane	$Cu(OTf)_2$ (1 equiv)	bpy	-	15
19	DMF	$CuSO_4$ (1 equiv)	bpy	-	52
20	DMF	$Cu(acac)_2$ (1 equiv)	bpy	-	35
21	DMF	$Cu(OAc)_2$ (1 equiv)	bpy	-	27
22	DMF	CuI (1 equiv)	bpy	-	33
23[c]	DMF	CuI (1 equiv)	bpy	-	0
24	DMF	CuTC (1 equiv)	bpy	-	64
25	DMF	$Cu(MeCN)_4PF_6$ (1 equiv)	bpy	-	61
26	DMF	$Cu(OTf)_2$ (1 equiv)	bpy-OMe	-	81
27	DMF	$Cu(OTf)_2$ (1 equiv)	dtbpy	-	79
28	DMF	$Cu(OTf)_2$ (1 equiv)	phen	-	78
29	DMF	$Cu(OTf)_2$ (1 equiv)	TMEDA	-	65

[a] Reaction conditions: boronic acid **3a** (0.10 mmol), Me_4NSeCF_3 (0.11 mmol), $Cu(OTf)_2$ (0.10 mmol) and bipyridine (0.11 mmol) in THF (1 mL) were stirred at RT for 18h; [b] Yields were determined by ^{19}F NMR analysis with $PhCF_3$ as internal standard; [c] Reaction under argon atmosphere; [d] Reaction under oxygen atmosphere;

4. Reaction with different nucleophiles:



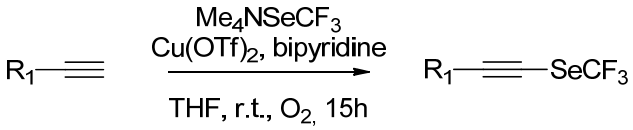
4a

Entry [a]	X	Yield (%) [b]
1	**-B(OH)$_2$**	**88**
2	**-B(Pin)**	**87**
3	**-B(Neop)**	**82**
4	-B(MIDA)	26
5	-B(DEAM)	52
6	-BF_3K	0
7	-$SnMe_3$	27

[a] Reaction conditions: nucleophile (0.10 mmol), Me_4NSeCF_3 (0.11 mmol), $Cu(OTf)_2$ (0.10 mmol) and bipyridine (0.11 mmol) in DMF (1 mL) were stirred at RT for 18h; [b] Yields were determined by ^{19}F NMR analysis with $PhCF_3$ as internal standard; *B(Pin)* – boronic acid pinacol ester, *B(Neop)* – boronic acid neopentyl glycol ester, *B(MIDA)* – boronic acid *N*-methyliminodiacetic ester, *B(DEAM)* – boronic acid *N*-methyldiethanolamine ester.

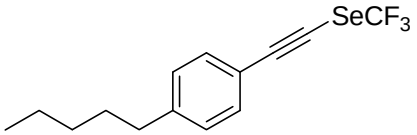
5. Trifluoromethylselenolation of alkynes by Me_4NSeCF_3

General procedure



The terminal alkyne (0.30 mmol, 1.0 equiv), copper (II) triflate (109 mg, 0.30 mmol, 1.0 equiv), bipyridine (51.5 mg, 0.33 mmol, 1.1 equiv) and tetramethylammonium trifluoromethylselenate (83.3 mg, 0.375 mmol, 1.25 equiv) were loaded into a tube under air and dissolved in THF (2 mL). The tube was closed with a septum, and the deep green solution was stirred at room temperature under oxygen atmosphere (balloon) for 18h. Upon completion of the reaction, the crude mixture was directly loaded onto a silica gel column and eluted with pentane. The fractions containing the product were carefully evaporated under reduced pressure (300 mbar, 30°C). The solvent was then evaporated under reduced pressure (200 mbar, 30°C) to give analytically pure samples.

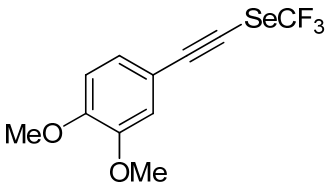
Preparation and characterisation of 1-(trifluoromethylseleno)ethynyl-4-pentylbenzene 2a



Prepared according to the general procedure on 0.3 mmol scale. Colourless oil, 90%.

FT-IR ν_{max}(ATR) 3031, 2929, 2860, 2327, 2166, 2064, 1907, 1606, 1506, 1460, 1409, 1377, 1280, 1152, 1088, 828, 739 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 0.90 (t, 3H, C<u>*H*</u>$_3$, *J* 7.1 Hz), 1.28-1.38 (m, 4H, 2 × C<u>*H*</u>$_2$), 1.59-1.64 (m, 2H, C<u>*H*</u>$_2$), 2.62 (t, 2H, C<u>*H*</u>$_2$, *J* 7.8 Hz), 7.17 (d, 2H, 2 × Ar-C<u>*H*</u>, *J* 8.1 Hz), 7.42 (d, 2H, 2 × Ar-C<u>*H*</u>, *J* 8.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.1 (<u>*C*</u>H$_3$), 22.7 (<u>*C*</u>H$_2$), 31.0 (<u>*C*</u>H$_2$), 31.6 (<u>*C*</u>H$_2$), 36.1 (<u>*C*</u>H$_2$), 61.0 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 3.0 Hz), 107.6 (<u>*C*</u>quat.), 119.3 (<u>*C*</u>quat.), 120.9 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 336.6 Hz), 128.7 (2 × Ar-<u>*C*</u>H), 132.3 (2 × Ar-<u>*C*</u>H), 145.1 (<u>*C*</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.4 (SeC<u>*F*</u>$_3$); **MS** (CI): *m/z* (%) 299.0 (7) $[M-F-2]^+$, 301.0 (16) $[M-F]^+$, 317.0 (19) $[M-3]^+$, 318.0 (42) $[M-2]^+$, 319.0 (32) $[M-1]^+$, 320.0 (100) $[M]^+$, 321.0 (86) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{14}H_{15}F_3{}^{80}Se]$ 320.0285, measured 320.0284.

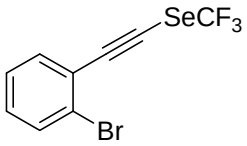
Preparation and characterisation of 4-(trifluoromethylseleno)ethynyl-1,2-dimethoxybenzene 2b



Prepared according to the general procedure on 0.14 mmol scale. Colourless oil, 80%. **FT-IR** ν_{max}(ATR) 3080, 3004, 2947, 2838, 2679, 2589, 2319, 2156, 1996, 1908, 1734, 1592, 1510, 1445, 1406, 1323,

1254, 1146, 1086, 1023, 947, 855, 808, 743 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.88 (s, 3H, C$\underline{H}_3$), 3.90 (s, 3H, C$\underline{H}_3$), 6.82 (d, 1H, Ar-C$\underline{H}$, *J* 8.3 Hz), 6.99 (d, 1H, Ar-C$\underline{H}$, *J* 1.8 Hz), 7.13 (dd, 1H, Ar-C$\underline{H}$, *J* 1.8, 8.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 56.1 ($\underline{C}H_3$), 56.1 ($\underline{C}H_3$), 60.3 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 3.1 Hz), 107.5 ($\underline{C}$quat.), 111.0 (Ar-$\underline{C}$H), 114.2 ($\underline{C}$quat.), 114.9 (Ar-$\underline{C}$H), 120.8 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 336.5 Hz), 126.3 (Ar-$\underline{C}$H), 148.7 ($\underline{C}$quat.), 150.7 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.4 (SeC$\underline{F}_3$); **MS** (CI): *m/z* (%) 160.9 (48) $[M-SeCF_3]^+$, 239.7 (89) $[M-CF_3-1]^+$, 240.9 (72) $[M-CF_3]^+$, 305.9 (24) $[M-4]^+$, 306.8 (30) $[M-3]^+$, 308.4 (31) $[M-2]^+$, 309.2 (39) $[M-1]^+$, 310.0 (38) $[M]^+$, 311.0 (41) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{11}H_9O_2F_3{}^{80}Se]$ 309.9714, measured 309.9713.

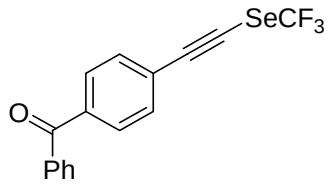
Preparation and characterisation of 1-bromo-2-(trifluoromethylseleno)ethynylbenzene 2c



Prepared according to the general procedure on 0.14 mmol scale. Colourless oil, 58%.

FT-IR ν_{max}(ATR) 3066, 2664, 2325, 2172, 2081, 1993, 1922, 1805, 1729, 1619, 1585, 1556, 1466, 1429, 1272, 1226, 1153, 1084, 945, 836, 749, 665 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.22 (app dt, 1H, Ar-C$\underline{H}$, *J* 1.7, 7.8 Hz), 7.29 (app dt, 1H, Ar-C$\underline{H}$, *J* 1.1, 7.6 Hz), 7.50 (dd, 1H, Ar-C$\underline{H}$, *J* 1.6, 7.7 Hz), 7.60 (dd, 1H, Ar-C$\underline{H}$, *J* 0.8, 8.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 67.1 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 3.0 Hz), 105.7 ($\underline{C}$quat.), 120.8 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 336.6 Hz),124.4 ($\underline{C}$quat.), 125.7 ($\underline{C}$quat.), 127.2 (Ar-$\underline{C}$H), 130.6 (Ar-$\underline{C}$H), 132.7 (Ar-$\underline{C}$H), 133.7 (Ar-$\underline{C}$H); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.6 (SeC$\underline{F}_3$); **MS** (CI): *m/z* (%) 258.3 (22) $[M-CF_3]^+$, 259.9 (18) $[M-CF_3+1]^+$, 323.9 (42) $[M-4]^+$, 325.0 (59) $[M-3]^+$, 326.0 (75) $[M-2]^+$, 327.2 (100) $[M-1]^+$, 328.1 (93) $[M]^+$, 329.1 (80) $[M+1]^+$, 330.0 (62) $[M+2]^+$, 331.0 (40) $[M+3]^+$; **HRMS** (EI): calc. for $[C_9H_4{}^{79}BrF_3{}^{80}Se]$ 327.8608, measured 327.8595.

Preparation and characterisation of 4-(trifluoromethylseleno)ethynylbenzophenone 2d

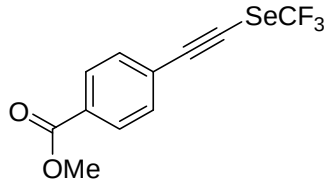


Prepared according to the general procedure on 0.3 mmol scale. Colourless solid, 95%.

m.p. 68-70 °C; **FT-IR** ν_{max}(ATR) 3066, 2320, 2170, 2073, 1930, 1738, 1643, 1596, 1446, 1402, 1278, 1142, 1082, 924, 846, 788, 736, 691 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.49 (t, 2H, 2 × Ar-C$\underline{H}$, *J* 8.7 Hz), 7.57-7.61 (m, 3H, 3 × Ar-C$\underline{H}$), 7.77-7.79 (m, 4H, 4 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 65.6 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 3.0 Hz), 106.5 ($\underline{C}$quat.), 120.7 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 336.5 Hz), 126.0 ($\underline{C}$quat.), 128.5 (2 × Ar-$\underline{C}$H), 130.1 (2 × Ar-$\underline{C}$H), 130.1 (2 × Ar-$\underline{C}$H), 131.6 (2 × Ar-$\underline{C}$H), 132.8 (Ar-$\underline{C}$H), 137.2 ($\underline{C}$quat.), 137.9 ($\underline{C}$quat.), 195.8 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.7 (SeC$\underline{F}_3$); **MS** (CI): *m/z* (%) 69.2

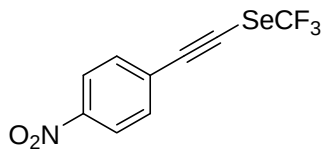
(74) $[CF_3]^+$, 105.2 (16) $[C_6H_5CO]^+$, 351.5 (43) $[M-3]^+$, 352.5 (76) $[M-2]^+$, 353.6 (89) $[M-1]^+$, 354.6 (100) $[M]^+$, 355.5 (98) $[M+1]^+$. Analytical data in accordance with literature.[11]

Preparation and characterisation of methyl 4-(trifluoromethylseleno)ethynylbenzoate 2e



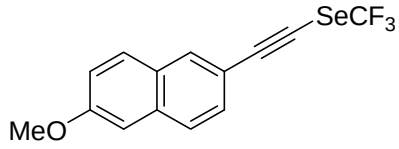
Prepared according to the general procedure on 0.3 mmol scale. Colourless solid, 87%. **m.p.** 38-40 °C; **FT-IR** ν_{max}(ATR) 2953, 2325, 2087, 1997, 1927, 1722, 1604, 1559, 1437, 1277, 1153, 1087, 966, 854, 764, 693 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.92 (s, 3H, C<u>H</u>$_3$), 7.52 (d, 2H, 2 × Ar-C<u>H</u>, *J* 8.3 Hz), 8.01 (d, 2H, 2 × Ar-C<u>H</u>, *J* 8.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 52.5 (<u>C</u>H$_3$), 65.5 (q, <u>C</u>quat., $J_{C\text{-}F}$ 3.0 Hz), 106.5 (<u>C</u>quat.), 120.7 (q, <u>C</u>quat., $J_{C\text{-}F}$ 336.6 Hz), 126.5 (<u>C</u>quat.), 129.7 (2 × Ar-<u>C</u>H), 130.6 (<u>C</u>quat.), 131.7 (2 × Ar-<u>C</u>H), 166.4 (<u>C</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.8 (SeC<u>F</u>$_3$); **MS** (CI): *m/z* (%) 69.2 (84) $[CF_3]^+$, 304,2 (33) $[M-4]^+$, 305.2 (50) $[M-3]^+$, 306.1 (63) $[M-2]^+$, 307.2 (100) $[M-1]^+$, 308.2 (95) $[M]^+$, 309.2 (93) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{11}H_7O_2F_3{}^{80}Se]$ 307.9557, measured 307.9555.

Preparation and characterisation of 4-(trifluoromethylseleno)ethynyl-1-nitrobenzene 2f



Prepared according to the general procedure on 0.3 mmol scale. Yellow solid, 91%.**m.p.** 68-70 °C; **FT-IR** ν_{max}(ATR) 3108, 2935, 2861, 2171, 1939, 1734, 1597, 1528, 1347, 1286, 1148, 1082, 855, 738, 683 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.61 (d, 2H, 2 × Ar-C<u>H</u>, *J* 8.9 Hz), 8.22 (d, 2H, 2 × Ar-C<u>H</u>, *J* 8.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 68.6 (q, <u>C</u>quat., $J_{C\text{-}F}$ 2.9 Hz), 105.4 (<u>C</u>quat.), 120.7 (q, <u>C</u>quat., $J_{C\text{-}F}$ 336.6 Hz), 123.8 (2 × Ar-<u>C</u>H), 128.6 (<u>C</u>quat.), 132.4 (2 × Ar-<u>C</u>H), 147.7 (<u>C</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.4 (SeC<u>F</u>$_3$); **MS** (CI): *m/z* (%) 69.3 (58) $[CF_3]^+$, 291.3 (68) $[M-4]^+$, 292.4 (46) $[M-3]^+$, 293.4 (94) $[M-2]^+$, 294.2 (73) $[M-1]^+$, 295.1 (76) $[M]^+$, 296.0 (100) $[M+1]^+$. Analytical data in accordance with literature.[11]

Preparation and characterisation of 6-(trifluoromethylseleno)ethynyl-2-methoxynaphthalene 2g

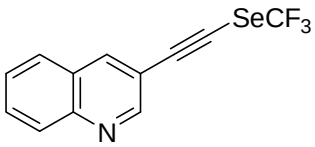


Prepared according to the general procedure on 0.3 mmol scale. Colourless solid, 84%. **m.p.** 109-111 °C; **FT-IR** ν_{max}(ATR) 3063, 2937, 2846, 2644, 2323, 2153, 1918, 1739, 1618, 1481,

[11] Cheng, C. et al., *Chem, Eur. J.*, **2014**, 20, 657-661
[11] Cheng, C. et al., *Chem, Eur. J.*, **2014**, 20, 657-661

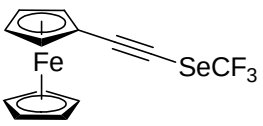
1388, 1240, 1142, 1079, 1031, 938, 895, 846, 810, 732, 664 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.93 (s, 3H, C<u>*H*</u>$_3$), 7.10 (d, 1H, Ar-C<u>*H*</u>, *J* 2.5 Hz), 7.18 (dd, 1H, Ar-C<u>*H*</u>, *J* 2.5, 8.9 Hz), 7.49 (dd, 1H, Ar-C<u>*H*</u>, *J* 1.6, 8.4 Hz), 7.69 (m, 2H, 2 × Ar-C<u>*H*</u>), 7.96 (s, 1H, Ar-C<u>*H*</u>); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 55.5 (<u>*C*</u>H_3), 61.3 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 3.0 Hz), 105.9 (Ar-<u>*C*</u>H), 108.0 (<u>*C*</u>quat.), 116.9 (<u>*C*</u>quat.), 119.8 (Ar-<u>*C*</u>H), 120.9 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 336.4 Hz), 127.1 (Ar-<u>*C*</u>H), 128.3 (<u>*C*</u>quat.), 129.0 (Ar-<u>*C*</u>H), 129.7 (Ar-<u>*C*</u>H), 132.6 (Ar-<u>*C*</u>H), 134.9 (<u>*C*</u>quat.), 158.9 (<u>*C*</u>quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.3 (SeC<u>*F*</u>$_3$); **MS** (CI): *m/z* (%) 69.1 (67) $[CF_3]^+$, 327.5 (37) $[M-3]^+$, 328.4 (63) $[M-2]^+$, 329.4 (56) $[M-1]^+$, 330.5 (100) $[M]^+$, 331.5 (60) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{14}H_9OF_3{}^{80}Se]$ 329.9765, measured 329.9762.

Preparation and characterisation of 3-(trifluoromethylseleno)ethynylquinoline 2h



Prepared according to the general procedure on 0.3 mmol scale. Colourless solid, 81%. **m.p.** 67-69 °C; **FT-IR** ν_{max}(ATR) 3459, 3014, 2308, 2184, 2110, 2030, 1980, 1910, 1738, 1614, 1565, 1484, 1442, 1365, 1217, 1098, 903, 746 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.57 (app t, 1H, Ar-C<u>*H*</u>, *J* 7.5 Hz), 7.74 (ddd, 1H, Ar-C<u>*H*</u>, *J* 1.3, 7.0, 8.3 Hz), 7.77 (d, 1H, Ar-C<u>*H*</u>, *J* 8.2 Hz), 8.09 (d, 1H, Ar-C<u>*H*</u>, *J* 8.5 Hz), 8.27 (d, 1H, Ar-C<u>*H*</u>, *J* 1.7 Hz), 8.92 (d, 1H, Ar-C<u>*H*</u>, *J* 2.0 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 65.9 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 3.0 Hz), 104.6 (<u>*C*</u>quat.), 116.2 (<u>*C*</u>quat.), 120.8 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 336.6 Hz), 127.0 (<u>*C*</u>quat.), 127.7 (Ar-<u>*C*</u>H), 127.9 (Ar-<u>*C*</u>H), 129.6 (Ar-<u>*C*</u>H), 130.9 (Ar-<u>*C*</u>H), 139.6 (Ar-<u>*C*</u>H), 147.3 (<u>*C*</u>quat.), 151.8 (Ar-<u>*C*</u>H); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.7 (SeC<u>*F*</u>$_3$); **MS** (CI): *m/z* (%) 69.2 (2) $[CF_3]^+$, 297.9 (56) $[M-3]^+$, 299.2 (46) $[M-2]^+$, 300.1 (78) $[M-1]^+$, 301.1 (54) $[M]^+$, 302.0 (100) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{12}H_6NF_3{}^{80}Se]$ 300.9612, measured 300.9614.

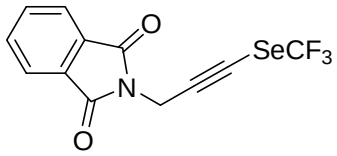
Preparation and characterisation of (trifluoromethylseleno)ethynylferrocene 2i



Prepared according to the general procedure on 0.3 mmol scale. Orange solid, 54%. **m.p.** 74-76 °C; **FT-IR** ν_{max}(ATR) 3931, 3101, 3015, 2653, 2306, 2149, 1906, 1739, 1368, 1228, 1140, 1083, 924, 819, 733 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 4.24 (s, 5H, 5 × Ar-C<u>*H*</u>), 4.29 (s, 2H, 2 × Ar-C<u>*H*</u>), 4.53 (s, 2H, 2 × Ar-C<u>*H*</u>); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 57.5 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 3.0 Hz), 63.0 (<u>*C*</u>quat.), 69.8 (2 × Ar-<u>*C*</u>H), 70.3 (5 × Ar-<u>*C*</u>H), 72.6 (2 × Ar-<u>*C*</u>H), 107.9 (<u>*C*</u>quat.), 120.3 (q, <u>*C*</u>quat., $J_{C\text{-}F}$ 336.9 Hz); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –37.2 (SeC<u>*F*</u>$_3$); **MS** (CI): *m/z* (%) 209.1 (18) $[M-SeCF_3]^+$, 288.0 (27)

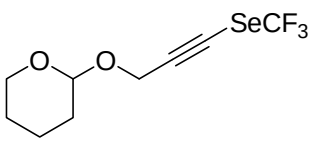
$[M-CF_3-1]^+$, 289.1 (18) $[M-CF_3]^+$, 355.5 (50) $[M-3]^+$, 356.5 (78) $[M-2]^+$, 357.6 (91) $[M-1]^+$, 358.5 (100) $[M]^+$, 359.6 (52) $[M+1]^+$. Analytical data in accordance with literature.[11]

Preparation and characterisation of 3-phthalimido-1-(trifluoromethylseleno)propyne 2j



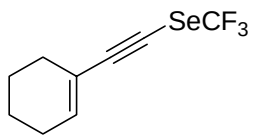
Prepared according to the general procedure on 0.3 mmol scale. Colourless solid, 52%. **m.p.** 71-73 °C; **FT-IR** ν_{max}(ATR) 3463, 3281, 3031, 2928, 2324, 2110, 1892, 1707, 1465, 1390, 1338, 1294, 1085, 929, 848, 794, 711 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 4.66 (s, 2H, C$\underline{H_2}$), 7.74 (dd, 2H, *J* 3.0, 5.4 Hz), 7.88 (dd, 2H, *J* 3.0, 5.4 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 28.4 (C$\underline{H_2}$), 57.2 (q, *C*quat., $J_{C\text{-}F}$ 3.0 Hz), 102.1 (*C*quat.), 120.6 (q, *C*quat., $J_{C\text{-}F}$ 336.0 Hz), 123.8 (2 × Ar-*C*H), 132.0 (2 × *C*quat.), 134.4 (2 × Ar-*C*H), 167.0 (2 × *C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.5 (SeC$\underline{F_3}$); **MS** (CI): *m/z* (%) 69.2 (1) $[CF_3]^+$, 185.1 (2) $[M-SeCF_3]^+$, 262.7 (13) $[M-CF_3-1]^+$, 263.7 (18) $[M-CF_3]^+$, 330.2 (42) $[M-3]^+$, 331.3 (43) $[M-2]^+$, 332.3 (74) $[M-1]^+$, 333.4 (59) $[M]^+$, 334.2 (100) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{12}H_6O_2N_1F_3{}^{80}Se]$ 332.9510, measured 332.9519.

Preparation and characterisation of 2-((3-((Trifluoromethyl)seleno)prop-2-yn-1-yl)oxy)tetrahydro-2H-pyran 2k



Prepared according to the general procedure on 0.3 mmol scale. Yellow oil, 50%. **FT-IR** ν_{max}(ATR) 3455, 2941, 2866, 2323, 2099, 1994, 1737, 1443, 1352, 1268, 1148, 1088, 1029, 899, 870, 812, 740 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.52-1.66 (m, 4H, 2 × C$\underline{H_2}$), 1.72-1.85 (m, 2H, C$\underline{H_2}$), 3.52-3.55 (m, 1H, C$\underline{H_a}H_b$), 3.81-3.85 (m, 1H, $CH_a\underline{H_b}$), 4.43-4.49 (m, 2H, AA' system), 4.81 (t, 1H, C$\underline{H}$, *J* 3.4 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 19.1 (C$\underline{H_2}$), 25.4 (C$\underline{H_2}$), 30.3 (C$\underline{H_2}$), 55.1 (C$\underline{H_2}$) 59.5 (q, *C*quat., $J_{C\text{-}F}$ 3.0 Hz), 62.2 (C$\underline{H_2}$), 97.1 (C$\underline{H}$), 105.3 (*C*quat.), 120.7 (q, *C*quat., $J_{C\text{-}F}$ 336.0 Hz); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.1 (SeC$\underline{F_3}$); **MS** (CI): *m/z* (%) 85.1 (39) $[C_5H_9O]^+$, 139.1 (2) $[M-SeCF_3]^+$, 169.2 (100) $[C_{10}H_{17}O_2]^+$, 217.0 (1) $[M-CF_3-2]^+$, 219.0 (1) $[M-CF_3]^+$, 286.9 (1) $[M-1]^+$, 288.9 $[M+1]^+$; **HRMS** (EI): calc. for $[C_9H_{11}O_2F_3{}^{80}Se]$ 287.9870, measured 287.9874.

Preparation and characterisation of 1-(trifluoromethylseleno)ethynylcyclohexene 2l



Prepared according to the general procedure on 0.3 mmol scale. Colourless oil, 58%. **FT-IR** ν_{max}(ATR) 3029, 2934, 2863, 2668, 2327,

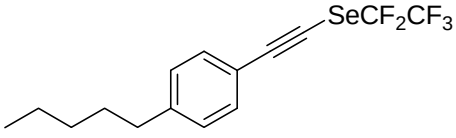
[11] Cheng, C. et al., *Chem, Eur. J.*, **2014**, 20, 657-661

2148, 1987, 1736, 1625, 1437, 1347, 1271, 1329, 1148, 1087 918, 843, 798, 739, 668 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.57-1.61 (m, 2H, C$\underline{H}_2$), 1.63-1.67 (m, 2H, C$\underline{H}_2$), 2.13-2.16 (m, 4H, 2 × C$\underline{H}_2$), 6.24-6.26 (m, 1H, C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 21.4 ($\underline{C}H_2$), 22.2 ($\underline{C}H_2$), 25.9 ($\underline{C}H_2$), 28.8 ($\underline{C}H_2$), 58.6 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 2.9 Hz), 109.3 ($\underline{C}$quat.), 120.5 ($\underline{C}$quat.), 120.8 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 336.4 Hz), 138.5 ($\underline{C}$H); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.8 (SeC$\underline{F}_3$); **MS** (CI): *m/z* (%) 69.1 (16) $[CF_3]^+$, 105.1 (55) $[M-SeCF_3]^+$, 233.0 (20) $[M-F-2]^+$, 234.9 (38) $[M-F]^+$, 250.9 (33) $[M-3]^+$, 252.0 (17) $[M-2]^+$, 252.9 (60) $[M-1]^+$, 253.9 (19) $[M]^+$, 254.9 (52) $[M+1]^+$; **HRMS** (EI): calc. for $[C_9H_9F_3{}^{80}Se]$ 253.9816, measured 253.9817.

One-pot procedure for reaction with terminal alkynes:

A suspension of red selenium (380 mg, 4.8 mmol, 1.6 equiv) in 10 mL of dry THF under air was cooled to −40 °C. $TMSCF_3$ (0.75 mL, 5.1 mmol, 1.7 equiv) was added followed by Me_4NF (450 mg, 4.8 mmol, 1.6 equiv). The reaction mixture was stirred for 10 min at −40 °C, warmed up to room temperature and stirred for further 30 min. 1-ethynyl-4-pentylbenzene (0.58 ml, 3.0 mmol, 1 equiv), bipyridine (515 mg, 3.3 mmol, 1.1 equiv) and $Cu(OTf)_2$ (1.085 g, 3 mmol, 1 equiv) were added and the flask was closed with a rubber septum. A balloon of oxygen was connected via needle and the reaction mixture was stirred at room temperature for 15h. The mixture was filtered through Celite eluting with diethyl ether (50 mL). The filtrate was washed with water (2 x 50 mL) and brine, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure.The crude product was purified by column chromatography (SiO_2, pentane) to provide **2a** (543 mg, 56%) as yellow oil.

