

Electronic Supplementary Information

Transition-Metal-Free Electrophilic Trifluoromethylthiolation with Sodium Trifluoromethanesulfinate at Room Temperature

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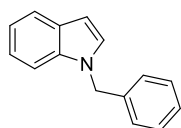
1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried Schlenk tubes. Dry solvents (water \leq 50 ppm) were purchased from Energy Chemical and stored over molecular sieves under argon atmosphere. Commercially available chemicals were used without any further purification. The products were purified by column chromatography over silica gel. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel, and compounds were detected by visualization under an ultraviolet lamp (254 nm). ^1H , ^{13}C and ^{19}F NMR spectra were recorded on an AVANCE III 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 470 MHz, respectively. Chemical shifts were reported in ppm. Coupling constants (J values) are reported in Hz. Low-resolution mass spectra (EI) were obtained at 70 eV on a 5975C Mass Selective Detector. Elemental analysis was performed on a C/H mode.

2. Synthesis of Starting Materials

1-Benzyl-1*H*-indole,¹ 2-phenyl-1*H*-pyrrole,² and 1-(4-methoxyphenyl)-1*H*-pyrrole³ were synthesized according to previous reported procedures.

1-Benzyl-1*H*-indole (1c).



Chemical Formula: $\text{C}_{15}\text{H}_{13}\text{N}$
Exact Mass: 207.1048
Elemental Analysis: C, 86.92; H, 6.32; N, 6.76

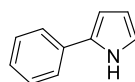
^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, $J = 7.7$ Hz, 1H), 7.37 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.19 – 7.09 (m, 4H), 6.61 (d, $J = 3.0$ Hz, 1H), 5.31 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 137.8, 136.6, 129.0, 128.5, 127.8, 127.0, 121.9, 121.2, 119.8, 109.9, 101.9, 50.3.

MS (EI) m/z : 207 (M^+).

Analytical data are in accordance with the literature values.¹

2-Phenyl-1*H*-pyrrole (4a).



Chemical Formula: $\text{C}_{10}\text{H}_9\text{N}$
Exact Mass: 143.0735
Elemental Analysis: C, 83.88; H, 6.34; N, 9.78

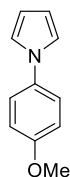
^1H NMR (500 MHz, CDCl_3) δ 8.38 (br, 1H), 7.50 (d, $J = 7.9$ Hz, 2H), 7.40 (t, $J = 7.7$ Hz, 2H), 7.26 (t, $J = 7.4$ Hz, 1H), 6.86 (q, $J = 2.4$ Hz, 1H), 6.60 (p, $J = 1.7$ Hz, 1H), 6.36 (q, $J = 2.9$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 132.9, 132.3, 129.1, 126.4, 124.0, 119.1, 110.3, 106.3.

MS (EI) m/z : 143 (M^+).

Analytical data are in accordance with the literature values.²

1-(4-Methoxyphenyl)-1H-pyrrole (4b).



Chemical Formula: C₁₁H₁₁NO
Exact Mass: 173.0841
Elemental Analysis: C, 76.28; H, 6.40; N, 8.09; O, 9.24

¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 8.9 Hz, 2H), 7.08 (t, *J* = 2.2 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 6.41 (t, *J* = 2.2 Hz, 2H), 3.88 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 157.9, 134.7, 122.3, 119.8, 114.8, 110.1, 55.7.

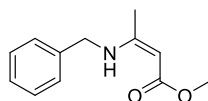
MS (EI) *m/z*: 173 (M⁺).

Analytical data are in accordance with the literature values.³

General procedure for the synthesis of enamines:

Enamines were synthesized according to a modified procedure of Brandt.⁴ Ketones (2 mmol), amine (3 mmol), and acetic acid (48 mg, 0.8 mmol) in 2 mL of ethanol were stirred at room temperature or refluxed overnight. The resulting mixture was concentrated *in vacuo*, dissolved with EtOAc (30 mL), washed with water (2 x 8 mL) and brine (2 x 8 mL). The organic phase was concentrated and purified by column chromatography.

Methyl (Z)-3-(benzylamino)but-2-enoate (5a).



Chemical Formula: C₁₂H₁₅NO₂
Exact Mass: 205.1103
Elemental Analysis: C, 70.22; H, 7.37; N, 6.82; O, 15.59

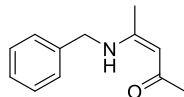
¹H NMR (500 MHz, CDCl₃) δ 8.95 (br, 1H), 7.36 – 7.31 (m, 2H), 7.29 – 7.22 (m, 3H), 4.54 (s, 1H), 4.42 (d, *J* = 6.4 Hz, 2H), 3.63 (s, 3H), 1.91 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 171.0, 162.1, 138.8, 128.9, 127.5, 126.8, 82.9, 50.1, 46.9, 19.5.

MS (EI) *m/z*: 205 (M⁺).

Analytical data are in accordance with the literature values.⁵

(Z)-4-(benzylamino)pent-3-en-2-one (5b).



Chemical Formula: C₁₂H₁₅NO
Exact Mass: 189.1154
Elemental Analysis: C, 76.16; H, 7.99; N, 7.40; O, 8.45

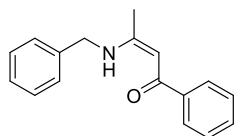
¹H NMR (500 MHz, CDCl₃) δ 11.14 (br, 1H), 7.34 – 7.27 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 3H), 5.01 (s, 1H), 4.40 (d, *J* = 6.4 Hz, 2H), 2.00 (s, 3H), 1.87 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 195.4, 163.2, 138.2, 128.9, 127.5, 126.8, 96.0, 46.8, 29.0, 19.0.

MS (EI) *m/z*: 189 (M⁺).

Analytical data are in accordance with the literature values.⁶

(Z)-3-(Benzylamino)-1-phenylbut-2-en-1-one (5c).



Chemical Formula: C₁₇H₁₇NO
Exact Mass: 251.1310
Elemental Analysis: C, 81.24; H, 6.82; N, 5.57; O, 6.37

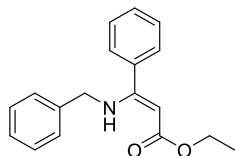
¹H NMR (500 MHz, CDCl₃) δ 11.79 (br, 1H), 7.92 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.34 (m, 2H), 7.30 (dd, *J* = 14.8, 7.2 Hz, 3H), 5.77 (s, 1H), 4.52 (d, *J* = 6.3 Hz, 2H), 2.05 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 188.2, 165.1, 140.5, 137.9, 130.7, 129.0, 128.3, 127.7, 127.1, 127.1, 92.8, 47.2, 19.7.

MS (EI) *m/z*: 251 (M⁺).

Analytical data are in accordance with the literature values.⁶

Ethyl (Z)-3-(benzylamino)-3-phenylacrylate (5e).



Chemical Formula: C₁₈H₁₉NO₂
Exact Mass: 281.1416
Elemental Analysis: C, 76.84; H, 6.81; N, 4.98; O, 11.37

¹H NMR (500 MHz, CDCl₃) δ 8.93 (br, 1H), 7.37 (dq, *J* = 18.6, 6.7, 5.7 Hz, 5H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 4.69 (s, 1H), 4.28 (d, *J* = 6.5 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 170.5, 164.9, 139.4, 136.1, 129.4, 128.7, 128.5, 128.0, 127.3, 127.0, 86.4, 58.9, 48.5, 14.7.

MS (EI) *m/z*: 281 (M⁺).

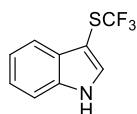
Analytical data are in accordance with the literature values.⁵

3. Experimental and Characterization of Reaction Products

General procedure for the electrophilic trifluoromethylthiolation with CF₃SO₂Na:

A 10-mL Schlenk tube with a magnetic stirring bar was charged with triphenylphosphine (0.6 mmol, 158 mg), chlorophthalimide (0.3 mmol, 55 mg) and sodium trifluoromethanesulfinate (0.3 mmol, 47 mg). The tube was evacuated and backfilled with dry nitrogen (this operation was repeated three times). Indole, pyrrole, or enamine (0.2 mmol) dissolved in dry acetonitrile (2 mL) was added by syringe. The resulting mixture was stirred at room temperature before the solvent was removed under reduced pressure. Purification of the crude product was achieved by column chromatography.

3-((Trifluoromethyl)thio)-1H-indole (3a).



Chemical Formula: C₉H₆F₃NS
Exact Mass: 217.0173
Elemental Analysis: C, 49.77; H, 2.78; F, 26.24; N, 6.45; S, 14.76

¹H NMR (500 MHz, CDCl₃) δ 8.45 (br, 1H), 7.92 – 7.79 (m, 1H), 7.51 (d, *J* = 2.8 Hz, 1H), 7.45 –

7.39 (m, 1H), 7.37 – 7.28 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 136.2, 133.0, 129.6 (q, $J = 309.7$ Hz), 129.6, 123.6, 121.8, 119.5, 111.8, 95.7.

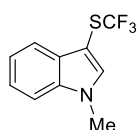
^{19}F NMR (470 MHz, CDCl_3) δ -44.5.

MS (EI) m/z : 217 (M^+).

Anal. Calcd for $\text{C}_9\text{H}_6\text{F}_3\text{NS}$: C, 49.77; H, 2.78. Found: C, 49.40; H, 2.87.

Analytical data are in accordance with the literature values.⁷

1-Methyl-3-((trifluoromethyl)thio)-1H-indole (3b).



Chemical Formula: $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$
Exact Mass: 231.0330
Elemental Analysis: C, 51.94; H, 3.49; F, 24.65; N, 6.06; S, 13.86

^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 7.6$ Hz, 1H), 7.40 – 7.31 (m, 4H), 3.80 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 137.4, 137.1, 129.6 (q, $J = 310.4$ Hz), 130.4, 123.1, 121.4, 119.5, 110.0, 93.2, 33.3.

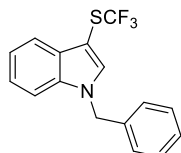
^{19}F NMR (470 MHz, CDCl_3) δ -44.8.

MS (EI) m/z : 231 (M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$: C, 51.94; H, 3.49. Found: C, 52.27; H, 3.58.

Analytical data are in accordance with the literature values.⁷

1-Benzyl-3-((trifluoromethyl)thio)-1H-indole (3c).



Chemical Formula: $\text{C}_{16}\text{H}_{12}\text{F}_3\text{NS}$
Exact Mass: 307.0643
Elemental Analysis: C, 62.53; H, 3.94; F, 18.55; N, 4.56; S, 10.43

^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 7.0$ Hz, 1H), 7.47 (s, 1H), 7.36 – 7.28 (m, 6H), 7.16 (d, $J = 6.5$ Hz, 2H), 5.34 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 137.0, 136.5, 136.2, 130.6, 129.4 (q, $J = 314.8$ Hz), 129.1, 128.3, 127.1, 123.3, 121.6, 119.7, 110.6, 94.2, 50.8.

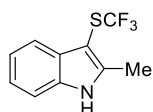
^{19}F NMR (470 MHz, CDCl_3) δ -44.7.

MS (EI) m/z : 307 (M^+).

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{NS}$: C, 62.53; H, 3.94. Found: C, 62.31; H, 4.03.

Analytical data are in accordance with the literature values.⁸

2-Methyl-3-((trifluoromethyl)thio)-1H-indole (3d).



Chemical Formula: $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$
Exact Mass: 231.0330
Elemental Analysis: C, 51.94; H, 3.49; F, 24.65; N, 6.06; S, 13.86

^1H NMR (500 MHz, CDCl_3) δ 8.29 (br, 1H), 7.73 (d, $J = 6.9$ Hz, 1H), 7.35 – 7.29 (m, 1H), 7.27 –

7.22 (m, 2H), 2.57 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 143.7, 135.2, 130.7, 129.9 (q, $J = 311.0$ Hz), 122.7, 121.5, 118.8, 110.9, 92.7, 12.2.

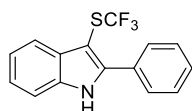
^{19}F NMR (470 MHz, CDCl_3) δ -44.4.

MS (EI) m/z : 231 (M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$: C, 51.94; H, 3.49. Found: C, 51.59; H, 3.55.

Analytical data are in accordance with the literature values.⁷

2-Phenyl-3-((trifluoromethyl)thio)-1H-indole (3e).



Chemical Formula: $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NS}$

Exact Mass: 293.0486

Elemental Analysis: C, 61.43; H, 3.44; F, 19.43; N, 4.78; S, 10.93

^1H NMR (500 MHz, CDCl_3) δ 8.56 (br, 1H), 7.93 – 7.86 (m, 1H), 7.83 – 7.74 (m, 2H), 7.58 – 7.52 (m, 2H), 7.52 – 7.47 (m, 1H), 7.43 (dt, $J = 7.4, 3.0$ Hz, 1H), 7.37 – 7.30 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 144.5, 135.5, 131.6, 130.8, 129.9 (q, $J = 310.8$ Hz), 129.4, 129.0, 128.9, 123.8, 122.0, 119.9, 111.4, 92.6.

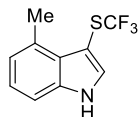
^{19}F NMR (470 MHz, CDCl_3) δ -43.4.

MS (EI) m/z : 293 (M^+).

Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NS}$: C, 61.43; H, 3.44. Found: C, 61.19; H, 3.51.

Analytical data are in accordance with the literature values.⁷

4-Methyl-3-((trifluoromethyl)thio)-1H-indole (3f).



Chemical Formula: $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$

Exact Mass: 231.0330

Elemental Analysis: C, 51.94; H, 3.49; F, 24.65; N, 6.06; S, 13.86

^1H NMR (500 MHz, CDCl_3) δ 8.47 (br, 1H), 7.50 (d, $J = 2.8$ Hz, 1H), 7.26 (d, $J = 8.1$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 7.1$ Hz, 1H), 2.88 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 136.5, 134.2, 131.8, 129.3 (q, $J = 309.3$ Hz), 126.9, 123.6, 109.9, 95.2, 19.5.

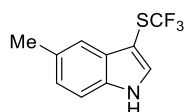
^{19}F NMR (470 MHz, CDCl_3) δ -45.8.

MS (EI) m/z : 231 (M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$: C, 51.94; H, 3.49. Found: C, 51.59; H, 3.55.

Analytical data are in accordance with the literature values.⁷

5-Methyl-3-((trifluoromethyl)thio)-1H-indole (3g).



Chemical Formula: $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$

Exact Mass: 231.0330

Elemental Analysis: C, 51.94; H, 3.49; F, 24.65; N, 6.06; S, 13.86

^1H NMR (500 MHz, CDCl_3) δ 8.39 (br, 1H), 7.62 (s, 1H), 7.47 (d, $J = 2.8$ Hz, 1H), 7.31 (d, $J = 8.3$ Hz, 1H), 7.15 (dd, $J = 8.3, 1.2$ Hz, 1H), 2.53 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 134.5, 133.0, 131.4, 129.8, 129.6 (q, $J = 310.2$ Hz), 125.2, 119.0, 111.5, 95.0, 21.7.

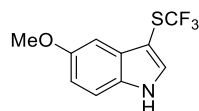
^{19}F NMR (470 MHz, CDCl_3) δ -44.6.

MS (EI) m/z : 231 (M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$: C, 51.94; H, 3.49. Found: C, 52.20; H, 3.40.

Analytical data are in accordance with the literature values.⁷

5-Methoxy-3-((trifluoromethyl)thio)-1H-indole (3h).



Chemical Formula: $\text{C}_{10}\text{H}_8\text{F}_3\text{NOS}$

Exact Mass: 247.0279

Elemental Analysis: C, 48.58; H, 3.26; F, 23.05; N, 5.67; O, 6.47; S, 12.97

^1H NMR (500 MHz, CDCl_3) δ 8.52 (br, 1H), 7.49 (d, $J = 2.8$ Hz, 1H), 7.30 (d, $J = 8.8$ Hz, 1H), 7.24 (d, $J = 2.4$ Hz, 1H), 6.95 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.91 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 155.7, 133.4, 131.1, 130.4, 129.6 (q, $J = 310.2$ Hz), 114.1, 112.7, 100.7, 95.1, 56.0.

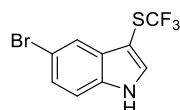
^{19}F NMR (470 MHz, CDCl_3) δ -44.6.

MS (EI) m/z : 247 (M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NOS}$: C, 48.58; H, 3.26. Found: C, 48.83; H, 3.37.

Analytical data are in accordance with the literature values.⁷

5-Bromo-3-((trifluoromethyl)thio)-1H-indole (3i).



Chemical Formula: $\text{C}_9\text{H}_5\text{BrF}_3\text{NS}$

Exact Mass: 294.9278

Elemental Analysis: C, 36.51; H, 1.70; Br, 26.99; F, 19.25; N, 4.73; S, 10.83

^1H NMR (500 MHz, CDCl_3) δ 8.59 (br, 1H), 7.99 – 7.89 (m, 1H), 7.54 (d, $J = 2.8$ Hz, 1H), 7.38 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.29 (d, $J = 8.6$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 134.8, 133.9, 131.3, 129.3 (q, $J = 310.2$ Hz), 126.7, 122.2, 115.4, 113.3, 95.6.

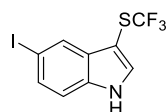
^{19}F NMR (470 MHz, CDCl_3) δ -44.5.

MS (EI) m/z : 295 (M^+).

Anal. Calcd for $\text{C}_9\text{H}_5\text{BrF}_3\text{NS}$: C, 36.51; H, 1.70. Found: C, 36.20; H, 1.76.

Analytical data are in accordance with the literature values.⁷

5-Iodo-3-((trifluoromethyl)thio)-1H-indole (3j).



