# Supporting Information

# Visible-Light Promoted Photocatalyst and Additive-Free Intermolecular Trifluoromethyl-thio(seleno)cyanation of Alkenes

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**1. General information:** Unless otherwise noted, reagents obtained from commercial suppliers were used without further purification. Reactions were monitored by silica gel thin-layer chromatography (TLC). Silica gel (100-200 mesh) packed in glass column was used for the column chromatography. NMR spectra were recorded at 400, 500 MHz (H) and at 101, 125 MHz (C), respectively. $^{31}P$ and $^{19}F$ NMR spectra were recorded at 162 and 376 MHz respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: $\delta$ = 7.26 and C: $\delta$ = 77.0 ppm) as internal standard, and coupling constants (*J*) are measured in hertz (Hz). High-resolution mass spectra (HRMS) were recorded using ESI-TOF techniques. Melting points of solids were recorded using Electrothermal (IA9100) melting point apparatus. Irradiation was performed with Penn *PhD* photoreactor m2 (PR m2) (blue LED, 450 nm) purchased from Sigma- Aldrich. UV/Vis experiments were conducted on UV-1800 SHIMADZU UV spectrophotometer.

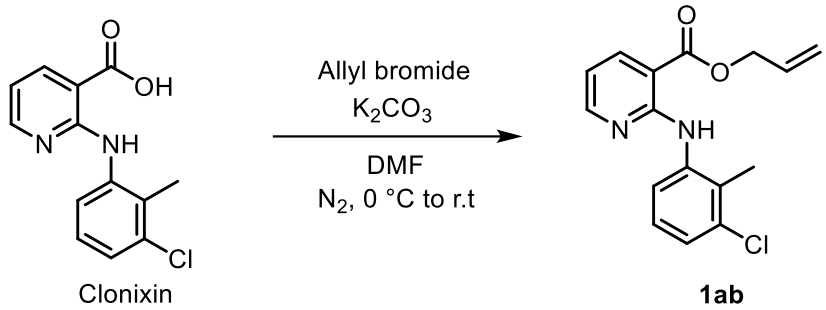
## 2. Experimental procedures:

### 2-1. Synthesis of substrates:

Alkenes **1a-1r** and **1z** are commercially available. Alkenes **1s-1y**[1] and **1aa**[2] and **1ac**[3] are synthesized from the known procedures available in the literature.

Alkene **1ab** is prepared by the following procedure.

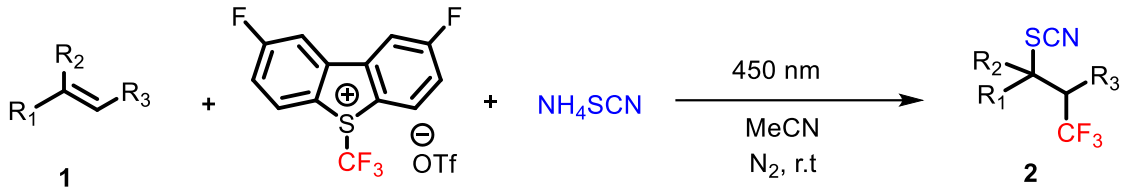
**Allyl 2-((3-chloro-2-methylphenyl)amino)nicotinate (1ab):**




Clonixin **1ab**

To a solution of clonixin (500 mg, 1.9 mmol) in anhydrous DMF (9.5ml, 0.2M) was added $K_2CO_3$ (656.5 mg, 4.75 mmol) and the solution was brought to 0 °C. Allyl bromide was added at once and the reaction mixture was stirred at room temperature for 12 hours. The reaction was diluted with ethyl acetate (25 mL) and washed with 2M HCl (2 x 10 mL) followed by brine solution. Organic layer was concentrated by rotary evaporation and the crude residue was recrystalized from hexane to get desired product as pale yellow crystalline solid (547mg, 95%); mp = 75-76 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.34 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.29 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.20 – 7.10 (m, 2H), 6.72 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.06 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.44 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.34 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.85 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.41 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.3, 156.6, 153.4, 140.3, 139.3, 134.8, 131.8, 128.8, 126.6, 124.9, 122.0, 118.8, 113.5, 107.1, 65.8, 15.2; HRMS (ESI) calcd for $C_{16}H_{16}N_2O_2Cl$ $[M+H]^+$: 303.0900; found: 303.0907.

**2-2. General procedure for the visible-light promoted trifluoromethylthiocyanation**:




Alkene **1** (0.3 mmol), Umemoto reagent II (0.45 mmol) and $NH_4SCN$ (0.45 mmol) were weighed in a screw capped vial and MeCN (3.0 mL) was added to this mixture. The vial was back filled with $N_2$ and it was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). After completion of reaction (4 hours), the reaction mixture was concentrated using rotary evaporation and the crude reaction mixture was purified by column chromatography to get the desired compound **2**.

**Analytical data of the trifluoromethylthiocyanated compounds 2:**

**1-(*tert*-Butyl)-4-(3,3,3-trifluoro-1-thiocyanatopropyl)benzene (2a):** Pale yellow syrup (80.2 mg, 93%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.64 (t, *J* = 7.3 Hz, 1H), 3.04 (qd, *J* = 9.7, 7.4 Hz, 2H), 1.32 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.0, 133.0, 126.9, 126.4, 124.7 (q, *J* = 278.1 Hz), 110.5, 46.1, 46.1, 39.9 (q, *J* = 29.1 Hz), 34.8, 31.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.8; HRMS (ESI) calcd for $C_{13}H_{16}F_3$ $[M\text{-}SCN]^+$: 229.1204; found: 229.1208.

**1-Methyl-4-(3,3,3-trifluoro-1-thiocyanatopropyl)benzene (2b):** White solid (51.5 mg, 70%); mp = 80-82 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.63 (t, *J* = 7.3 Hz, 1H), 3.15 – 2.91 (m, 2H), 2.36 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.9, 133.0, 130.1, 127.1, 124.7 (q, *J* = 278.3 Hz), 110.5, 46.2 (q, *J* = 2.9 Hz), 39.9 (q, *J* = 29.1 Hz), 21.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.8; HRMS (ESI) calcd for $C_{10}H_{10}F_3$ $[M\text{-}SCN]^+$: 187.0735; found: 187.0733.

**1-Chloro-4-(3,3,3-trifluoro-1-thiocyanatopropyl)benzene (2c):** Sticky mass (57.2 mg, 72%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 4.62

(t, *J* = 7.4 Hz, 1H), 3.01 (qd, *J* = 9.6, 7.4 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.9, 134.6, 129.7, 128.6, 124.5 (q, *J* = 278.3 Hz), 109.9, 45.5, 45.5, 39.7 (q, *J* = 29.4 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.7; HRMS (ESI) calcd for $C_{10}H_6NF_3SCl$ $[M-H]^-$: 263.9862; found: 263.9874.

**1-Bromo-4-(3,3,3-trifluoro-1-thiocyanatopropyl)benzene (2d):** white solid (85.6 mg, 92%); mp = 56-58 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 4.60 (t, *J* = 7.4 Hz, 1H), 3.01 (qd, *J* = 9.6, 7.4 Hz, 2H).; $^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.1, 132.7, 128.9, 124.5 (q, *J* = 278.1 Hz), 124.0, 109.8, 45.6, 45.6, 39.6 (q, *J* = 29.4 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.7; HRMS (ESI) calcd for $C_9H_7F_3Br$ $[M-SCN]^+$: 250.9683; found: 250.9681.

**1-(3,3,3-Trifluoro-1-thiocyanatopropyl)-4-(trifluoromethyl)benzene (2e):** Colorless syrup (55.6 mg, 62%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 4.66 (t, *J* = 7.3 Hz, 1H), 3.04 (qd, *J* = 9.6, 7.5 Hz, 2H).; $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.2, 131.9 (q, *J* = 33.0 Hz), 127.8, 126.5, 126.5, 124.5 (q, *J* = 278.2 Hz), 123.5 (q, *J* = 272.6 Hz), 109.6, 45.3, 45.3, 39.5 (q, *J* = 29.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.0, -63.8; HRMS (ESI) calcd for $C_{10}H_7F_6$ $[M-SCN]^+$: 241.0452; found: 241.0457.

**1-Methoxy-4-(3,3,3-trifluoro-1-thiocyanatopropyl)benzene (2f):** Yellow syrup (58.7 mg, 75%); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.66 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.07 – 2.97 (m, 2H).; $^{13}$C NMR (101 MHz, $CDCl_3$) δ 160.5, 128.6, 127.7, 124.7 (q, *J* = 278.1 Hz), 114.8, 110.6, 55.4, 46.24, 46.2, 39.9 (q, *J* = 29.8 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.8; HRMS (ESI) calcd for $C_{10}H_{10}OF_3$ $[M-SCN]^+$: 203.0684; found: 203.0684.

**1-Chloro-3-(3,3,3-trifluoro-1-thiocyanatopropyl)benzenee (2g):** Yellow syrup (43.7 mg, 55%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 3H), 7.30 – 7.22 (m, 1H), 4.59 (t, *J* = 7.3 Hz, 1H), 3.01 (qd, *J* = 9.6, 7.4 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.1, 135.4, 130.8,

130.0, 127.4, 125.4, 124.5 (q, *J* = 278.2 Hz), 109.7, 45.5 (q, *J* = 2.8 Hz), 39.7 (q, *J* = 29.5 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.8; HRMS (ESI) calcd for $C_9H_7ClF_3$ $[M\text{-}SCN]^+$: 207.0188; found: 207.0187.

**1-chloro-2-(3,3,3-trifluoro-1-thiocyanatopropyl)benzene (2h):** Yellow syrup (38.2 mg, 48%) ; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 1H), 7.45 – 7.41 (m, 1H), 7.41 – 7.32 (m, 2H), 5.10 (t, *J* = 7.3 Hz, 1H), 3.10 (qd, *J* = 9.6, 7.3 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.8, 133.4, 130.7, 130.6, 127.8, 124.6 (q, *J* = 278.1 Hz), 109.8, 42.0, 38.8 (q, *J* = 29.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.0; HRMS (ESI) calcd for $C_9H_7ClF_3$ $[M\text{-}SCN]^+$: 207.0188; found: 207.0190

**1,3-Dimethyl-5-(3,3,3-trifluoro-1-thiocyanatopropyl)benzene (2i):** White solid (48.2 mg, 62%); mp = 62-64 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 4.91 (t, *J* = 7.3 Hz, 1H), 3.13 – 3.01 (m, 2H), 2.39 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.6, 135.8, 132.2, 130.7, 127.8, 126.1, 124.8 (q, *J* = 277.7 Hz), 110.6, 42.2, 39.7 (q, *J* = 28.9 Hz), 21.1, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.0; HRMS (ESI) calcd for $C_{12}H_{12}NF_3NaS$ $[M+Na]^+$: 282.0540; found: 282.0538.

**(3,3,3-Trifluoro-1-thiocyanatopropyl)benzene (2j):** Yellow syrup (35.4 mg, 51%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 3H), 7.39 – 7.34 (m, 2H), 4.65 (t, *J* = 7.3 Hz, 1H), 3.14 – 2.94 (m, 2H); $^{13}$C NMR ($CDCl_3$, 101 MHz): δ 136.1, 129.8, 129.5, 127.2, 124.7 (q, *J* = 278.2 Hz), 110.3, 46.3 (q, *J* = 2.9 Hz), 39.9 (q, *J* = 29.2 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.8; HRMS (ESI) calcd for $C_9H_8F_3$ $[M\text{-}SCN]^+$: 173.0578; found: 173.0584.

**(3,3,3-Trifluoro-2-methyl-1-thiocyanatopropyl)benzene (2k):** (2:1 diastereomers) Yellow syrup (35.3 mg, 48%);

Major isomer: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 5H), 4.61 (d, *J* = 6.9 Hz, 1H), 3.05 – 2.89 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 137.5, 129.4,

129.3, 127.6, 126.4 (q, $J$ = 281.4 Hz), 110.7, 53.7, 43.8 (q, $J$ = 26.4 Hz), 11.5 (q, $J$ = 2.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -69.1.

Minor isomer: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 3H), 7.32 – 7.27 (m, 2H), 4.70 (d, $J$ = 6.9 Hz, 1H), 3.07 – 2.88 (m, 1H), 1.20 (d, $J$ = 7.1 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 134.7, 129.5, 129.2, 128.3, 126.4 (q, $J$ = 281.3 Hz), 110.7, 51.7, 43.0 (q, $J$ = 26.4 Hz), 10.8 (q, $J$ = 2.5 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.9.

HRMS (ESI) calcd for $C_{10}H_{10}F_3$ $[M\text{-}SCN]^+$: 187.0735; found: 187.0737.

**1-Thiocyanato-2-(trifluoromethyl)-2,3-dihydro-1H-indene (2l):** Yellow syrup (32.8 mg, 45%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 4.88 (d, $J$ = 5.0 Hz, 1H), 3.50 – 3.37 (m, 2H), 3.24 – 3.15 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.4, 137.2, 130.1, 128.3, 128.0, 126.6 (q, $J$ = 277.5 Hz), 125.1, 125.0, 110.0, 52.1, 51.0 (q, $J$ = 27.9 Hz), 31.6; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -71.3; HRMS (ESI) calcd for $C_{10}H_8F_3$ $[M\text{-}SCN]^+$: 185.0581; found: 185.0578.

**(4,4,4-Trifluoro-2-thiocyanatobutyl)benzene (2m):** Colorless syrup (50.0 mg, 68%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 3H), 7.25 – 7.19 (m, 2H), 3.55 – 3.45 (m, 1H), 3.22 (dd, $J$ = 14.4, 6.4 Hz, 1H), 3.10 (dd, $J$ = 14.4, 8.5 Hz, 1H), 2.76 – 2.57 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.8, 129.2, 129.1, 127.9, 125.1 (q, $J$ = 277.7 Hz), 109.8, 44.3 (q, $J$ = 2.4 Hz), 41.3, 38.8 (q, $J$ = 29.3 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.4; HRMS (ESI) calcd for $C_{10}H_{10}F_3$ $[M\text{-}SCN]^+$: 187.0735; found: 187.0743.

**1,2-Dimethoxy-4-(4,4,4-trifluoro-2-thiocyanatobutyl)benzene (2n):** Yellow syrup (69.5 mg, 76%); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, $J$ = 8.2 Hz, 1H), 6.76 (dd, $J$ = 8.1, 2.1 Hz, 1H), 6.71 (d, $J$ = 2.0 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.48 (quin, $J$ = 6.7 Hz, 1H), 3.15 (dd, $J$ = 14.4, 6.7 Hz, 1H), 3.05 (dd, $J$ = 14.5, 8.3 Hz, 1H), 2.71 – 2.59 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.3, 148.7, 128.2, 125.2 (q, $J$ = 277.8 Hz), 121.4, 112.1, 111.5, 109.9, 56.0,

55.9, 44.4, 44.4, 41.0, 38.6 (q, *J* = 29.2 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.4; HRMS (ESI) calcd for $C_{13}H_{18}N_2O_2F_3S$ $[M+NH_4]^+$: 323.1041; found: 323.1044.

**(5,5,5-Trifluoro-3-thiocyanatopentyl)benzene (2o):** Pale yellow syrup (69.1 mg, 89%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.19 (m, 2H), 3.24 – 3.14 (m, 1H), 2.95 (ddd, *J* = 13.9, 12.0, 7.6 Hz, 1H), 2.82 – 2.52 (m, 3H), 2.31 – 2.20 (m, 1H), 2.19 – 2.07 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.1, 128.9, 128.7, 128.4, 126.8, 125.0 (q, *J* = 277.8 Hz), 109.4, 42.3, 39.9 (q, *J* = 29.0 Hz), 36.2, 32.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.5; HRMS (ESI) calcd for $C_{11}H_{12}F_3$ $[M-SCN]^+$: 201.0891; found: 201.0894.

**(3,3,3-Trifluoro-1-thiocyanatopropyl)cyclooctane (2p):** Pale yellow syrup (34.2 mg, 43%); $^1$H NMR (400 MHz, $CDCl_3$) δ 3.47 – 3.39 (m, 1H), 2.72 – 2.47 (m, 2H), 2.17 – 2.08 (m, 1H), 1.82 – 1.70 (m, 2H), 1.69 – 1.60 (m, 5H), 1.55 – 1.38 (m, 7H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 125.4 (q, *J* = 277.7 Hz), 111.2, 51.4, 41.2, 36.9 (q, *J* = 29.2 Hz), 31.3, 29.7, 29.3, 26.5, 26.2, 26.0, 25.9, 25.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -68.6; HRMS (ESI) calcd for $C_{11}H_{18}F_3$ $[M-SCN]^+$: 207.1361; found: 207.1354.

**1,1,1-Trifluoro-3-thiocyanatoheptane (2q):** Colorless syrup (32.9 mg, 52%); $^1$H NMR (400 MHz, $CDCl_3$) δ 3.39 – 3.16 (m, 1H), 2.78 – 2.51 (m, 2H), 2.03 – 1.87 (m, 1H), 1.86 – 1.76 (m, 1H), 1.60 – 1.48 (m, 1H), 1.48 – 1.33 (m, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 125.2 (q, *J* = 277.7 Hz), 109.8, 43.3, 43.2, 39.8 (q, *J* = 28.9 Hz), 34.6, 28.7, 21.9, 13.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.7; HRMS (ESI) calcd for $C_8H_{11}NF_3S$ $[M-H]^-$: 210.0564; found: 210.0560.

**1,1,1-Trifluoro-3-thiocyanatohenicosane (2r):** Pale yellow sticky mass (56.2 mg, 46%); $^1$H NMR (400 MHz, $CDCl_3$) δ 3.33 – 3.23 (m, 1H), 2.78 – 2.46 (m, 2H), 1.97 – 1.85 (m, 1H), 1.84 – 1.74 (m, 1H), 1.65 – 1.49 (m, 2H), 1.47 – 1.38 (m, 1H), 1.35 – 1.21 (m, 29H), 0.88 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 101 MHz) δ 125.2 (q, *J* = 277.9 Hz), 109.8, 43.3, 39.8 (q, *J* = 29.0

Hz), 34.9, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 28.8, 26.7, 22.7, 14.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.6; HRMS (ESI) calcd for $C_{20}H_{40}NF_3SCl$ $[M+Cl]^-$: 442.2522; found: 442.2510.

**Benzyl 7,7,7-trifluoro-5-thiocyanatoheptanoate (2s):** Colorless syrup (50.6 mg, 51%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 5.13 (s, 2H), 3.33 – 3.19 (m, 1H), 2.76 – 2.49 (m, 2H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.01 – 1.89 (m, 2H), 1.88 – 1.70 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.4, 135.7, 128.7, 128.4, 128.4, 125.0 (q, *J* = 277.8 Hz), 109.5, 66.6, 42.9, 42.9, 39.7 (q, *J* = 29.1 Hz), 34.2, 33.2, 22.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.6; HRMS (ESI) calcd for $C_{15}H_{17}NO_2F_3S$ $[M+H]^+$: 332.0932; found: 332.0920.

**6,6,6-Trifluoro-4-thiocyanatohexyl 4-methylbenzenesulfonate (2t):** Colorless syrup (80.4 mg, 73%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.14 – 4.04 (m, 2H), 3.27 – 3.20 (m, 1H), 2.74 – 2.63 (m, 1H), 2.63 – 2.49 (m, 1H), 2.46 (s, 3H), 2.04 – 1.92 (m, 2H), 1.85 – 1.78 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.2, 132.7, 130.04, 127.90, 124.9 (q, *J* = 277.9 Hz), 109.1, 68.9, 42.6, 39.8 (q, *J* = 29.2 Hz), 31.1, 26.2, 21.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.6; HRMS (ESI) calcd for $C_{14}H_{20}N_2O_3F_3S_2$ $[M+NH_4]^+$: 385.0867; found: 385.0873.

**2-(6,6,6-Trifluoro-4-thiocyanatohexyl)isoindoline-1,3-dione (2u):** White crystalline solid (72.8 mg, 67%); mp = 74-76 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.76 (t, *J* = 6.3 Hz, 2H), 3.43 – 3.33 (m, 1H), 2.77 – 2.50 (m, 2H), 2.08 – 1.92 (m, 2H), 1.92 – 1.79 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.3, 134.2, 131.9, 125.0 (q, *J* = 277.9 Hz), 123.4, 109.3, 42.5 (q, *J* = 2.9 Hz), 40.23, 39.8 (q, *J* = 29.2 Hz), 36.6, 32.1, 25.8; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.6; HRMS (ESI) calcd for $C_{15}H_{14}N_2O_2F_3S$ $[M+H]^+$: 343.0728; found: 343.0729.

**Diethyl (6,6,6-trifluoro-4-thiocyanatohexyl) phosphate (2v):** Pale yellow sticky mass (86.9 mg, 83%); $^1$H NMR (400 MHz, $CDCl_3$) δ 4.18 – 4.05 (m, 6H), 3.39 – 3.29 (m, 1H), 2.81 – 2.53 (m, 2H), 2.15 – 2.07 (m, 1H), 2.04 – 1.80 (m, 3H), 1.35 (t, *J* = 7.1, 3H), 1.34 (t, *J* = 7.1, 3H);

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 125.0 (q, *J* = 277.9 Hz), 109.3, 66.1 (d, *J* = 5.8 Hz), 64.0 (d, *J* = 5.8 Hz), 42.8 (q, *J* = 2.6 Hz), 39.9 (q, *J* = 29.2 Hz), 31.2, 27.4 (d, *J* = 6.9 Hz), 16.1 (d, *J* = 6.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.6; $^{31}$P NMR (162 MHz, $CDCl_3$) δ -1.0; HRMS (ESI) calcd for $C_{11}H_{20}NO_4SF_3P$ $[M+H]^+$: 350.0803; found: 350.0810.

**Benzyl 4,4,4-trifluoro-2-methyl-2-thiocyanatobutanoate (2w):** Colorless syrup (62.7 mg, 69%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 5H), 5.25 (s, 2H), 3.17 – 3.01 (m, 1H), 2.96 – 2.80 (m, 1H), 1.83 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.7, 134.0, 129.0, 128.8, 128.7, 124.3 (q, *J* = 278.6 Hz), 109.4, 69.3, 53.6, 42.2 (q, *J* = 29.5 Hz), 24.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.4; HRMS (ESI) calcd for $C_{13}H_{13}NO_2F_3S$ $[M+H]^+$: 304.0619; found: 304.0622.

**Benzyl 4,4,4-trifluoro-2-phenyl-2-thiocyanatobutanoate (2x):** Pale yellow syrup (66.8 mg, 61%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.37 – 7.29 (m, 6H), 7.23 – 7.16 (m, 2H), 5.23 (dd, *J* = 18.6, 12.0 Hz, 2H), 3.60 – 3.37 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.2, 136.4, 133.6, 129.8, 129.3, 129.0, 128.8, 128.7, 128.6, 128.4, 125.8, 125.1, 110.5, 69.7, 62.3, 39.7 (q, *J* = 29.5); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -60.2; HRMS (ESI) calcd for $C_{18}H_{15}NO_2F_3S$ $[M+H]^+$: 366.0776; found: 366.0779.

**Benzyl 2-benzyl-4,4,4-trifluoro-2-thiocyanatobutanoate (2y):** White sticky mass (70.5 mg, 62%); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.34 (m, 3H), 7.33 – 7.17 (m, 5H), 7.10 (d, *J* = 6.8 Hz, 2H), 5.15 (dd, *J* = 26.6, 11.9 Hz, 2H), 3.45 – 3.11 (m, 3H), 3.03 – 2.87 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.6, 133.5, 132.5, 130.3, 129.2, 129.1, 128.8, 128.6, 128.3, 124.3 (q, *J* = 278.1), 110.9, 69.5, 61.5, 61.5, 41.9 (q, *J* = 29.3), 41.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -60.7; HRMS (ESI) calcd for $C_{19}H_{17}NO_2F_3S$ $[M+H]^+$: 380.0932; found: 380.0934.

**(*E*)-1-(3,3,3-Trifluoroprop-1-en-1-yl)pyrrolidin-2-one (2z):** Pale yellow syrup (22.5 mg, 42%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 14.4, 1.8 Hz, 1H), 5.01 (dq, *J* = 14.3, 6.3 Hz, 1H), 3.54 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 8.2 Hz, 2H), 2.25 – 2.13 (m, 2H); $^{13}$C NMR (101

MHz, $CDCl_3$) δ 174.1, 131.1 (q, *J* = 7.3 Hz), 124.3 (q, *J* = 267.5 Hz), 98.4 (q, *J* = 34.9 Hz), 44.8, 30.9, 17.4; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -60.4; HRMS (ESI) calcd for $C_7H_9NOF_3$ $[M+H]^+$: 180.0636; found: 180.0638.

**13-Methyl-3-(3,3,3-trifluoro-1-thiocyanatopropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2aa):** (1:1 diastereomeric mixture) Sticky mass (70.8 mg, 58%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.07 (s, 1H), 4.60 (t, *J* = 7.3 Hz, 1H), 3.10 – 2.98 (m, 2H), 2.93 (dd, *J* = 8.4, 3.7 Hz, 2H), 2.52 (dd, *J* = 18.7, 8.5 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.36 – 2.25 (m, 1H), 2.21 – 1.93 (m, 4H), 1.69 – 1.40 (m, 6H), 0.92 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 220.6, 141.6, 137.8, 133.4, 133.4, 127.8, 127.7, 126.5, 126.1, 124.7 (q, *J* = 278.1 Hz), 124.5, 124.4, 110.5, 50.5, 47.9, 46.2, 44.4, 39.8 (q, *J* = 29.2 Hz), 37.9, 35.8, 31.6, 29.7, 29.3, 26.3, 25.6, 21.6, 13.9; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -63.8, -63.8 (1:1 ratio); HRMS (ESI) calcd for $C_{22}H_{28}N_2OF_3S$ $[M+NH_4]^+$: 425.1874; found: 425.1846.

**4,4,4-trifluoro-2-thiocyanatobutyl 2-((3-chloro-2-methylphenyl)amino)nicotinate (2ab):** Pale yellow syrup (87.5 mg, 68%); $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.38 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.30 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.23 – 7.12 (m, 2H), 6.77 (dd, *J* = 7.8, 4.7 Hz, 1H), 4.73 – 4.58 (m, 2H), 3.84 – 3.67 (m, 1H), 2.88 – 2.73 (m, 2H), 2.39 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 166.6, 156.7, 154.3, 140.6, 138.7, 135.0, 129.4, 126.7, 125.5, 124.8 (q, *J* = 277.7 Hz), 122.5, 113.6, 108.9, 105.6, 65.4, 40.9, 36.5 (q, *J* = 30.3), 15.2; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -63.7; HRMS (ESI) calcd for $C_{18}H_{16}N_3O_2F_3SCl$ $[M+H]^+$: 430.0612; found: 430.0604.

**2-3. General procedure for the visible-light promoted trifluoromethylselenocyanation**:

Alkene **1** (0.3 mmol), Umemoto reagent II (0.45 mmol) and KSeCN (0.45 mmol) were weighed in a screw capped vial and MeCN (3.0 mL) was added to this mixture. The vial was back filled with $N_2$ and it was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). After completion of reaction (5 hours), the reaction mixture was concentrated using rotary evaporation and the crude reaction mixture was purified by column chromatography to get the desired compound **3**.

**Analytical data of the trifluoromethylselenocyanated compounds 3:**

**1-Bromo-4-(3,3,3-trifluoro-1-selenocyanatopropyl)benzene (3a):** Yellow solid (64.3 mg, 60%); mp = 65-67 ºC; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.84 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.27 – 3.00 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.6, 132.7, 128.8, 124.8 (q, *J* = 278.9 Hz), 123.8, 100.8, 40.9, 40.5 (q, *J* = 28.6 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.9; HRMS (ESI) calcd for $C_9H_7F_3Br$ $[M\text{-}SeCN]^+$: 250.9683; found: 250.9684.

**1-Selenocyanato-2-(trifluoromethyl)-2,3-dihydro-1H-indene (3b):** Pale brownish syrup (39.1 mg, 45%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 1H), 7.35 – 7.27 (m, 3H), 5.18 (d, *J* = 3.5 Hz, 1H), 3.65 – 3.44 (m, 2H), 3.22 (dd, *J* = 16.1, 3.3 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.2, 129.9, 128.2, 126.8 (q, *J* = 279.1 Hz), 125.2, 125.0, 100.6, 51.6 (q, *J* = 27.7 Hz), 48.0, 31.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -71.8; HRMS (ESI) calcd for $C_{10}H_8F_3$ $[M\text{-}SeCN]^+$: 185.0578; found: 185.0581.

**(4,4,4-trifluoro-2-selenocyanatobutyl)benzene (3c):** Pale brownish syrup (42.9 mg, 49%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 3H), 7.24 – 7.18 (m, 2H), 3.80 – 3.65 (m, 1H), 3.33 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.16 (dd, *J* = 14.5, 8.6 Hz, 1H), 2.89 – 2.68 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 136.6, 129.1, 129.0, 127.9, 125.5 (q, *J* = 278.1 Hz), 100.2, 42.1, 41.1 (q, *J* = 2.2 Hz), 39.9 (q, *J* = 29.1 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.3; HRMS (ESI) calcd for $C_{10}H_{10}F_3$ $[M\text{-}SeCN]^+$: 187.0735; found: 187.0732.

**1,2-Dimethoxy-4-(4,4,4-trifluoro-2-selenocyanatobutyl)benzene (3d):** Pale brownish syrup (50.8 mg, 48%); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.1 Hz, 1H), 6.75 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.70 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.81 – 3.66 (m, 1H), 3.27 (dd, *J* = 14.5, 6.7 Hz, 1H), 3.11 (dd, *J* = 14.5, 8.4 Hz, 1H), 2.86 – 2.69 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.3, 148.7, 129.0, 125.3 (q, *J* = 278.1 Hz), 121.2, 112.0, 111.5, 100.4, 56.0, 55.9, 41.7, 41.3 (q, *J* = 2.2 Hz), 39.7 (q, *J* = 29.0 Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (ESI) calcd for $C_{13}H_{18}N_2O_2F_3Se$ $[M+NH_4]^+$: 371.0486; found: 371.0486.

**(5,5,5-Trifluoro-3-selenocyanatopentyl)benzene (3e):** Pale brownish syrup (39.5 mg, 43%); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.22 – 7.16 (m, 2H), 3.47 – 3.32 (m, 1H), 2.93 (ddd, *J* = 14.0, 8.7, 5.2 Hz, 1H), 2.88 – 2.66 (m, 3H), 2.40 – 2.27 (m, 1H), 2.26 – 2.13 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.2, 128.9, 128.5, 126.8, 125.4 (q, *J* = 279.0 Hz), 99.6, 41.1 (q, *J* = 28.9 Hz), 39.6 (q, *J* = 2.4 Hz), 33.6; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.5; HRMS (ESI) calcd for $C_{12}H_{12}NF_3ClSe$ $[M+Cl]^-$: 341.9776; found: 341.9778.

**(3,3,3-Trifluoro-1-selenocyanatopropyl)cyclooctane (3f):** Pale brownish syrup (38.5 mg, 41%); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.69 (td, *J* = 6.9, 3.4 Hz, 1H), 2.84 – 2.61 (m, 2H), 2.15 – 2.09 (m, 1H), 1.85 – 1.71 (m, 2H), 1.71 – 1.58 (m, 5H), 1.57 – 1.44 (m, 6H), 1.44 – 1.34 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 125.6 (q, *J* = 278.1 Hz), 101.1, 50.0 (q, *J* = 2.1 Hz), 41.4, 38.0 (q, *J* = 29.0 Hz), 32.7, 30.0, 26.5, 26.2, 26.0, 25.9, 25.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.8; HRMS (ESI) calcd for HRMS (ESI) calcd for $C_{11}H_{18}F_3$ $[M-SeCN]^+$: 207.1361; found: 207.1364.

**2-(6,6,6-Trifluoro-4-selenocyanatohexyl)isoindoline-1,3-dione (3g):** White solid (66.7 mg, 57%); mp = 128-130 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 3.60 – 3.49 (m, 1H), 2.87 – 2.62 (m, 2H), 2.09 – 1.80 (m, 4H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.3, 134.2, 131.9, 125.3 (q, *J* = 278.1

Hz), 123.4, 99.5, 40.9 (q, $J$ = 29.0 Hz), 39.6, 36.6, 33.1, 26.8; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.6; HRMS (ESI) calcd for $C_{15}H_{14}N_2O_2F_3Se$ $[M+H]^+$: 391.0173; found: 391.0178.

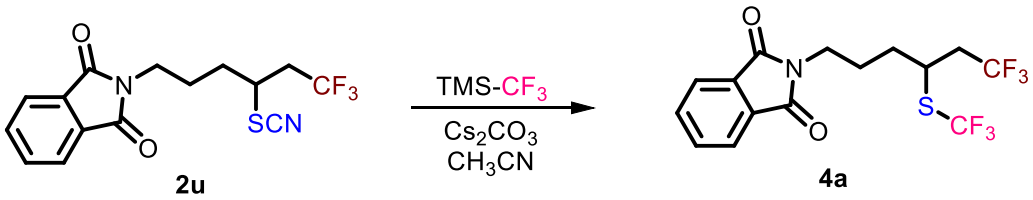
**Benzyl 4,4,4-trifluoro-2-methyl-2-selenocyanatobutanoate (3h):** Pale brownish syrup (63.9 mg, 61%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 5H), 5.24 (s, 2H), 3.24 – 2.91 (m, 2H), 1.97 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.0, 134.0, 129.0, 128.8, 128.7, 124.5 (q, $J$ = 279.0 Hz), 101.3, 69.3, 51.2, 43.4 (q, $J$ = 29.0 Hz), 25.9. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.6; HRMS (ESI) calcd for $C_{13}H_{16}N_2O_2F_3Se$ $[M+NH_4]^+$: 369.0329; found: 369.0336.

**2-4. One mmol scale trifluoromethylthiocyanation:**

Alkene **1u** (215 mg, 1.0 mmol), Umemoto reagent II (657 mg, 1.5 mmol) and $NH_4SCN$ (114 mg, 1.5 mmol) were weighed in a 25 mL round bottom flask and MeCN (10 mL) was added to this mixture. The flask was sealed with a septum, degassed with nitrogen and introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). After completion of reaction (4 hours), the reaction mixture was concentrated using rotary evaporation and the crude reaction mixture was purified by column chromatography to get the desired compound **2u** (232 mg, 68% yield).

**2-5. Tansformation of trifluoromethyl-thiocyanation product:**

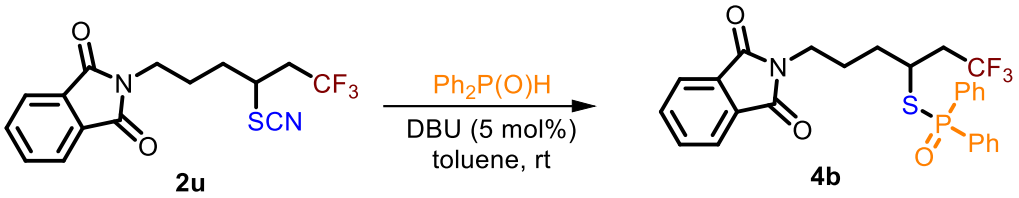
**2-(6,6,6-trifluoro-4-((trifluoromethyl)thio)hexyl)isoindoline-1,3-dione (4a):**




To a solution of **2u** (50 mg, 0.15 mmol) in $CH_3CN$ (1.5 ml) was added $Cs_2CO_3$ (98 mg, 0.3 mmol) and cooled to 0 °C. Then trifluoromethyltrimethylsilane (42.7 mg, 0.3 mmol) was added at once via syringe and the mixture was then stirred at ambient temperature for 16 h. The resulting mixture was extracted into EtOAc (15 mL) and washed with water (10 mL) followed

by brine solution (10 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated. The crude compound was purified by column chromatography. White solid (44.5 mg, 77%); mp =71-73 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.74 (t, *J* = 6.7 Hz, 2H), 3.51 – 3.42 (m, 1H), 2.72 – 2.44 (m, 2H), 2.04 – 1.70 (m, 4H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.3, 134.1, 132.0, 130.5 (q, *J* = 306.6 Hz), 125.3 (q, *J* = 277.9 Hz), 123.33, 40.2 (q, *J* = 28.4 Hz), 39.1, 37.0, 31.5, 25.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -39.6, -63.7; HRMS (ESI) calcd for $C_{15}H_{14}NO_2SF_6$ $[M+H]^+$: 386.0649; found: 386.0651.

**(6-(1,3-Dioxoisoindolin-2-yl)-1,1,1-trifluorohexan-3-yl) diphenylphosphinothioate (4b):**




To a mixture of **2u** (50 mg, 0.15 mmol) and diphenylphosphine oxide (30 mg, 0.15 mmol) in toluene (1.5 mL) was added DBU (1 mg, 0.0075 mmol) at room temperature and stirred at the same temperature for 2 hours. The reaction mixture was concentrated and the crude mass was purified by column chromatography. Colorless sticky mass (33.3 mg, 43%), $^1$H NMR (400 MHz, $CDCl_3$) 8.06 – 7.77 (m, 6H), 7.72 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.57 – 7.50 (m, 6H), 3.66 – 3.54 (br, 2H), 3.52 – 3.37 (br, 1H), 2.88 – 2.69 (br, 1H), 2.53 – 2.37 (br, 1H), 1.93 – 1.79 (m, 2H), 1.76 – 1.63 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.3, 134.0, 132.7, 132.6, 132.1, 131.9, 131.5, 128.9, 125.5 (q, *J* = 278.6 Hz), 123.3, 40.6 (q, *J* = 28.6 Hz), 39.3, 37.3, 32.5, 25.4; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.9; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 42.0; HRMS (ESI) calcd for $C_{26}H_{24}NO_3SF_3P$ $[M+H]^+$: 518.1167; found: 518.1168.

## 3. Mechanistic investigations:

### 3-1. UV/Vis absorbance studies:

UV absorption spectra of alkene **1a (**0.0066 M), Umemoto reagent II (0.0066 M) and mixture of alkene **1a** and Umemoto reagent II in acetonitrile were recorded (Figure S1). There was no increase in UV absorbance upon mixing the alkene **1a** and Umemoto reagent II. This clearly indicates there is no EDA complex between alkene and Umemoto ragent II.

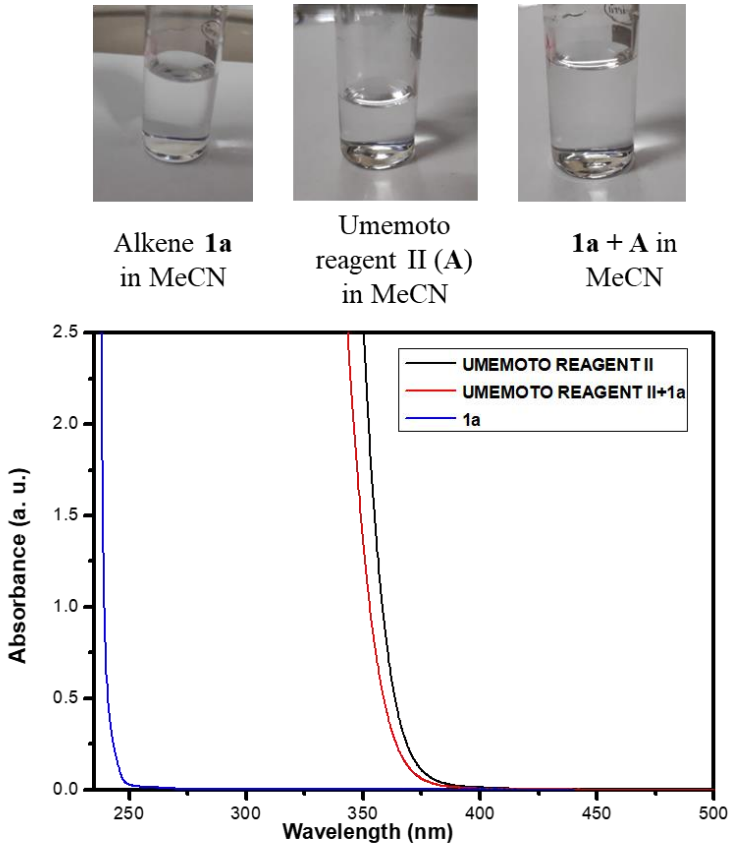
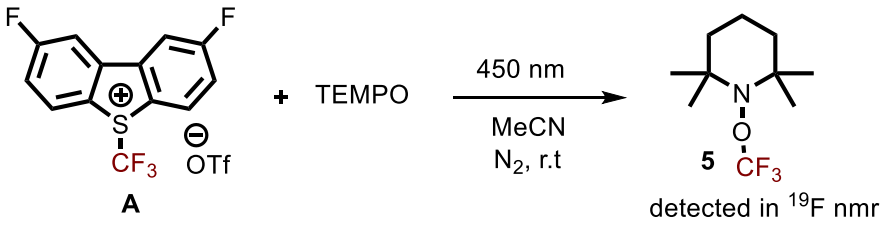



**Figure S1** (Top) photographs of alkene **1a**, Umemoto reagent II (**A**) and mixture of **1a**+**A** in acetonitrile. (There was no formation of colored solution upon mixing **1a** and **A**)

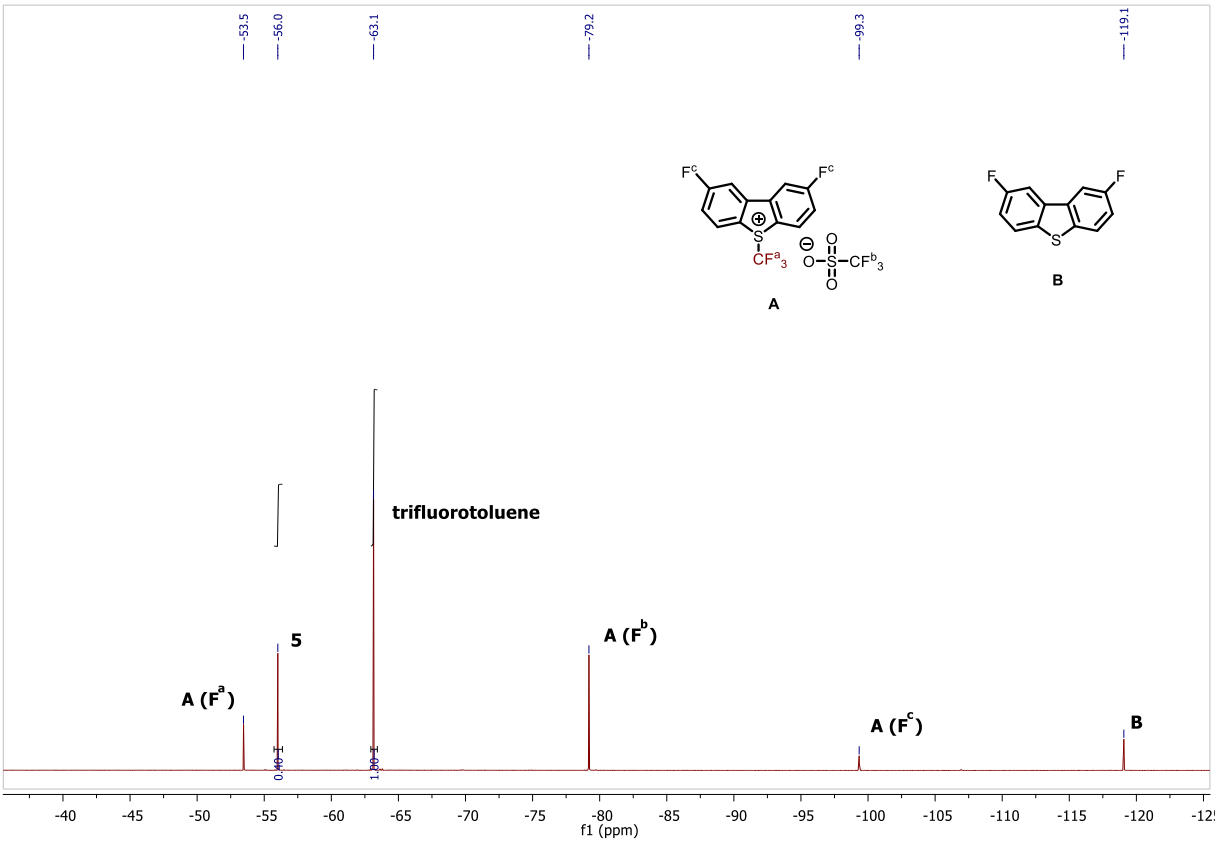
(Bottom) UV-Vis absorption of alkene **1a** (0.0066 M), **A** (0.0066 M) and mixture of **1a** and **A.** (There was no increase in UV absorbance upon mixing **1a** and **A**)

### 3-2. Radical trapping experiments:

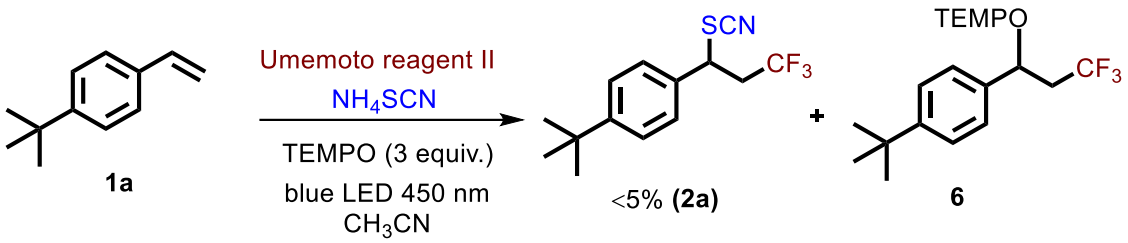
### a. Detection of $CF_3$-TEMPO adduct:



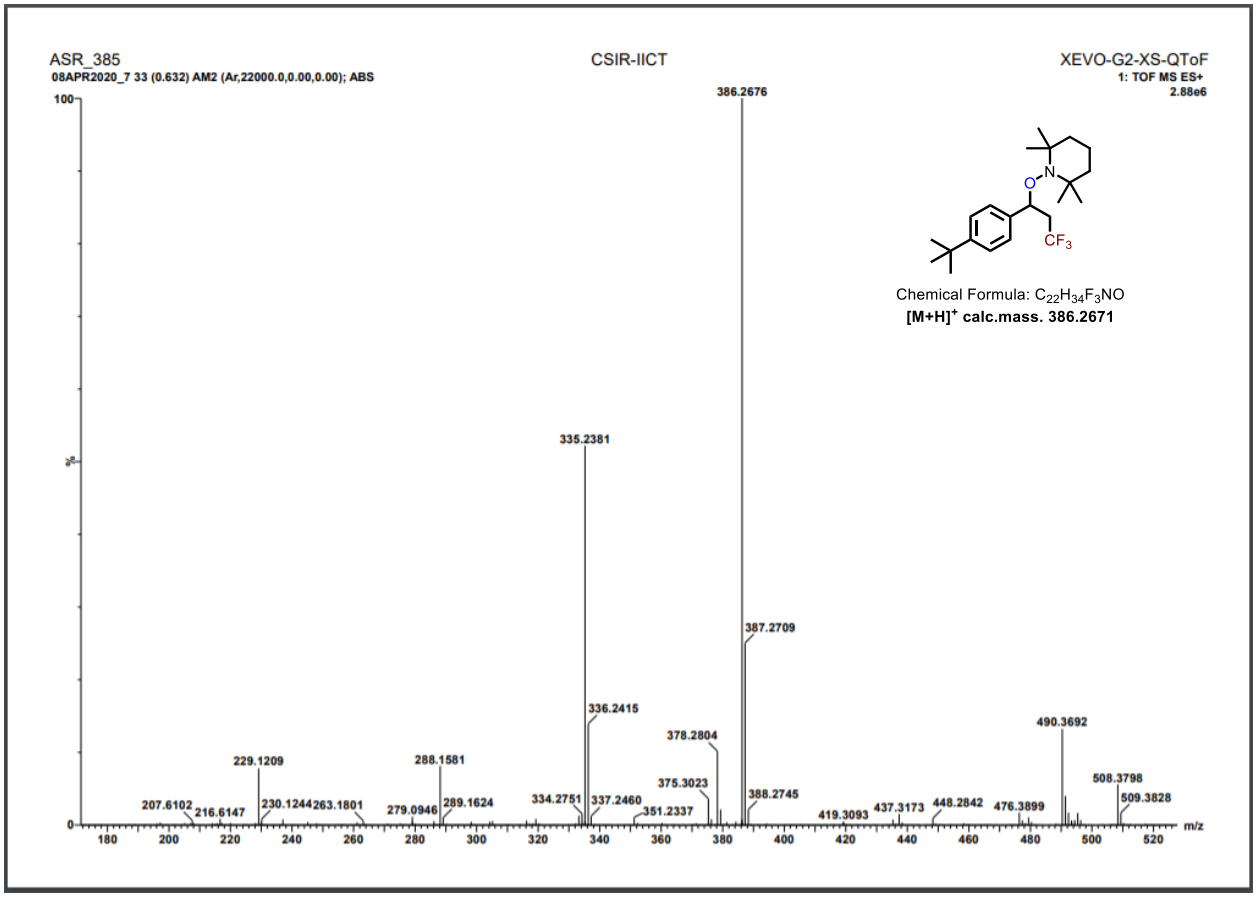

A mixture of Umemoto reagent II (**A**) (19.7 mg, 0.045 mmol) and TEMPO (7 mg, 0.045 mmol) in $CH_3CN$ was irradiated in PR m2 (blue LED, 450 nm) for 4 hours. The reaction mixture was concentrated and dissolved in $CDCl_3$ to record $^{19}F$ nmr. $CF_3$-TEMPO adduct was detected in an yield of 40% (using trifluorotoluene as internal standard) in $^{19}F$ nmr.



**b. Detection of $CF_3$-TEMPO difunctionalized product:**

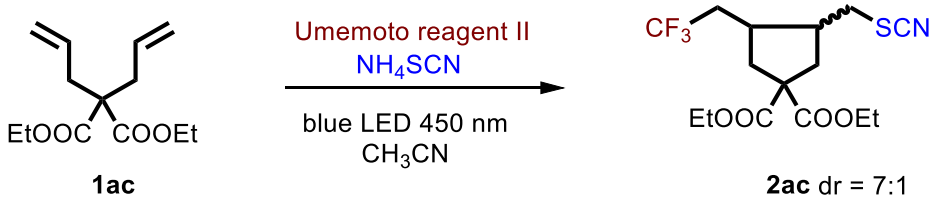



Alkene **1a** (48 mg, 0.3 mmol), Umemoto reagent II (197 mg, 0.45 mmol), $NH_4SCN$ (34 mg, 0.45 mmol) and TEMPO (141 mg, 0.9 mmol) were weighed in a screw capped vial and MeCN (3.0 mL) was added to this mixture. The vial was back filled with $N_2$ and it was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). After 4 hours, the HRMS of crude reaction mixture revealed the formation of compound **6**.



### 3-3. Radical clock cyclization experiment:

**Diethyl 3-(thiocyanatomethyl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (2ac):**




**1ac** **2ac** dr = 7:1

Following the general procedure for the trifluoromethylthiocyanation, the alkene **1ac** was converted into the radical cyclized product **2ac**. Pale yellow syrup (34 mg, 45%); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.28 – 4.13 (m, 4H), 3.10 (dd, *J* = 12.6, 4.2 Hz, 1H), 2.74 – 2.62 (m, 2H), 2.62 – 2.49 (m, 2H), 2.48 (d, *J* = 5.0 Hz, 2H), 2.27 – 2.09 (m, 2H), 2.04 (dd, *J* = 14.0, 9.7 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.5, 171.6, 126.5 (q, *J* = 276.9 Hz), 111.6, 62.1, 62.0, 58.1, 42.3, 38.2, 37.4, 36.7, 33.9, 33.4 (q, *J* = 28.6 Hz), 14.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.6; HRMS (ESI) calcd for $C_{15}H_{21}NO_4F_3S$ $[M+H]^+$: 368.1143; found: 368.1146.

### 4. X-ray crystallography of 2u:

X-ray data for KA973 (**2u**) was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H or 1.2$U_{eq}$(C) for other H atoms].

**Figure S2 Captions**

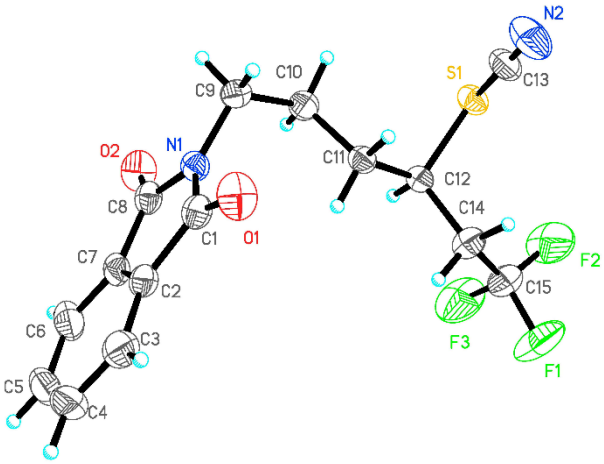



Fig.S2. A view of **KA973** (**2u**), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

**Crystal structure determination of 2u [KA973_0m]:**

**Crystal Data** for $C_{15}H_{13}N_2O_2F_3S$ ($M$ =342.33 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 12.0991(2) Å, $b$ = 12.9247(2) Å, $c$ = 10.4969(2) Å, $\beta$ = 100.4740(7)°, $V$ = 1614.12(5) Å$^3$, $Z$ = 4, $T$ = 294.15 K, μ(MoKα) = 0.241 mm$^{-1}$, $Dcalc$ = 1.409 g/cm$^3$, 18639 reflections measured (5.05° ≤ 2Θ ≤ 61.004°), 4444 unique ($R_{int}$ = 0.0548, $R_{sigma}$ = 0.0528) which were used in all calculations. The final $R_1$ was 0.0619 (I > 2σ(I)) and $wR_2$ was 0.1791 (all data). CCDC 2004626 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].


1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

2. Sheldrick G. M. (2015**)** Acta Crystallogr C71: 3-8.

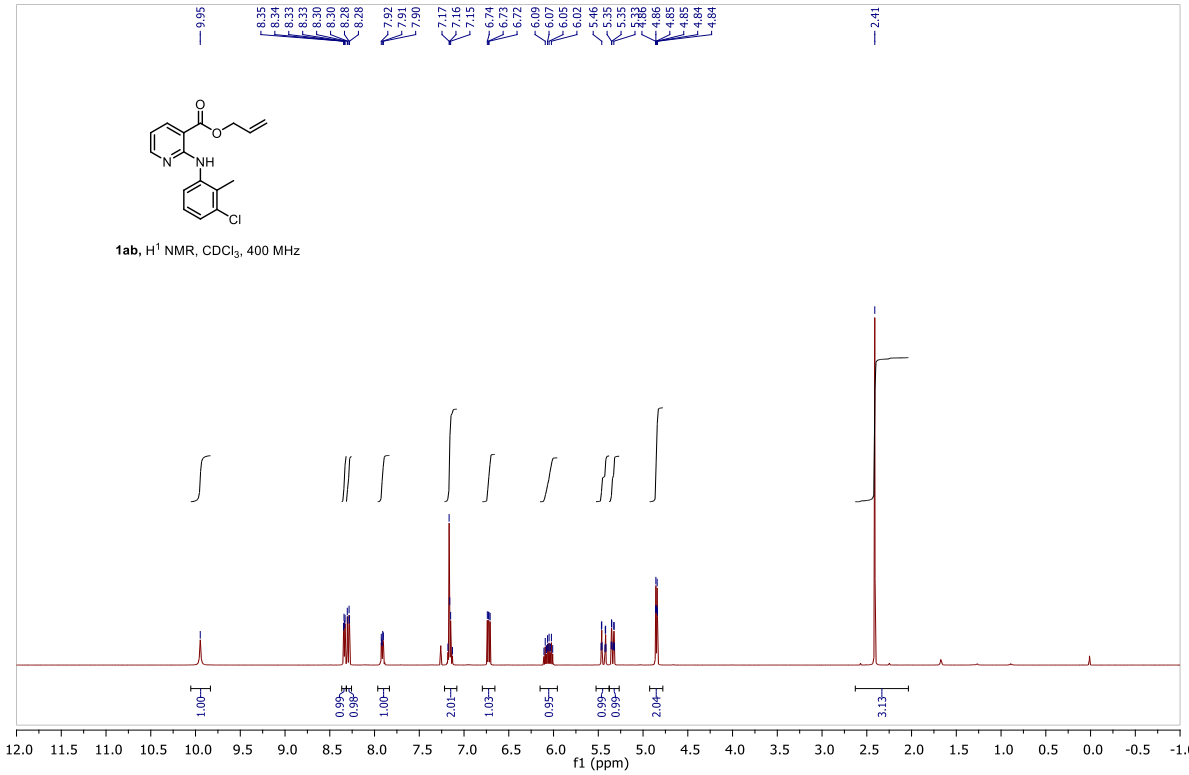
## 5. References:

1. a) B. R. Kusuma, L. B. Peterson, H. Zhao, G. Vielhauer, J. Holzbeierlein and B. S. J. Blagg, *J. Med. Chem.*, 2011, **54**, 6234–6253; b) G. Ma, W. Wan, J. Li, Q. Hu, H. Jiang, S. Zhu, J. Wang and J. Hao, *Chem. Commun.*, 2014, **50**, 9749–9752; c) E. M. Stang and M. C. White, *J. Am. Chem. Soc.*, 2011, **133**, 14892–14895; d) T. Balalas, C. Peperidou, D. J. Hadjipavlou-Litina and K. E. Litinas, *Synthesis.*, 2016, **48**, 281–292; e) C. S. Buxton, D. C. Blakemore and J. F. Bower, *Angew. Chemie Int. Ed.*, 2017, **56**, 13824–13828.