Preparation and characterisation of 1-(pentafluoroethylseleno)ethynyl-4-pentylbenzene 12a:

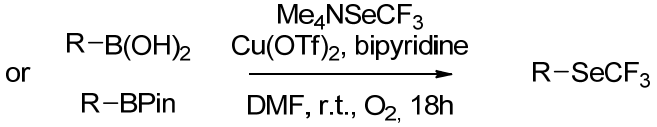


A suspension of red selenium (38.0 mg, 0.48 mmol, 1.6 equiv) in 1 mL of dry THF under air was cooled to −40 °C. $TMSC_2F_5$ (84 µL, 0.48 mmol, 1.6 equiv) was added followed by Me_4NF (45 mg, 0.48 mmol, 1.6 equiv). The reaction mixture was stirred for 10 min at −40 °C, warmed up to room temperature and stirred for further 30 min. 1-ethynyl-4-pentylbenzene (58 µl, 0.3 mmol, 1 equiv), bipyridine (51.5 mg, 0.33 mmol, 1.1 equiv) and $Cu(OTf)_2$ (108.5 mg, 0.3 mmol, 1 equiv) were added and the flask was closed with a rubber septum. A balloon of oxygen was connected via needle and the reaction mixture was stirred at room temperature for 15h. The mixture was filtered through Celite eluting with diethyl ether (25 mL). The filtrate was concentrated under reduced pressure to ca. 1 mL and directly purified by column chromatography (SiO_2, pentane) to provide **11a** (56 mg, 51%) as pale yellow oil. **m.p.** 34-36 °C, **FT-IR** ν_{max}(ATR) 2934, 2863, 2158, 1925, 1738, 1603, 1502, 1463, 1411, 1322, 1207, 1106, 1018, 931, 836, 739 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 0.91 (t, 3H, C$\underline{H}_3$, *J* 7.1 Hz), 1.27-1.39 (m, 4H, 2 × C$\underline{H}_2$),

1.58-1.66 (m, 2H, C$\underline{H}_2$), 2.62 (t, 2H, C$\underline{H}_2$, *J* 7.8 Hz), 7.17 (d, 2H, 2 × Ar-C$\underline{H}$, *J* 8.2 Hz), 7.41 (d, 2H, 2 × Ar-C$\underline{H}$, *J* 8.2 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 14.0 ($\underline{C}H_3$), 22.5 ($\underline{C}H_2$), 30.9 ($\underline{C}H_2$), 31.4 ($\underline{C}H_2$), 35.9 ($\underline{C}H_2$), 61.2 (t, $\underline{C}$quat., $J_{C\text{-}F}$ 6.0 Hz), 107.2 ($\underline{C}$quat.), 114.7 (tq, $\underline{C}$quat. $J_{C\text{-}F}$ 308.7, 42.4 Hz), 118.5 (qt, $\underline{C}$quat., $J_{C\text{-}F}$ 286.1, 34.1 Hz), 119.1 ($\underline{C}$quat.), 128.5 (2 × Ar-$\underline{C}$H), 132.1 (2 × Ar-$\underline{C}$H), 145.0 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –92.9 (q, 2F, SeC$\underline{F}_2$CF$_3$, $J_{F\text{-}F}$ 3.4 Hz), –83.3 (t, 3F, SeCF$_2$C$\underline{F}_3$, $J_{F\text{-}F}$ 3.4 Hz); **MS** (CI): *m/z* (%) 171.0 (6) $[M-SeC_2F_5]^+$, 250.9 (11) $[M-C_2F_5]^+$, 251.9 (11) $[M-C_2F_5+1]^+$, 366.9 (30) $[M-3]^+$, 367.9 (50) $[M-2]^+$, 368.9 (54) $[M-1]^+$, 370.0 (85) $[M]^+$, 371.0 (100) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{15}H_{15}F_5{}^{80}Se]$ 370.0253, measured 370.0253.

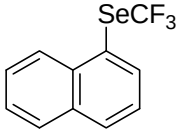
6. Trifluoromethylselenolation of boron derivatives by Me_4NSeCF_3

General procedure



The boron derivative (boronic acid or pinacol ester, 0.30 mmol, 1.0 equiv), copper (II) triflate (109 mg, 0.30 mmol, 1.0 equiv), bipyridine (51.5 mg, 0.33 mmol, 1.1 equiv) and tetramethylammonium trifluoromethylselenate (83.3 mg, 0.375 mmol, 1.25 equiv) were loaded into a tube under air and dissolved in DMF (2 mL). The tube was closed with a septum, and the deep green solution was stirred at room temperature under oxygen atmosphere (balloon) for 18h. Upon completion of the reaction, the crude mixture was directly loaded onto a silica gel column and eluted with pentane. The fractions containing the product were carefully evaporated under reduced pressure (200-300 mbar, 30°C). to give analytically pure samples.

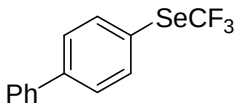
Preparation and characterisation of 1-(trifluoromethylseleno)naphthalene 4a



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid. Yellow oil, 73%. **FT-IR** ν_{max}(ATR) 3167, 3059, 2172, 1737, 1612, 1503, 1375, 1323, 1253, ,1083, 959, 872, 793, 769 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.48 (dd, 1H, Ar-C$\underline{H}$, *J* 7.2, 8.2 Hz), 7.58 (ddd, 1H, Ar-C$\underline{H}$, *J* 1.2, 6.9, 8.1 Hz), 7.65 (ddd, 1H, Ar-C$\underline{H}$, *J* 1.4, 6.9, 8.4 Hz), 7.89 (d, 1H, Ar-C$\underline{H}$, *J* 8.1 Hz), 8.00 (d, 1H, Ar-C$\underline{H}$, *J* 8.2 Hz), 8.09 (dd, 1H, Ar-C$\underline{H}$, *J* 1.0, 7.2 Hz), 8.51 (d, 1H, Ar-C$\underline{H}$, *J* 8.4 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 122.1 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 1.3 Hz), 122.6 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 334.1 Hz), 125.8 (Ar-$\underline{C}$H), 126.7 (Ar-$\underline{C}$H), 127.6 (Ar-$\underline{C}$H), 128.1 (Ar-$\underline{C}$H), 128.6 (Ar-$\underline{C}$H), 132.0 (Ar-$\underline{C}$H), 134.4 ($\underline{C}$quat.), 135.3 ($\underline{C}$quat.), 138.5 (Ar-$\underline{C}$H); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –35.9 (SeC$\underline{F}_3$); **MS**

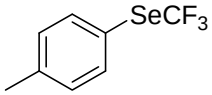
(CI): *m/z* (%) 128.1 (12) $[M-SeCF_3+1]^+$, 255.0 (9) $[M-F-2]^+$, 256.9 (20) $[M-F]^+$, 273.0 (10) $[M-3]^+$, 274.0 (28) $[M-2]^+$, 275.0 (13) $[M-1]^+$, 276.0 (100) $[M]^+$, 277.0 (53) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{11}H_7F_3{}^{80}Se]$ 275.9659, measured 275.9663.

Preparation and characterisation of 4-(trifluoromethylseleno)biphenyl 4b



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid. Colourless oil, 63%. **FT-IR** ν_{max}(ATR) 3023, 2330, 2078, 1911, 1743, 1590, 1473, 1389, 1276, 1087, 1002, 832, 751, 691 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.40 (t, 1H, Ar-C*H*, *J* 7.4 Hz), 7.48 (t, 2H, 2 × Ar-C*H*, *J* 7.6 Hz), 7.60-7.63 (m, 4H, 4 × Ar-C*H*), 7.82 (d, 2H, 2 × Ar-C*H*, *J* 8.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 121.3 (*C*quat.), 122.7 (q, *C*quat., J_{C-F} 332.9 Hz), 127.7 (2 × Ar-*C*H), 128.2 (2 × Ar-*C*H), 128.4 (2 × Ar-*C*H), 129.1 (2 × Ar-*C*H), 137.6 (Ar-*C*H), 139.9 (*C*quat.), 143.5 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.1 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 69.2 (17) $[CF_3]^+$, 153.3 (8) $[M-SeCF_3]^+$, 232.8 (13) $[M-CF_3]^+$, 300.0 (88) $[M-2]^+$, 301.2 (85) $[M-1]^+$, 302.2 (100) $[M]^+$, 303.2 (54) $[M+1]^+$. Analytical data in accordance with literature.[11]

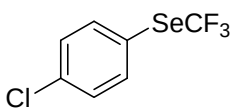
Preparation and characterisation of 4-(trifluoromethylseleno)toluene 4c



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid. Colourless oil, 62%.

FT-IR ν_{max}(ATR) 3458, 2924, 2856, 2651, 2324, 2107, 1987, 1909, 1739, 1448, 1367, 1216, 1090, 902, 792, 714 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 2.39 (s, 3H, C*H*$_3$), 7.20 (d, 2H, 2 × Ar-C*H*, *J* 8.1 Hz), 7.63 (d, 2H, 2 × Ar-C*H*, *J* 8.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 21.5 (*C*H$_3$), 119.2 (q, *C*quat., J_{C-F} 0.9 Hz), 122.7 (q, *C*quat., J_{C-F} 332.8 Hz), 130.5 (2 × Ar-*C*H), 137.2 (2 × Ar-*C*H), 140.9 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.6 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 91.2 (100) $[M-SeCF_3]^+$, 169.2 (17) $[M-CF_3-2]^+$, 171.2 (25) $[M-CF_3]^+$, 237.1 (13) $[M-3]^+$, 238.1 $[M-2]^+$, 239.1 (31) $[M-1]^+$, 240. 0 (12) $[M]^+$, 241.1 (55) $[M+1]^+$. Analytical data in accordance with literature.

Preparation and characterisation of 4-chloro-1-(trifluoromethylseleno)benzene 4d

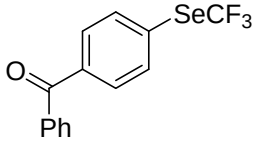


Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid. Colourless oil, 58%. **FT-IR** ν_{max}(ATR) 3459,

[11] Cheng, C. et al., *Chem, Eur. J.*, **2014**, 20, 657-661

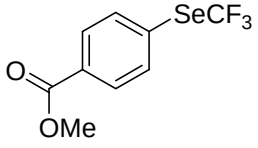
3014, 2929, 2856, 2653, 2319, 2108, 1986, 1739, 1583, 1440, 1366, 1217, 1093, 902 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.37 (d, 2H, 2 × Ar-C*H*, *J* 8.4 Hz), 7.67 (d, 2H, 2 × Ar-C*H*, *J* 8.4 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 120.7 (q, *C*quat., J_{C-F} 1.1 Hz), 122.5 (q, *C*quat., J_{C-F} 332.9 Hz), 130.0 (2 × Ar-*C*H), 137.3 (*C*quat.), 138.5 (2 × Ar-*C*H); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.2 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 69.2 (57) $[CF_3]^+$, 189.0 (29) $[M- CF_3-2]^+$, 191.0 (52) $[M-CF_3]^+$, 192.9 (77) $[M- CF_3+2]^+$, 239.0 (30) $[M-F-2]^+$, 241.0 (49) $[M-F]^+$, 243.0 (22) $[M-F+2]^+$, 257 (12) $[M-3]^+$, 257.9 (15) $[M-2]^+$, 259.0 (31) $[M-1]^+$, 259.9 (17) $[M]^+$, 260.9 (54) $[M+1]^+$, 261.9 (10) $[M+2]^+$, 263.9 (26) $[M+3]^+$. Analytical data in accordance with literature.[12]

Preparation and characterisation of 4-(trifluoromethylseleno)benzophenone 4e



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid pinacol ester. Colourless oil, 70%. **FT-IR** ν_{max}(ATR) 3069, 2929, 2647, 2290, 2102, 1926, 1738, 1650, 1586, 1448, 1389, 1277, 1091, 921, 843, 789, 728, 693 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.50 (t, 2H, 2 × Ar-C*H*, *J* 7.8 Hz), 7.62 (t, 1H, Ar-C*H*, *J* 7.5 Hz), 7.79-7.81 (m, 4H, 4 × Ar-C*H*), 7.85 (d, 2H, 2 × Ar-C*H*, *J* 8.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 122.5 (q, *C*quat., J_{C-F} 332.8 Hz), 127.4 (q, *C*quat, J_{C-F} 1.0 Hz), 128.6 (2 × Ar-*C*H), 130.20 (2 × Ar-*C*H), 130.9 (2 × Ar-*C*H), 133.1 (Ar-*C*H), 136.5 (2 × Ar-*C*H), 137.0 (*C*quat.), 139.1 (*C*quat.), 195.8 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.2 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 69.2 (11) $[CF_3]^+$, 261.0 (9) $[M-CF_3]^+$, 262.0 (11) $[M-CF_3+1]^+$, 328.3 (69) $[M-2]^+$, 329.4 (96) $[M-1]^+$, 330.4 (100) $[M]^+$, 331.4 (99) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{14}H_9OF_3{}^{80}Se]$ 329.9765, measured 329.9767.

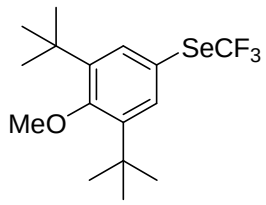
Preparation and characterisation of methyl 4-(trifluoromethylseleno)benzoate 4f



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid. Colourless oil, 69%. **FT-IR** ν_{max}(ATR) 3438, 2954, 2663, 2322, 2088, 1994, 1928, 1725, 1593, 1437, 1394, 1276, 1094, 1013, 966, 845, 754, 689 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.94 (s, 3H, C*H*$_3$), 7.80 (d, 2H, 2 × Ar-C*H*, *J* 8.3 Hz), 8.04 (d, 2H, 2 × Ar-C*H*, *J* 8.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 52.6 (*C*H$_3$), 122.5 (q, *C*quat., J_{C-F} 332.7 Hz), 128.2 (q, *C*quat., J_{C-F} 1.0 Hz), 130.6 (2 × Ar-*C*H), 131.9 (*C*quat.), 136.6 (2 × Ar-*C*H), 166.3 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.3 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 69.2 (100) $[CF_3]^+$, 282.1 (29) $[M-2]^+$, 283.0 (54) [M−1]+, 284.0 (34) $[M]^+$, 284.9 (41) $[M+1]^+$; **HRMS** (EI): calc. for $[C_9H_7O_2F_3{}^{80}Se]$ 283.9557, measured 283.9558.

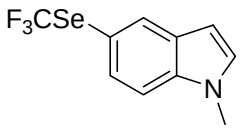
[12] Blond, G., Billard, T., Langlois, B. R., *Tetrahedron Lett.*, **2001**, 42, 2473-2475

Preparation and characterisation of 2,6-di(*tert*-butyl)-4-(trifluoromethylseleno)anisole 4g



Prepared according to the general procedure on 0.1 mmol scale from the corresponding boronic acid. Colourless oil, 67%. **FT-IR** ν_{max}(ATR) 3363, 2956, 2319, 2167, 2104, 2010, 1942, 1671, 1597, 1457, 1402, 1256, 1221, 1091, 1013, 877, 804, 741, 695 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 1.43 (s, 18H, 6 × C$\underline{H}_3$), 3.71 (s, 3H, C$\underline{H}_3$), 7.58 (s, 2H, 2 × Ar-C$\underline{H}$); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 32.0 (6 × $\underline{C}H_3$), 36.0 (2 × $\underline{C}$quat.), 64.6 ($\underline{C}H_3$), 116.6 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 0.8 Hz), 122.8 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 333.0 Hz), 135.8 (2 × Ar-$\underline{C}$H), 145.5 (2 × $\underline{C}$quat.), 161.7 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.6 (SeC$\underline{F}_3$); **MS** (CI): *m/z* (%) 83.1 (100) $[H_3Se]^+$, 347.6 (23) $[M-F-2]^+$, 349.2 (51) $[M-F]^+$, 365.6 (47) $[M-2]^+$, 366.8 (42) $[M-1]^+$, 367.8 (65) $[M]^+$, 368.8 (69) $[M+1]^+$, 369.7 (61) $[M+2]^+$. Analytical data in accordance with literature.

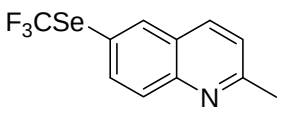
Preparation and characterisation of *N*-methyl-5-(trifluoromethylseleno)indole 4h



Prepared according to the general procedure on 0.1 mmol scale from the corresponding boronic acid. Colourless solid, 84%.

m.p. 54-56 °C; **FT-IR** ν_{max}(ATR) 2937, 2658, 2325, 2100, 1867, 1711, 1600, 1472, 1425, 1327, 1276, 1242, 1087, 880, 792, 722 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 3.82 (s, 3H, C$\underline{H}_3$), 6.53 (d, 1H, Ar-C$\underline{H}$, *J* 3.1 Hz), 7.11 (d, 1H, Ar-C$\underline{H}$, *J* 3.1 Hz), 7.33 (d, 1H, Ar-C$\underline{H}$, *J* 8.5 Hz), 7.57 (dd, 1H, Ar-C$\underline{H}$, *J* 1.3, 8.5 Hz), 8.05 (d, 1H, Ar-C$\underline{H}$, *J* 1.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 33.1 ($\underline{C}H_3$), 101.6 (Ar-$\underline{C}$H), 110.4 (Ar-$\underline{C}$H), 112.0 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 0.9 Hz), 122.9 (q, $\underline{C}$quat., $J_{C\text{-}F}$ 333.1 Hz), 129.6 ($\underline{C}$quat.), 130.2 (Ar-$\underline{C}$H), 130.3 (Ar-$\underline{C}$H), 131.1 (Ar-$\underline{C}$H), 137.4 ($\underline{C}$quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –37.3 (SeC$\underline{F}_3$); **MS** (CI): *m/z* (%) 130.5 (100) $[M-SeCF_3]^+$, 275.0 (29) $[M-4]^+$, 276.1 (29) $[M-3]^+$, 277.1 (44) $[M-2]^+$, 278.1 (49) $[M-1]^+$, 279.1 (41) $[M]^+$, 280.0 (39) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{10}H_8NF_3{}^{80}Se]$ 278.9768, measured 278.9764.

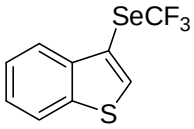
Preparation and characterisation of 2-methyl-6-(trifluoromethylseleno)quinoline 4i



Prepared according to the general procedure on 0.1 mmol scale from the corresponding boronic acid pinacol ester. Colourless solid, 75%. **m.p.** 84-86 °C; **FT-IR** ν_{max}(ATR) 2926, 2856, 2218, 2023, 1921, 1737, 1601, 1481, 1375, 1301, 1216, 1093, 975, 914, 822, 731 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 2.78 (s, 3H, C$\underline{H}_3$), 7.37 (d, 1H, Ar-C$\underline{H}$, *J* 8.4 Hz), 7.96 (dd, 1H, Ar-C$\underline{H}$, *J* 1.7, 8.7 Hz), 8.03 (d, 1H, Ar-C$\underline{H}$, *J* 8.7 Hz), 8.07 (d, 1H,

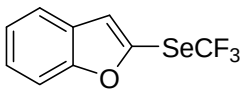
Ar-C*H*, *J* 8.4 Hz), 8.21 (d, 1H, Ar-C*H*, *J* 1.7 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 25.6 (*C*H_3), 119.7 (*C*quat.), 122.7 (q, *C*quat., $J_{C\text{-}F}$ 333.1 Hz), 123.1 (Ar-*C*H), 127.0 (*C*quat.), 130.0 (Ar-*C*H), 136.4 (Ar-*C*H), 136.8 (Ar-*C*H), 137.2 (Ar-*C*H), 148.0 (*C*quat.), 161.2 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.8 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 269.9 (34) $[M-F-2]^+$, 271.5 (53) $[M-F]^+$, 286.7 (47) $[M-4]^+$, 288.1 (61) $[M-3]^+$, 289.2 (28) $[M-2]^+$, 290.0 (100) $[M-1]^+$, 291.2 (60) $[M]^+$, 292.0 (71) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{11}H_8NF_3{}^{80}Se]$ 290.9768, measured 290.9766.

Preparation and characterisation of 3-(trifluoromethylseleno)benzothiophene 4j



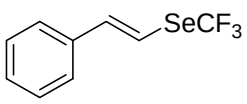
Prepared according to the general procedure on 0.1 mmol scale from the corresponding boronic acid pinacol ester. Colourless oil, 76%. **FT-IR** ν_{max}(ATR) 3102, 2926, 1676, 1572, 1418, 1313, 1255, 1084, 936, 823, 740 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.43-7.46 (m, 1H, Ar-C*H*), 7.50-7.53 (m, 1H, Ar-C*H*), 7.92 (d, 1H, Ar-C*H*, *J* 8.1 Hz), 7.97 (s, 1H, Ar-C*H*), 8.02 (d, 1H, Ar-C*H*, *J* 8.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 112.9 (*C*quat.), 122.3 (q, *C*quat., $J_{C\text{-}F}$ 334.6 Hz), 122.8 (Ar-*C*H), 124.0 (Ar-*C*H), 125.4 (Ar-*C*H), 125.4 (Ar-*C*H), 137.5 (Ar-*C*H), 139.6 (*C*quat.), 140.3 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.7 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 69.2 (13) $[CF_3]^+$, 134.2 (34) $[M-SeCF_3+1]^+$, 261.0 (47) $[M-F-2]^+$, 262.9 (42) $[M-F]^+$, 278.2 (35) $[M-4]^+$, 279.1 (69) $[M-3]^+$, 280.2 (95) $[M-2]^+$, 281.0 (100) $[M-1]^+$, 282.0 (91) $[M]^+$, 282.9 (74) $[M+1]^+$; **HRMS** (EI): calc. for $[C_9H_5F_3{}^{32}S{}^{80}Se]$ 281.9223, measured 281.9210.

Preparation and characterisation of 2-(trifluoromethylseleno)benzofuran 4k



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid. Colourless oil, 62%. **FT-IR** ν_{max}(ATR) 3067, 2681, 2325, 2100, 1993, 1740, 1610, 1527, 1438, 1358, 1250, 1142, 1090, 918, 878, 819, 742 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.25-7.30 (m, 2H, 2 × Ar-C*H*), 7.37-7.40 (m, 1H, Ar-C*H*), 7.55 (d, 1H, Ar-C*H*, *J* 8.4 Hz), 7.62 (d, 1H, Ar-C*H*, *J* 7.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 111.8 (Ar-*C*H), 120.7 (Ar-*C*H), 121.6 (Ar-*C*H), 121.8 (q, *C*quat., $J_{C\text{-}F}$ 335.7 Hz), 123.6 (Ar-*C*H), 126.4 (Ar-*C*H), 128.0 (*C*quat.), 136.4 (q, *C*quat., $J_{C\text{-}F}$ 1.7 Hz), 158.1 (*C*quat.); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –35.4 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 118.0 (56) $[M-SeCF_3]^+$, 194.9 (19) $[M-CF_3-2]^+$, 196.9 (38) $[M-CF_3]^+$, 244.9 (33) $[M-F-2]^+$, 246.8 (69) $[M-F]^+$, 262.9 (22) $[M-3]^+$, 263.8 (23) $[M-2]^+$, 264.9 (51) $[M-1]^+$, 265.9 (17) $[M]^+$, 266.9 (100) $[M+1]^+$; **HRMS** (EI): calc. for $[C_9H_5OF_3{}^{80}Se]$ 265.9452, measured 265.9446.

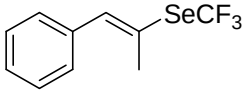
Preparation and characterisation of *β*-(trifluoromethylseleno)styrene 4l



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid. Yellow oil, 75%.

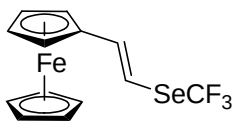
FT-IR ν_{max}(ATR) 3038, 2663, 2320, 2101, 1880, 1741, 1574, 1493, 1445, 1367, 1283, 1218, 1092, 951, 809, 731, 689 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.10 (d, 1H, *J* 15.6 Hz, AA' system), 7.16 (d, 1H, *J* 15.6 Hz, AA' system), 7.31-7.42 (m, 5H, 5 × Ar-C*H*); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ_C 109.4 (q, *C*H, J_{C-F} 2.3 Hz), 122.3 (q, *C*quat., J_{C-F} 332.5 Hz), 126.8 (2 × Ar-*C*H), 128.8 (2 × Ar-*C*H), 129.1 (Ar-*C*H), 135.7 (*C*quat.), 143.4 (q, *C*H, J_{C-F} 1.1 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F –36.1 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 69.2 (20) $[CF_3]^+$, 103.1 (54) $[M-SeCF_3]^+$,, 181.0 (26) $[M-CF_3-2]^+$, 182.9 (48) $[M-CF_3]^+$, 249.0 (14) $[M-3]^+$, 250.0 (14) $[M-2]^+$, 250.9 (32) $[M-1]^+$, 251.9 (13) $[M]^+$, 253.0 (56) $[M+1]^+$; **HRMS** (EI): calc. for $[C_9H_7F_3{}^{80}Se]$ 251.9659, measured 251.9658.

Preparation and characterisation of *β*-methyl-*β*-(trifluoromethylseleno)styrene 4m



Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid pinacol ester. Colourless oil, 62%. **FT-IR** ν_{max}(ATR) 3029, 2924, 2661, 2325, 2084, 1994, 1742, 1589, 1490, 1442, 1378, 1273 ,1101, 919, 865, 747, 697 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 2.48 (s, 3H, C*H*$_3$), 7.23 (s, 1H, C*H*), 7.29-7.33 (m, 3H, 3 × Ar-C*H*), 7.39 (t, 2H, 2 × Ar-C*H*, *J* 7.6 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 23.9 (*C*H$_3$), 123.2 (q, *C*quat., J_{C-F} 333.6 Hz), 124.6 (*C*quat.), 128.1 (Ar-*C*H), 128.6 (2 × Ar-*C*H), 128.9 (2 × Ar-*C*H), 136.2 (*C*quat.), 142.8 (q, *C*H, J_{C-F} 1.1 Hz); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –34.3 (SeC*F*$_3$); **MS** (CI): *m/z* (%) 69.2 (100) $[CF_3]^+$, 117.2 (13) $[M-SeCF_3]^+$, 263.0 (7) $[M-3]^+$, 264.1 (10) $[M-2]^+$, 265.0 (11) $[M-1]^+$, 265.9 (10) $[M]^+$, 266.9 (5) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{10}H_9F_3{}^{80}Se]$ 265.9816, measured 265.9817.

Preparation and characterisation of *β*-(trifluoromethylseleno)vinylferrocene 4n



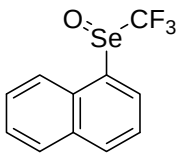
Prepared according to the general procedure on 0.3 mmol scale from the corresponding boronic acid pinacol ester. Orange oil, 71%. **FT-IR** ν_{max}(ATR) 3924, 3093, 2924, 2667, 2323, 2095, 1996, 1768, 1595, 1457, 1410, 1289, 1232, 1094, 952, 817, 736 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 4.17 (s, 5H, 5 × C*H*), 4.34 (s, 2H, 2 × C*H*), 4.43 (s, 2H, 2 × C*H*), 6.62 (d, 1H, C*H*, *J* 14.7 Hz), 7.06 (d, 1H, C*H*, *J* 14.7 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 67.5 (2 × *C*H), 69.5 (5 × *C*H), 70.0 (2 × *C*H), 80.7 (*C*quat.), 103.1 (*C*H), 122.0 (q, *C*quat., J_{C-F} 333.1 Hz), 146.1 (*C*H); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –36.6

(SeC<u>F</u>$_3$); **MS** (CI): *m/z* (%) 211.2 (60) [M−SeCF$_3$]$^+$, 289.2 (35) [M−CF$_3$−2]$^+$, 291.4 (39) [M−CF$_3$]$^+$, 355.8 (40) [M−4]$^+$, 356.7 (27) [M−3]$^+$, 357.7 (63) [M−2]$^+$, 358.5 (53) [M−1]$^+$, 359.5 (91) [M]$^+$, 360.5 (100) [M+1]$^+$; **HRMS** (EI): calc. for [$C_{13}H_{11}F_3{}^{56}Fe^{80}Se$] 359.9322, measured 359.9326.

One-pot procedure for reaction with boronic acids:

A suspension of red selenium (380 mg, 4.8 mmol, 1.6 equiv) in 10 mL of dry DMF under air was cooled to −40 °C. TMSCF$_3$ (0.75 mL, 5.1 mmol, 1.7 equiv) was added followed by Me$_4$NF (450 mg, 4.8 mmol, 1.6 equiv). The reaction mixture was stirred for 10 min at −40 °C, warmed up to room temperature and stirred for further 30 min. 1-naphthylboronic acid (516 mg, 3.0 mmol, 1 equiv), bipyridine (515 mg, 3.3 mmol, 1.1 equiv) and Cu(OTf)$_2$ (1.085 g, 3 mmol, 1 equiv) were added and the flask was closed with a rubber septum. A balloon of oxygen was connected via needle and the reaction mixture was stirred at room temperature for 15h. The mixture was filtered through Celite eluting with diethyl ether (50 mL). The filtrate was washed with water (2 x 50 mL) and brine. the organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, pentane) to provide **4a** (660 mg, 80%) as a light yellow oil.

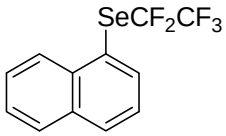
Oxidation of 4a to 1-(trifluoromethylseleninyl)naphthalene 13a



1-trifluoromethylselenonaphthalene **2a** (27.5 mg, 0.1 mmol, 1.0 equiv) was dissolved in 1 mL of dry DCM under argon. The reaction mixture was cooled to 0 °C, and *m*-CPBA (≤ 77% purity, 24.7 mg, 0.11 mmol, 1.1 equiv) was added in one portion. The mixture was stirred at 0 °C for 30 minutes, and at room-temperature for 30 additional minutes. The organic phase was washed with a saturated aqueous solution of potassium carbonate (1 mL) and the aqueous phase was extracted with DCM (3 × 1 mL). The organics were combined and concentrated under reduced pressure. The residue was purified by column chromatography (pentane/ethyl acetate 10:1 to 1:1) to provide **13a** (25 mg, 86%) as a colourless solid. **m.p.** 110-112 °C; **FT-IR** ν_{max}(ATR) 3426, 3050, 2924, 2853, 2664, 2324, 2193, 2105, 1931, 1725, 1588, 1504, 1458, 1375, 1265, 1144, 1093, 971, 920, 827, 797, 758, 731 cm^{-1}; **^{1}H NMR** (CDCl$_3$, 600 MHz) δ_H 7.63-7.69 (m, 2H, 2 × Ar-C<u>H</u>), 7.75 (t, 1H, Ar-C<u>H</u>, *J* 7.7 Hz), 7.97-8.01 (m, 2H, 2 × Ar-C<u>H</u>), 8.11 (d, 1H, Ar-C<u>H</u>, *J* 8.1 Hz), 8.38 (d, 1H, Ar-C<u>H</u>, *J* 7.3 Hz); **^{13}C NMR** (CDCl$_3$, 150 MHz) δ_C 122.2 (Ar-<u>C</u>H), 123.0 (q, <u>C</u>quat., $J_{C\text{-}F}$ 363.5 Hz), 126.0 (Ar-<u>C</u>H), 126.3 (Ar-<u>C</u>H), 127.4 (Ar-<u>C</u>H), 128.4 (Ar-<u>C</u>H), 129.4 (Ar-<u>C</u>H), 131.4 (<u>C</u>quat.), 132.8 (<u>C</u>quat.), 133.5 (Ar-<u>C</u>H), 134.1 (<u>C</u>quat.); **^{19}F NMR** (CDCl$_3$, 564 MHz) δ_F –62.7 (Se(O)C<u>F</u>$_3$); **MS** (CI): *m/z* (%) 128.0 (18) [M−SeCF$_3$+1]$^+$, 221.0 (21) [M−CF$_3$−2]$^+$, 222.0 (18) [M−CF$_3$−1]$^+$, 223.0

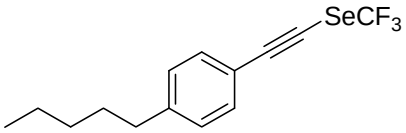
(32) $[M-CF_3]^+$, 223.9 (37) $[M-CF_3+1]^+$, 273.9.0 (20) $[M-O-2]^+$, 275.9 (23) $[M-O]^+$, 288.9 (54) $[M-3]^+$, 289.9 (50) $[M-2]^+$, 290.9 (96) $[M-1]^+$, 291.9 (18) $[M]^+$, 292.9 (100) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{11}H_7OF_3{}^{80}Se]$ 291.9608, measured 291.9610.