Chemical Formula: $\text{C}_9\text{H}_5\text{F}_3\text{INS}$

Exact Mass: 342.9139

Elemental Analysis: C, 31.51; H, 1.47; F, 16.61; I, 36.99; N, 4.08; S, 9.34

^1H NMR (500 MHz, CDCl_3) δ 8.59 (br, 1H), 8.13 (s, 1H), 7.55 (dd, $J = 8.5, 1.4$ Hz, 1H), 7.52 – 7.47 (m, 1H), 7.23 – 7.17 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 135.3, 133.5, 132.1, 132.0, 129.3 (q, $J = 309.5$ Hz), 128.4, 113.7,

95.2, 85.6.

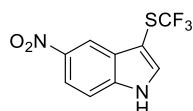
^{19}F NMR (470 MHz, CDCl_3) δ -44.4.

MS (EI) m/z : 343 (M^+).

Anal. Calcd for $\text{C}_9\text{H}_5\text{F}_3\text{NS}$: C, 31.51; H, 1.47. Found: C, 31.87; H, 1.52.

Analytical data are in accordance with the literature values.⁸

5-Nitro-3-((trifluoromethyl)thio)-1H-indole (3k).



Chemical Formula: $\text{C}_9\text{H}_5\text{F}_3\text{N}_2\text{O}_2\text{S}$

Exact Mass: 262.0024

Elemental Analysis: C, 41.23; H, 1.92; F, 21.74; N, 10.68; O, 12.20; S, 12.23

^1H NMR (500 MHz, CD_3OD) δ 8.56 (d, $J = 2.2$ Hz, 1H), 8.12 (dd, $J = 9.0, 2.2$ Hz, 1H), 7.90 (s, 1H), 7.59 (d, $J = 9.0$ Hz, 1H).

^{13}C NMR (125 MHz, CD_3OD) δ 142.9, 139.9, 137.6, 129.4 (q, $J = 309.4$ Hz), 129.0, 117.8, 115.0, 112.5, 95.9.

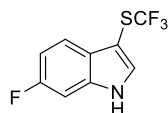
^{19}F NMR (470 MHz, CD_3OD) δ -46.6.

MS (EI) m/z : 262 (M^+).

Anal. Calcd for $\text{C}_9\text{H}_5\text{F}_3\text{N}_2\text{O}_2\text{S}$: C, 41.23; H, 1.92. Found: C, 41.12; H, 1.97.

Analytical data are in accordance with the literature values.⁸

6-Fluoro-3-((trifluoromethyl)thio)-1H-indole (3l).



Chemical Formula: $\text{C}_9\text{H}_5\text{F}_4\text{NS}$

Exact Mass: 235.0079

Elemental Analysis: C, 45.96; H, 2.14; F, 32.31; N, 5.96; S, 13.63

^1H NMR (500 MHz, CDCl_3) δ 8.54 (br, 1H), 7.72 (dd, $J = 8.8, 5.2$ Hz, 1H), 7.52 (d, $J = 2.7$ Hz, 1H), 7.11 (dd, $J = 9.2, 2.3$ Hz, 1H), 7.05 (ddd, $J = 9.5, 8.8, 2.2$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 160.7 (d, $J = 239.8$ Hz), 136.1 (d, $J = 12.3$ Hz), 133.2, 129.5 (q, $J = 309.8$ Hz), 126.0, 120.5 (d, $J = 10.2$ Hz), 110.7 (d, $J = 24.9$ Hz), 98.2 (d, $J = 26.8$ Hz), 96.1.

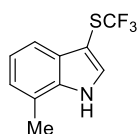
^{19}F NMR (470 MHz, CDCl_3) δ -44.5, -119.1.

MS (EI) m/z : 235 (M^+).

Anal. Calcd for $\text{C}_9\text{H}_5\text{F}_4\text{NS}$: C, 45.96; H, 2.14. Found: C, 45.61; H, 2.10.

Analytical data are in accordance with the literature values.⁸

7-Methyl-3-((trifluoromethyl)thio)-1H-indole (3m).



Chemical Formula: $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$

Exact Mass: 231.0330

Elemental Analysis: C, 51.94; H, 3.49; F, 24.65; N, 6.06; S, 13.86

^1H NMR (500 MHz, CDCl_3) δ 8.44 (br, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.52 (t, $J = 2.2$ Hz, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 7.1$ Hz, 1H), 2.51 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 135.8, 132.6, 129.6 (q, $J = 309.7$ Hz), 129.2, 124.1, 121.9, 121.0,

117.2, 96.1, 16.4.

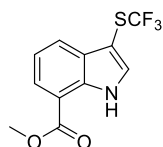
^{19}F NMR (470 MHz, CDCl_3) δ -44.5.

MS (EI) m/z : 231 (M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NS}$: C, 51.94; H, 3.49. Found: C, 52.24; H, 3.59.

Analytical data are in accordance with the literature values.⁷

Methyl 3-((trifluoromethyl)thio)-1H-indole-7-carboxylate (3n).



Chemical Formula: $\text{C}_{11}\text{H}_8\text{F}_3\text{NO}_2\text{S}$

Exact Mass: 275.0228

Elemental Analysis: C, 48.00; H, 2.93; F, 20.71; N, 5.09; O, 11.63; S, 11.65

^1H NMR (500 MHz, CD_3OD) δ 7.88 (q, $J = 7.2$ Hz, 2H), 7.71 (s, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 3.96 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 166.9, 135.4, 135.1, 130.8, 129.6 (q, $J = 309.1$ Hz), 125.3, 124.0, 120.3, 113.8, 94.0, 51.2.

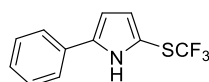
^{19}F NMR (470 MHz, CD_3OD) δ -46.7.

MS (EI) m/z : 275 (M^+).

Anal. Calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{NO}_2\text{S}$: C, 48.00; H, 2.93. Found: C, 47.93; H, 3.05.

Analytical data are in accordance with the literature values.⁸

2-Phenyl-5-((trifluoromethyl)thio)-1H-pyrrole (6a).



Chemical Formula: $\text{C}_{11}\text{H}_8\text{F}_3\text{NS}$

Exact Mass: 243.0330

Elemental Analysis: C, 54.32; H, 3.32; F, 23.43; N, 5.76; S, 13.18

^1H NMR (500 MHz, CDCl_3) δ 8.59 (br, 1H), 7.55 – 7.49 (m, 2H), 7.43 (dd, $J = 8.6, 7.0$ Hz, 2H), 7.35 – 7.28 (m, 1H), 6.73 (dd, $J = 3.7, 2.6$ Hz, 1H), 6.59 (dd, $J = 3.6, 2.8$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 136.9, 130.4, 128.1, 127.4 (q, $J = 311.3$ Hz), 126.7, 123.5, 122.1, 107.3.

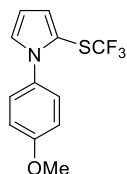
^{19}F NMR (470 MHz, CDCl_3) δ -45.0.

MS (EI) m/z : 243 (M^+).

Anal. Calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{NS}$: C, 54.32; H, 3.32. Found: C, 54.09; H, 3.27.

Analytical data are in accordance with the literature values.⁷

1-(4-Methoxyphenyl)-2-((trifluoromethyl)thio)-1H-pyrrole (6b).



Chemical Formula: $\text{C}_{12}\text{H}_{10}\text{F}_3\text{NOS}$

Exact Mass: 273.0435

Elemental Analysis: C, 52.74; H, 3.69; F, 20.86; N, 5.13; O, 5.85; S, 11.73

^1H NMR (500 MHz, CDCl_3) δ 7.25 – 7.20 (m, 2H), 7.08 (t, $J = 2.4$ Hz, 1H), 6.99 – 6.95 (m, 2H),

6.82 (dd, $J = 3.8, 1.8$ Hz, 1H), 6.35 (t, $J = 3.3$ Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 159.4, 132.0, 129.1, 128.4, 128.3 (q, $J = 311.3$ Hz), 123.6, 114.1, 111.1, 109.9, 55.6.

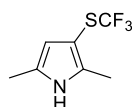
^{19}F NMR (470 MHz, CDCl_3) δ -45.3.

MS (EI) m/z : 273 (M^+).

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{NOS}$: C, 52.74; H, 3.69. Found: C, 52.45; H, 3.77.

Analytical data are in accordance with the literature values.⁸

2,5-Dimethyl-3-((trifluoromethyl)thio)-1H-pyrrole (6c).



Chemical Formula: $\text{C}_7\text{H}_9\text{F}_3\text{NS}$
Exact Mass: 195.0330
Elemental Analysis: C, 43.07; H, 4.13; F, 29.20; N, 7.18; S, 16.42

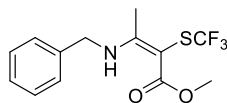
^1H NMR (500 MHz, CDCl_3) δ 7.92 (br, 1H), 5.96 (s, 1H), 2.31 (s, 3H), 2.22 (s, 3H).

^{19}F NMR (470 MHz, CDCl_3) δ -46.3.

MS (EI) m/z : 195 (M^+).

Analytical data are in accordance with the literature values.⁹

Methyl (E)-3-(benzylamino)-2-((trifluoromethyl)thio)but-2-enoate (7a).



Chemical Formula: $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}$
Exact Mass: 305.0697
Elemental Analysis: C, 51.14; H, 4.62; F, 18.67; N, 4.59; O, 10.48; S, 10.50

^1H NMR (500 MHz, CDCl_3) δ 10.77 (br, 1H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.26 (d, $J = 7.4$ Hz, 2H), 4.53 (d, $J = 5.9$ Hz, 2H), 3.74 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 171.7, 171.4, 137.0, 130.1 (q, $J = 311.8$ Hz), 129.2, 128.1, 127.0, 76.3, 51.7, 48.5, 17.9.

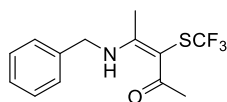
^{19}F NMR (470 MHz, CDCl_3) δ -47.3.

MS (EI) m/z : 305 (M^+).

Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2\text{S}$: C, 51.14; H, 4.62. Found: C, 51.41; H, 4.54.

Analytical data are in accordance with the literature values.¹⁰

(E)-4-(benzylamino)-3-((trifluoromethyl)thio)pent-3-en-2-one (7b).



Chemical Formula: $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NOS}$
Exact Mass: 289.0748
Elemental Analysis: C, 53.97; H, 4.88; F, 19.70; N, 4.84; O, 5.53; S, 11.08

^1H NMR (500 MHz, CDCl_3) δ 12.91 (br, 1H), 7.38 – 7.24 (m, 5H), 4.54 (d, $J = 5.9$ Hz, 2H), 2.44 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 199.9, 172.4, 136.4, 130.1 (q, $J = 311.5$ Hz), 129.2, 128.1, 127.0, 88.7, 48.5, 29.2, 17.9.

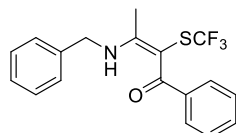
^{19}F NMR (470 MHz, CDCl_3) δ -47.2.

MS (EI) m/z : 289 (M^+).

Anal. Calcd for C₁₃H₁₄F₃NOS: C, 53.97; H, 4.88. Found: C, 54.06; H, 4.96.

Analytical data are in accordance with the literature values.¹⁰

(E)-3-(Benzylamino)-1-phenyl-2-((trifluoromethyl)thio)but-2-en-1-one (7c).



Chemical Formula: C₁₈H₁₆F₃NOS

Exact Mass: 351.0905

Elemental Analysis: C, 61.53; H, 4.59; F, 16.22; N, 3.99; O, 4.55; S, 9.12

¹H NMR (500 MHz, CDCl₃) δ 13.04 (br, 1H), 7.49 – 7.29 (m, 10H), 4.63 (t, *J* = 4.8 Hz, 2H), 2.51 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 197.9, 174.0, 142.3, 136.1, 129.8 (q, *J* = 311.6 Hz), 129.3, 129.2, 128.2, 127.7, 127.6, 127.2, 88.0, 48.8, 18.4.

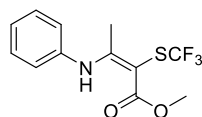
¹⁹F NMR (470 MHz, CDCl₃) δ -47.5.

MS (EI) *m/z*: 351 (M⁺).

Anal. Calcd for C₁₈H₁₆F₃NOS: C, 61.53; H, 4.59. Found: C, 61.90; H, 4.73.

Analytical data are in accordance with the literature values.¹⁰

Methyl (E)-3-(phenylamino)-2-((trifluoromethyl)thio)but-2-enoate (7d).



Chemical Formula: C₁₂H₁₂F₃NO₂S

Exact Mass: 291.0541

Elemental Analysis: C, 49.48; H, 4.15; F, 19.57; N, 4.81; O, 10.98; S, 11.01

¹H NMR (500 MHz, CDCl₃) δ 11.99 (br, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 3H), 2.35 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 171.2, 170.1, 138.3, 130.1 (q, *J* = 312.0 Hz), 129.5, 127.1, 126.0, 78.5, 51.9, 19.4.

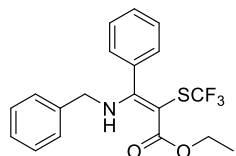
¹⁹F NMR (470 MHz, CDCl₃) δ -46.6.

MS (EI) *m/z*: 291 (M⁺).

Anal. Calcd for C₁₂H₁₂F₃NO₂S: C, 49.48; H, 4.15. Found: C, 49.16; H, 4.01.

Analytical data are in accordance with the literature values.¹⁰

Ethyl (E)-3-(benzylamino)-3-phenyl-2-((trifluoromethyl)thio)acrylate (7e).



Chemical Formula: C₁₉H₁₈F₃NO₂S

Exact Mass: 381.1010

Elemental Analysis: C, 59.83; H, 4.76; F, 14.94; N, 3.67; O, 8.39; S, 8.41

¹H NMR (500 MHz, CDCl₃) δ 10.62 (br, 1H), 7.42 (dd, *J* = 4.9, 1.7 Hz, 3H), 7.35 – 7.24 (m, 3H), 7.12 (dd, *J* = 17.0, 5.5 Hz, 4H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.13 (d, *J* = 6.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 173.1, 171.0, 137.6, 134.2, 129.6 (q, *J* = 311.2 Hz), 129.3, 128.9, 128.5, 127.8, 127.2, 78.2, 60.6, 49.7, 14.5.

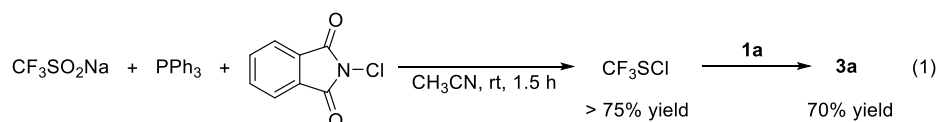
^{19}F NMR (470 MHz, CDCl_3) δ -46.6.

MS (EI) m/z : 381 (M^+).

Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NO}_2\text{S}$: C, 59.83; H, 4.76. Found: C, 59.48; H, 4.87.

Analytical data are in accordance with the literature values.¹⁰

4. Experiments for the Mechanistic Study



A 10-mL Schlenk tube with a magnetic stirring bar was charged with triphenylphosphine (0.6 mmol, 158 mg), chlorophthalimide (0.3 mmol, 55 mg) and sodium trifluoromethanesulfinate (0.3 mmol, 47 mg). The tube was evacuated and backfilled with dry nitrogen (this operation was repeated three times). Dry acetonitrile (2 mL) was added by syringe. The resulting mixture was stirred at room temperature and monitored by ^{19}F and ^{31}P NMR spectroscopies with PhCF_3 as the internal standard. As can be seen from Figure S1 and S2, triphenylphosphine converted completely into triphenylphosphine oxide after 1.5 hours, and CF_3SCl was afforded in 75% yield determined by ^{19}F NMR. Considering the volatility of CF_3SCl , the yield should be greater than 75%. Indole (**1a**, 0.2 mmol) was added to this mixture under nitrogen, and then the mixture was stirred for 14 hours. Trifluoromethylthiolated product **3a** was afforded in 70% based on **1a** after the reaction.

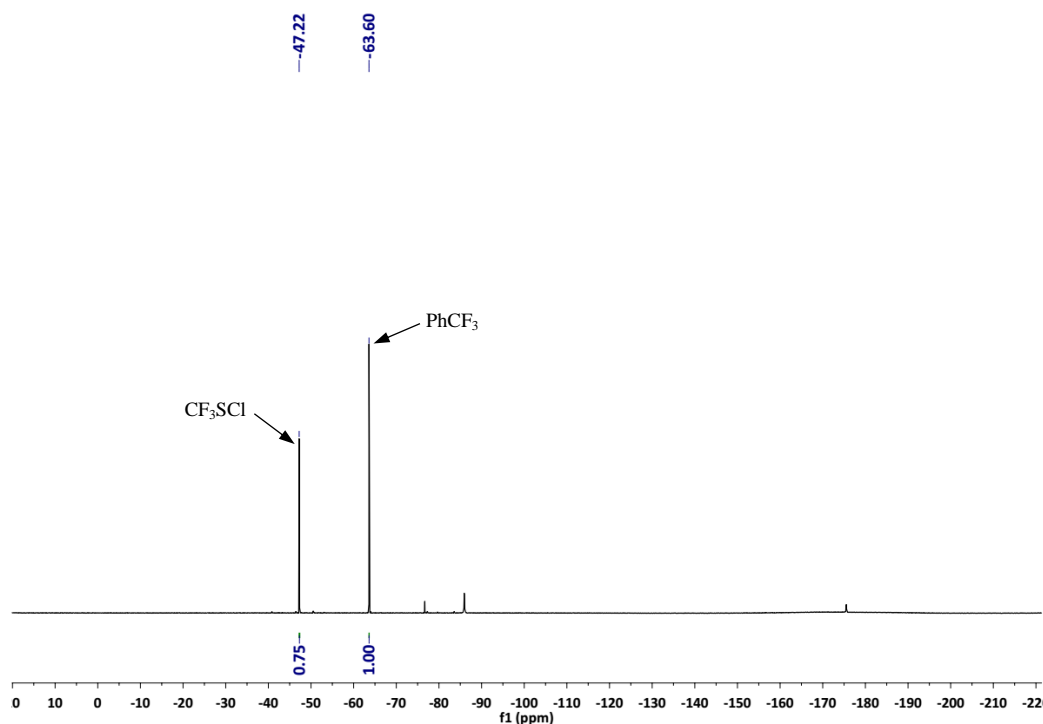


Figure S1. ^{19}F NMR spectrum of reaction mixture (after a reaction time of 1.5 h).