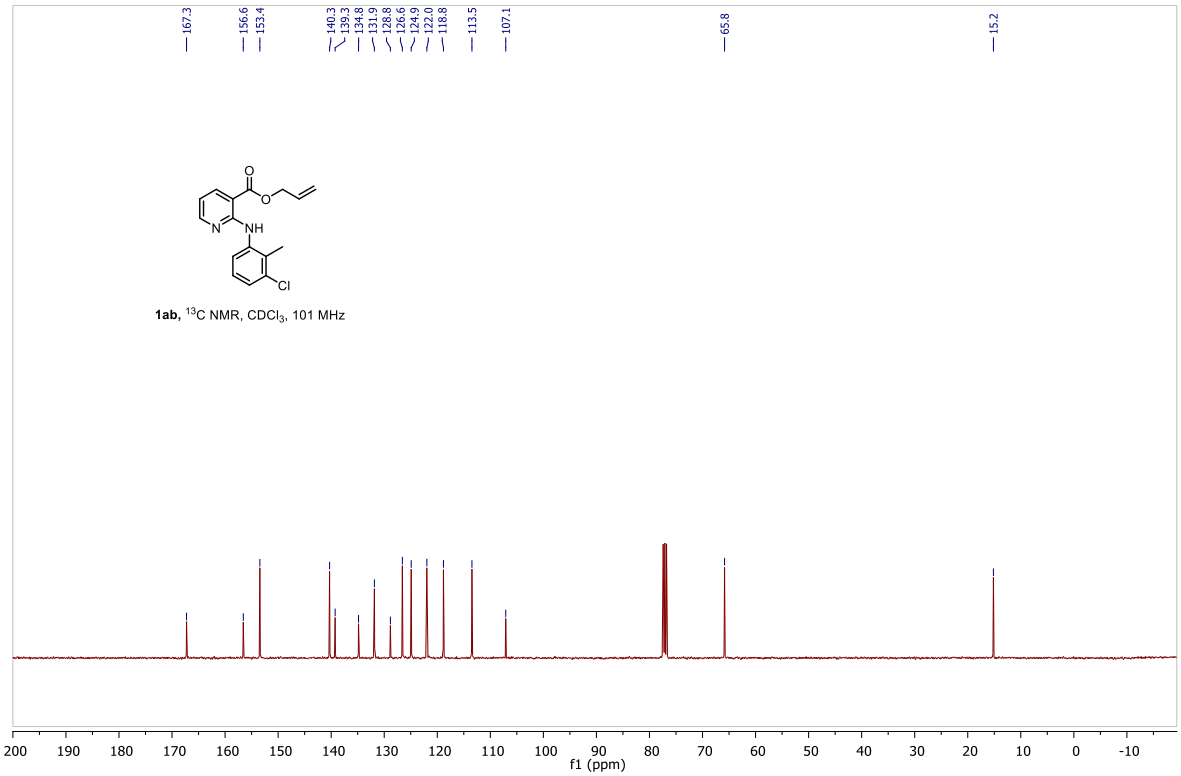
2. Z. Liang, F. Wang, P. Chen and G. Liu, *Org. Lett.*, 2015, **17**, 2438–2441.

3. V. A. Schmidt and E. J. Alexanian, *J. Am. Chem. Soc.*, 2011, **133**, 11402–11405.

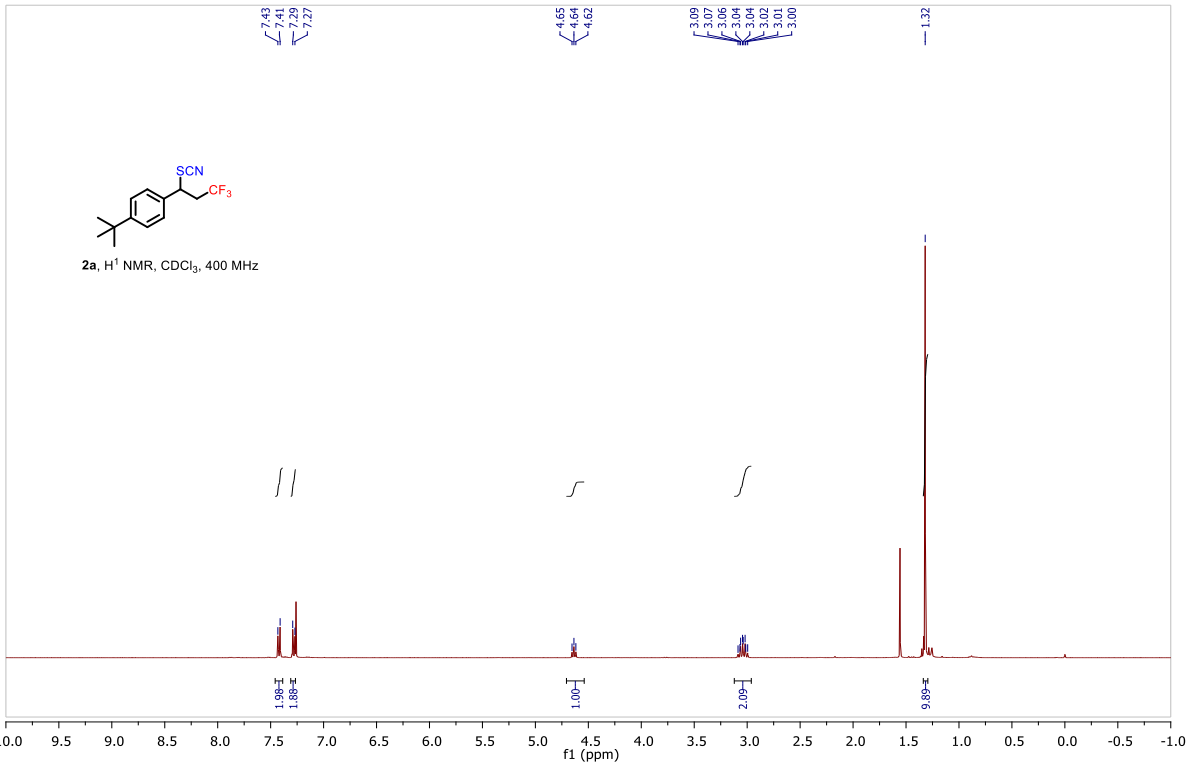
## 6. NMR spectra:



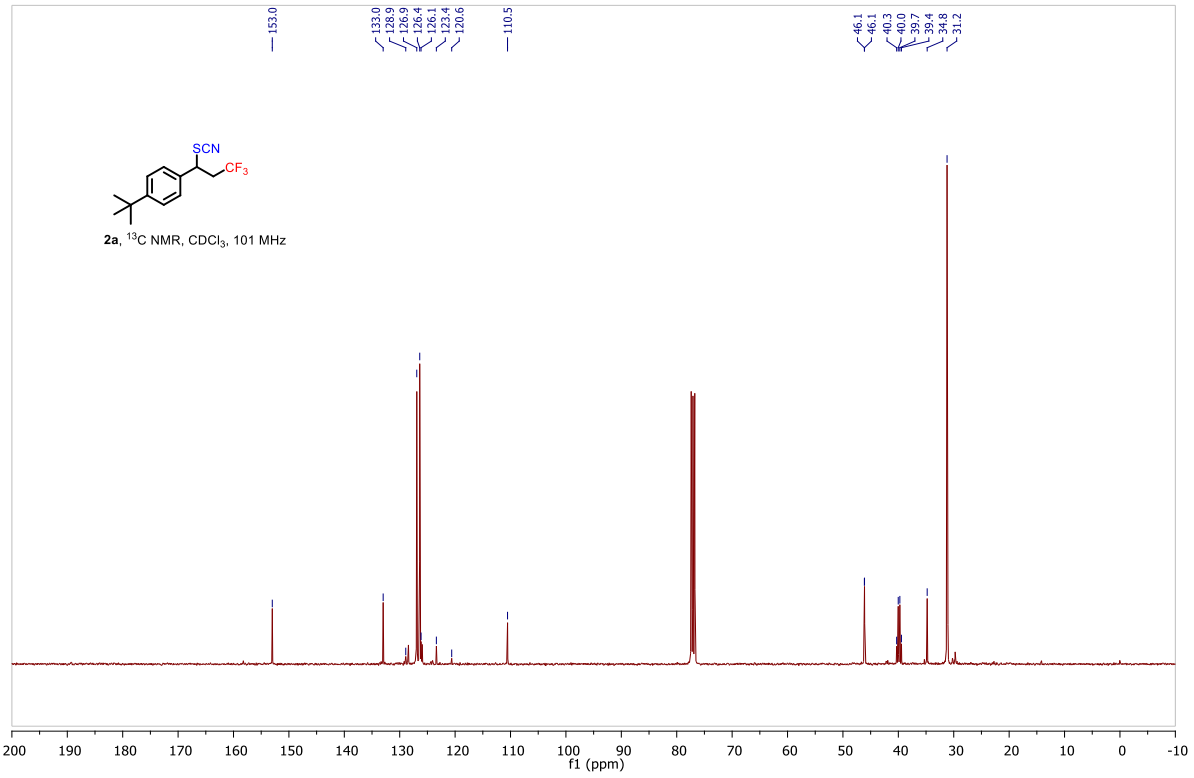

**1ab,** $H^1$ NMR, $CDCl_3$, 400 MHz



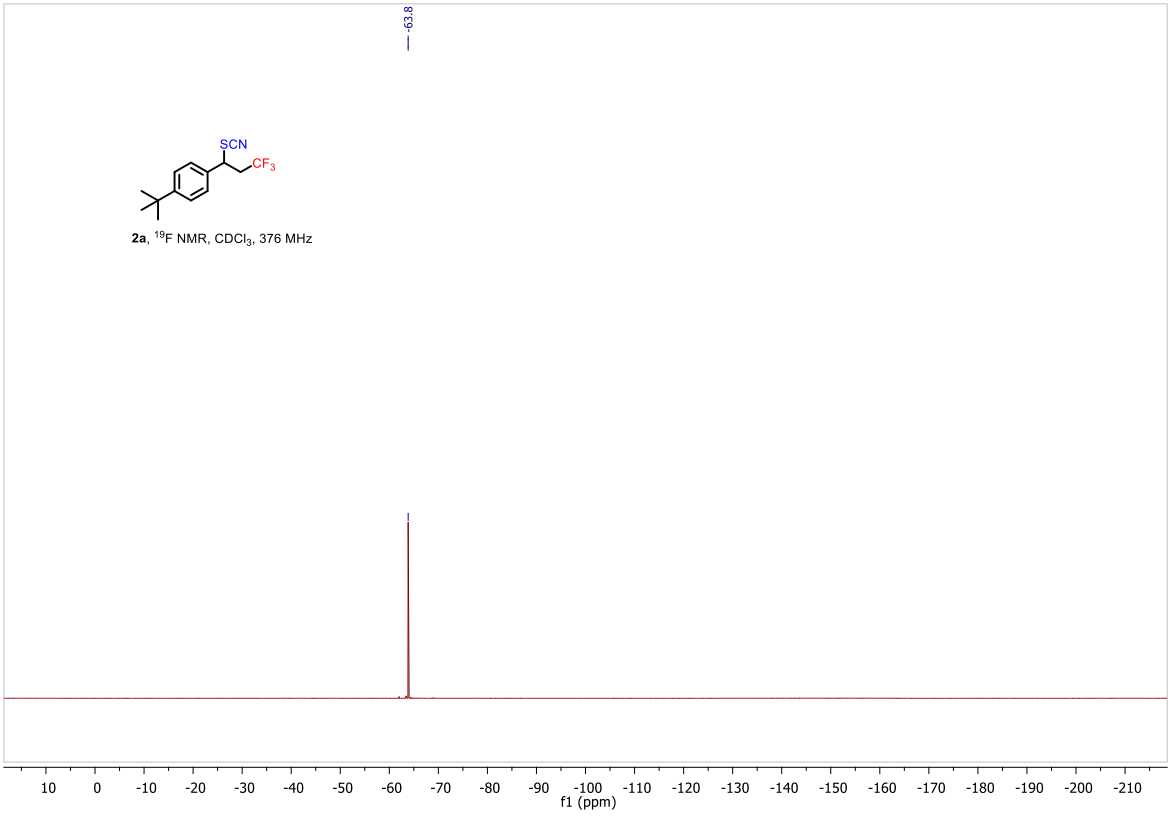

**1ab,** $^{13}C$ NMR, $CDCl_3$, 101 MHz



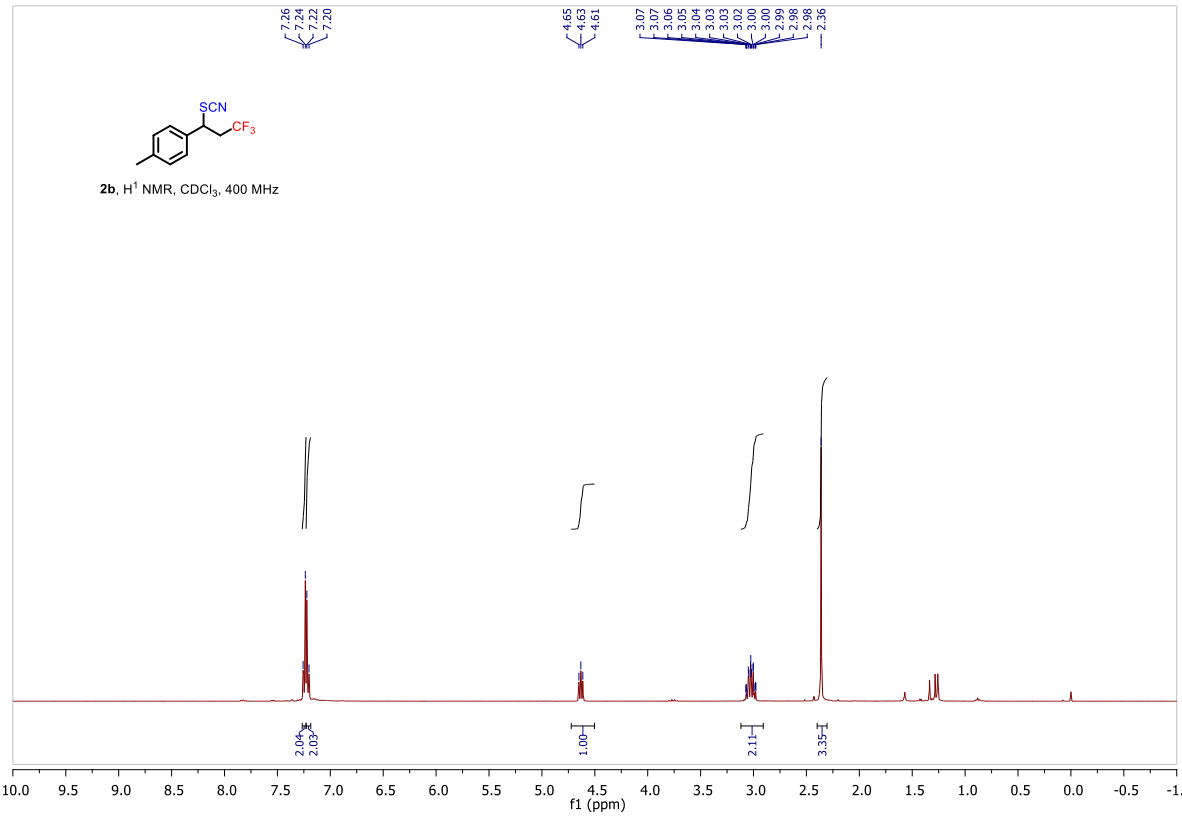

**2a**, $H^1$ NMR, $CDCl_3$, 400 MHz



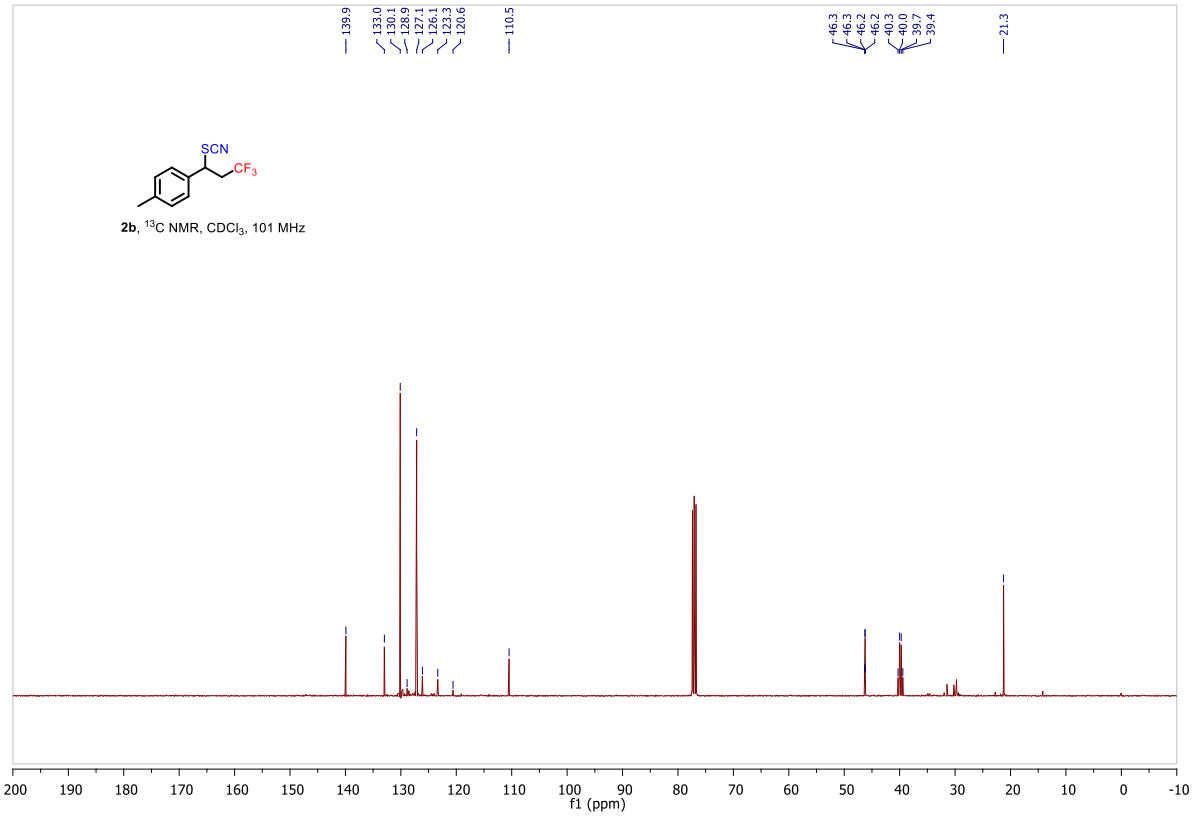

**2a**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



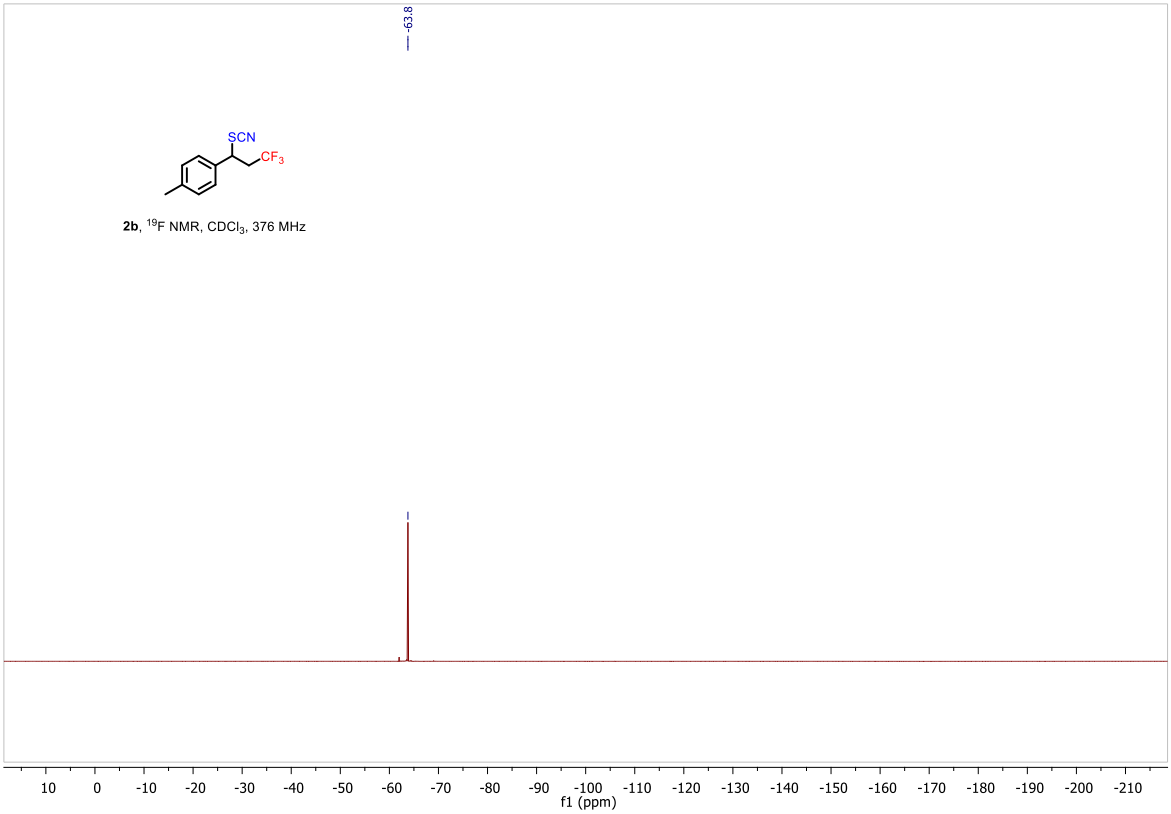

**2a**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



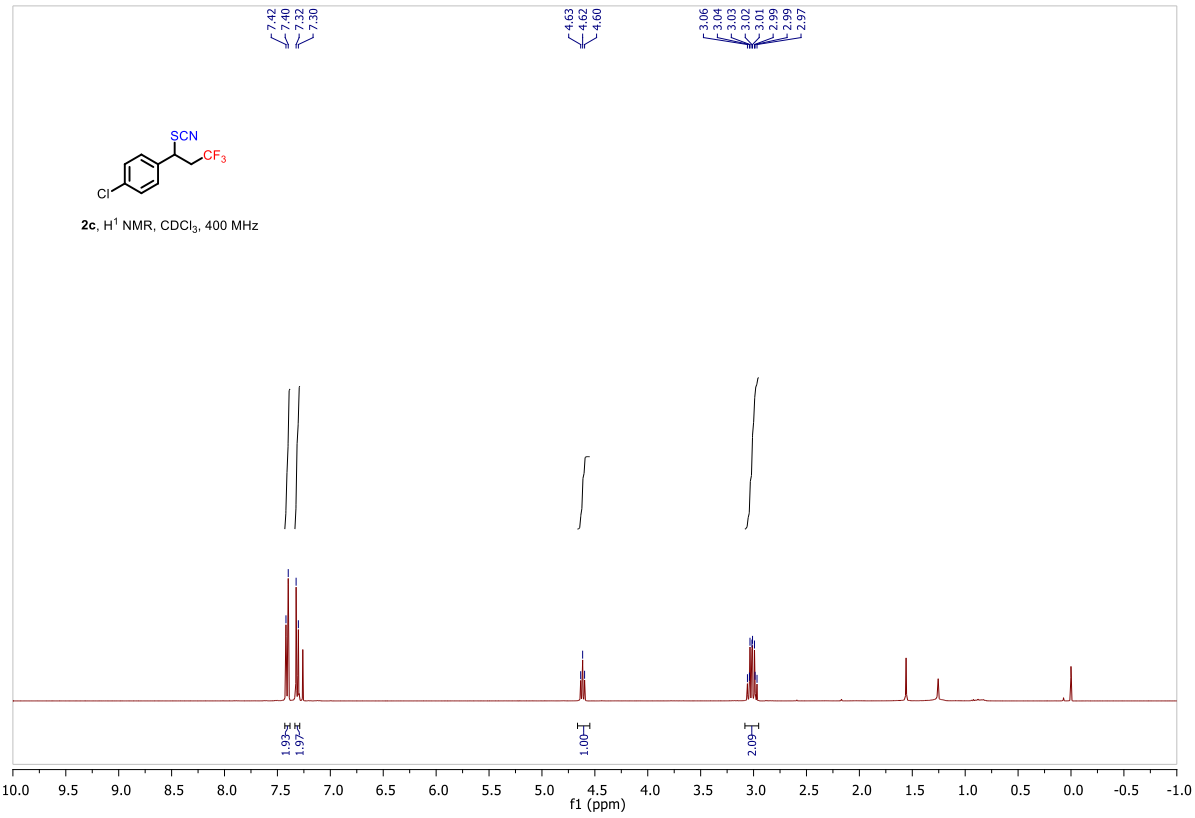

**2b**, $H^1$ NMR, $CDCl_3$, 400 MHz



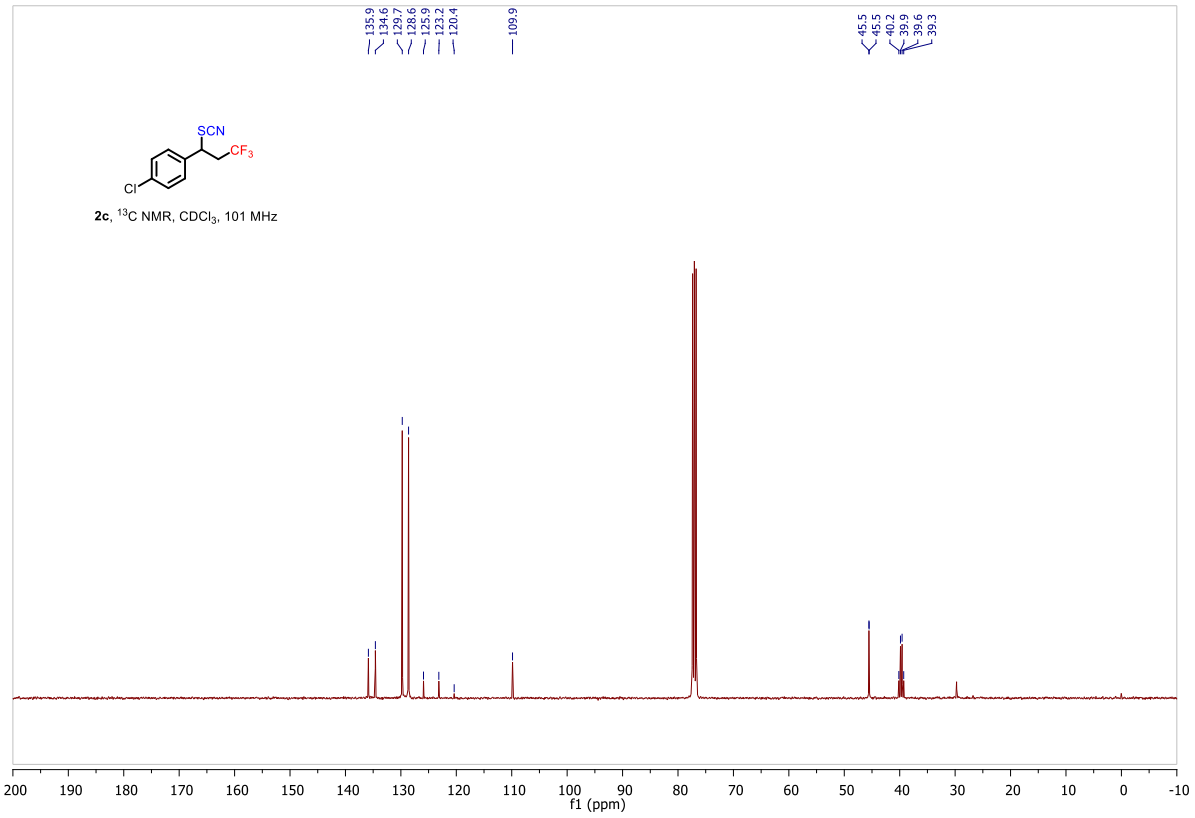

**2b**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



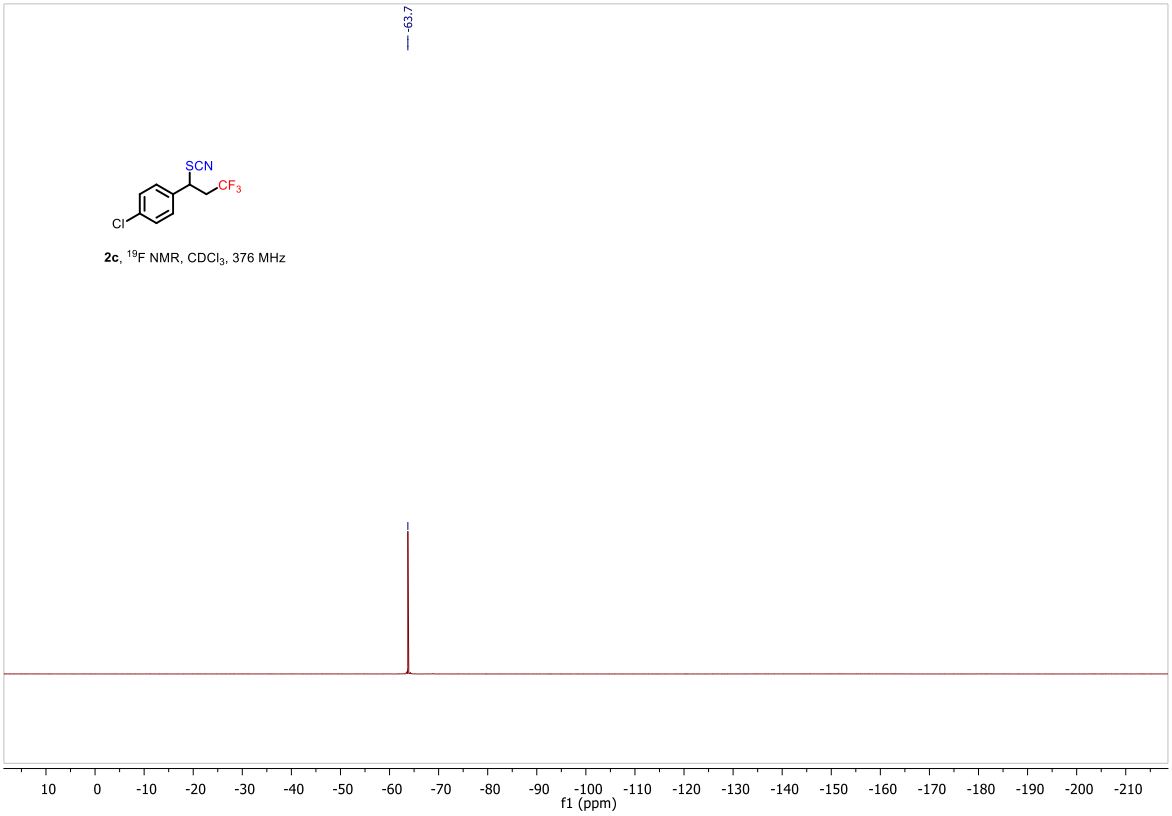

**2b**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



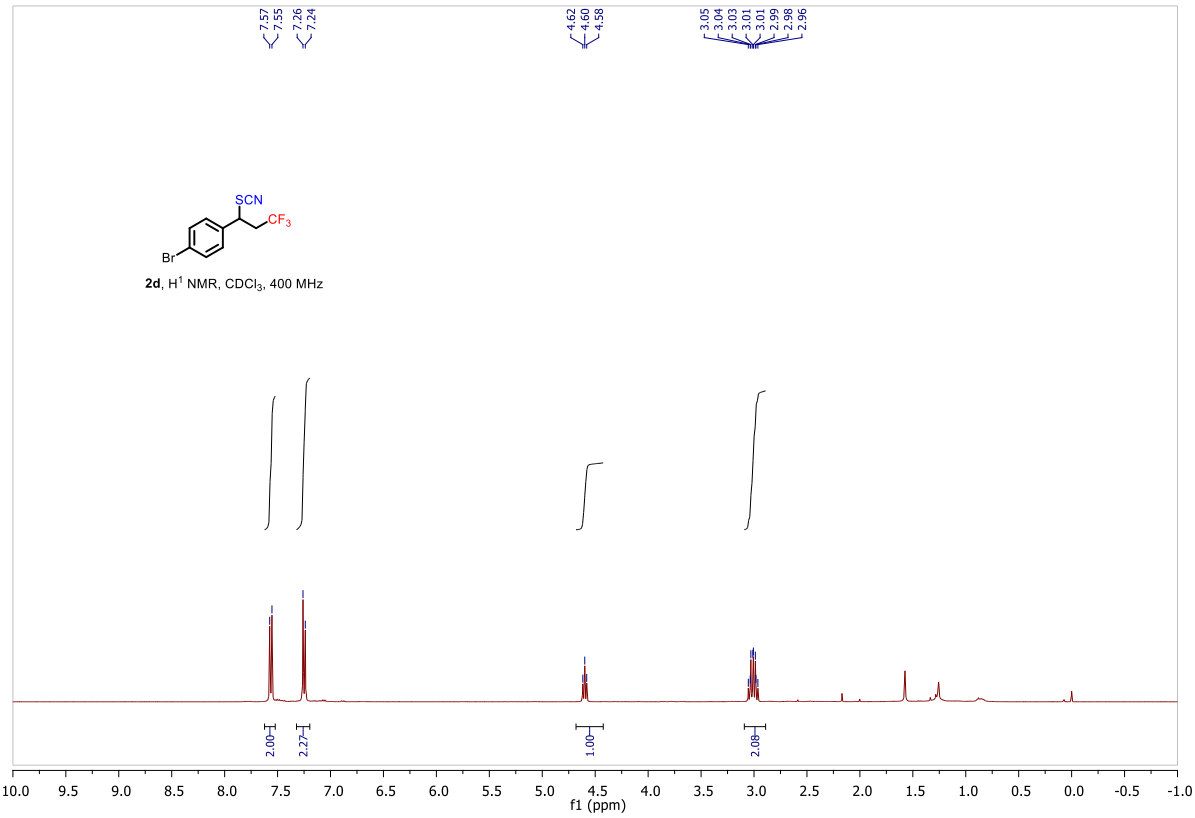

**2c**, $H^1$ NMR, $CDCl_3$, 400 MHz




**2c**, $^{13}C$ NMR, $CDCl_3$, 101 MHz




**2c**, $^{19}F$ NMR, $CDCl_3$, 376 MHz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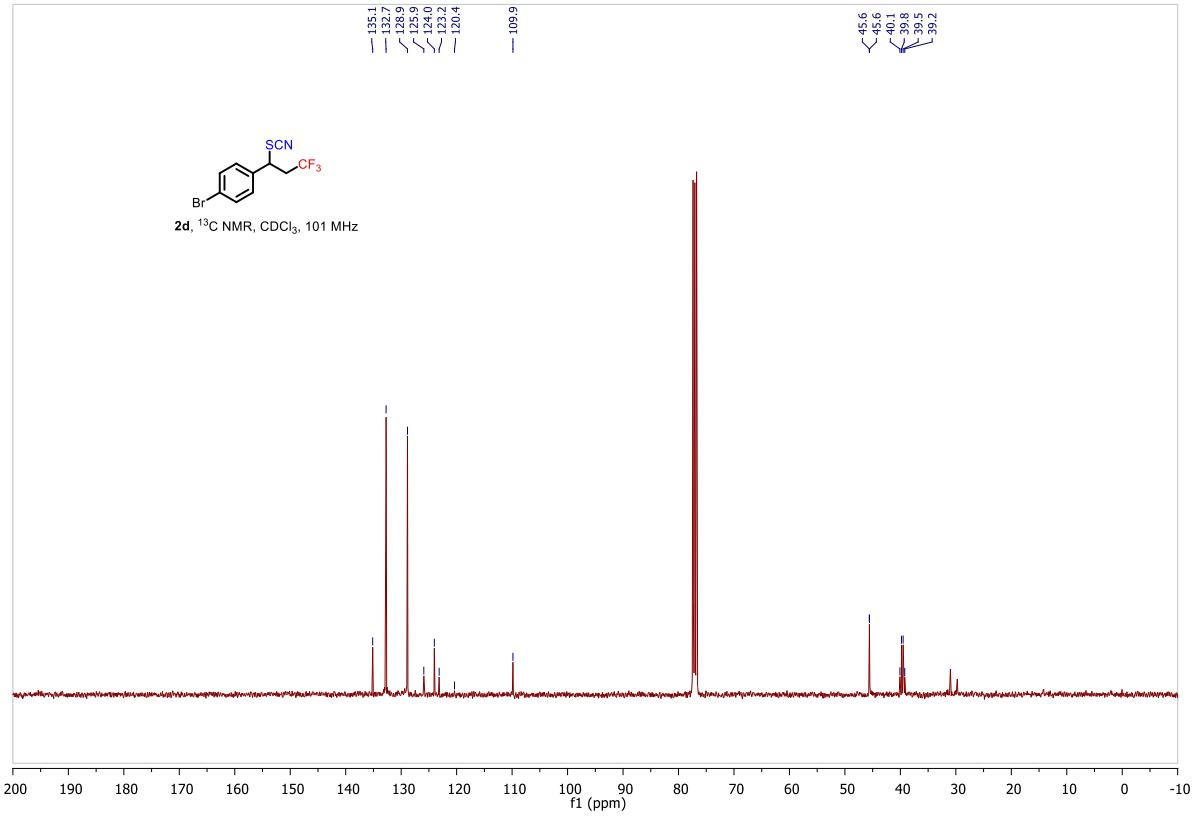
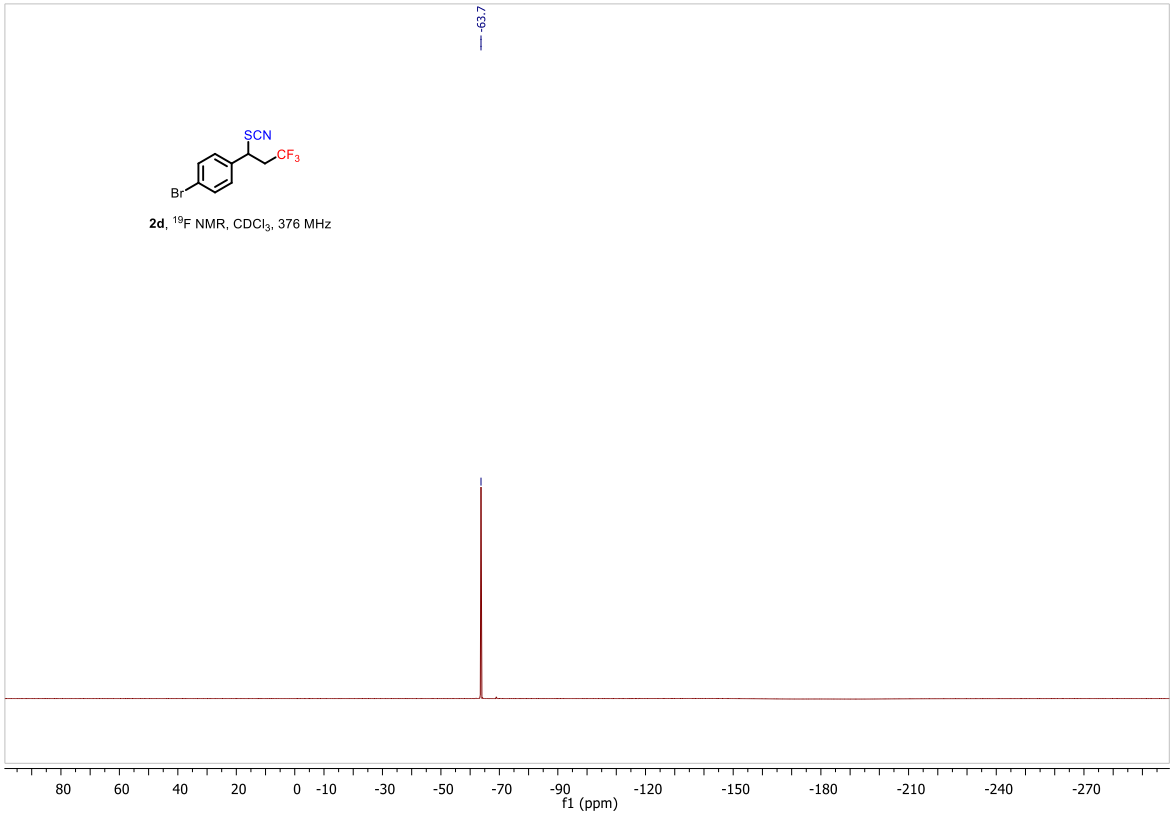
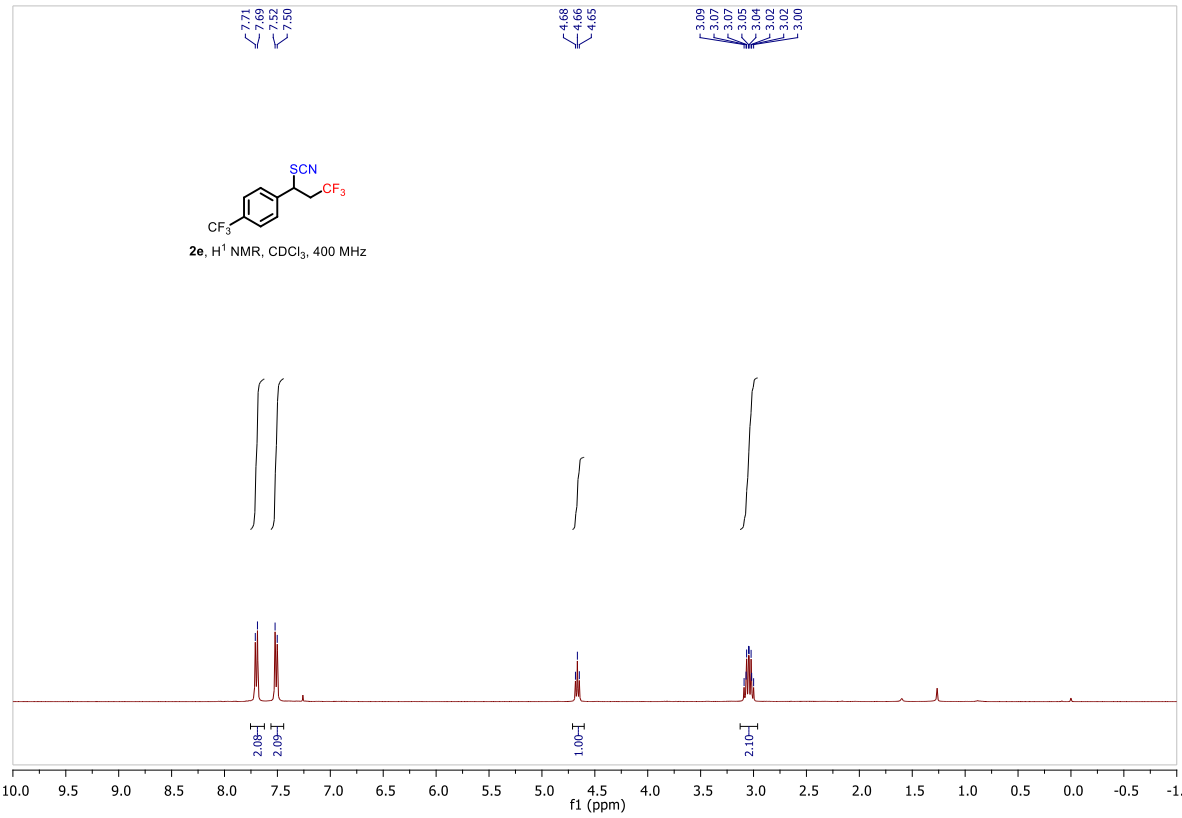
7.55
7.26
7.24
4.62
4.60
4.58
3.05
3.04
3.03
3.01
3.01
2.99
2.98
2.96
SCN
CF3
Br
2d, H1 NMR, CDCl3, 400 MHz
2.00
2.27
1.00
2.08
f1 (ppm)

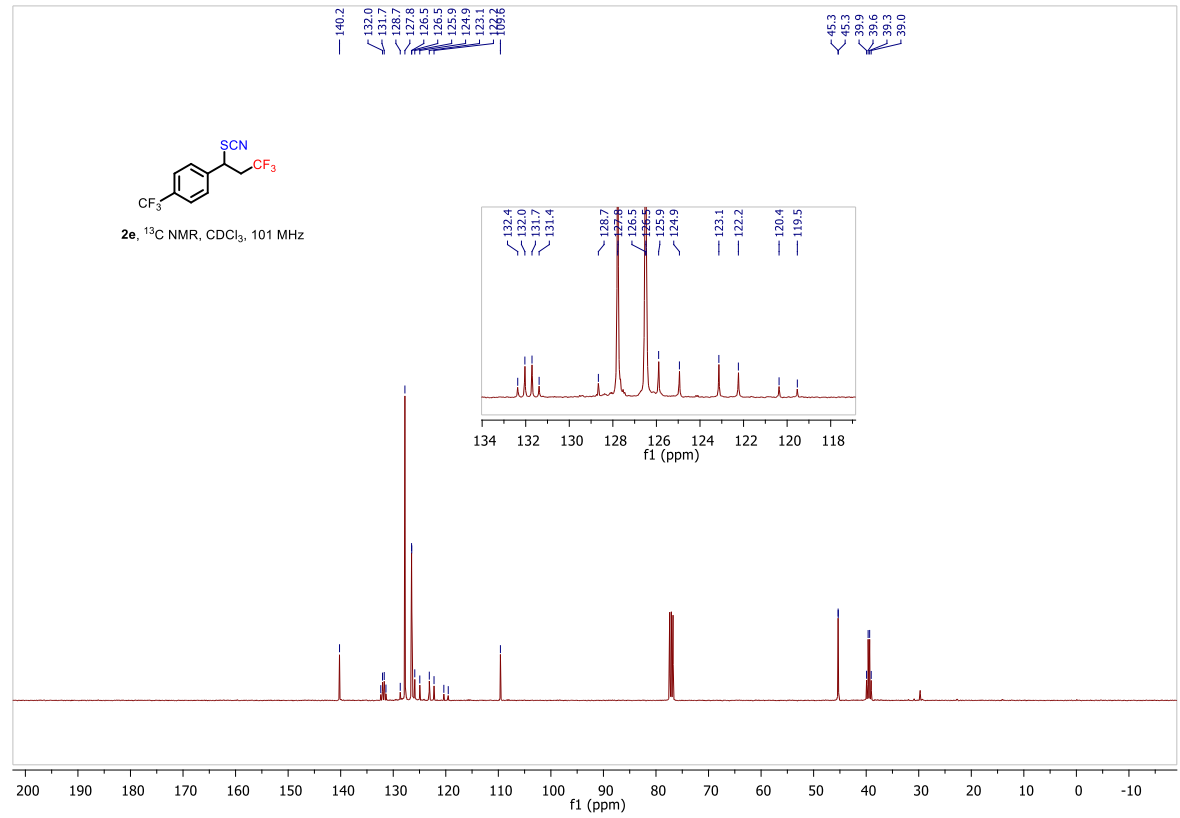

135.1
132.7
128.9
125.9
124.0
123.2
120.4
109.9
45.6
45.6
40.1
39.8
39.5
39.2
SCN
CF3
Br
2d, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



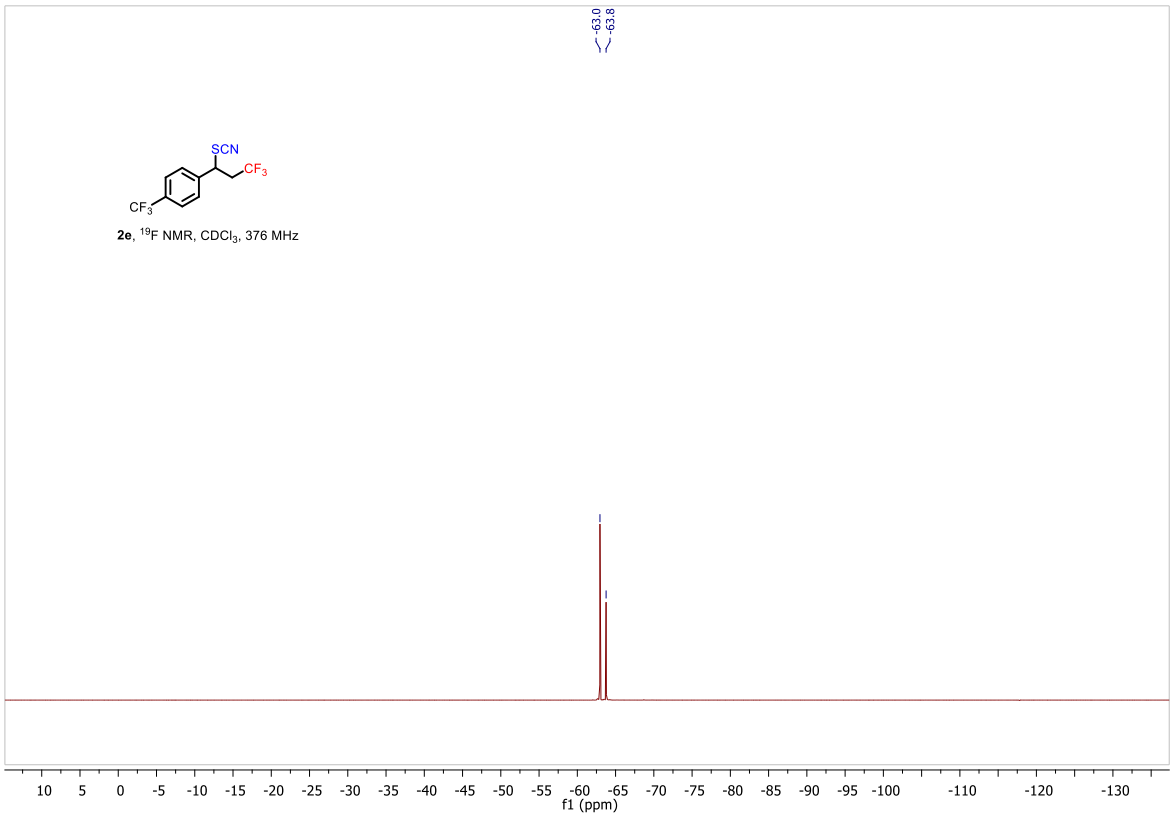

**2d**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



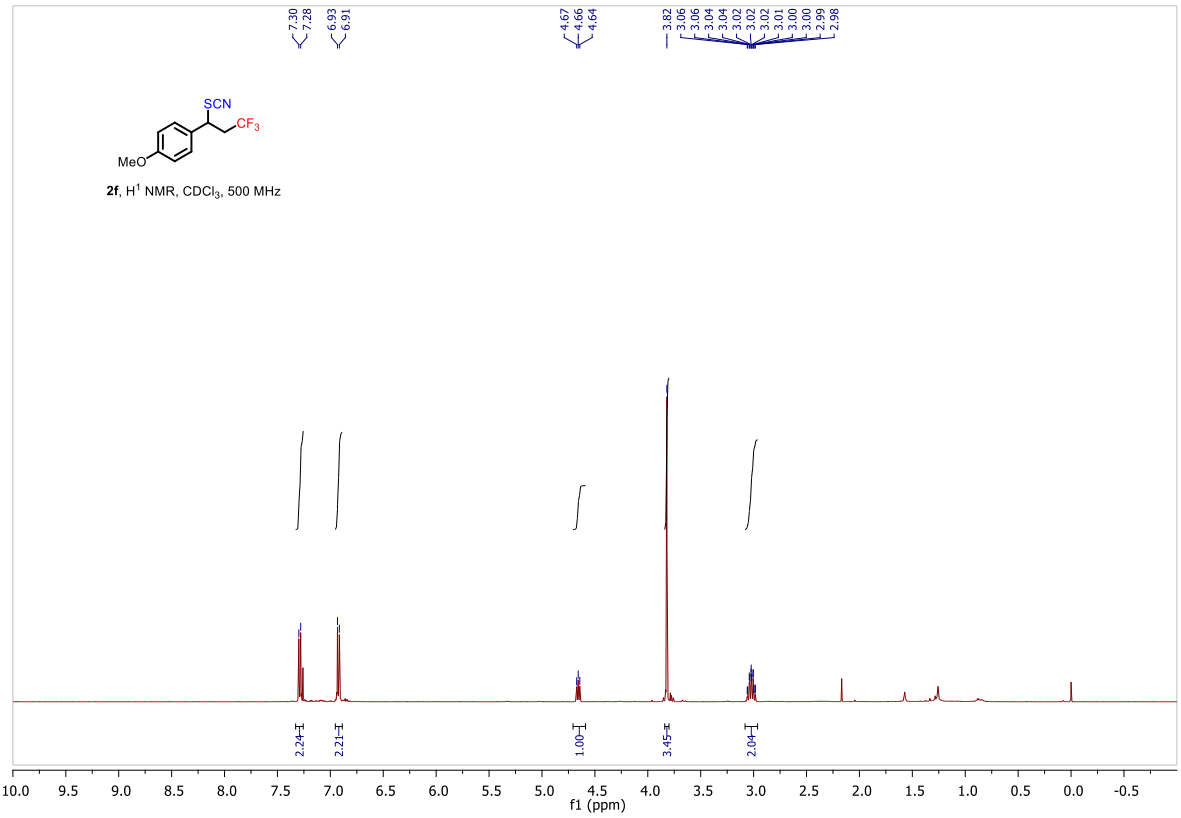

**2e**, $H^1$ NMR, $CDCl_3$, 400 MHz

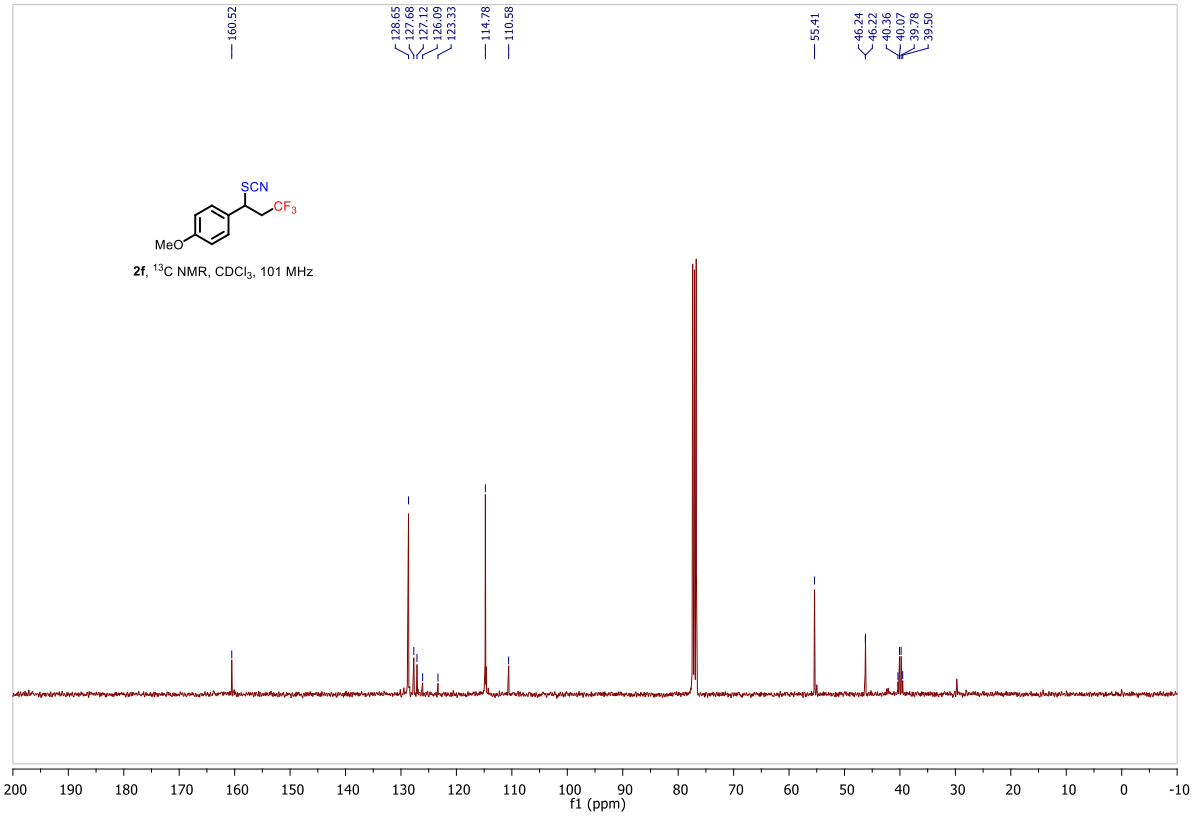


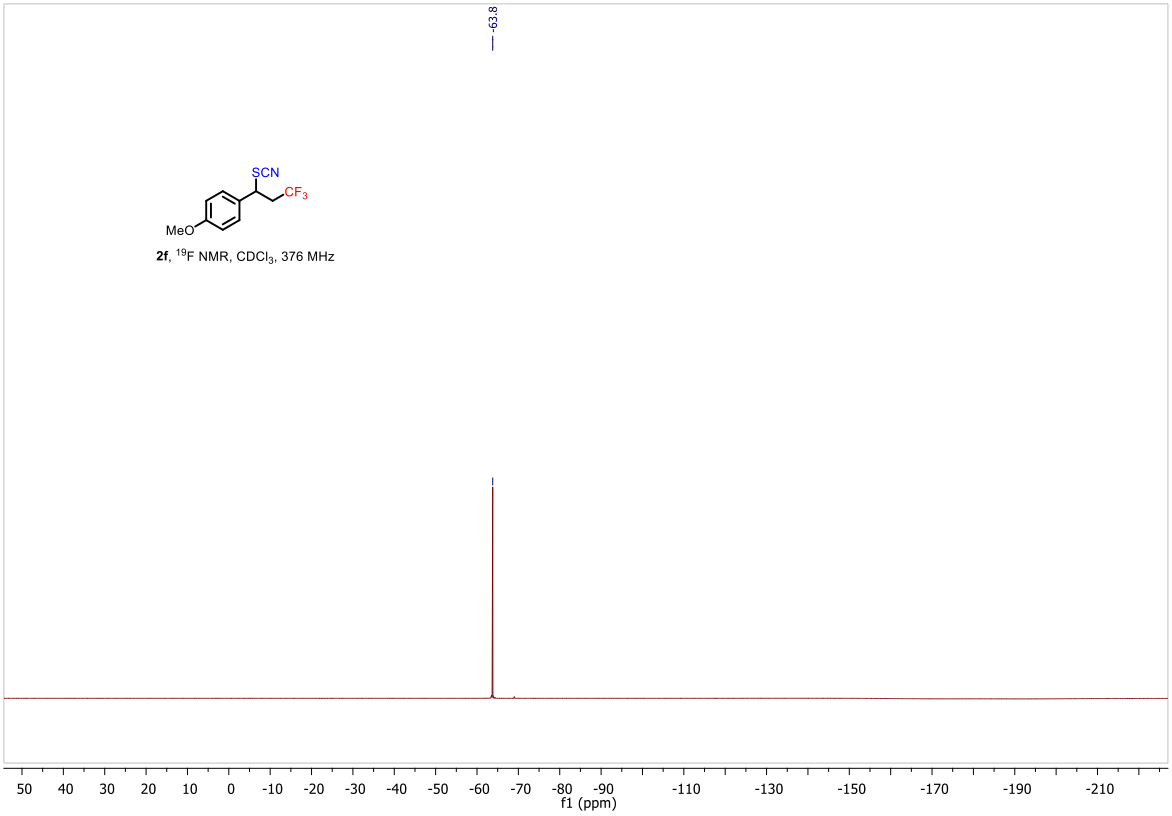

**2e**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



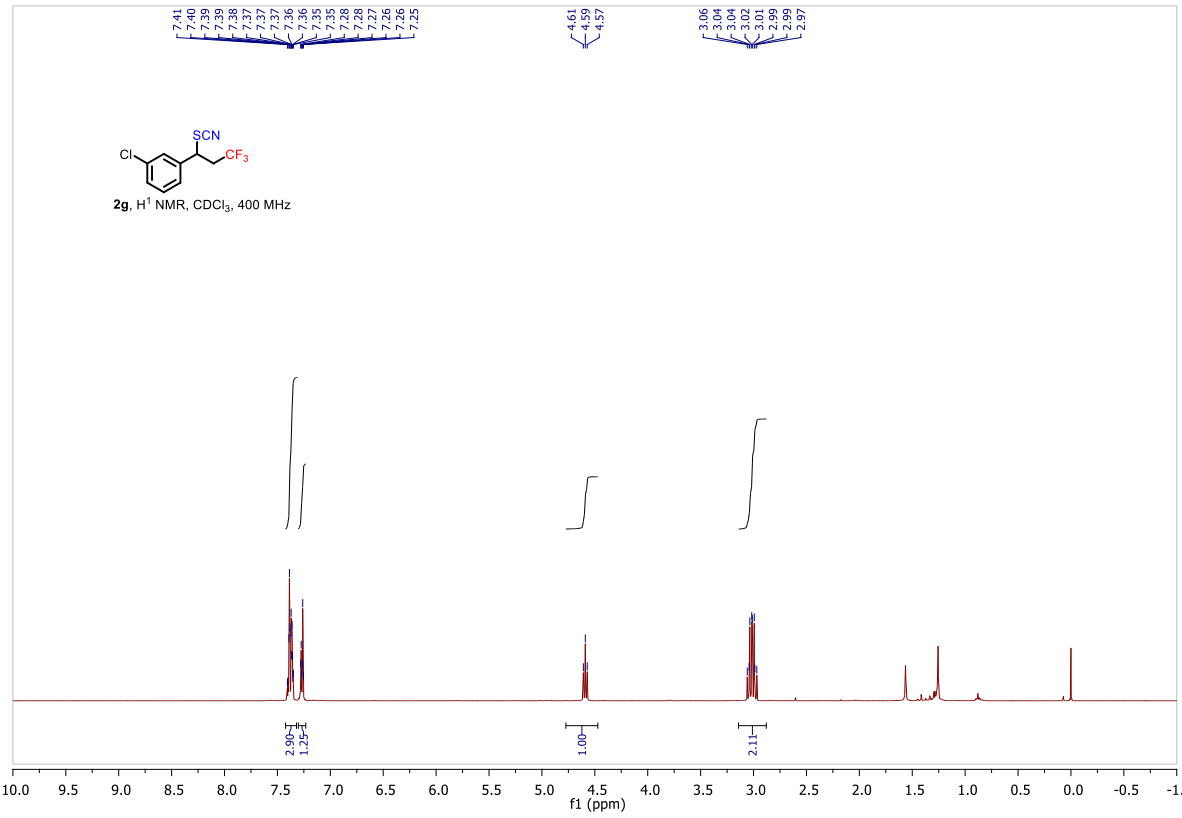

**2e**, $^{19}F$ NMR, $CDCl_3$, 376 MHz


7.30
7.28
6.93
6.91
4.67
4.66
4.64
3.82
3.06
3.06
3.04
3.04
3.02
3.02
3.02
3.01
3.00
3.00
2.99
2.98
SCN
CF3
MeO
2f, H1 NMR, CDCl3, 500 MHz
2.24
2.21
1.00
3.45
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