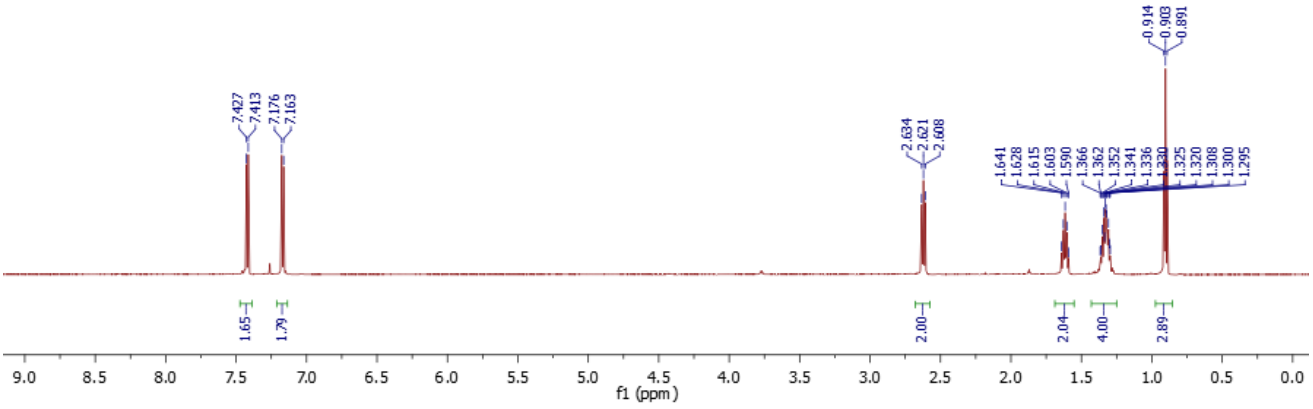
Preparation and characterisation of 1-(pentafluoroethylseleno)naphthalene 12a:



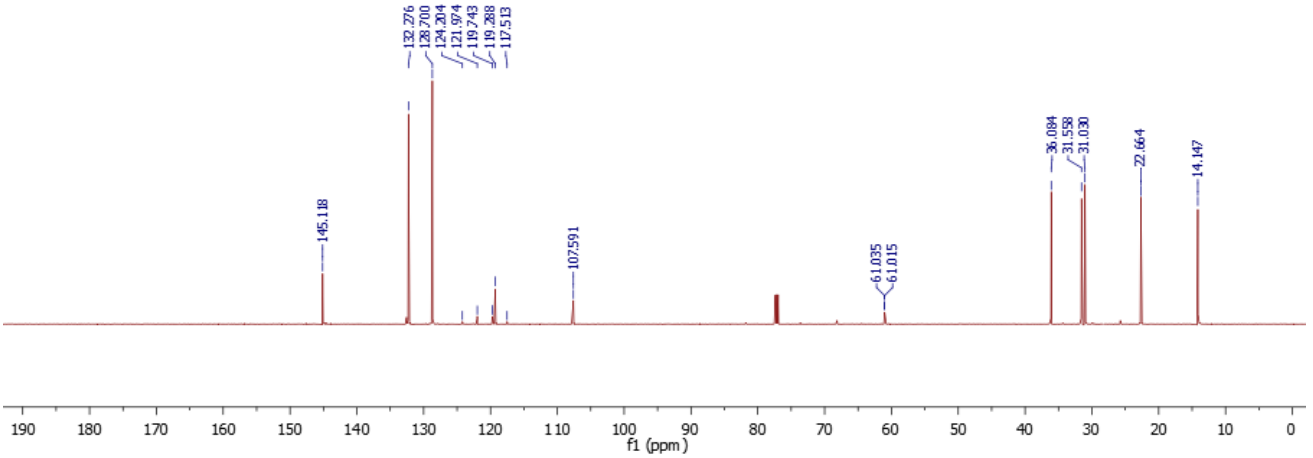
A suspension of red selenium (38.0 mg, 0.48 mmol, 1.6 equiv) in 1 mL of dry THF under air was cooled to −40 °C. $TMSC_2F_5$ (84 µL, 0.48 mmol, 1.6 equiv) was added followed by Me_4NF (45 mg, 0.48 mmol, 1.6 equiv). The reaction mixture was stirred for 10 min at −40 °C, warmed up to room temperature and stirred for further 30 min. 1a (58 µl, 0.30 mmol, 1 equiv), bipyridine (51.5 mg, 0.33 mmol, 1.1 equiv) and $Cu(OTf)_2$ (108.5 mg, 0.3 mmol, 1 equiv) were added and the flask was closed with a rubber septum. A balloon of oxygen was connected via needle and the reaction mixture was stirred at room temperature for 15h. The mixture was filtered through Celite eluting with diethyl ether (25 mL). The filtrate was concentrated under reduced pressure to ca. 1 mL and directly purified by column chromatography (SiO_2, pentane) to provide **12a** (68 mg, 69%) as pale yellow oil.**FT-IR** ν_{max}(ATR) 3058, 2930, 2663, 2325, 2090, 1998, 1933, 1738, 1590, 1501, 1448, 1372, 1319, 1205, 1094, 931, 767 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 600 MHz) δ_H 7.47 (dd, 1H, Ar-C*H*, *J* 7.1, 8.1 Hz), 7.58 (ddd, 1H, Ar-C*H*, *J* 1.1, 6.8, 8.2 Hz), 7.65 (ddd, 1H, Ar-C*H*, *J* 1.2, 6.8, 8.5 Hz), 7.89 (d, 1H, Ar-C*H*, *J* 8.1 Hz), 8.01 (d, 1H, Ar-C*H*, J 8.2 Hz), 8.07 (d, 1H, Ar-C*H*, *J* 7.1 Hz, 1H), 8.51 (d, 1H, Ar-C*H*, *J* 8.5 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ_C 116.0 (tq, *C*quat. J_{C-F} 42.0, 304.7 Hz), 118.9 (qt, *C*quat., J_{C-F} 34.6, 285.6 Hz), 121.0 (t, *C*quat., J_{C-F} 2.5 Hz), 125.7 (Ar-*C*H), 126.7 (Ar-*C*H), 127.6 (Ar-*C*H), 128.2 (Ar-*C*H), 128.6 (Ar-*C*H), 132.2 (Ar-*C*H), 134.2 (*C*quat.), 135.8 (*C*quat.), 139.2 (Ar-*C*H); **^{19}F NMR** ($CDCl_3$, 564 MHz) δ_F –91.1 (q, 2F, $SeCF_2CF_3$, J_{F-F} 4.1 Hz), –83.3 (t, 3F, $SeCF_2CF_3$, J_{F-F} 4.1 Hz); **MS** (CI): *m/z* (%) 128.1 (100) $[M-SeC_2F_5+1]^+$, 204.9 (10) $[M-C_2F_5-2]^+$, 206.9 (18) $[M-C_2F_5]^+$, 322.9 (12) $[M-3]^+$, 323.9 (23) $[M-2]^+$, 324.9 (14) $[M-1]^+$, 325.9 (25) $[M]^+$, 326.9 (28) $[M+1]^+$; **HRMS** (EI): calc. for $[C_{12}H_7F_5{}^{80}Se]$ 325.9627, measured 325.9631.

7. ^{1}H, ^{13}C and ^{19}F NMR spectra of new compounds

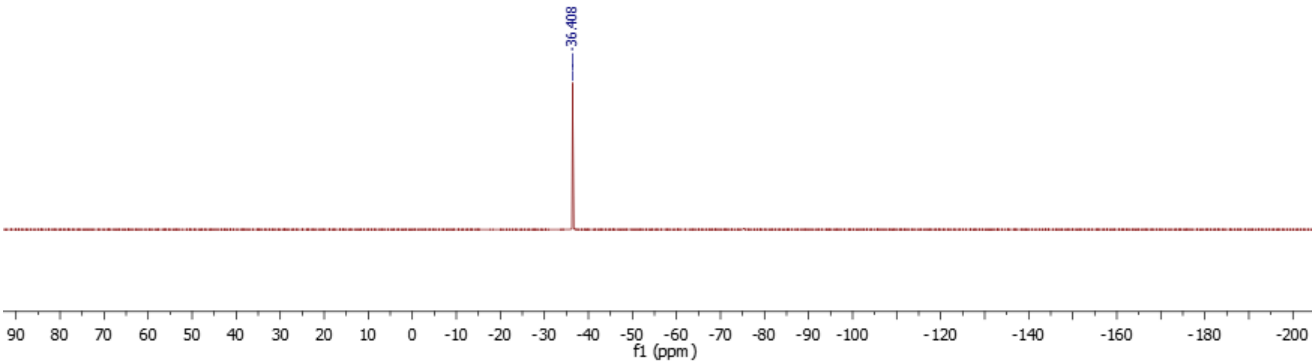




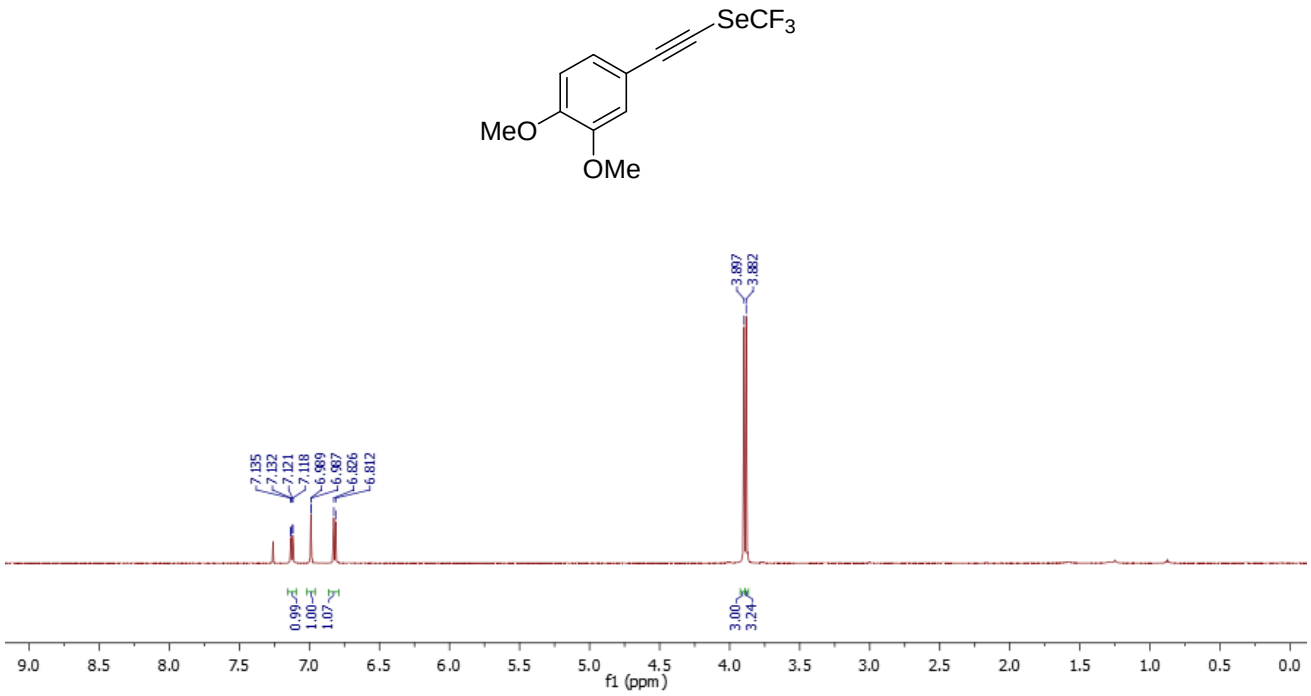
^{1}H NMR spectrum of 1-(trifluoromethylseleno)ethynyl-4-pentylbenzene 2a



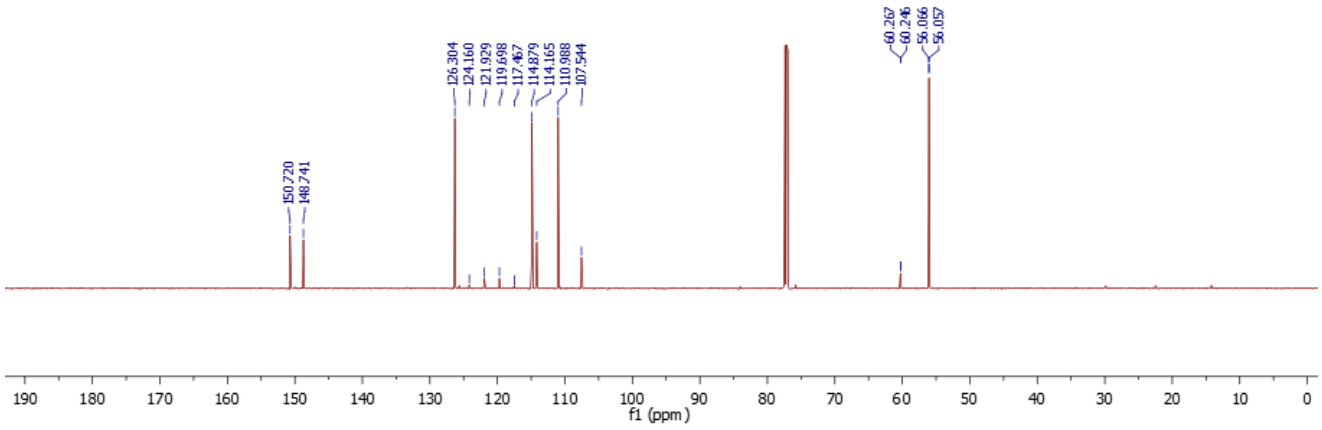
^{13}C NMR spectrum of 1-(trifluoromethylseleno)ethynyl-4-pentylbenzene 2a



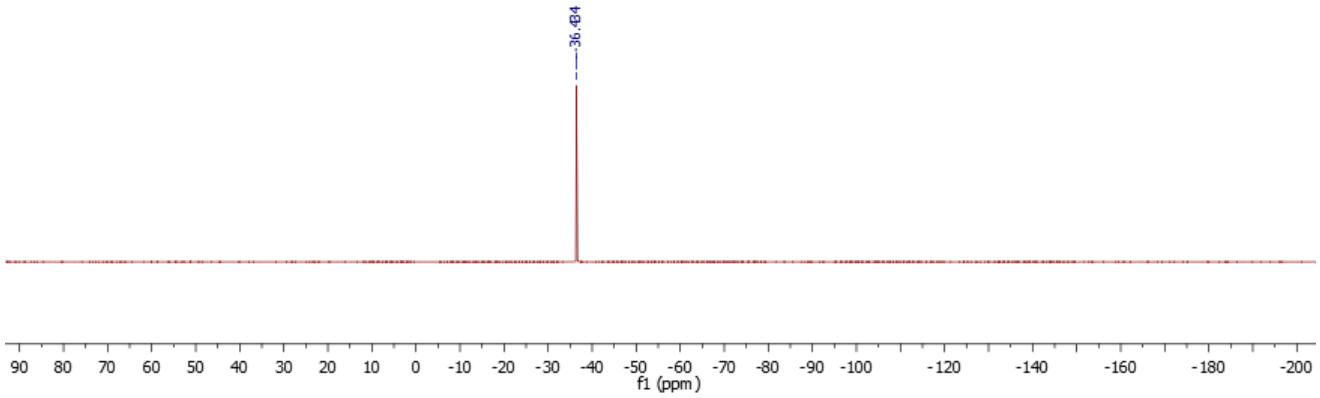
^{19}F NMR spectrum of 1-(trifluoromethylseleno)ethynyl-4-pentylbenzene 2a



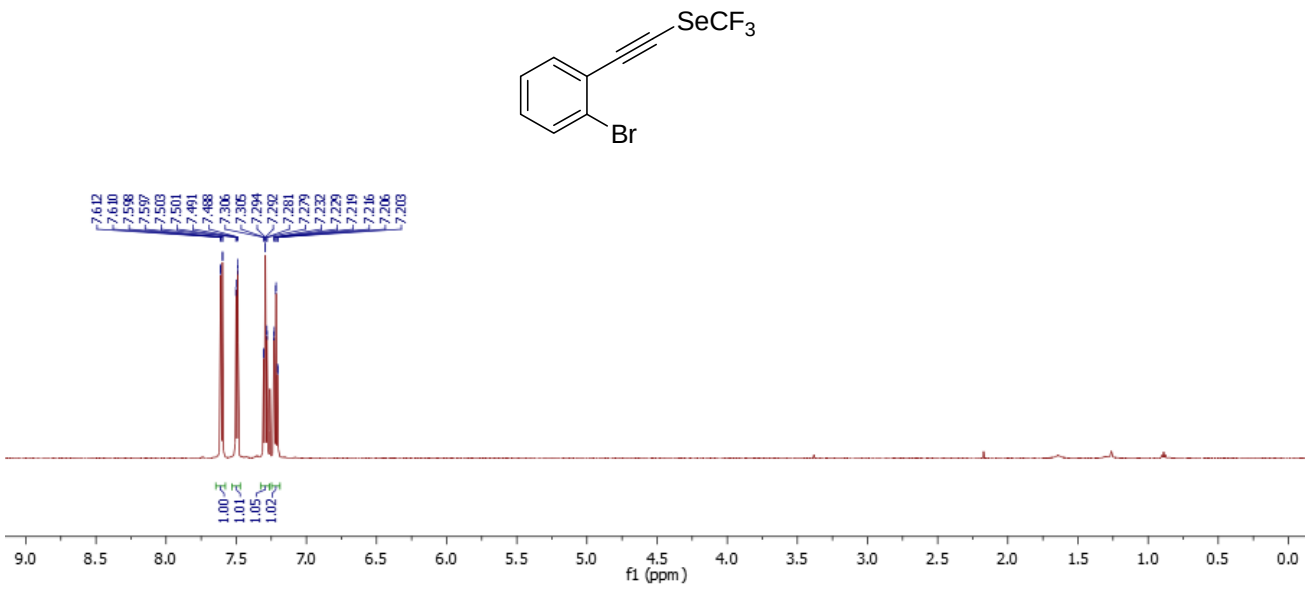
^{1}H NMR spectrum of 4-(trifluoromethylseleno)ethynyl-1,2-dimethoxybenzene 2b



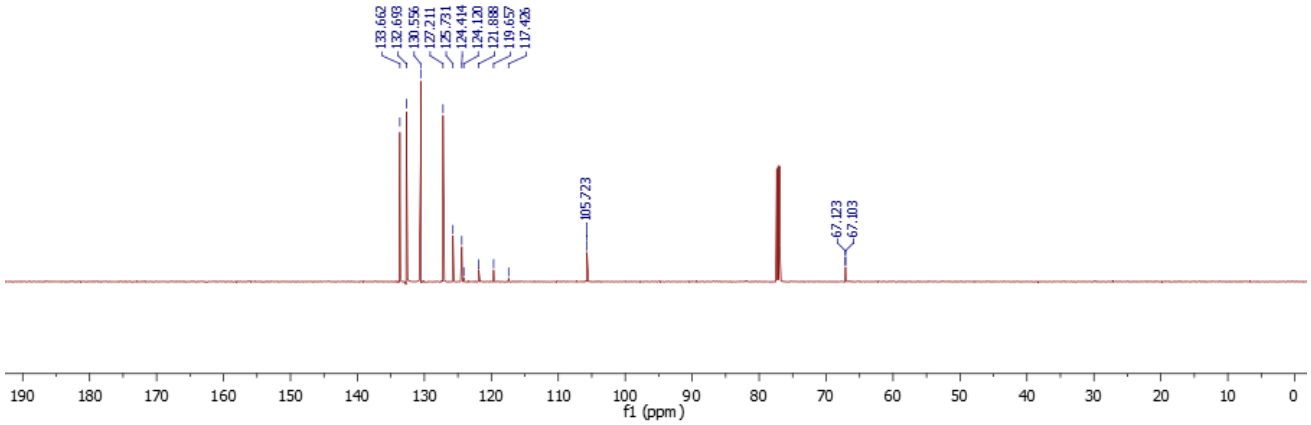
^{13}C NMR spectrum of 4-(trifluoromethylseleno)ethynyl-1,2-dimethoxybenzene 2b



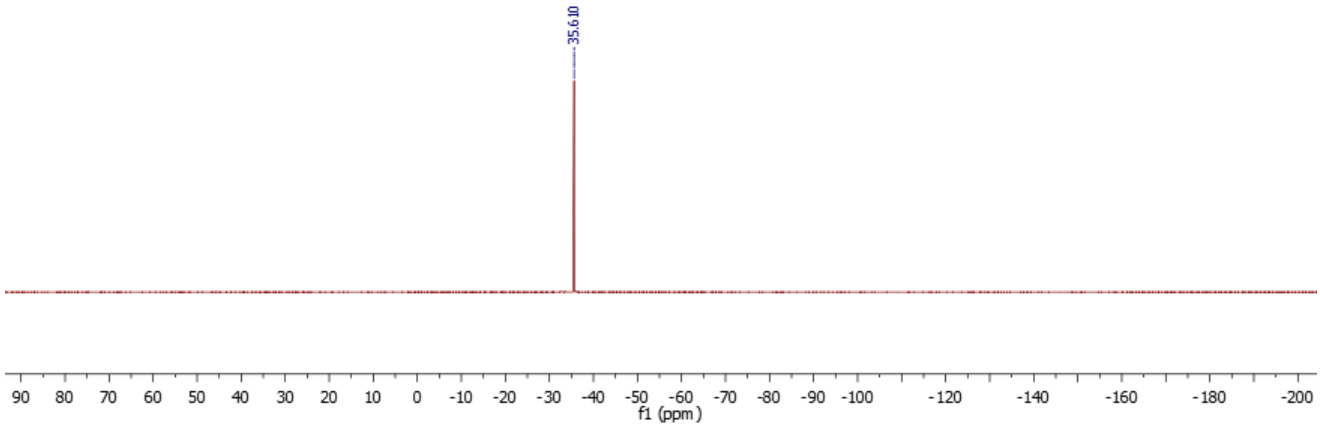
^{19}F NMR spectrum of 4-(trifluoromethylseleno)ethynyl-1,2-dimethoxybenzene 2b



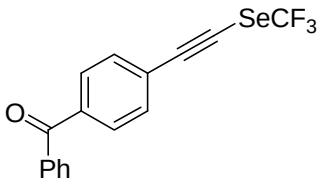
^{1}H NMR spectrum of 1-bromo-2-(trifluoromethylseleno)ethynylbenzene 2c

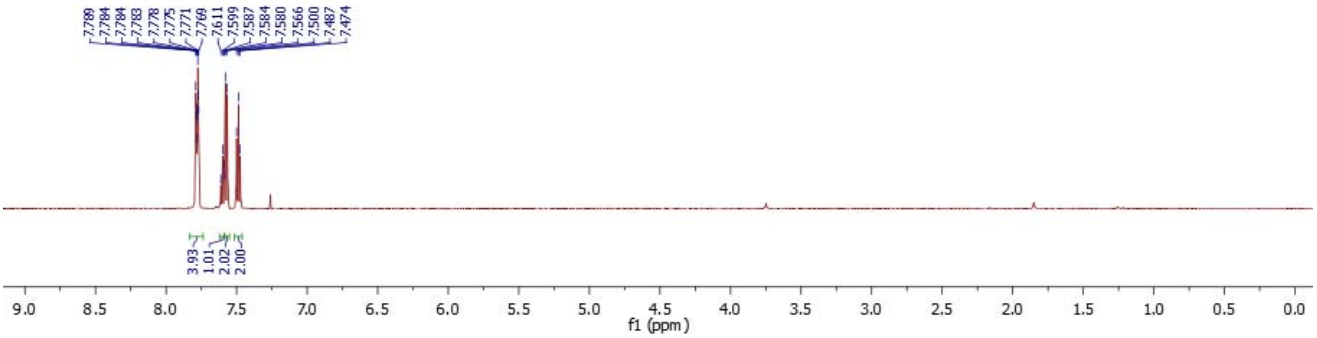


^{13}C NMR spectrum of 1-bromo-2-(trifluoromethylseleno)ethynylbenzene 2c

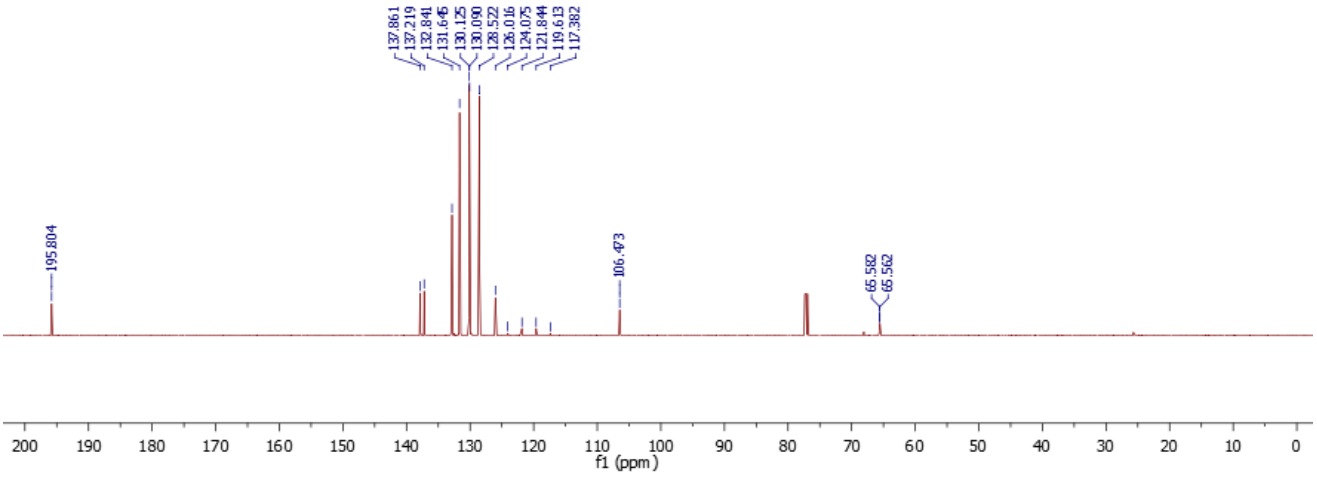


^{19}F NMR spectrum of 1-bromo-2-(trifluoromethylseleno)ethynylbenzene 2c

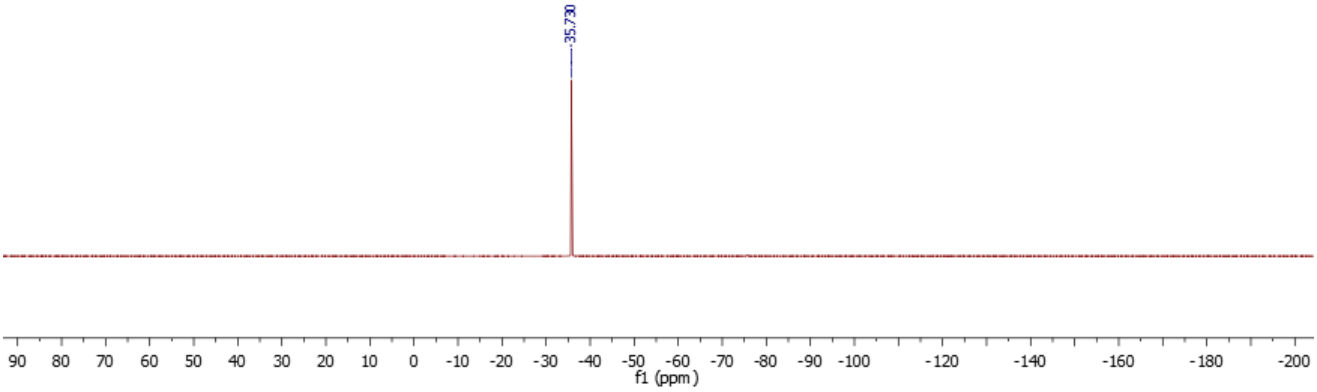




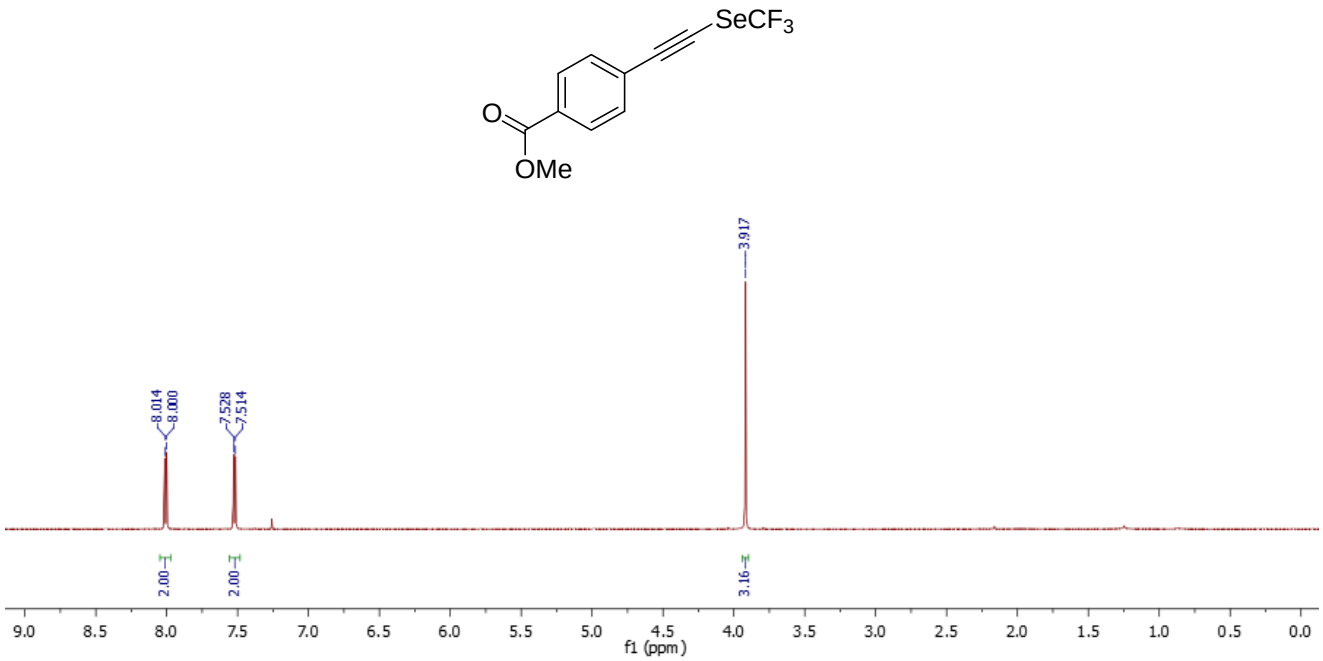
^{1}H NMR spectrum of 4-(trifluoromethylseleno)ethynylbenzophenone 2d