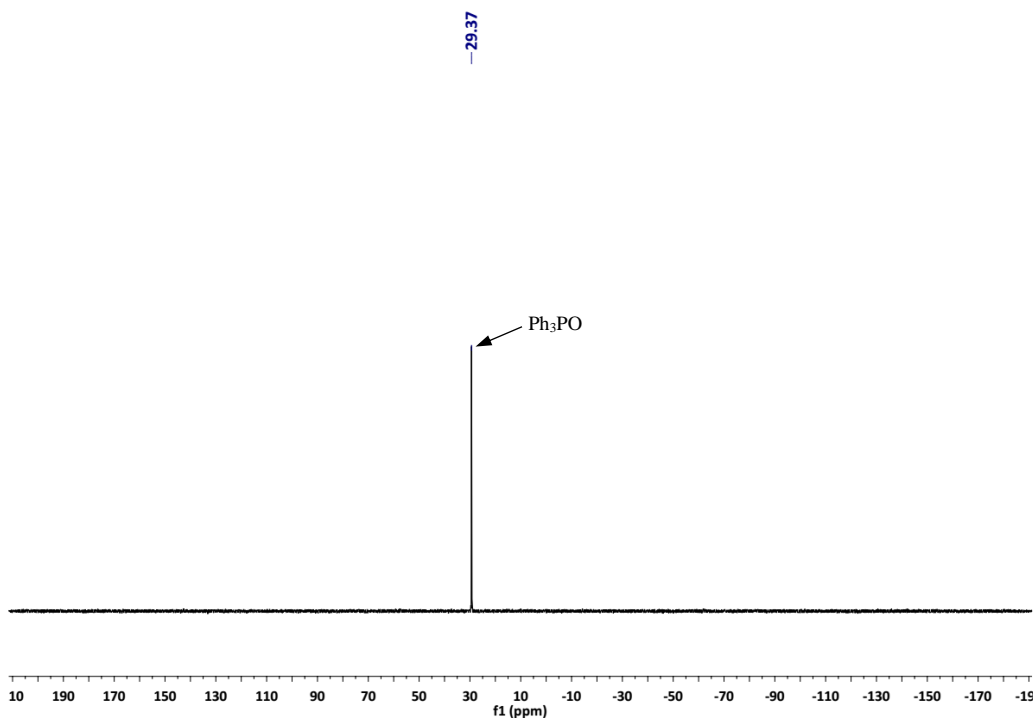
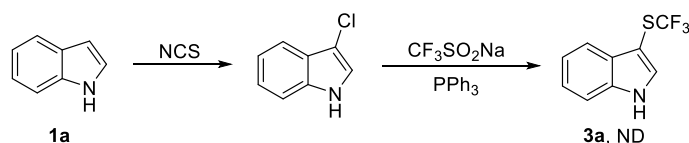
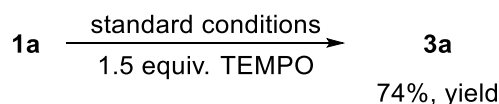


Figure S2. ³¹P NMR spectrum of reaction mixture (after a reaction time of 1.5 h).



To a 100 mL round-bottom flask with indole (1.00 g, 8.54 mmol, 1.0 equiv) in DMF (35 mL) was added *N*-chlorosuccinimide (1.23 g, 8.96 mmol, 1.05 equiv) at room temperature. After 1 h, water (40 mL) was added and the aqueous layer was extracted with EtOAc (3 × 35 mL). The combined organic layers were washed with brine (50 mL), and concentrated *in vacuo*. Purification of 3-chloroindole was achieved by column chromatography.

A 10-mL Schlenk tube with a magnetic stirring bar was charged with triphenylphosphine (0.6 mmol, 158 mg), and sodium trifluoromethanesulfinate (0.3 mmol, 47 mg). The tube was evacuated and backfilled with dry nitrogen (this operation was repeated three times). 3-Chloroindole dissolved in dry acetonitrile (2 mL) was added by syringe. The reaction mixture was stirred at room temperature for 14 hours. No trifluoromethylthiolated product **3a** could be detected after the reaction.



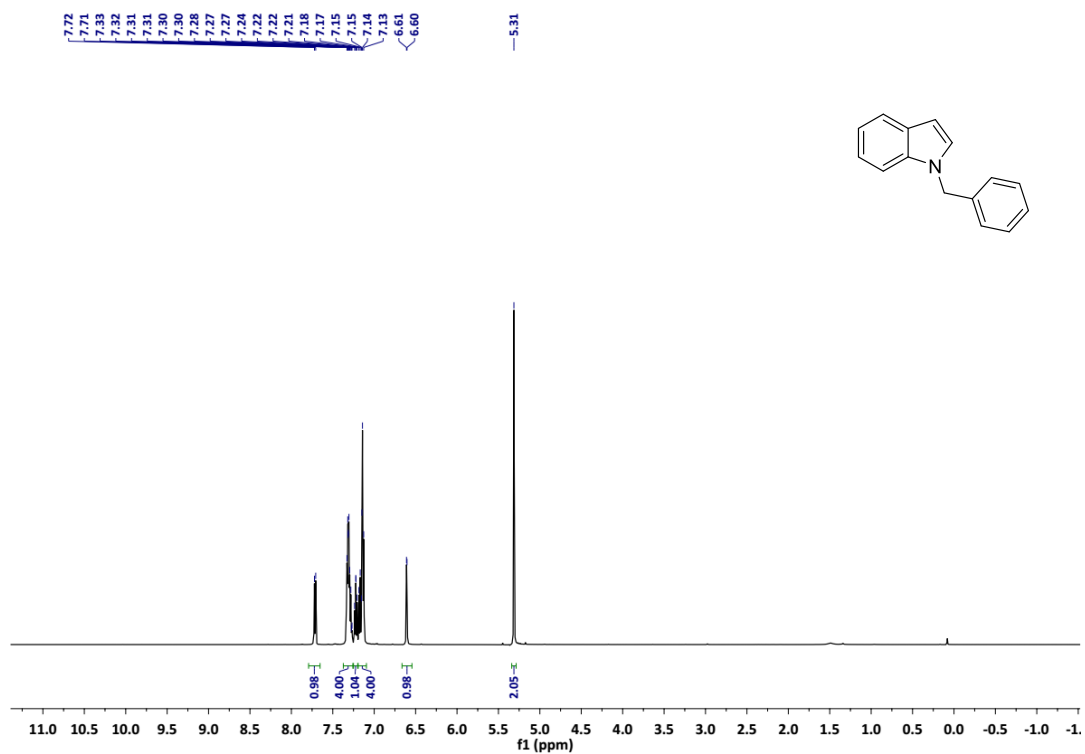
A 10-mL Schlenk tube with a magnetic stirring bar was charged with triphenylphosphine (0.6 mmol, 158 mg), chlorophthalimide (0.3 mmol, 55 mg) and sodium trifluoromethanesulfinate (0.3 mmol, 47 mg). The tube was evacuated and backfilled with dry nitrogen (this operation was repeated three times). Indole (**1a**, 0.2 mmol, 24 mg) and TEMPO (0.3 mmol, 47 mg) dissolved in dry acetonitrile

(2 mL) was added by syringe. The resulting mixture was stirred at room temperature before the solvent was removed under reduced pressure. A 74% yield of 3-((trifluoromethyl)thio)-1*H*-indole (**3a**) was achieved by column chromatography.

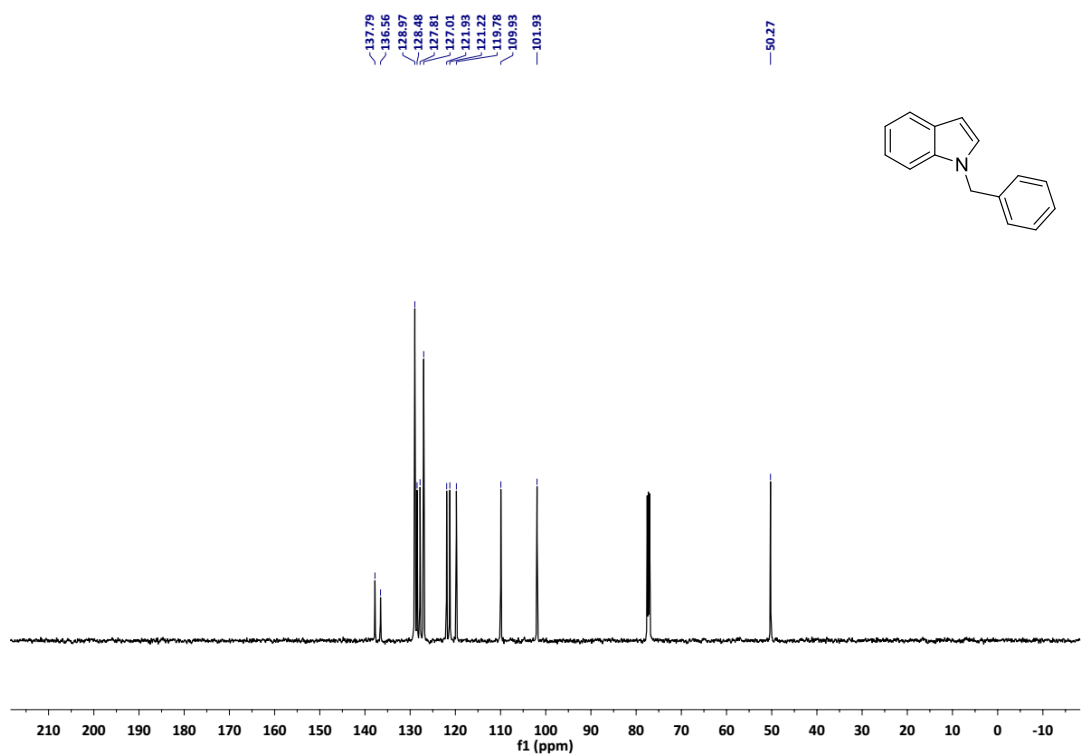
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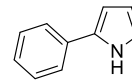
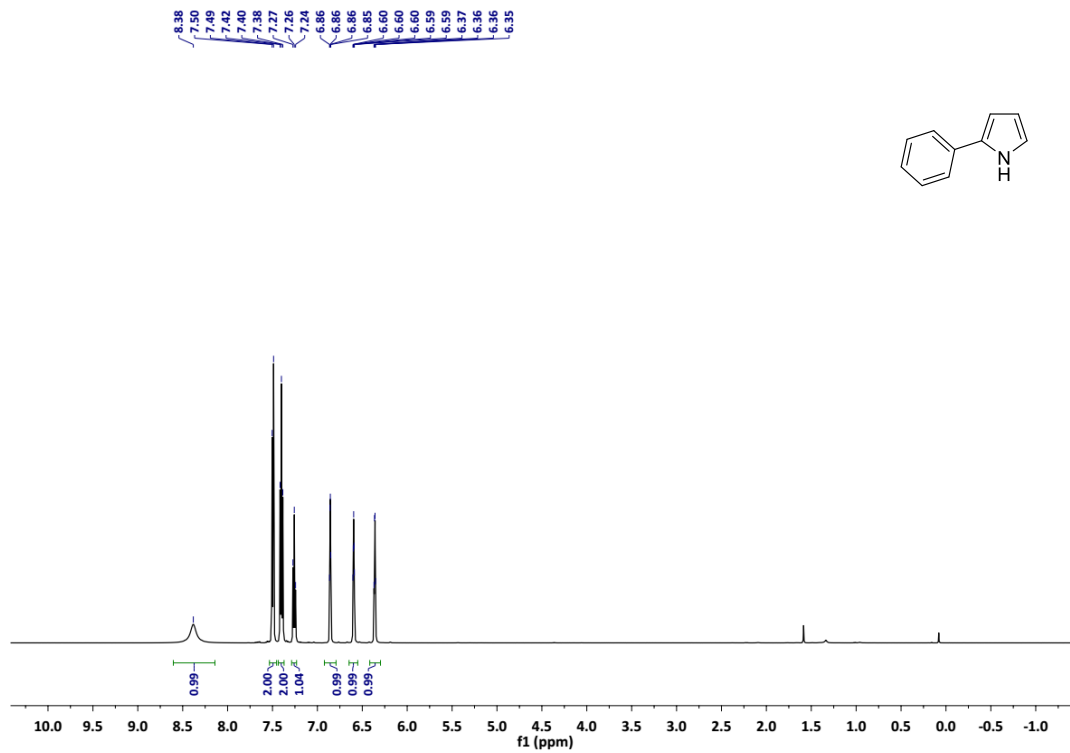
6. Copies of NMR Spectra



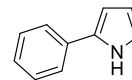
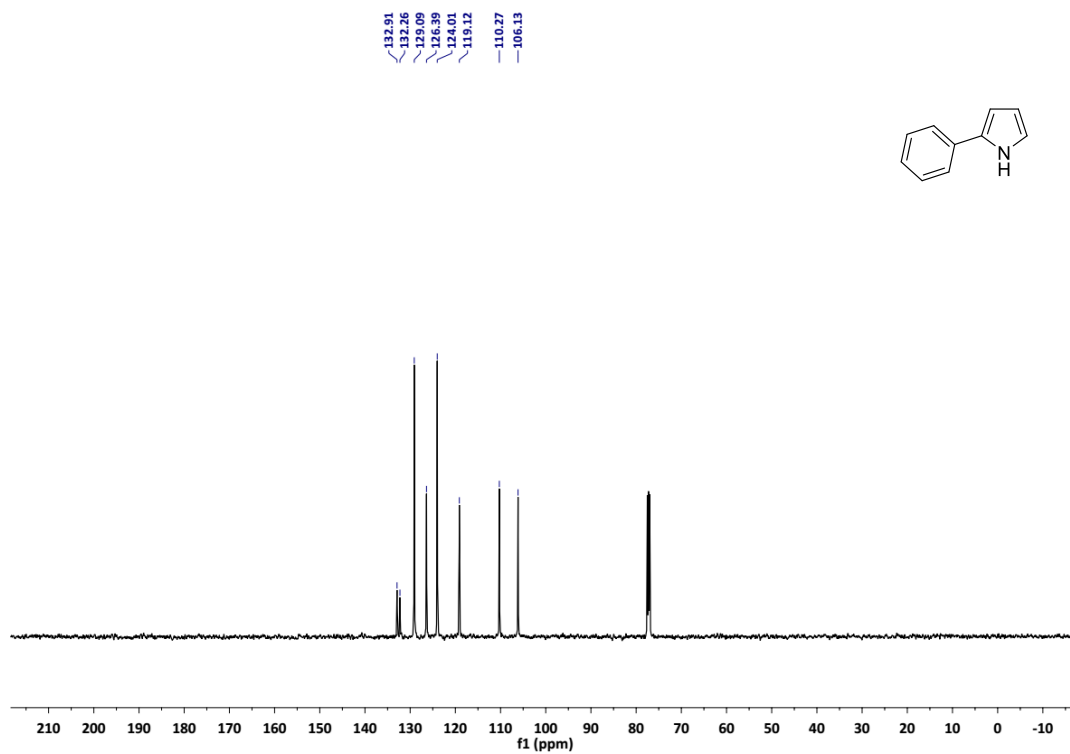
¹H NMR spectrum (500 MHz, CDCl₃) of **1c**



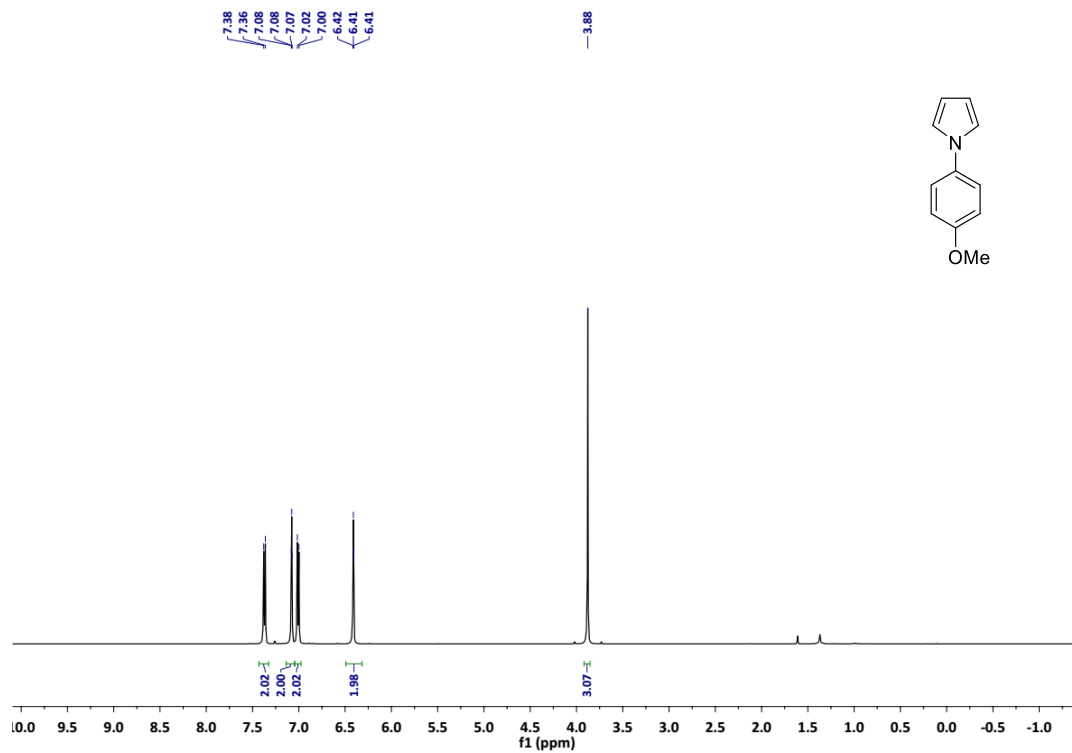
¹³C NMR spectrum (125 MHz, CDCl₃) of **1c**