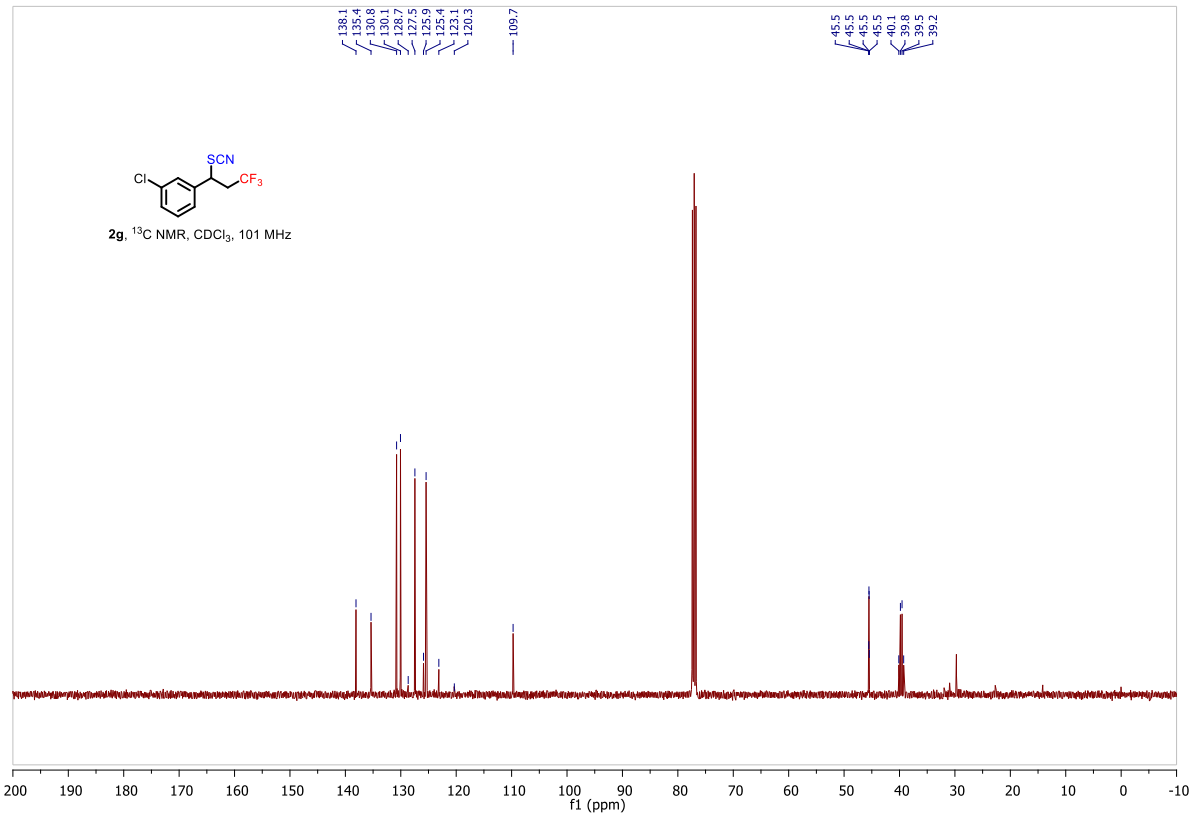

160.52
128.65
127.68
127.12
126.09
123.33
114.78
110.58
55.41
46.24
46.22
40.36
40.07
39.78
39.50
SCN
CF3
MeO
2f, 13C NMR, CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



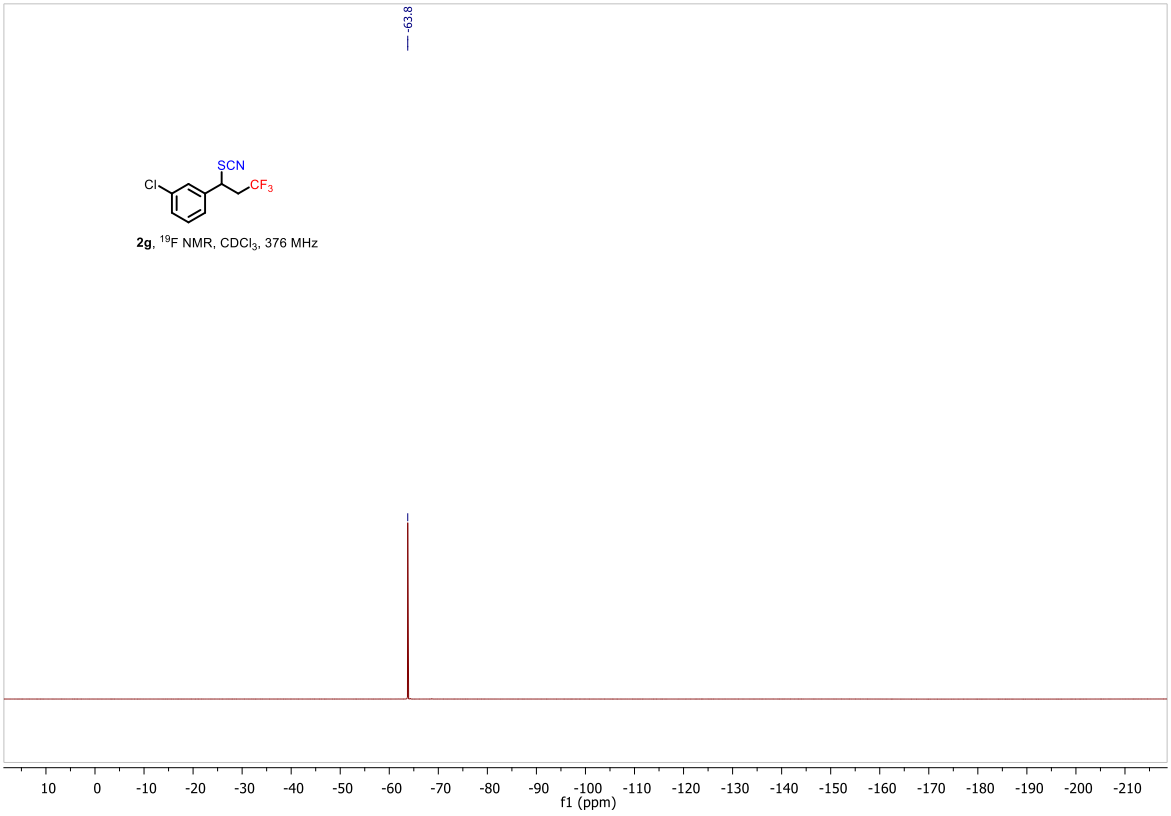

**2f**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



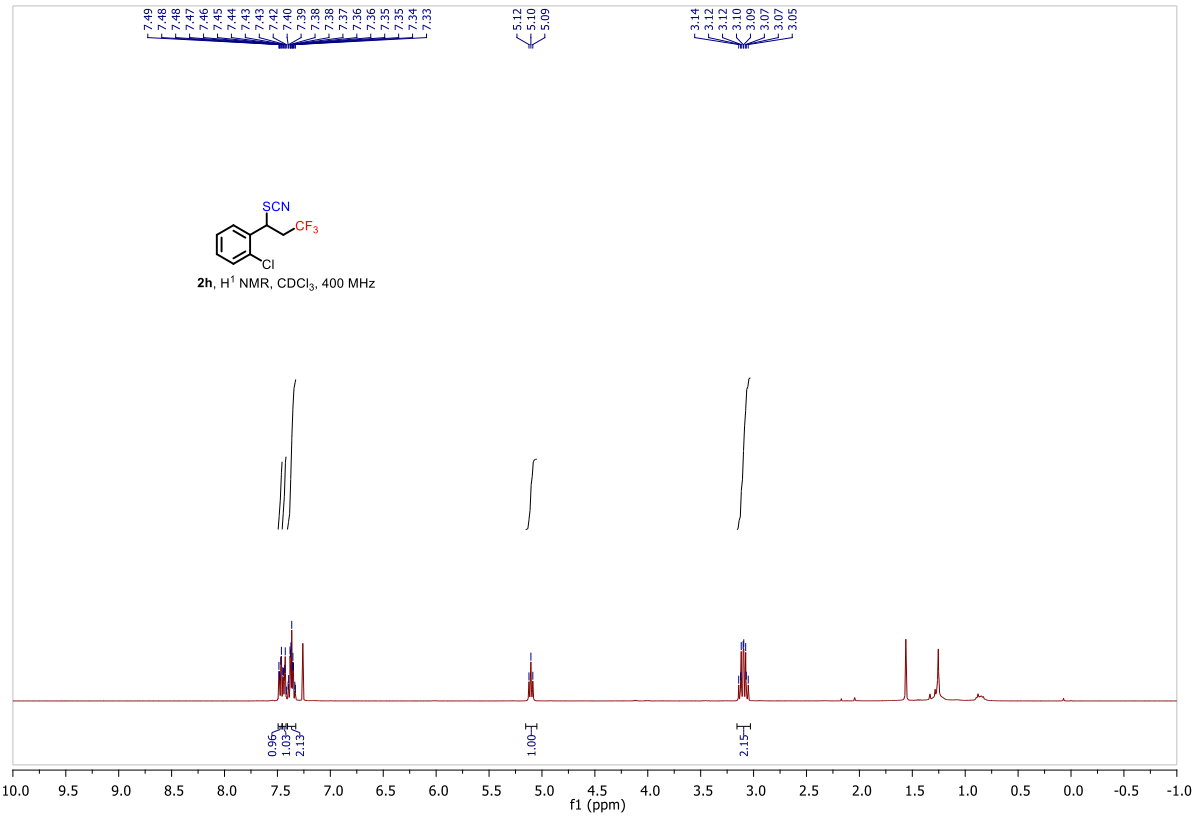

**2g**, $H^1$ NMR, $CDCl_3$, 400 MHz

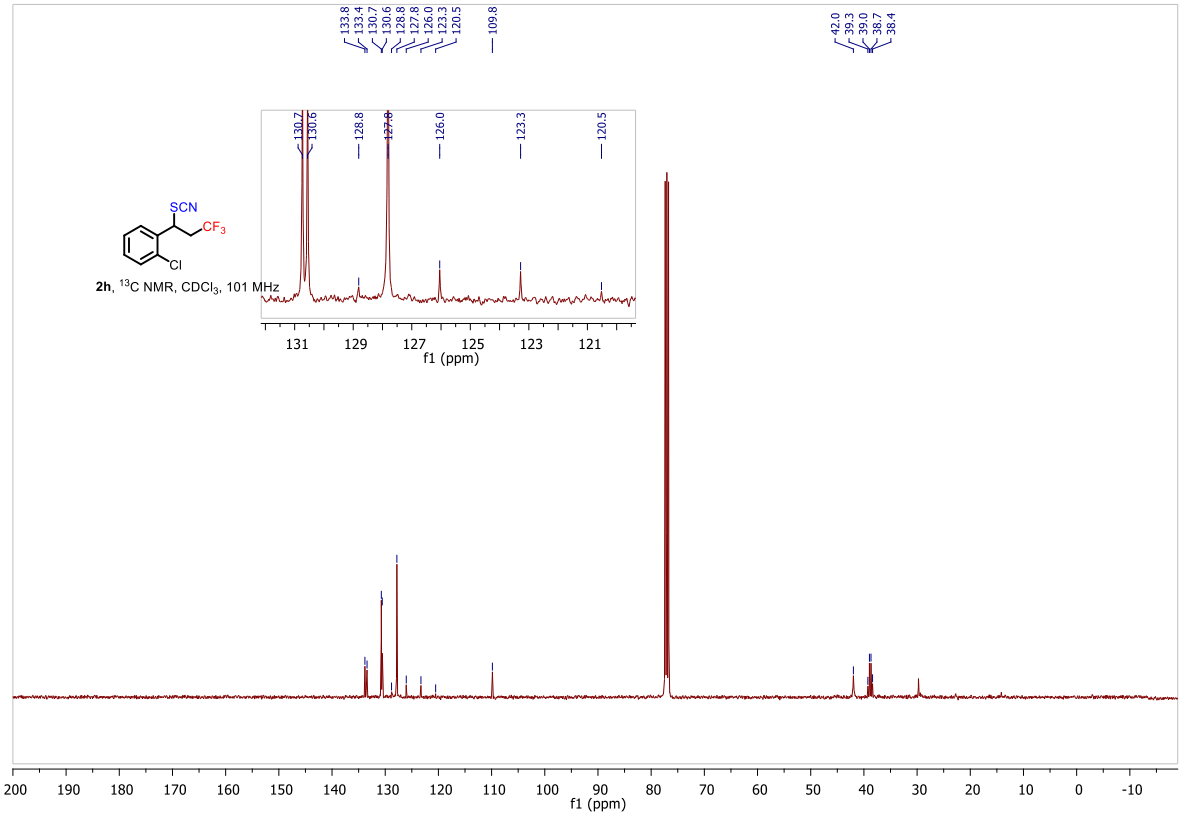


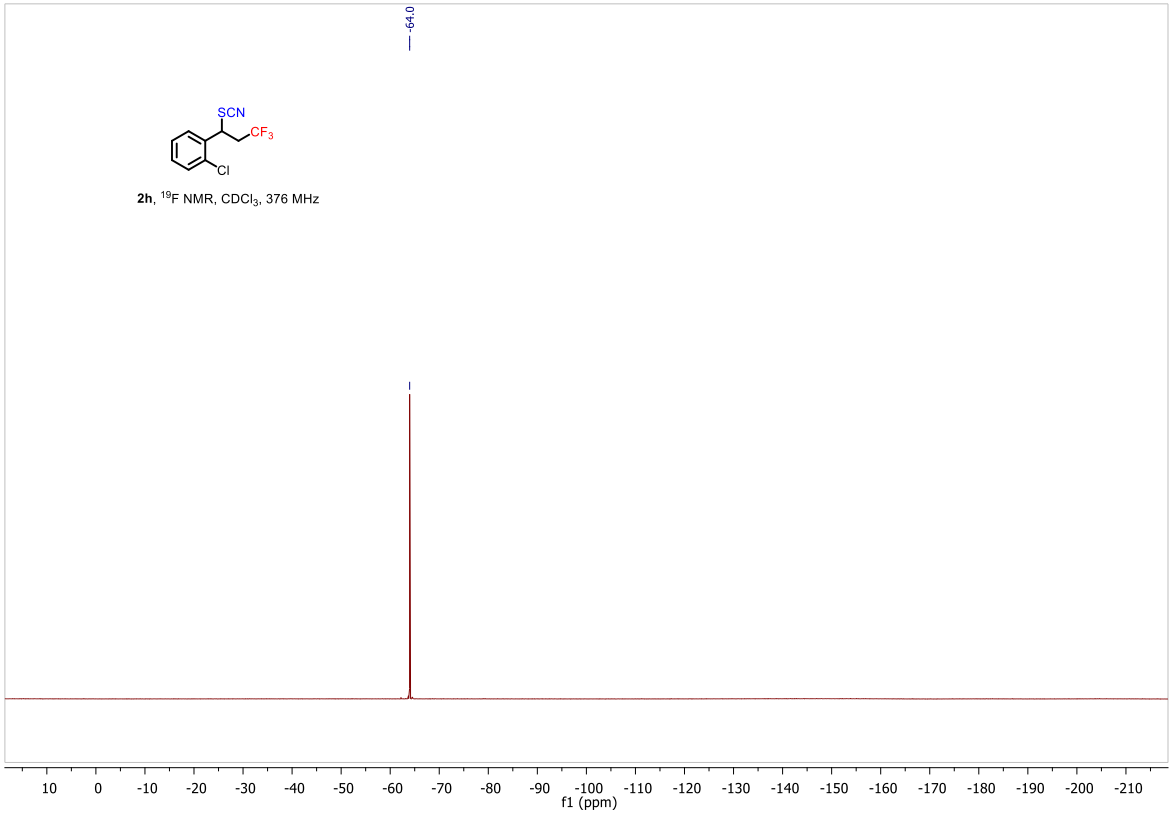

**2g**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



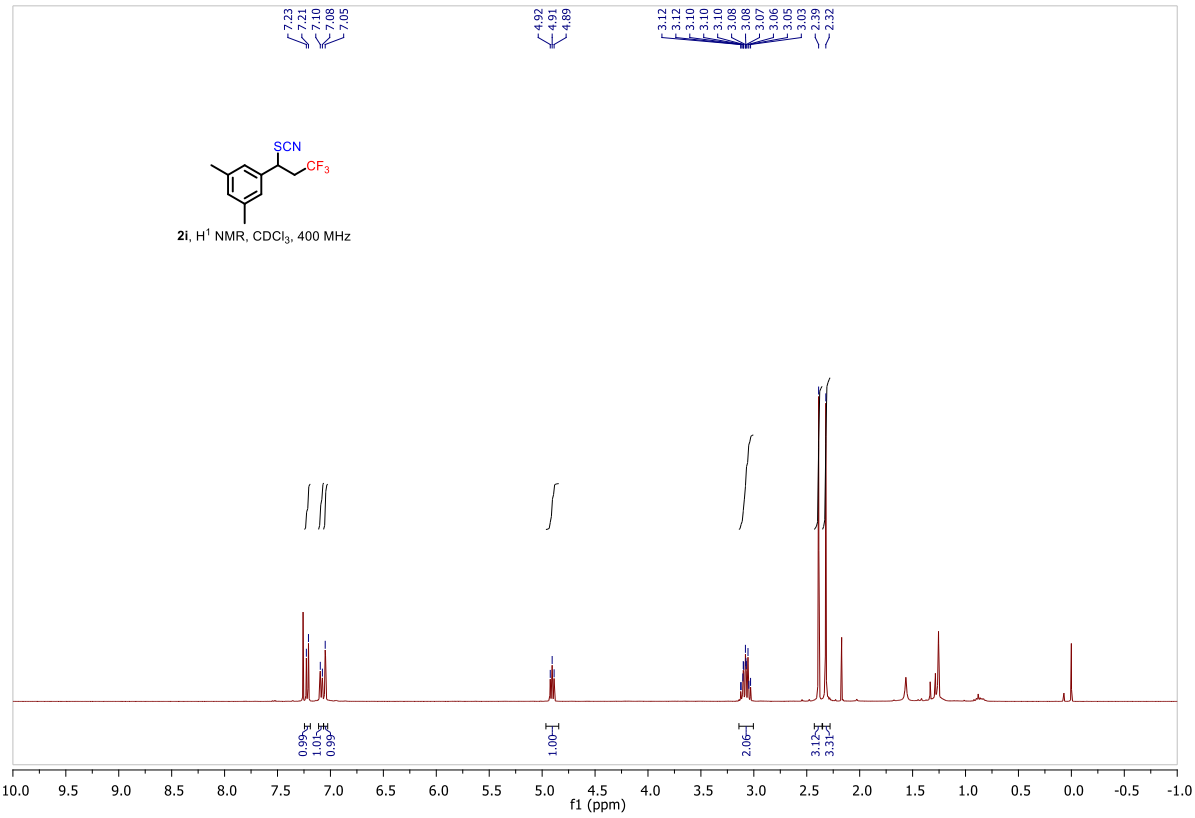

**2g**. $^{19}F$ NMR, $CDCl_3$, 376 MHz


7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.43
7.43
7.42
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
5.12
5.10
5.09
3.14
3.12
3.12
3.10
3.09
3.07
3.07
3.07
3.05
SCN
CF3
Cl
2h, H1 NMR, CDCl3, 400 MHz
0.96
1.03
2.13
1.00
2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

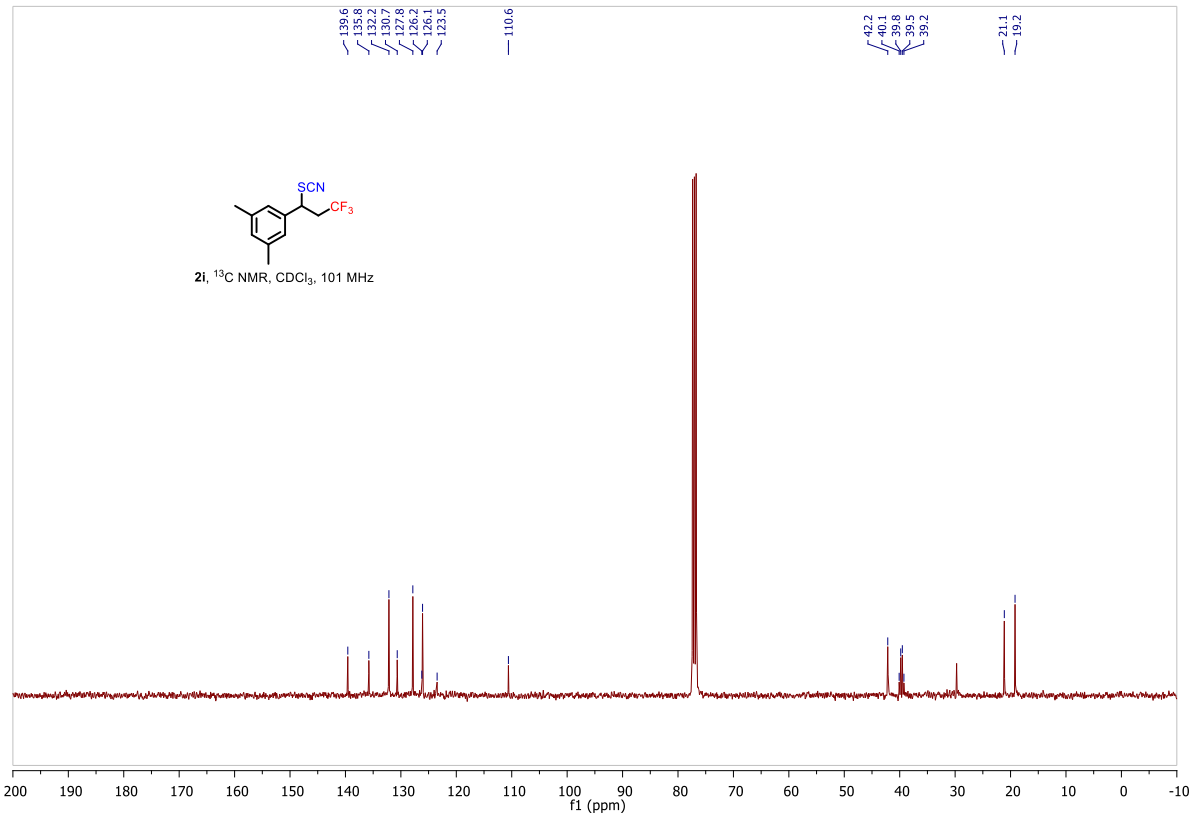

133.8
133.4
130.7
130.6
128.8
127.8
126.0
123.3
120.5
109.8
42.0
39.3
39.0
38.7
38.4
130.7
130.6
128.8
127.8
126.0
123.3
120.5
SCN
CF3
Cl
2h, 13C NMR, CDCl3, 101 MHz
131 129 127 125 123 121
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



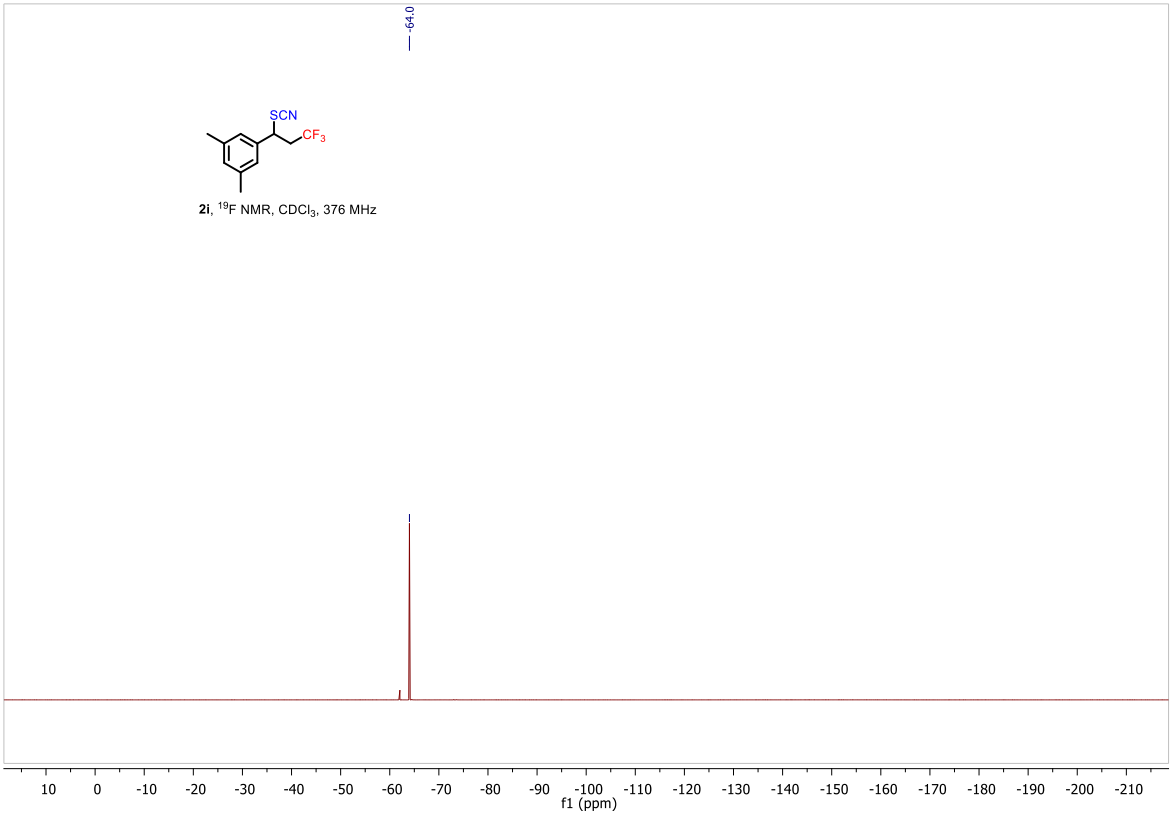

**2h**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



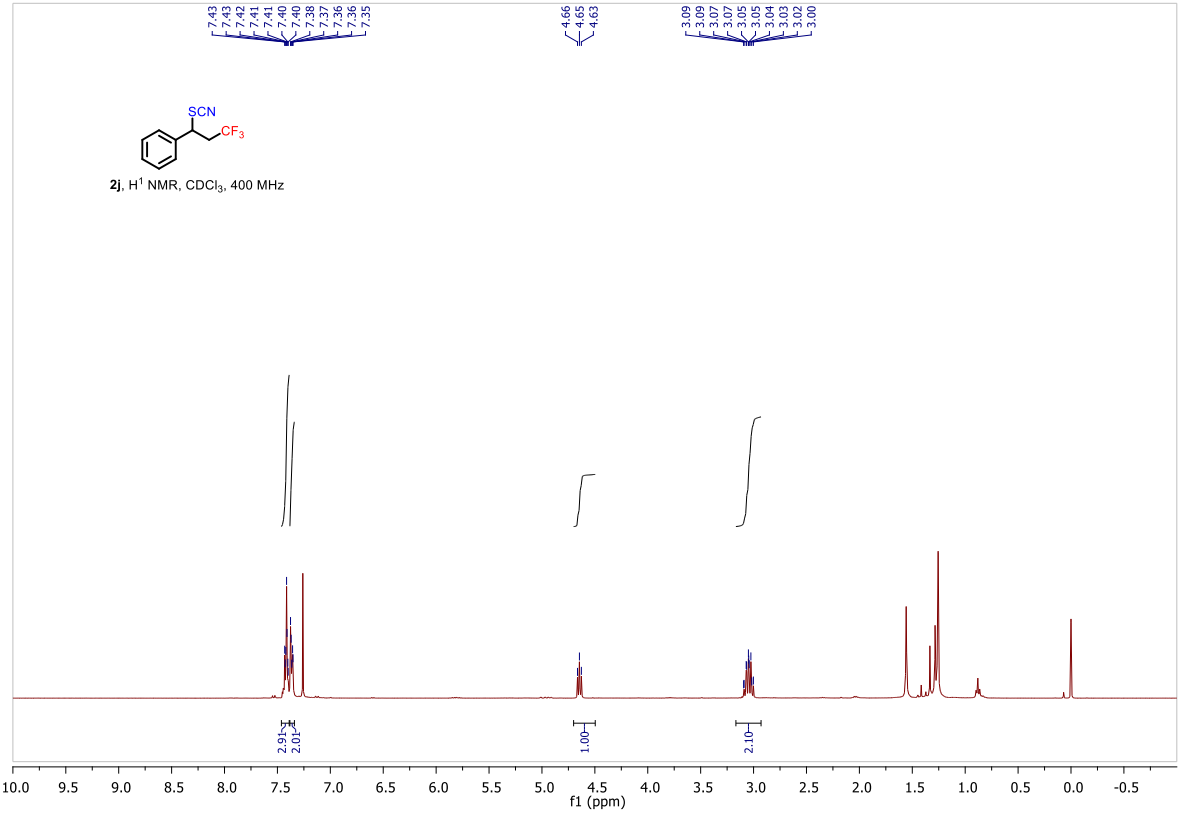

**2i**, $H^1$ NMR, $CDCl_3$, 400 MHz

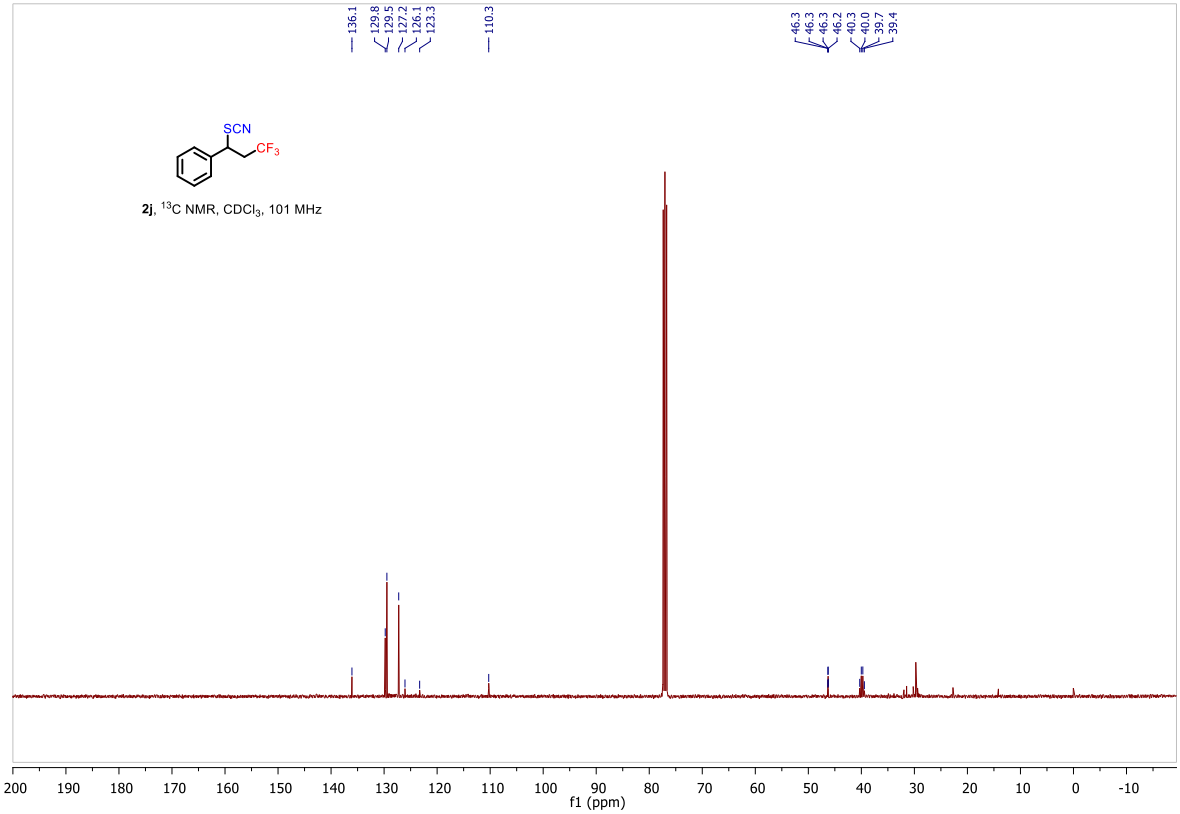


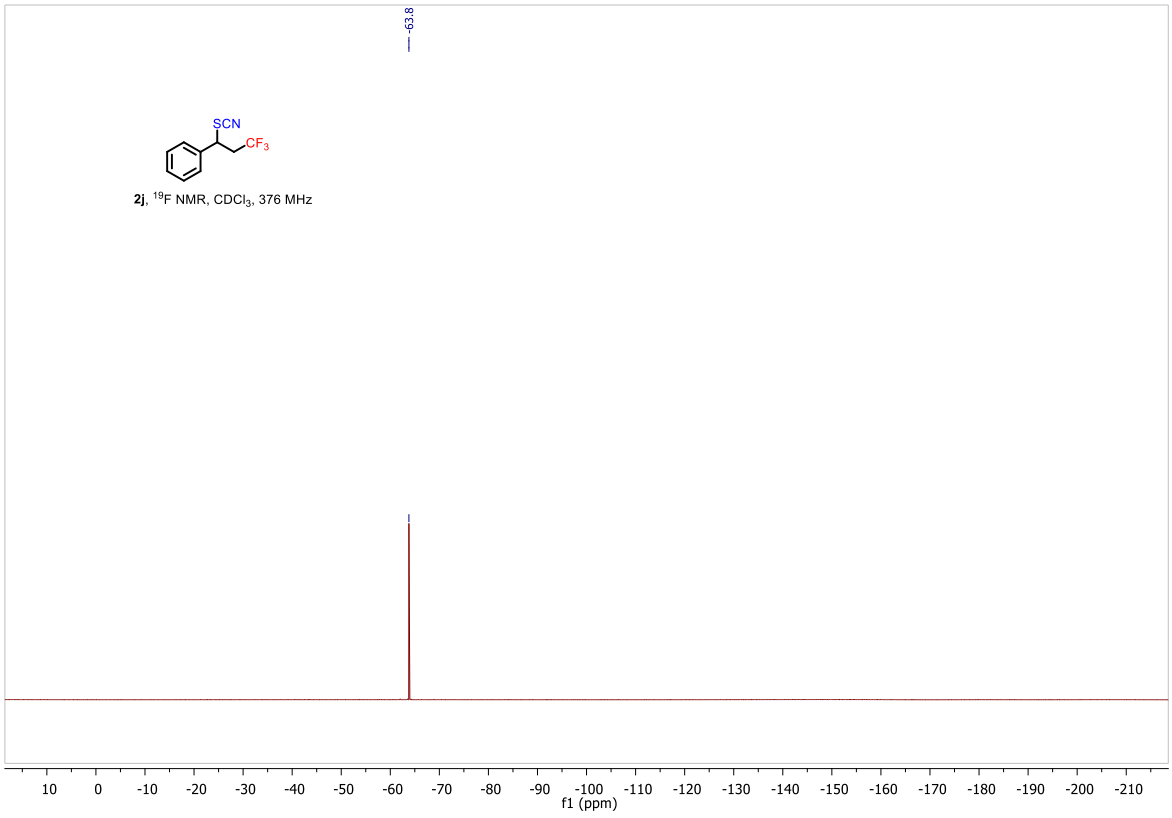

**2i**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



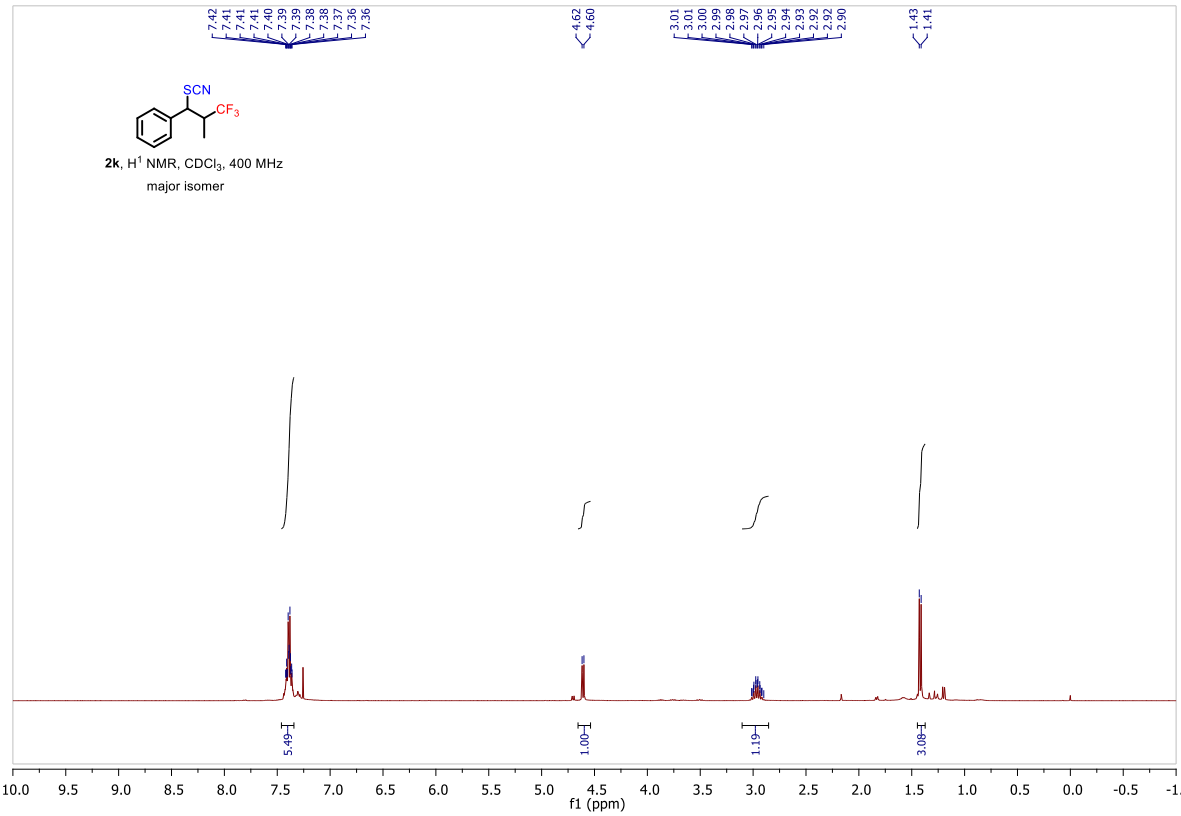

**2i**, $^{19}F$ NMR, $CDCl_3$, 376 MHz

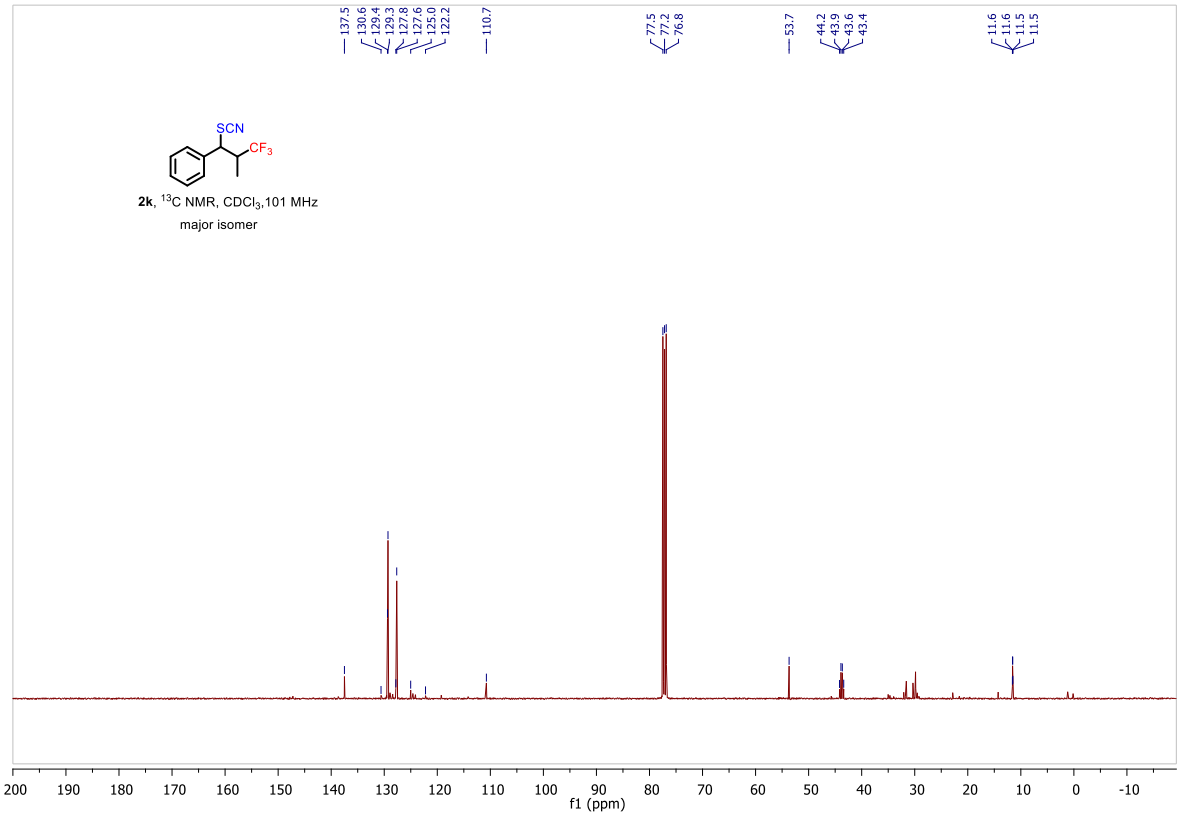

7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.38
7.37
7.36
7.36
7.35
4.66
4.65
4.63
3.09
3.09
3.07
3.07
3.05
3.05
3.04
3.03
3.02
3.00
SCN
CF3
2j, H1 NMR, CDCl3, 400 MHz
2.91
2.01
1.00
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

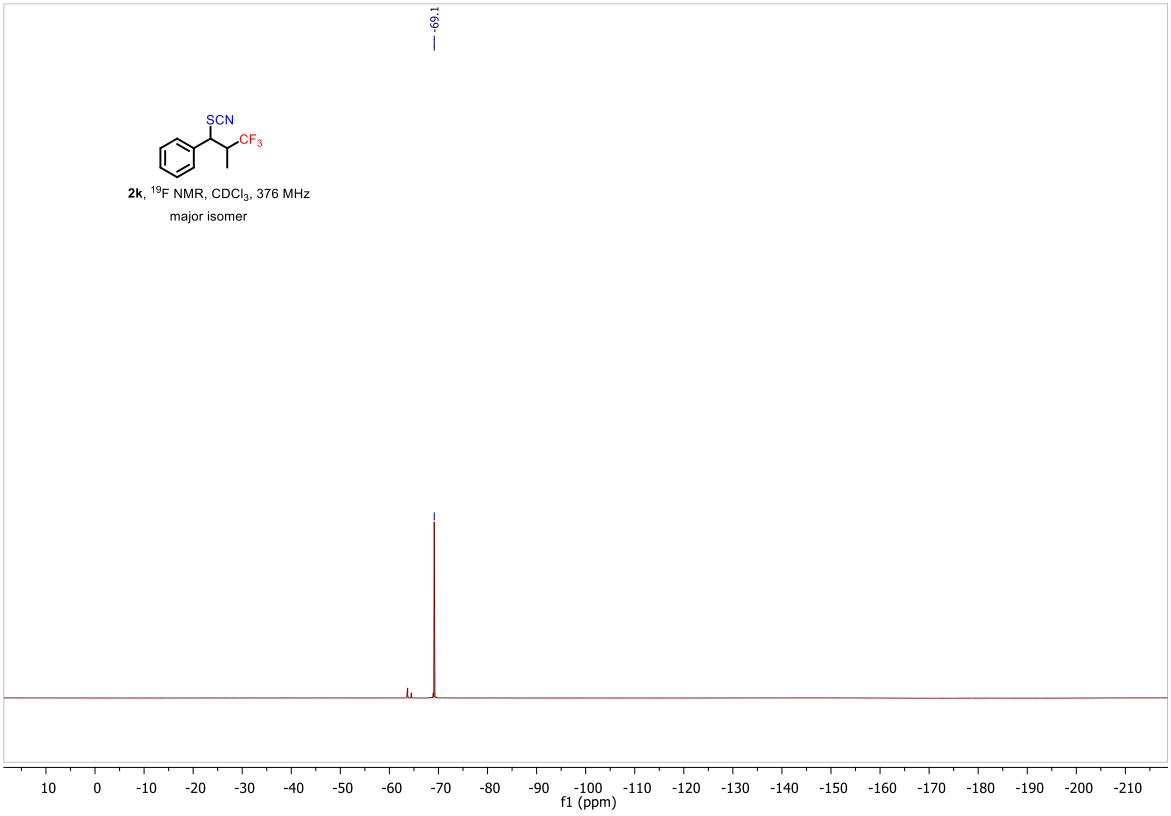

136.1
129.8
129.5
127.2
126.1
123.3
110.3
46.3
46.3
46.3
46.2
40.3
40.0
39.7
39.4
SCN
CF3
2j, 13C NMR, CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



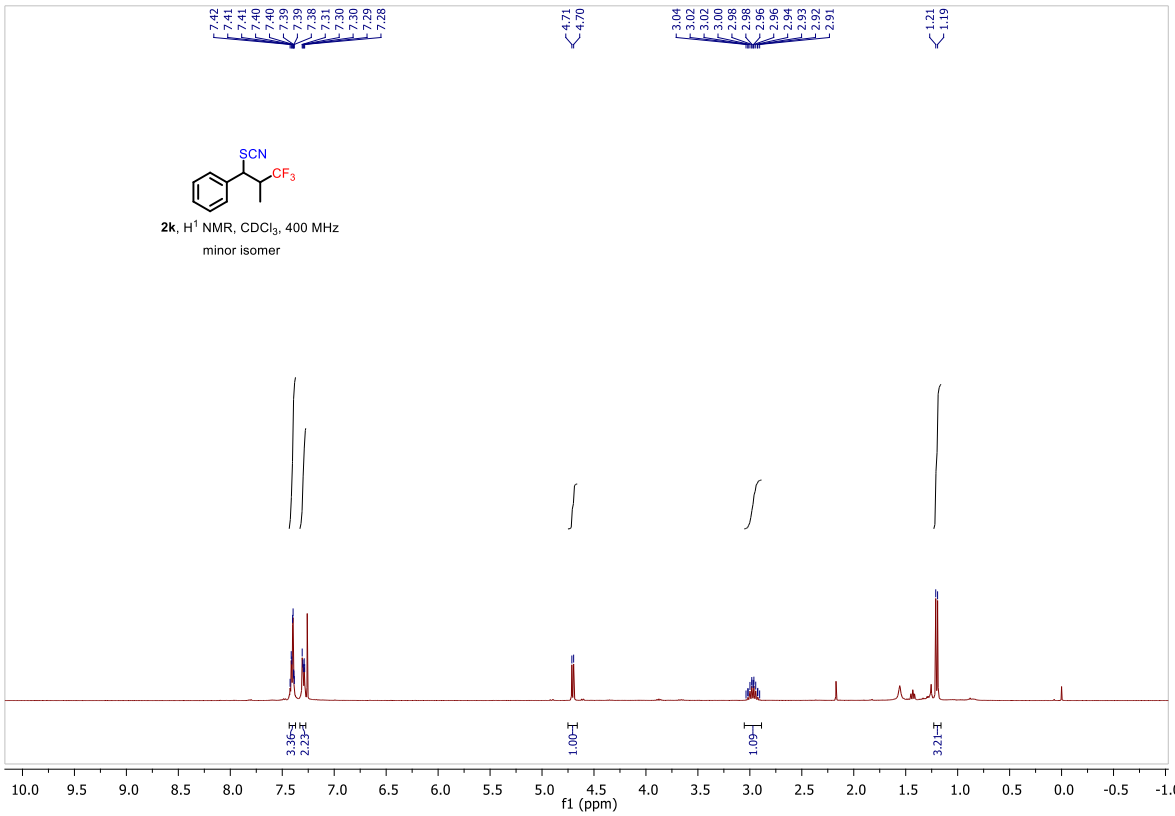

**2j**, $^{19}F$ NMR, $CDCl_3$, 376 MHz


7.42
7.41
7.41
7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.36
4.62
4.60
3.01
3.01
3.00
2.99
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.92
2.90
1.43
1.41
SCN
CF3
2k, H1 NMR, CDCl3, 400 MHz
major isomer
5.49
1.00
1.19
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

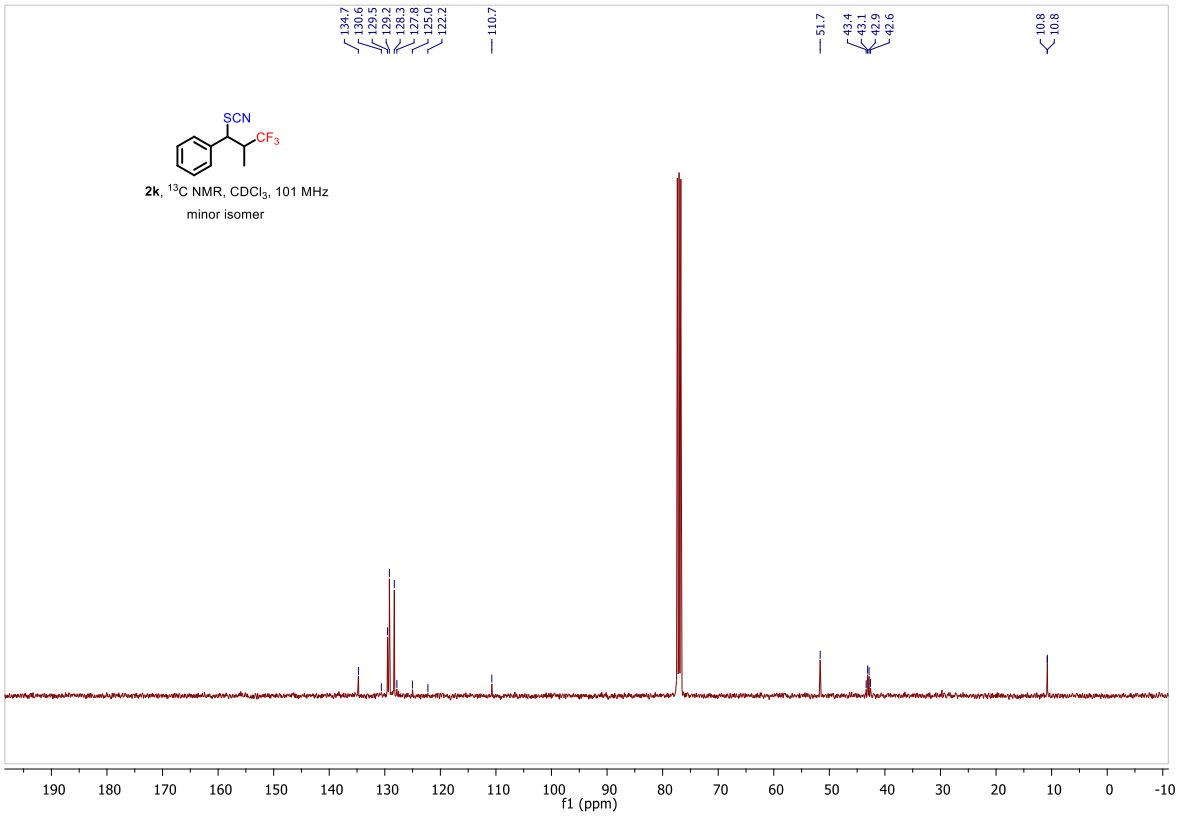

137.5
130.6
129.4
129.3
127.8
127.6
125.0
122.2
110.7
77.5
77.2
76.8
53.7
44.2
43.9
43.6
43.4
11.6
11.6
11.5
11.5
SCN
CF3
2k, 13C NMR, CDCl3,101 MHz
major isomer
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