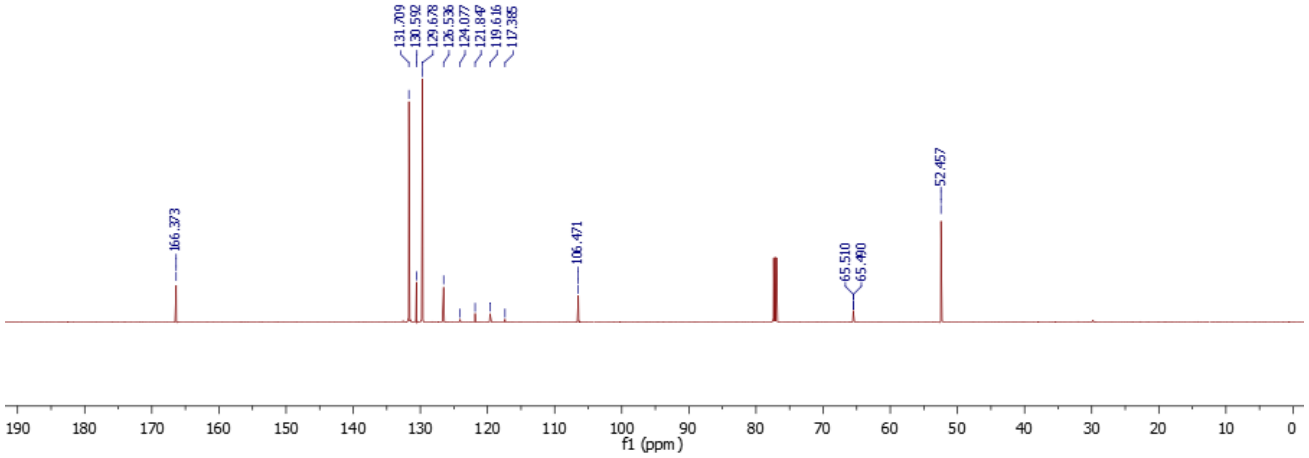
^{13}C NMR spectrum of 4-(trifluoromethylseleno)ethynylbenzophenone 2d



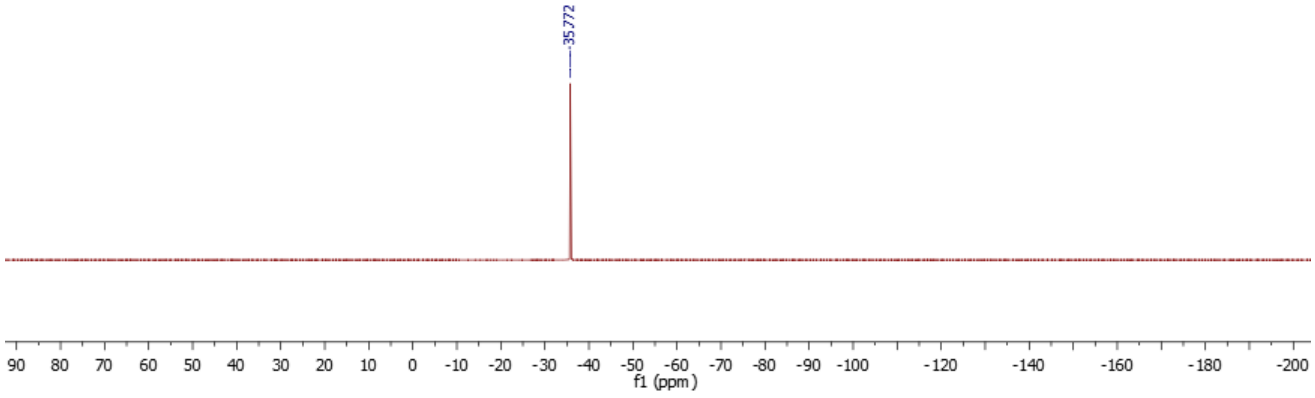
^{19}F NMR spectrum of 4-(trifluoromethylseleno)ethynylbenzophenone 2d



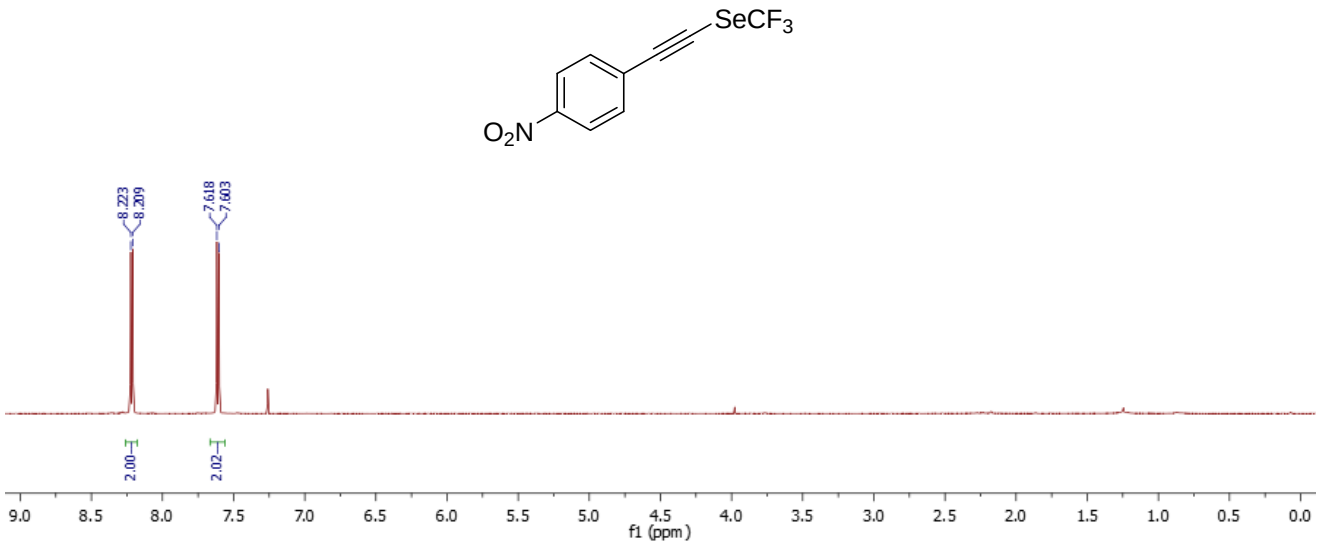
^{1}H NMR spectrum of methyl 4-(trifluoromethylseleno)ethynylbenzoate 2e



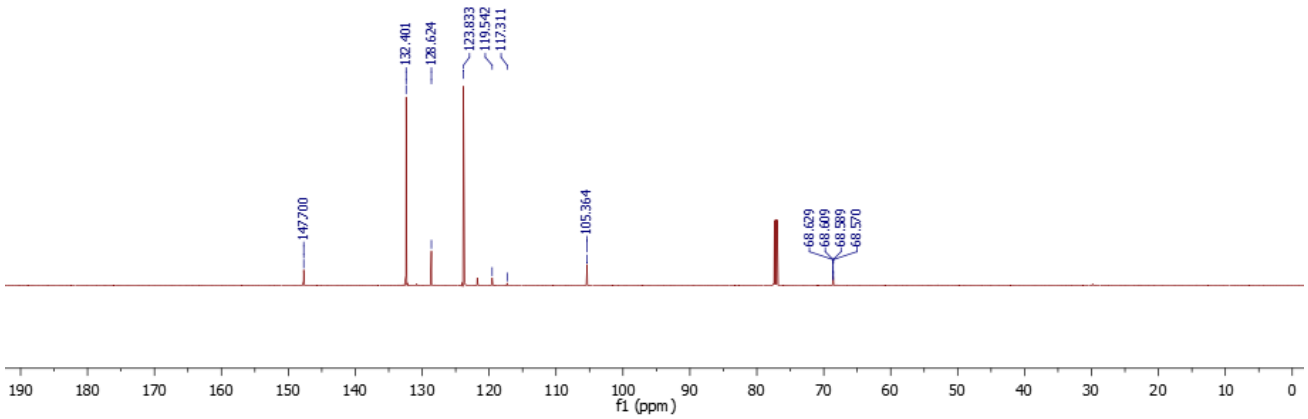
^{13}C NMR spectrum of methyl 4-(trifluoromethylseleno)ethynylbenzoate 2e



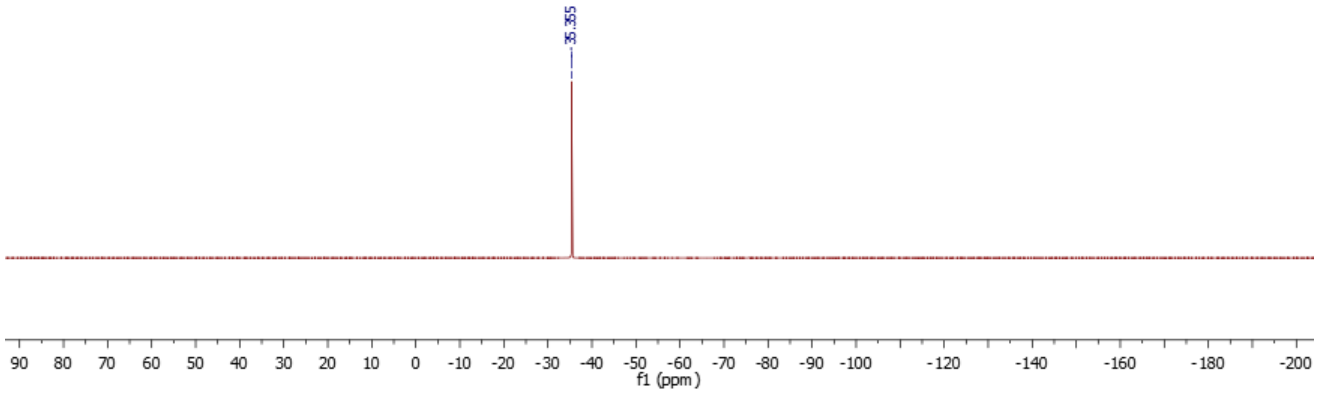
^{19}F NMR spectrum of methyl 4-(trifluoromethylseleno)ethynylbenzoate 2e



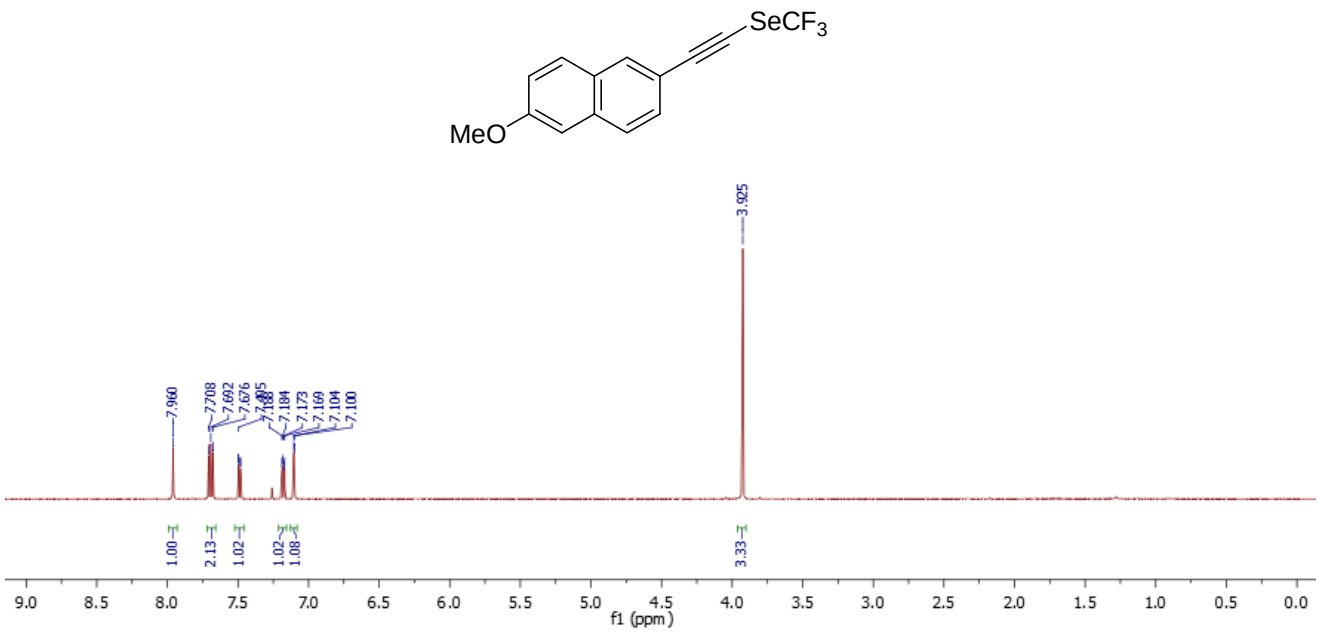
^{1}H NMR spectrum of 4-(trifluoromethylseleno)ethynyl-1-nitrobenzene 2f



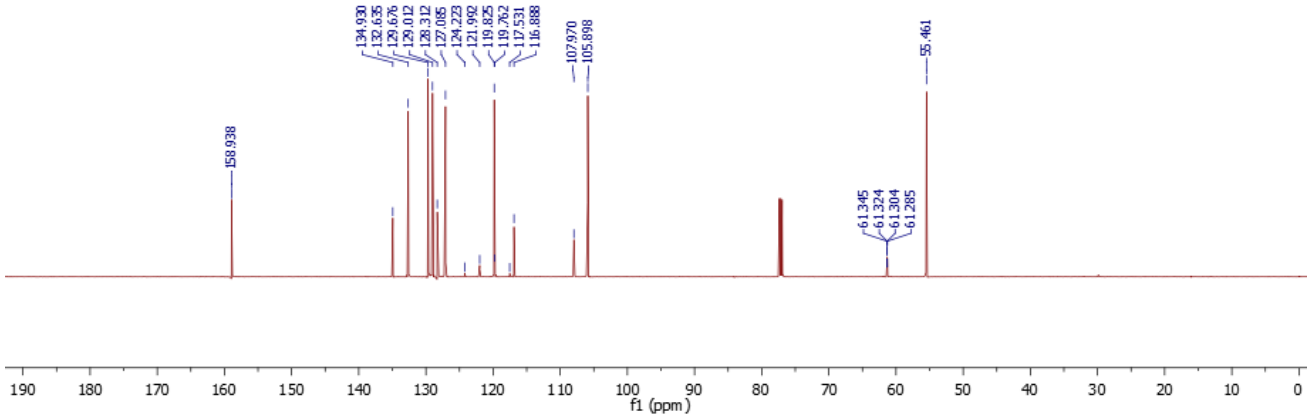
^{13}C NMR spectrum of 4-(trifluoromethylseleno)ethynyl-1-nitrobenzene 2f



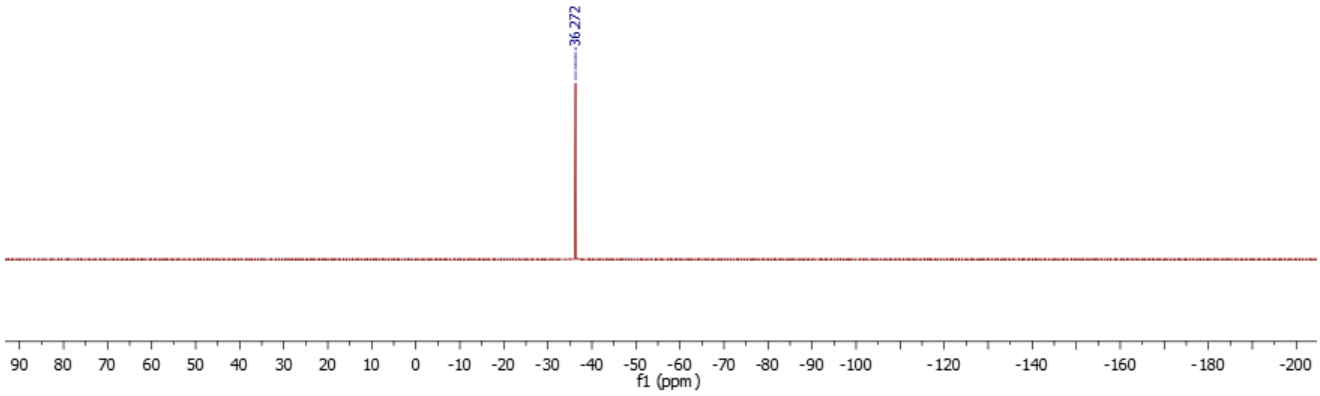
^{19}F NMR spectrum of 4-(trifluoromethylseleno)ethynyl-1-nitrobenzene 2f



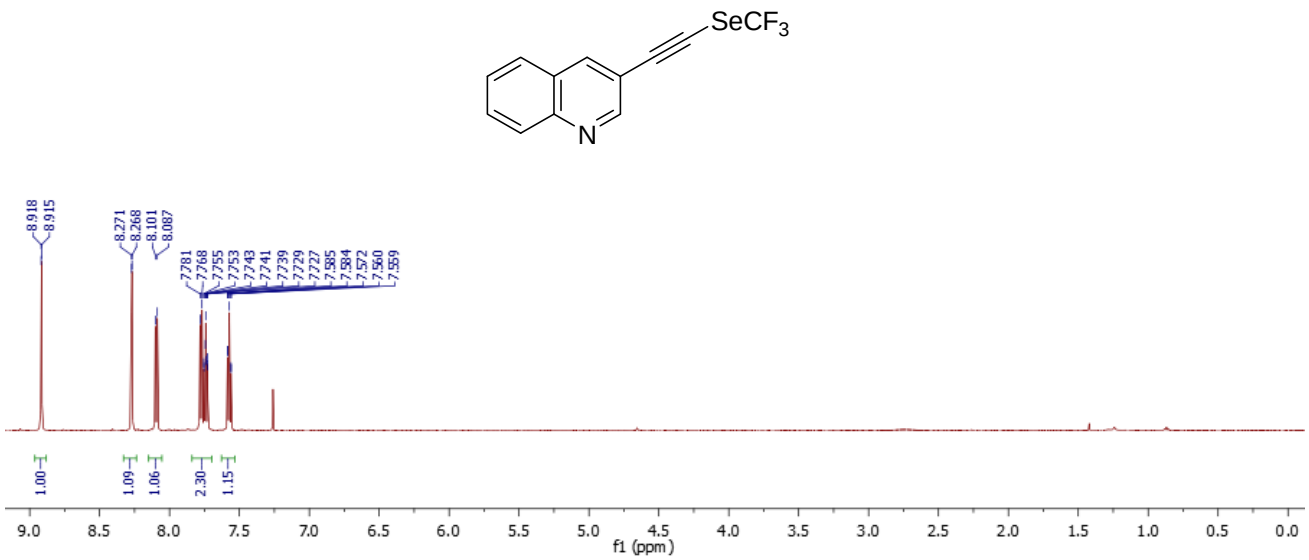
^{1}H NMR spectrum of 6-(trifluoromethylseleno)ethynyl-2-methoxynaphthalene 2g



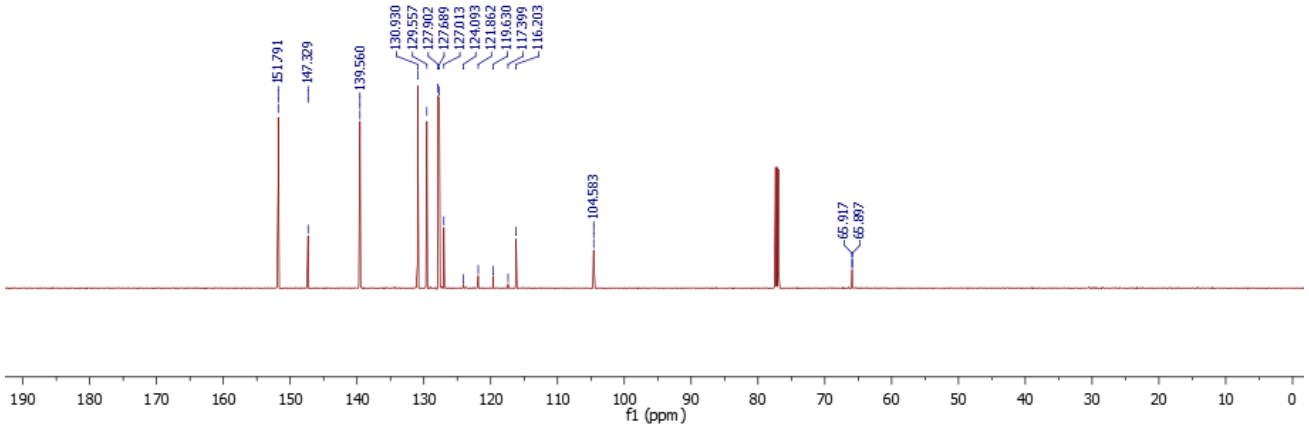
^{13}C NMR spectrum of 6-(trifluoromethylseleno)ethynyl-2-methoxynaphthalene 2g



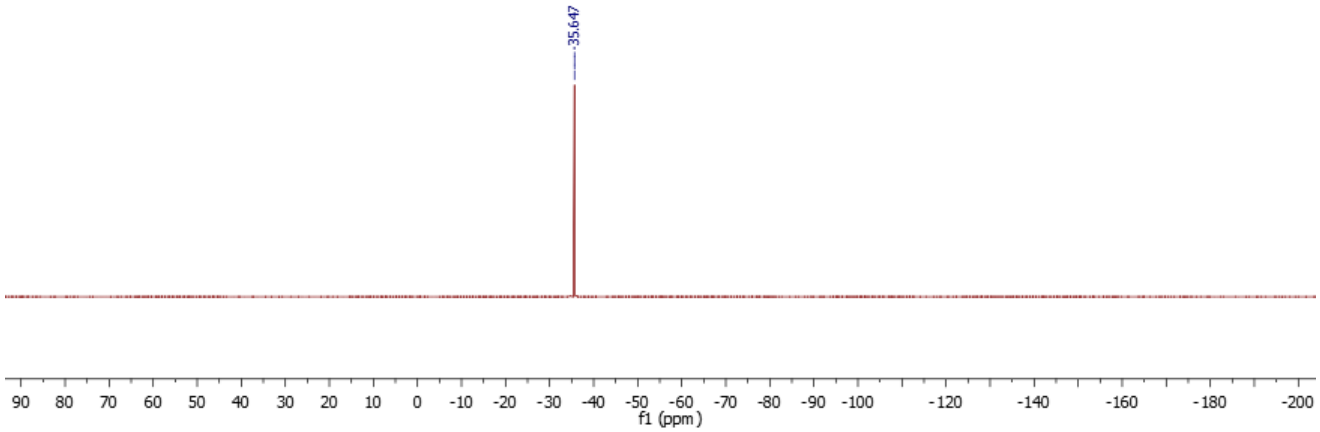
^{19}F NMR spectrum of 6-(trifluoromethylseleno)ethynyl-2-methoxynaphthalene 2g



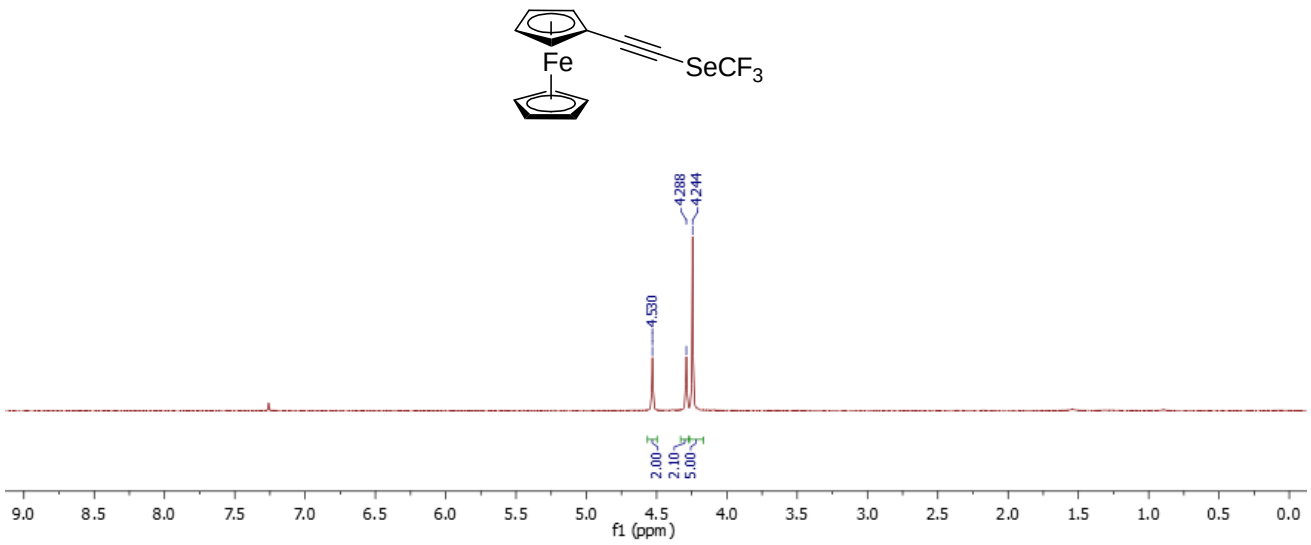
^{1}H NMR spectrum of 3-(trifluoromethylseleno)ethynylquinoline 2h



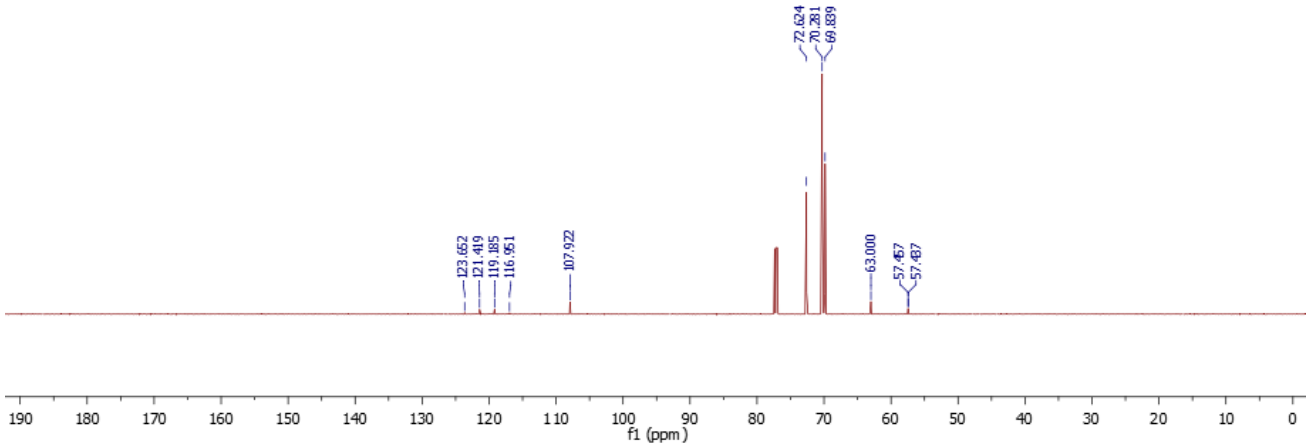
^{13}C NMR spectrum of 3-(trifluoromethylseleno)ethynylquinoline 2h



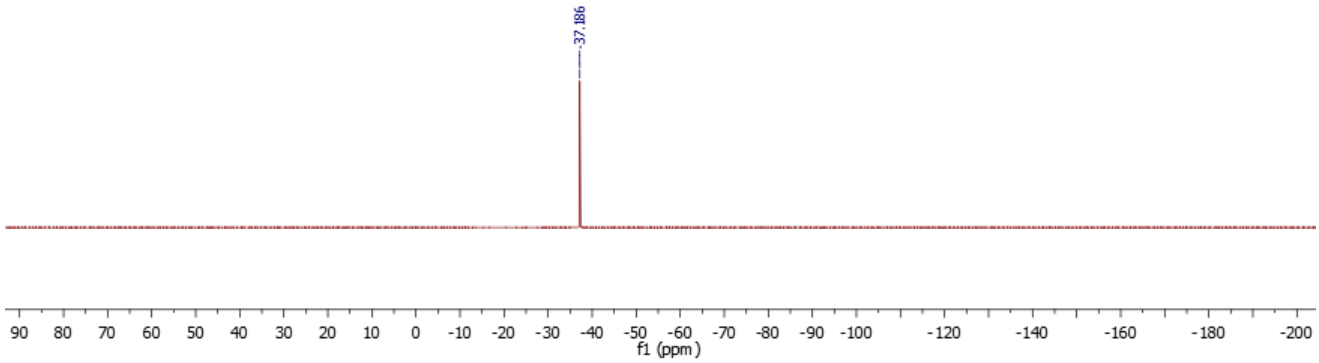
^{19}F NMR spectrum of 3-(trifluoromethylseleno)ethynylquinoline 2h