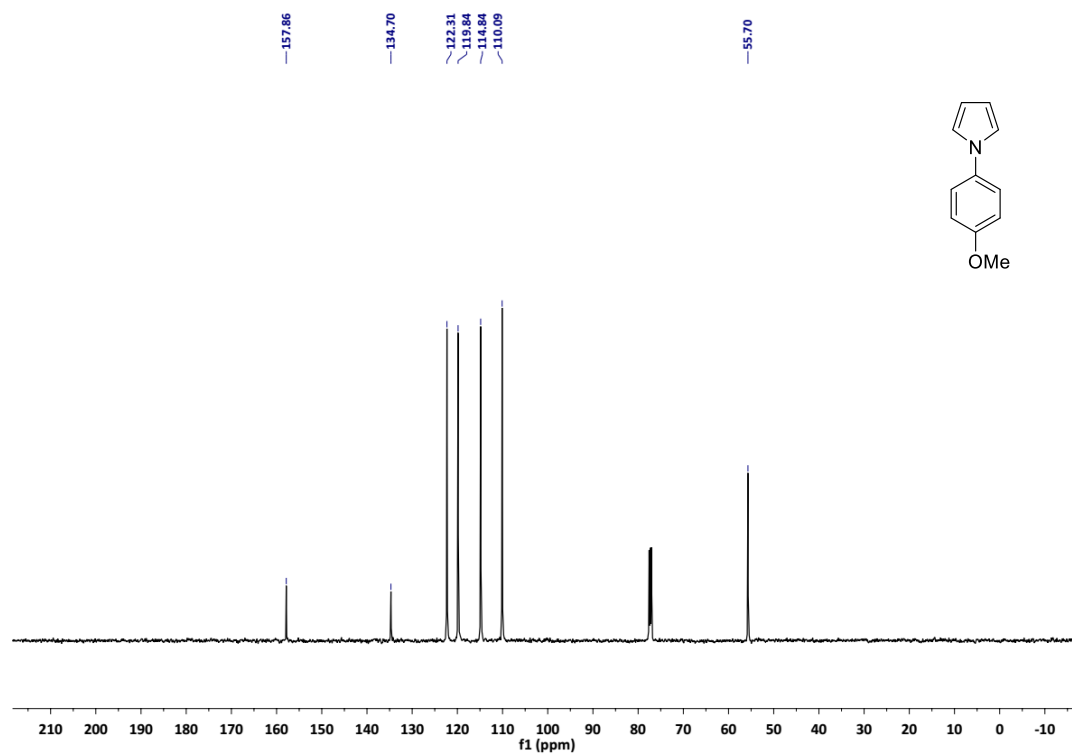
¹H NMR spectrum (500 MHz, CDCl₃) of **4a**



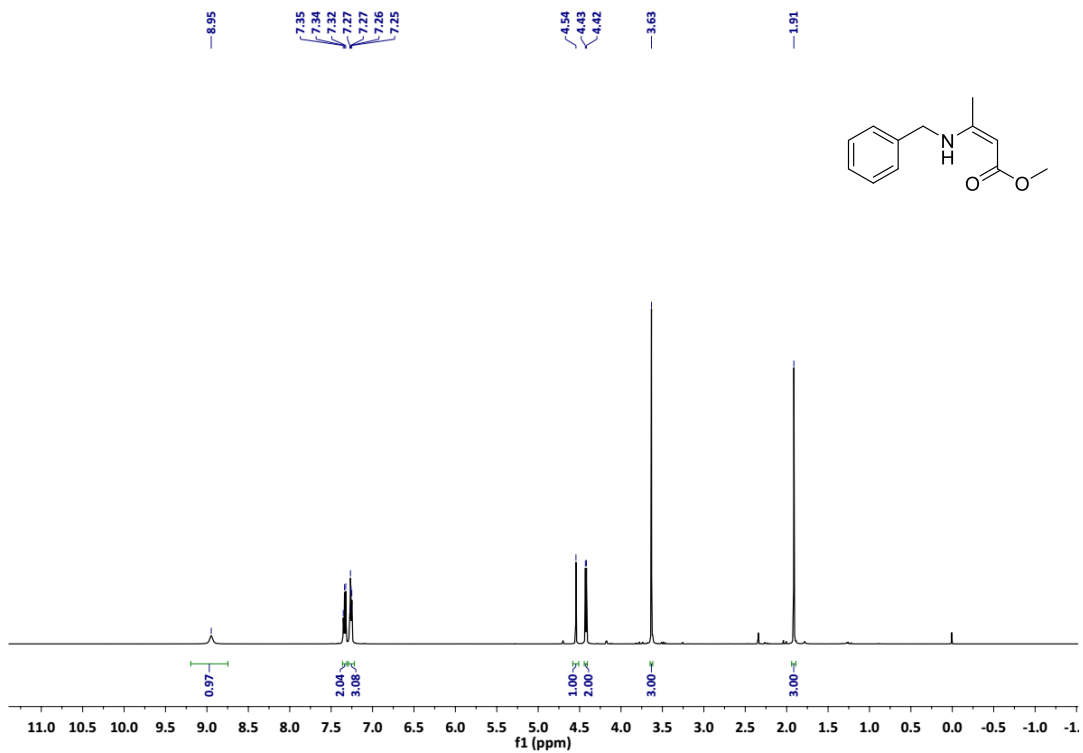
¹³C NMR spectrum (125 MHz, CDCl₃) of **4a**



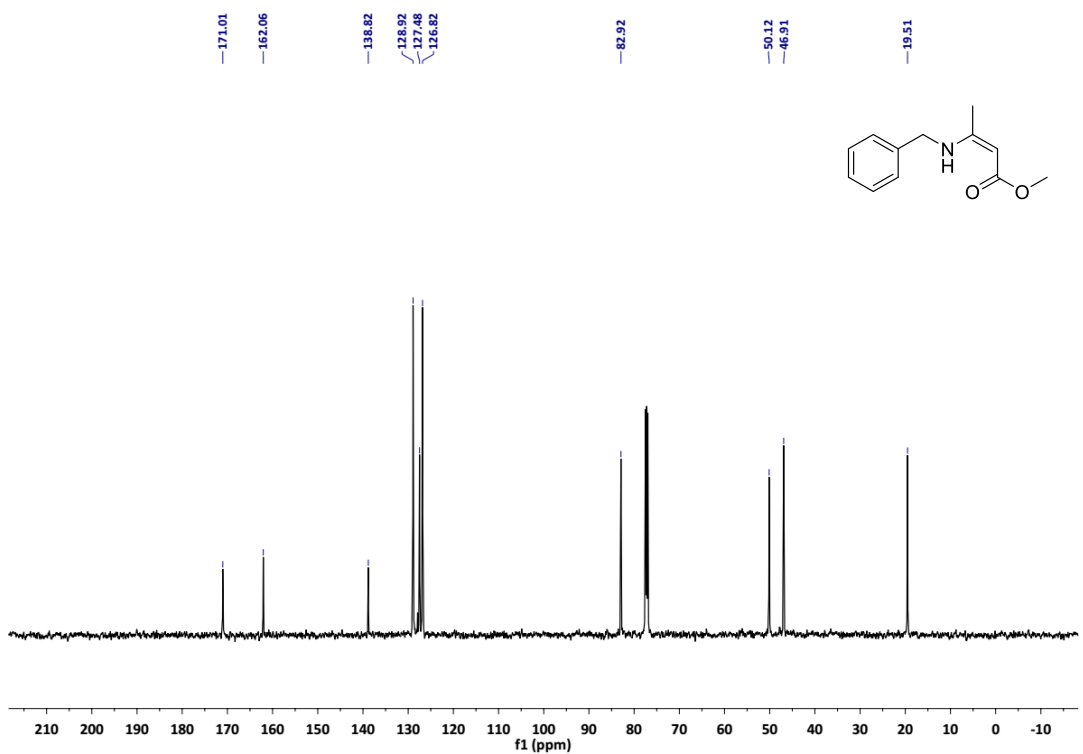
^1H NMR spectrum (500 MHz, CDCl_3) of **4b**



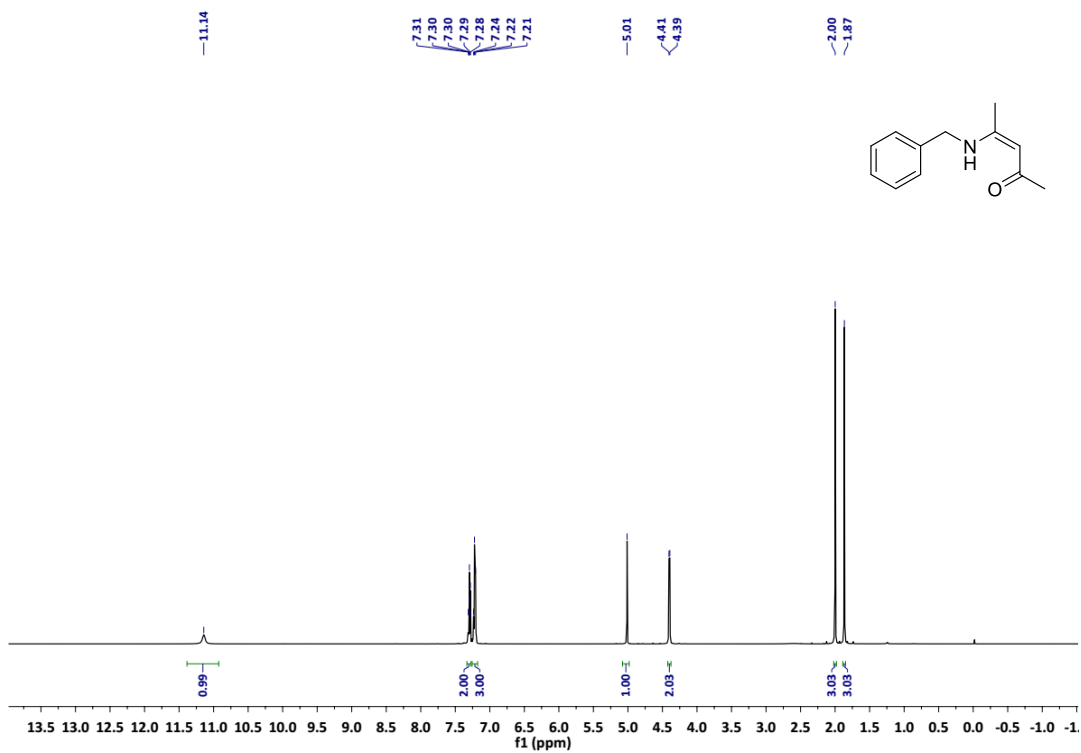
^{13}C NMR spectrum (125 MHz, CDCl_3) of **4b**



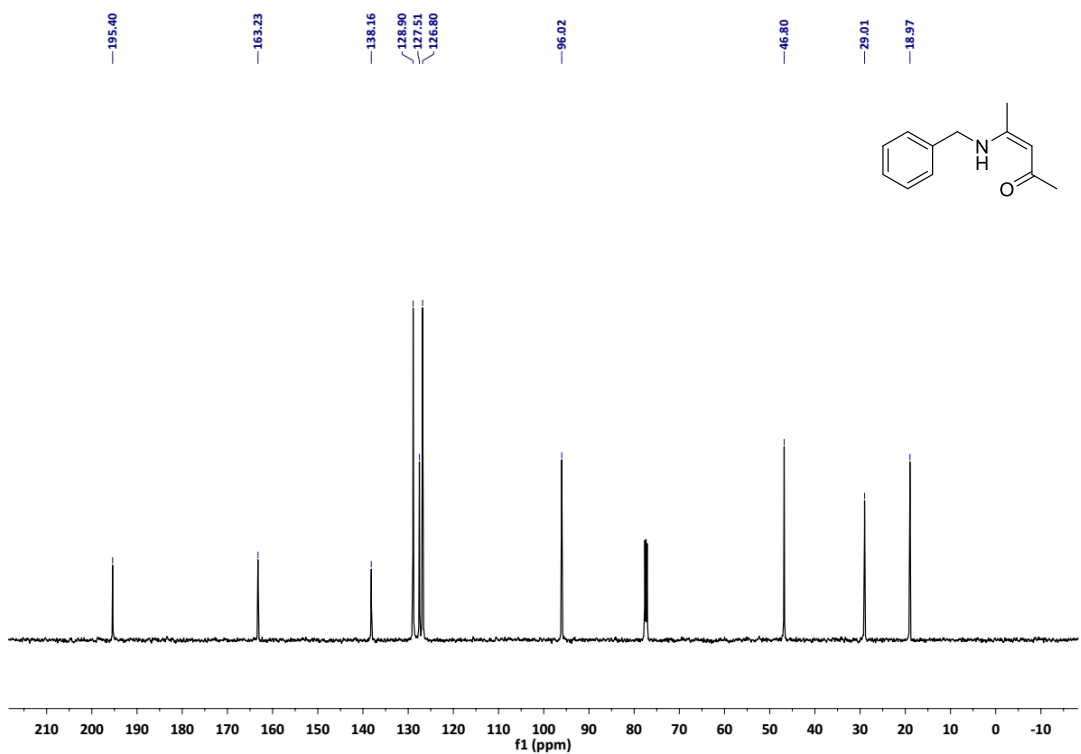
^1H NMR spectrum (500 MHz, CDCl_3) of **5a**



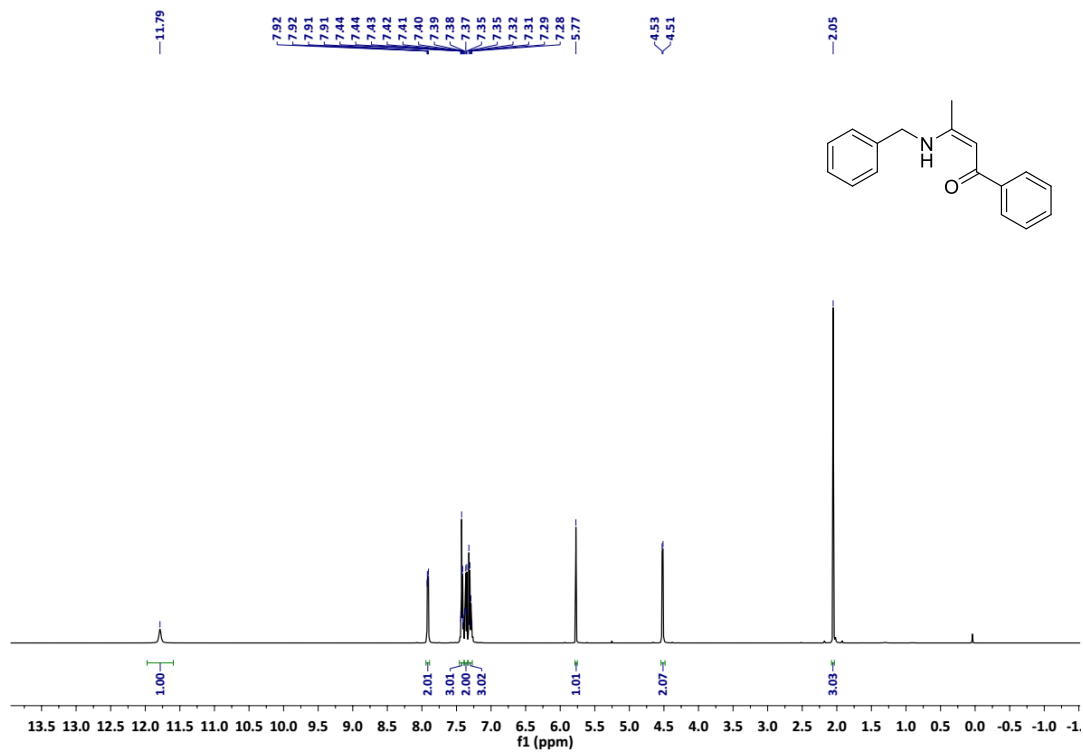
^{13}C NMR spectrum (125 MHz, CDCl_3) of **5a**