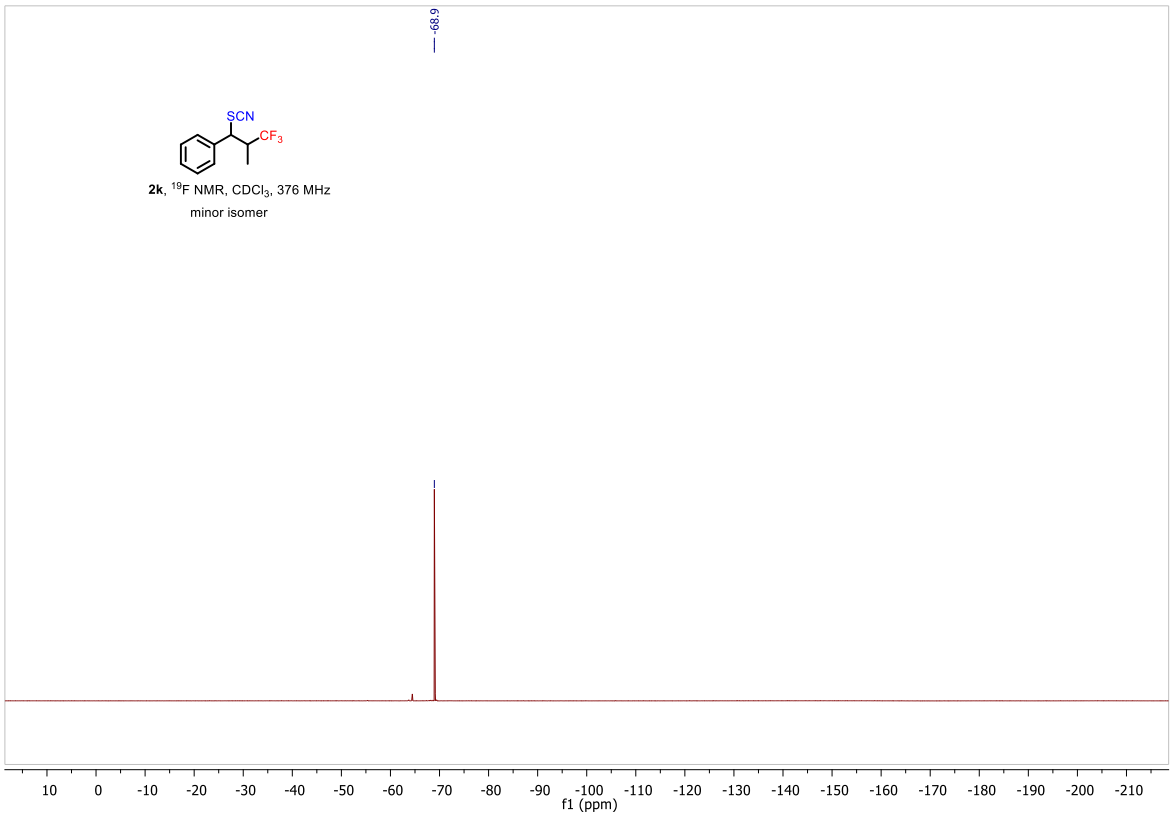

**2k**, $^{19}F$ NMR, $CDCl_3$, 376 MHz
major isomer



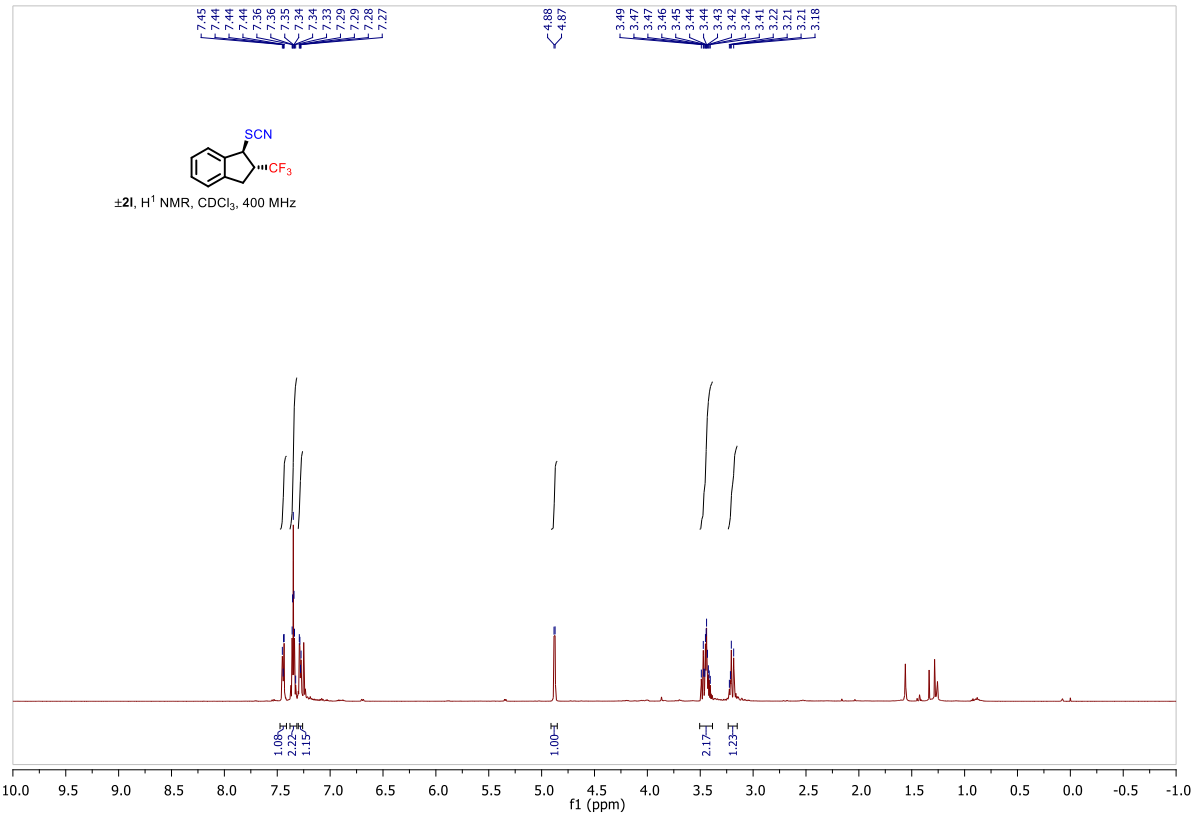

**2k**, $H^1$ NMR, $CDCl_3$, 400 MHz
minor isomer

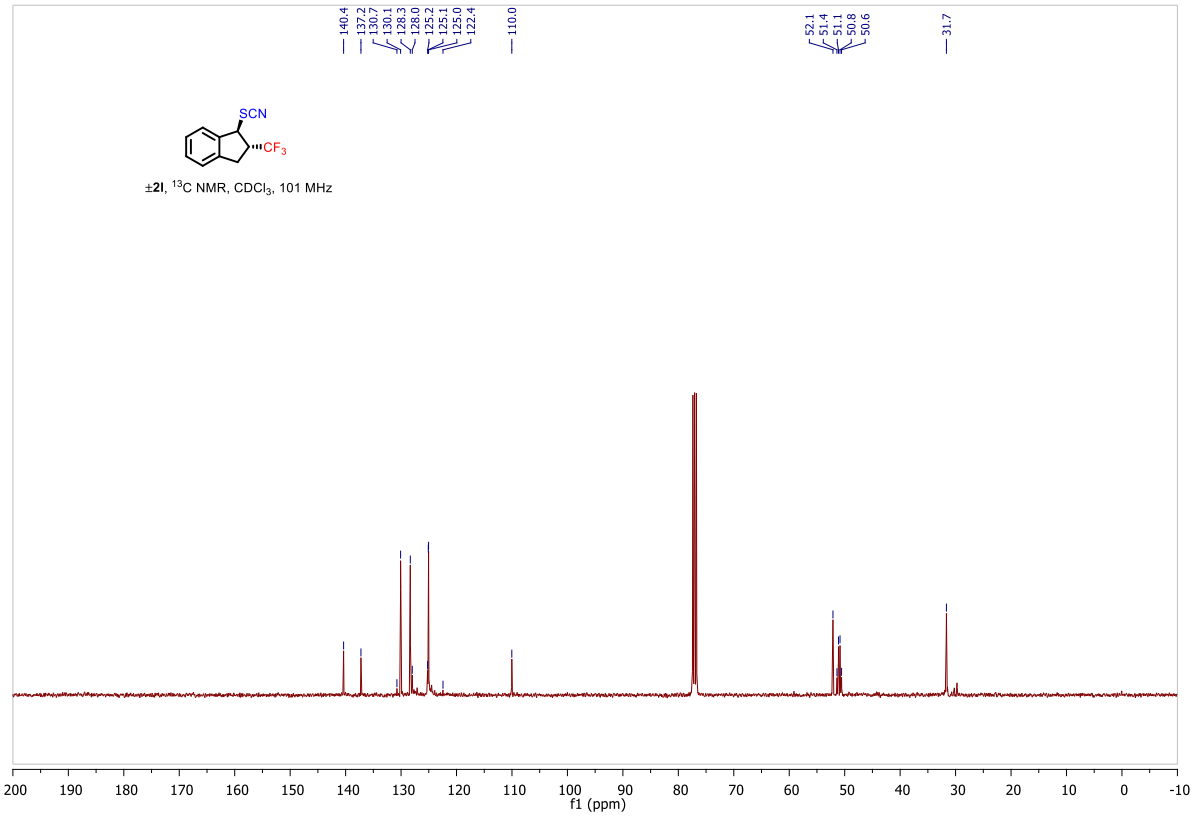


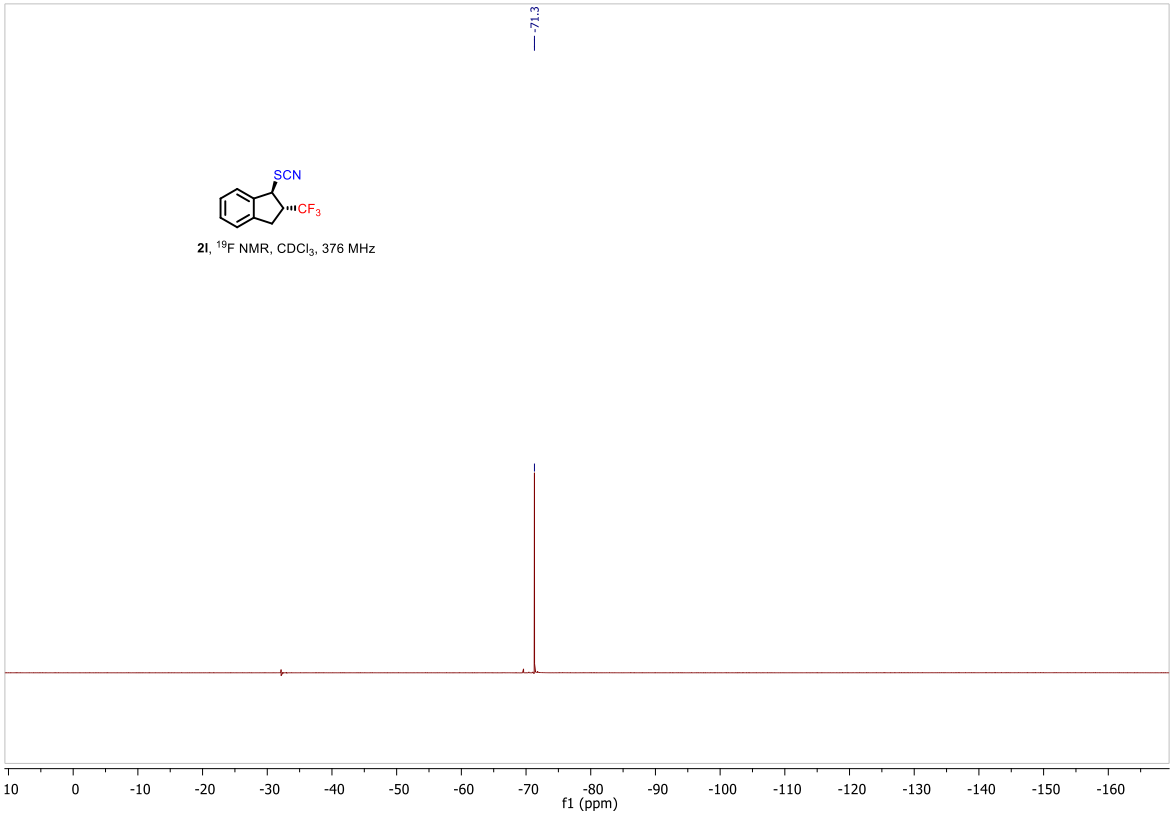

**2k**, $^{13}C$ NMR, $CDCl_3$, 101 MHz
minor isomer



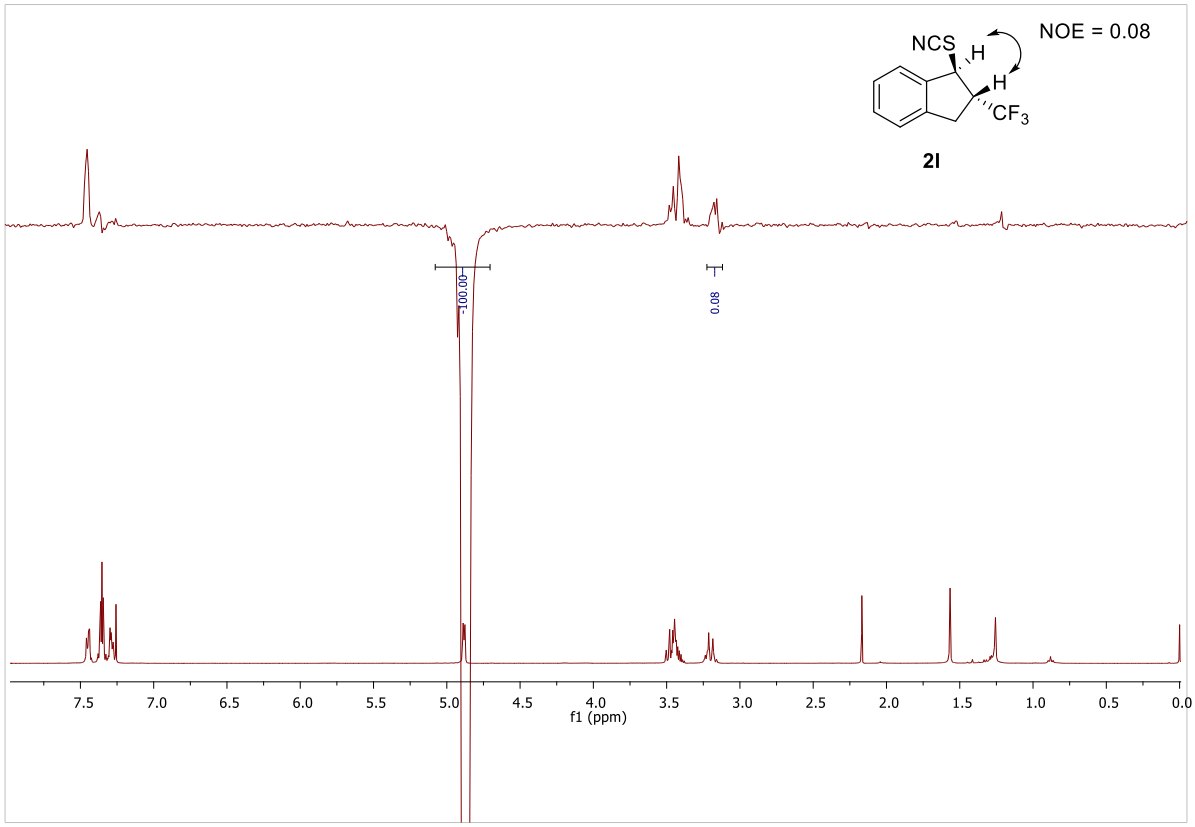

**2k**, $^{19}F$ NMR, $CDCl_3$, 376 MHz
minor isomer


7.45
7.44
7.44
7.44
7.36
7.35
7.35
7.34
7.34
7.33
7.29
7.29
7.28
7.27
4.88
4.87
3.49
3.47
3.47
3.46
3.45
3.44
3.44
3.43
3.42
3.42
3.41
3.22
3.21
3.21
3.18
SCN
CF3
±2l, H1 NMR, CDCl3, 400 MHz
1.08
2.22
1.15
1.00
2.17
1.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

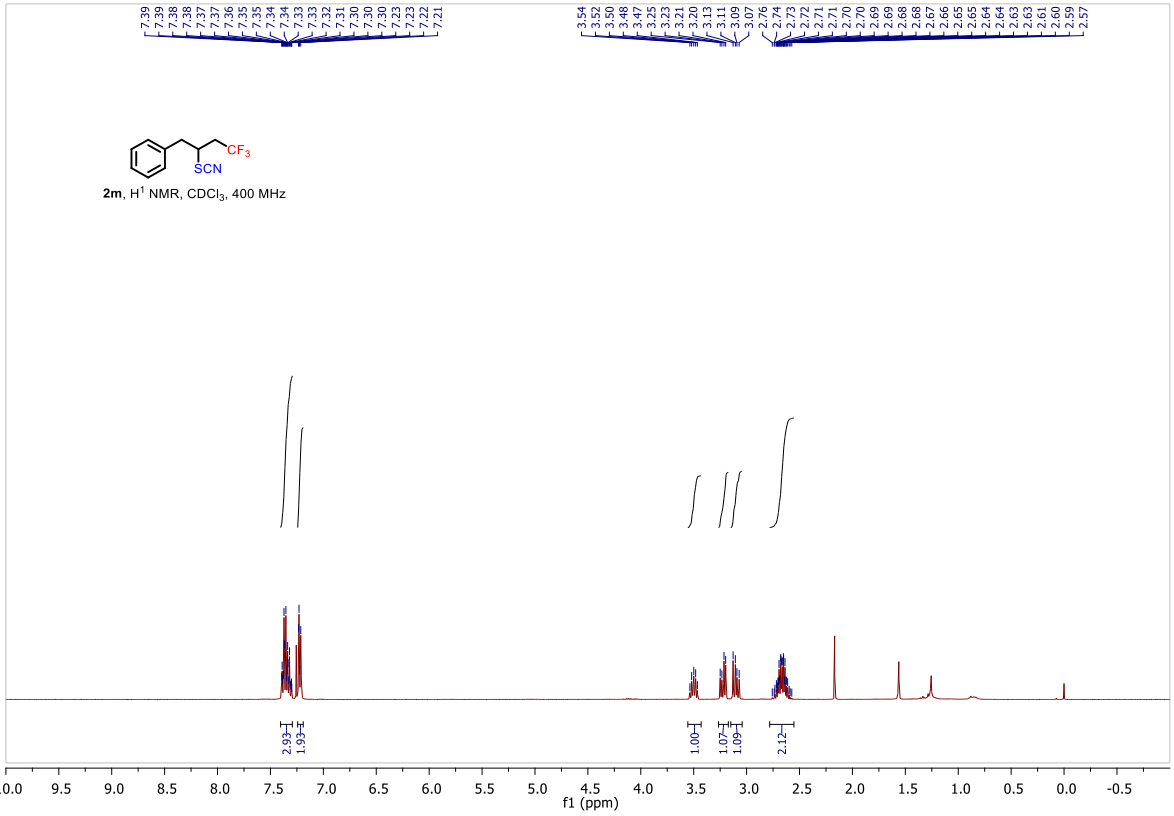

140.4
137.2
130.7
130.1
128.3
128.0
125.2
125.1
125.0
122.4
110.0
52.1
51.4
51.1
50.8
50.6
31.7
SCN
CF3
±2l, 13C NMR, CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

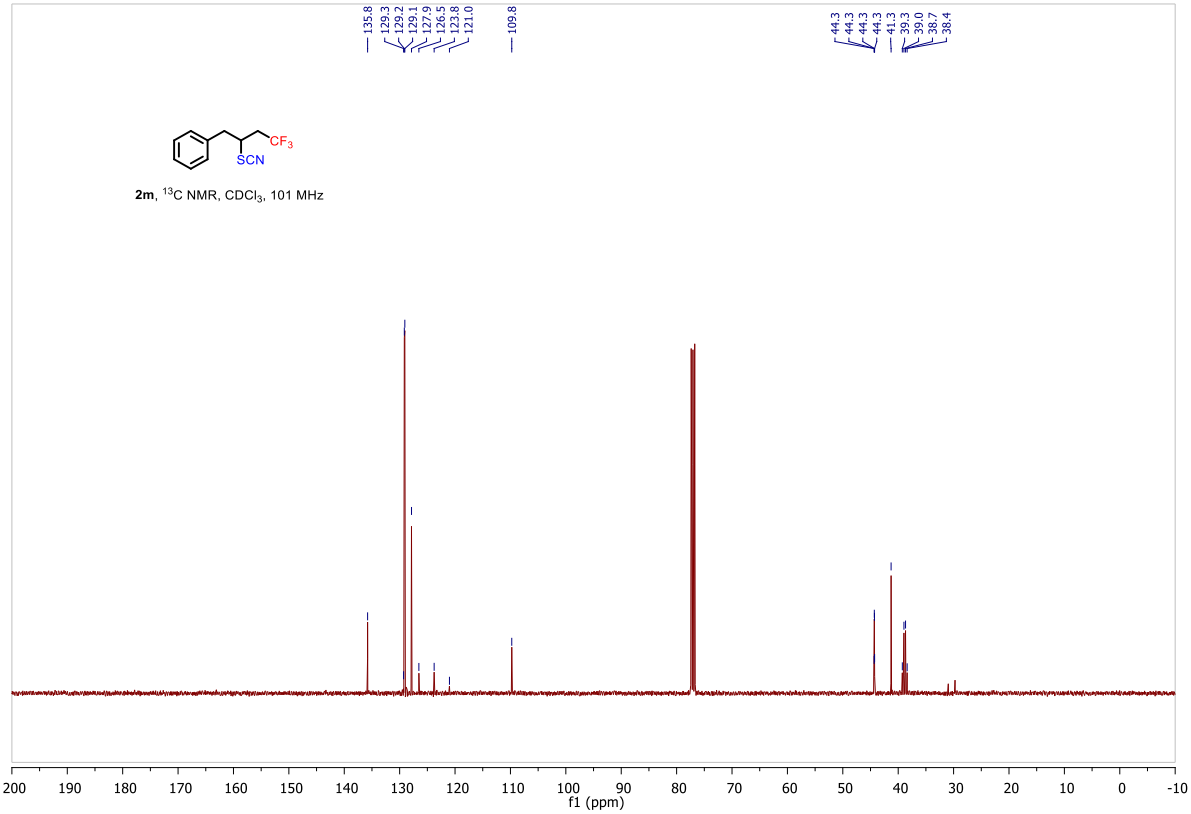


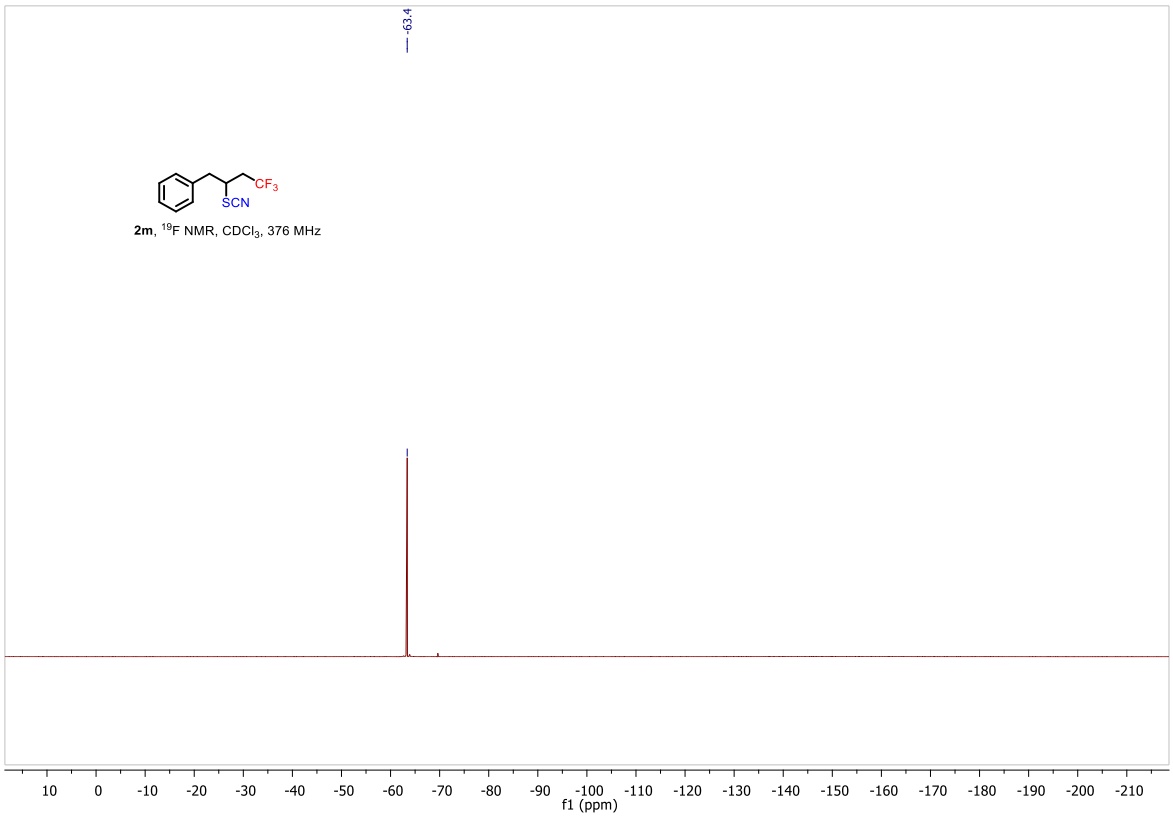

**2l**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



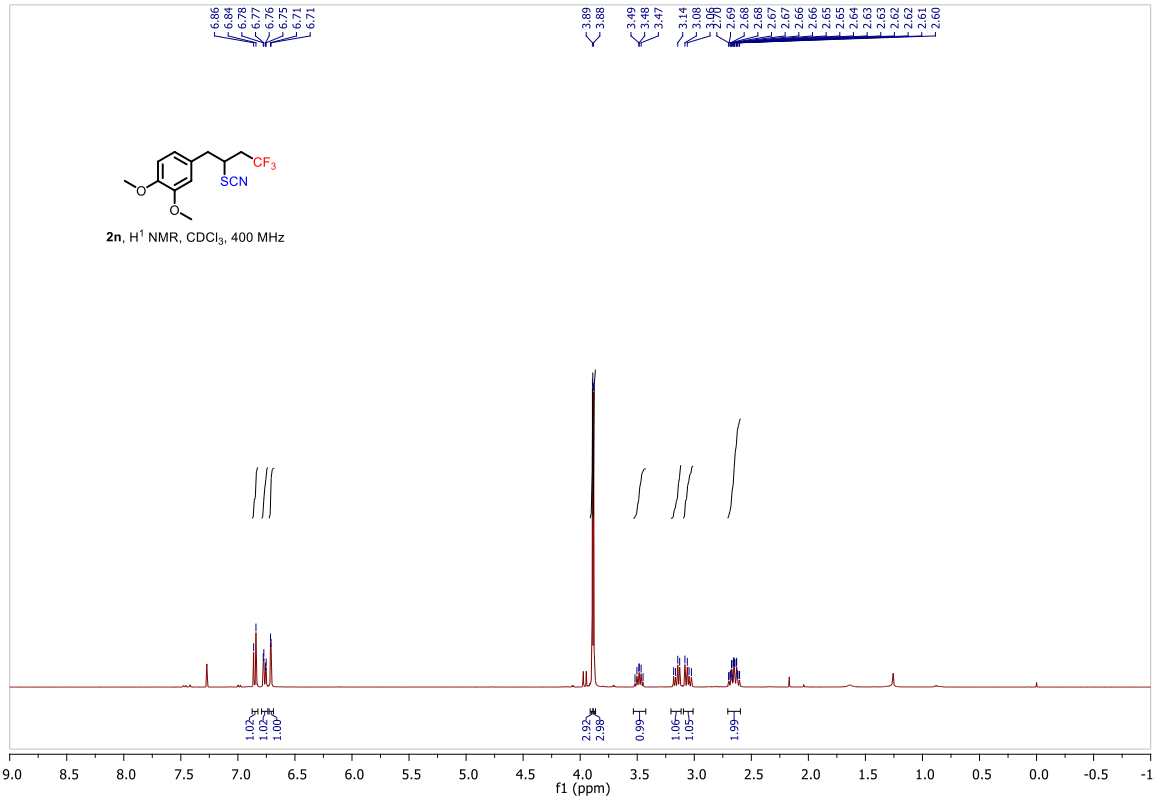

**2l**


7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.23 7.23 7.22 7.21
3.54 3.52 3.50 3.48 3.47 3.25 3.23 3.21 3.20 3.13 3.11 3.09 3.07 2.76 2.74 2.73 2.72 2.71 2.71 2.70 2.70 2.69 2.69 2.68 2.68 2.67 2.66 2.65 2.65 2.64 2.64 2.63 2.63 2.61 2.60 2.59 2.57
CF3
SCN
2m, H1 NMR, CDCl3, 400 MHz
2.93
1.93
1.00
1.07
1.09
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

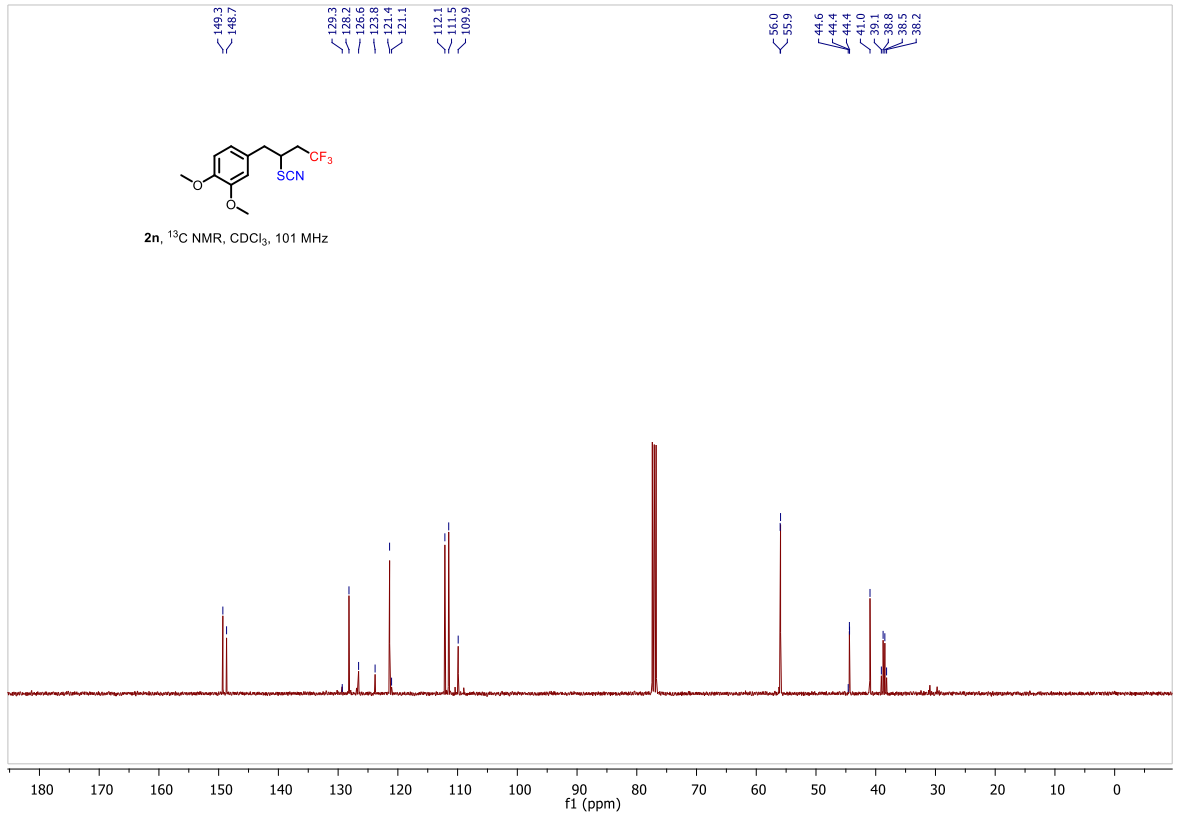

135.8 129.3 129.2 129.1 127.9 126.5 123.8 121.0 109.8
44.3 44.3 44.3 44.3 41.3 39.3 39.0 38.7 38.4
CF3
SCN
2m, 13C NMR, CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



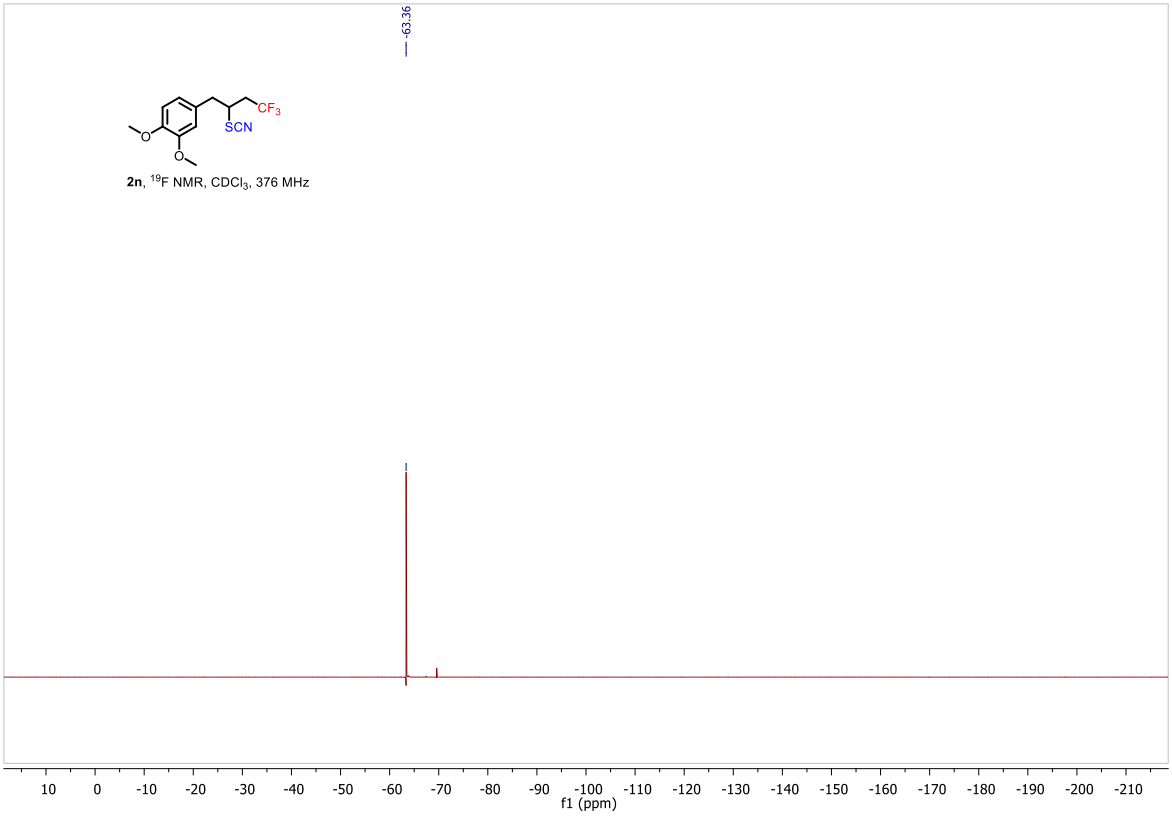

**2m**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



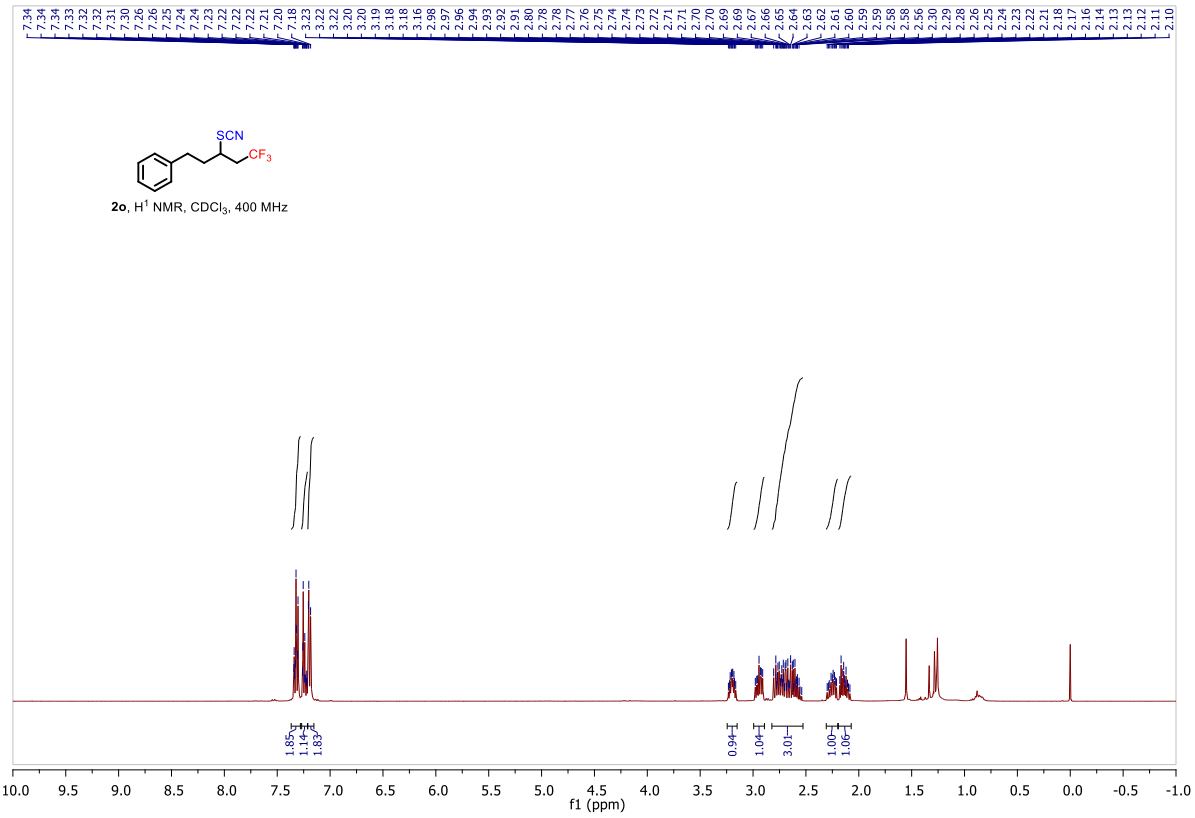

**2n**, $H^1$ NMR, $CDCl_3$, 400 MHz



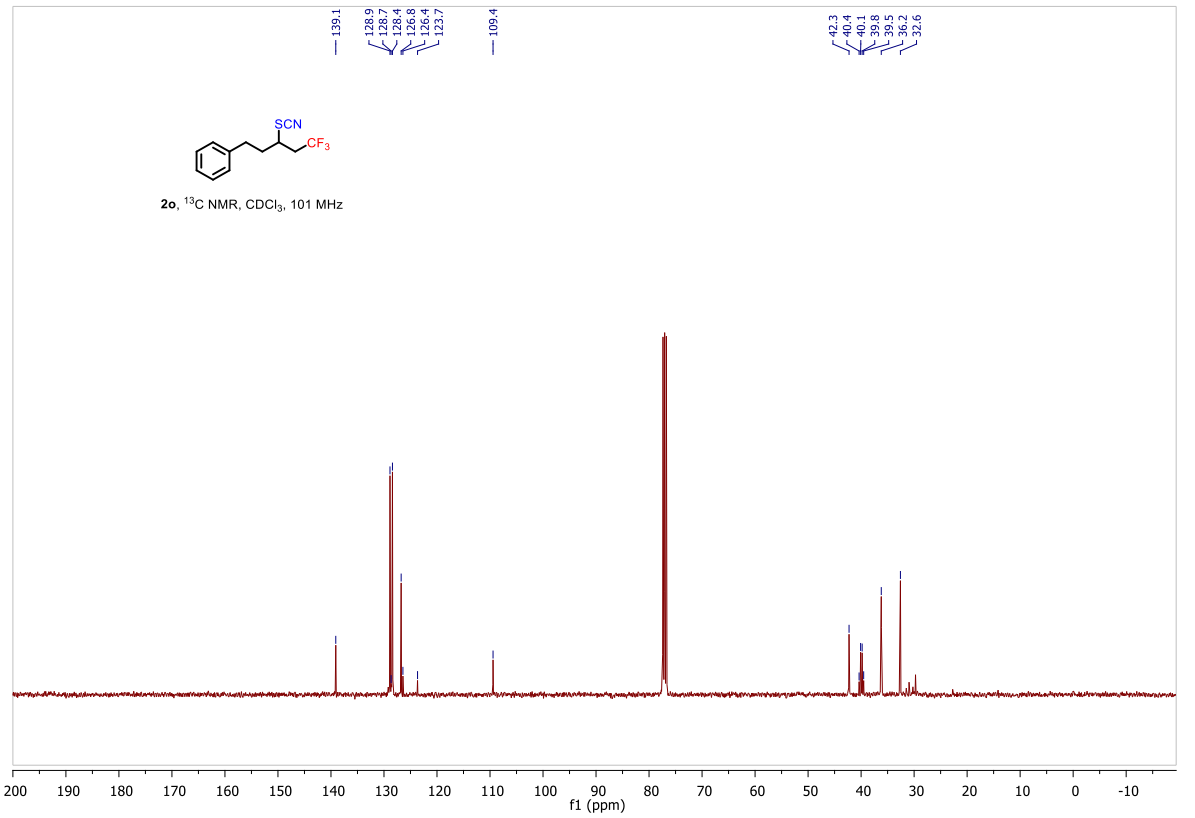

**2n**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



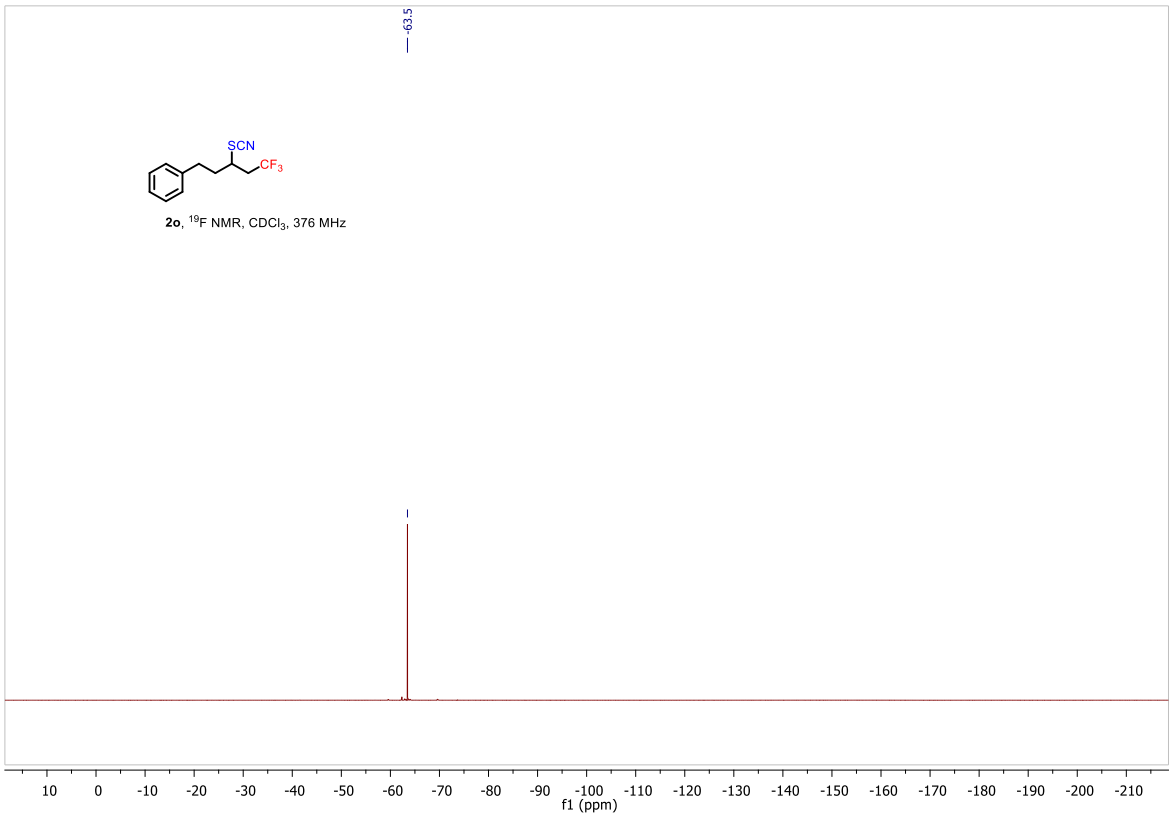

**2n**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



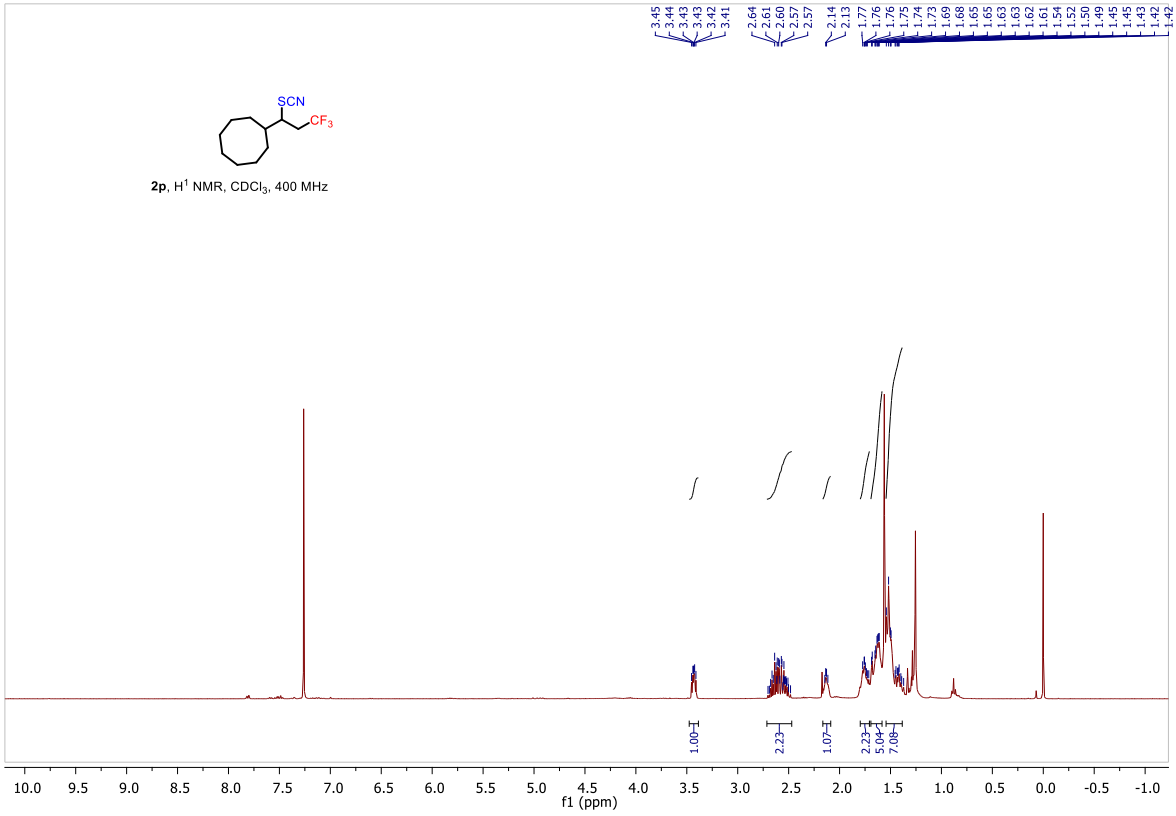

**2o**, $H^1$ NMR, $CDCl_3$, 400 MHz

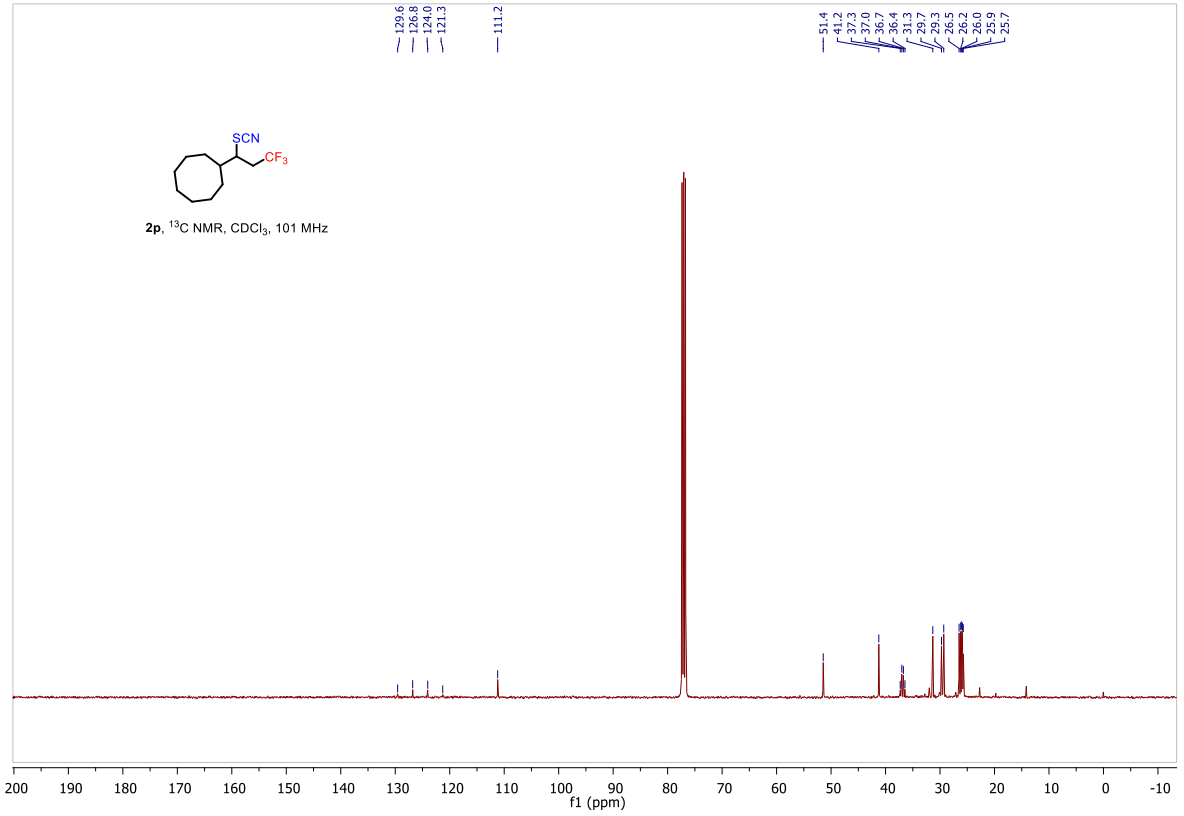


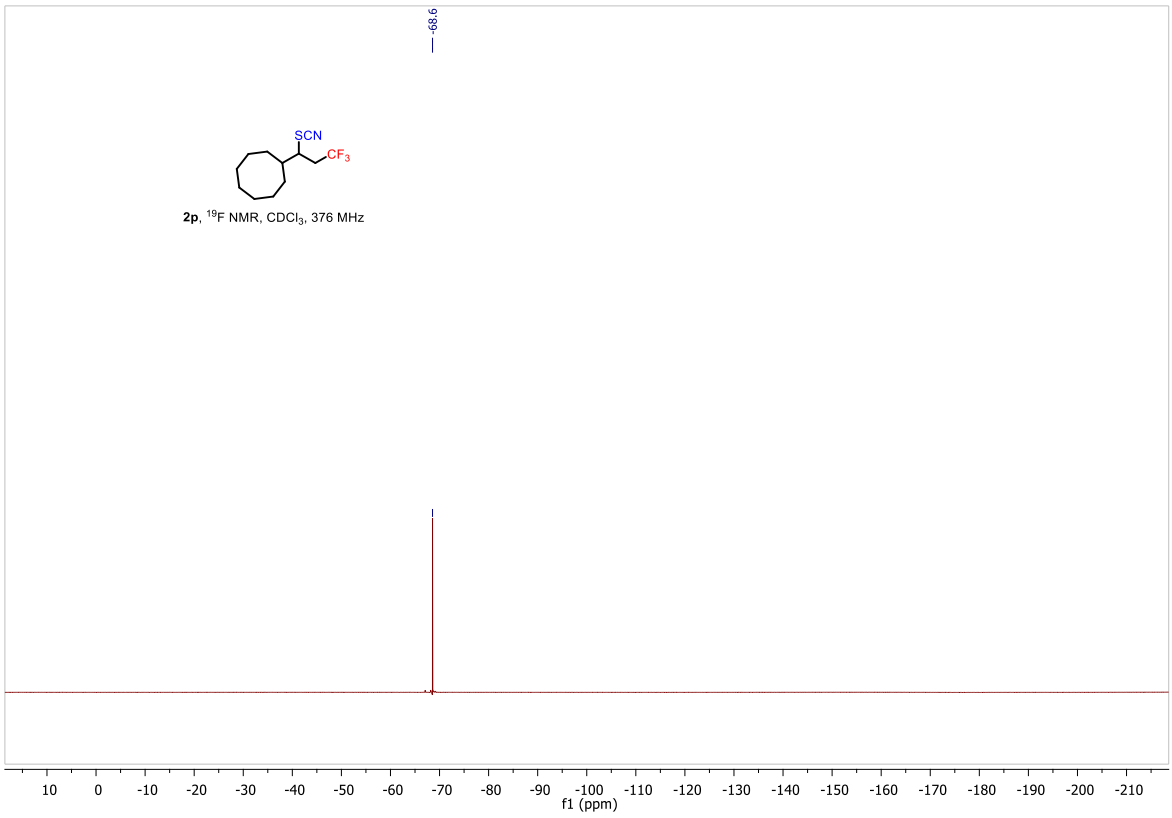

**2o**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



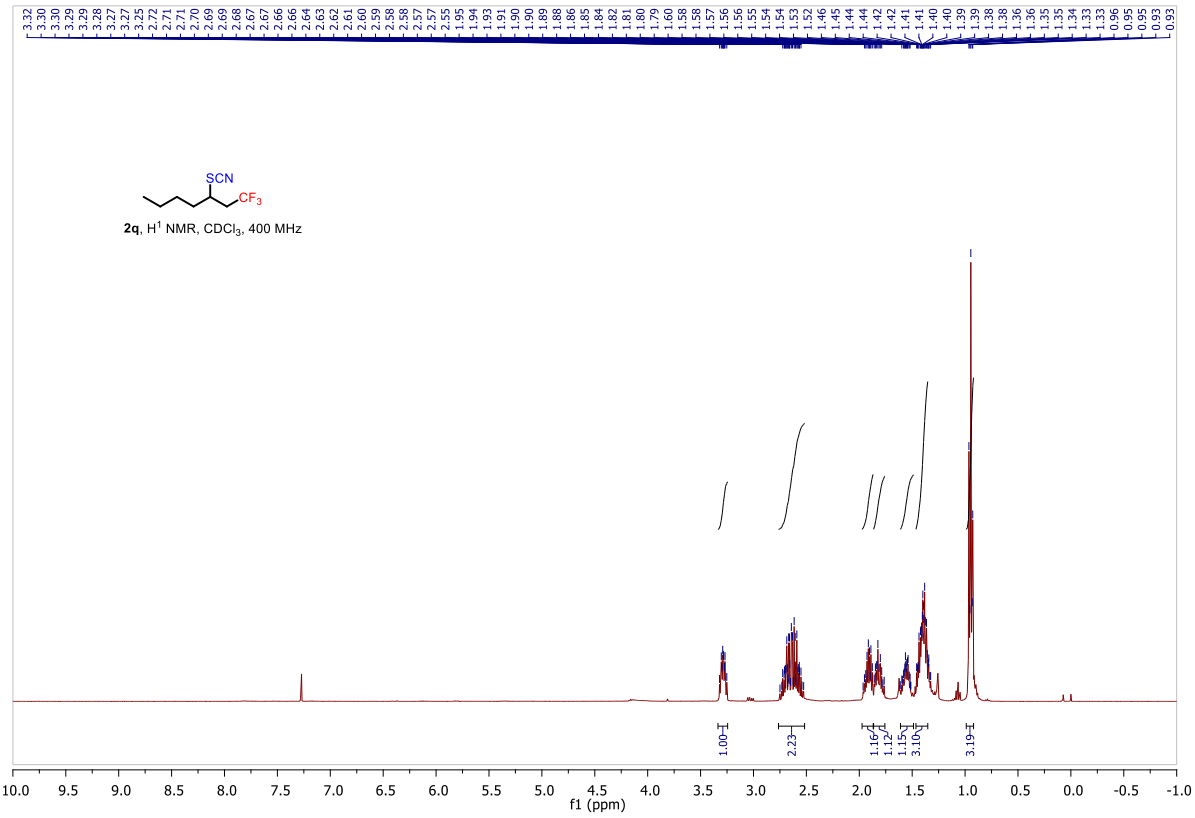

**2o**, $^{19}F$ NMR, $CDCl_3$, 376 MHz

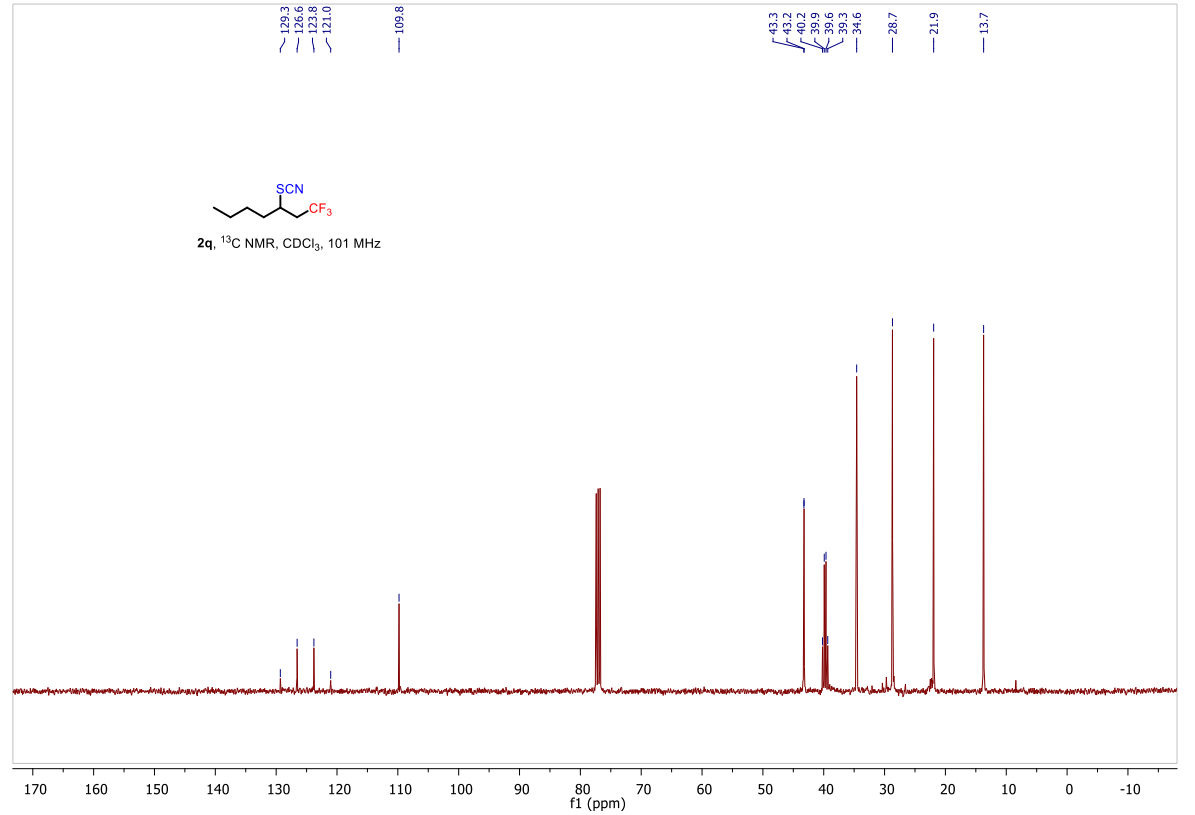

SCN
CF3
2p, H1 NMR, CDCl3, 400 MHz
f1 (ppm)