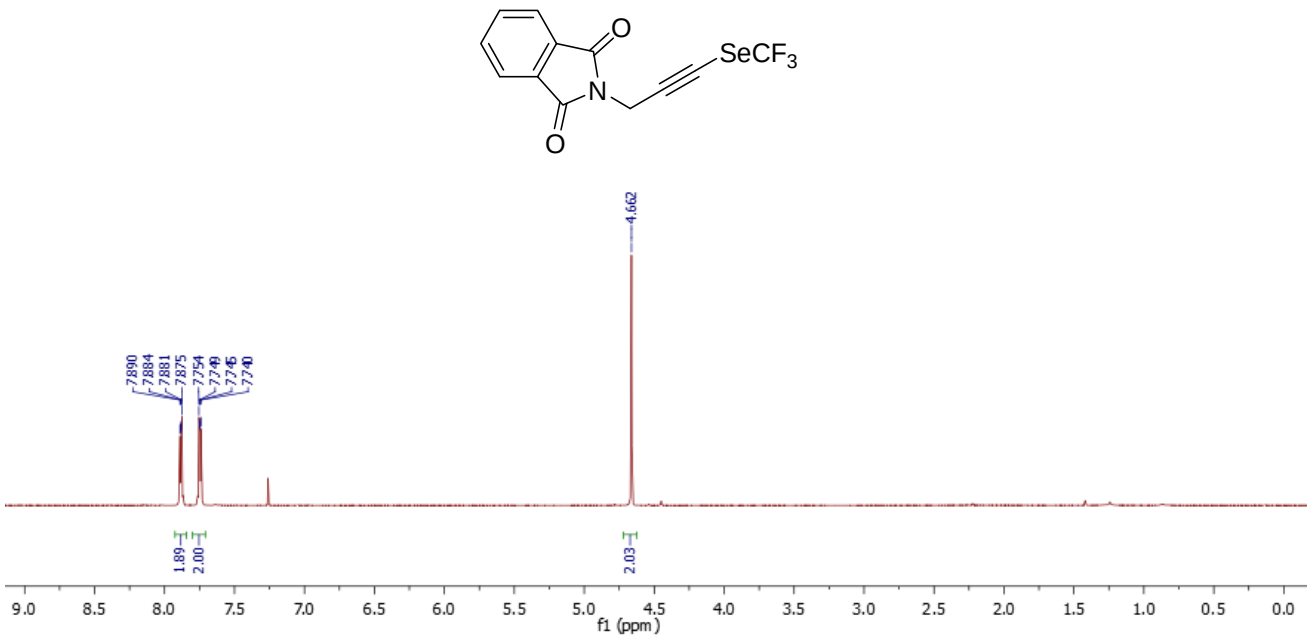
^{1}H NMR spectrum of (trifluoromethylseleno)ethynylferrocene 2i



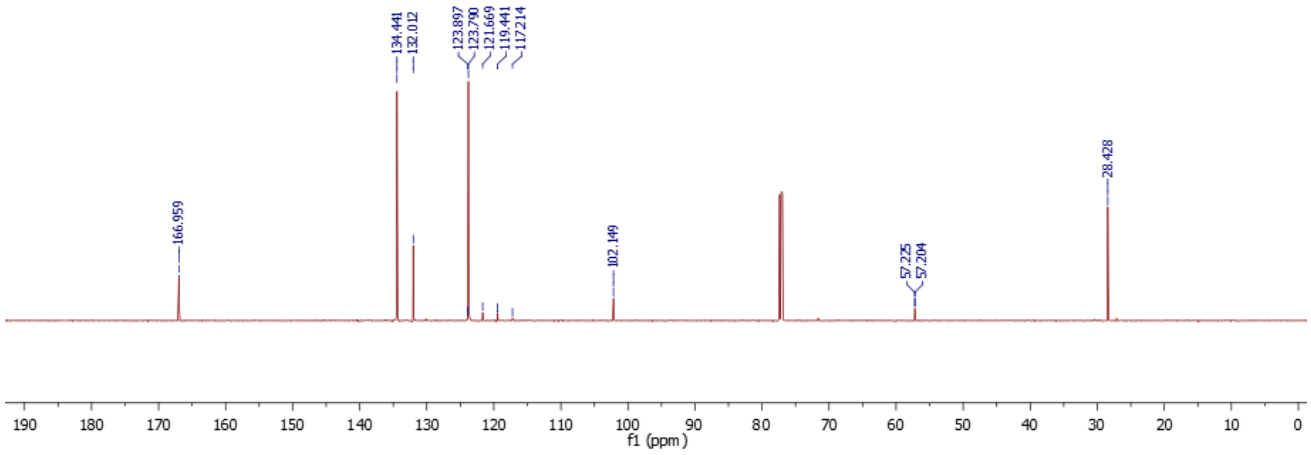
^{13}C NMR spectrum of (trifluoromethylseleno)ethynylferrocene 2i



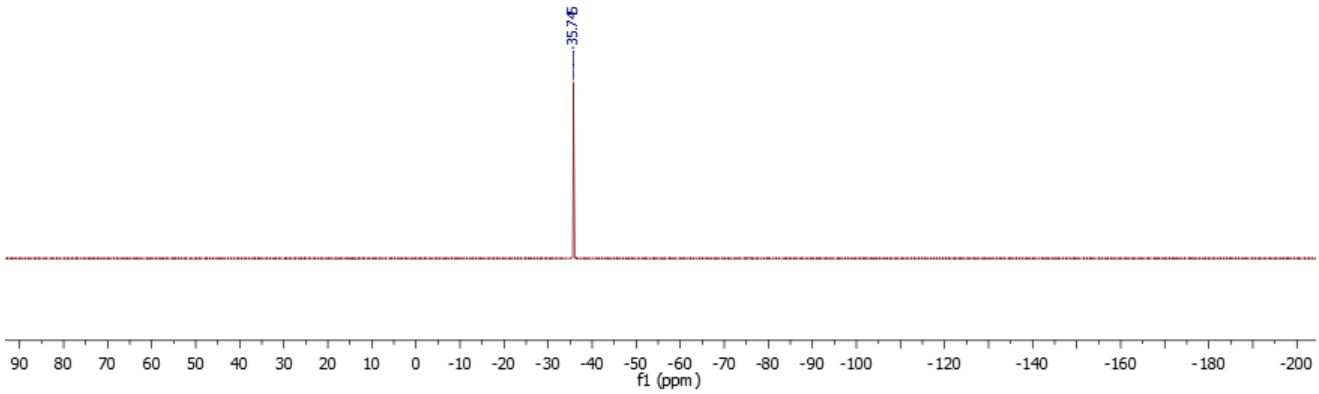
^{19}F NMR spectrum of (trifluoromethylseleno)ethynylferrocene 2i



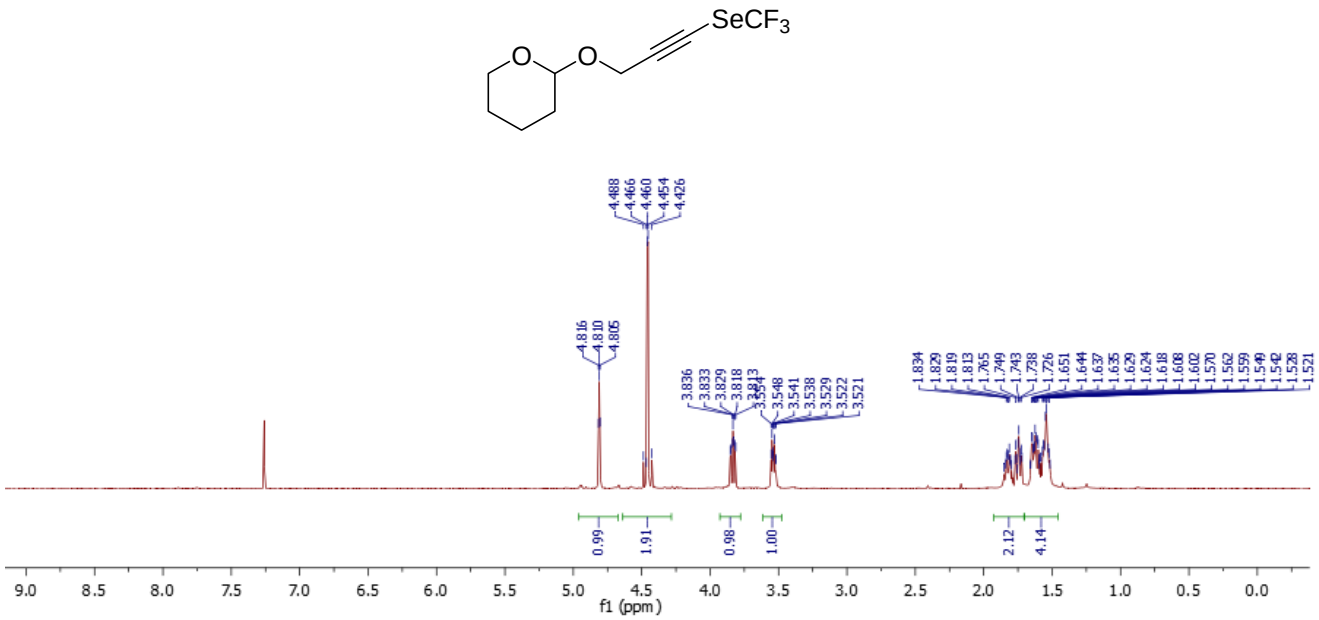
^{1}H NMR spectrum of 3-phthalimido-1-(trifluoromethylseleno)propyne 2j



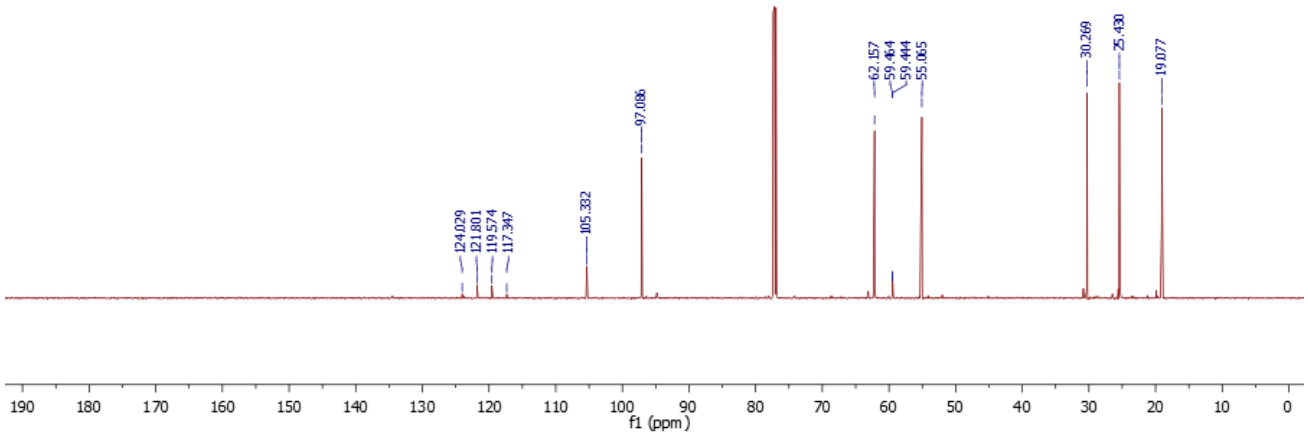
^{13}C NMR spectrum of 3-phthalimido-1-(trifluoromethylseleno)propyne 2j



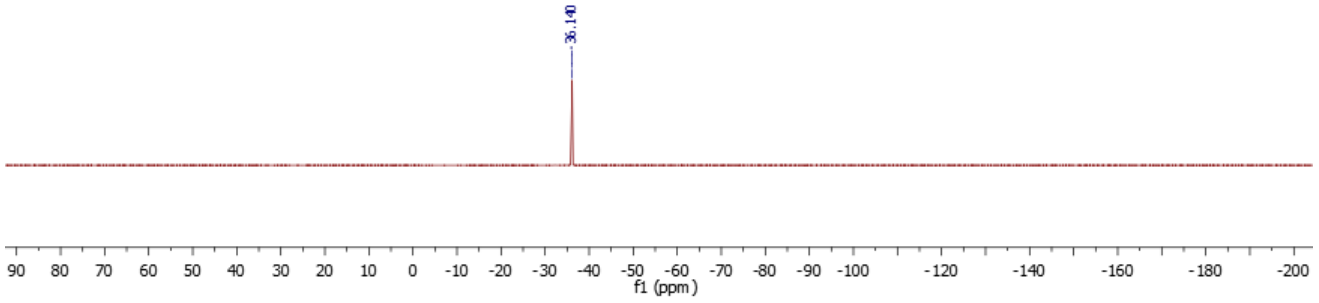
^{19}F NMR spectrum of 3-phthalimido-1-(trifluoromethylseleno)propyne 2j



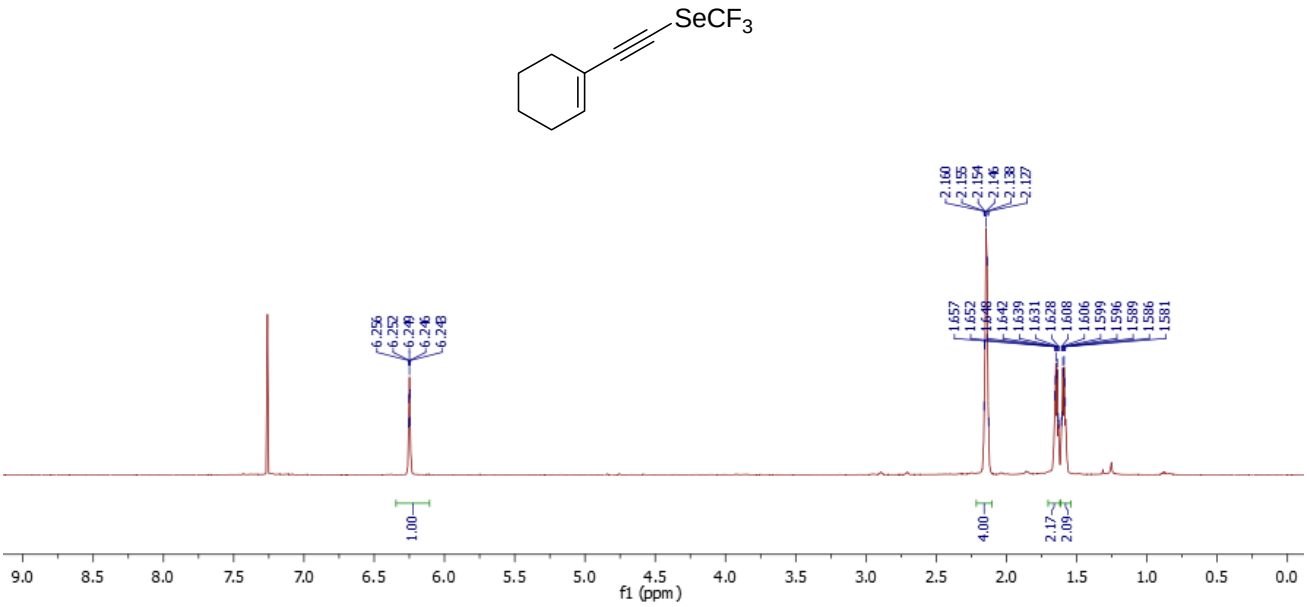
[1]H NMR spectrum of 2-((3-((Trifluoromethyl)seleno)prop-2-yn-1-yl)oxy)tetrahydro-2H-pyran 2k



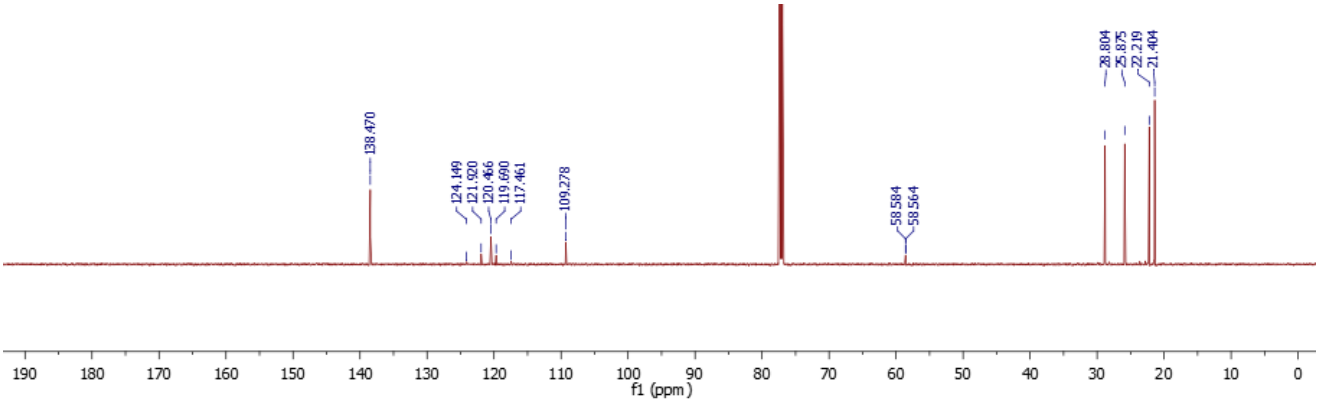
[13]C NMR spectrum of 2-((3-((Trifluoromethyl)seleno)prop-2-yn-1-yl)oxy)tetrahydro-2H-pyran 2k



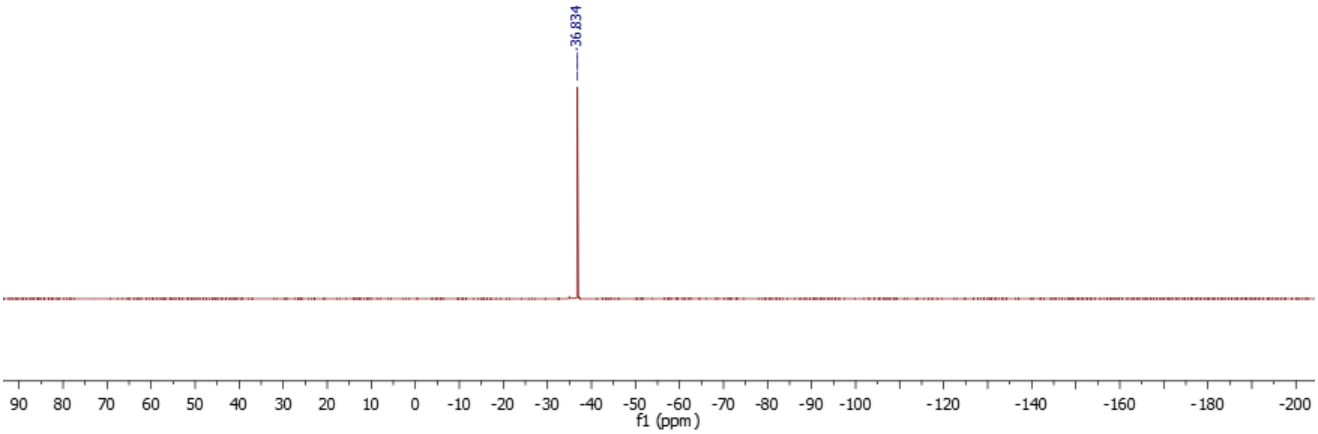
[19]F NMR spectrum of 2-((3-((Trifluoromethyl)seleno)prop-2-yn-1-yl)oxy)tetrahydro-2H-pyran 2k



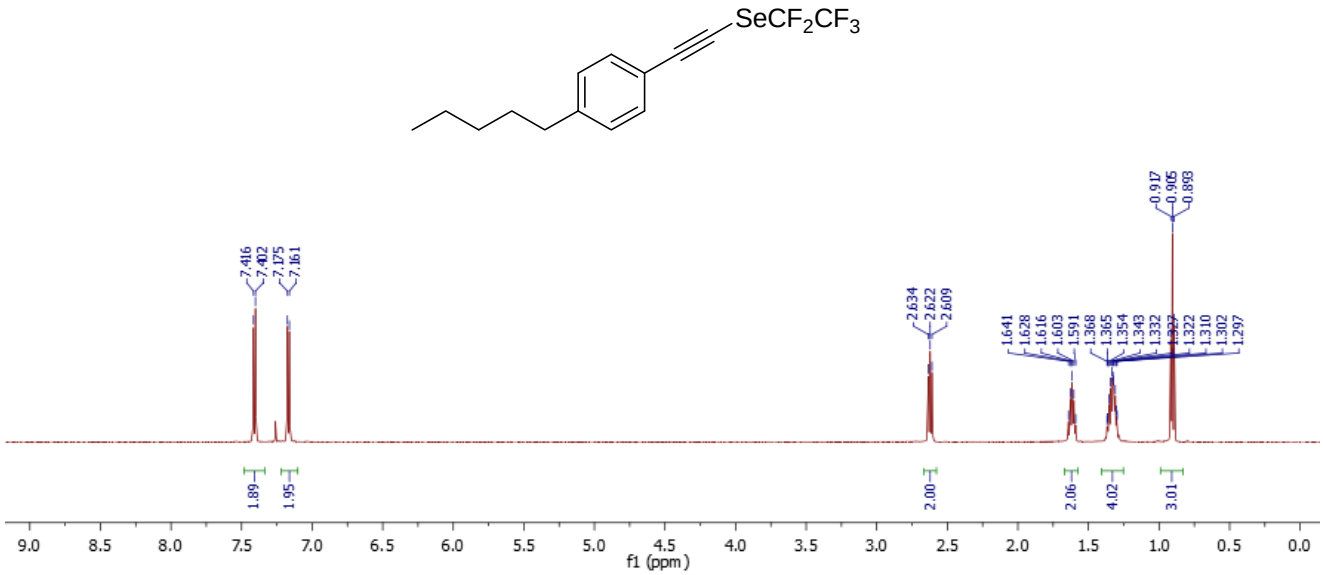
^{1}H NMR spectrum of 1-(trifluoromethylseleno)ethynylcyclohexene 2l



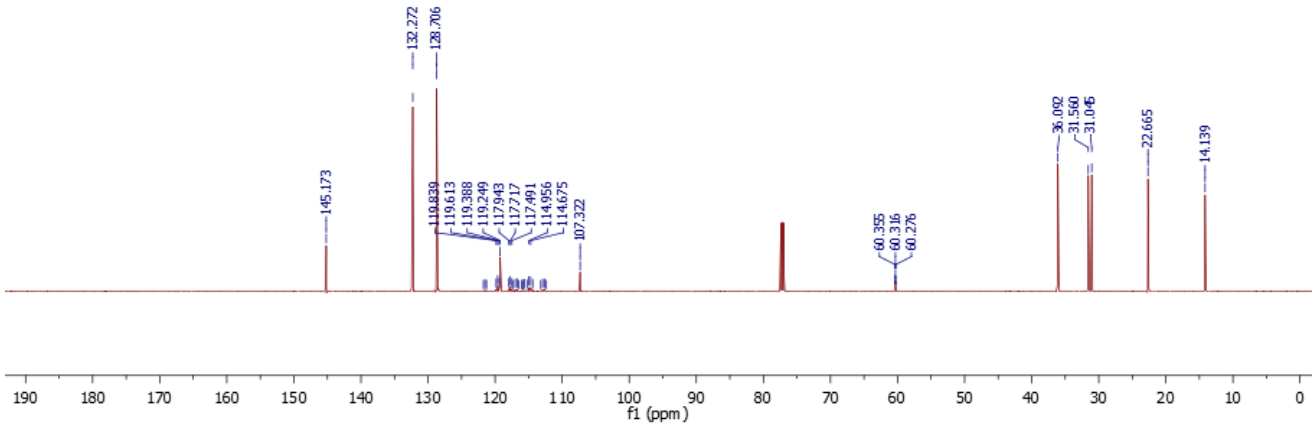
^{13}C NMR spectrum of 1-(trifluoromethylseleno)ethynylcyclohexene 2l



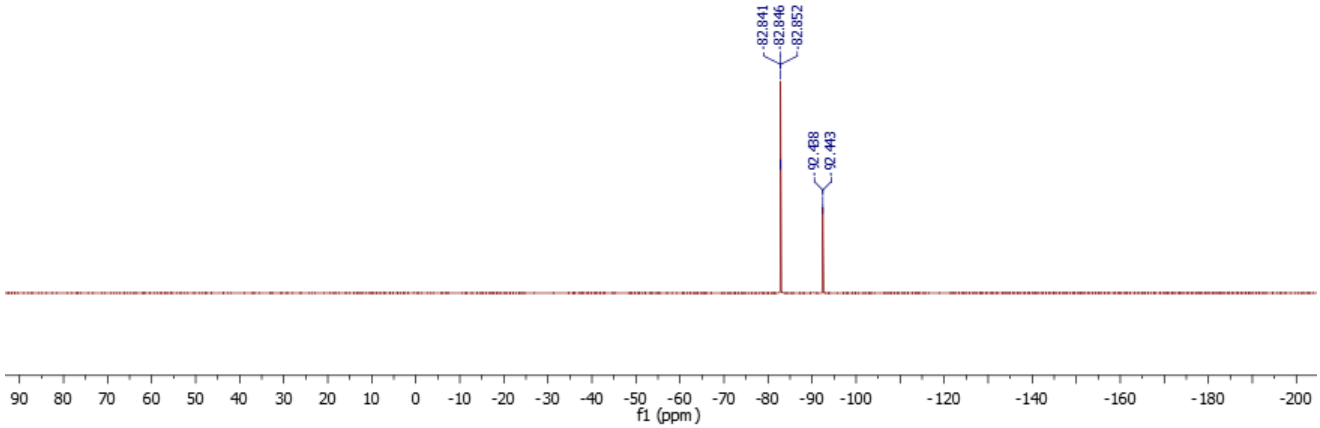
^{19}F NMR spectrum of 1-(trifluoromethylseleno)ethynylcyclohexene 2l



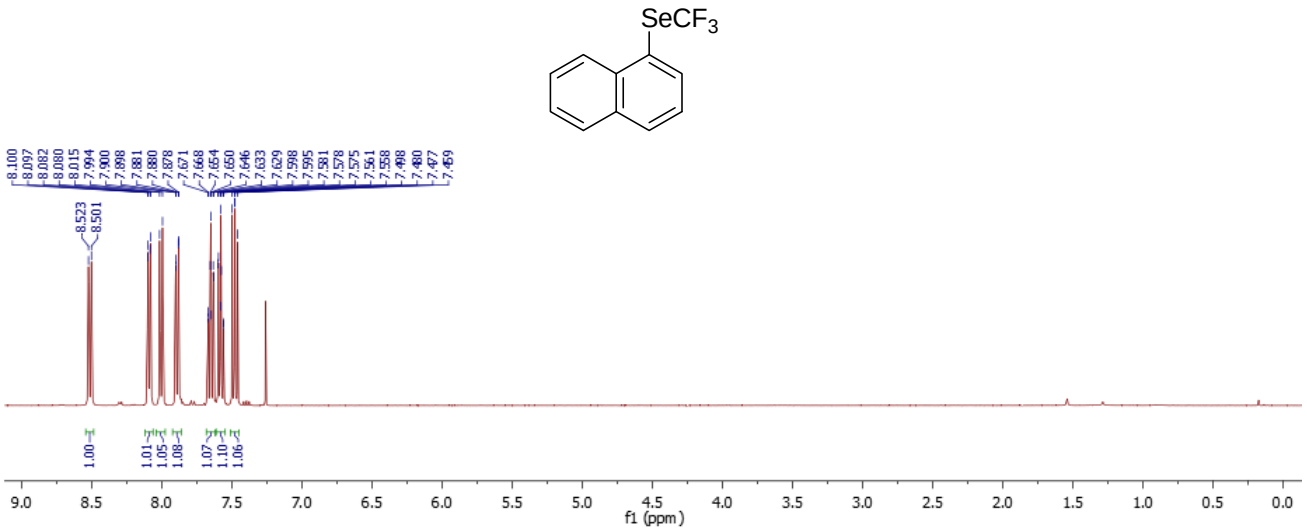
^{1}H NMR spectrum of 1-(pentafluoroethylseleno)ethynyl-4-pentylbenzene 11a



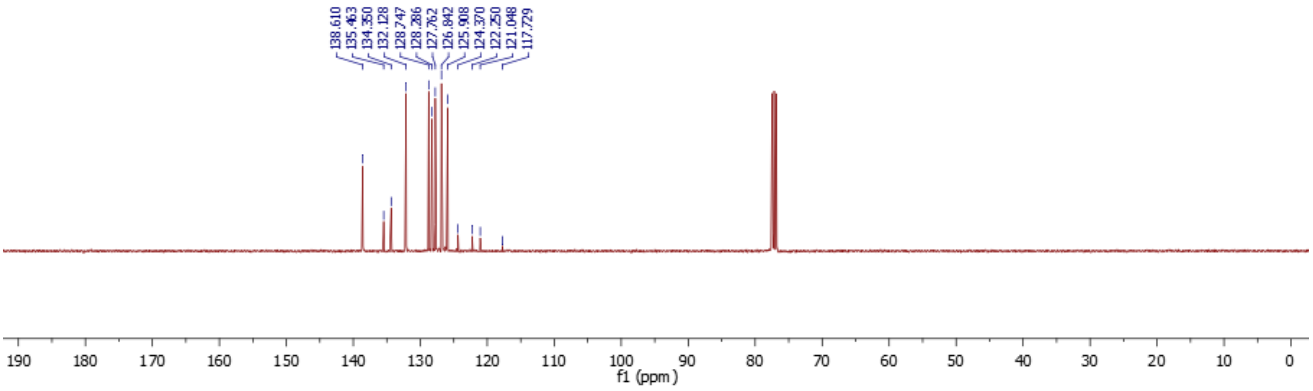
^{13}C NMR spectrum of 1-(pentafluoroethylseleno)ethynyl-4-pentylbenzene 11a