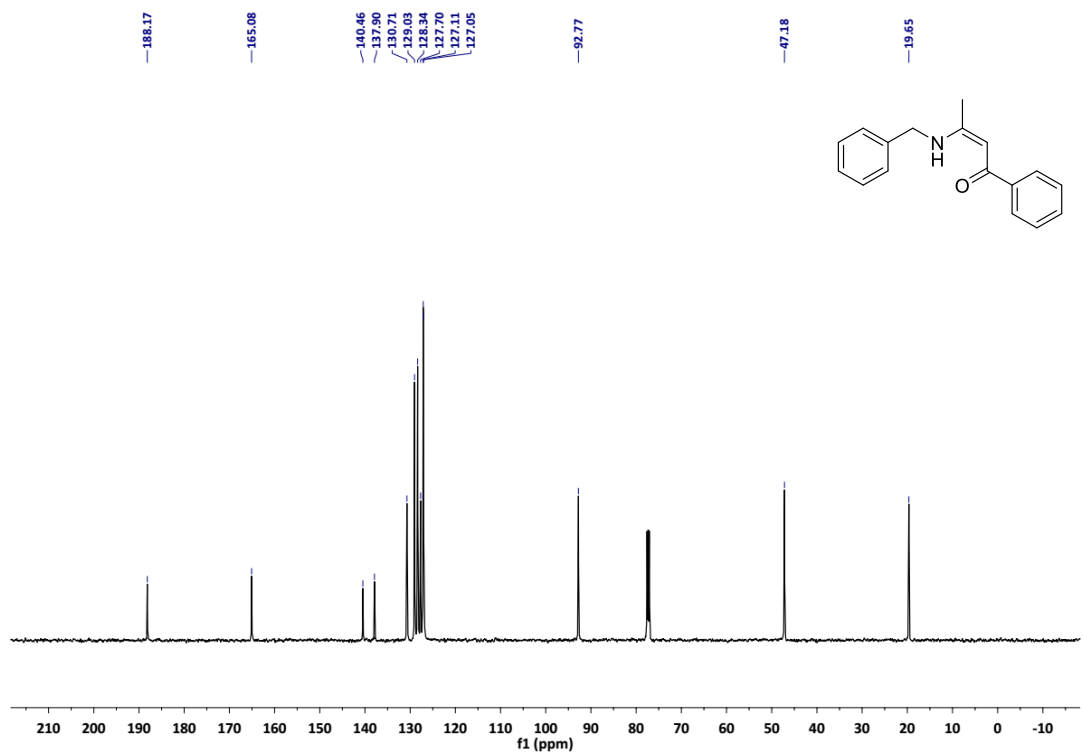
^1H NMR spectrum (500 MHz, CDCl_3) of **5b**



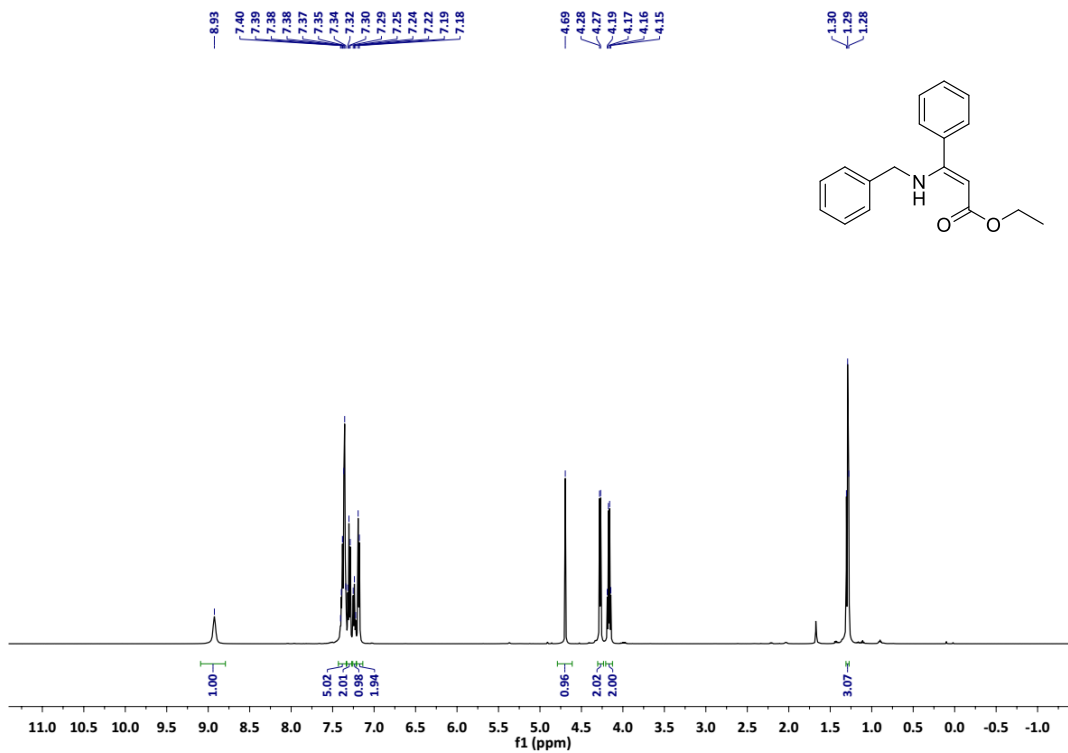
^{13}C NMR spectrum (125 MHz, CDCl_3) of **5b**



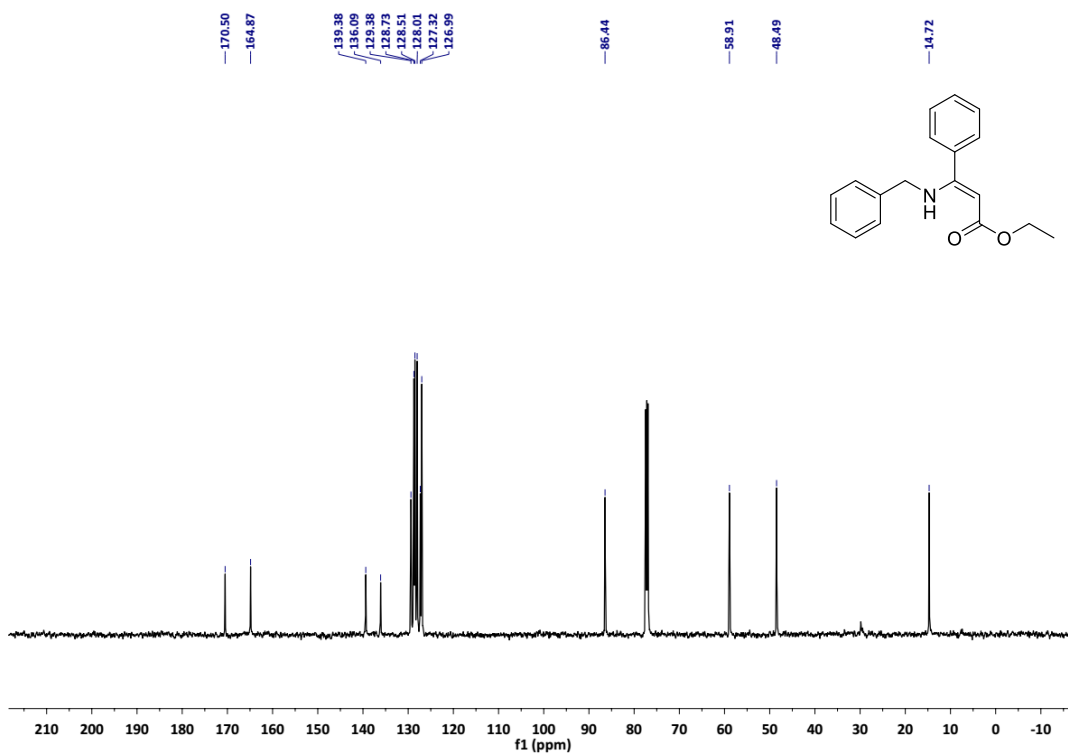
¹H NMR spectrum (500 MHz, CDCl₃) of **5c**



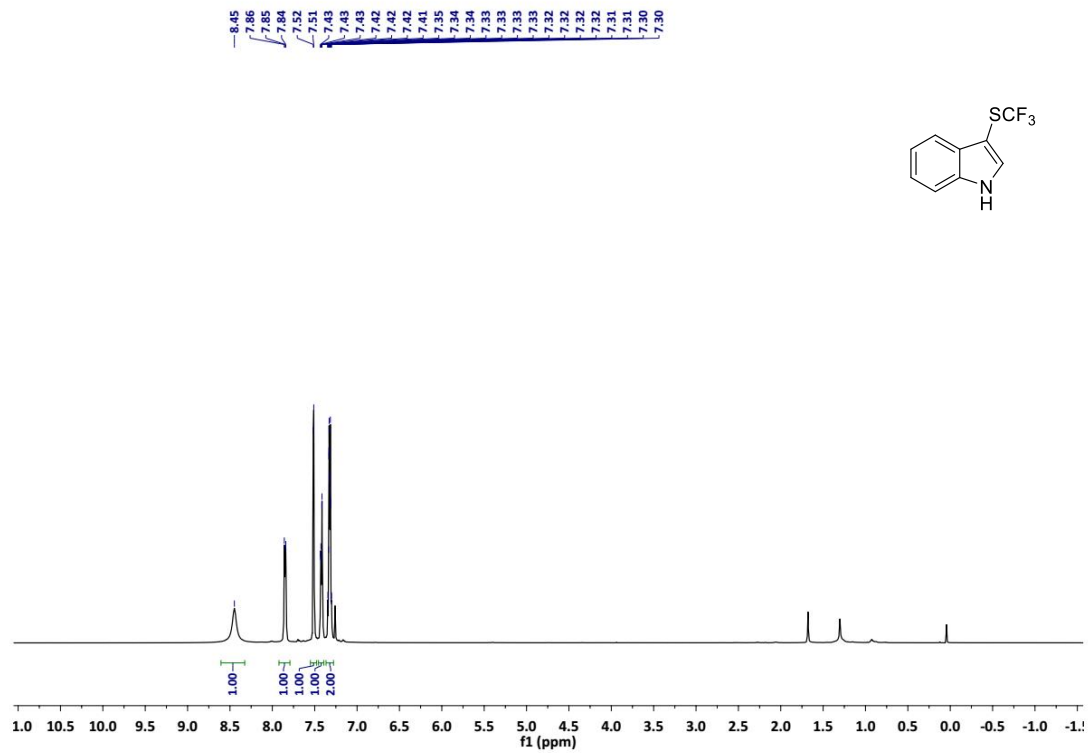
¹³C NMR spectrum (125 MHz, CDCl₃) of **5c**



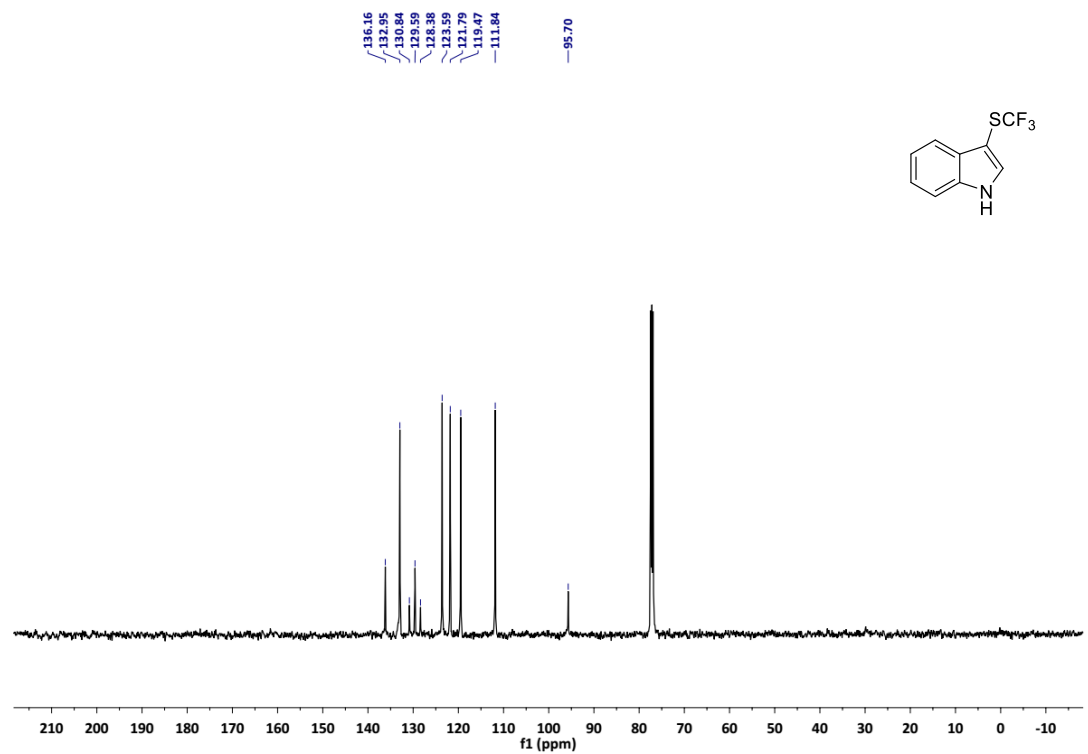
^1H NMR spectrum (500 MHz, CDCl_3) of **5e**



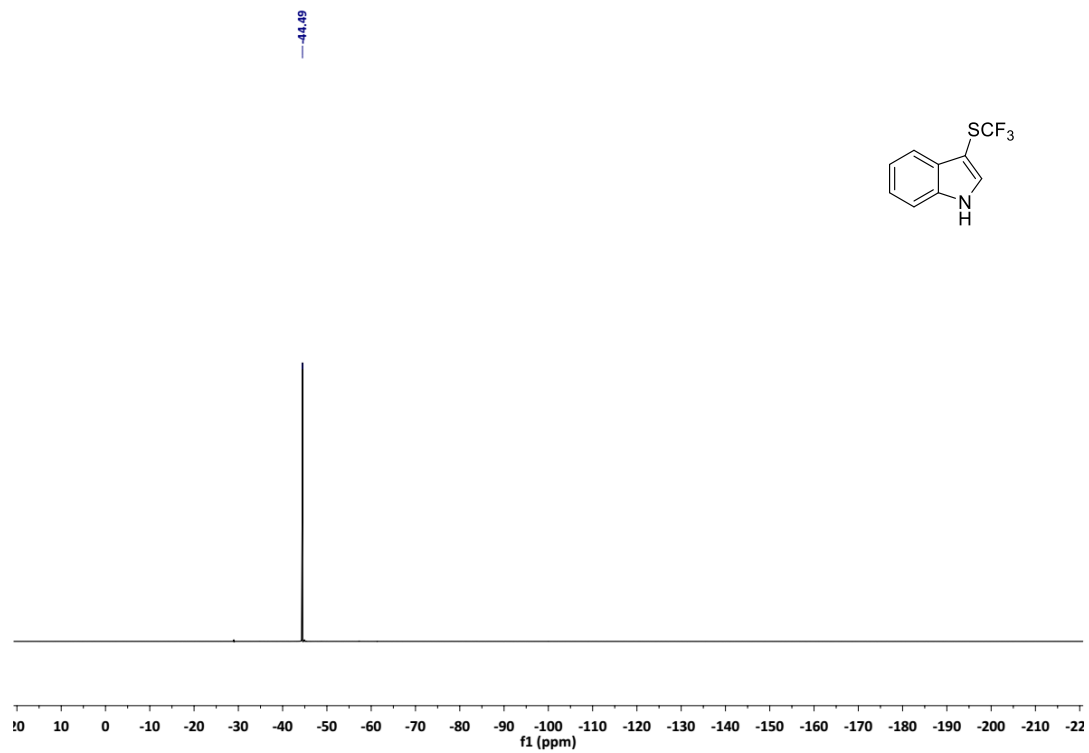
^{13}C NMR spectrum (125 MHz, CDCl_3) of **5e**



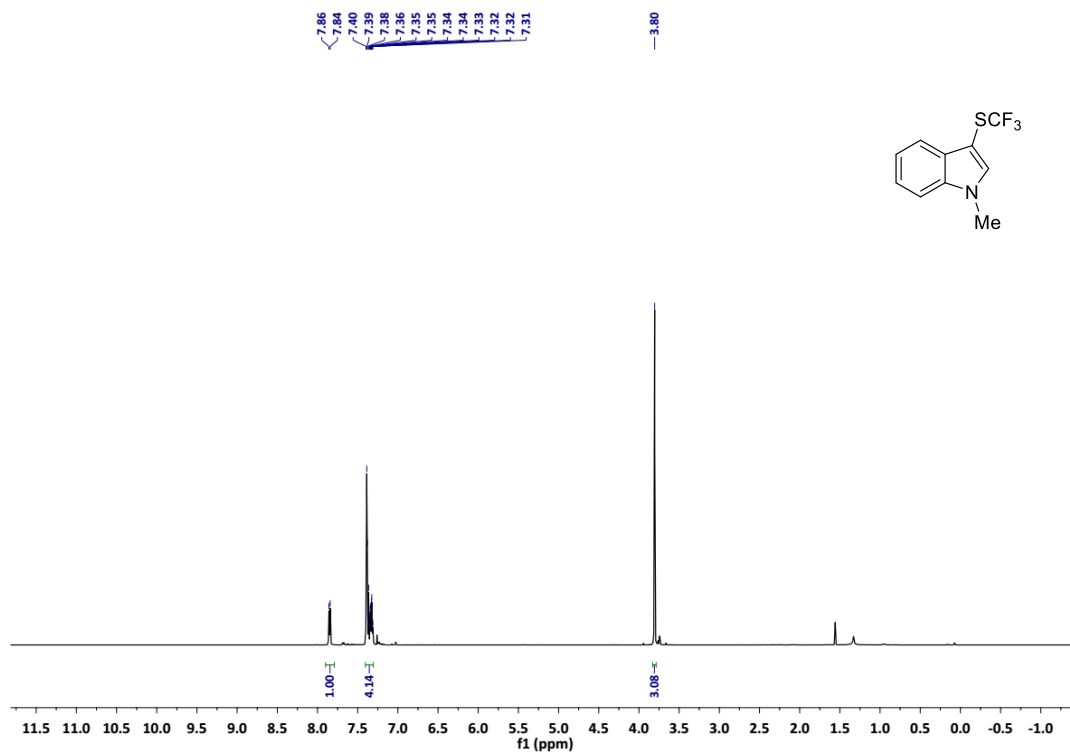
¹H NMR spectrum (500 MHz, CDCl₃) of **3a**