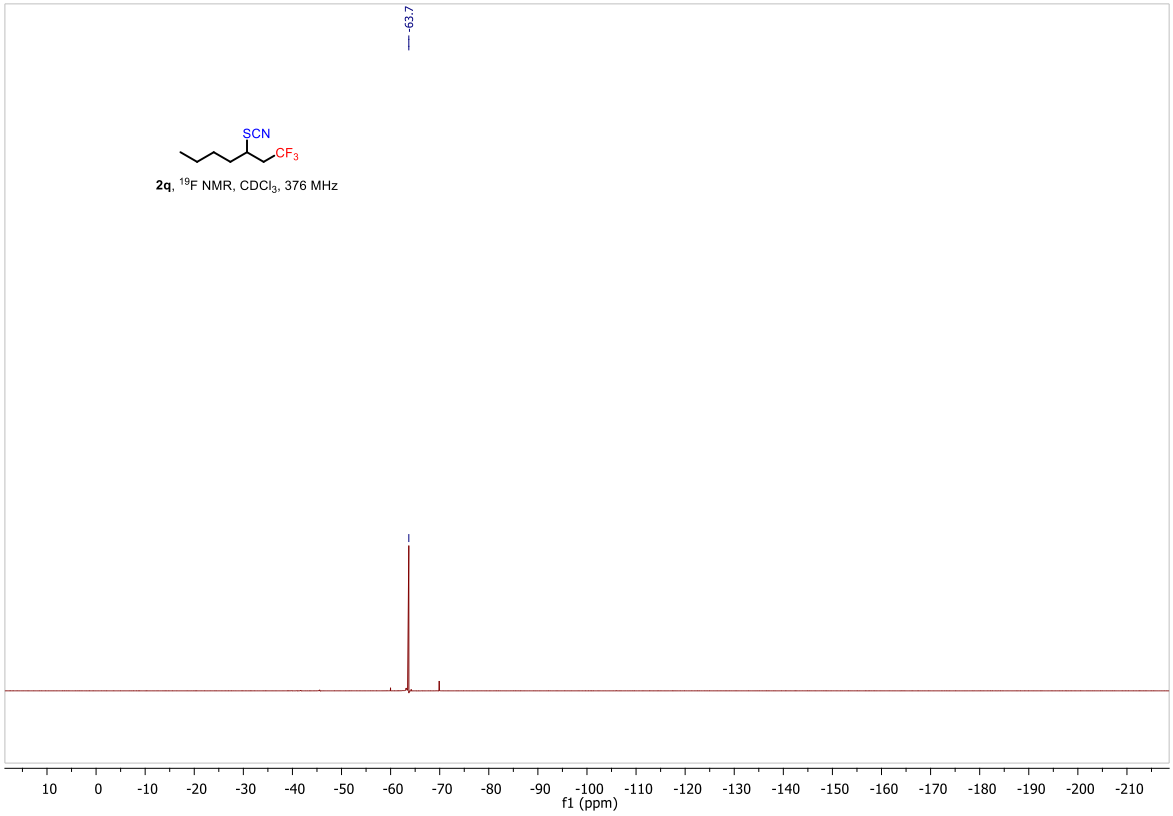

SCN
CF3
2p, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



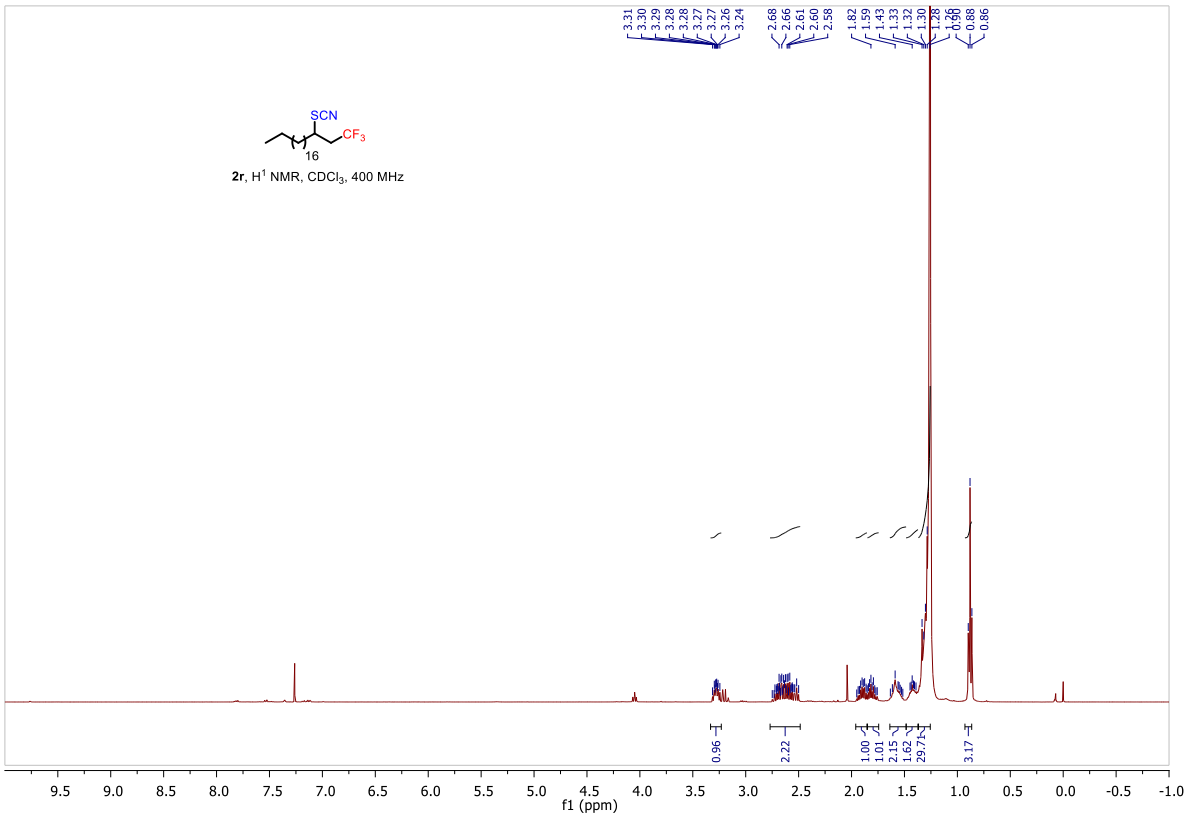

**2p**, $^{19}F$ NMR, $CDCl_3$, 376 MHz

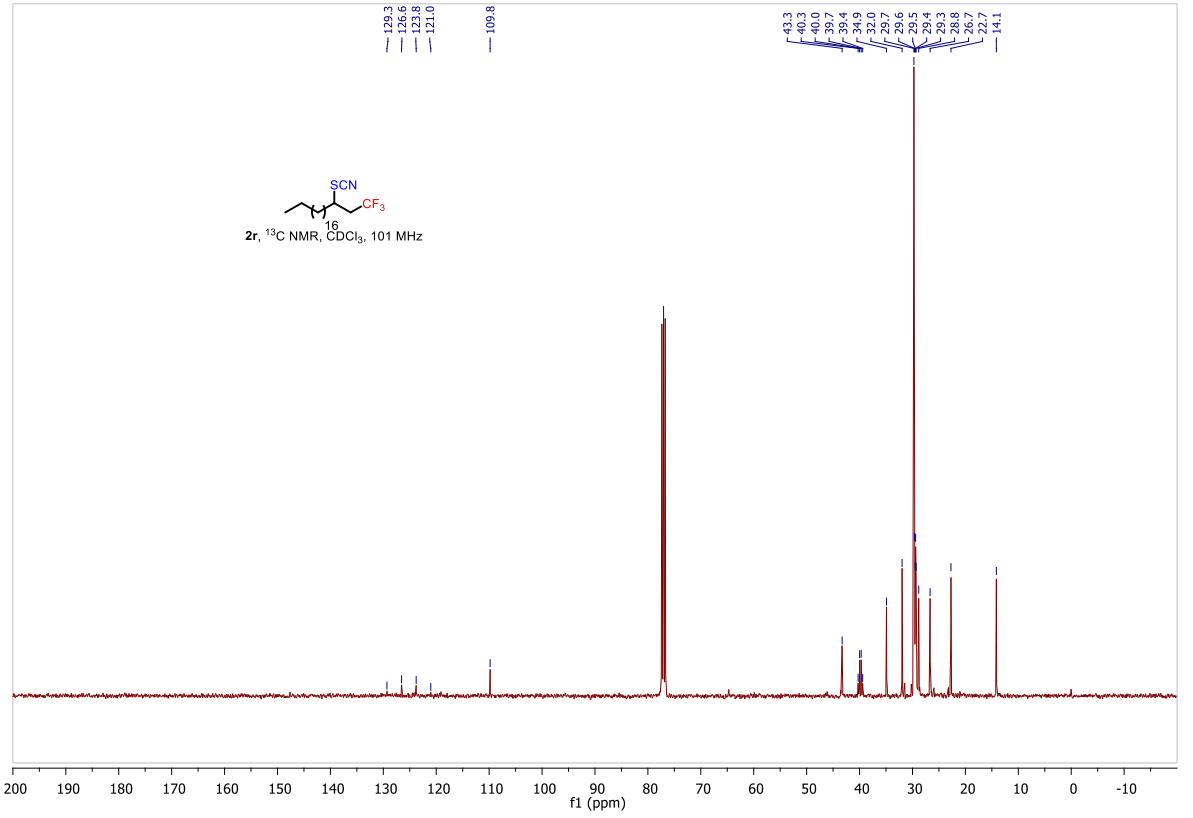

SCN
CF3
2q, H1 NMR, CDCl3, 400 MHz
1.00
2.23
1.16
1.12
1.15
3.10
3.19
f1 (ppm)

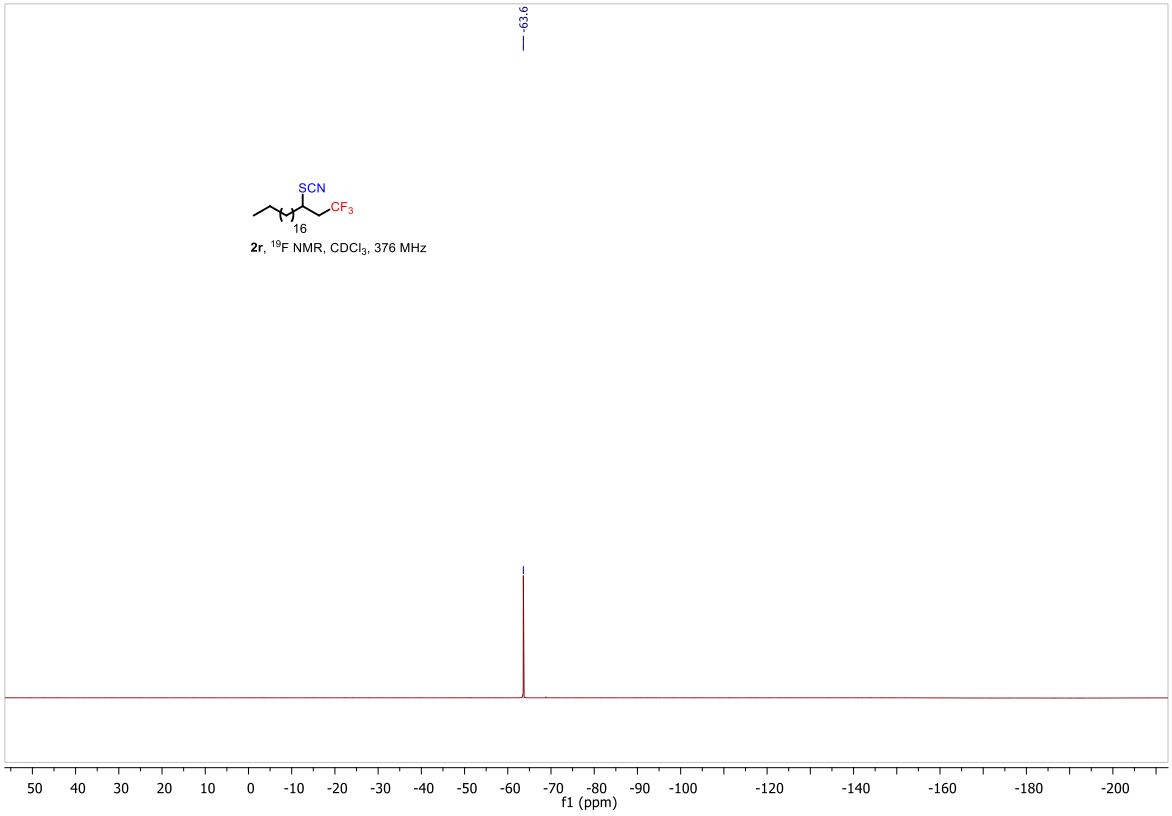

SCN
CF3
2q, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



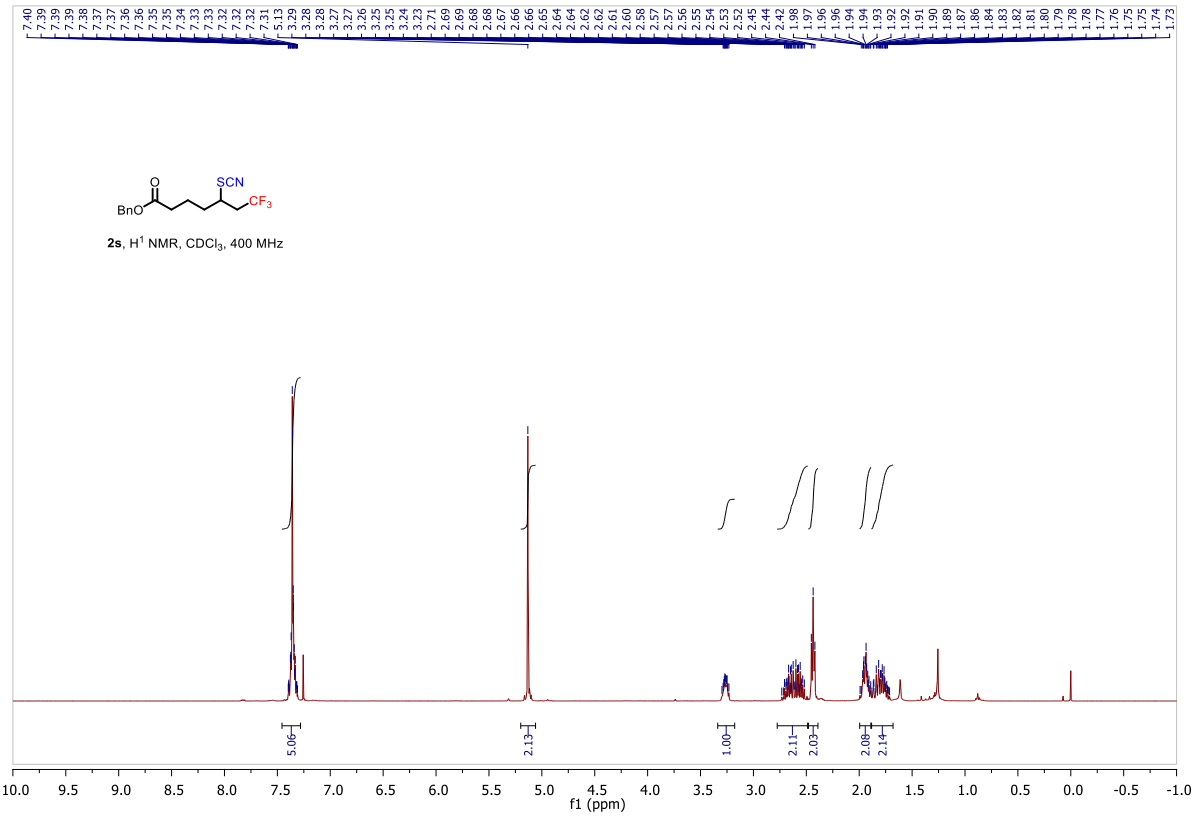

**2q**, $^{19}F$ NMR, $CDCl_3$, 376 MHz

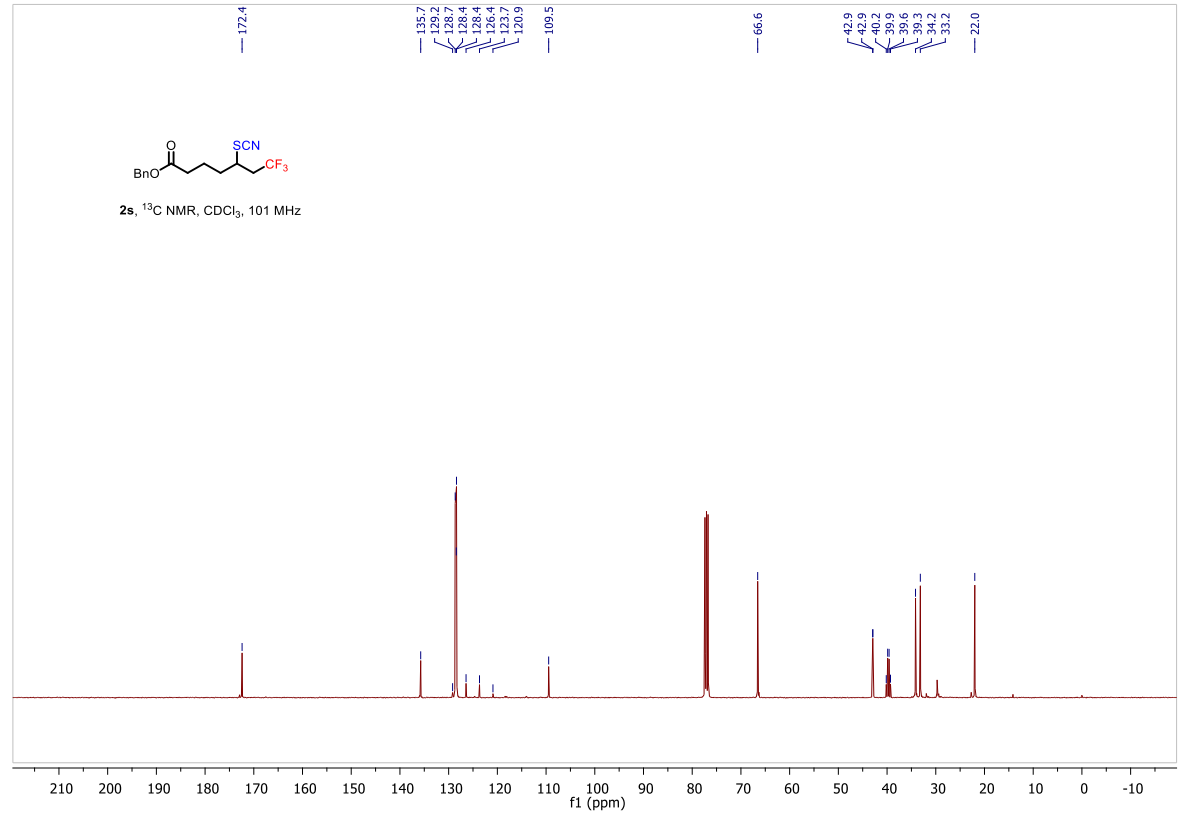

SCN
CF3
16
2r, H1 NMR, CDCl3, 400 MHz
f1 (ppm)

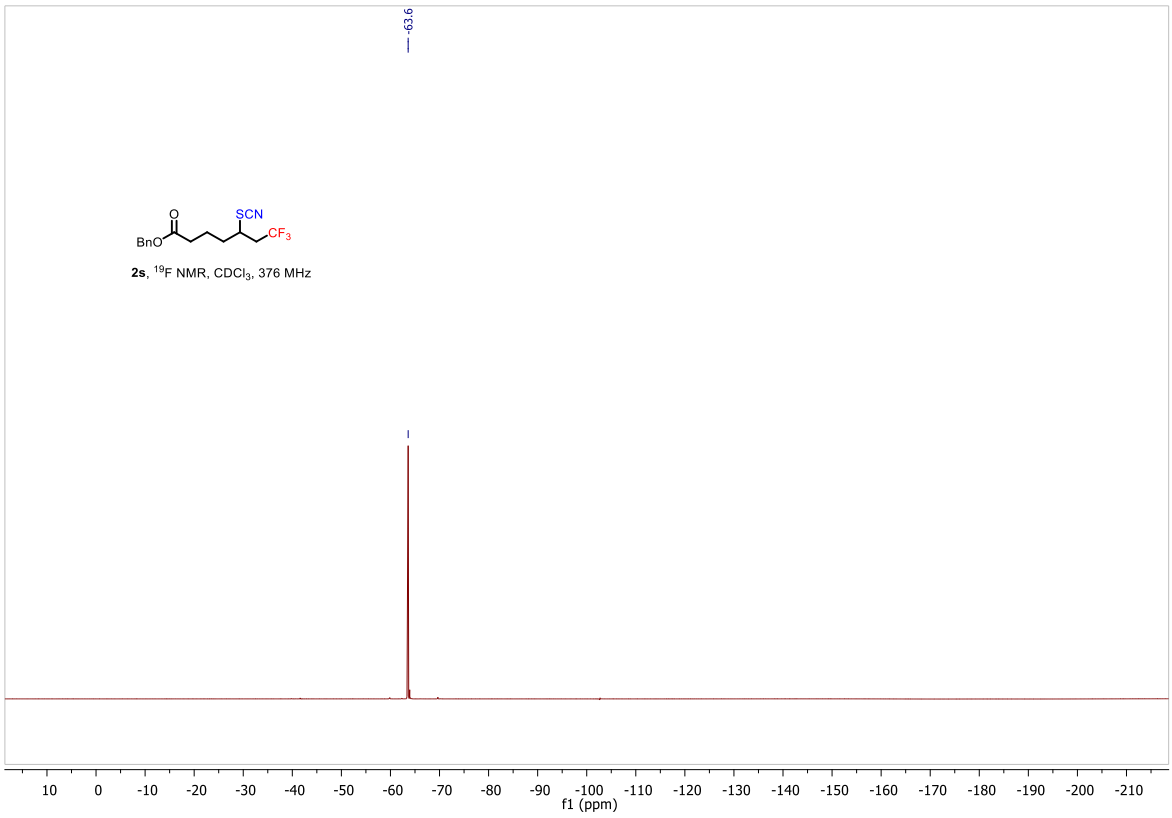

SCN
CF3
16
2r, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



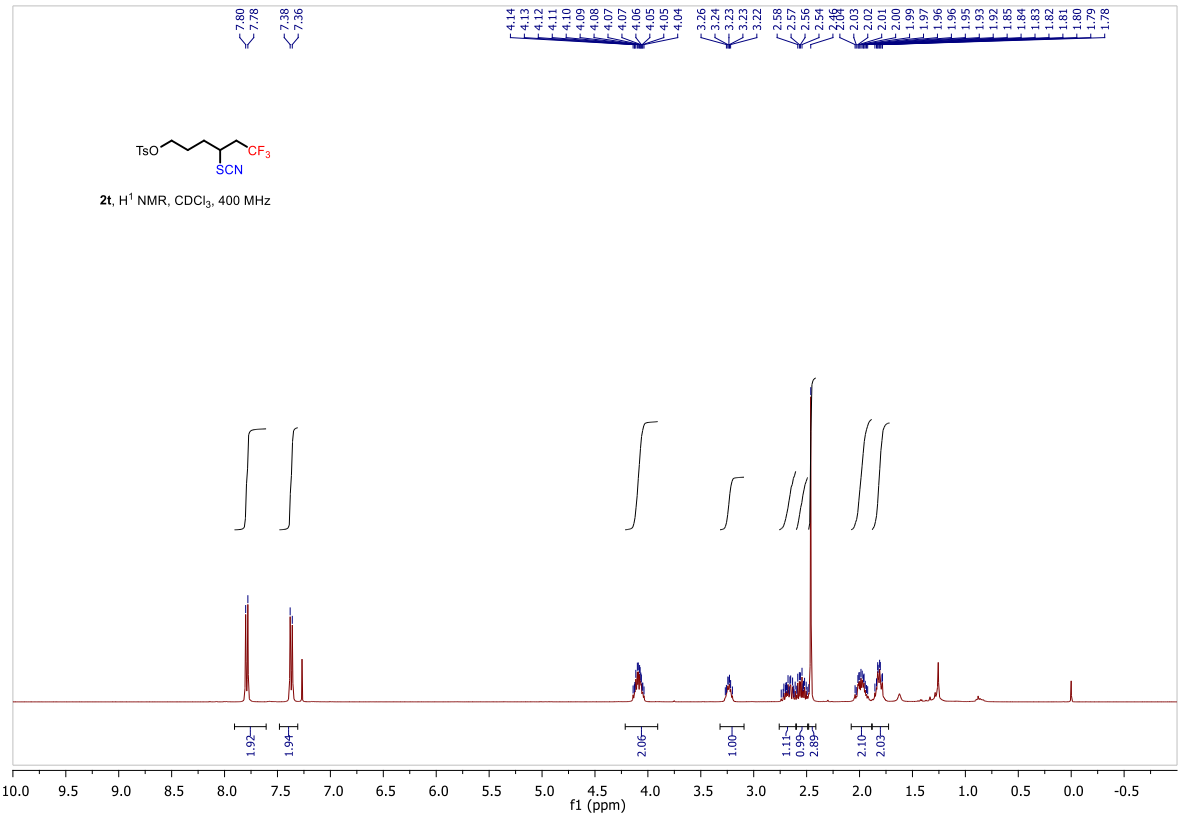

**2r**, $^{19}F$ NMR, $CDCl_3$, 376 MHz

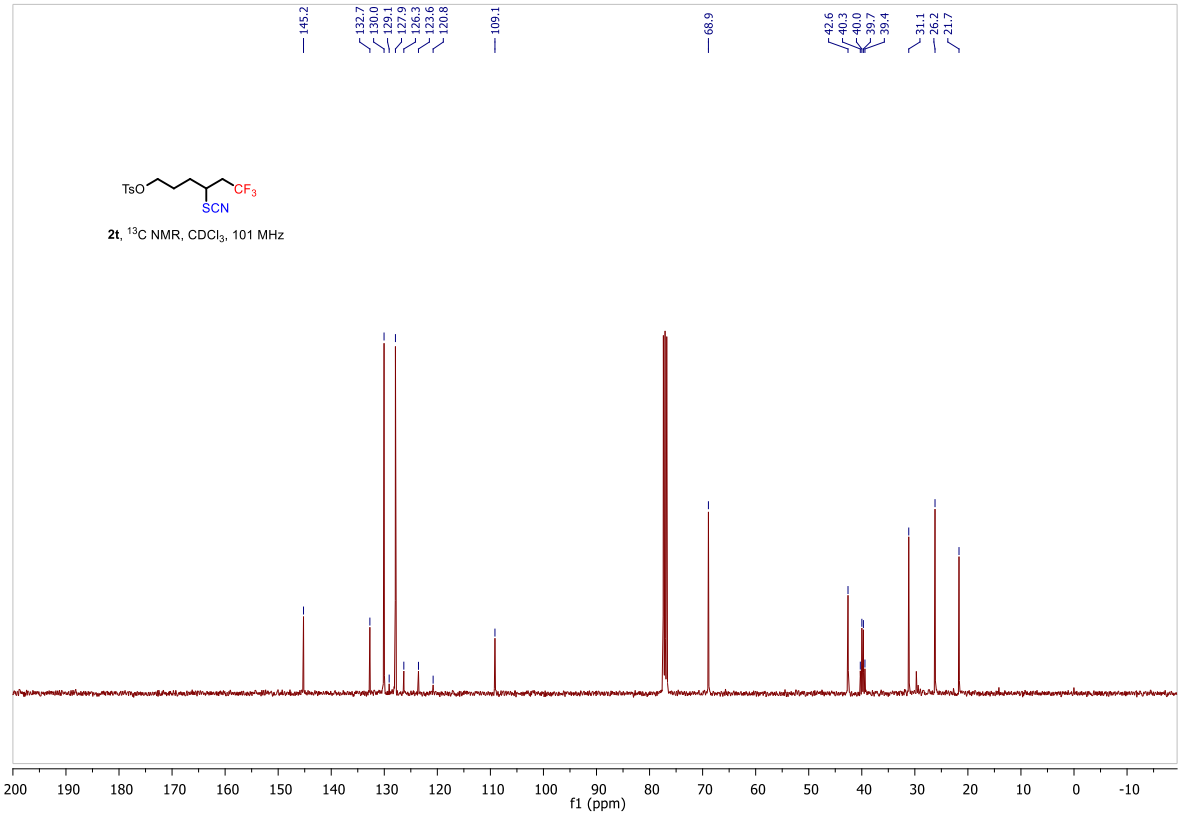

SCN
CF3
BnO
2s, H1 NMR, CDCl3, 400 MHz
5.06
2.13
1.00
2.11
2.03
2.08
2.14
f1 (ppm)

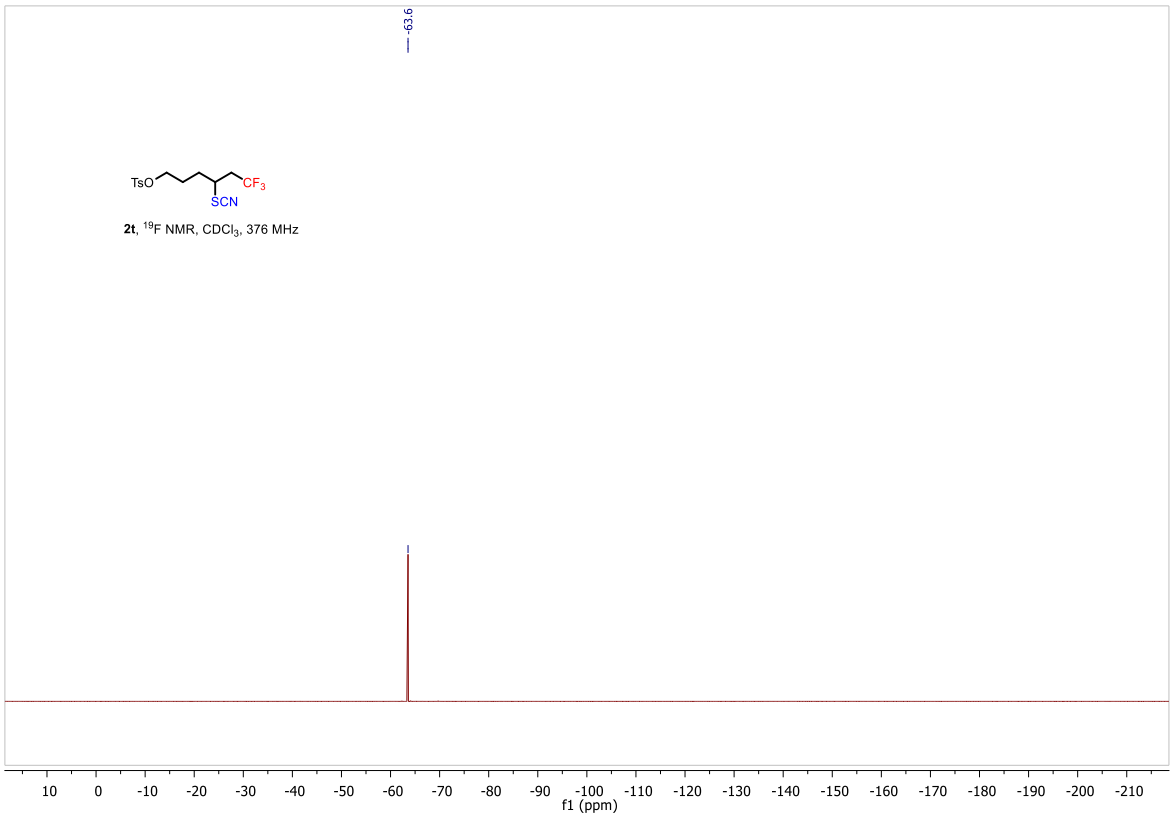

SCN
CF3
BnO
2s, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



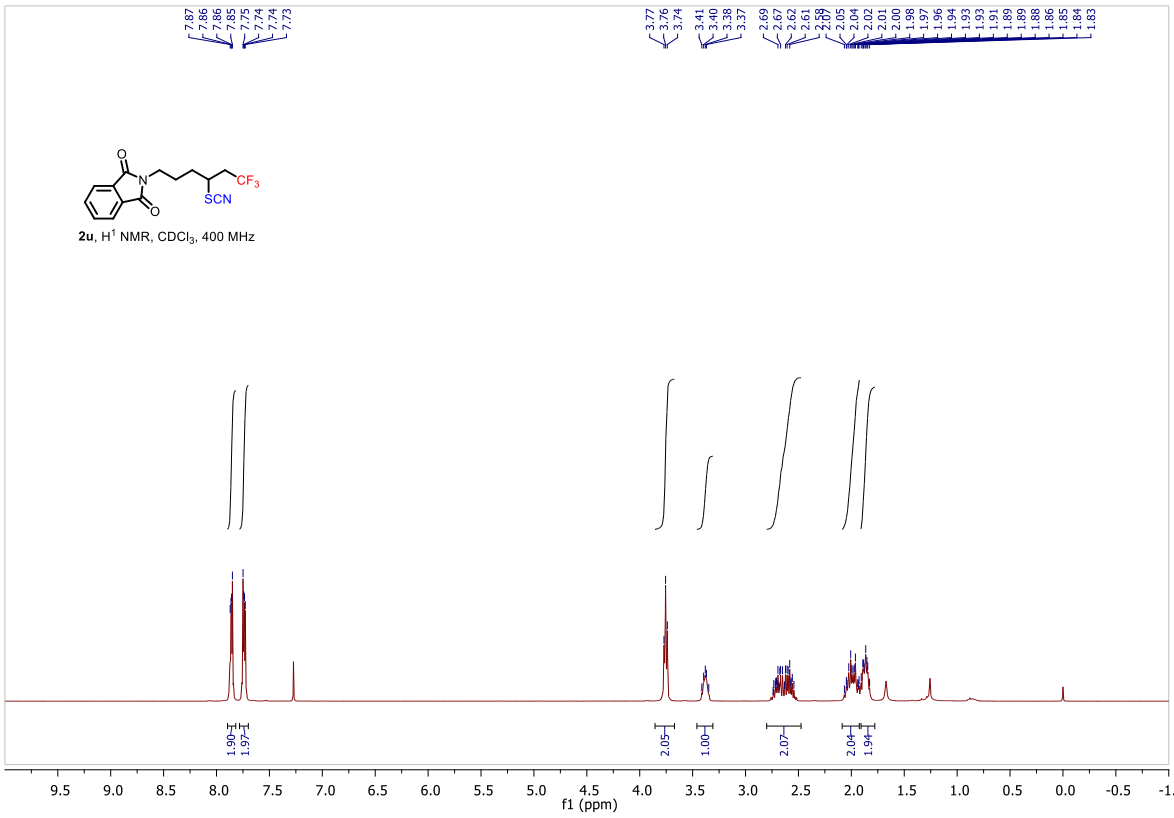

**2s**, $^{19}F$ NMR, $CDCl_3$, 376 MHz


TsO
CF3
SCN
2t, H1 NMR, CDCl3, 400 MHz
f1 (ppm)

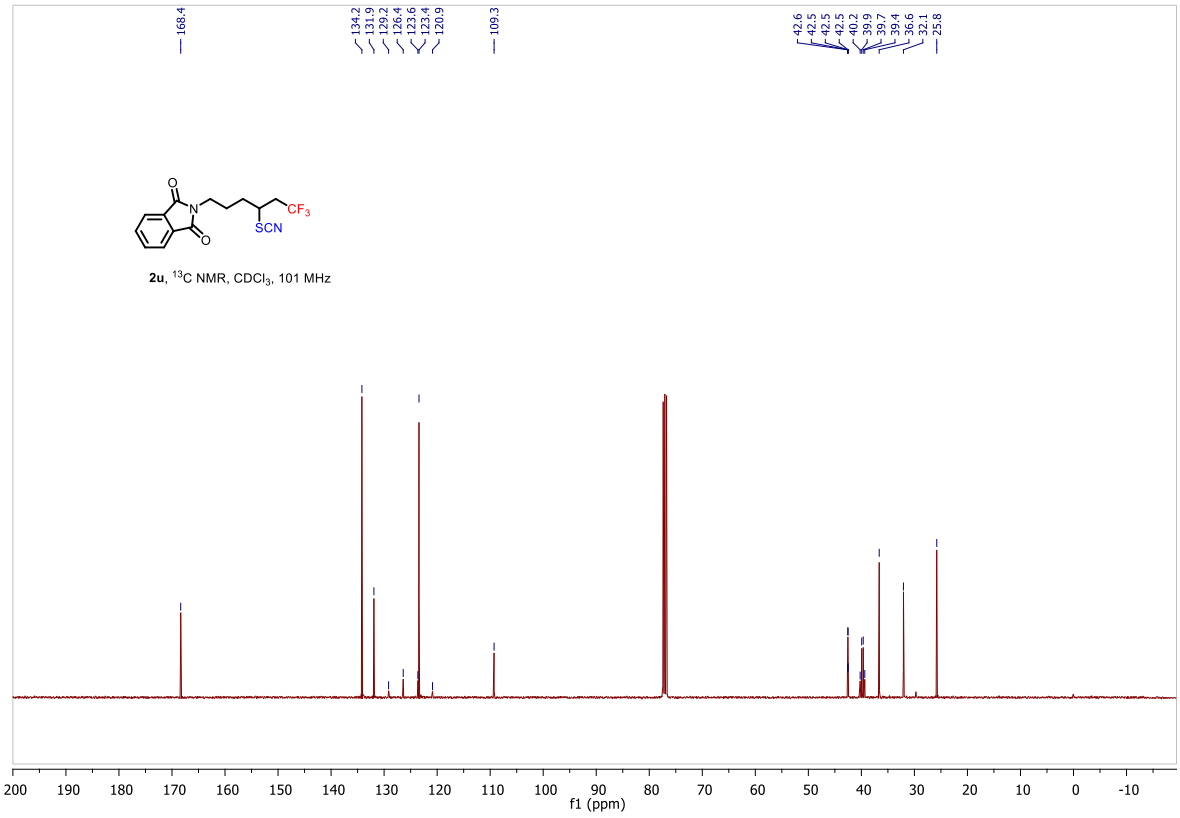

TsO
CF3
SCN
2t, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



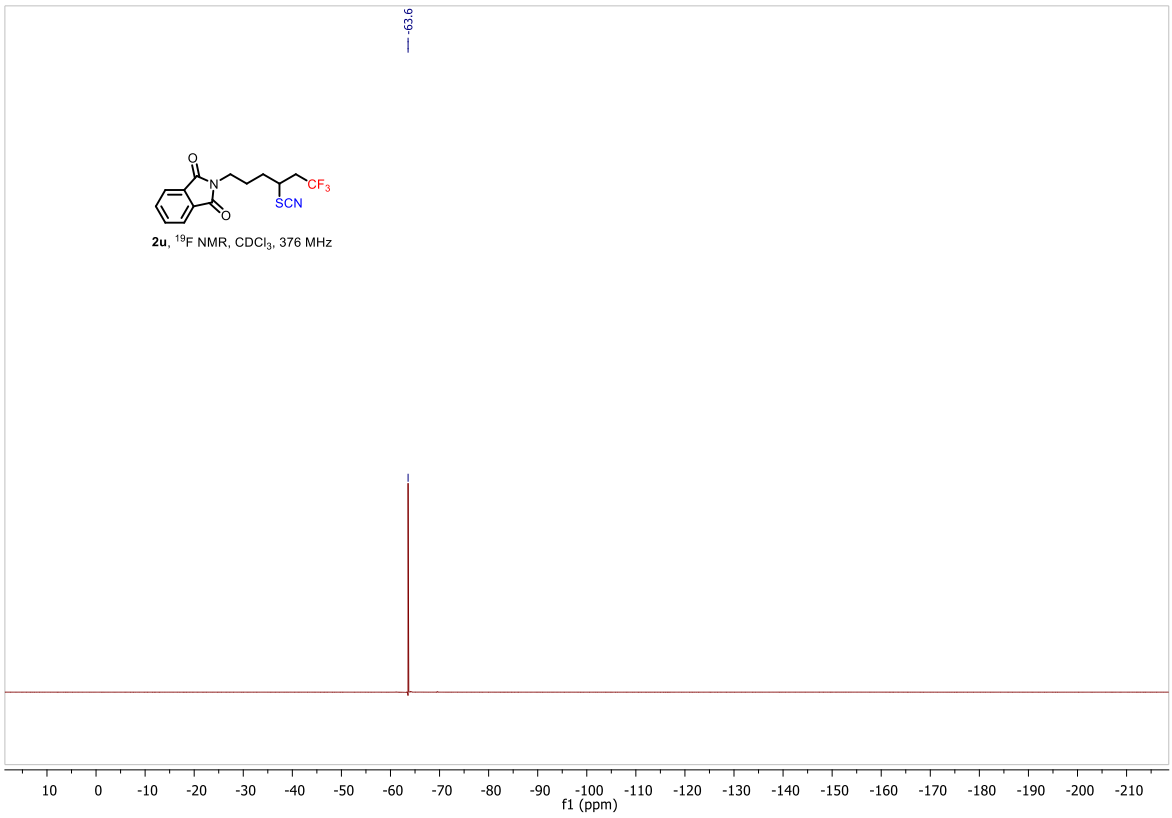

**2t**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



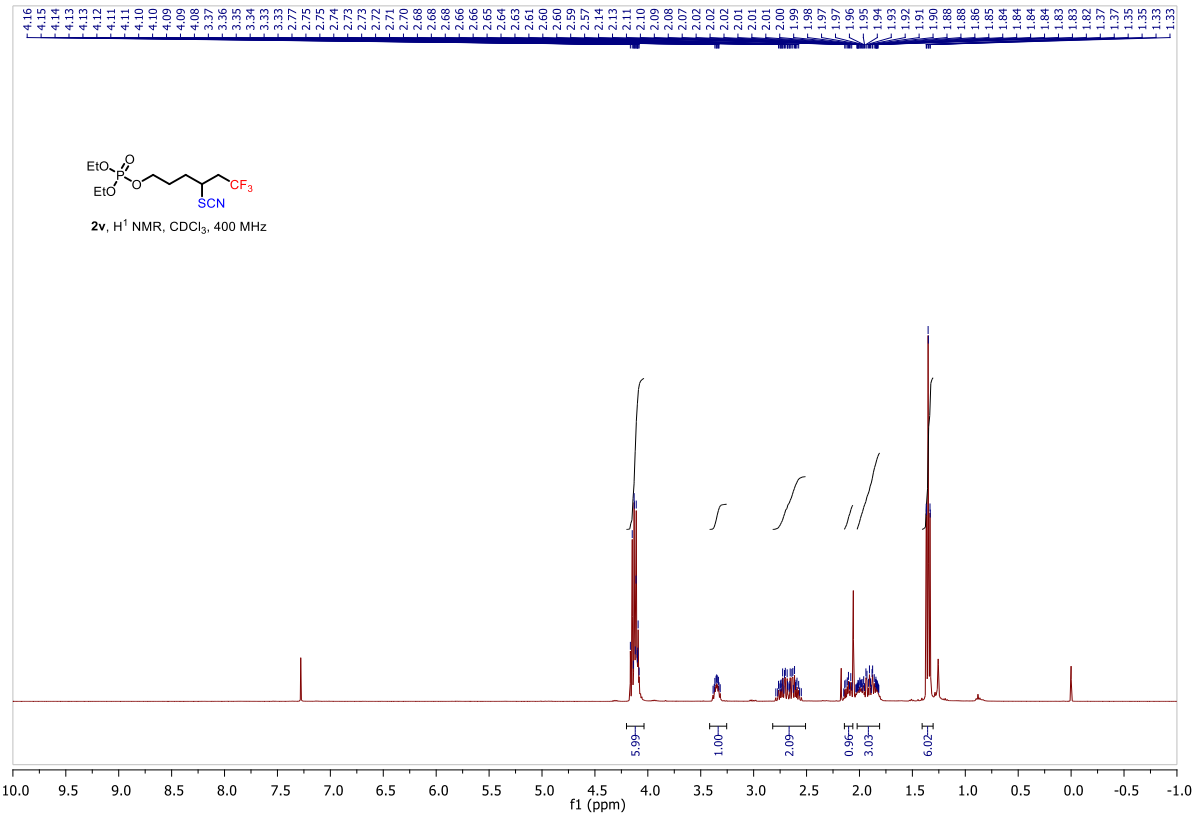

**2u**, $H^1$ NMR, $CDCl_3$, 400 MHz

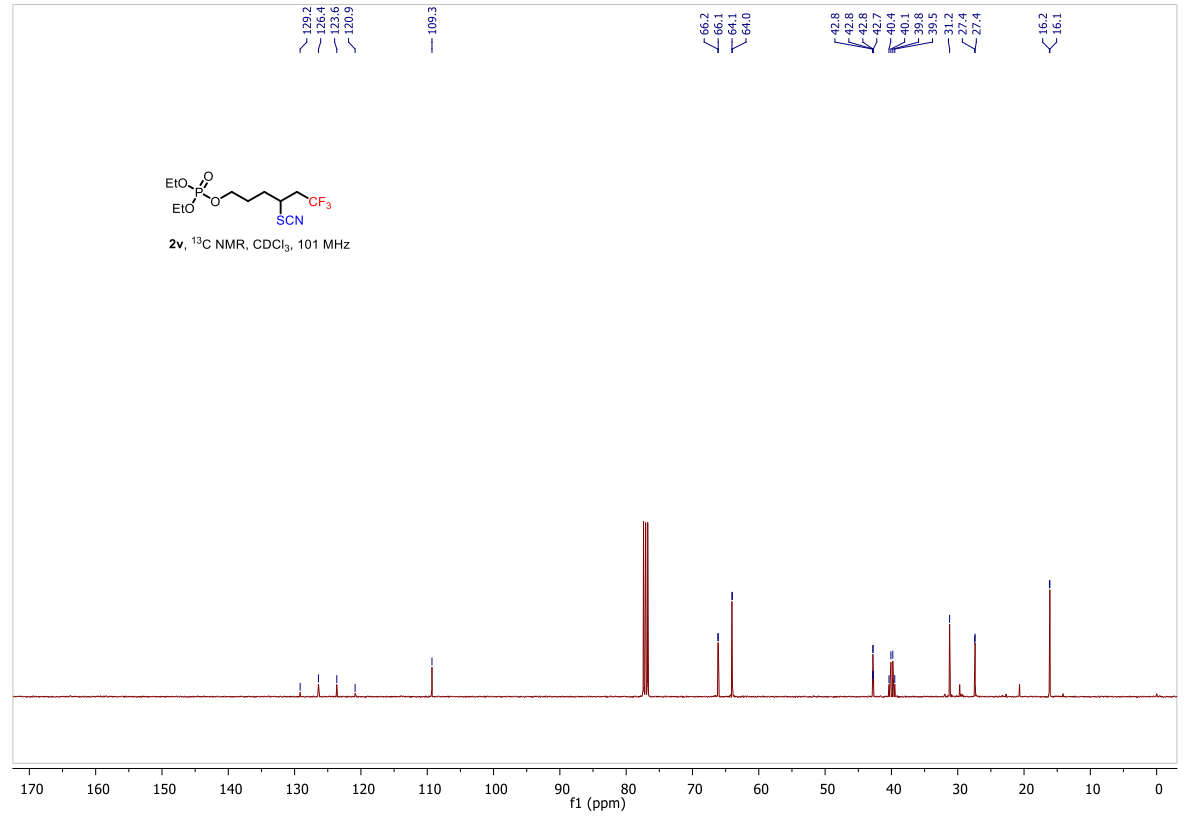


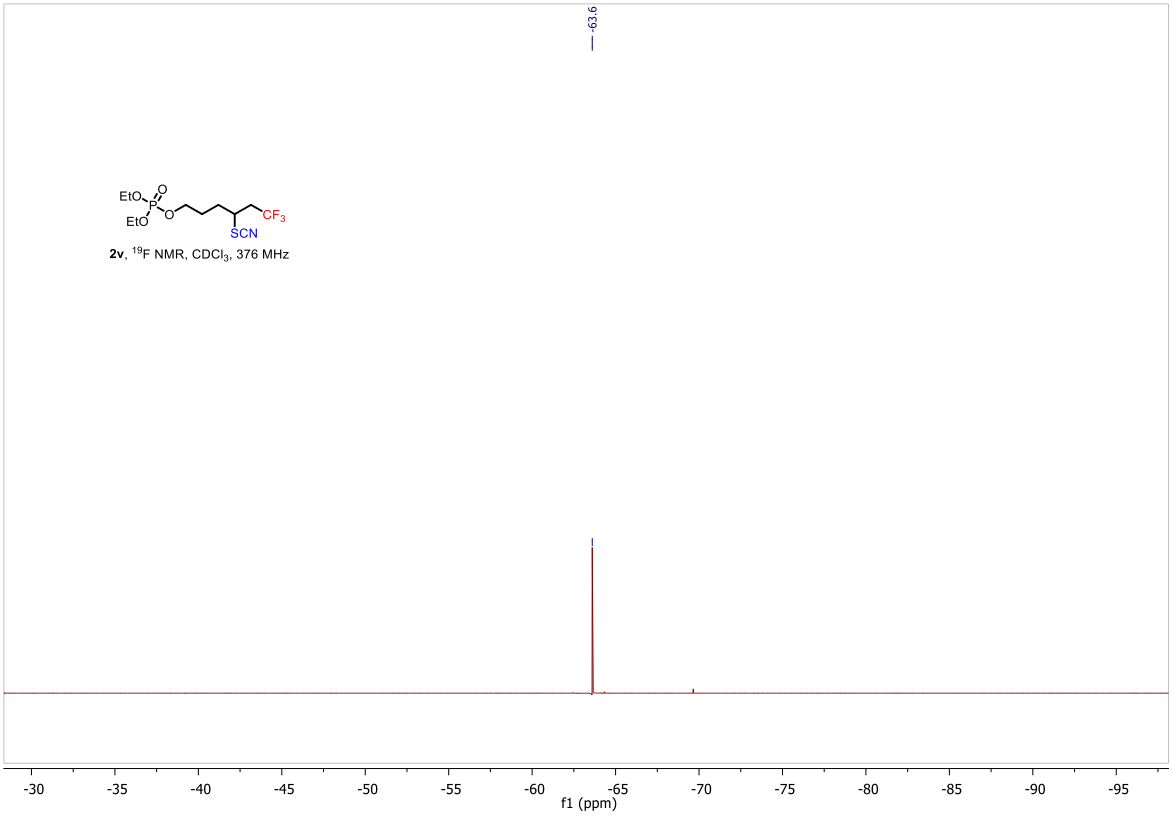

**2u**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



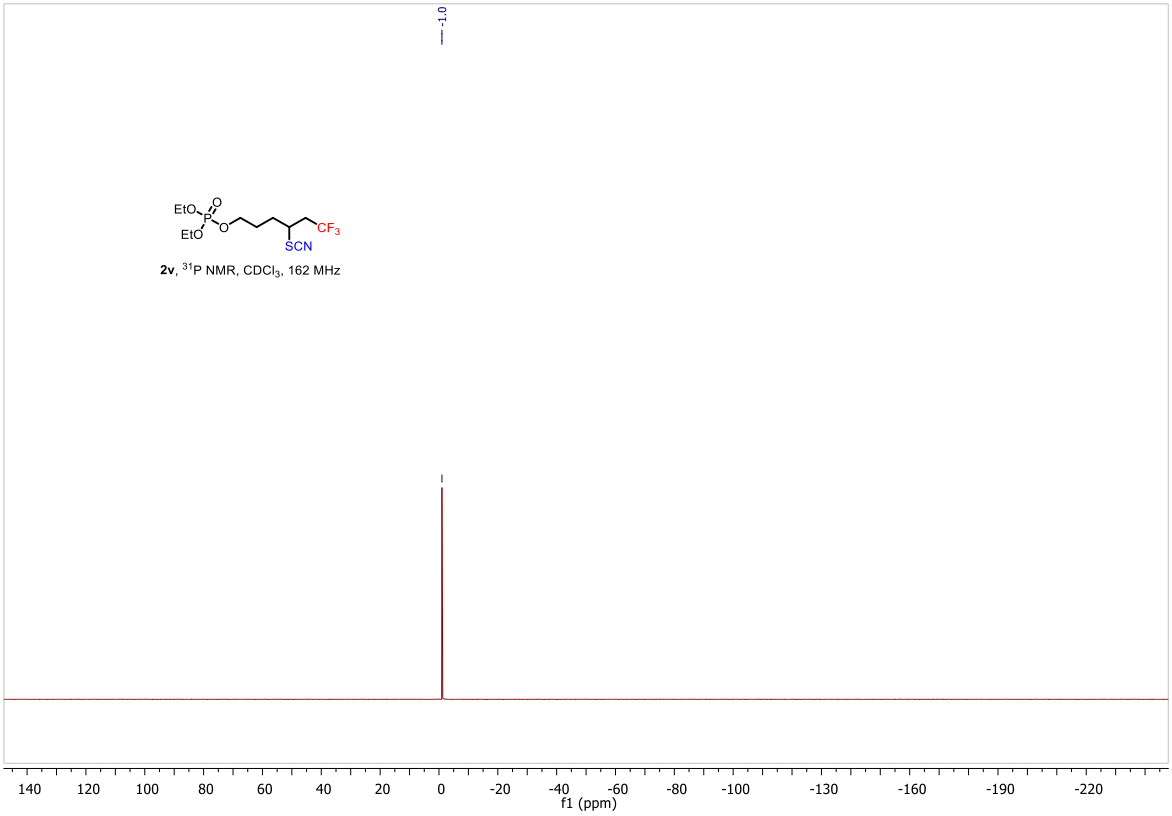

**2u**, $^{19}F$ NMR, $CDCl_3$, 376 MHz


EtO
EtO
O
P
O
CF3
SCN
2v, H1 NMR, CDCl3, 400 MHz
5.99
1.00
2.09
0.96
3.03
6.02
f1 (ppm)