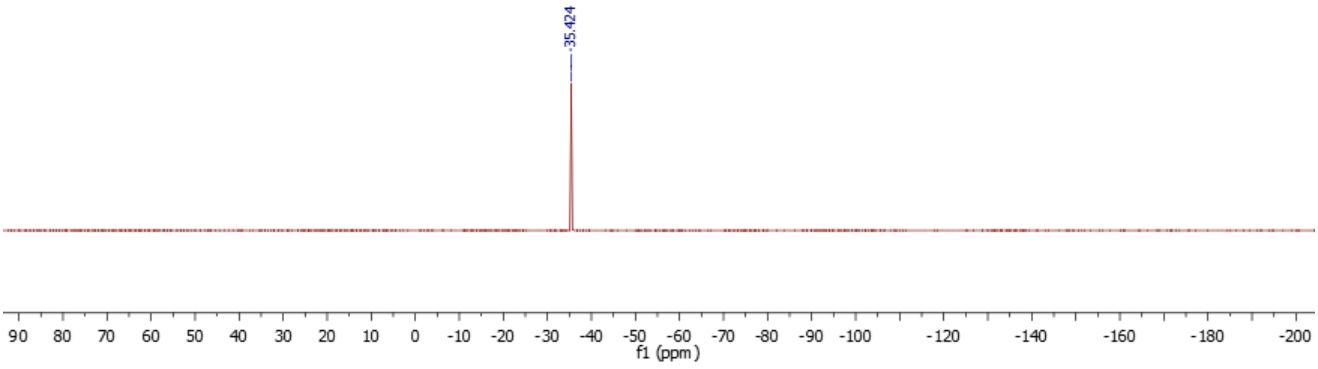
^{19}F NMR spectrum of 1-(pentafluoroethylseleno)ethynyl-4-pentylbenzene 11a



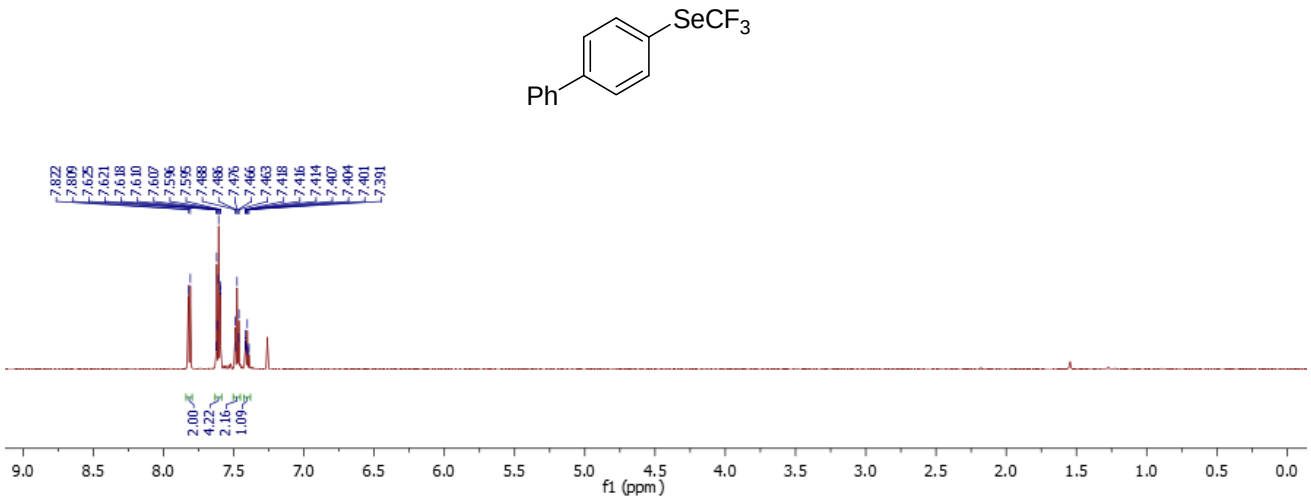
^{1}H NMR spectrum of 1-(trifluoromethylseleno)naphthalene 4a



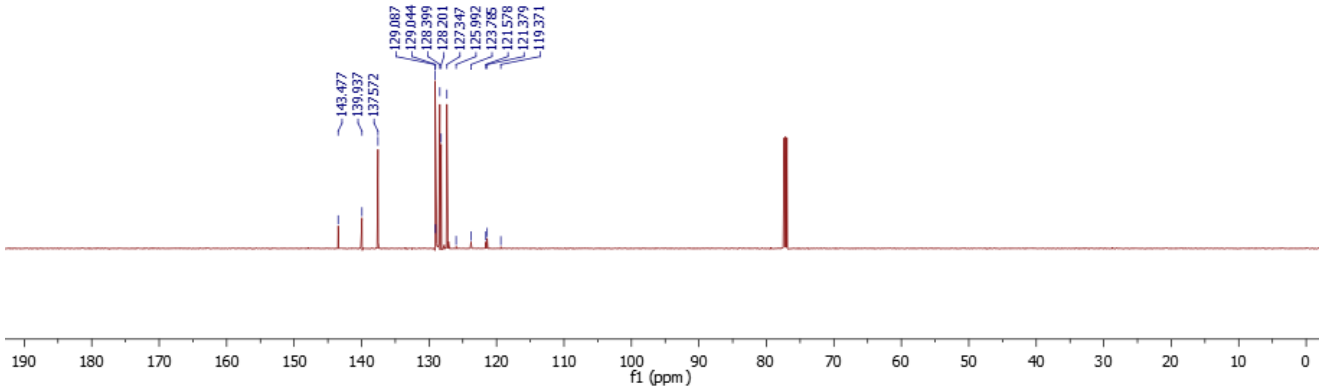
^{13}C NMR spectrum of 1-(trifluoromethylseleno)naphthalene 4a



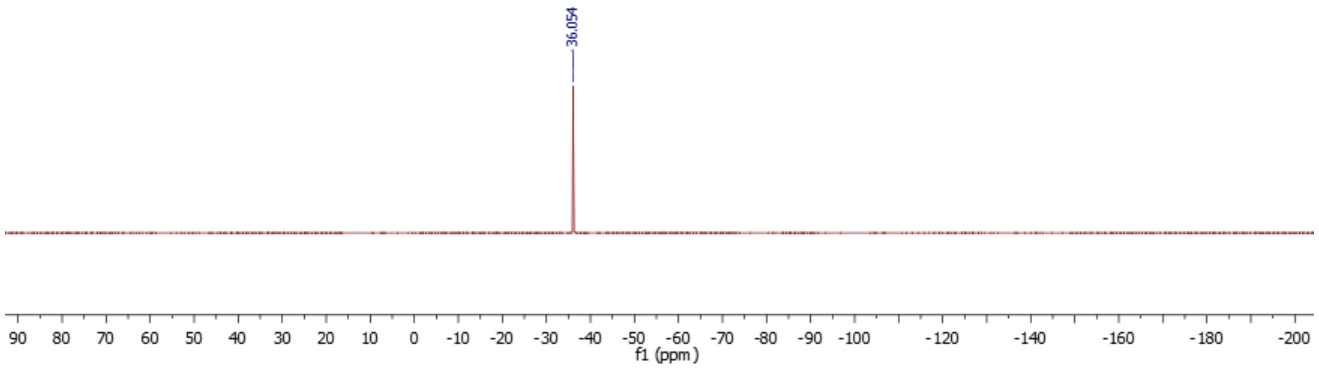
^{19}F NMR spectrum of 1-(trifluoromethylseleno)naphthalene 4a



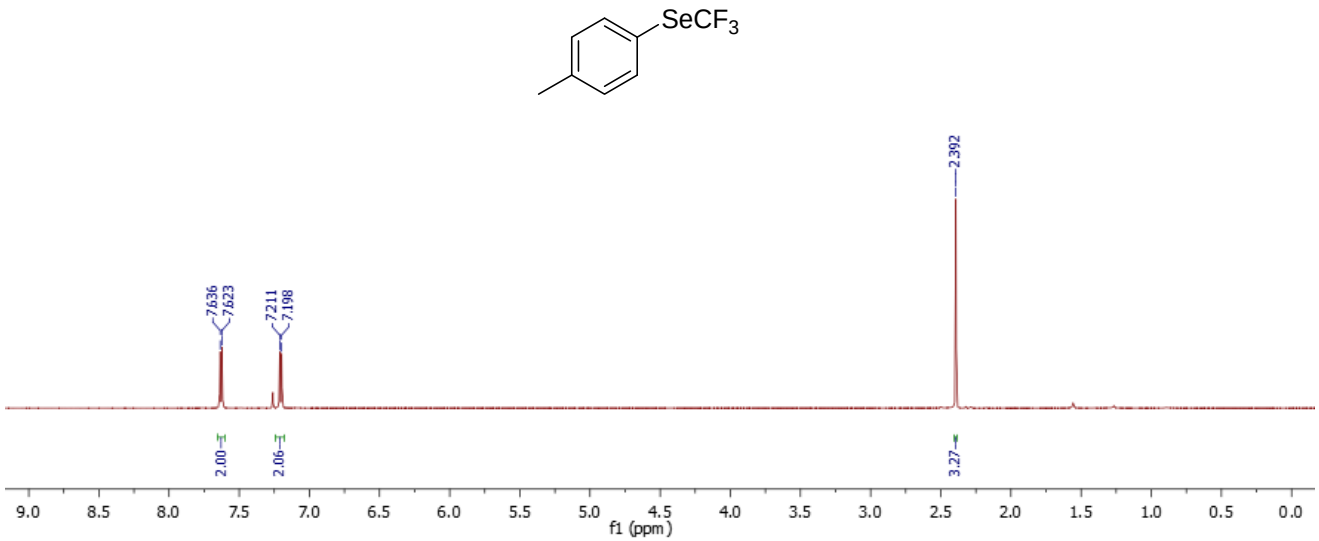
^{1}H NMR spectrum of 4-(trifluoromethylseleno)biphenyl 4b



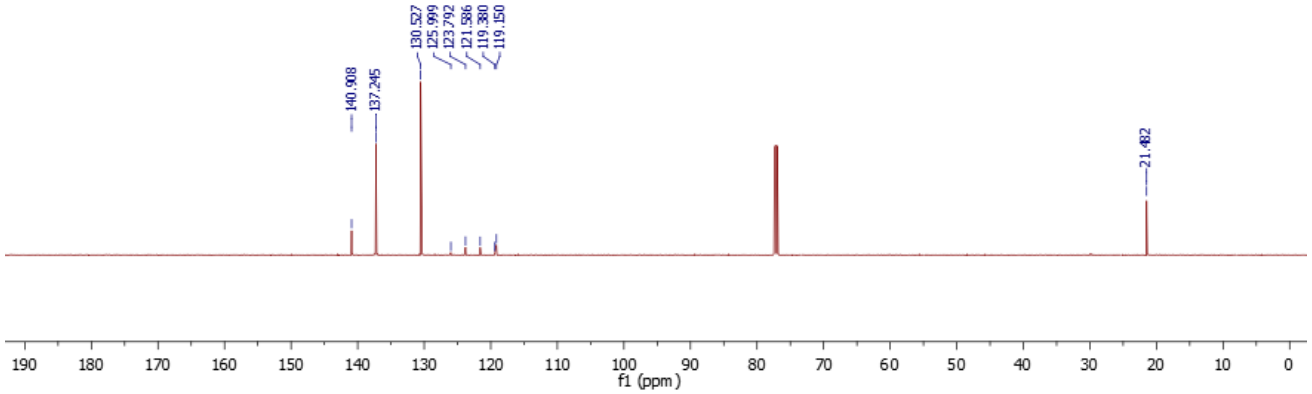
^{13}C NMR spectrum of 4-(trifluoromethylseleno)biphenyl 4b



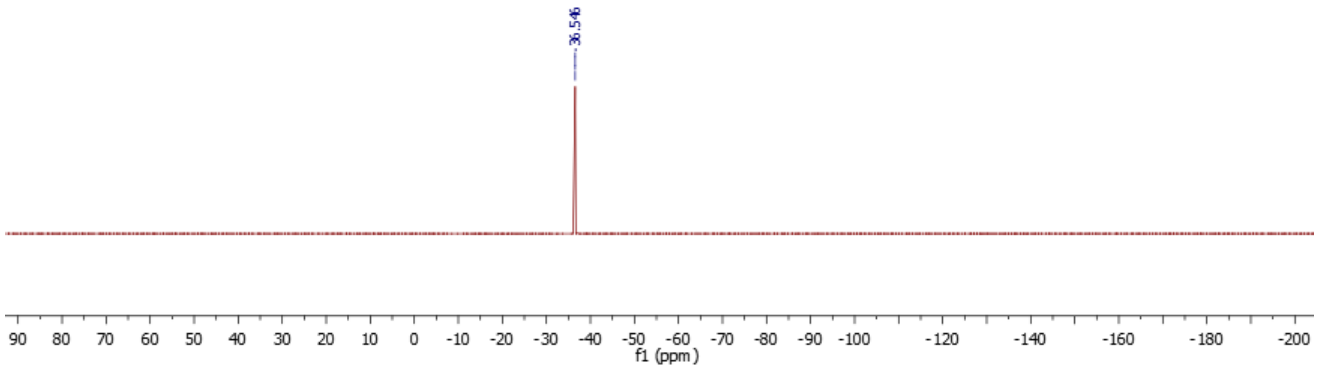
^{19}F NMR spectrum of 4-(trifluoromethylseleno)biphenyl 4b



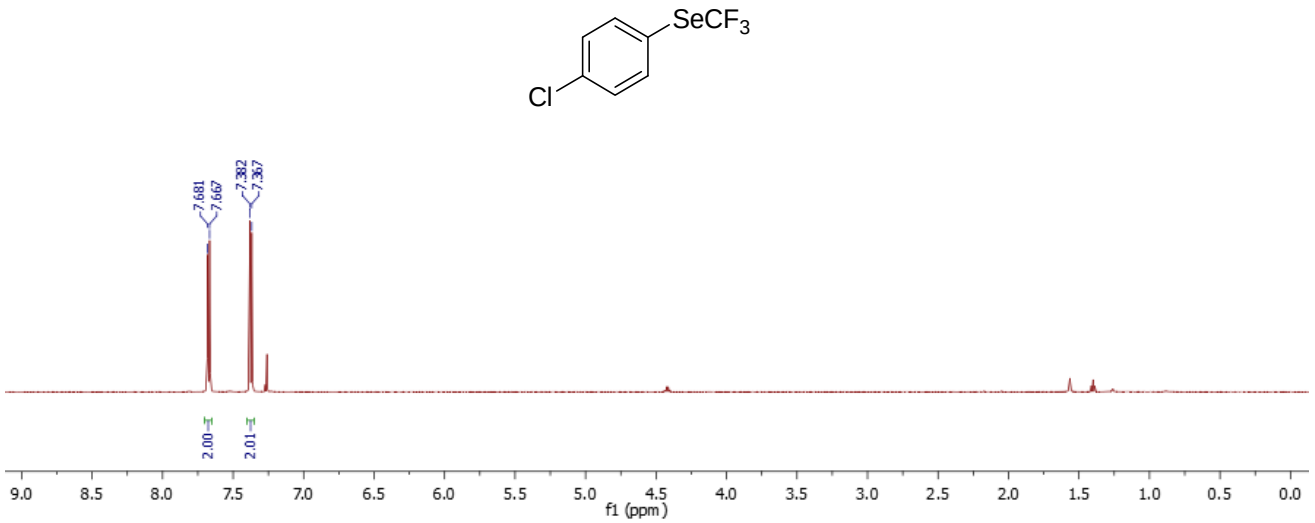
^{1}H NMR spectrum of 4-(trifluoromethylseleno)toluene 4c



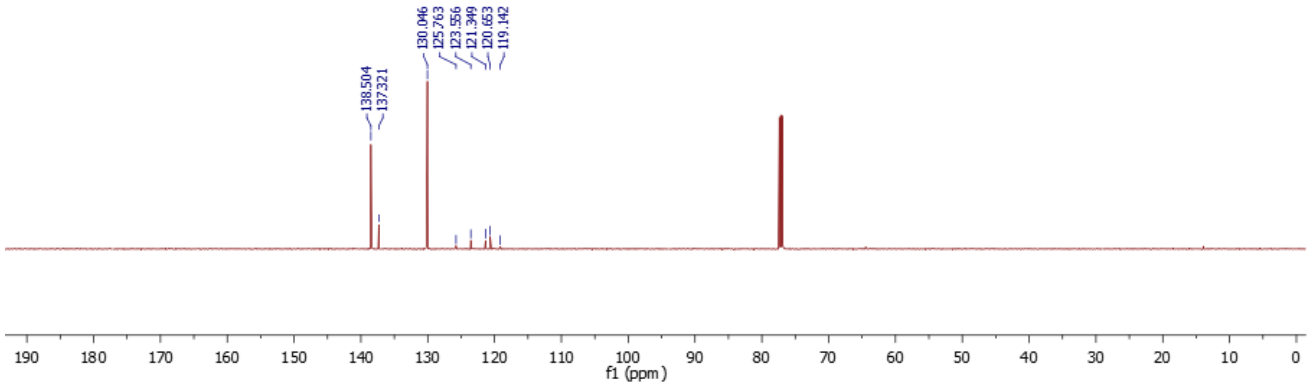
^{13}C NMR spectrum of 4-(trifluoromethylseleno)toluene 4c



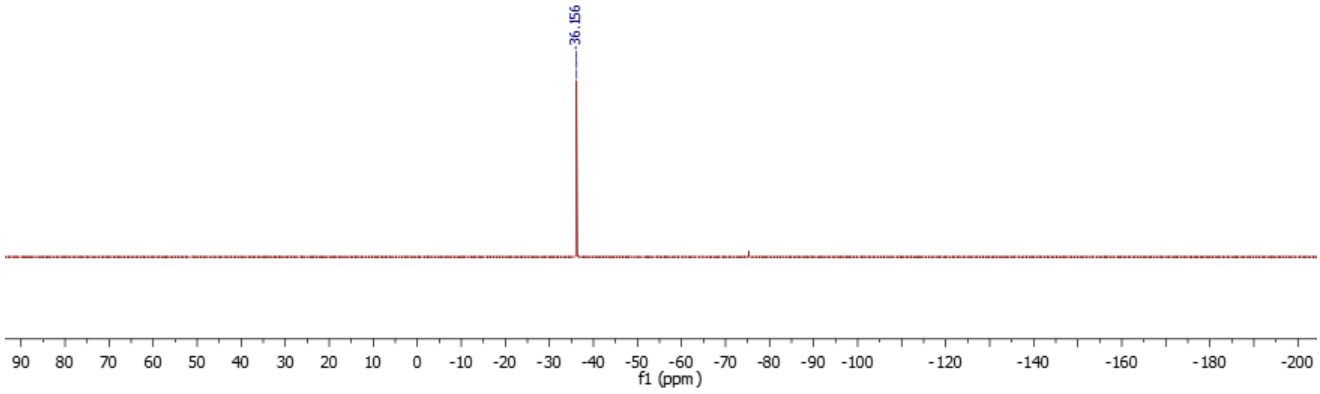
^{19}F NMR spectrum of 4-**(trifluoromethylseleno)toluene 4c**



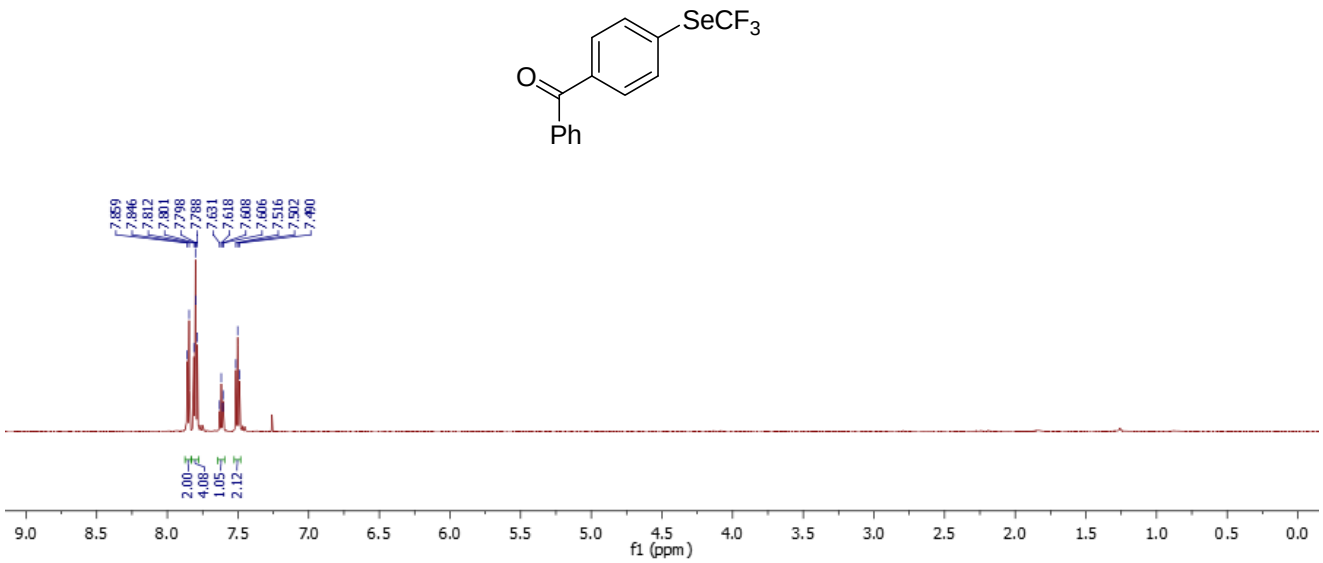
^{1}H NMR spectrum of 4-chloro-1-(trifluoromethylseleno)benzene 4d



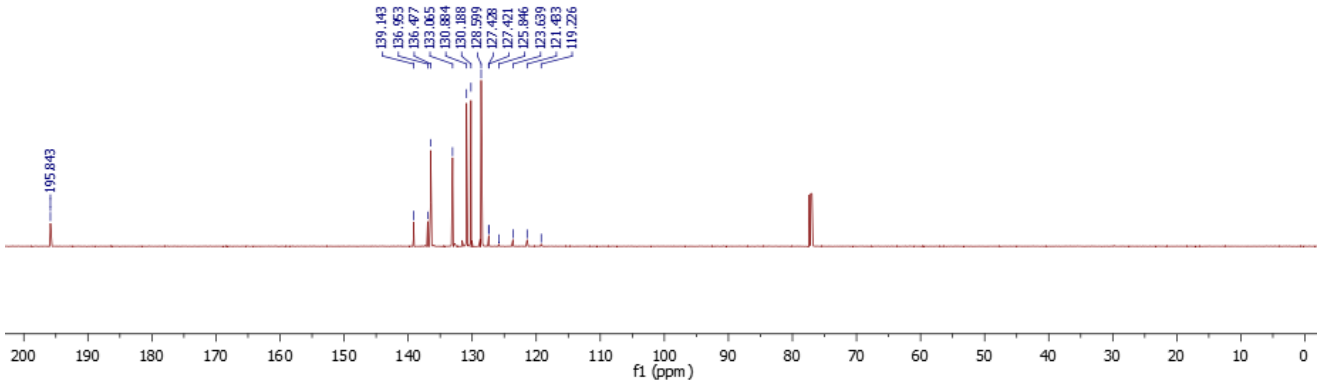
^{13}C NMR spectrum of 4-chloro-1-(trifluoromethylseleno)benzene 4d



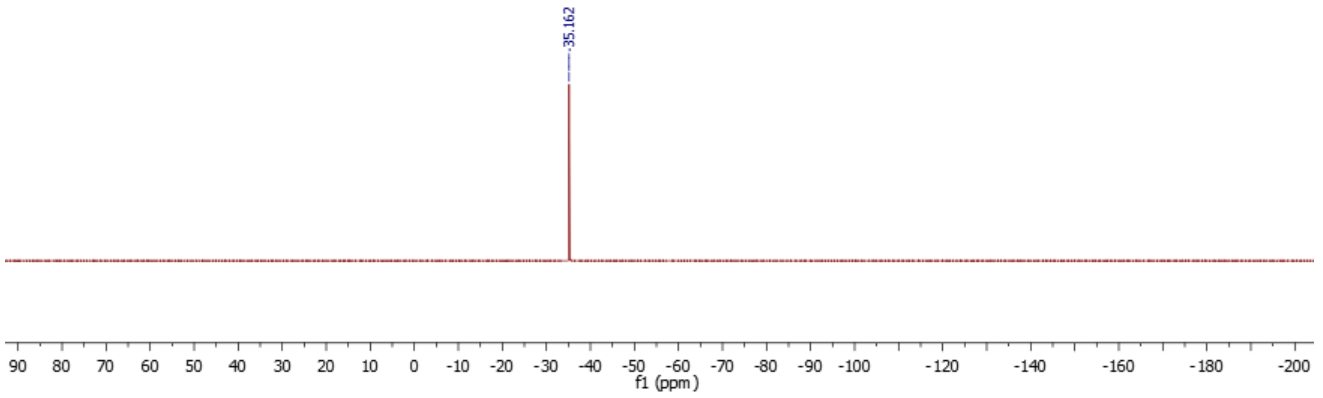
^{19}F NMR spectrum of 4-chloro-1-(trifluoromethylseleno)benzene 4d



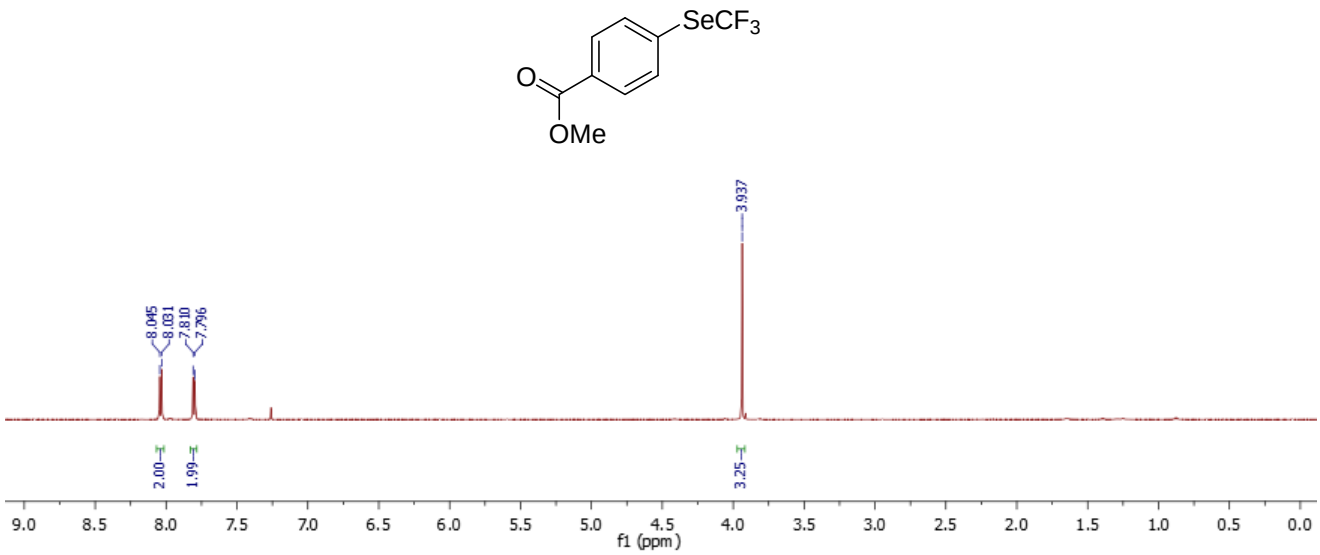
^{1}H NMR spectrum of 4-(trifluoromethylseleno)benzophenone 4e



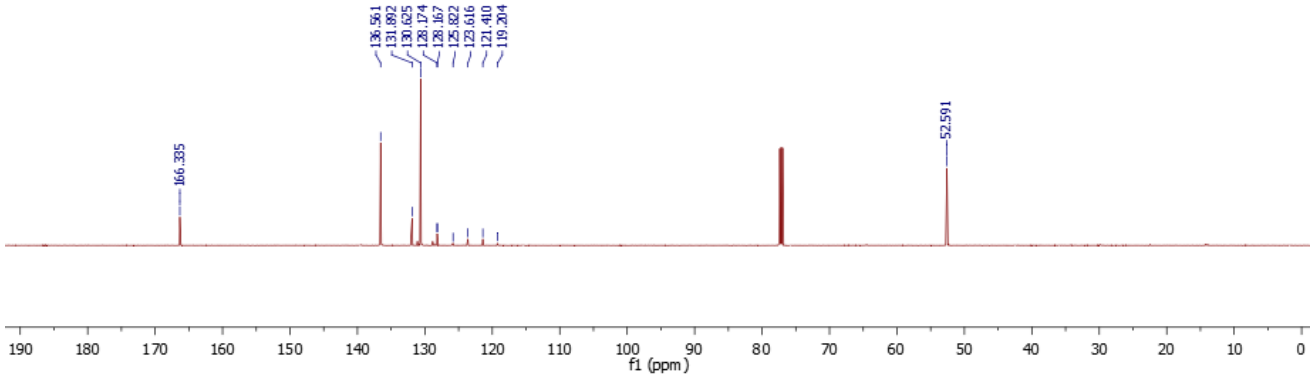
^{13}C NMR spectrum of 4-(trifluoromethylseleno)benzophenone 4e



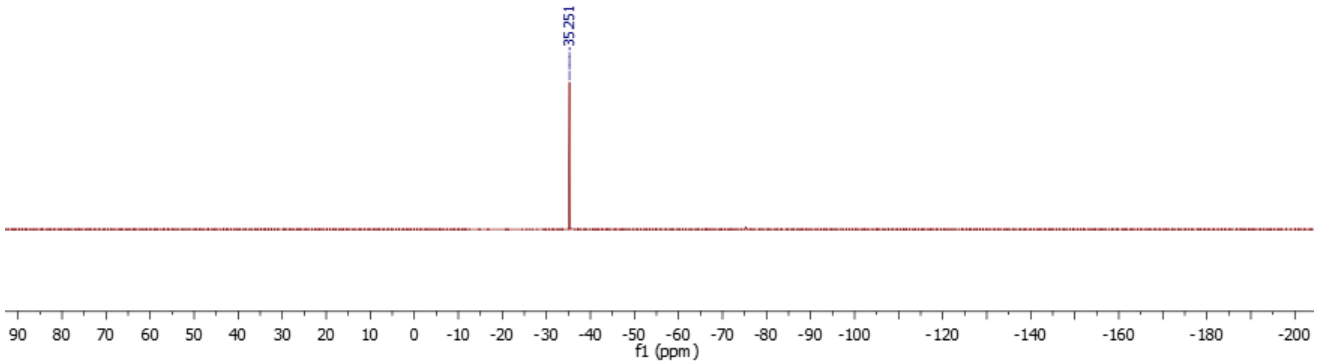
^{19}F NMR spectrum of 4-(trifluoromethylseleno)benzophenone 4e