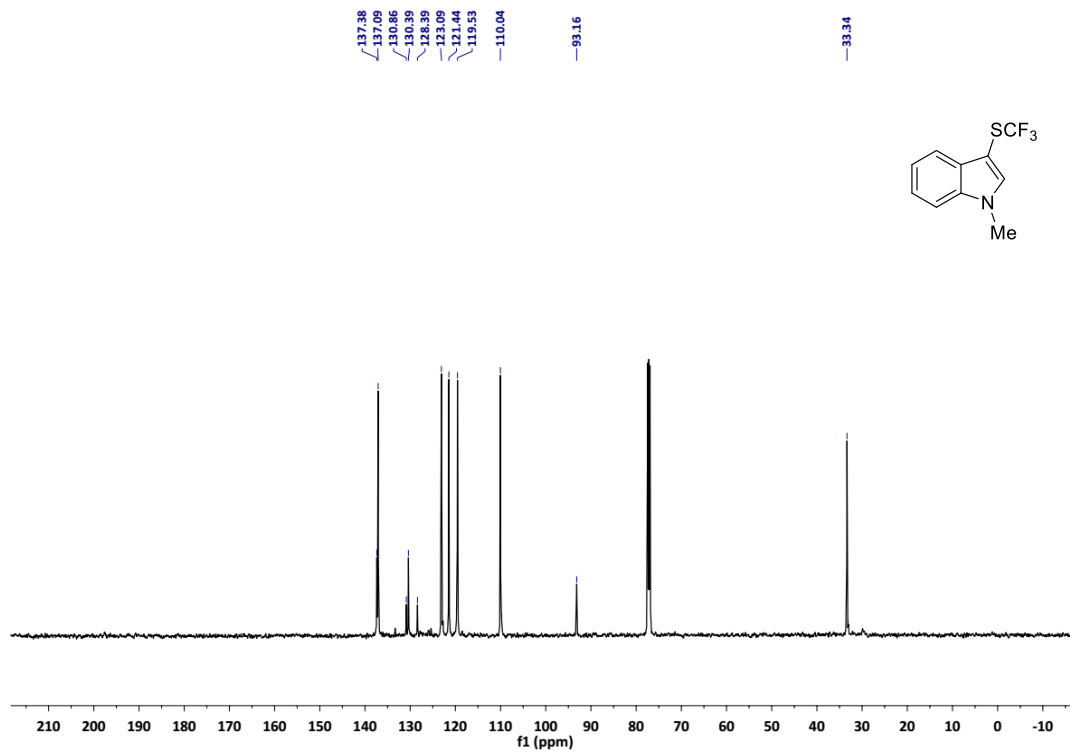
¹³C NMR spectrum (125 MHz, CDCl₃) of **3a**



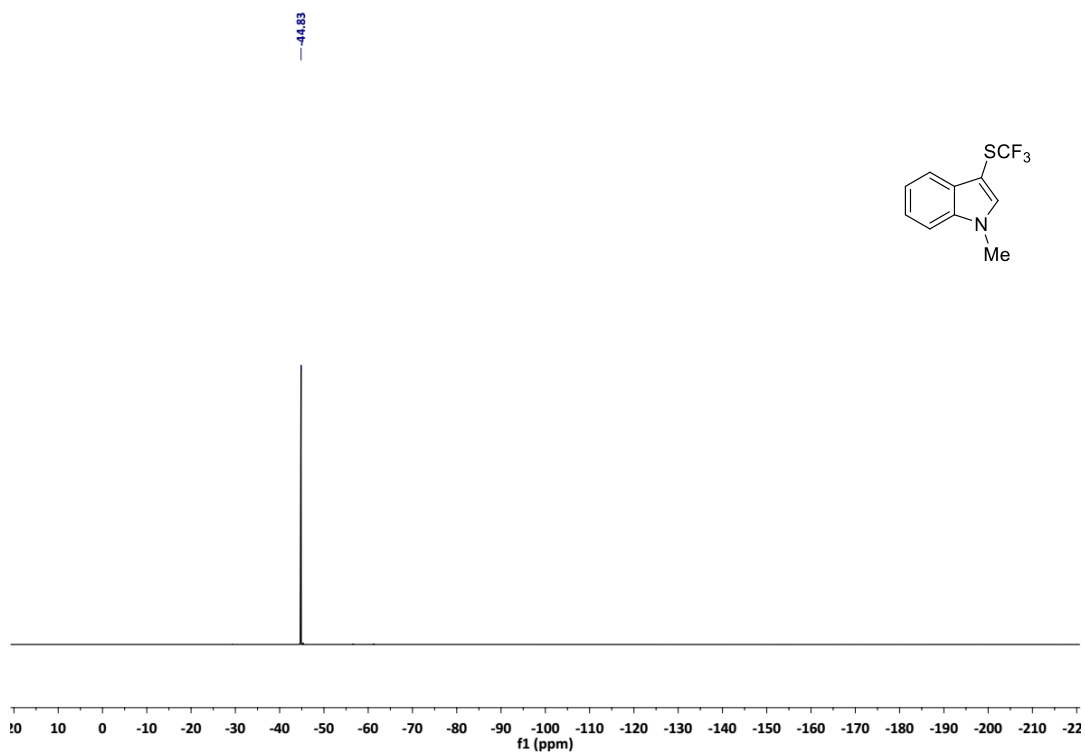
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3a**



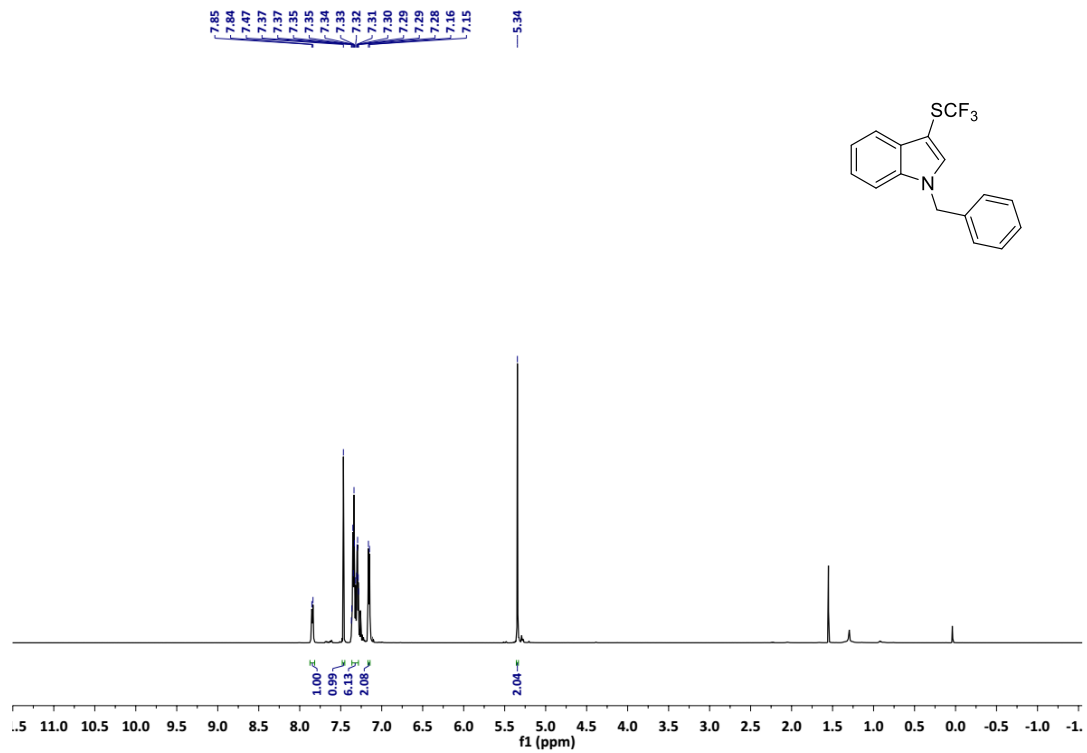
¹H NMR spectrum (500 MHz, CDCl₃) of **3b**



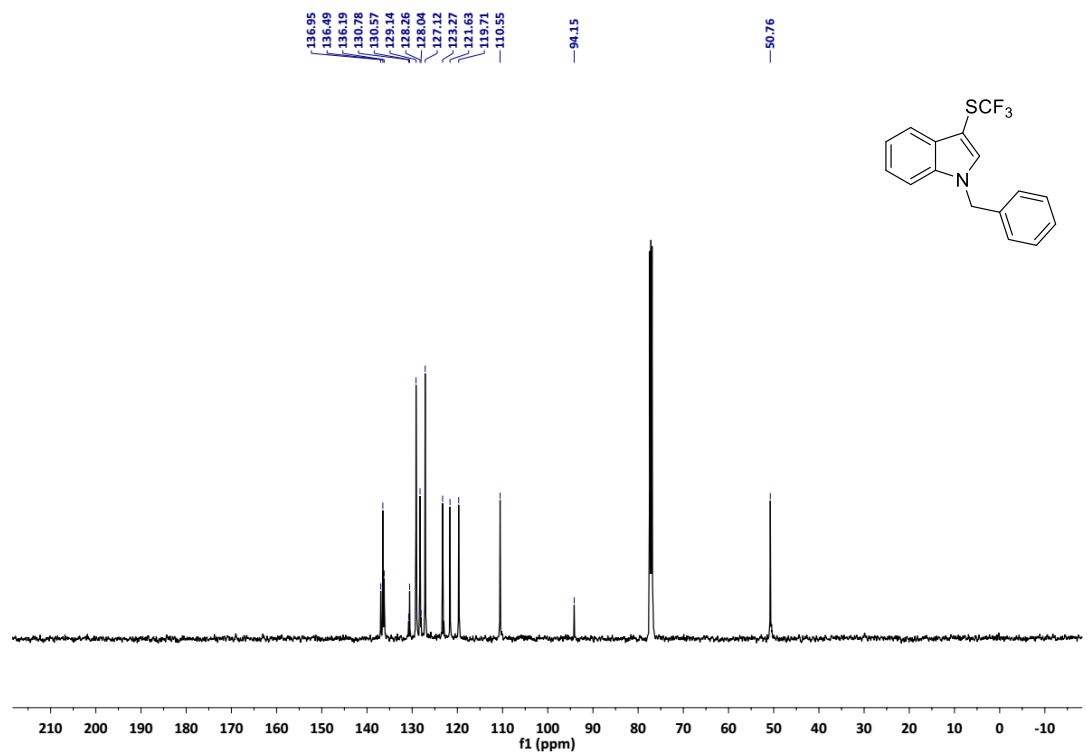
¹³C NMR spectrum (125 MHz, CDCl₃) of **3b**



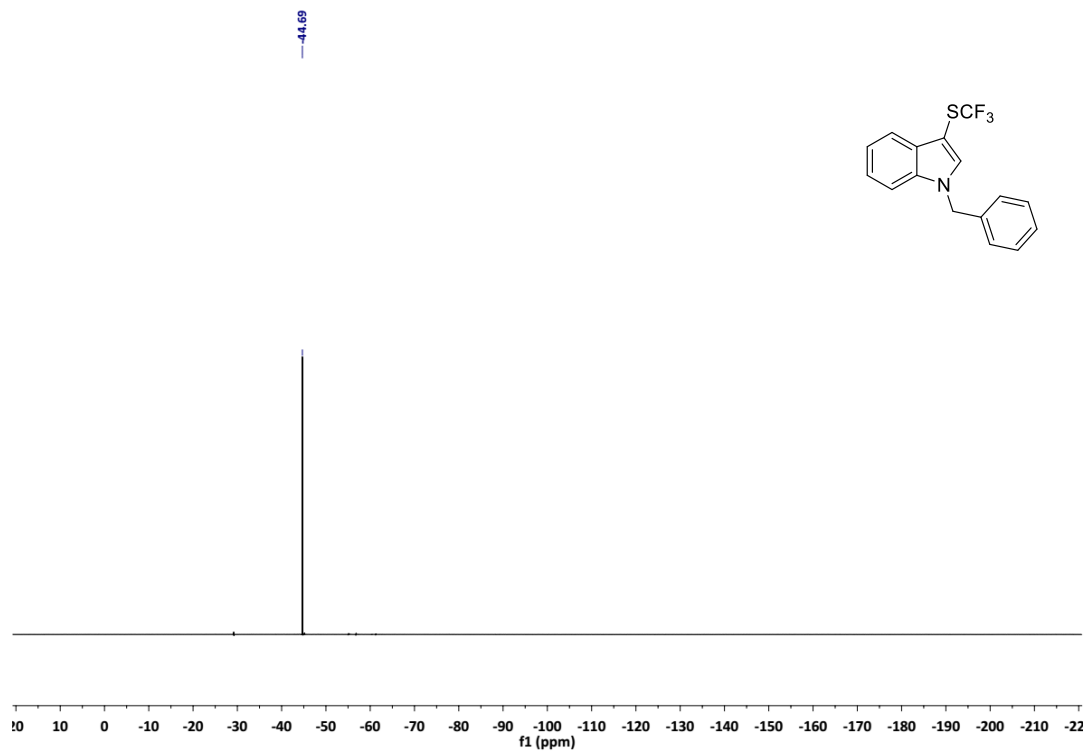
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3b**



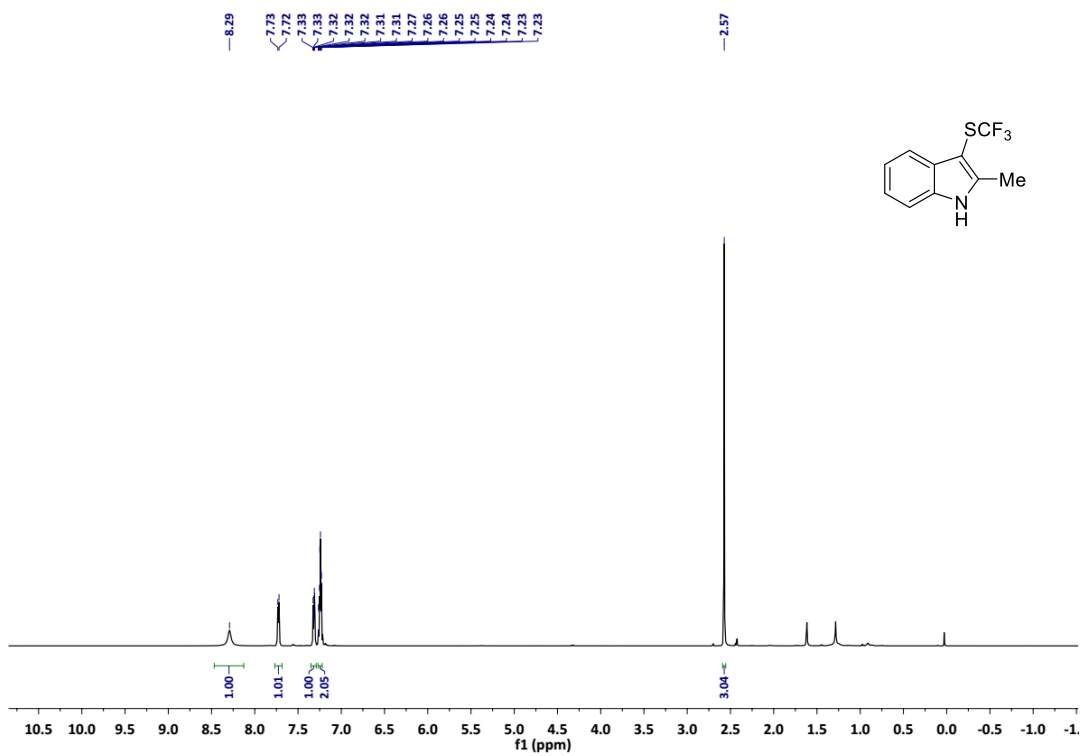
¹H NMR spectrum (500 MHz, CDCl₃) of **3c**



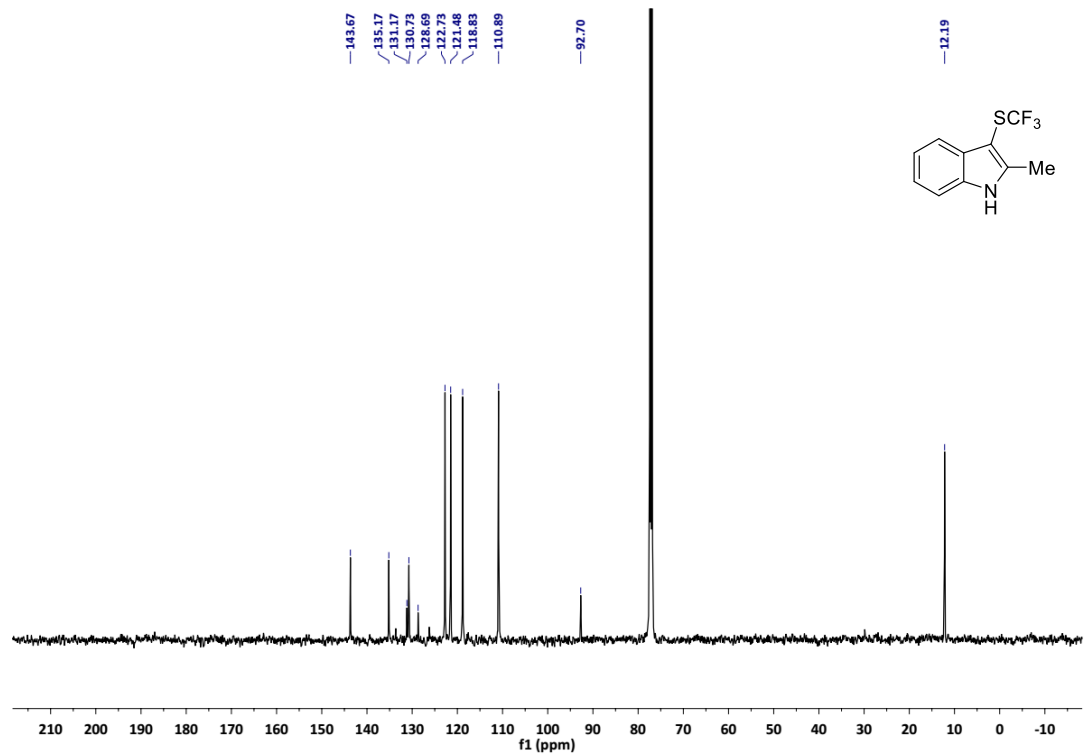
¹³C NMR spectrum (125 MHz, CDCl₃) of **3c**