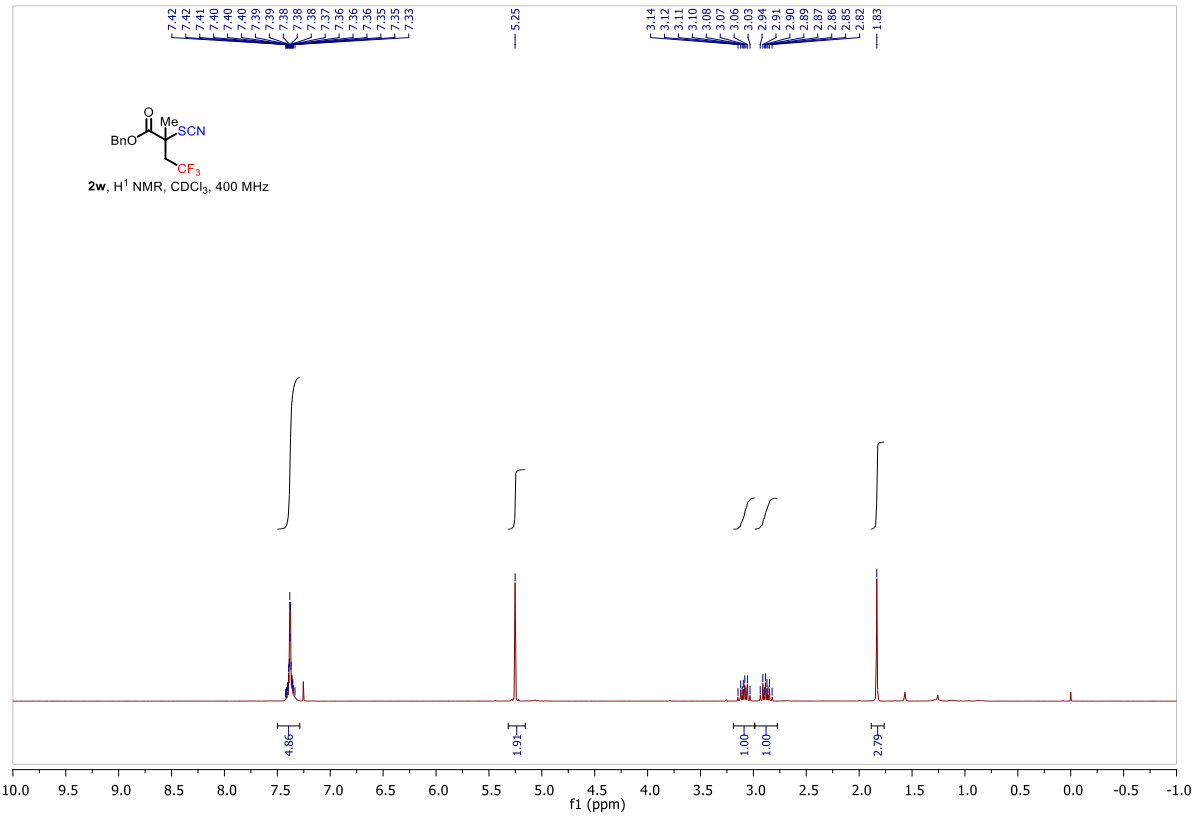

EtO
EtO
O
P
O
CF3
SCN
2v, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



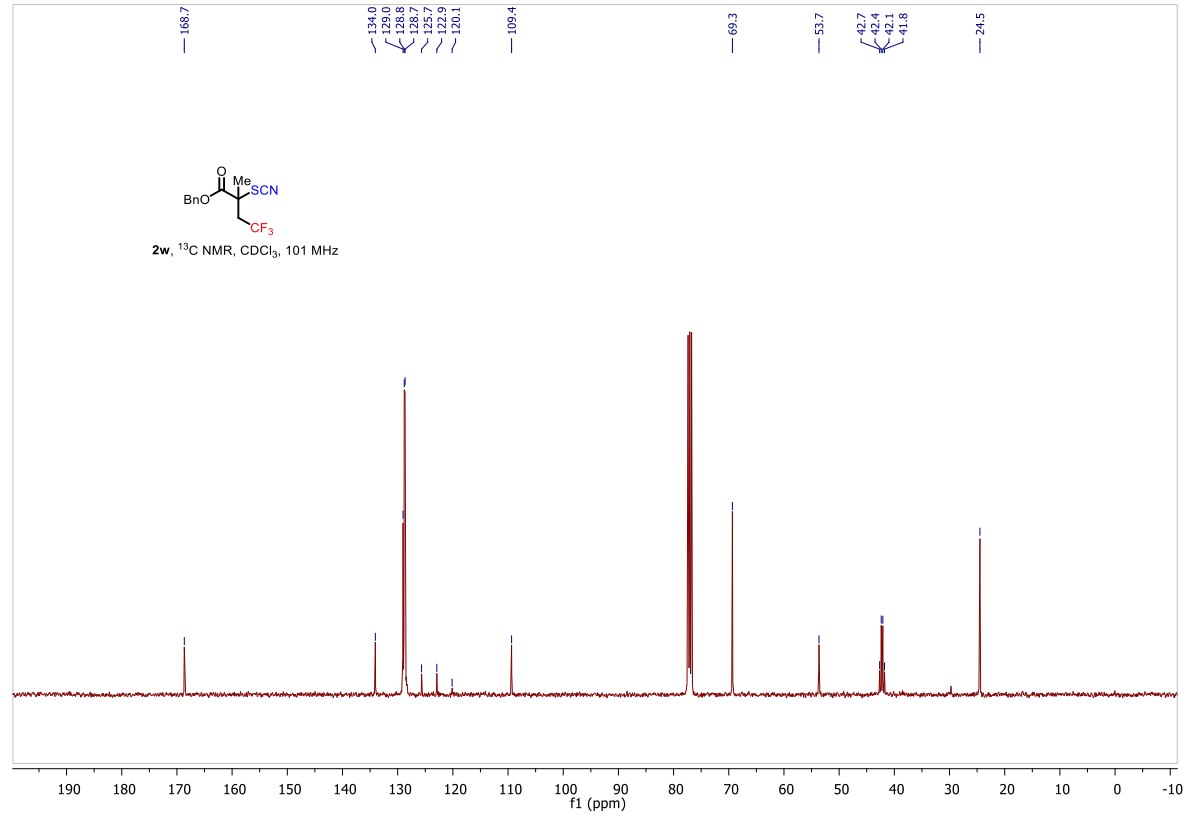

**2v**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



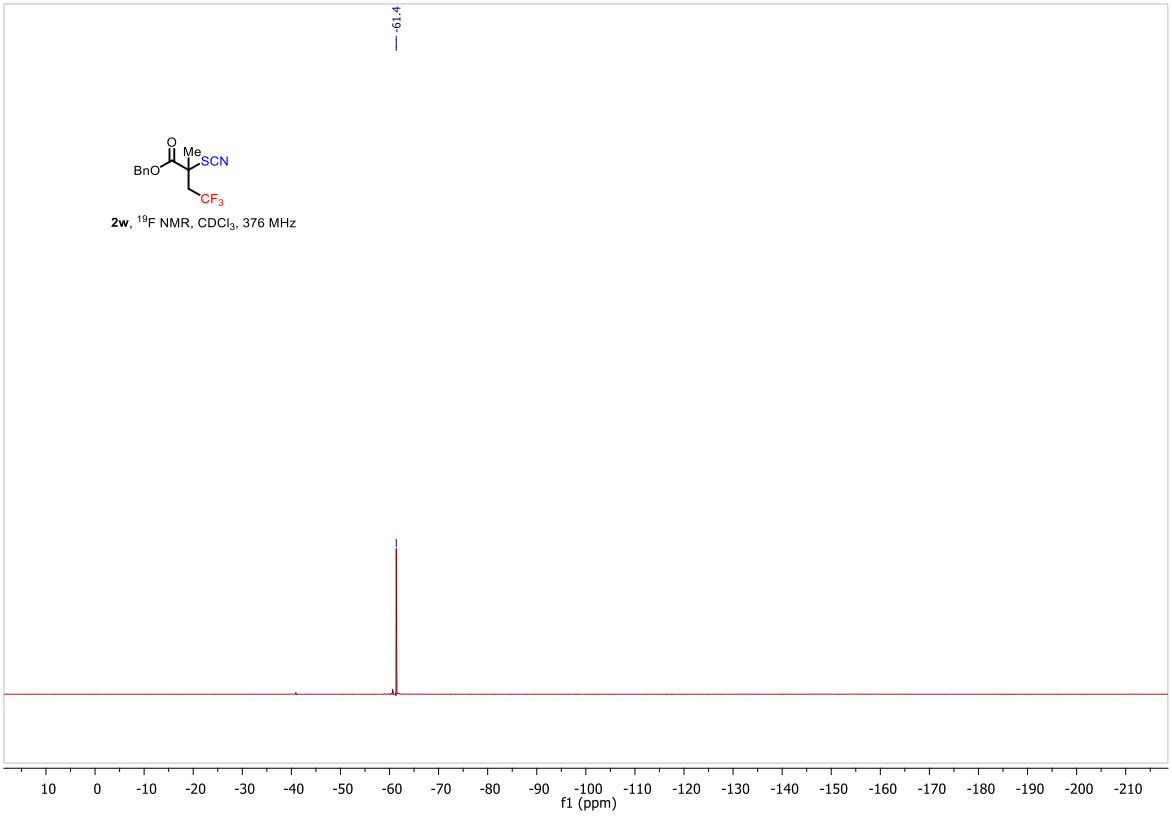

**2v**, $^{31}P$ NMR, $CDCl_3$, 162 MHz



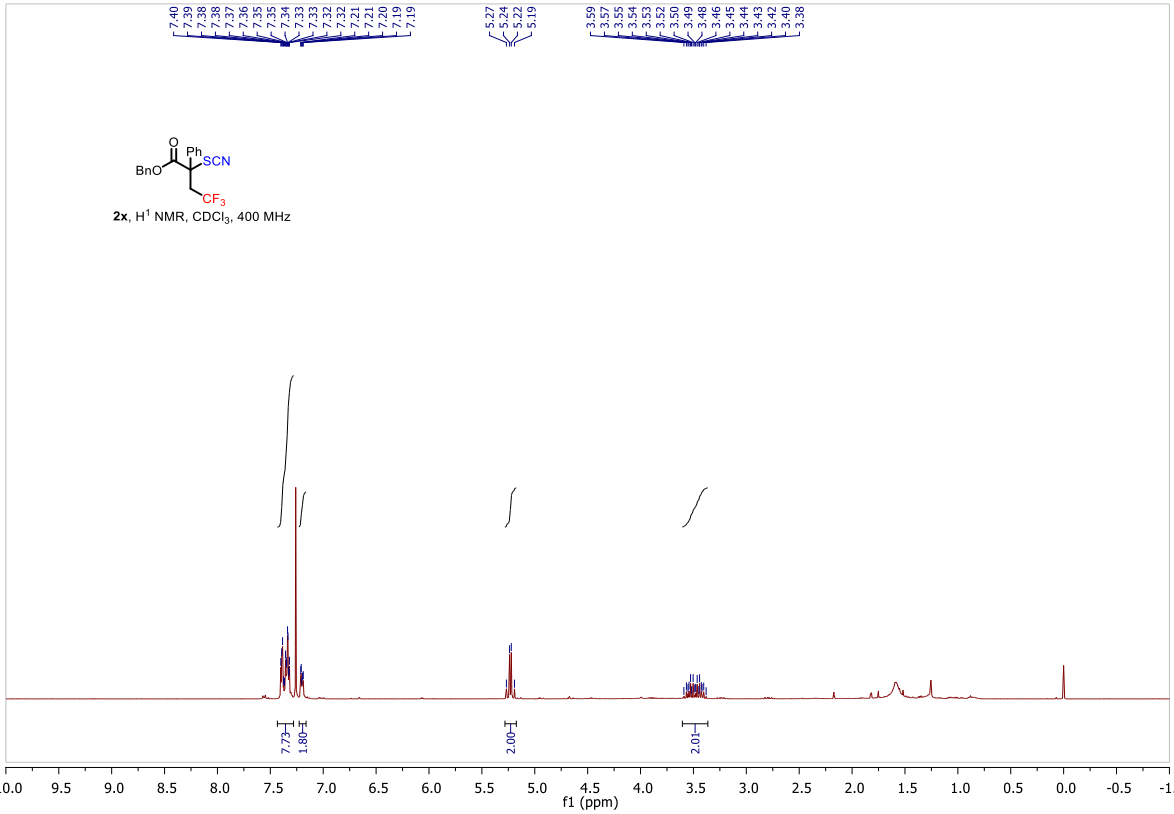

**2w**, $H^1$ NMR, $CDCl_3$, 400 MHz



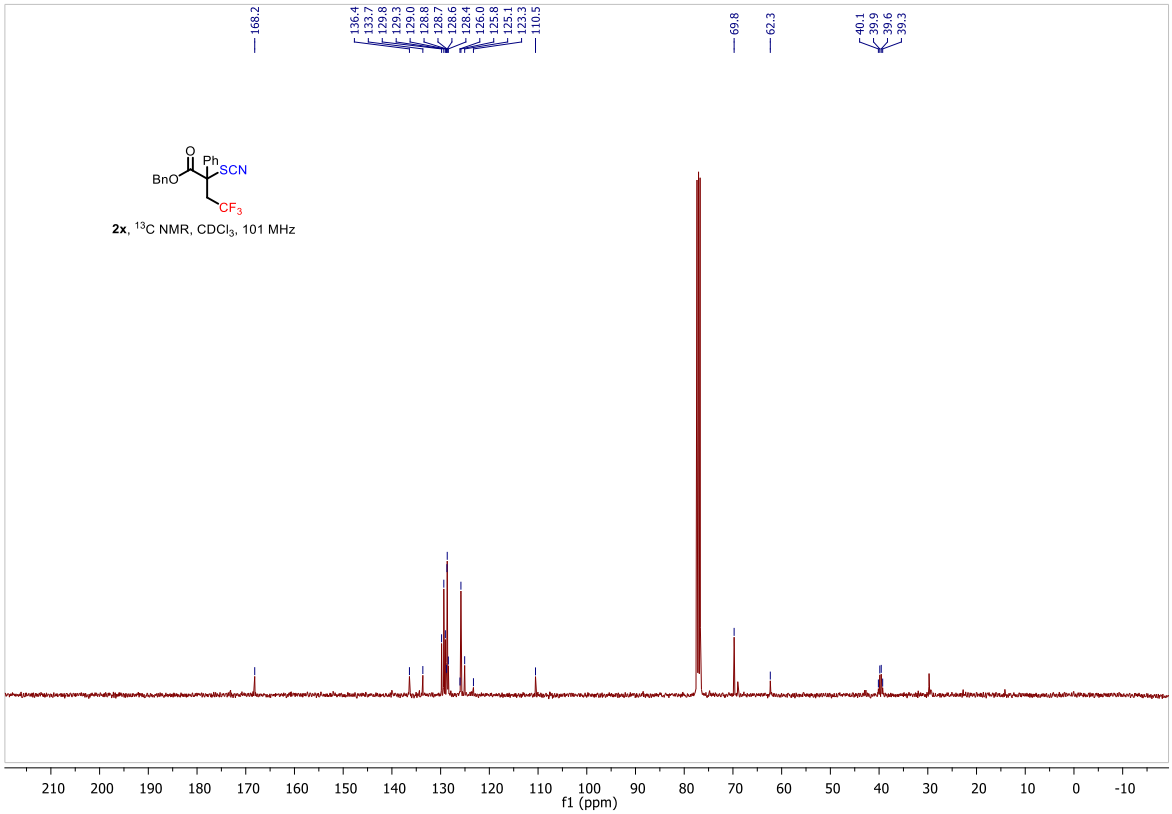

**2w**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



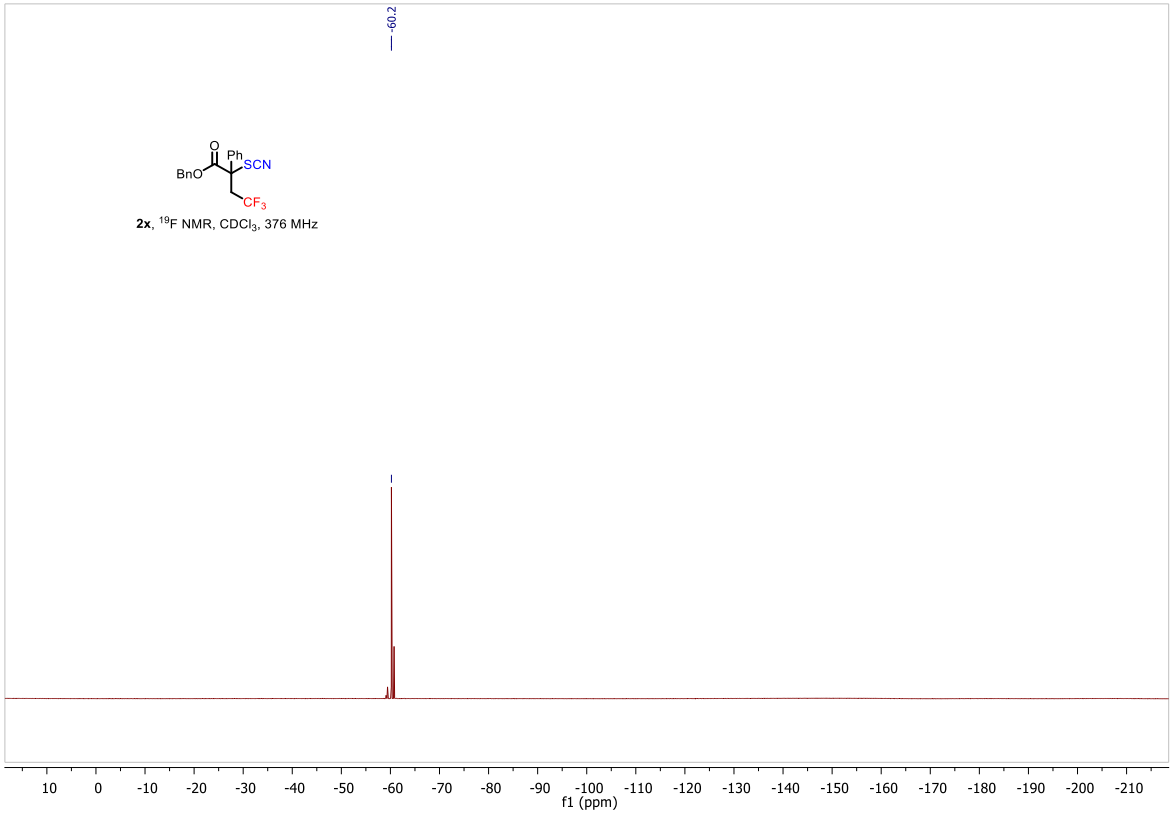

**2w**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



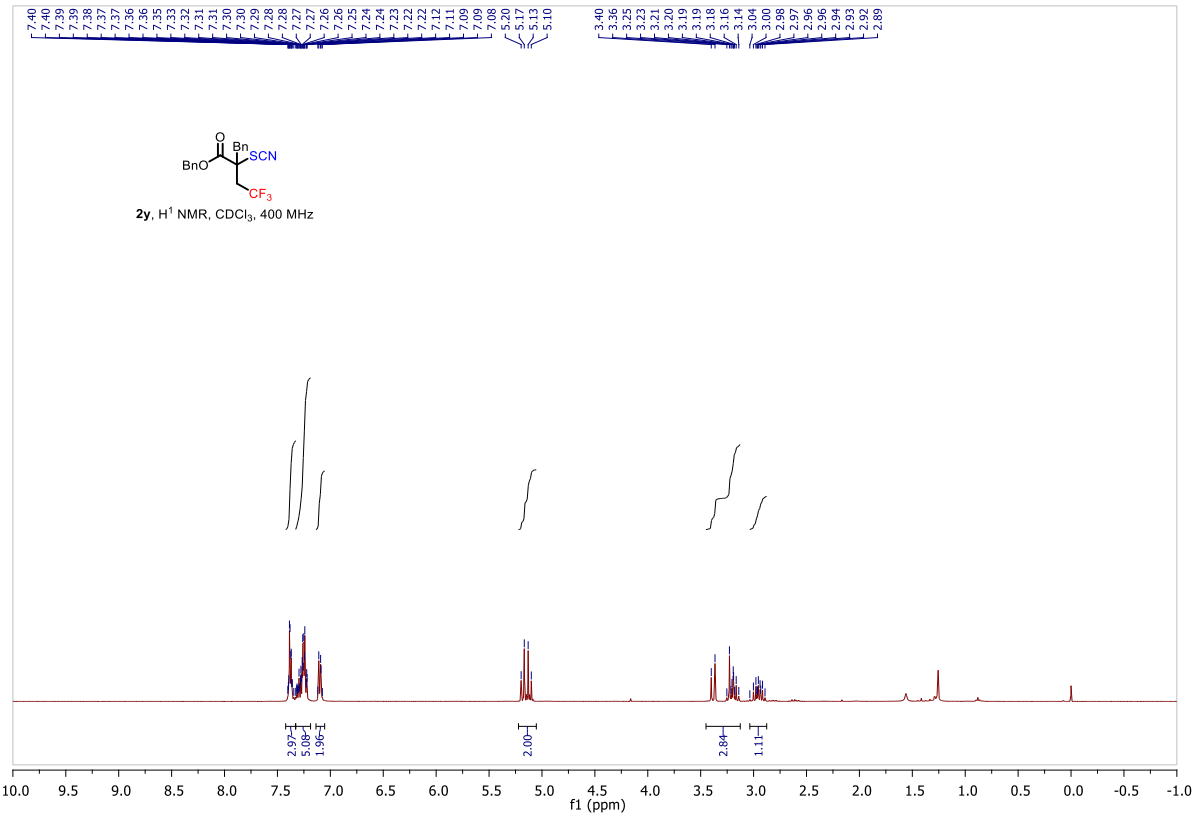

**2x**, $H^1$ NMR, $CDCl_3$, 400 MHz

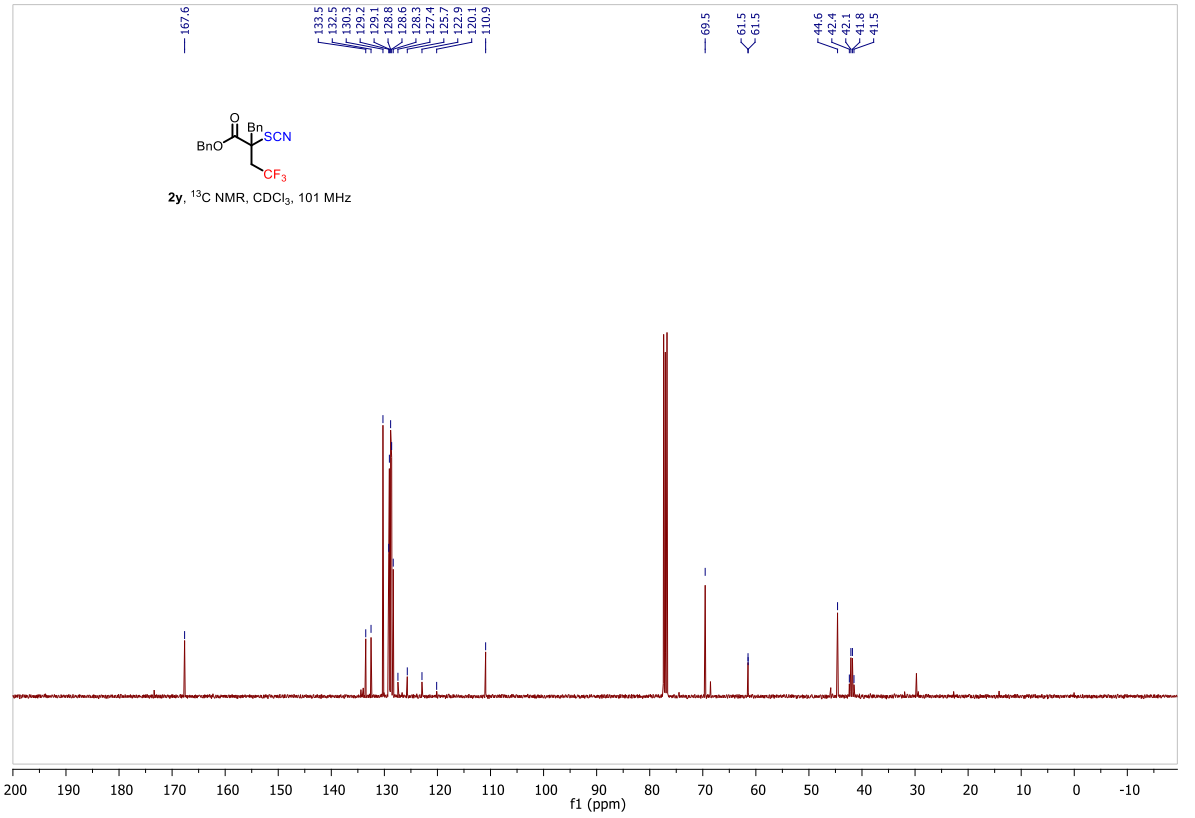


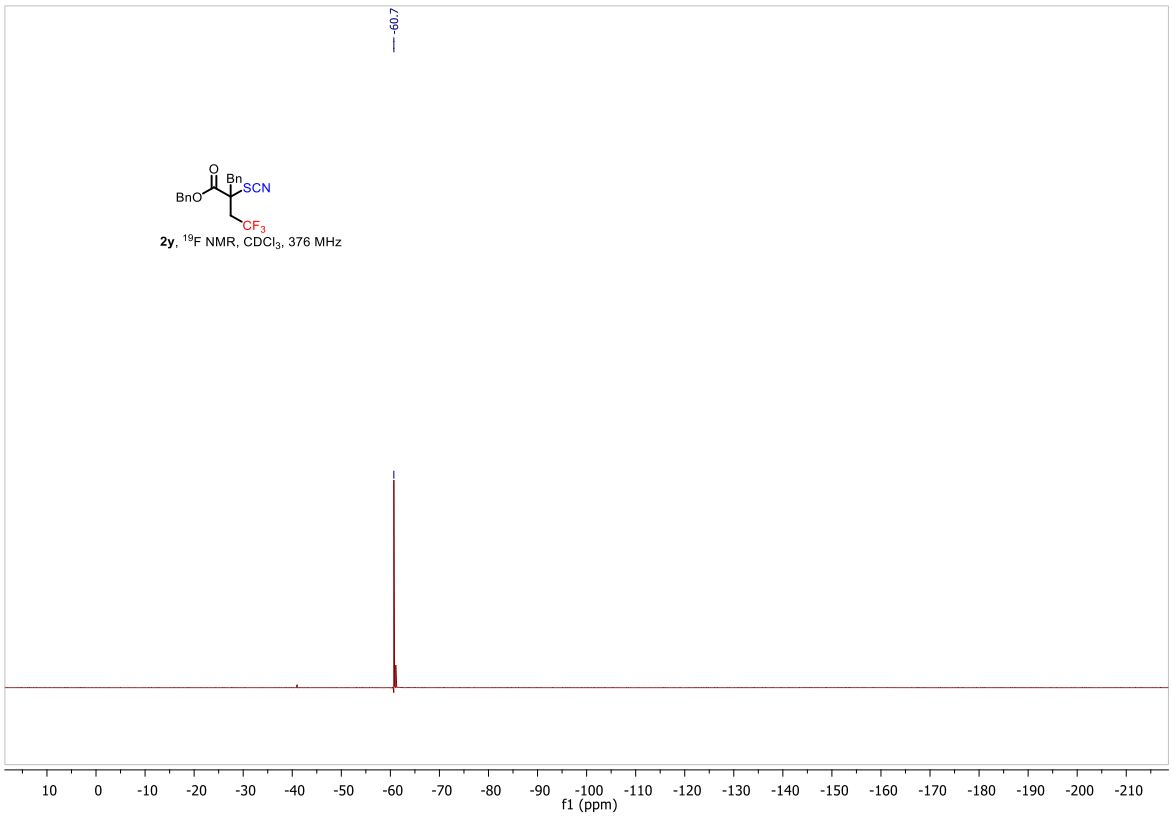

**2x**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



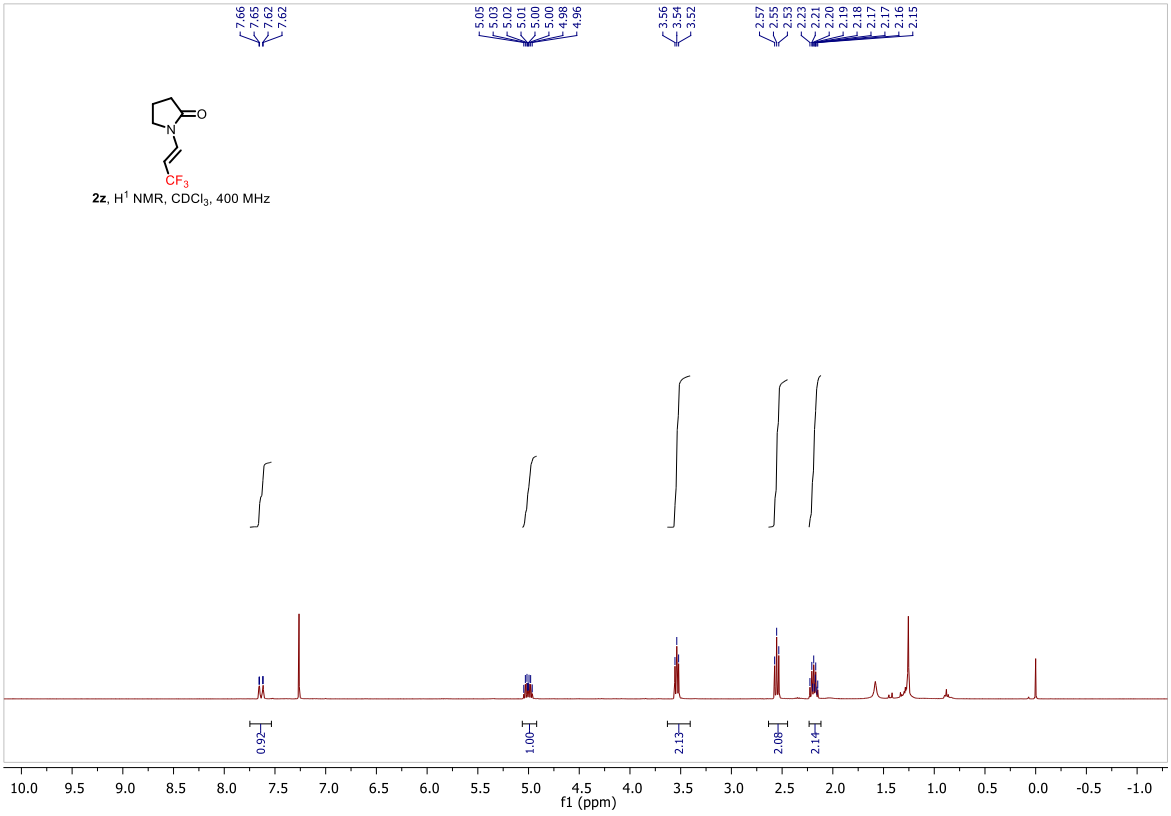

**2x**, $^{19}F$ NMR, $CDCl_3$, 376 MHz


7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.22 7.12 7.11 7.09 7.09 7.08 5.20 5.17 5.13 5.10
3.40 3.36 3.25 3.23 3.21 3.20 3.19 3.19 3.18 3.16 3.14 3.04 3.00 2.98 2.97 2.96 2.94 2.93 2.92 2.89
BnO
O
Bn
SCN
CF3
2y, H1 NMR, CDCl3, 400 MHz
2.97 5.08 1.96 2.00 2.84 1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

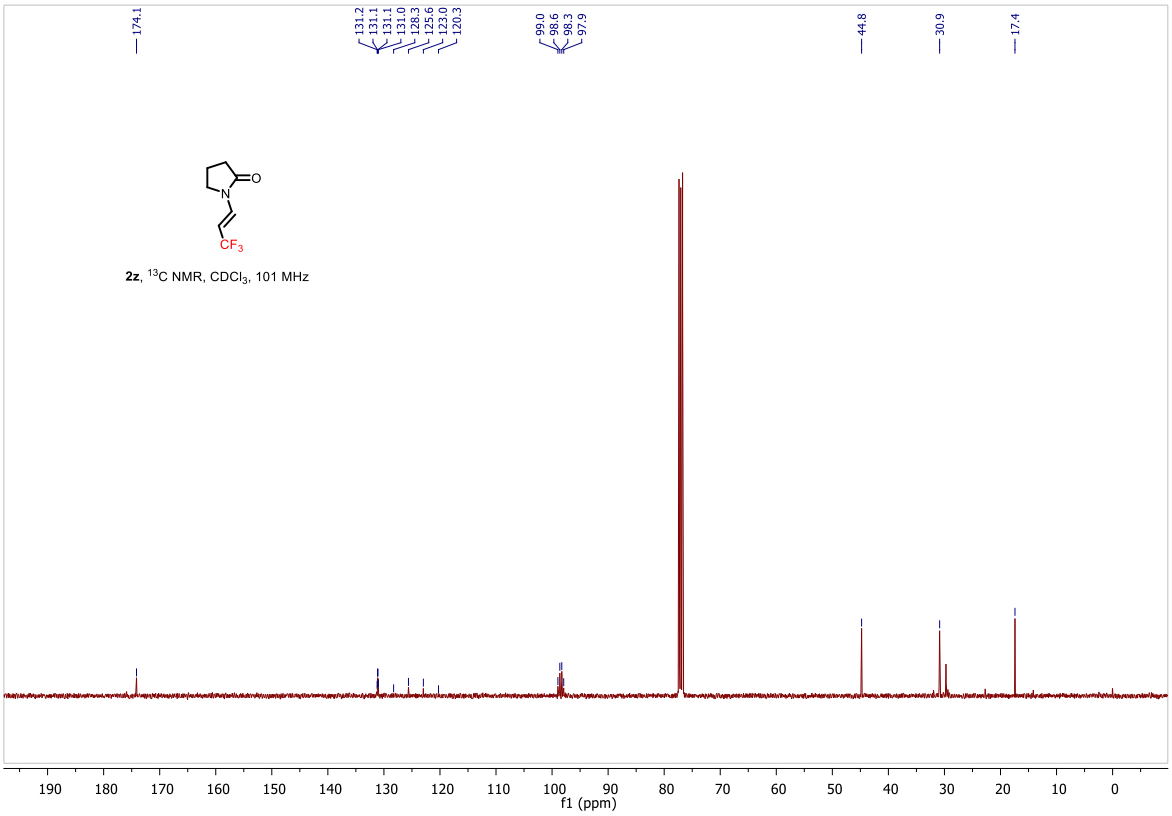

167.6
133.5 132.5 130.3 129.2 129.1 128.8 128.6 128.3 127.4 125.7 122.9 120.1 110.9
69.5
61.5 61.5
44.6 42.4 42.1 41.8 41.5
BnO
O
Bn
SCN
CF3
2y, 13C NMR, CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