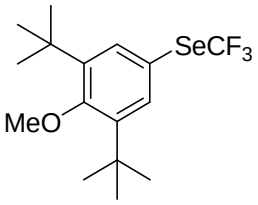
^{1}H NMR spectrum of methyl 4-(trifluoromethylseleno)benzoate 4f

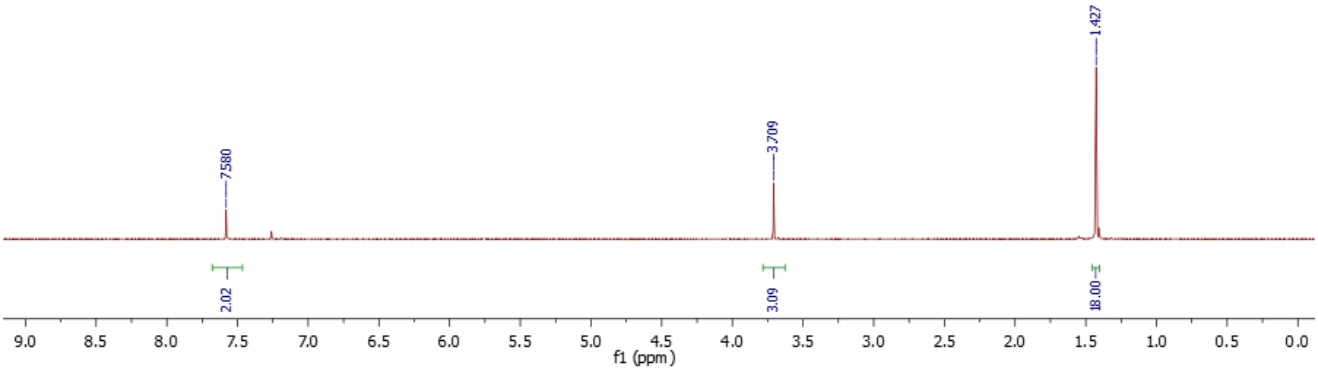


^{13}C NMR spectrum of methyl 4-(trifluoromethylseleno)benzoate 4f

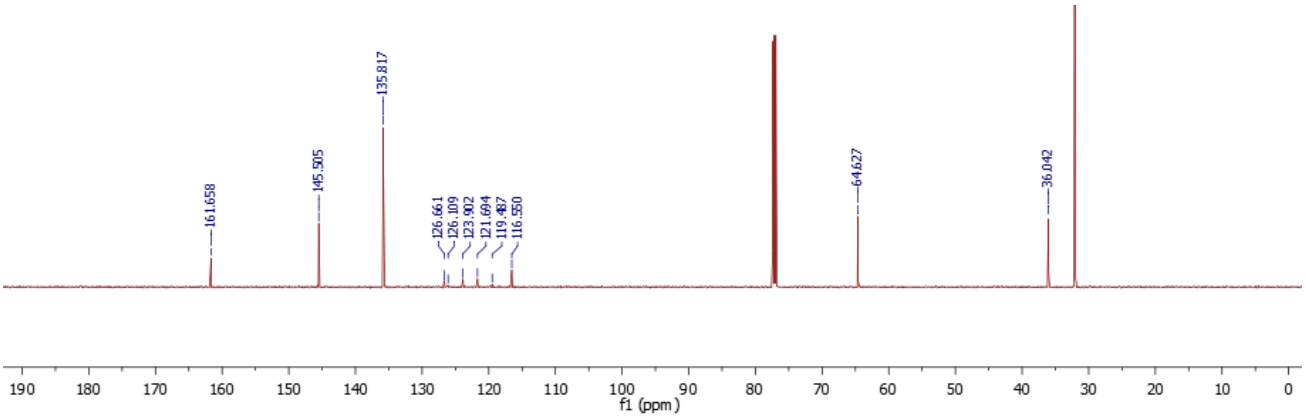


^{19}F NMR spectrum of methyl 4-(trifluoromethylseleno)benzoate 4f

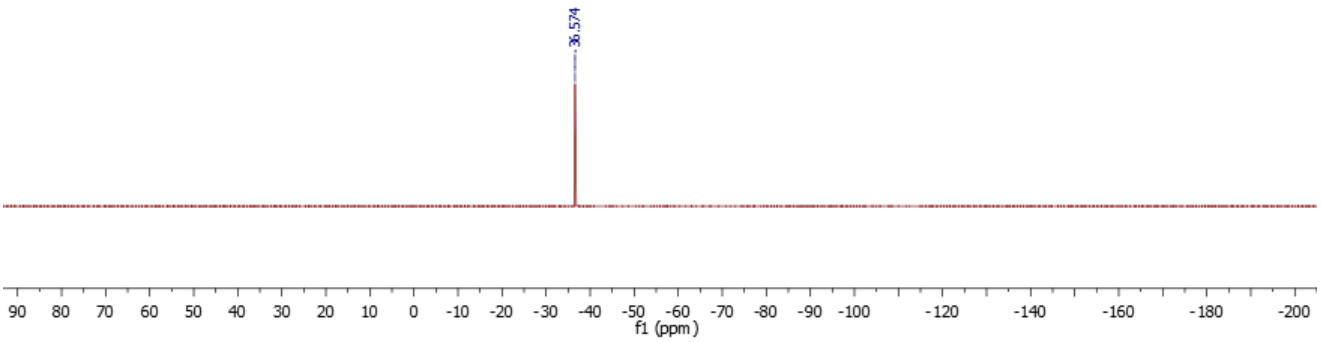




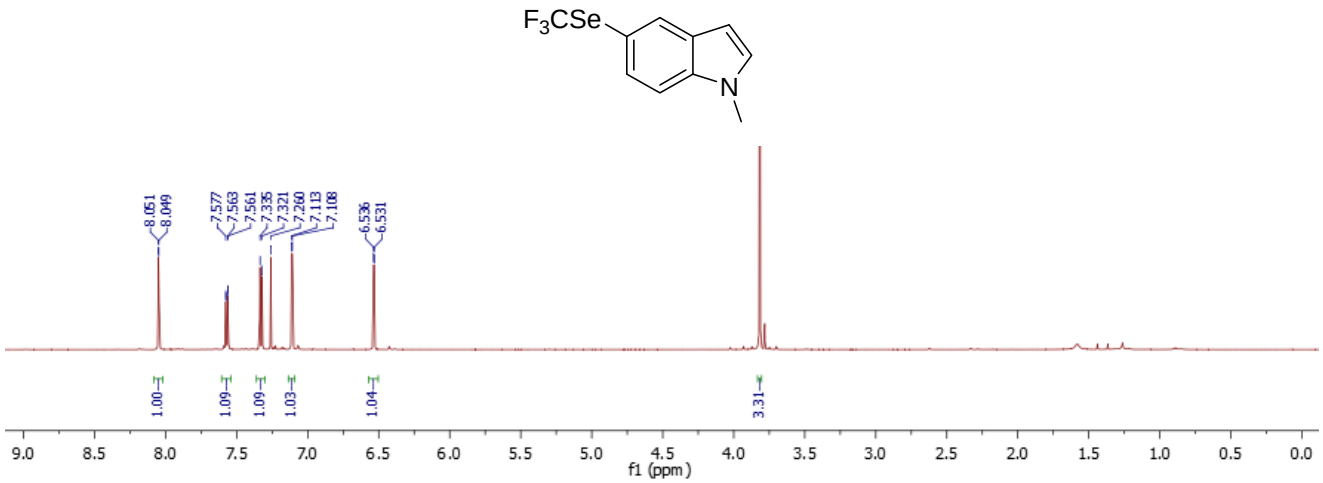
^{1}H NMR spectrum of 2,6-di(*tert*-butyl)-4-(trifluoromethylseleno)anisole 4g



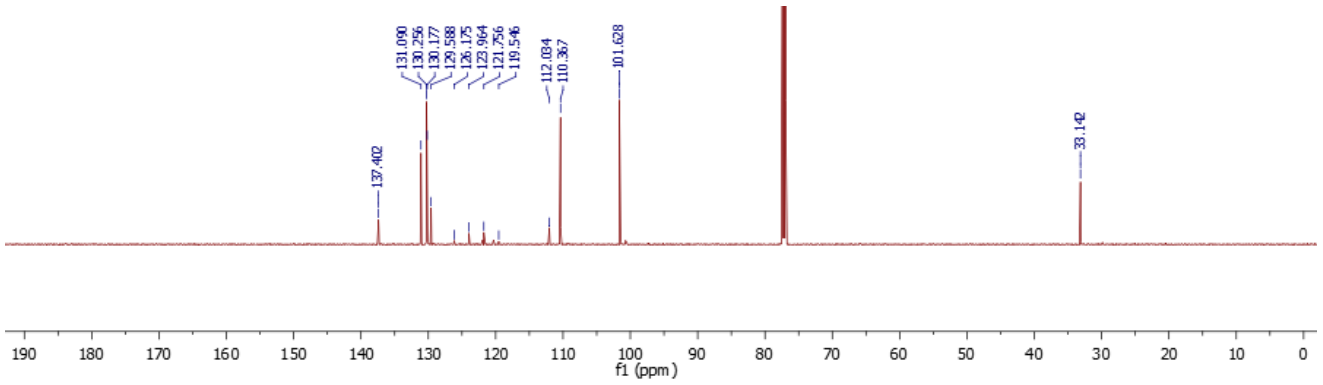
^{13}C NMR spectrum of 2,6-di(*tert*-butyl)-4-(trifluoromethylseleno)anisole 4g



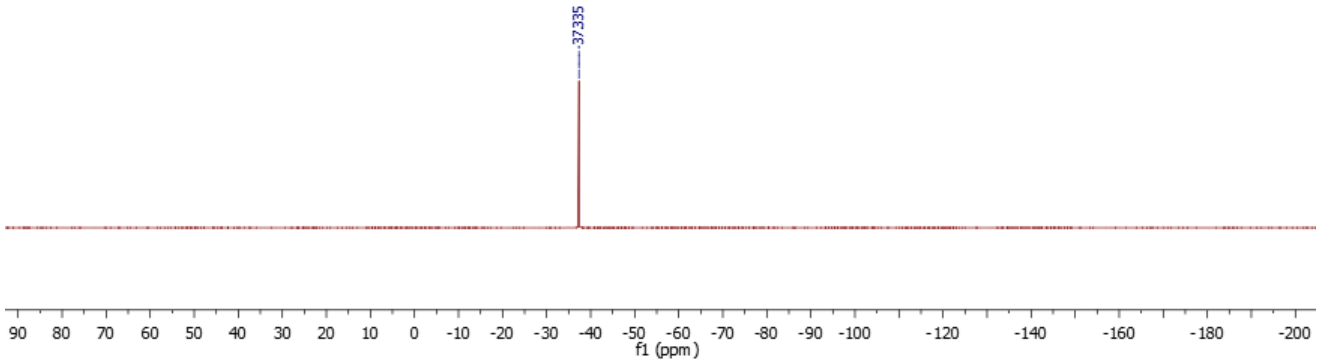
^{19}F NMR spectrum of 2,6-di(*tert*-butyl)-4-(trifluoromethylseleno)anisole 4g



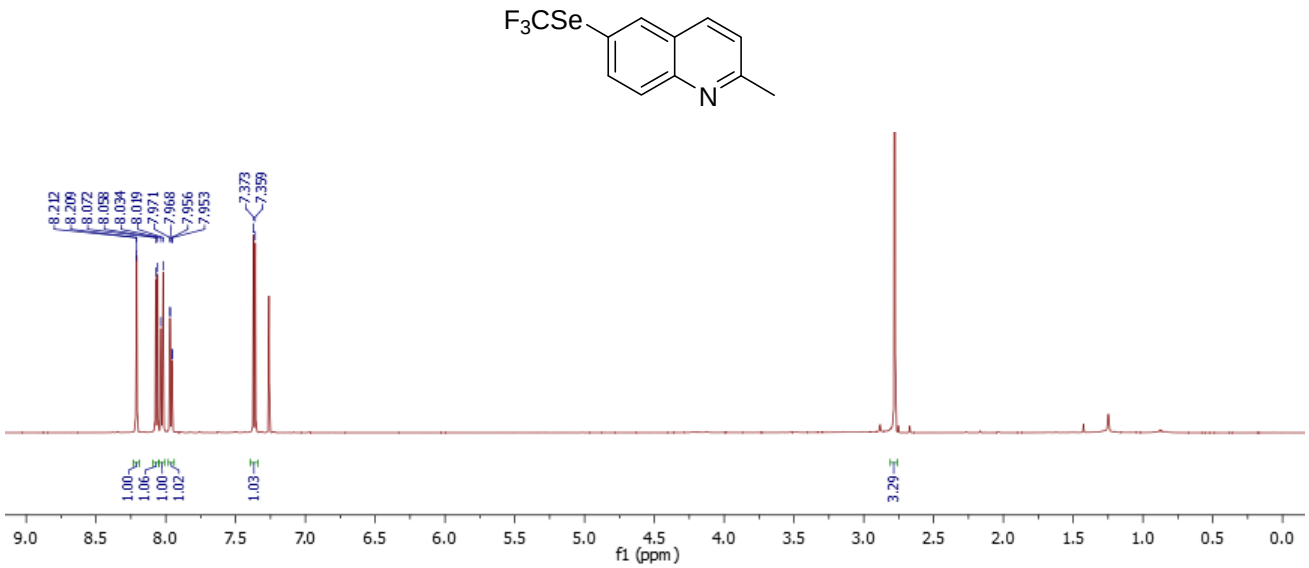
^{1}H NMR spectrum of *N*-methyl-5-(trifluoromethylseleno)indole 4h



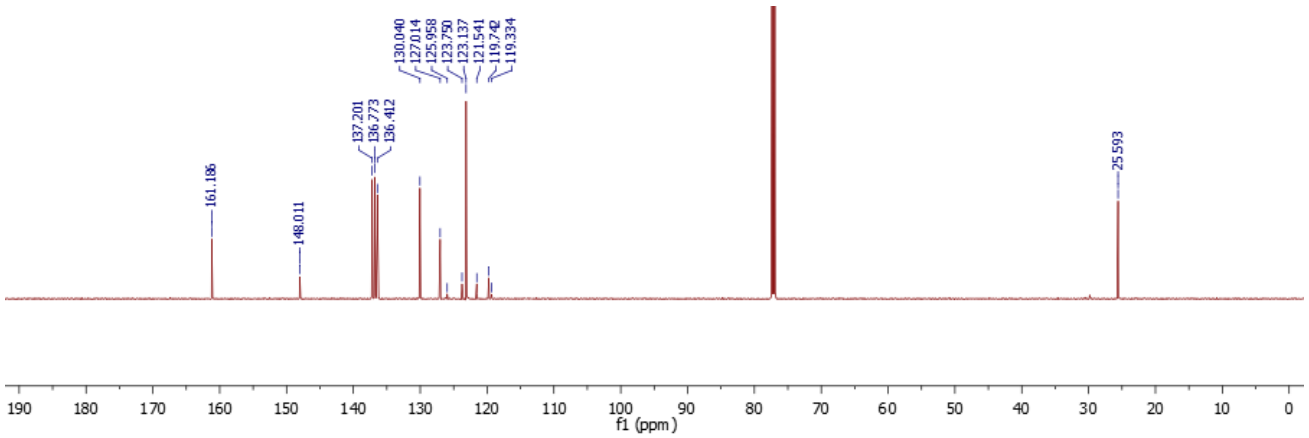
^{13}C NMR spectrum of *N*-methyl-5-(trifluoromethylseleno)indole 4h



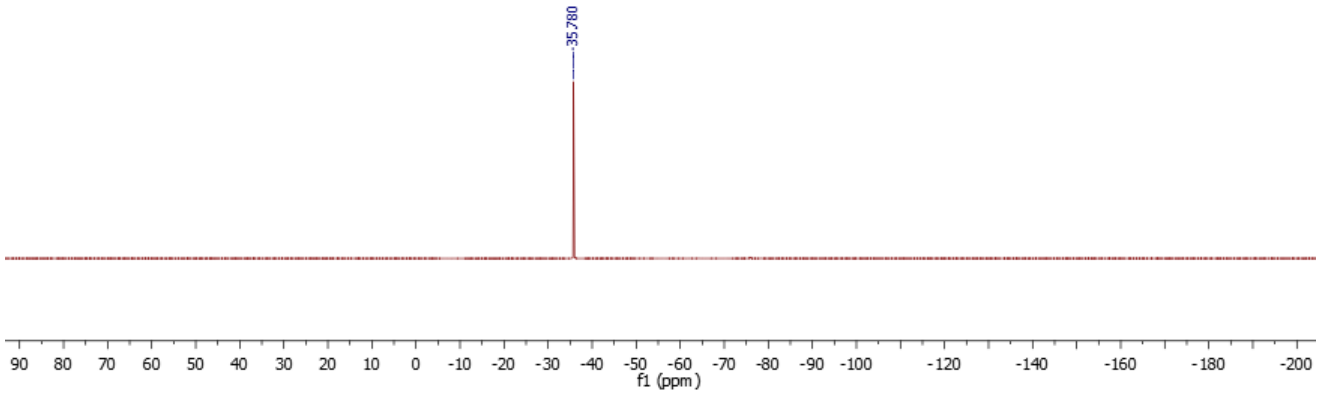
^{19}F NMR spectrum of *N*-methyl-5-(trifluoromethylseleno)indole 4h



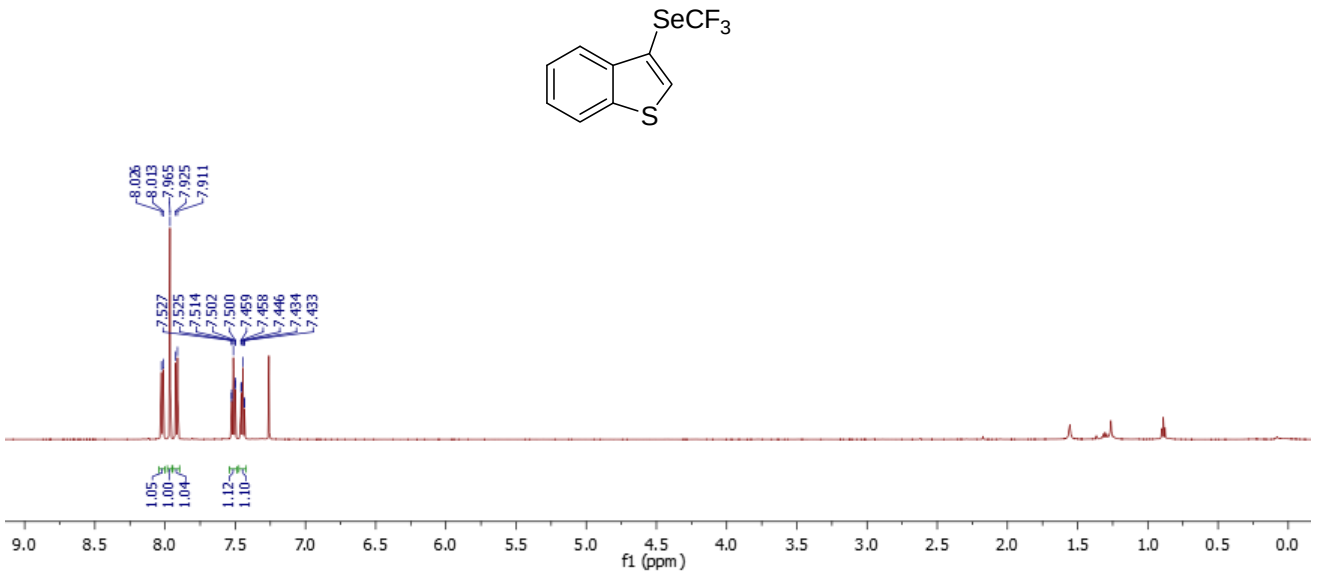
^{1}H NMR spectrum of 2-methyl-6-(trifluoromethylseleno)quinoline 4i



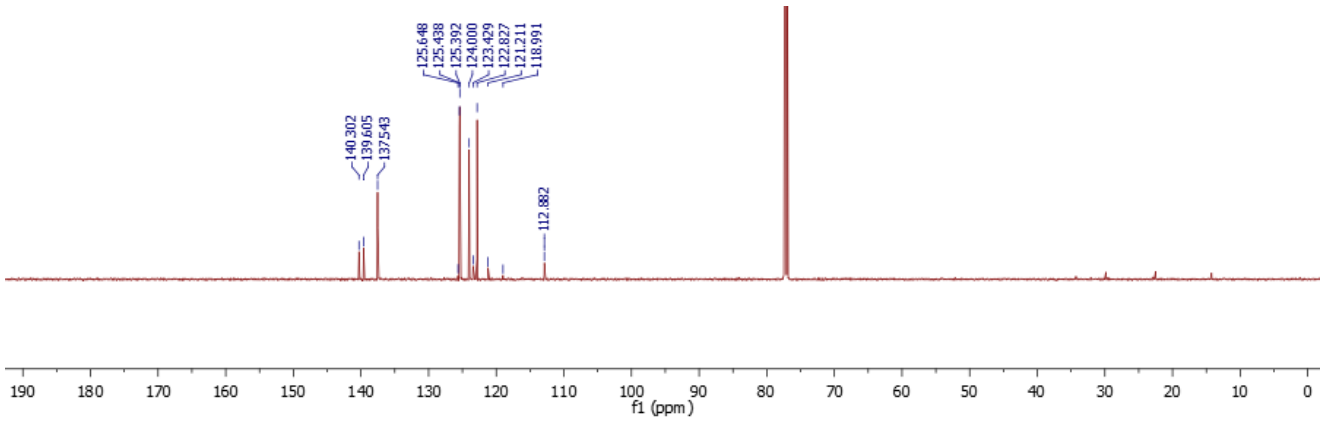
^{13}C NMR spectrum of 2-methyl-6-(trifluoromethylseleno)quinoline 4i



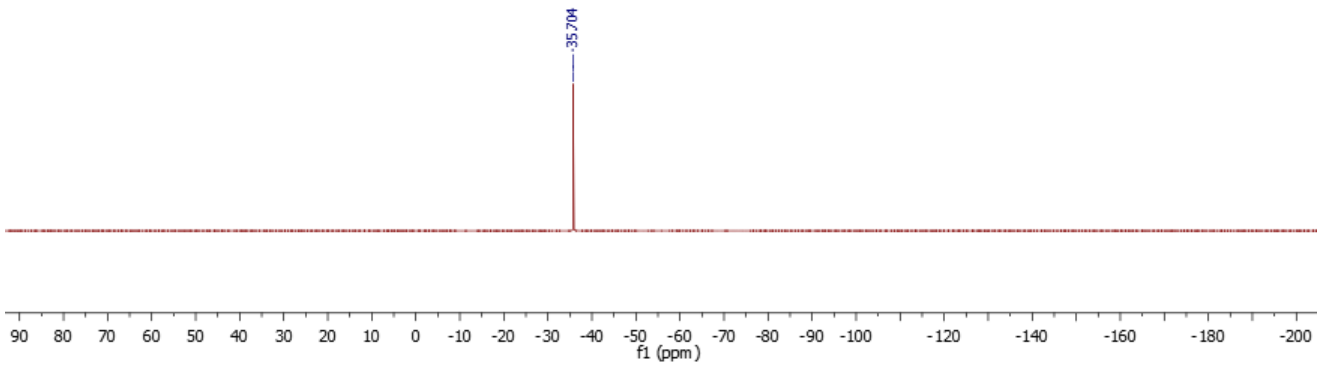
^{19}F NMR spectrum of 2-methyl-6-(trifluoromethylseleno)quinoline 4i



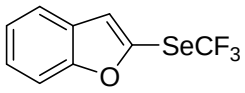
^{1}H NMR spectrum of 3-(trifluoromethylseleno)benzothiophene 4j

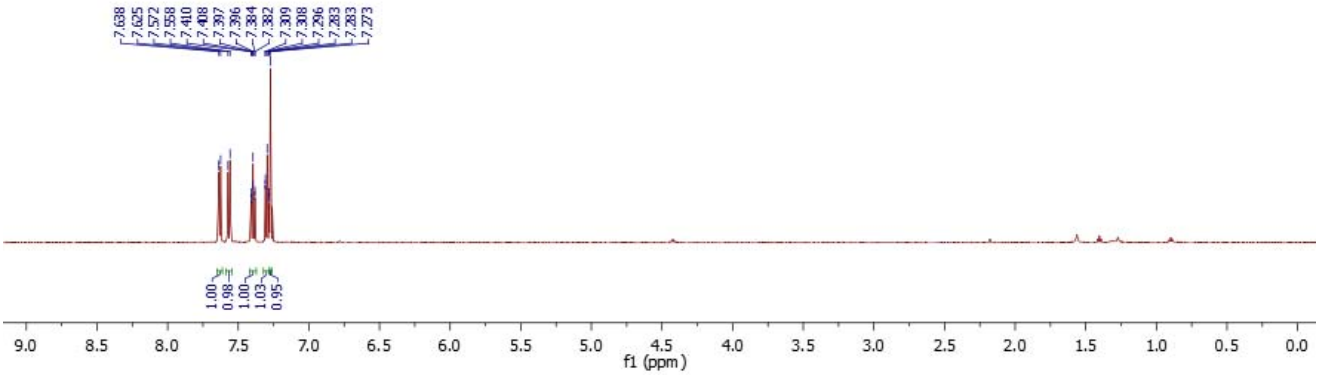


^{13}C NMR spectrum of 3-(trifluoromethylseleno)benzothiophene 4j

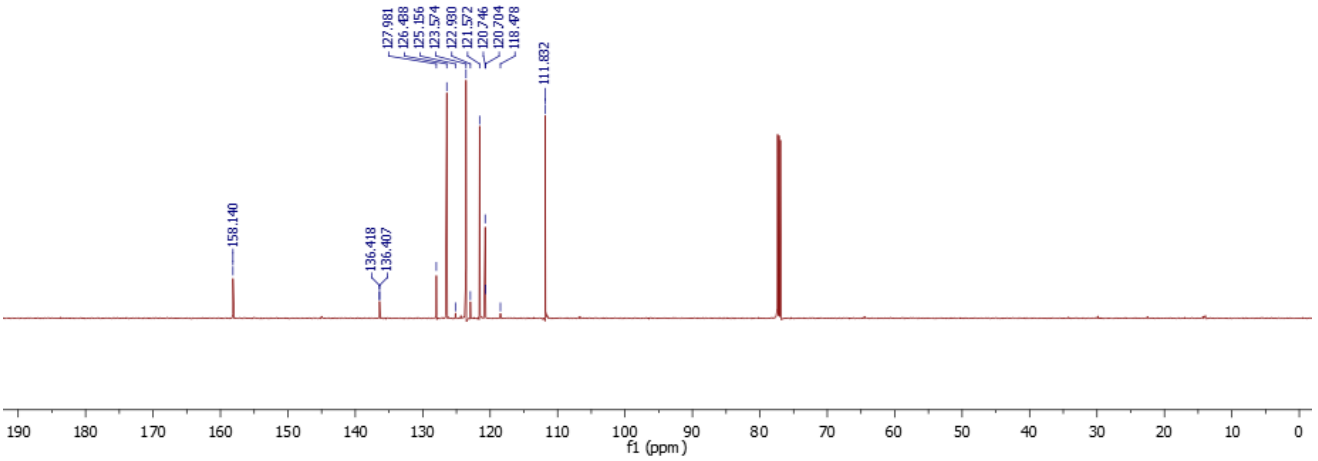


^{19}F NMR spectrum of 3-(trifluoromethylseleno)benzothiophene 4j

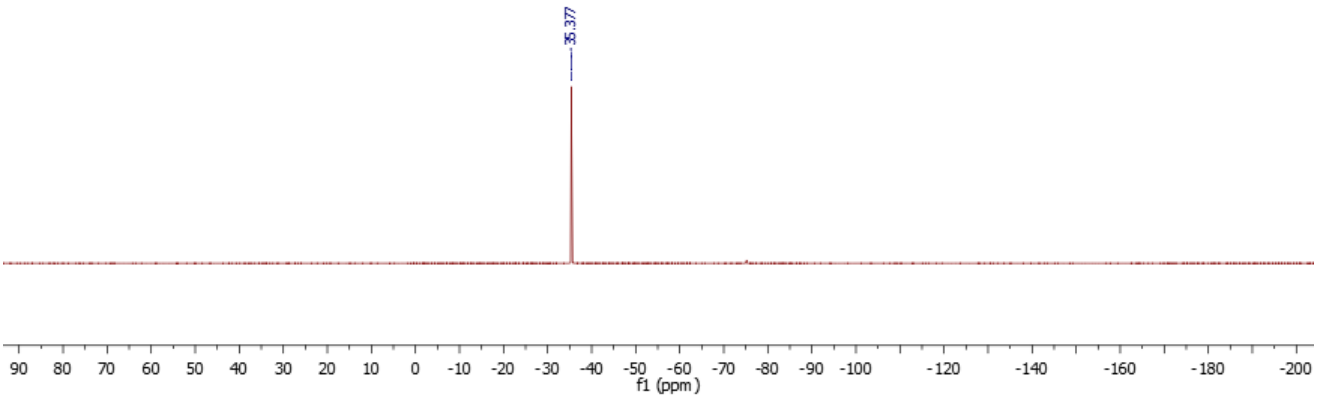




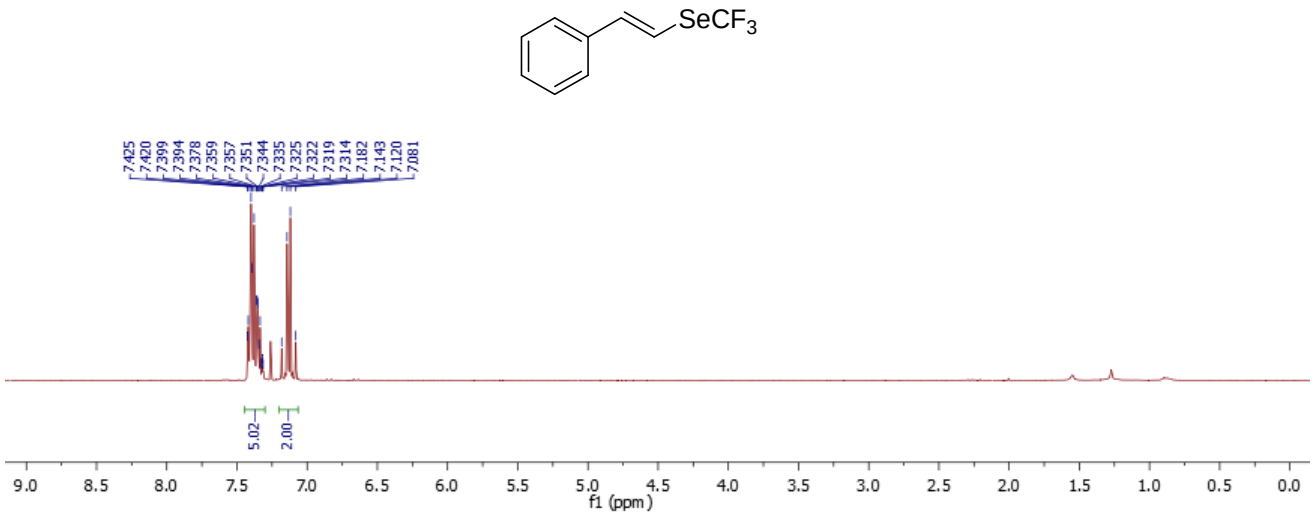
^{1}H NMR spectrum of 2-(trifluoromethylseleno)benzofuran 4k