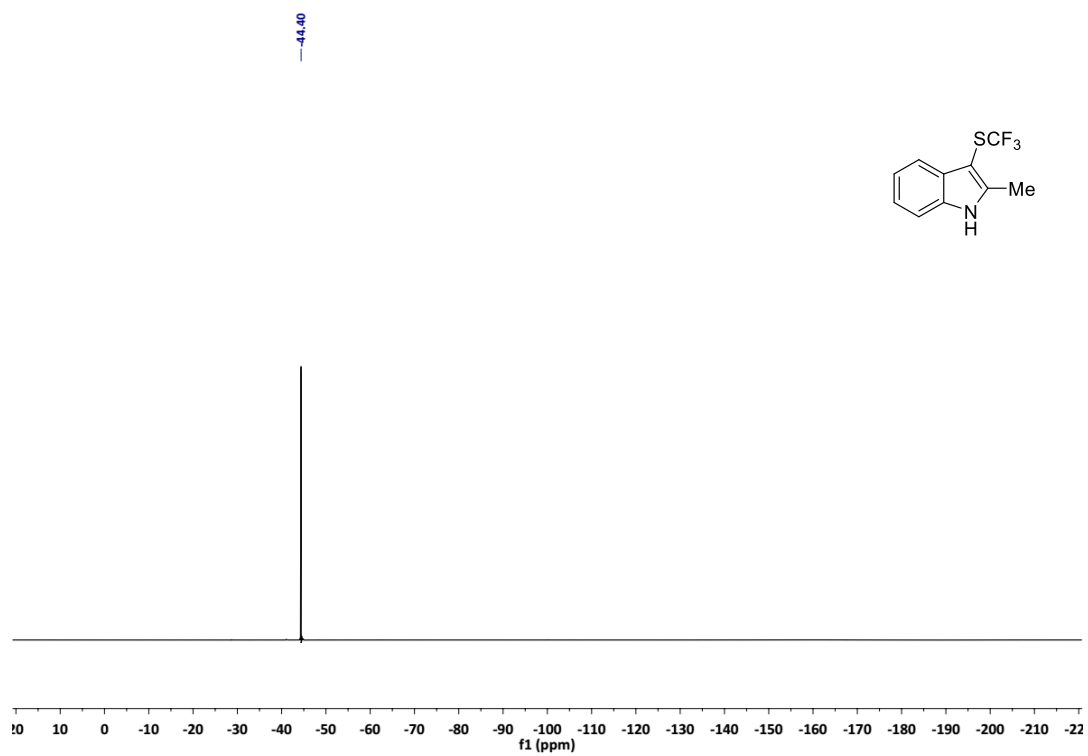
^{19}F NMR spectrum (470 MHz, CDCl_3) of **3c**



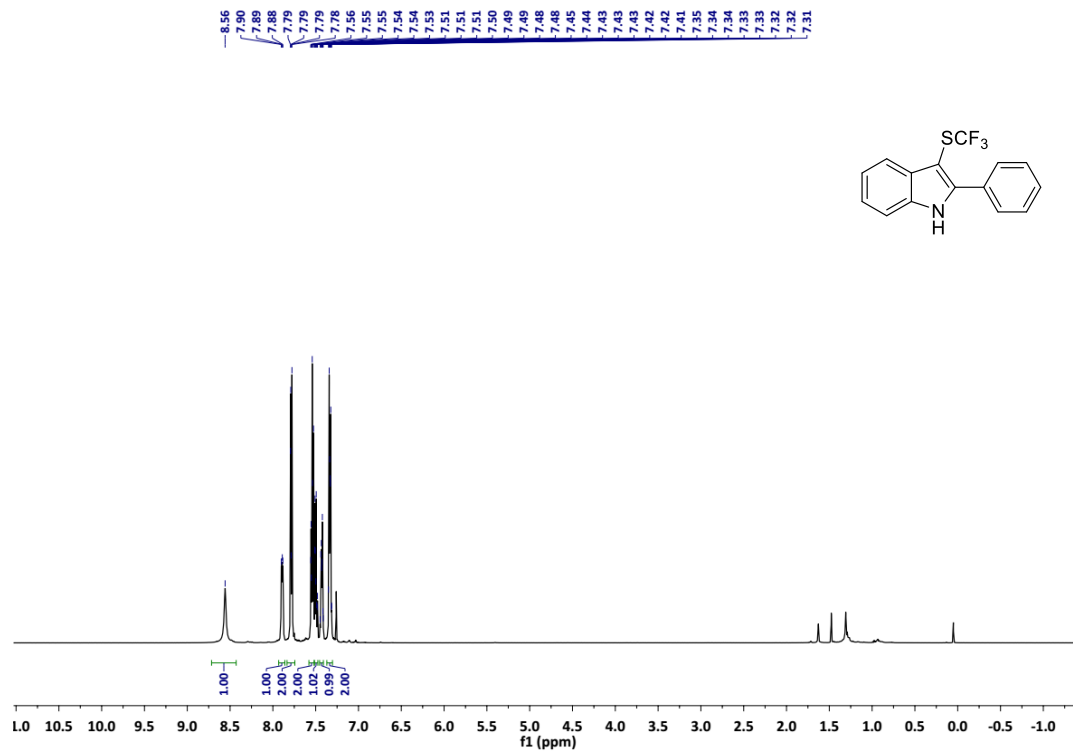
^1H NMR spectrum (500 MHz, CDCl_3) of **3d**



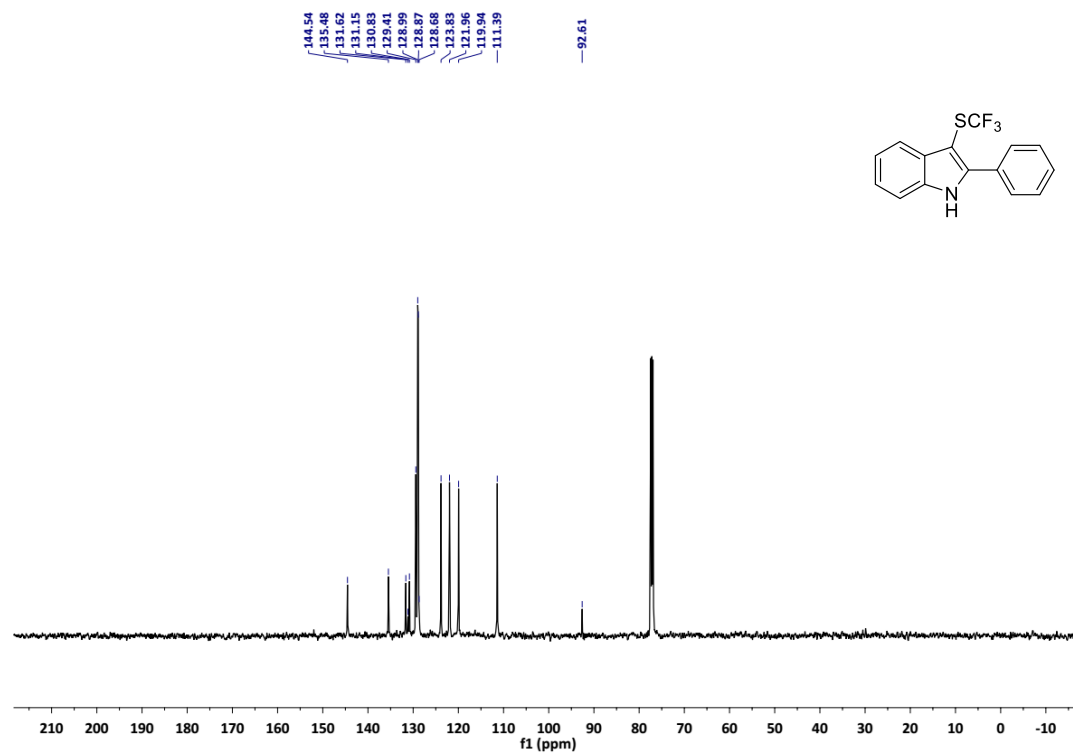
^{13}C NMR spectrum (125 MHz, CDCl_3) of **3d**



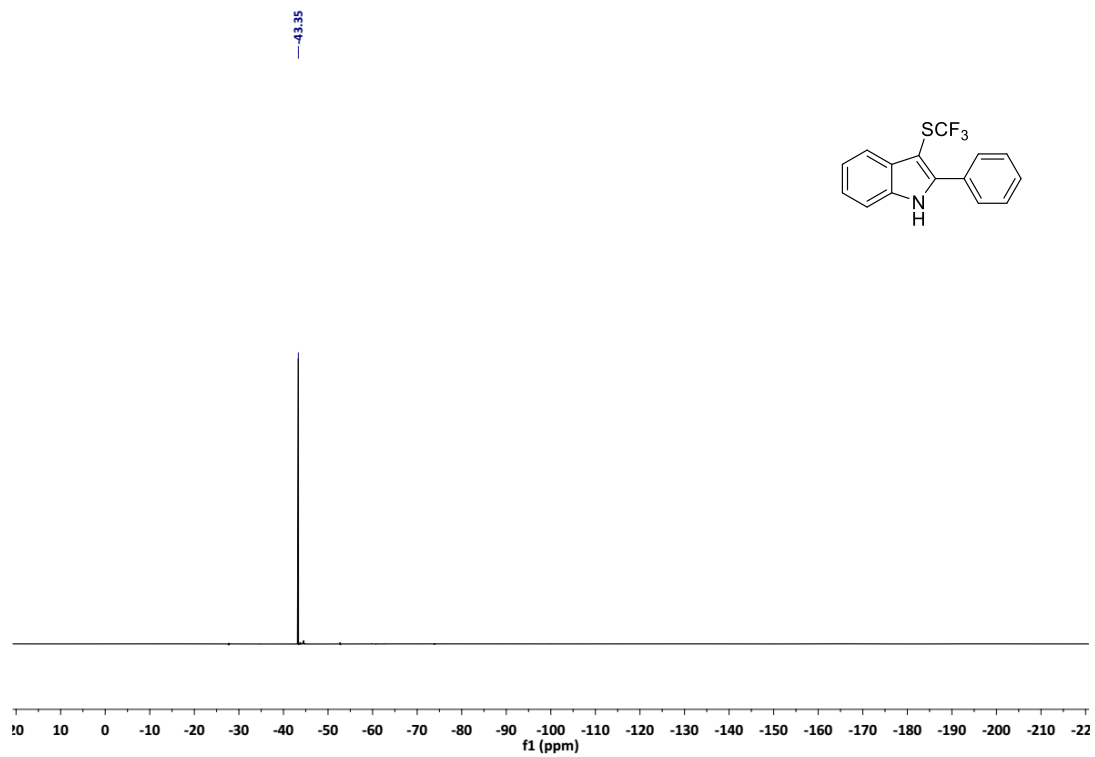
^{19}F NMR spectrum (470 MHz, CDCl_3) of **3d**



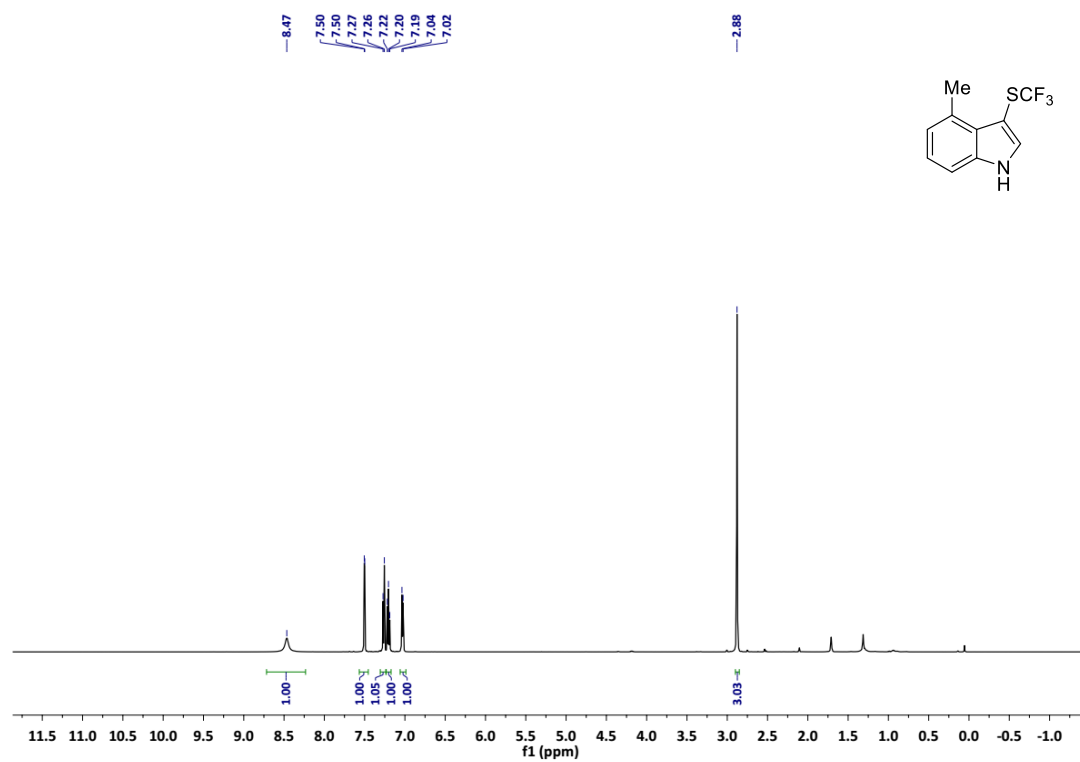
¹H NMR spectrum (500 MHz, CDCl₃) of 3e



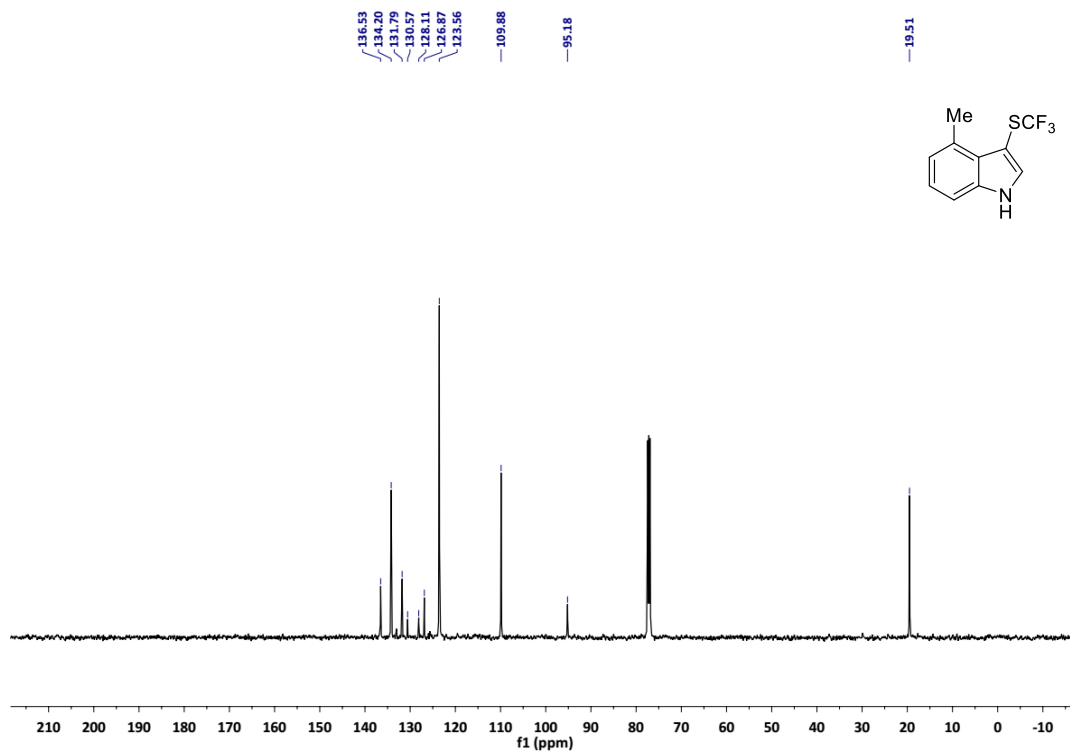
¹³C NMR spectrum (125 MHz, CDCl₃) of 3e



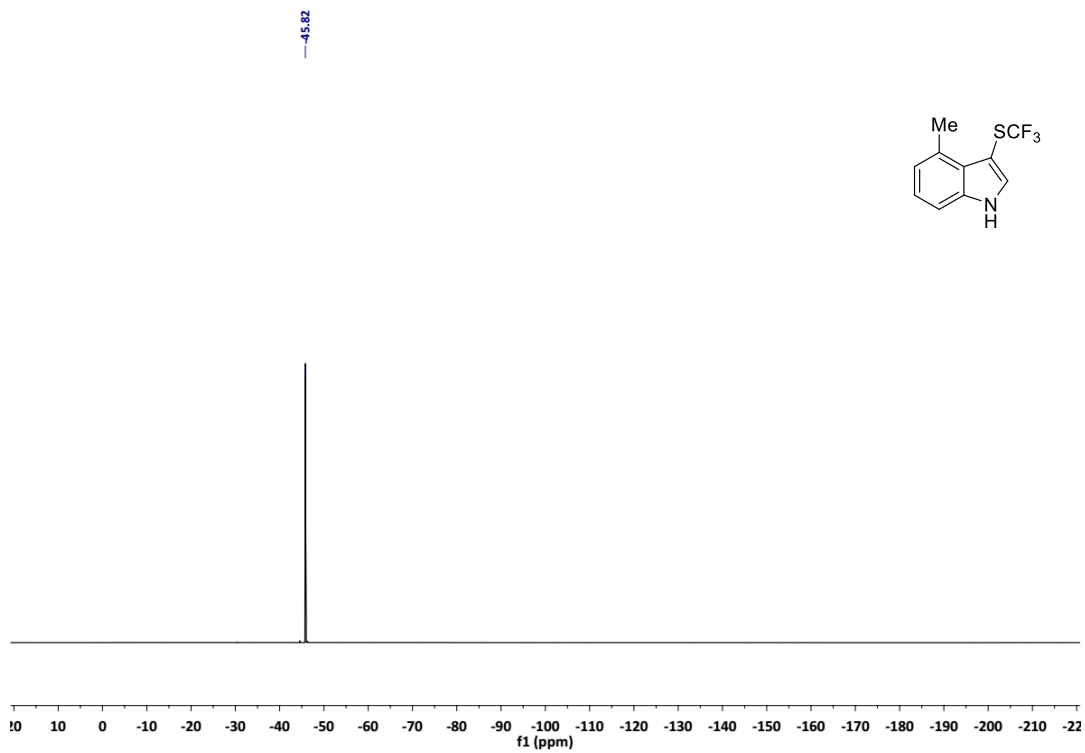
^{19}F NMR spectrum (470 MHz, CDCl_3) of **3e**