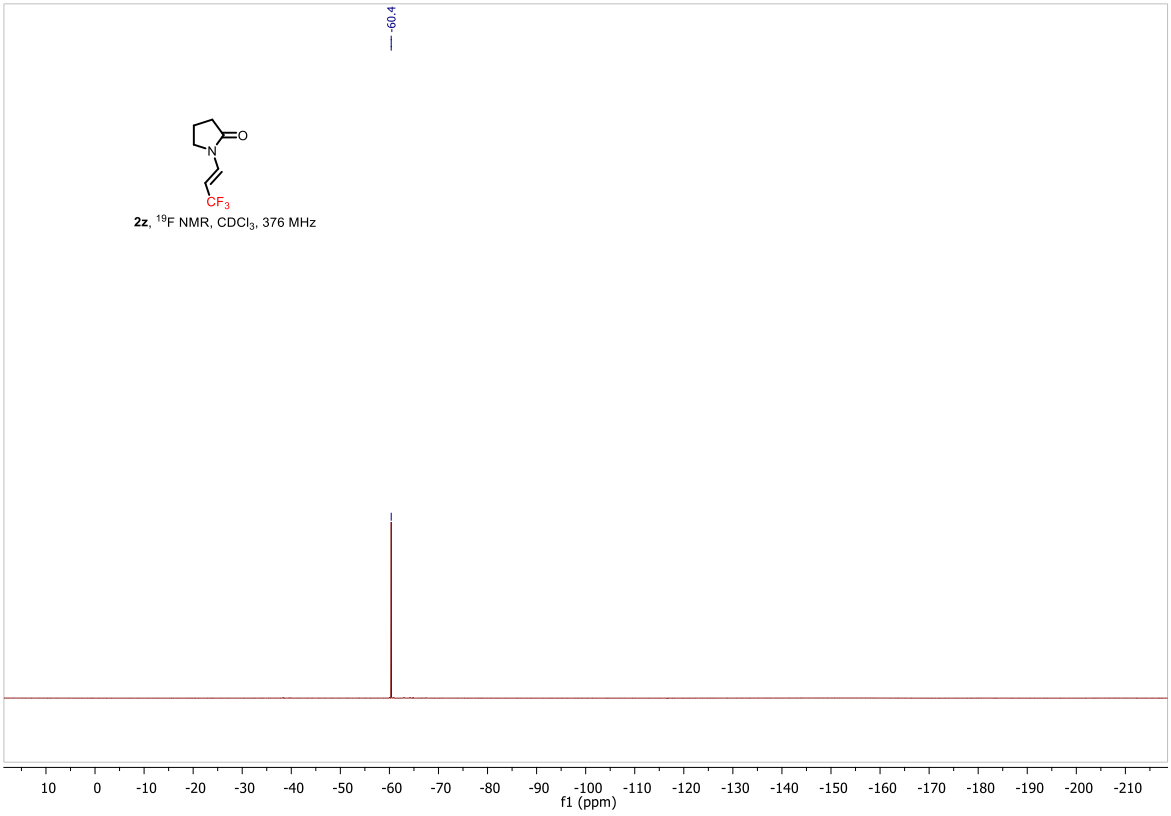

**2y**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



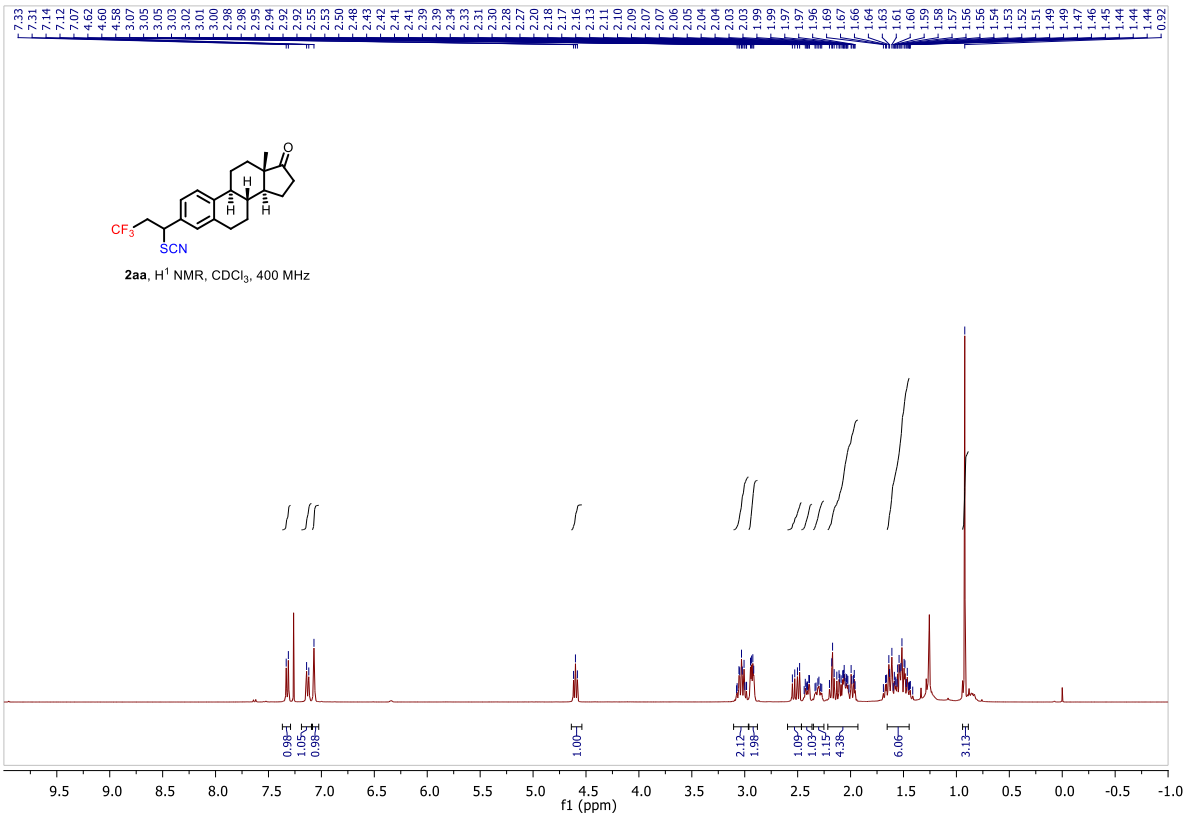

**2z**, $H^1$ NMR, $CDCl_3$, 400 MHz



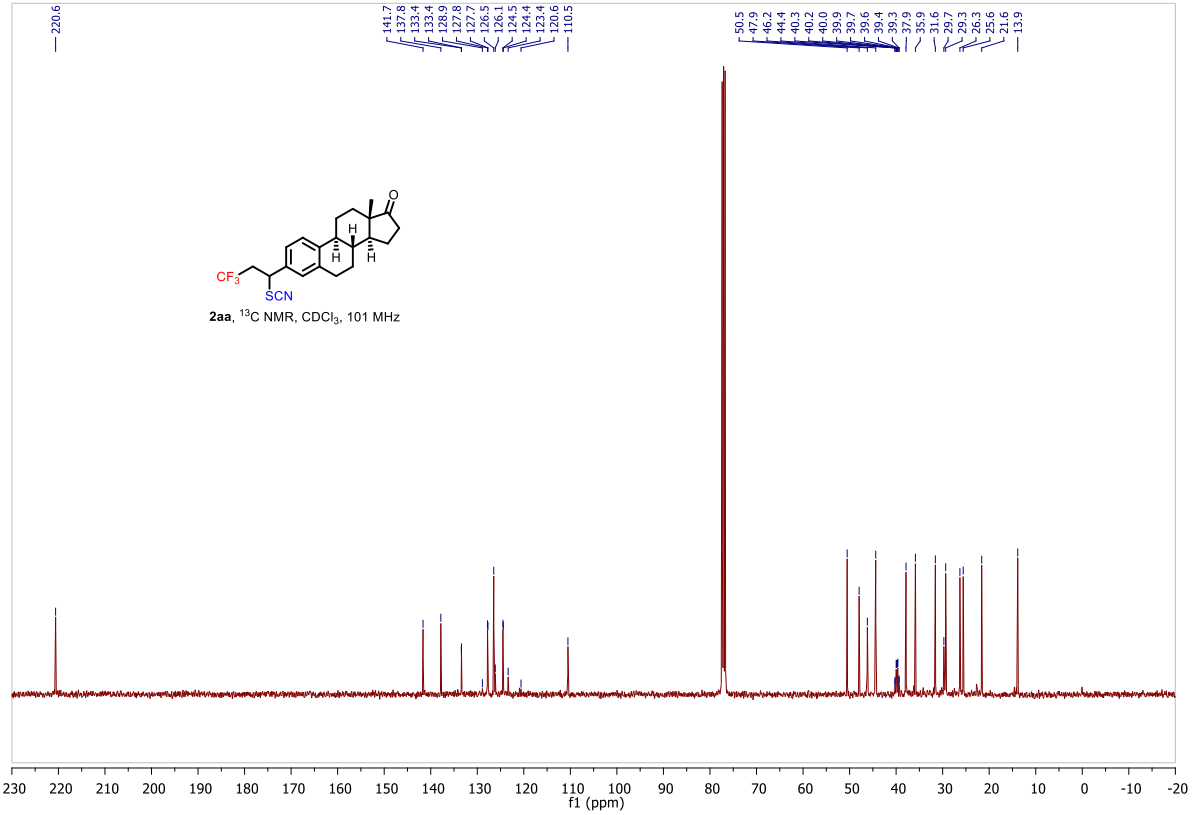

**2z**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



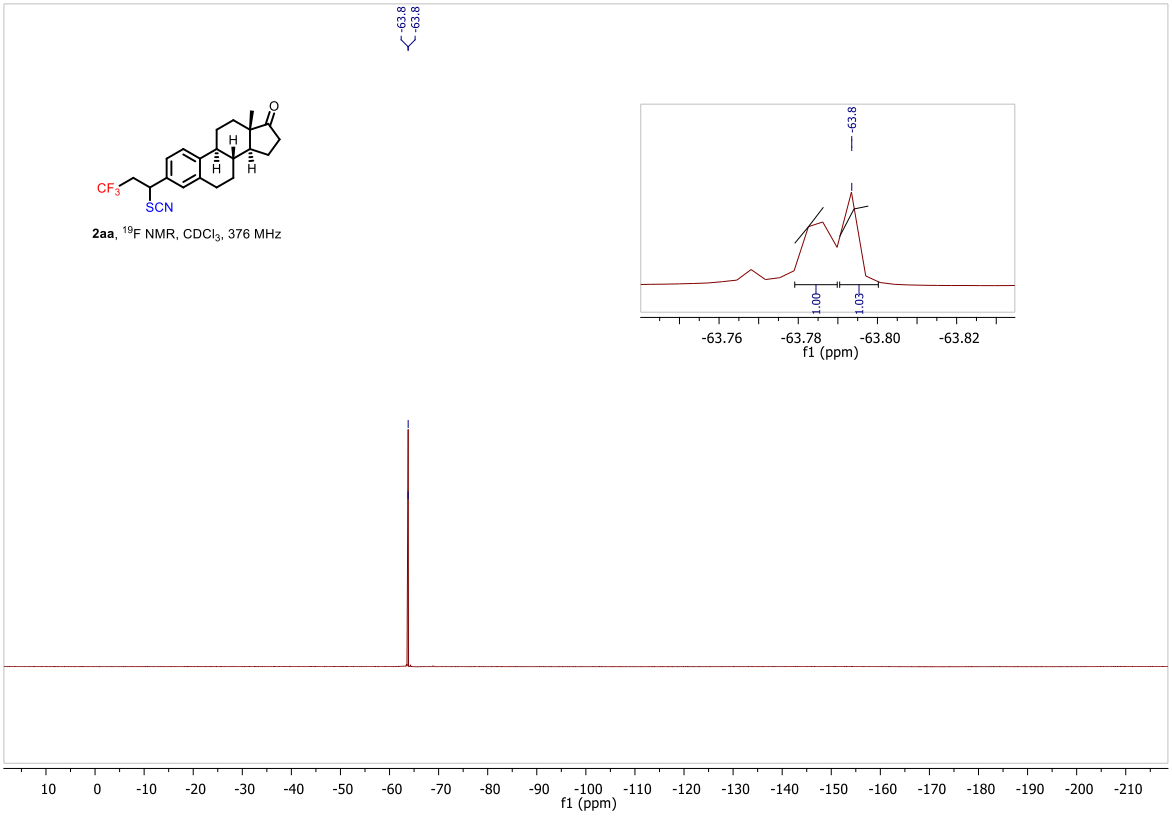

**2z**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



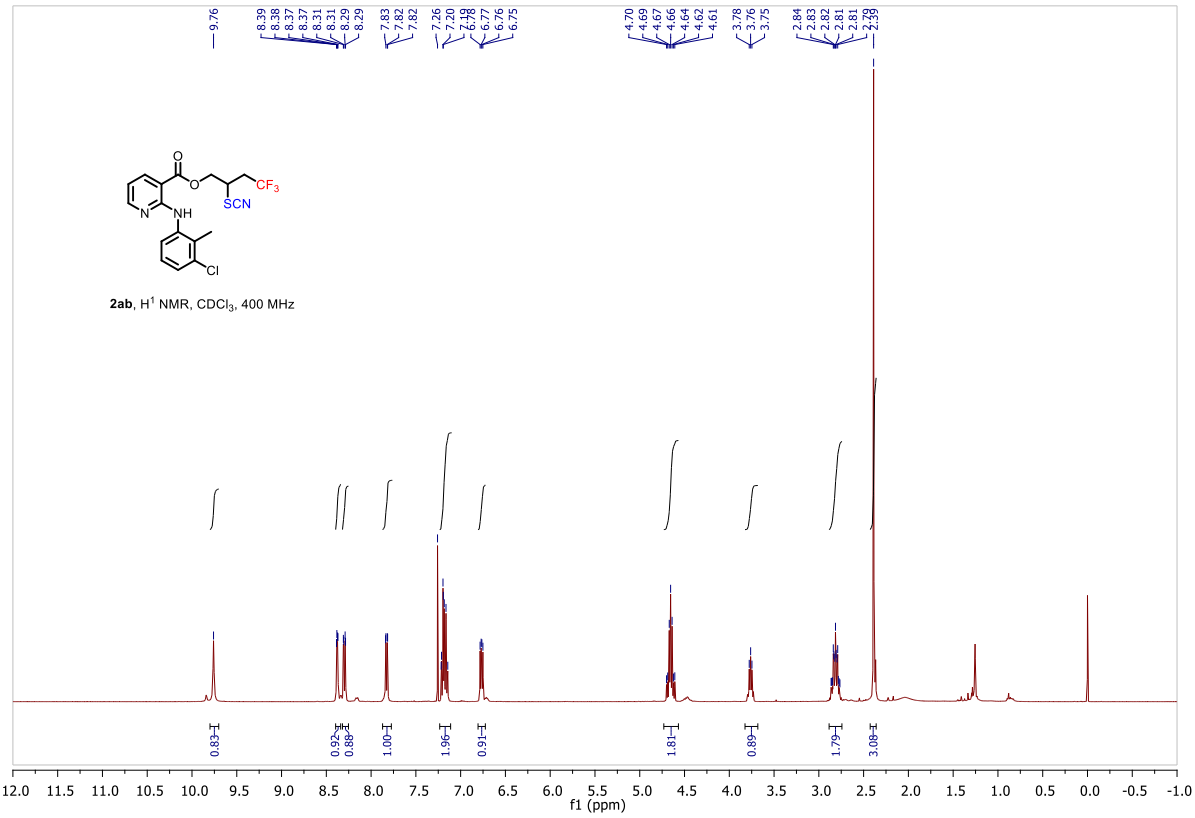

**2aa**, $H^1$ NMR, $CDCl_3$, 400 MHz



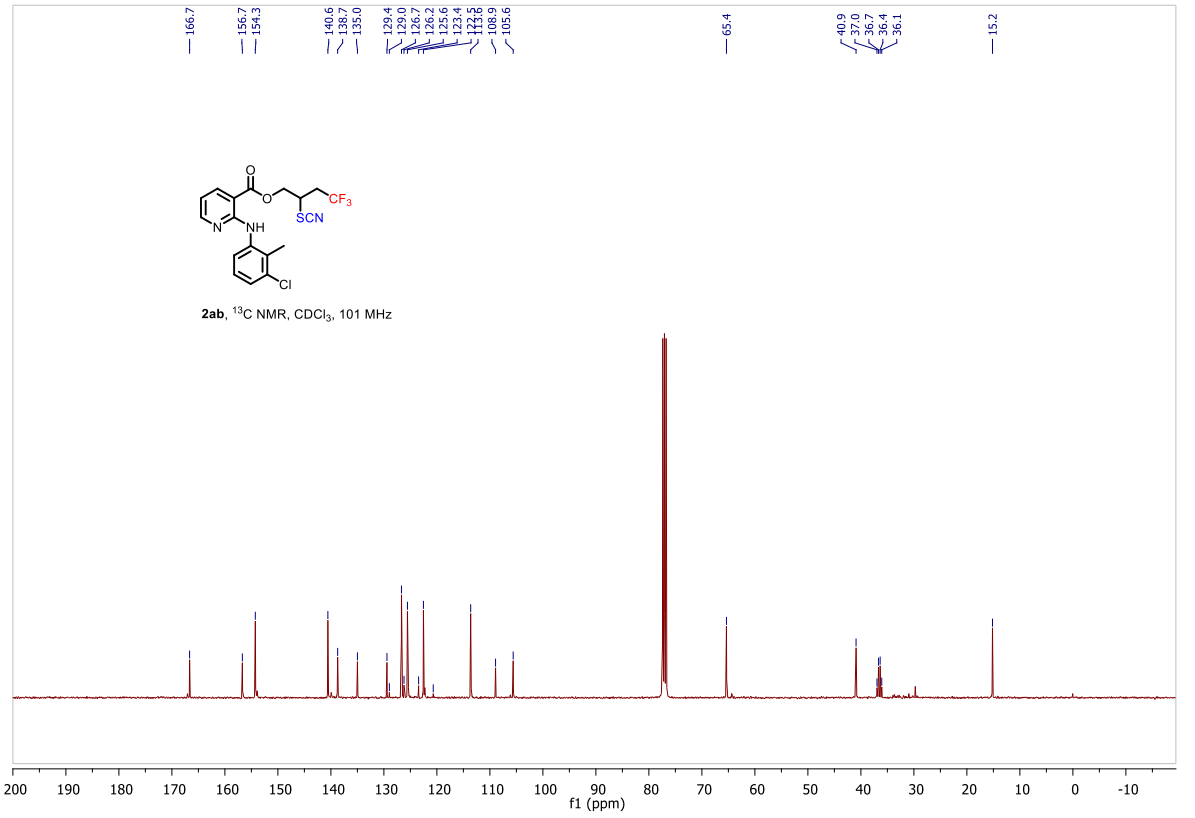

**2aa**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



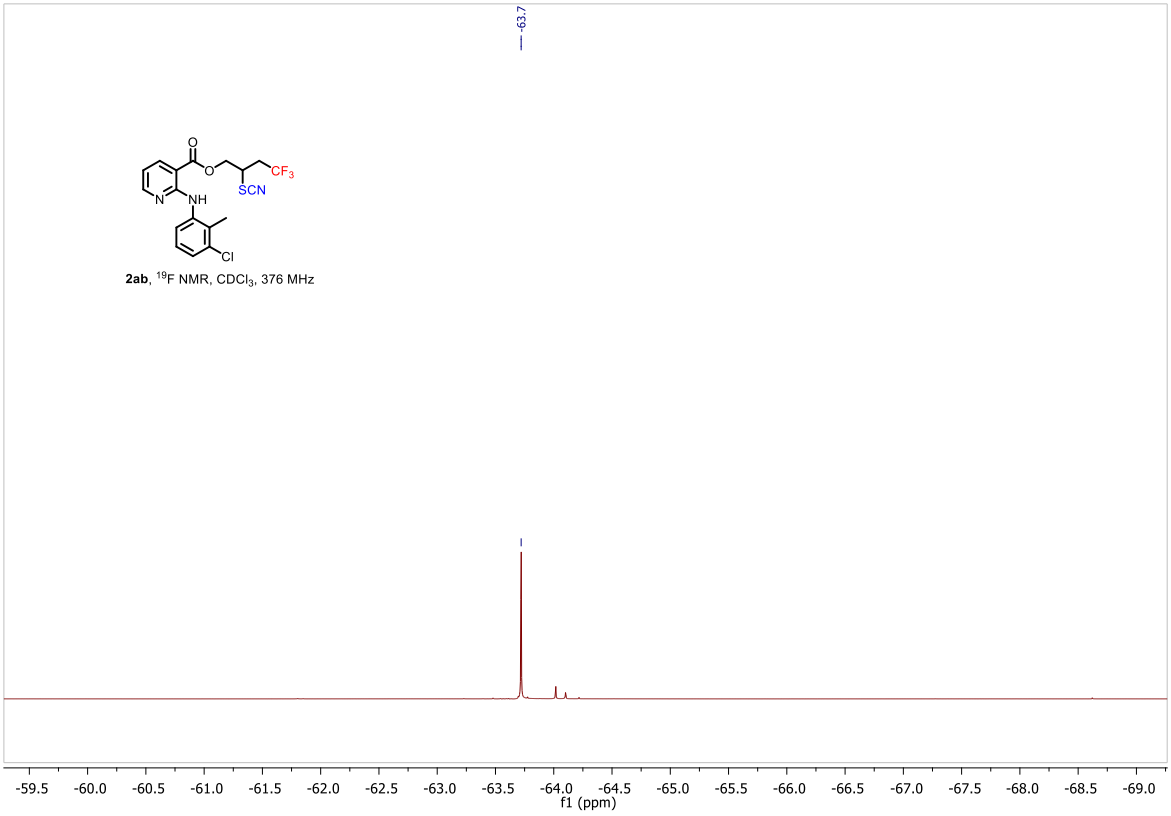

**2aa**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



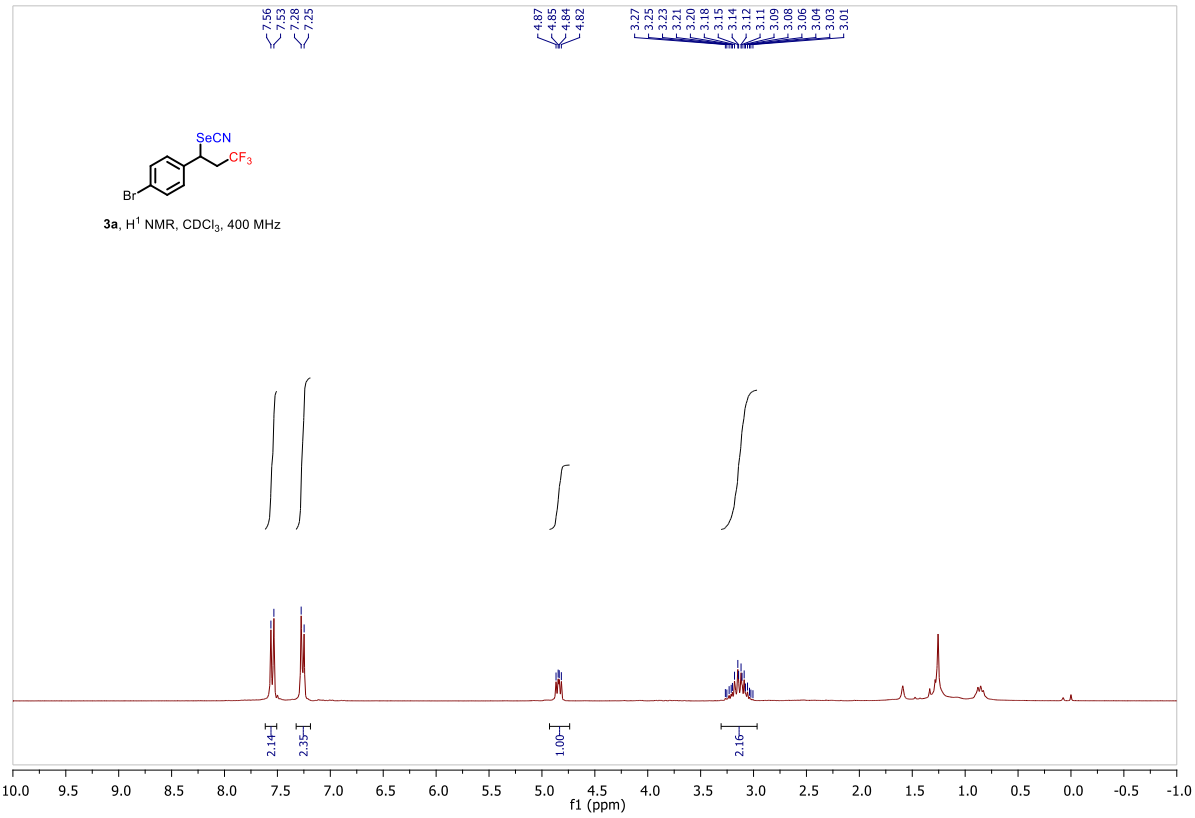

**2ab**, $H^1$ NMR, $CDCl_3$, 400 MHz

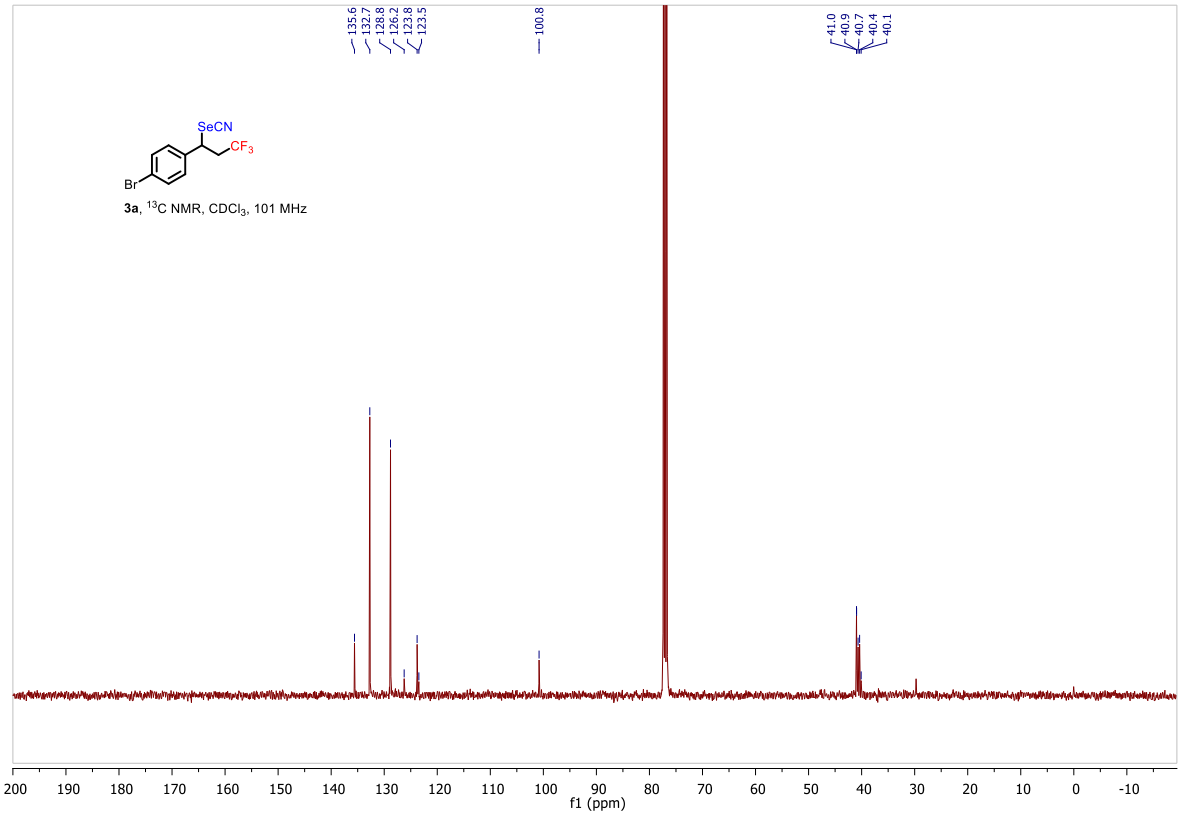


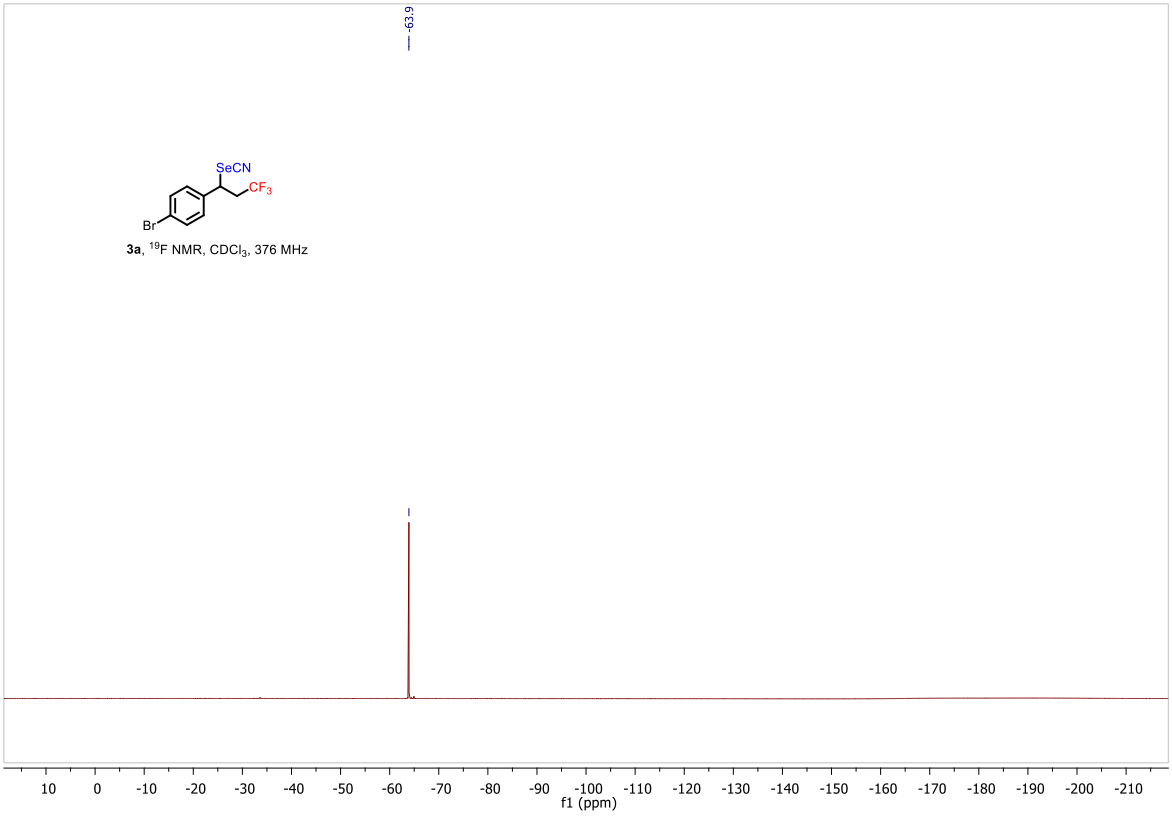

**2ab**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



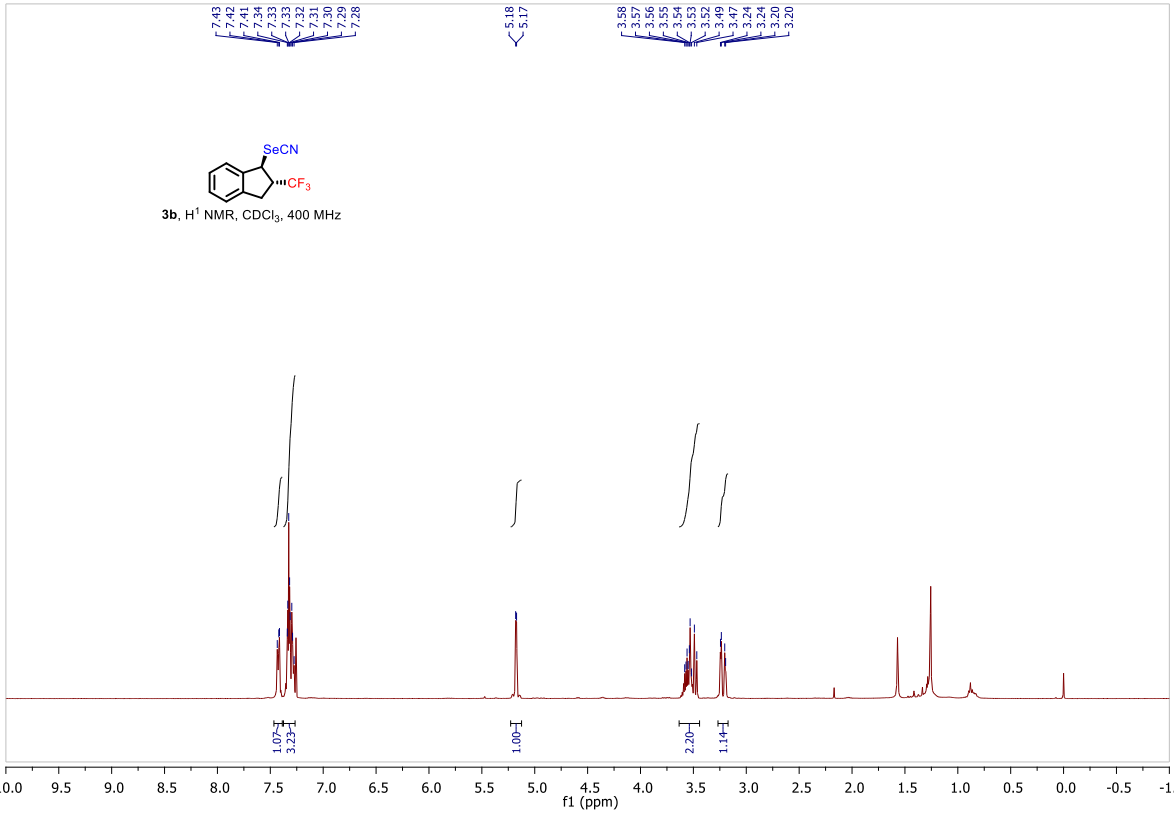

**2ab**, $^{19}F$ NMR, $CDCl_3$, 376 MHz


7.56
7.53
7.28
7.25
4.87
4.85
4.84
4.82
3.27
3.25
3.23
3.21
3.20
3.18
3.15
3.14
3.12
3.11
3.09
3.08
3.06
3.04
3.03
3.01
SeCN
CF3
Br
3a, H1 NMR, CDCl3, 400 MHz
2.14
2.35
1.00
2.16
f1 (ppm)

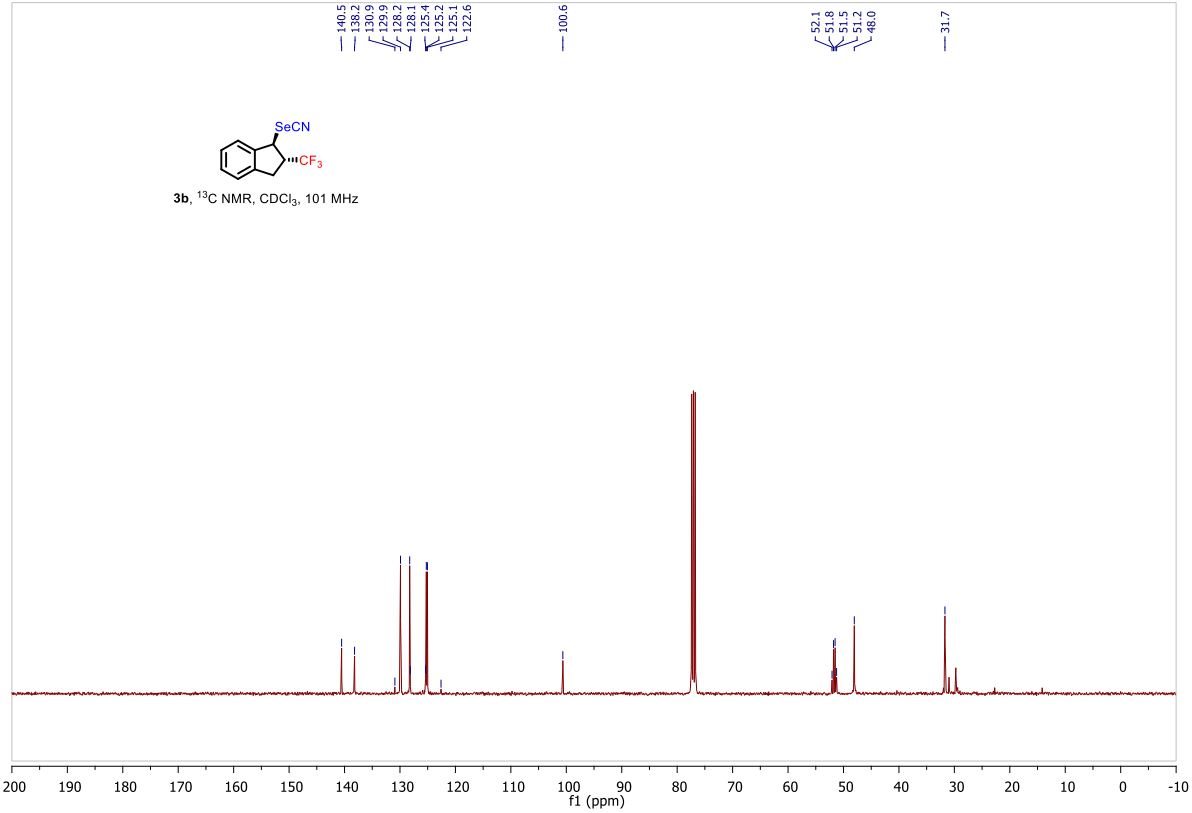

135.6
132.7
128.8
126.2
123.8
123.5
100.8
41.0
40.9
40.7
40.4
40.1
SeCN
CF3
Br
3a, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



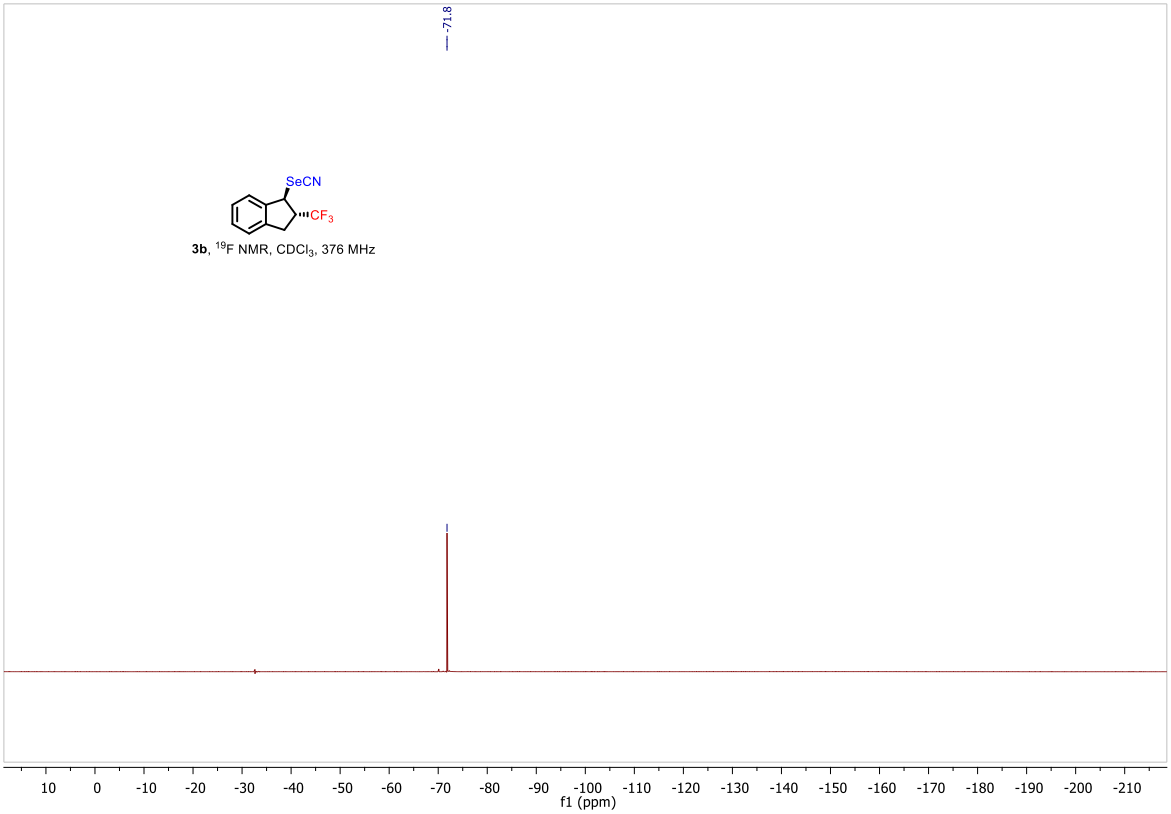

**3a**, $^{19}F$ NMR, $CDCl_3$, 376 MHz

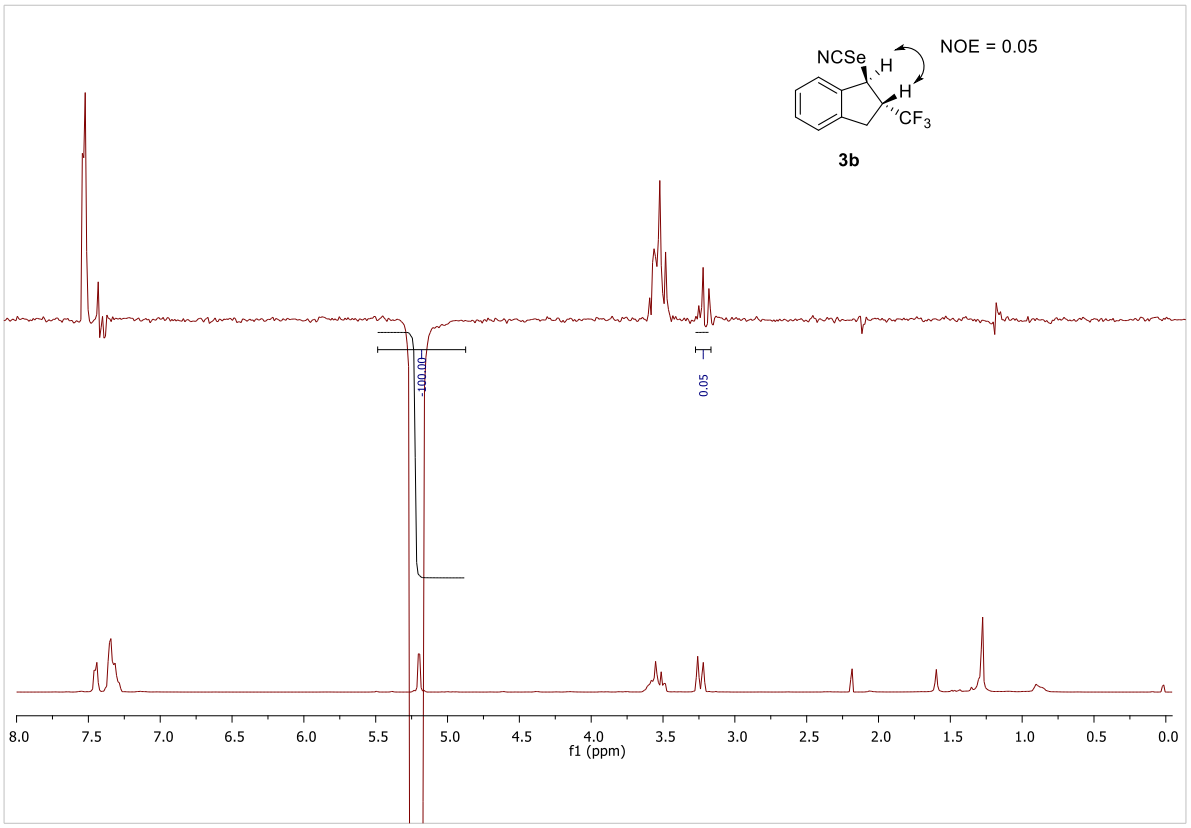


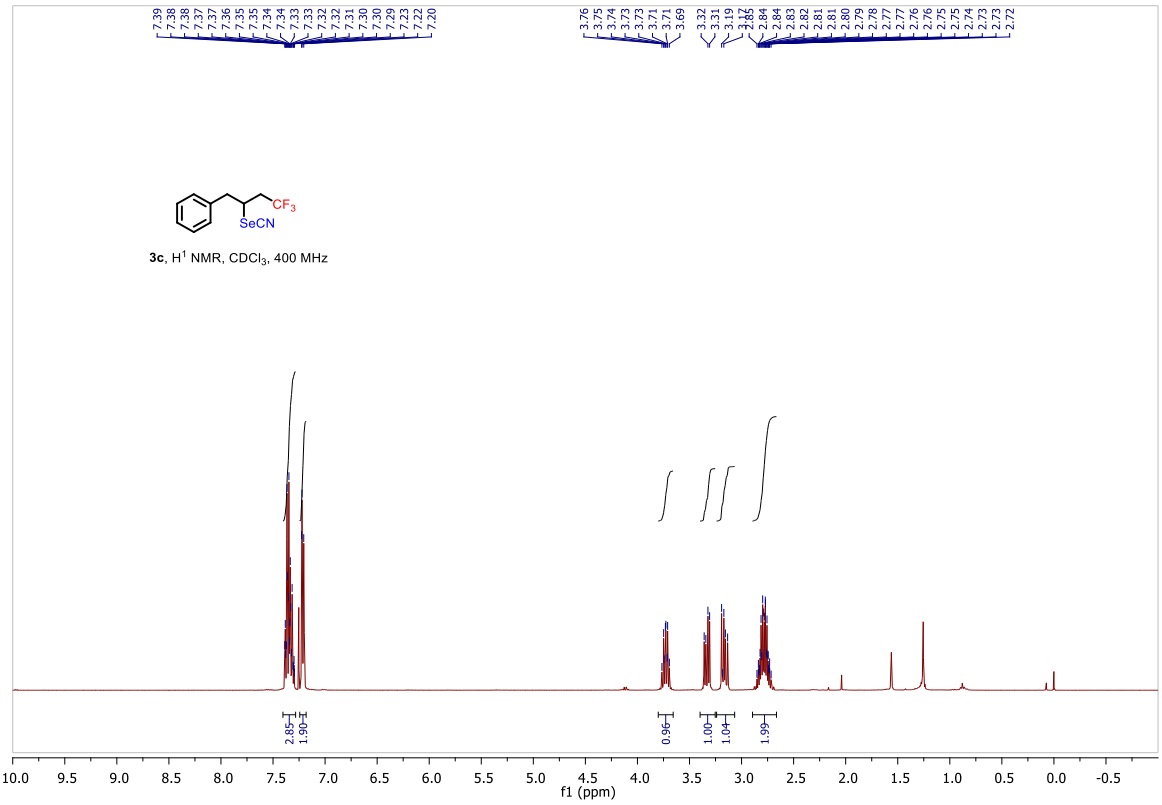

**3b**, $H^1$ NMR, $CDCl_3$, 400 MHz



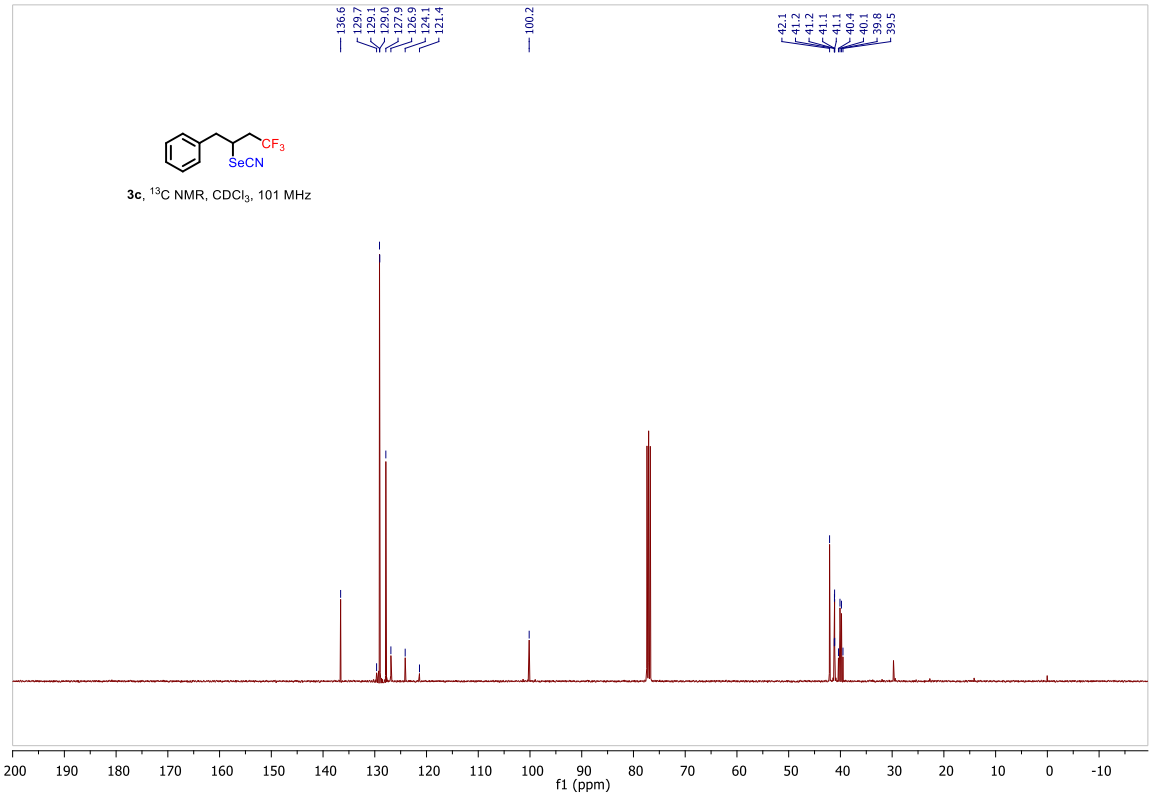

**3b**, $^{13}C$ NMR, $CDCl_3$, 101 MHz


-71.8
SeCN
CF3
3b, 19F NMR, CDCl3, 376 MHz
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

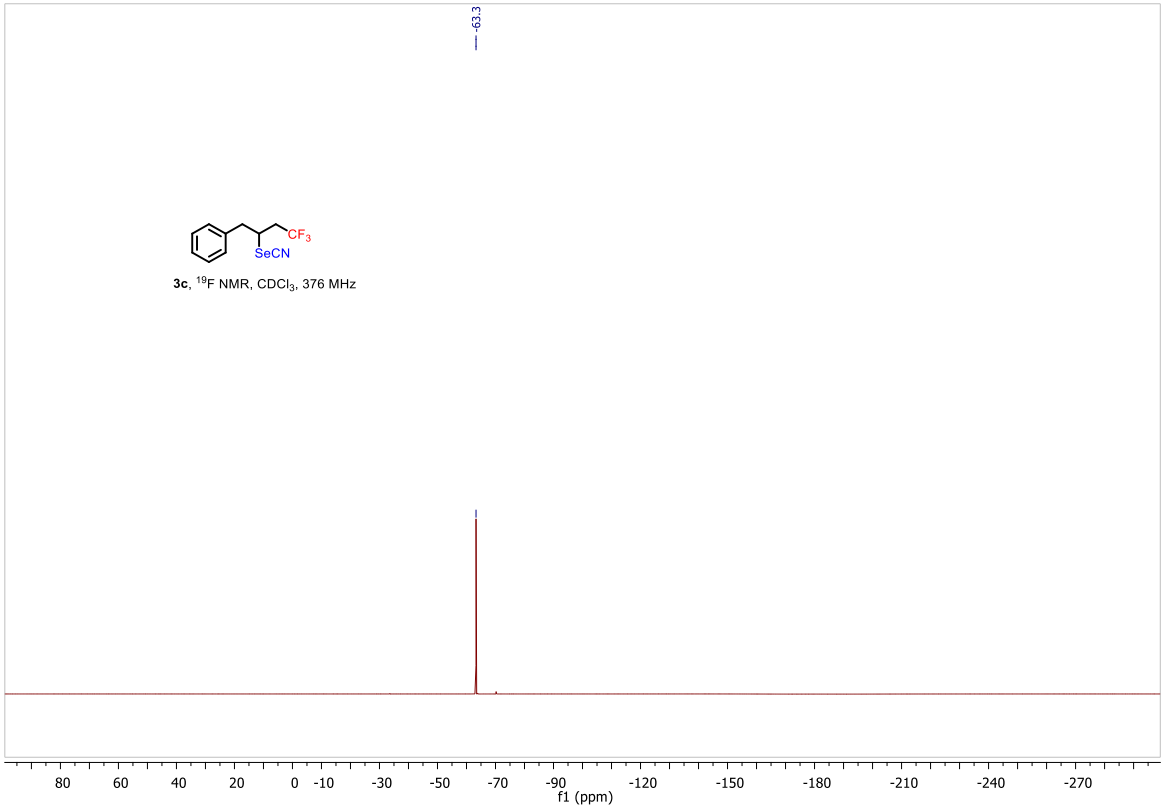

NCSe
H
H
CF3
NOE = 0.05
3b
-100.00
0.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



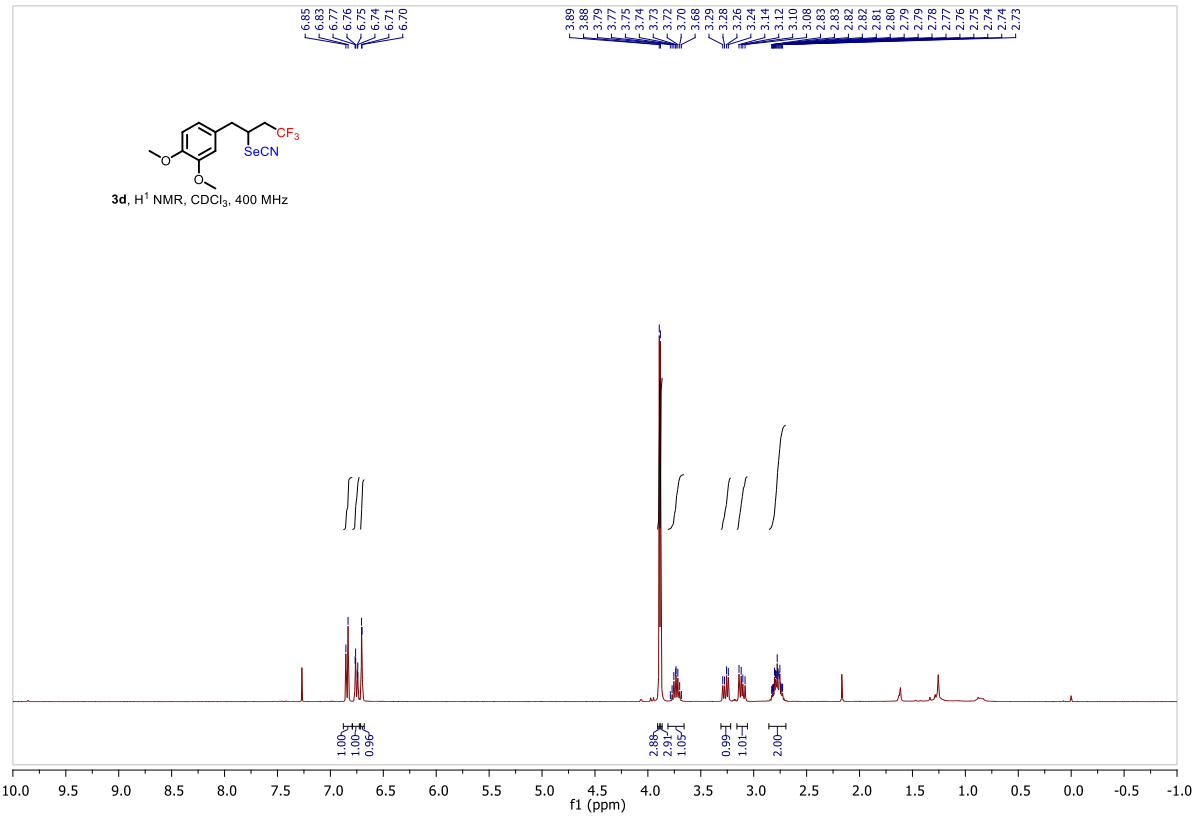

**3c**, $H^1$ NMR, $CDCl_3$, 400 MHz



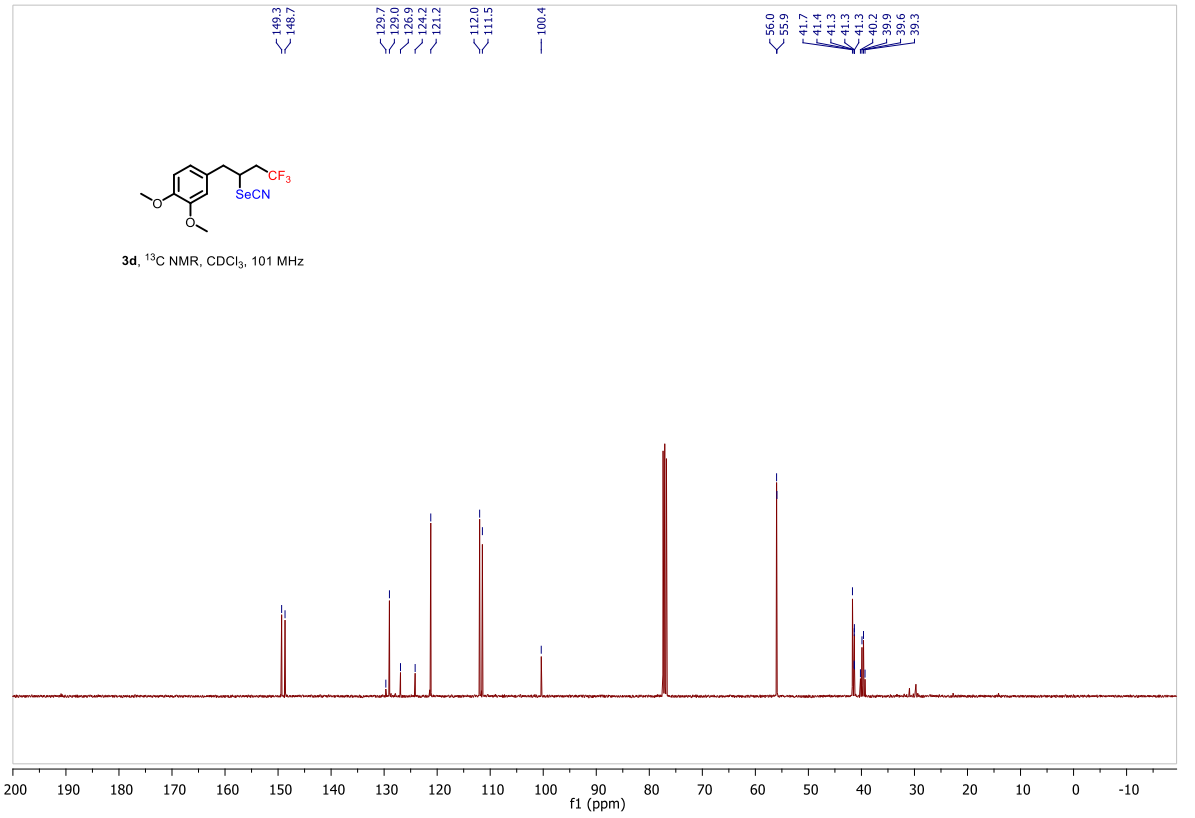

**3c**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



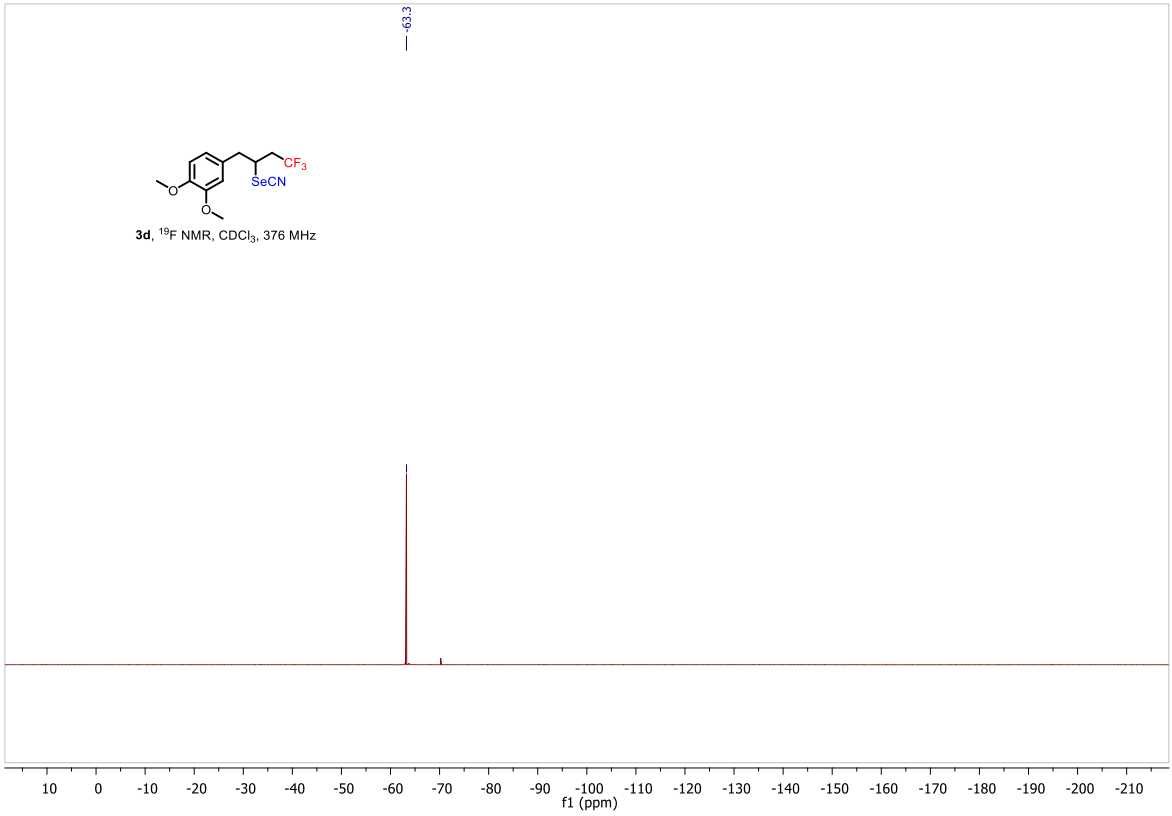

**3c**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



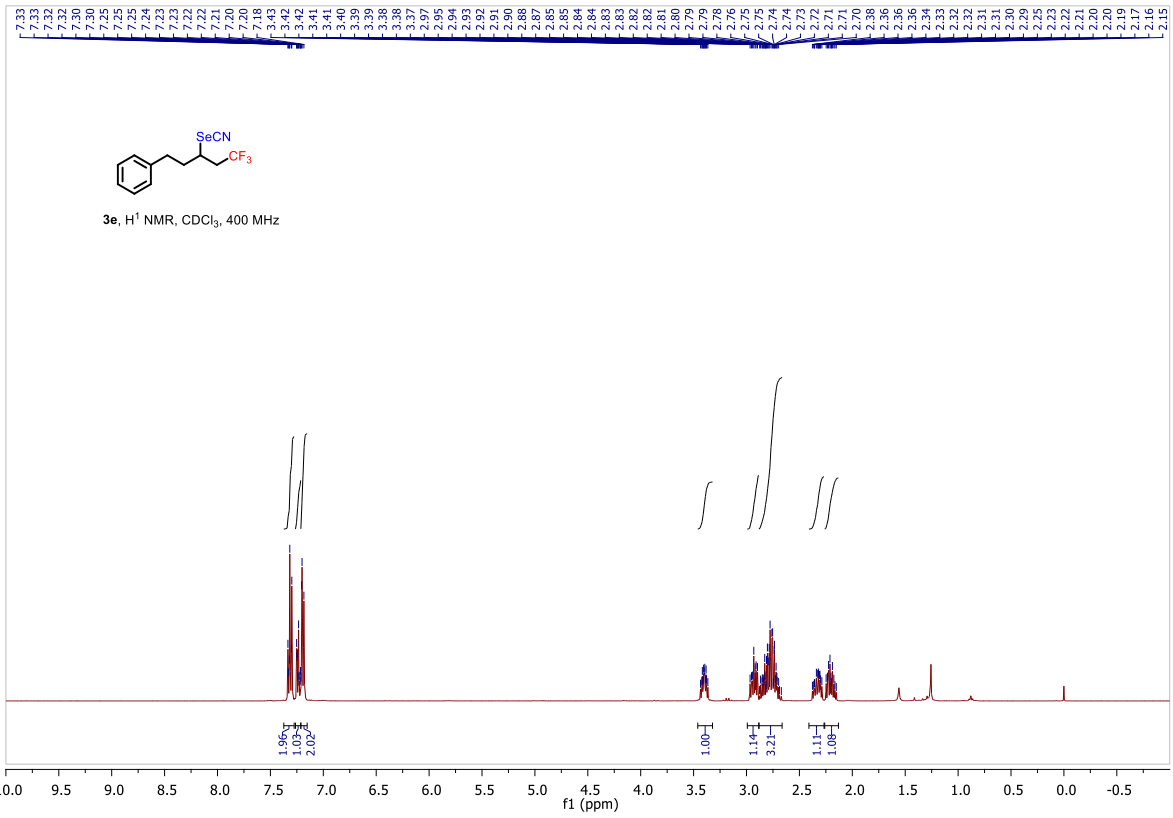

**3d**, $H^1$ NMR, $CDCl_3$, 400 MHz

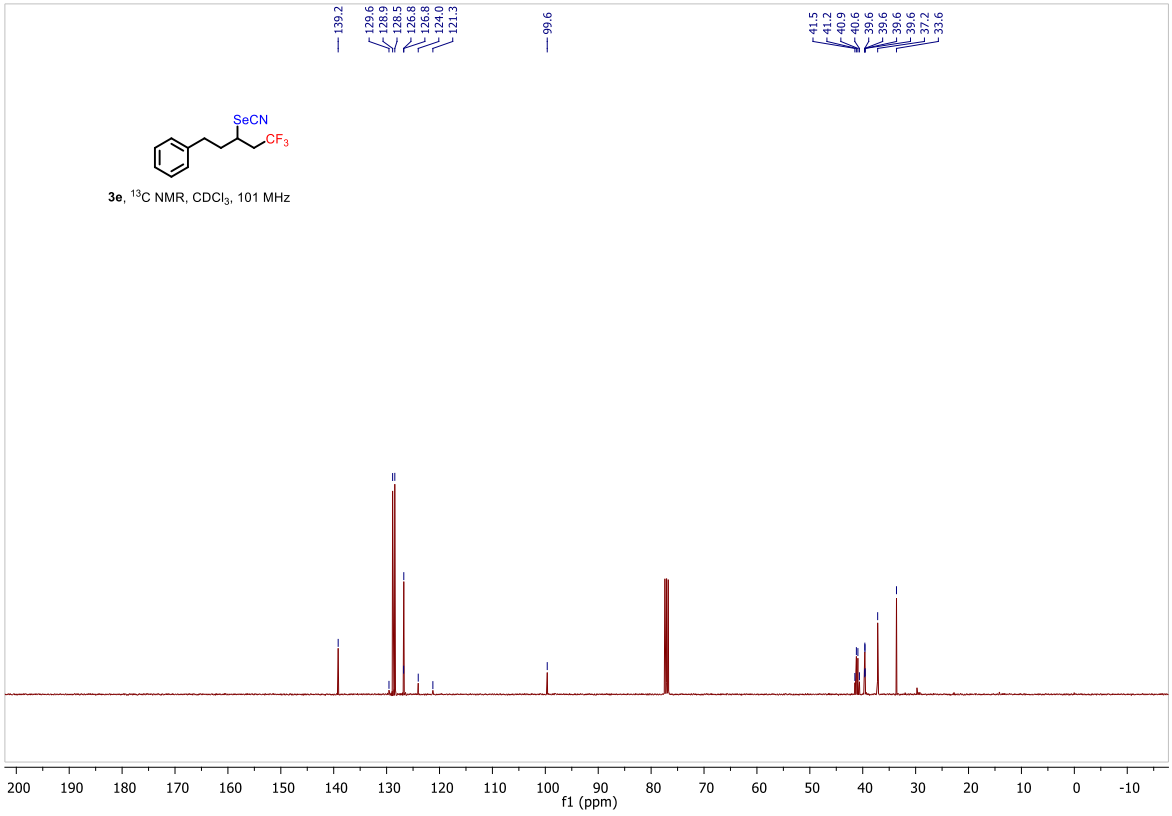


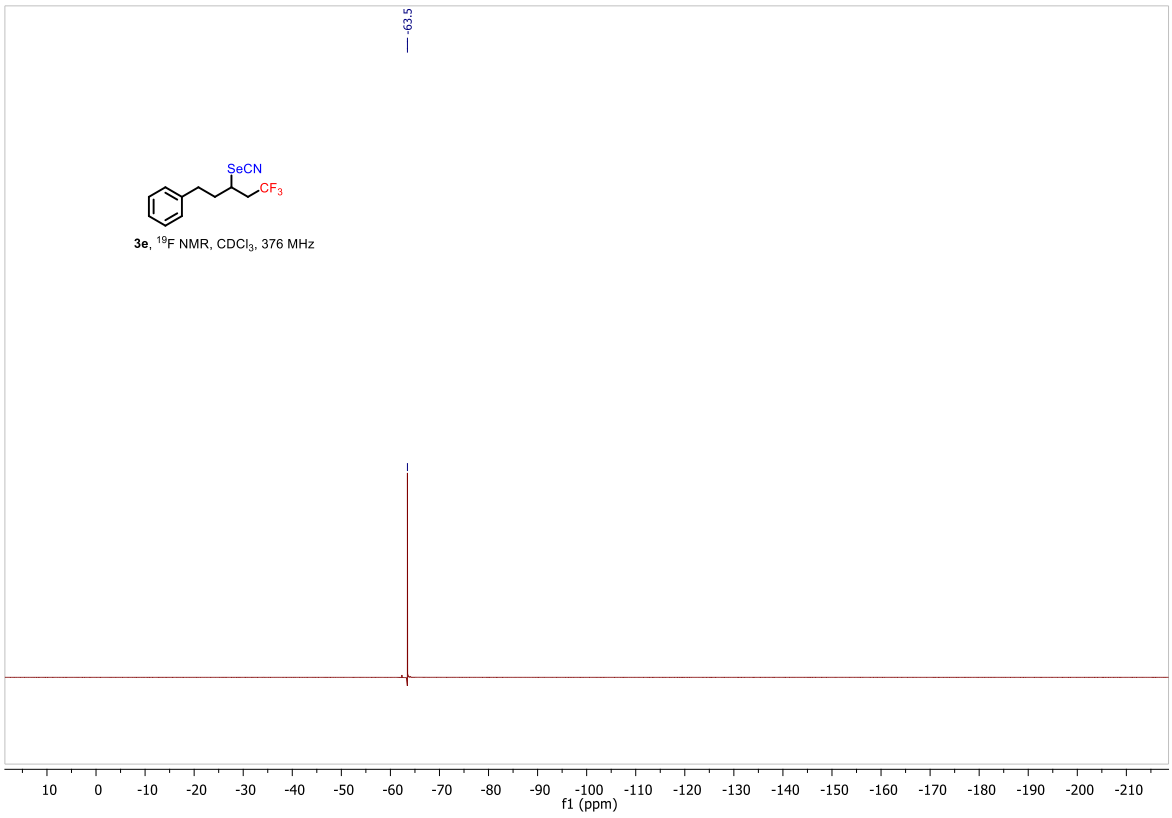

**3d**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



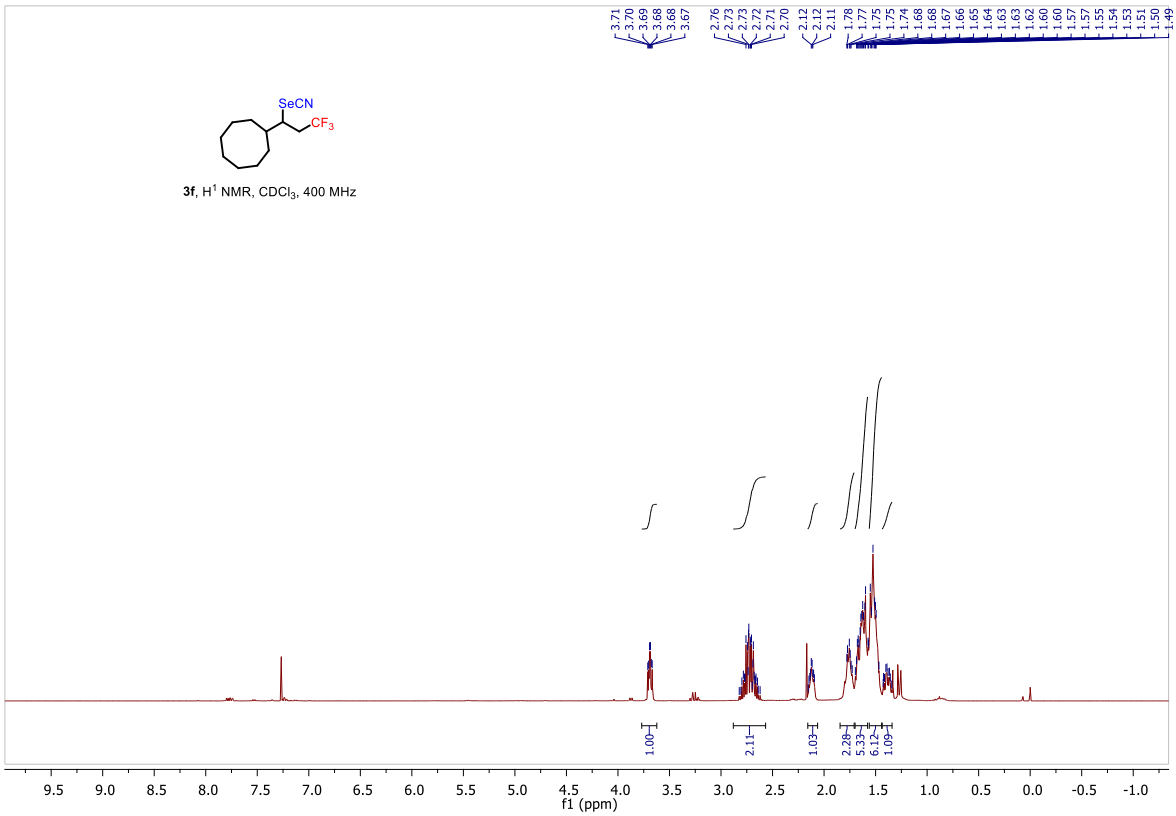

**3d**, $^{19}F$ NMR, $CDCl_3$, 376 MHz


SeCN
CF3
3e, H1 NMR, CDCl3, 400 MHz
1.96
1.03
2.02
1.00
1.14
3.21
1.11
1.08
f1 (ppm)

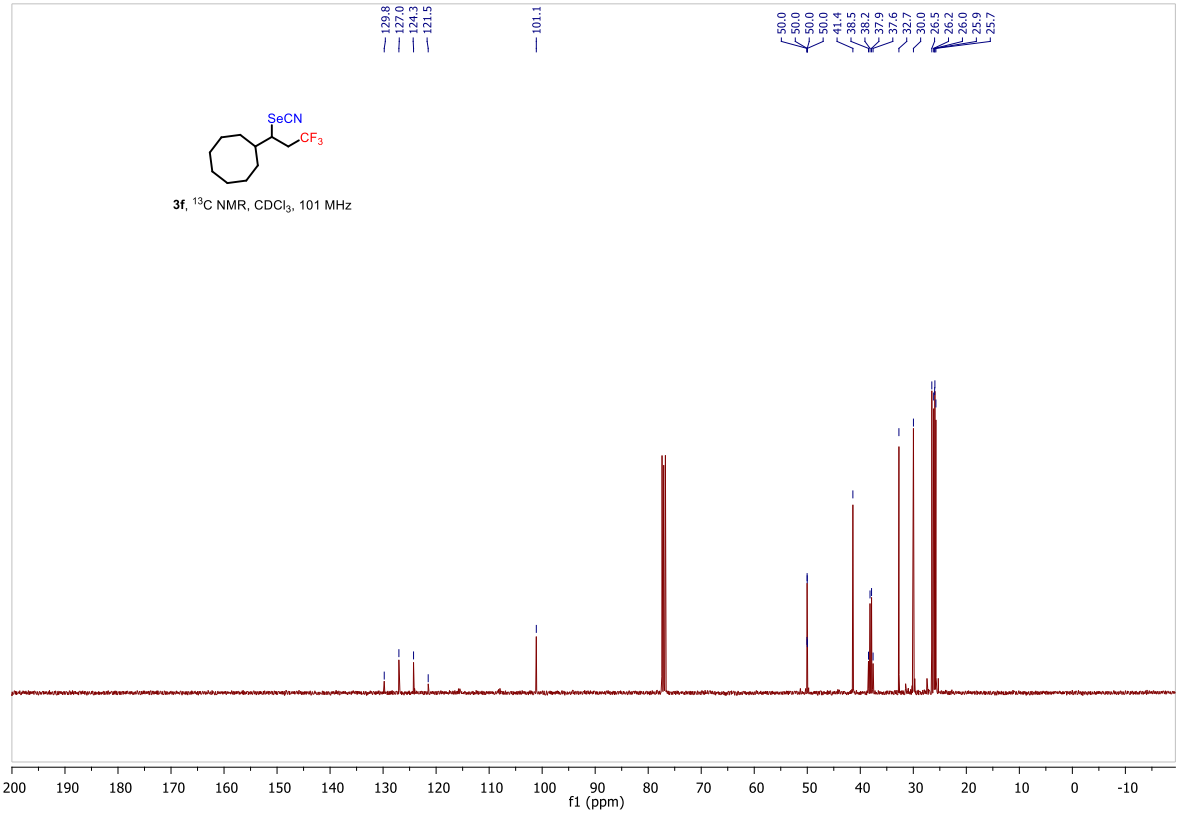

SeCN
CF3
3e, 13C NMR, CDCl3, 101 MHz
f1 (ppm)