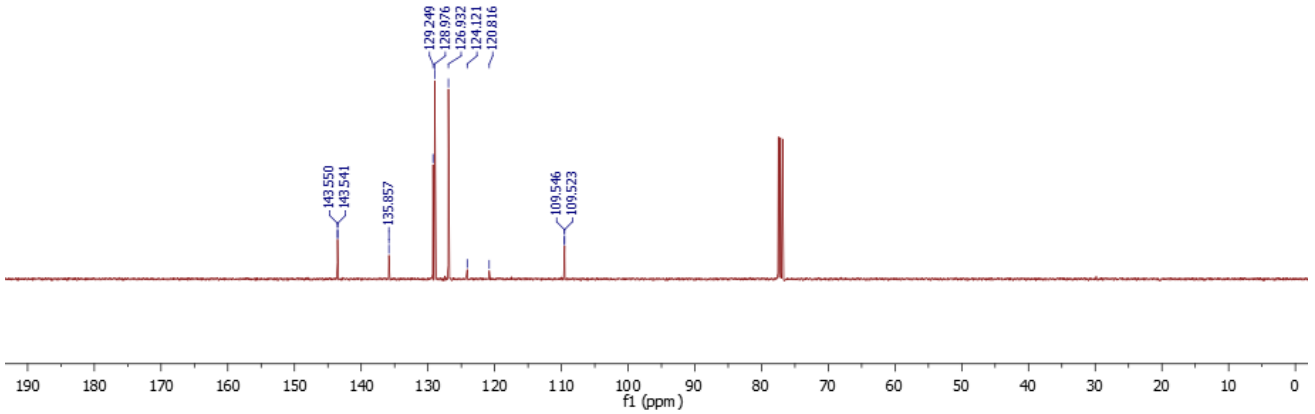
^{13}C NMR spectrum of 2-(trifluoromethylseleno)benzofuran 4k



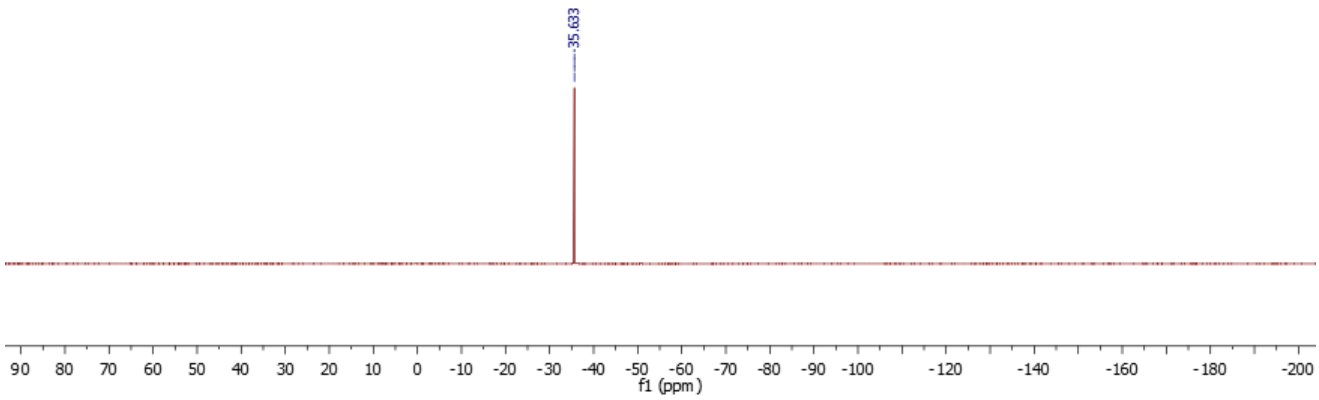
^{19}F NMR spectrum of 2-(trifluoromethylseleno)benzofuran 4k



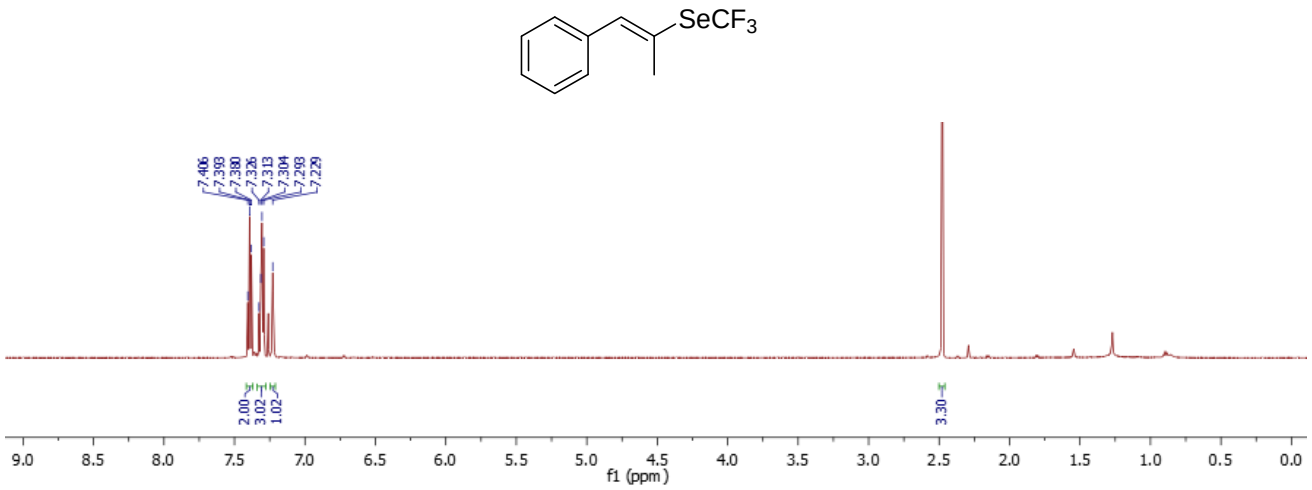
^{1}H NMR spectrum of *β*-(trifluoromethylseleno)styrene 4l



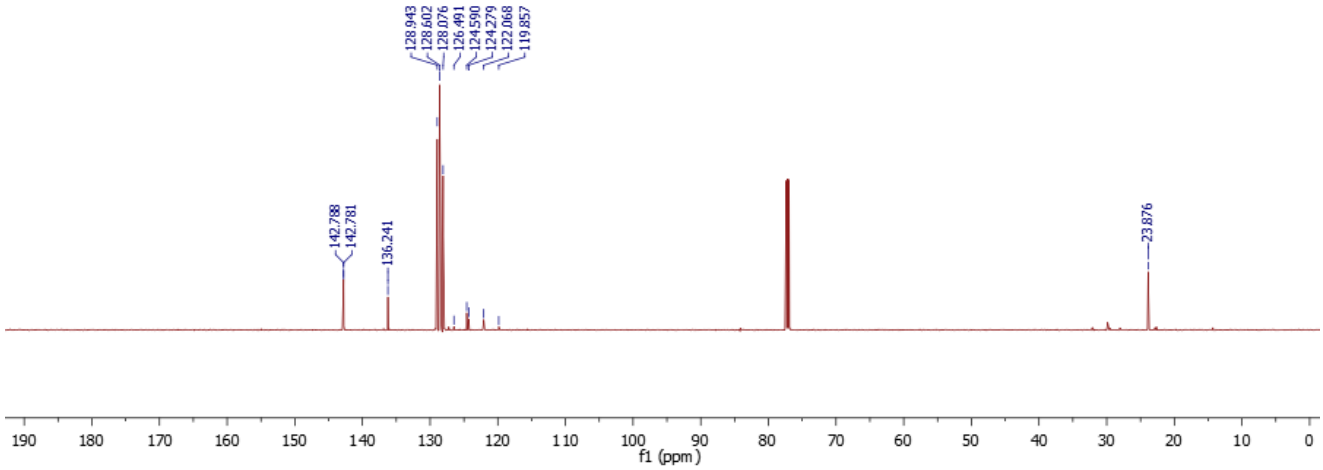
^{13}C NMR spectrum of *β*-(trifluoromethylseleno)styrene 4l



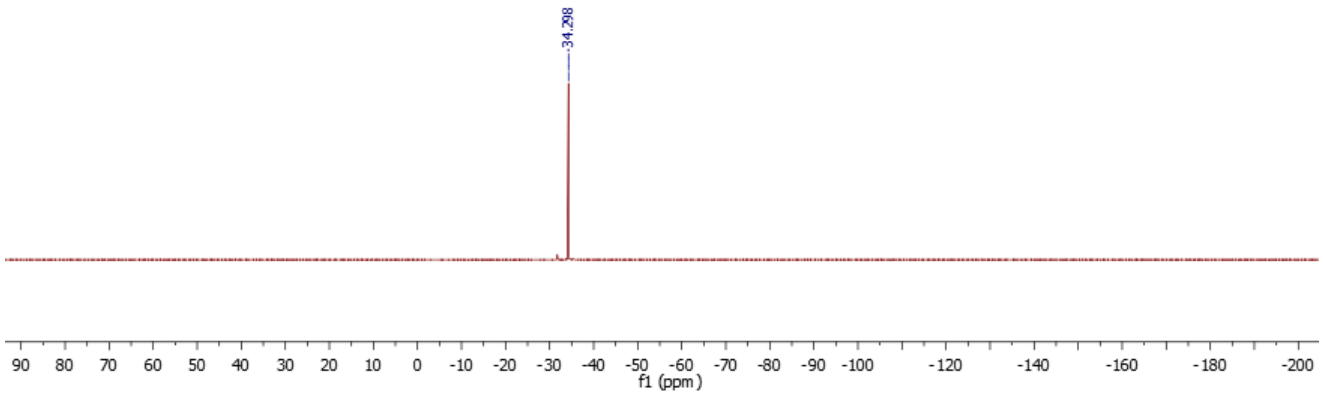
^{19}F NMR spectrum of *β*-(trifluoromethylseleno)styrene 4l



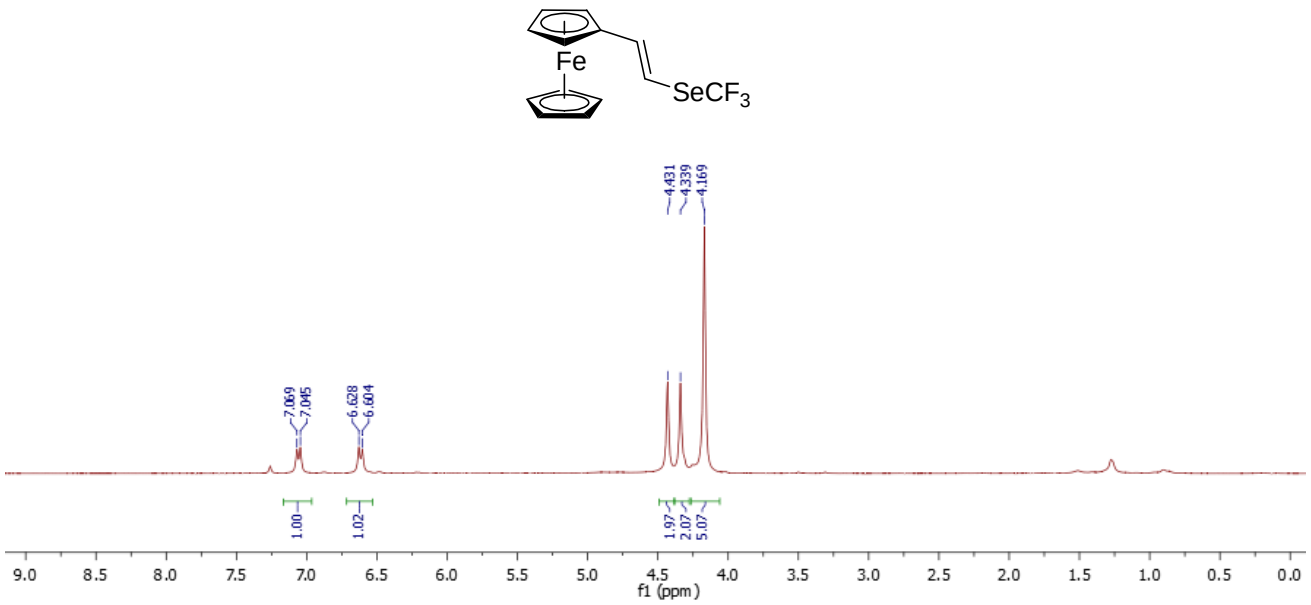
^{1}H NMR spectrum of *β*-methyl-*β*-(trifluoromethylseleno)styrene 4m



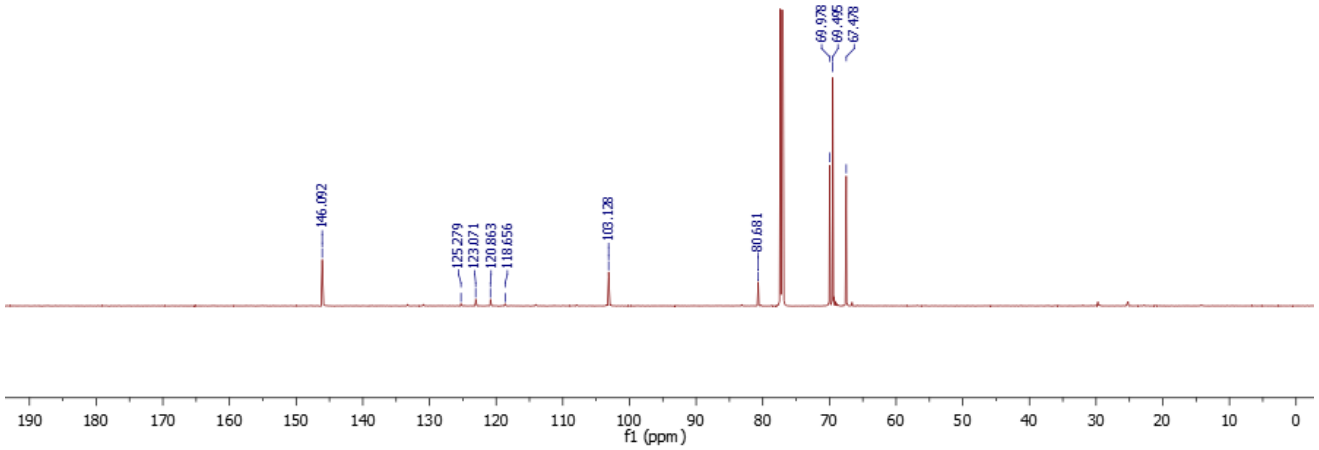
^{13}C NMR spectrum of *β*-methyl-*β*-(trifluoromethylseleno)styrene 4m



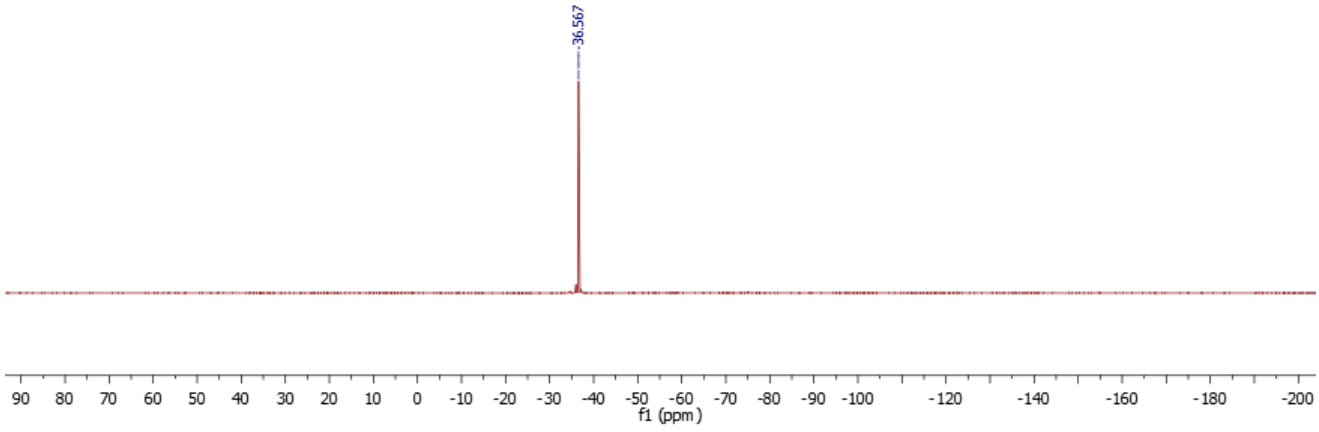
^{19}F NMR spectrum of *β*-methyl-*β*-(trifluoromethylseleno)styrene 4m



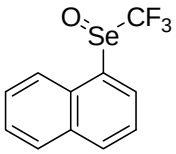
^{1}H NMR spectrum of *β*-(trifluoromethylseleno)vinylferrocene 4n

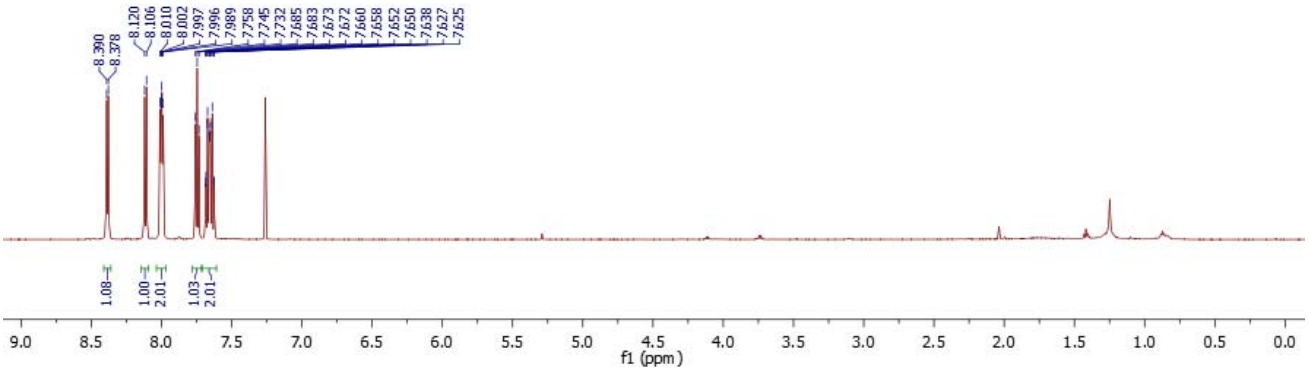


^{13}C NMR spectrum of *β*-(trifluoromethylseleno)vinylferrocene 4n

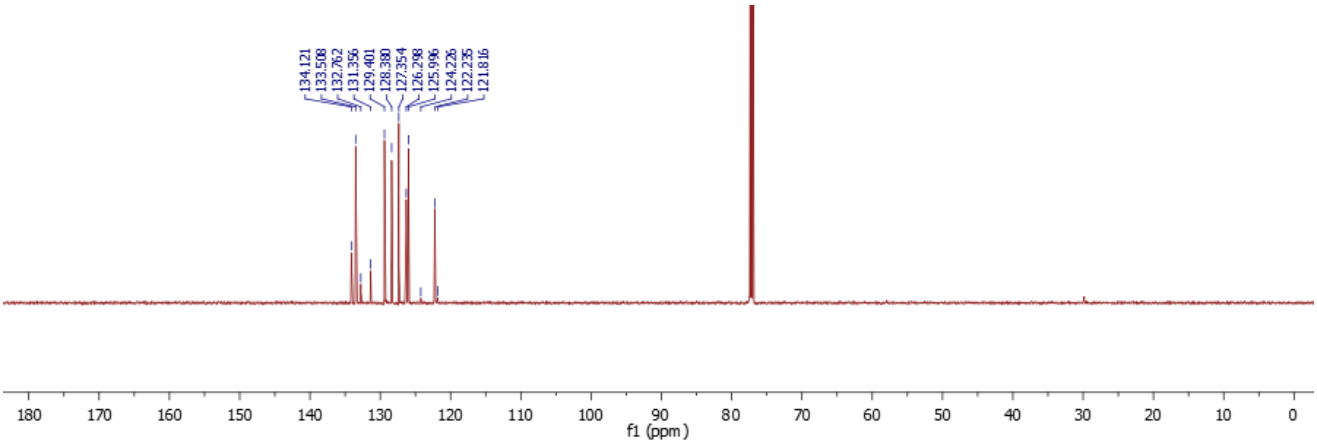


^{19}F NMR spectrum of *β*-(trifluoromethylseleno)vinylferrocene 4n

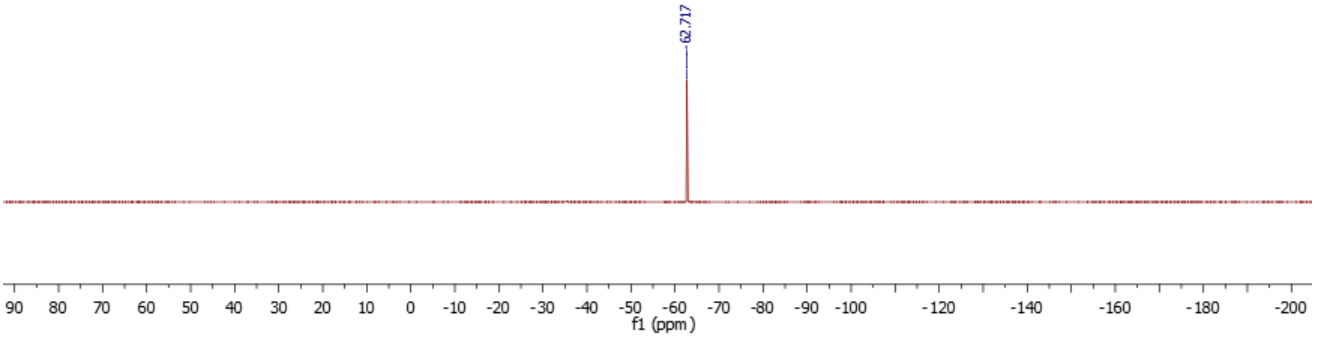




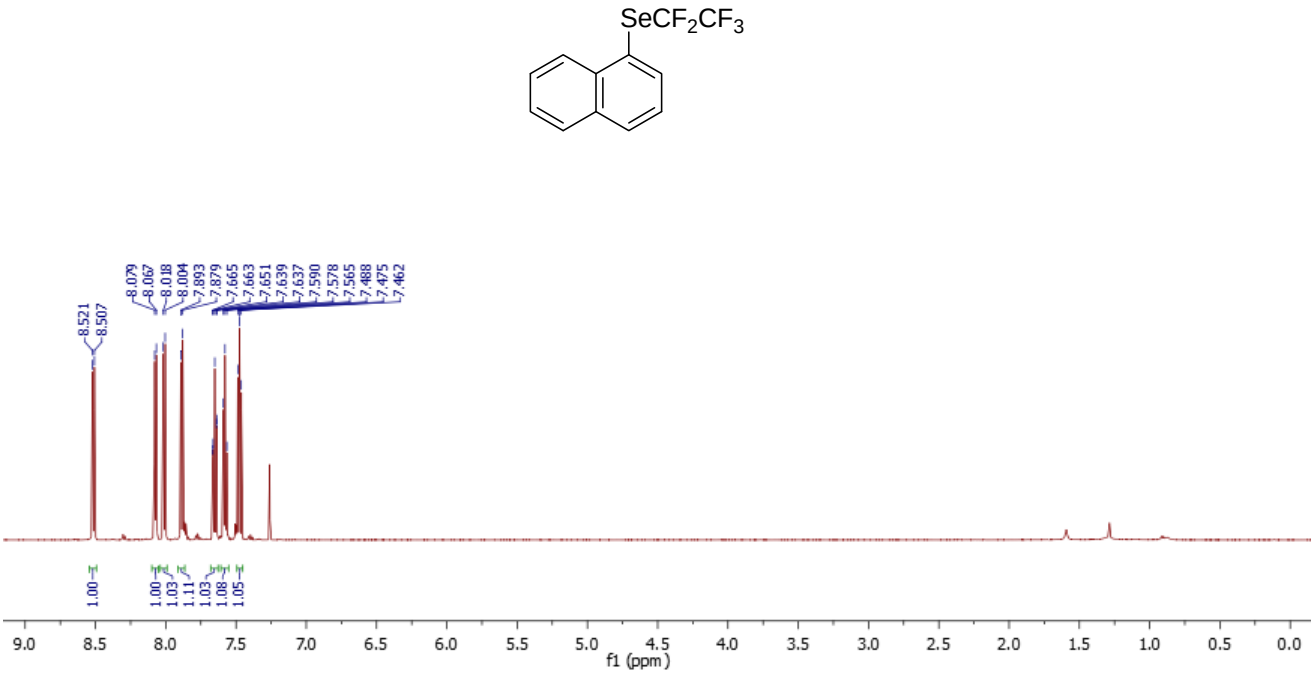
^{1}H NMR spectrum of 1-(trifluoromethylseleninyl)naphthalene 13a



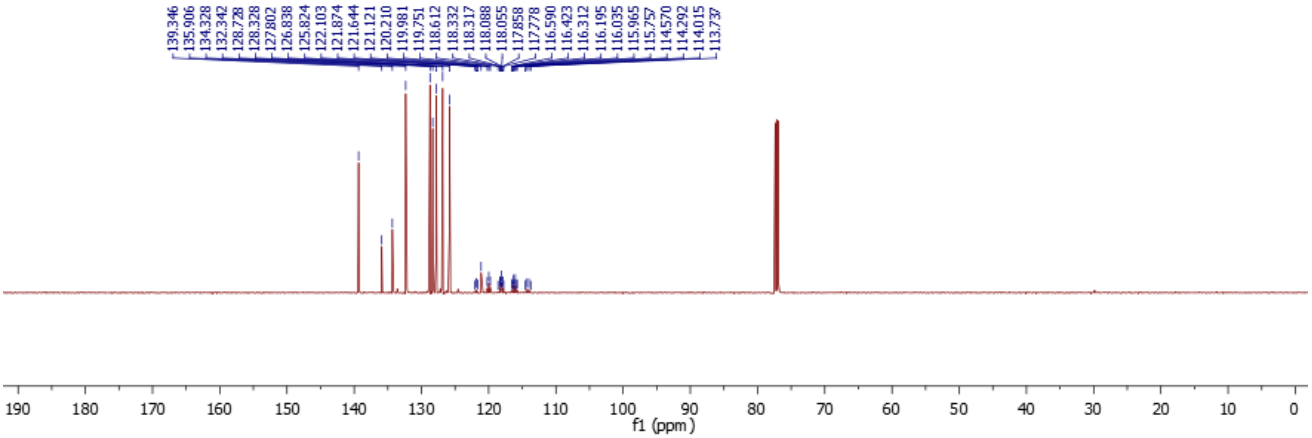
^{13}C NMR spectrum of 1-(trifluoromethylseleninyl)naphthalene 13a



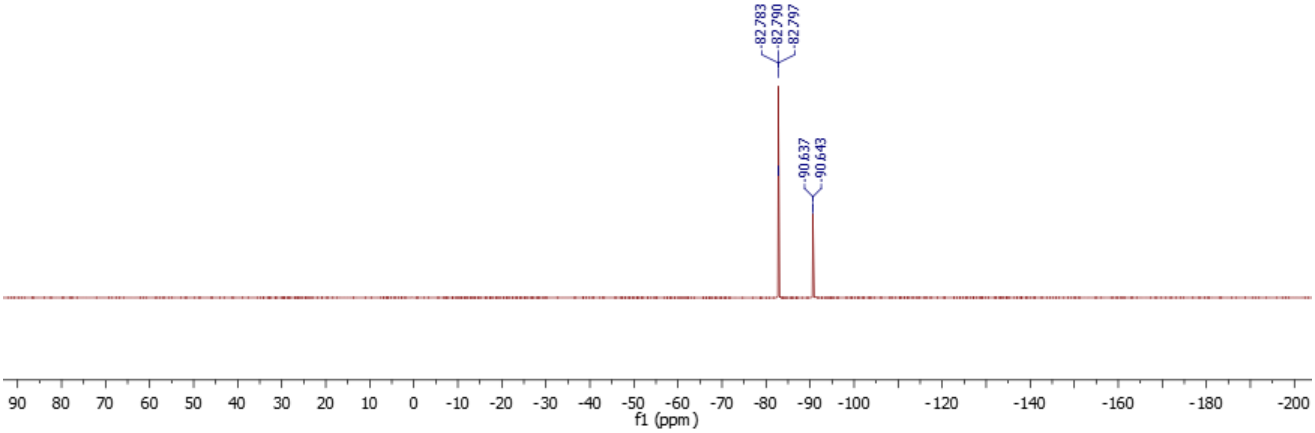
^{19}F NMR spectrum of 1-(trifluoromethylseleninyl)naphthalene 13a



^{1}H NMR spectrum of 1-(pentafluoroethylseleno)naphthalene 12a



^{13}C NMR spectrum of 1-(pentafluoroethylseleno)naphthalene 12a



^{19}F NMR spectrum of 1-(pentafluoroethylseleno)naphthalene 12a