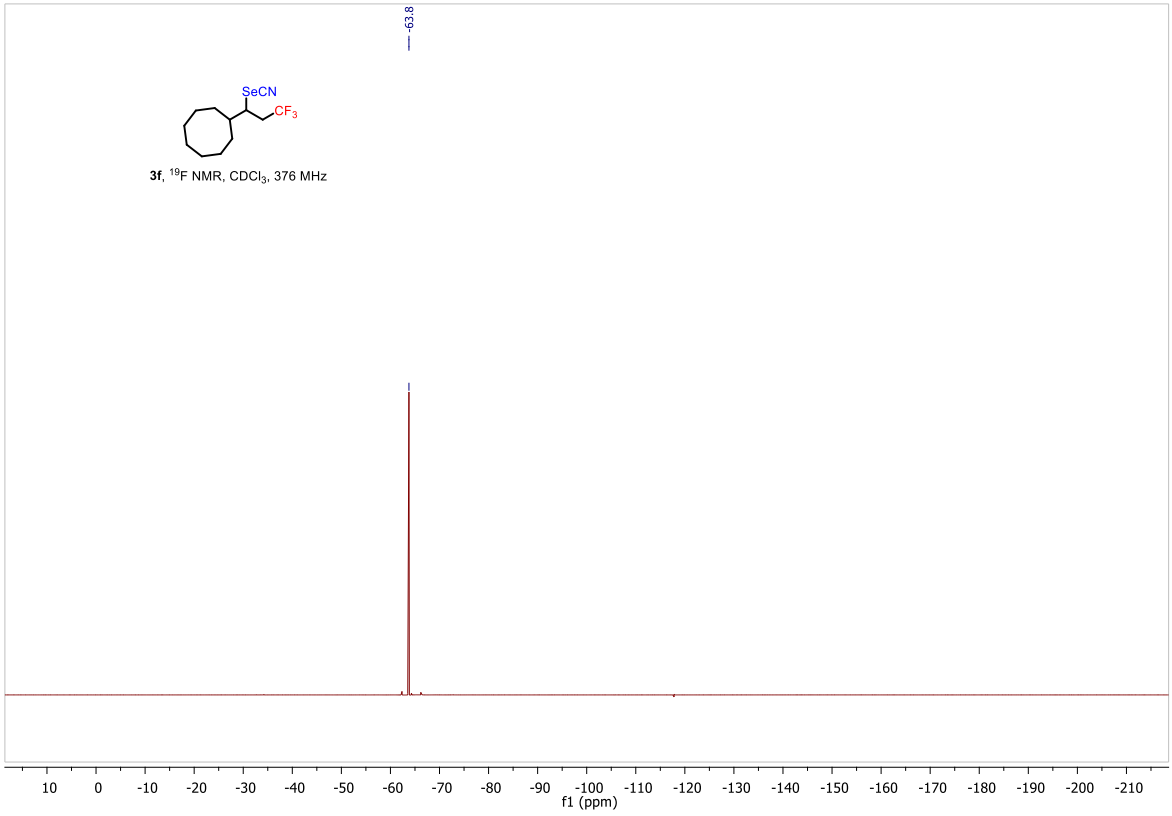

**3e**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



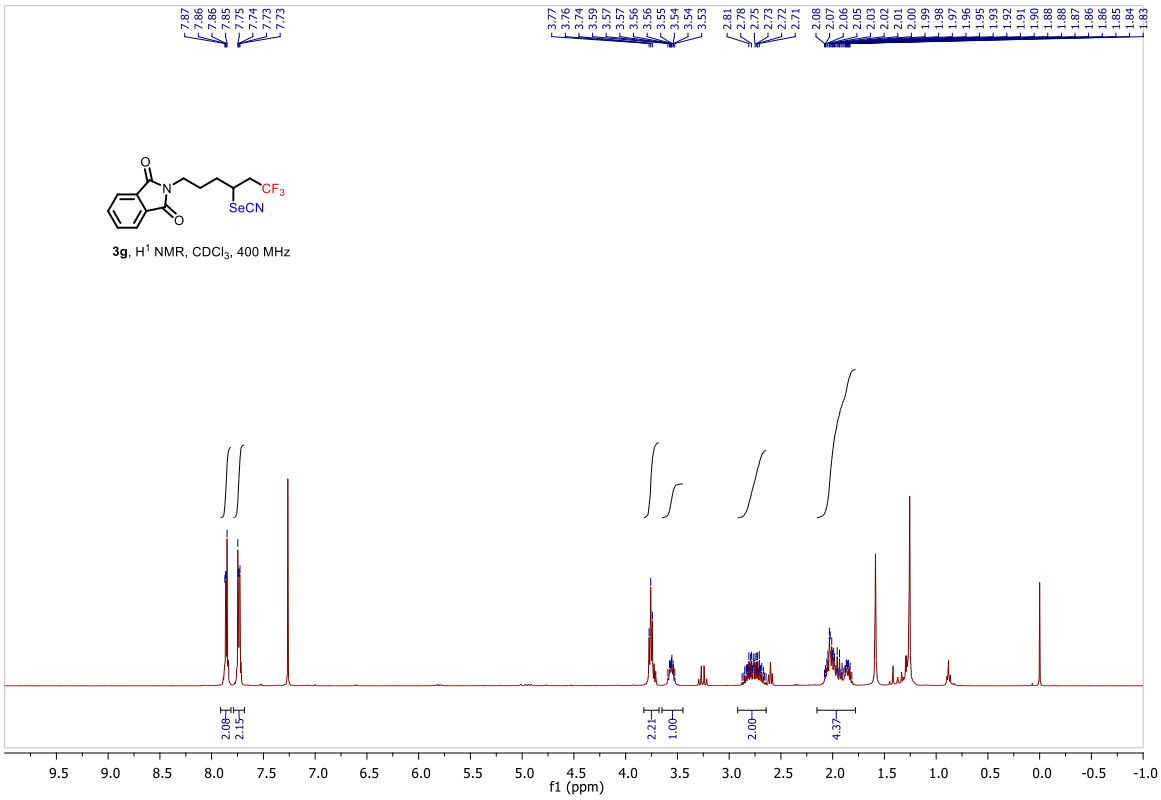

**3f**, $H^1$ NMR, $CDCl_3$, 400 MHz



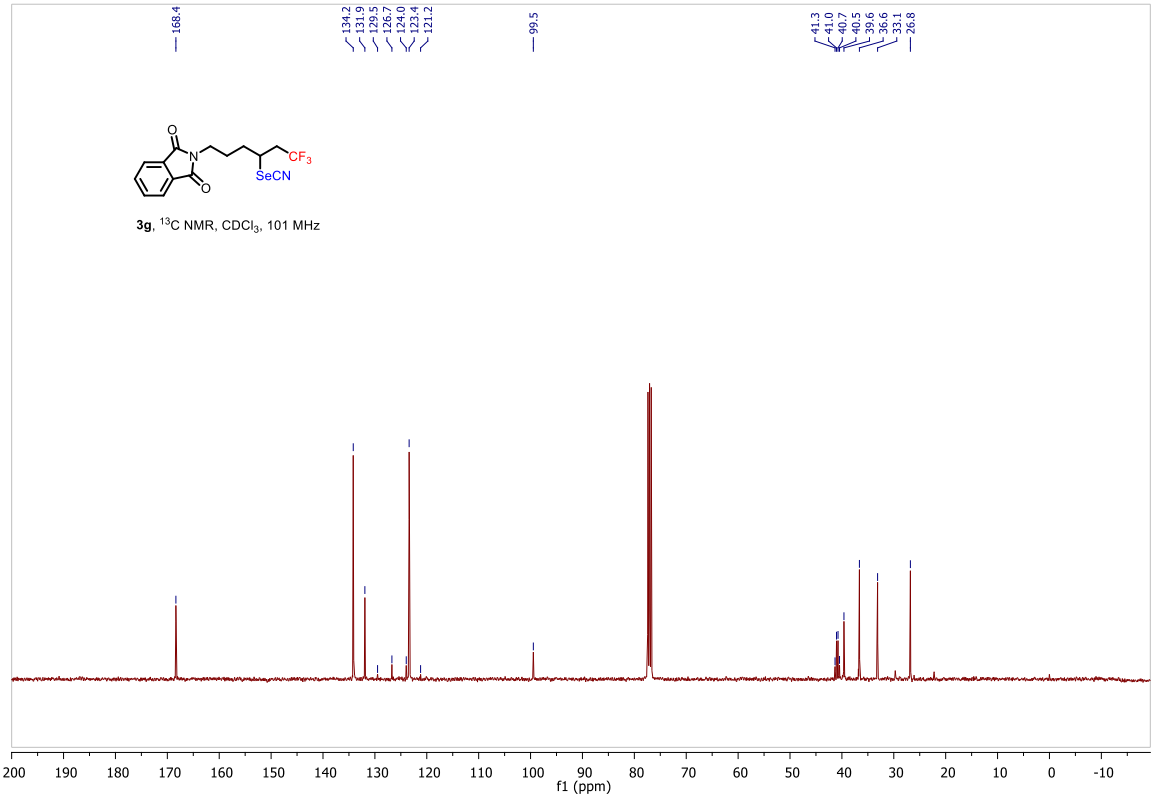

**3f**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



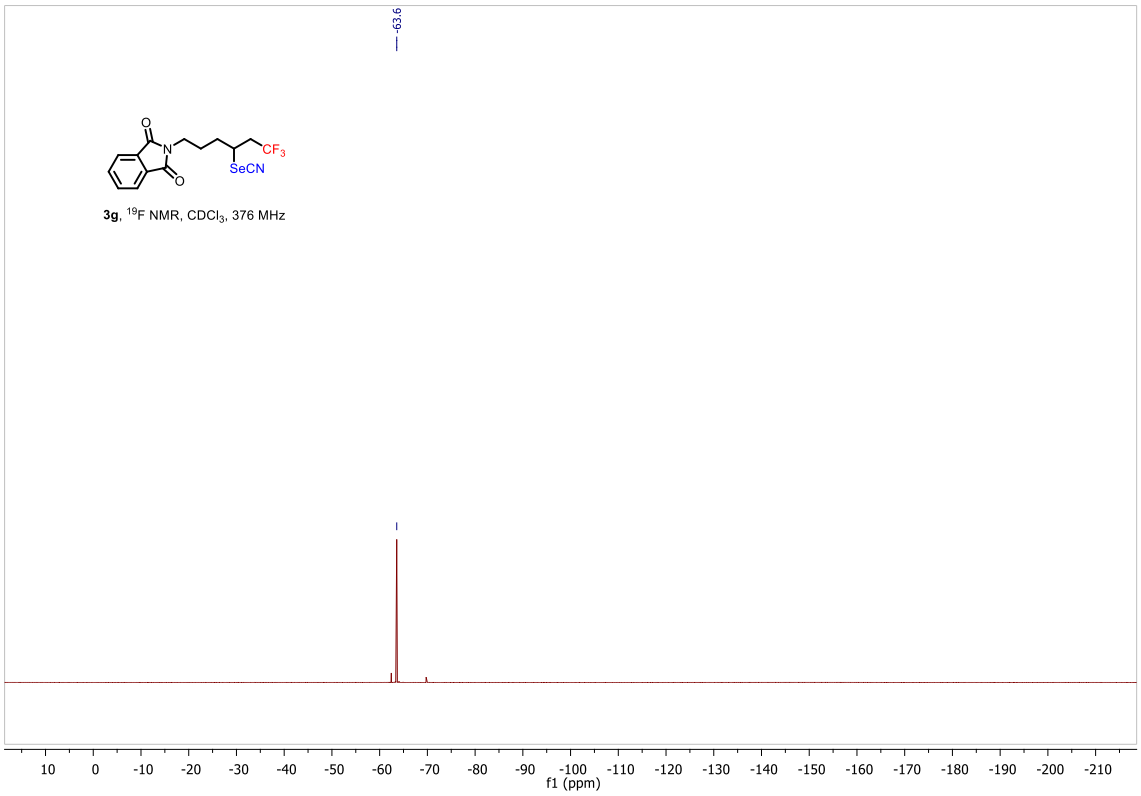

**3f**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



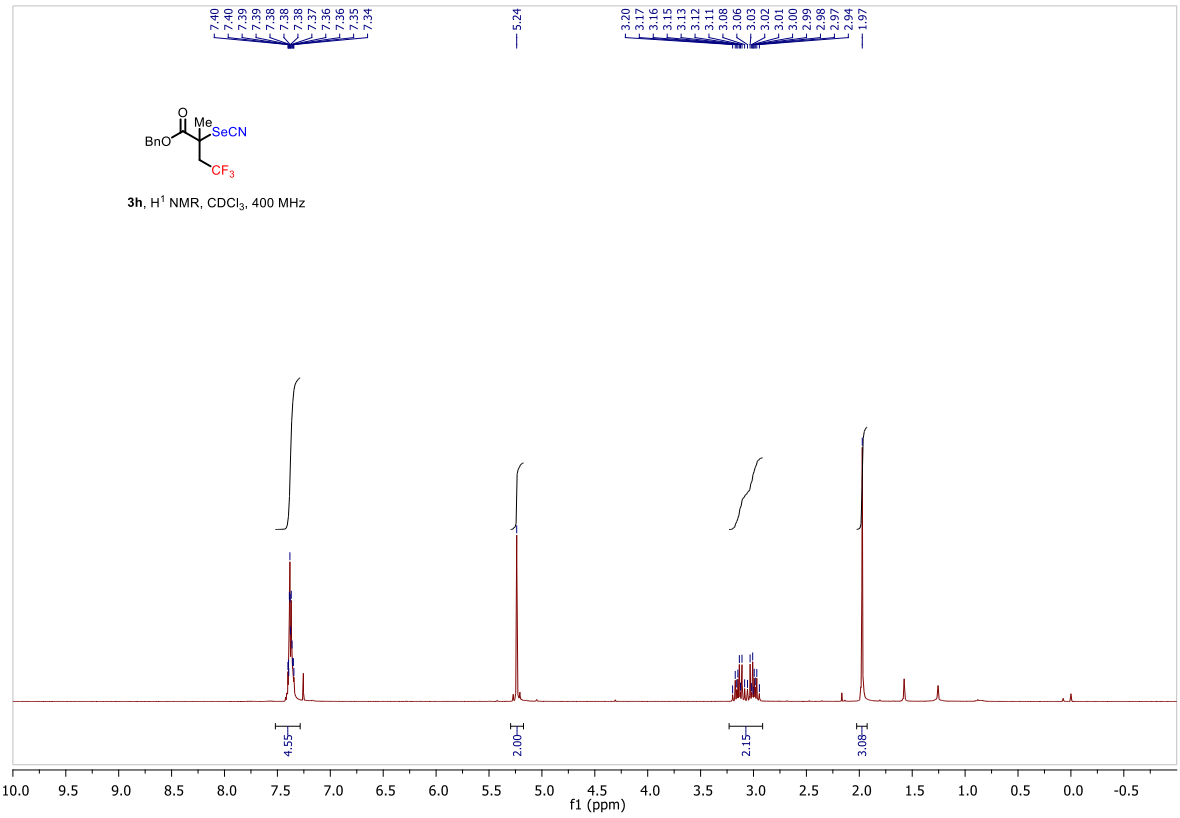

**3g**, $H^1$ NMR, $CDCl_3$, 400 MHz



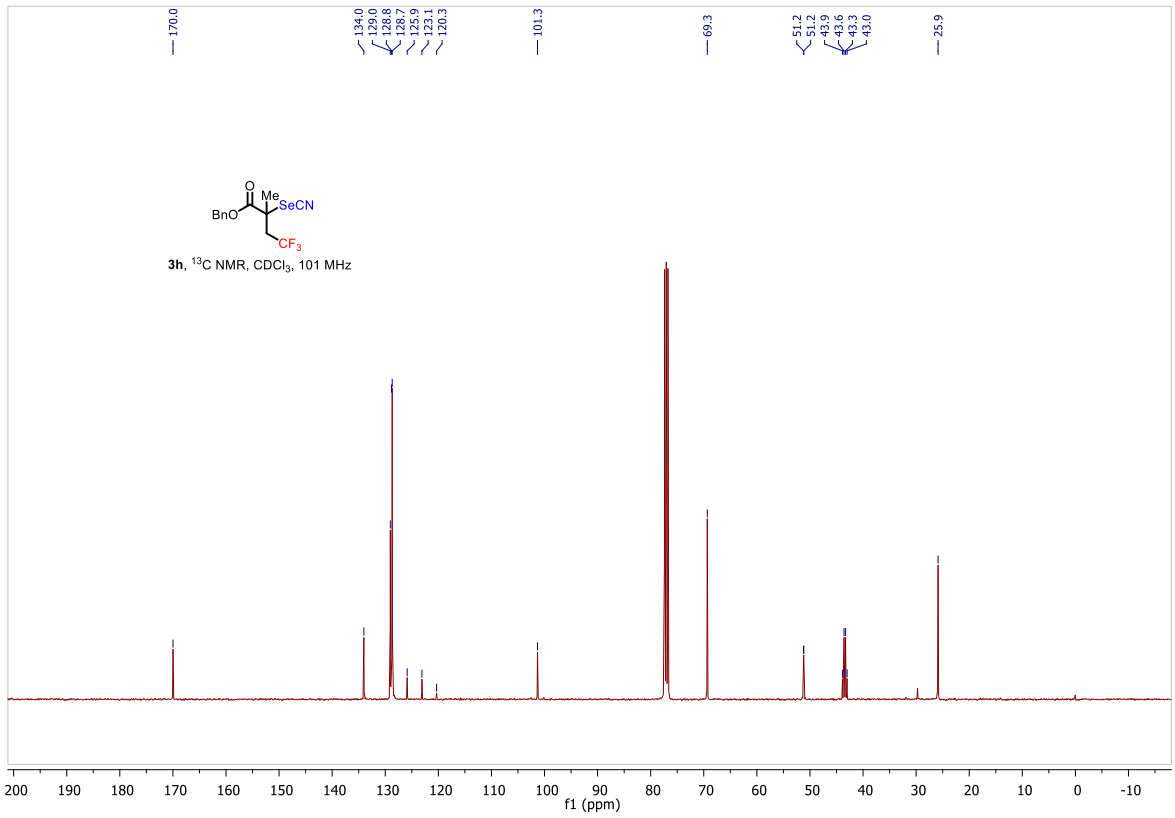

**3g**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



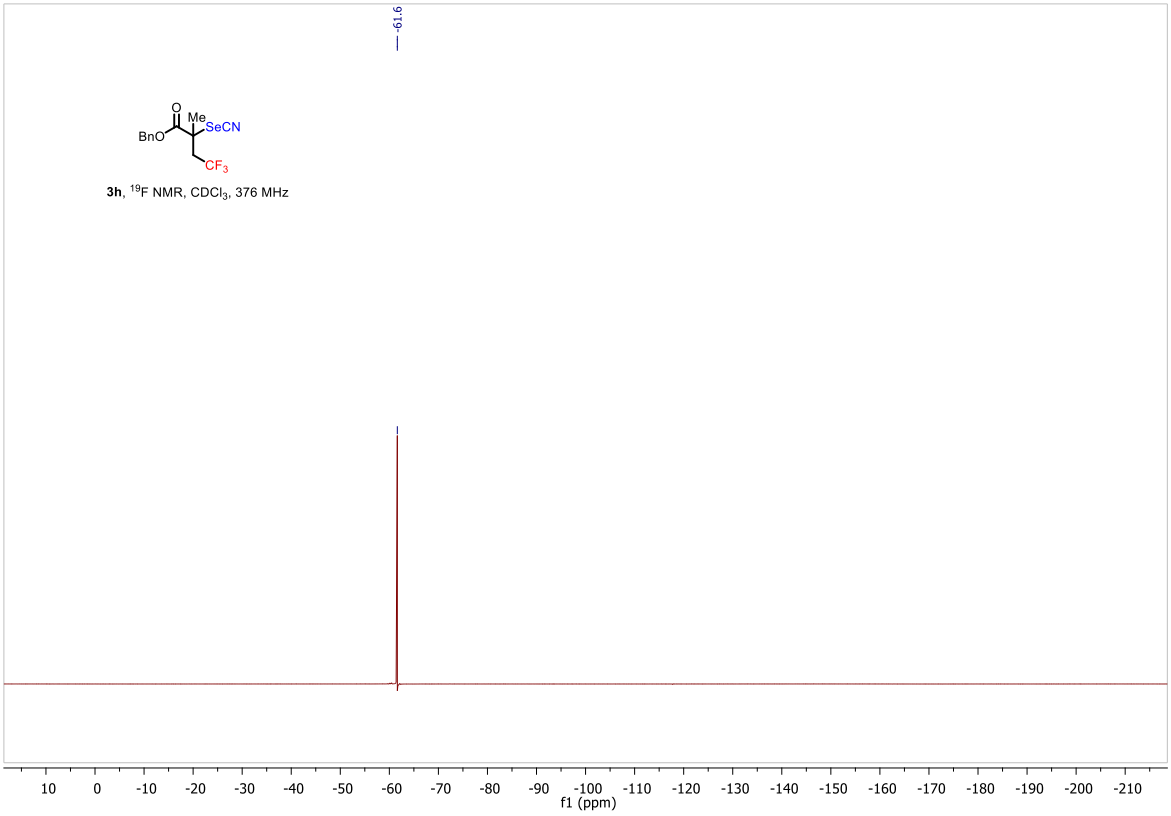

**3g**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



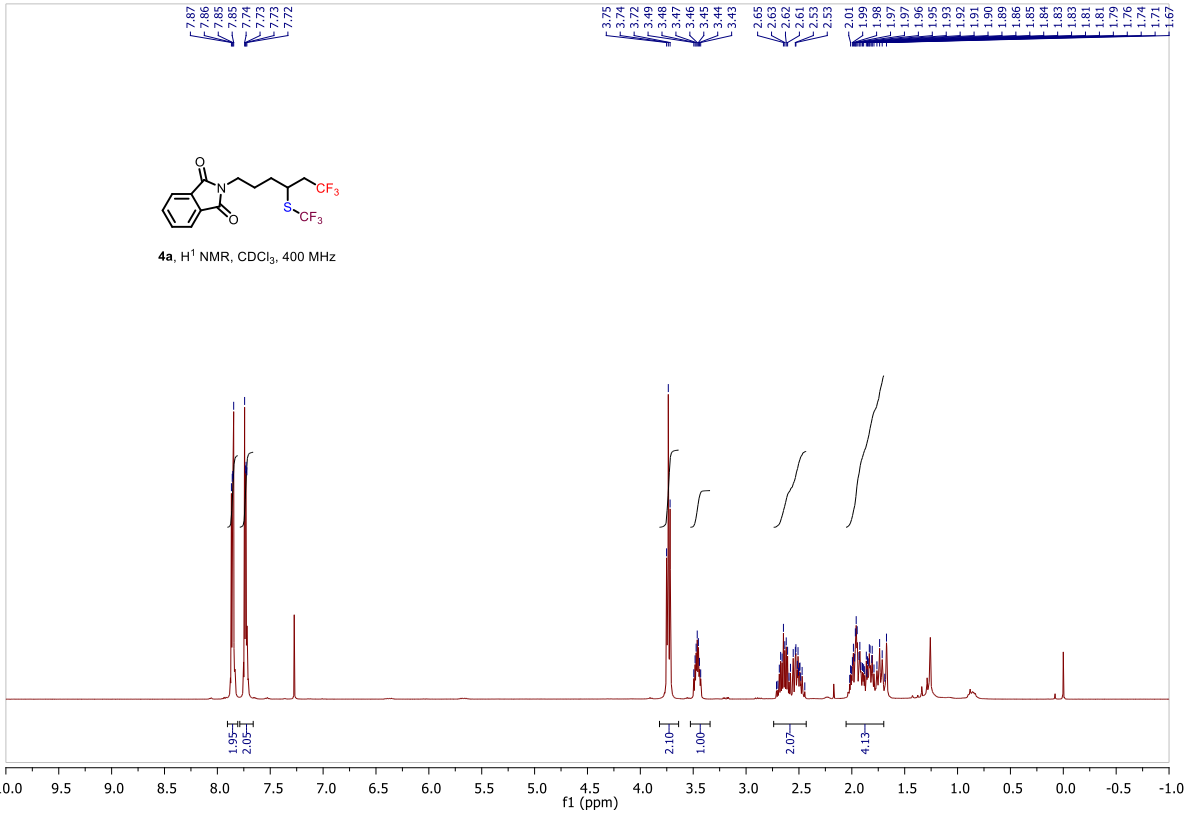

**3h**, $H^1$ NMR, $CDCl_3$, 400 MHz



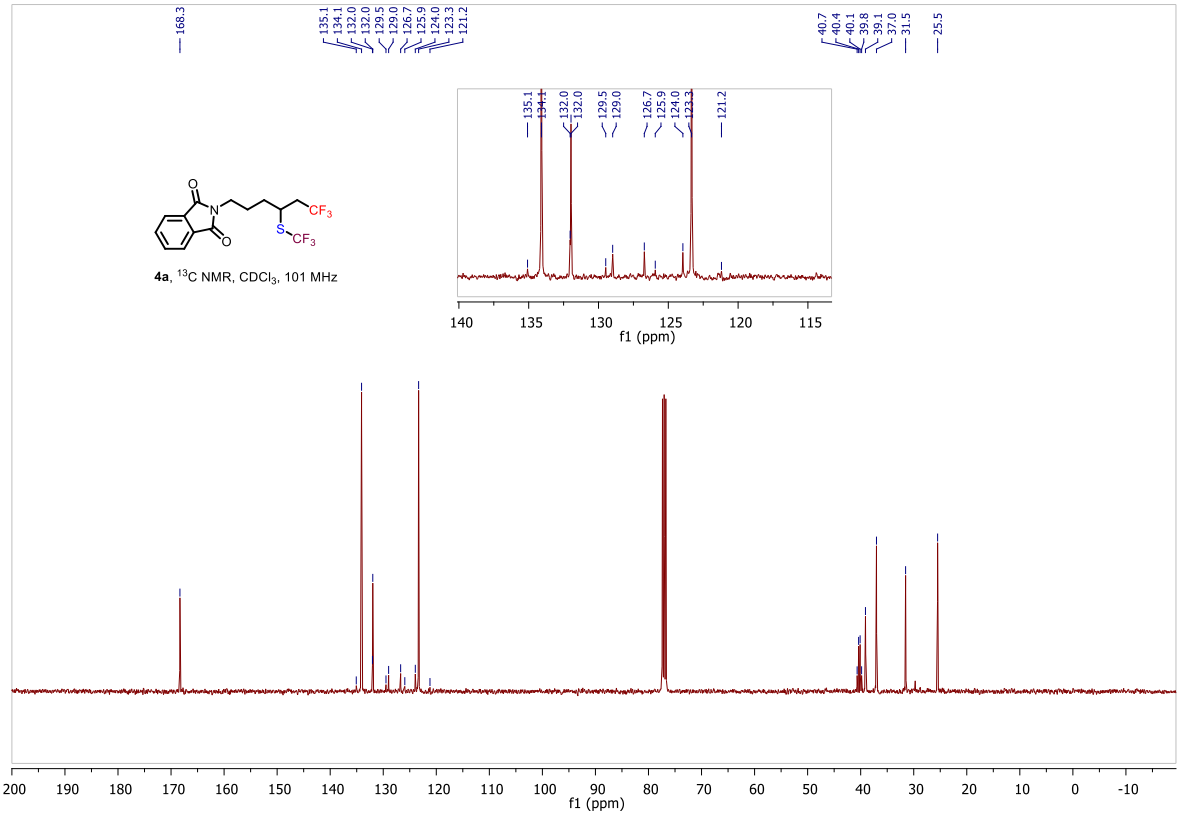

**3h**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



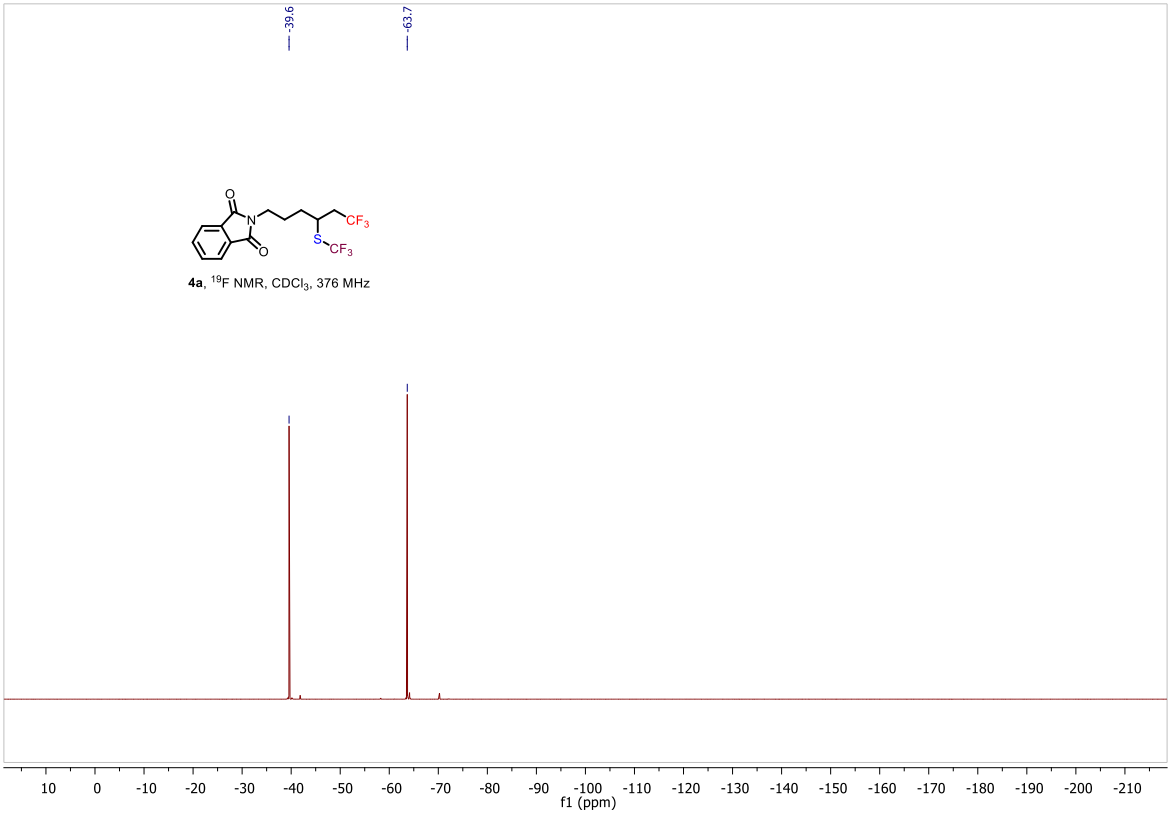

**3h**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



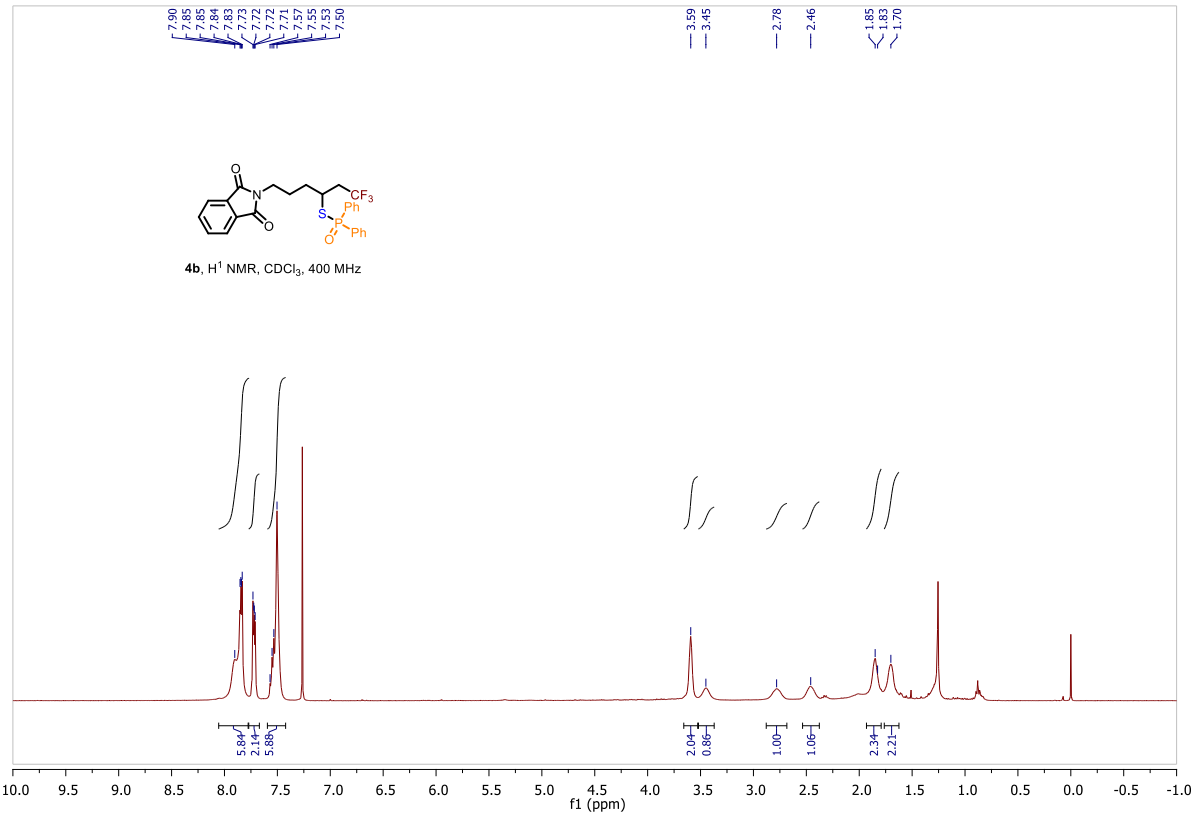

**4a**, $H^1$ NMR, $CDCl_3$, 400 MHz



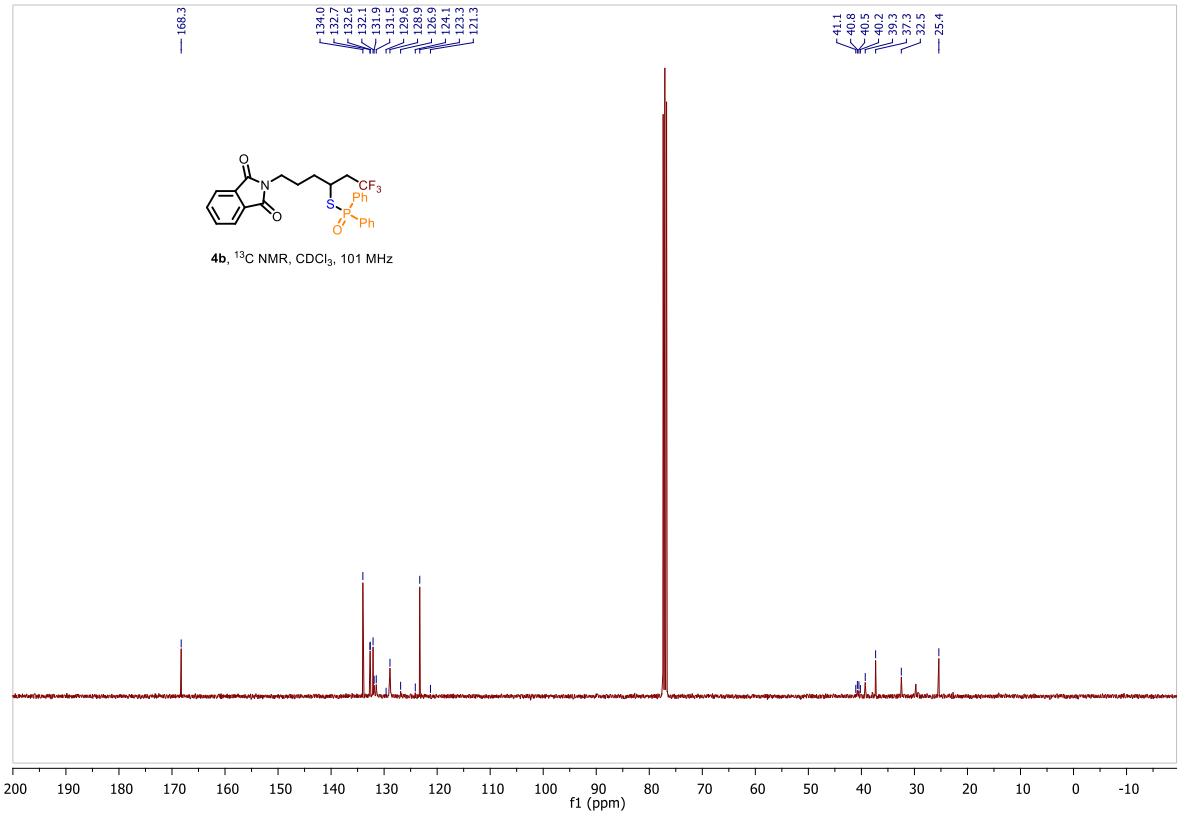

**4a**, $^{13}C$ NMR, $CDCl_3$, 101 MHz



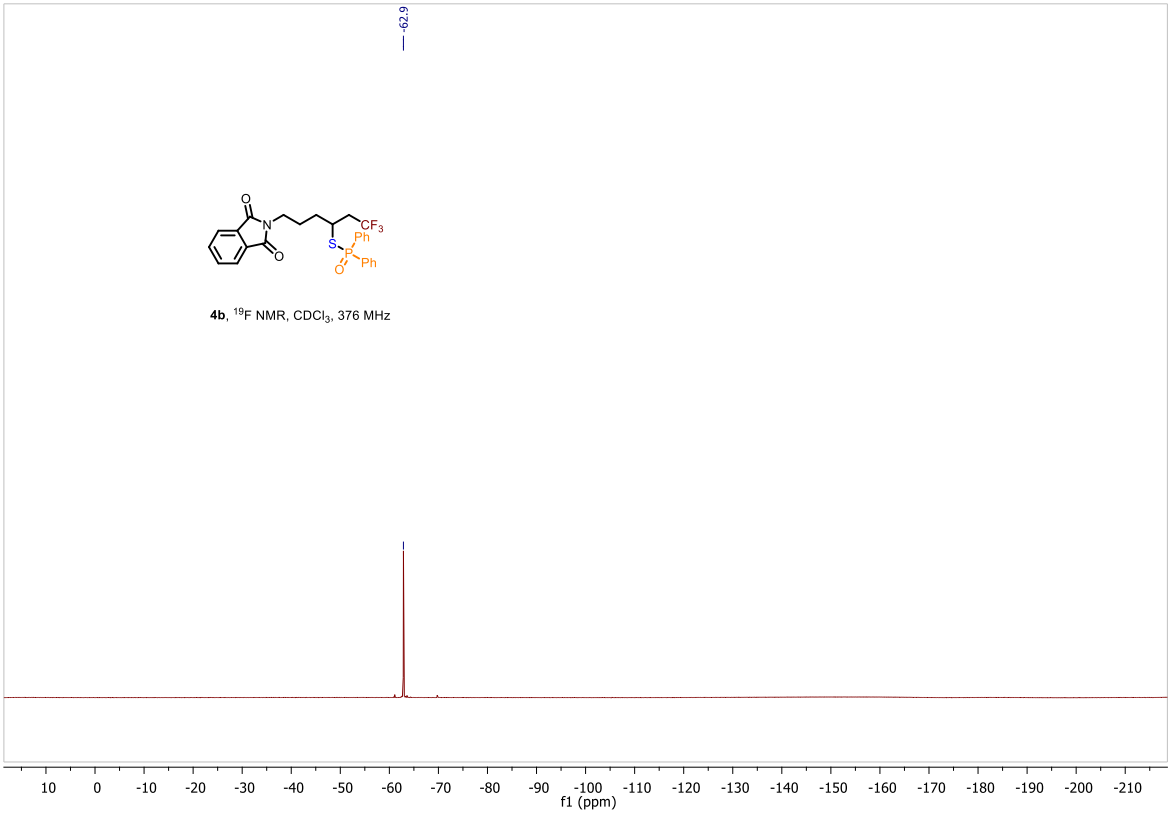

**4a**, $^{19}F$ NMR, $CDCl_3$, 376 MHz



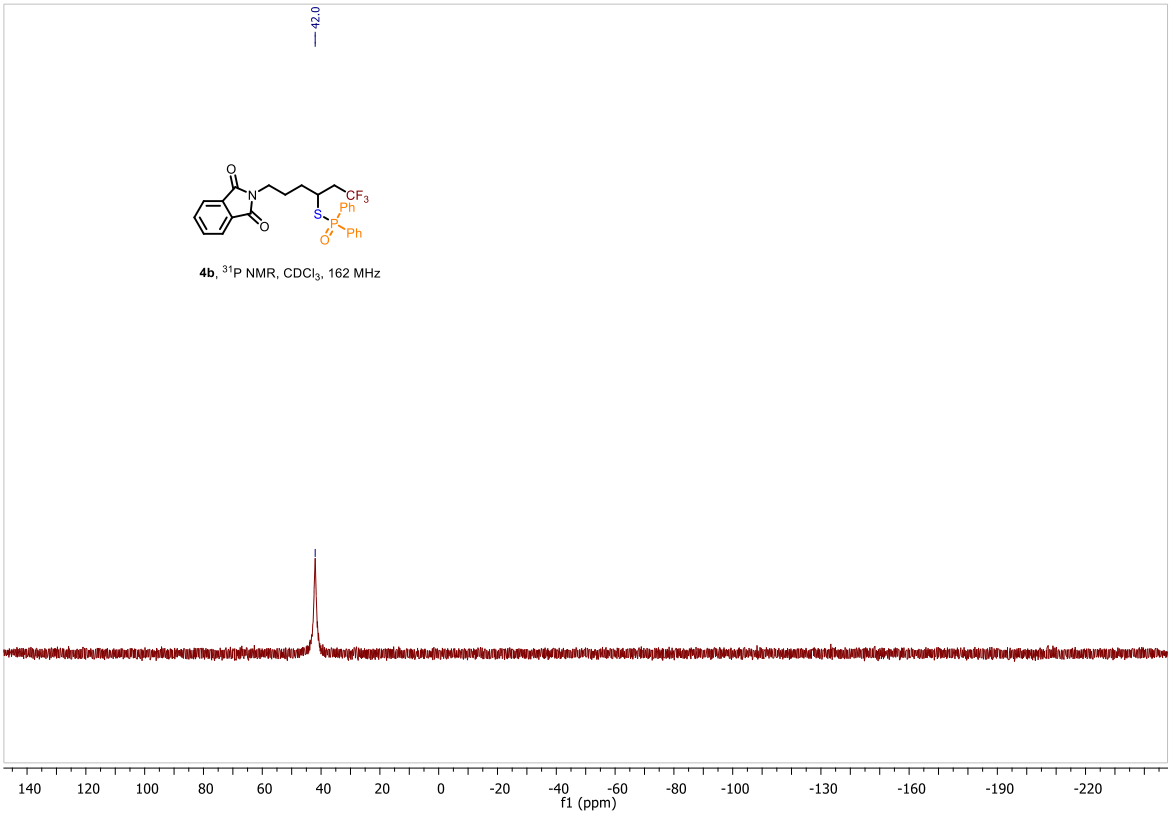

**4b**, $H^1$ NMR, $CDCl_3$, 400 MHz



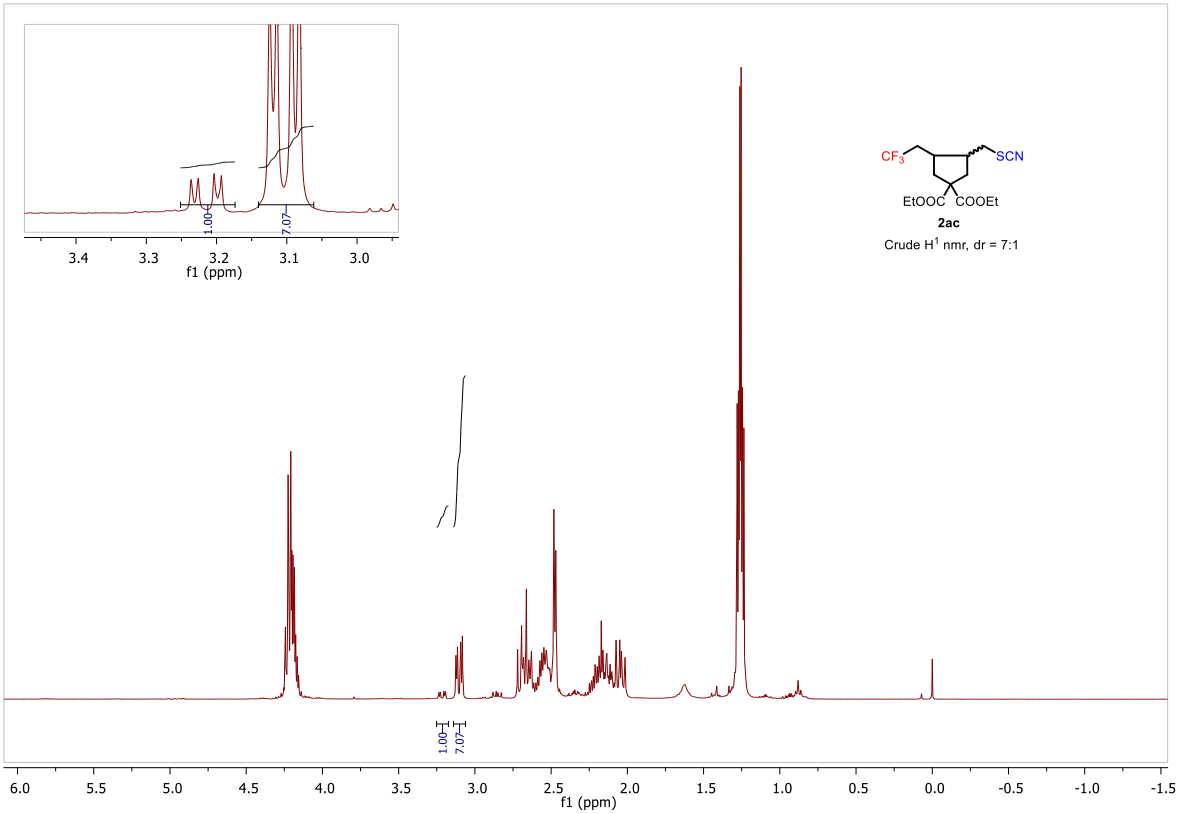

**4b**, $^{13}C$ NMR, $CDCl_3$, 101 MHz

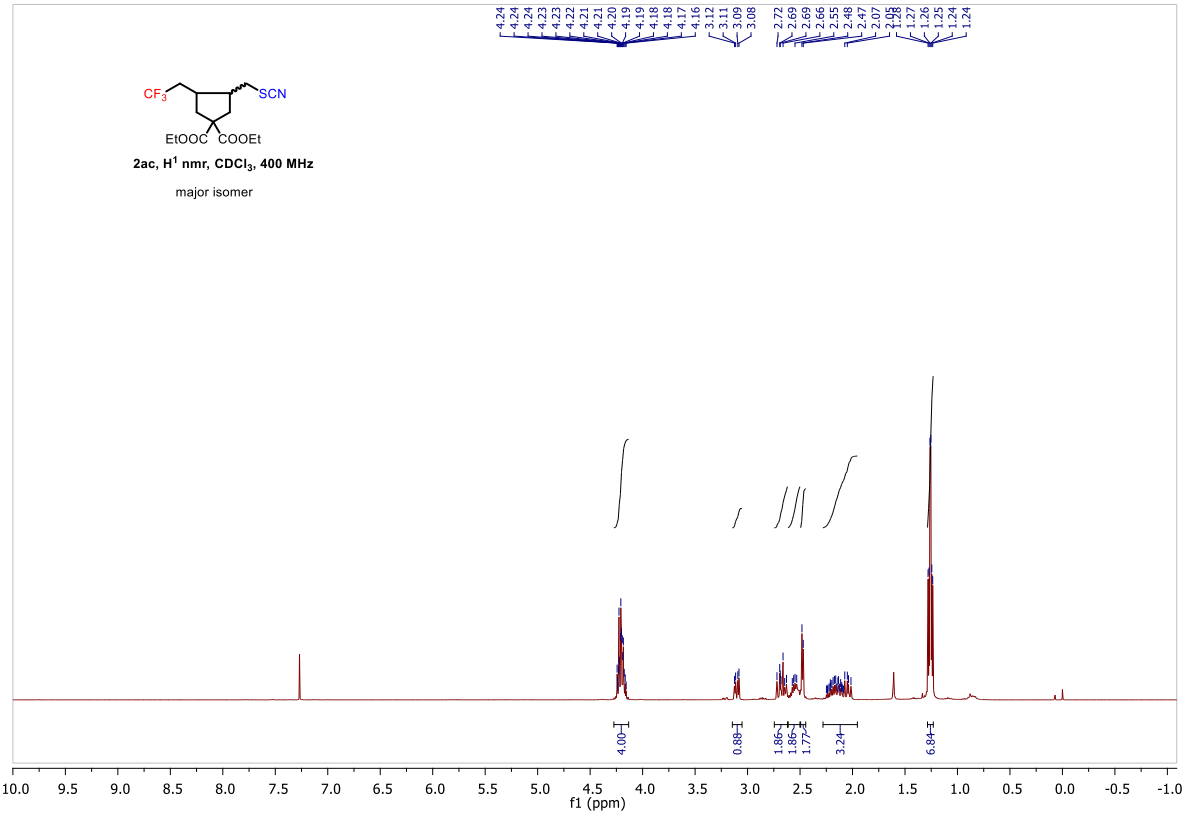


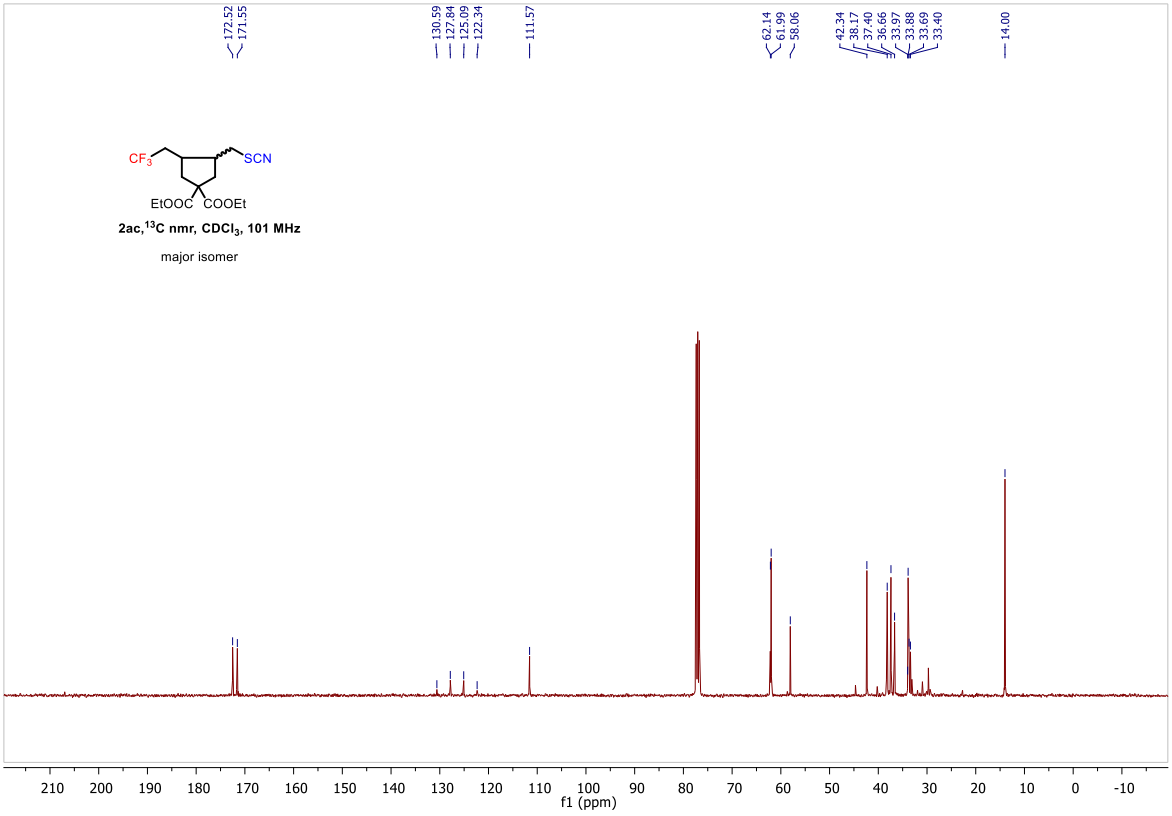

**4b**, $^{19}F$ NMR, $CDCl_3$, 376 MHz

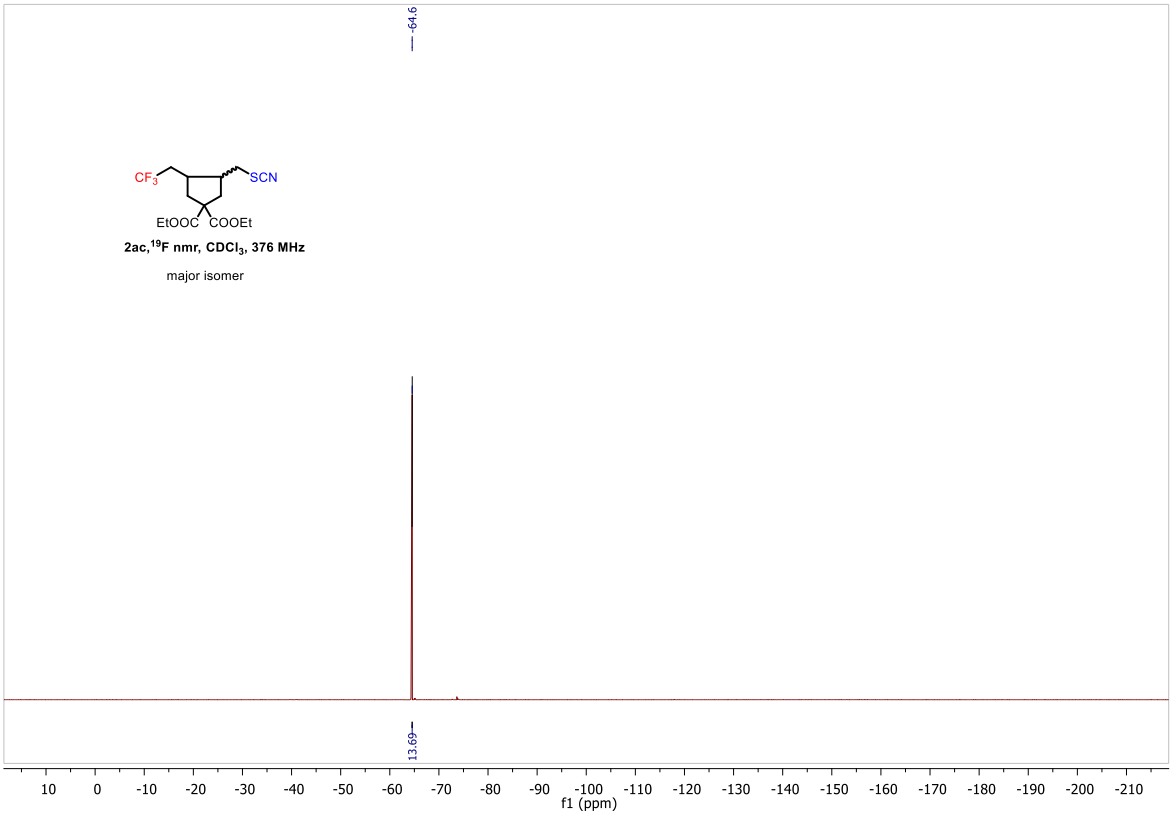



**4b**, $^{31}P$ NMR, $CDCl_3$, 162 MHz


CF3
SCN
EtOOC COOEt
2ac
Crude H1 nmr, dr = 7:1
f1 (ppm)


CF3
SCN
EtOOC COOEt
2ac, H1 nmr, CDCl3, 400 MHz
major isomer
f1 (ppm)


172.52
171.55
130.59
127.84
125.09
122.34
111.57
62.14
61.99
58.06
42.34
38.17
37.40
36.66
33.97
33.88
33.69
33.40
14.00
CF3
SCN
EtOOC COOEt
2ac,13C nmr, CDCl3, 101 MHz
major isomer
f1 (ppm)


-64.6
13.69
CF3
SCN
EtOOC COOEt
2ac,19F nmr, CDCl3, 376 MHz
major isomer
f1 (ppm)