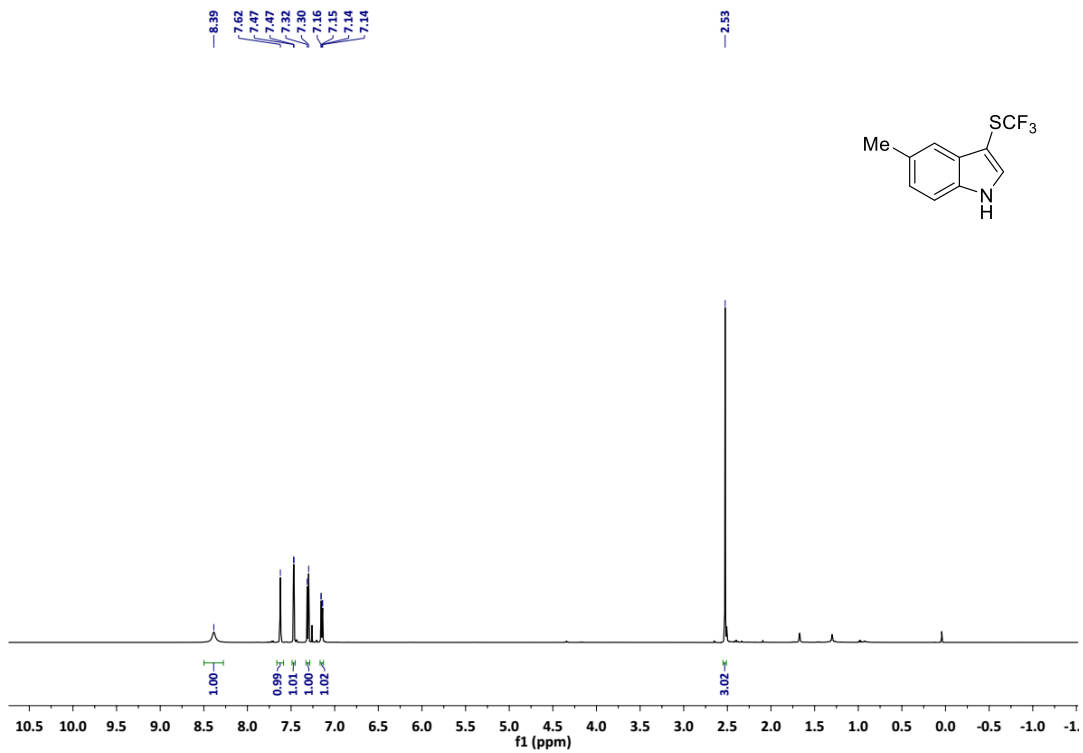
^1H NMR spectrum (500 MHz, CDCl_3) of **3f**



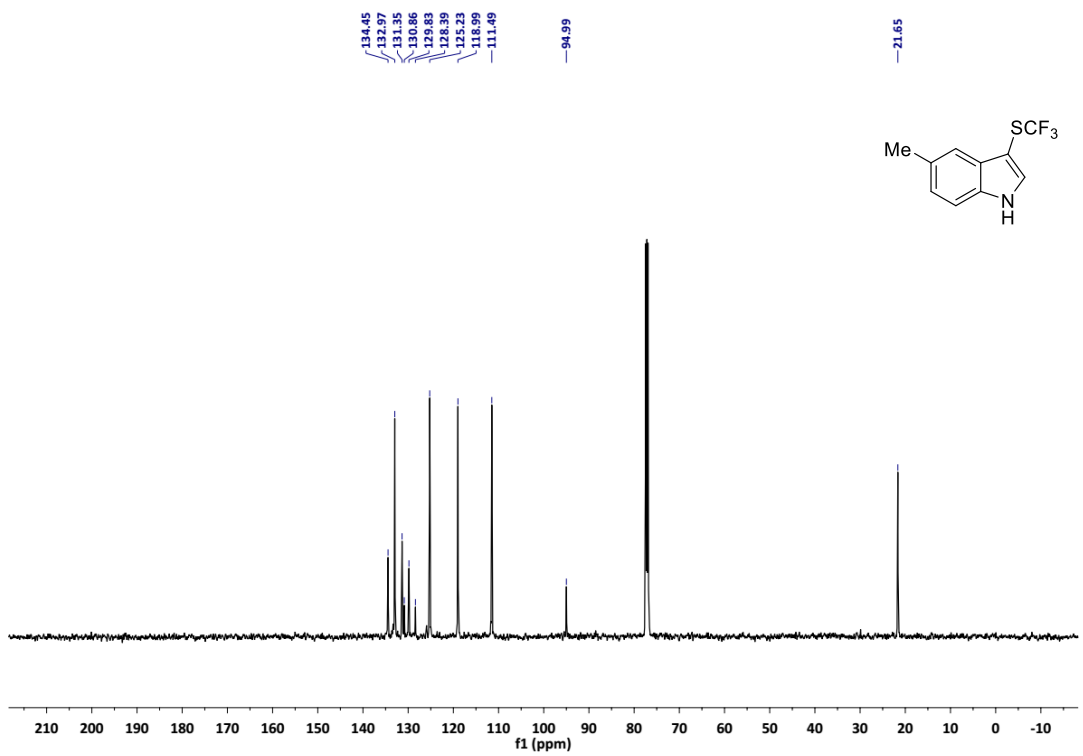
¹³C NMR spectrum (125 MHz, CDCl₃) of **3f**



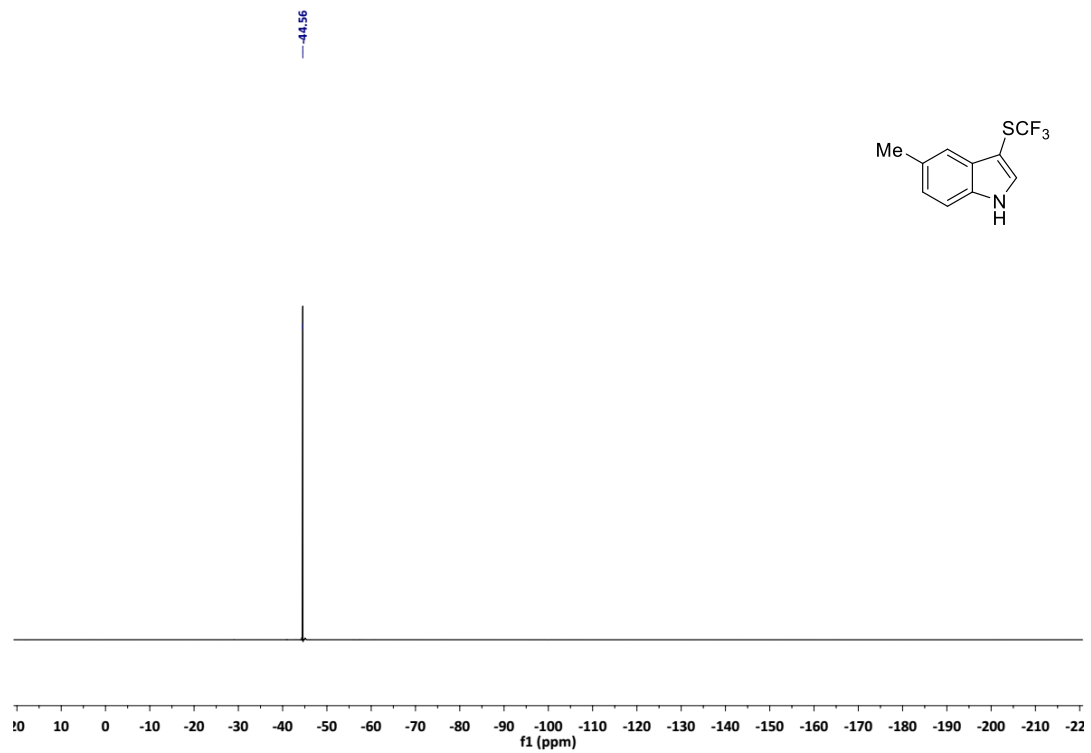
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3f**



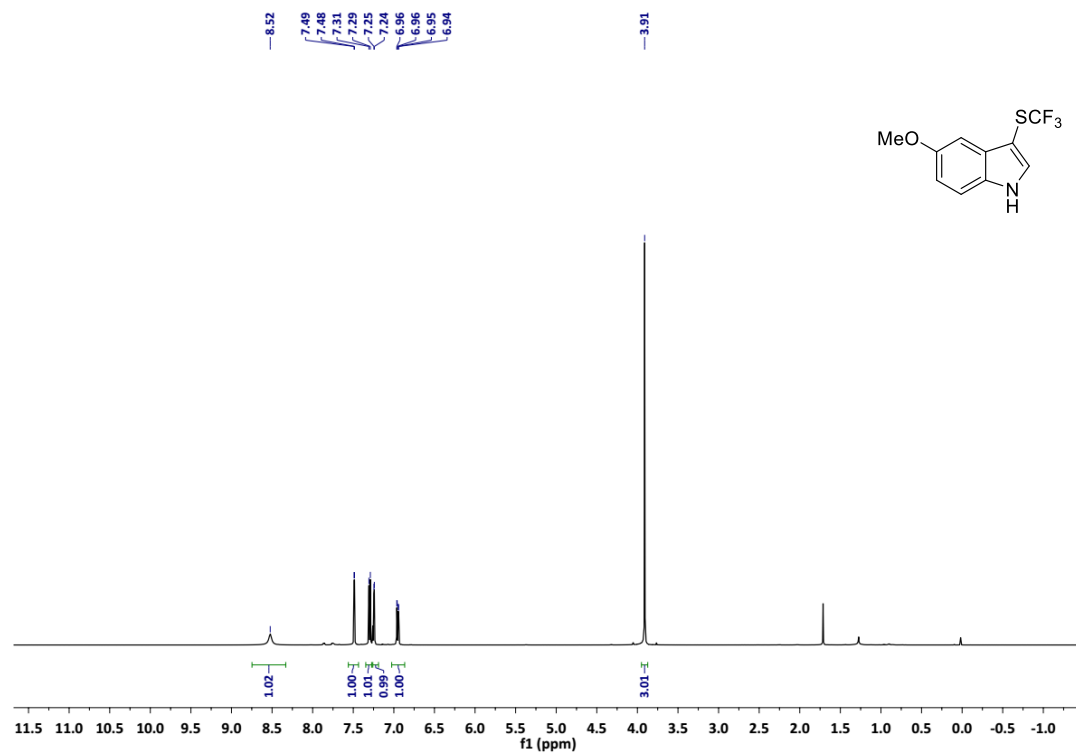
¹H NMR spectrum (500 MHz, CDCl₃) of **3g**



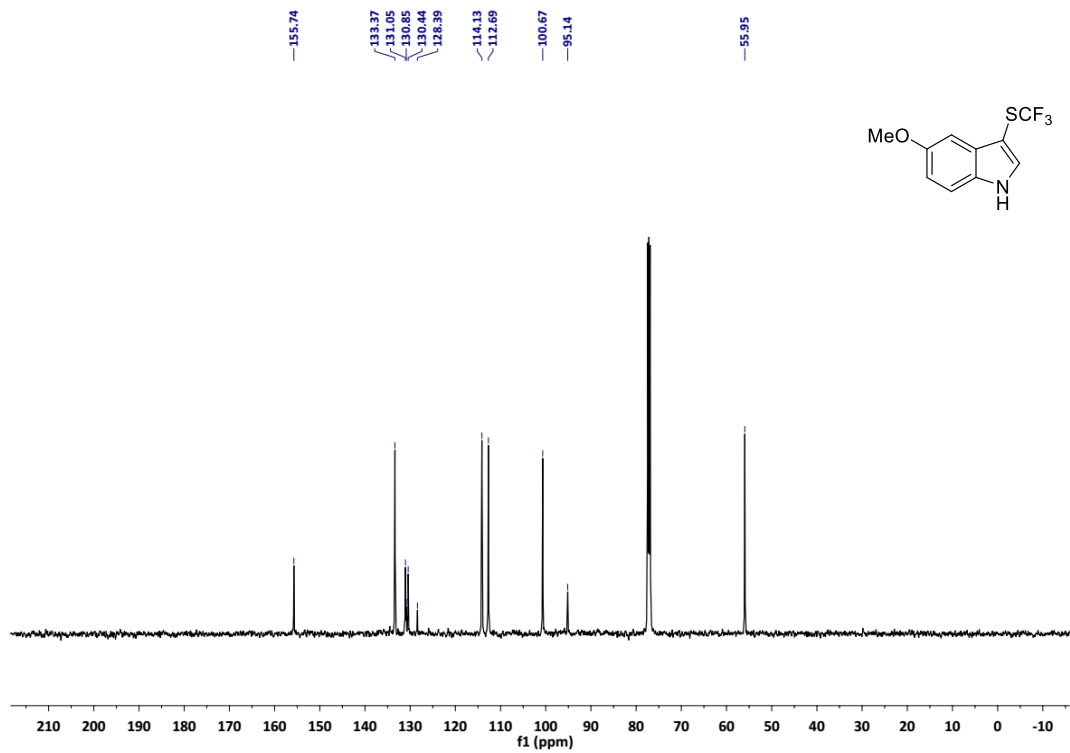
¹³C NMR spectrum (125 MHz, CDCl₃) of **3g**



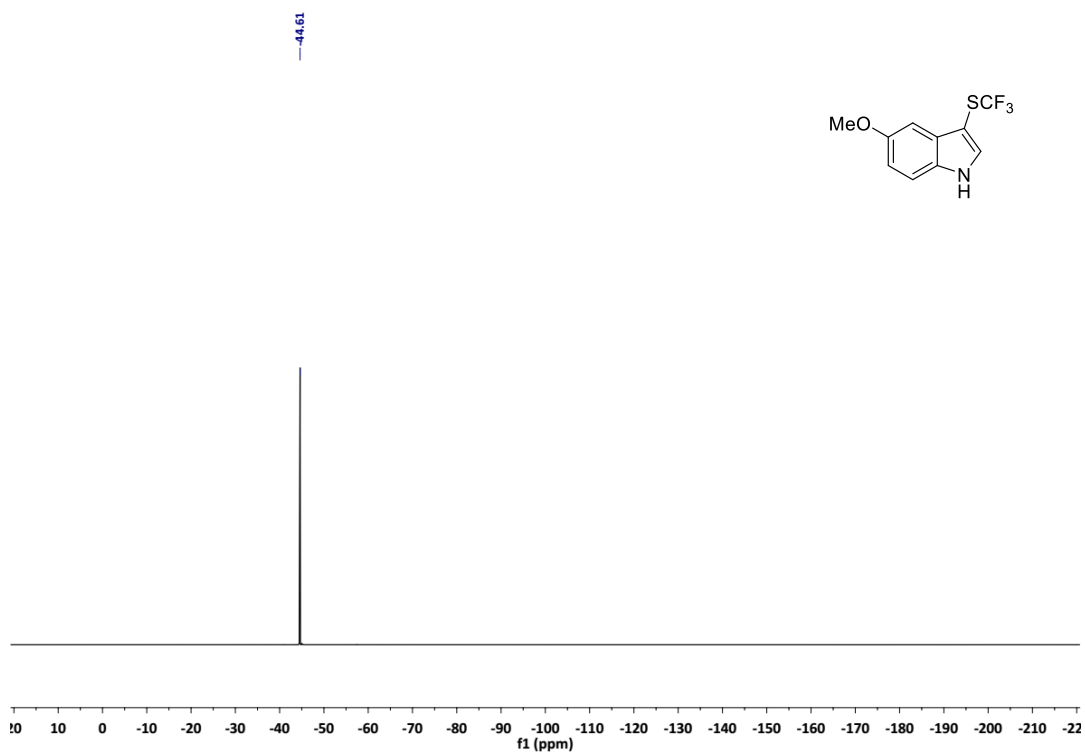
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3g**



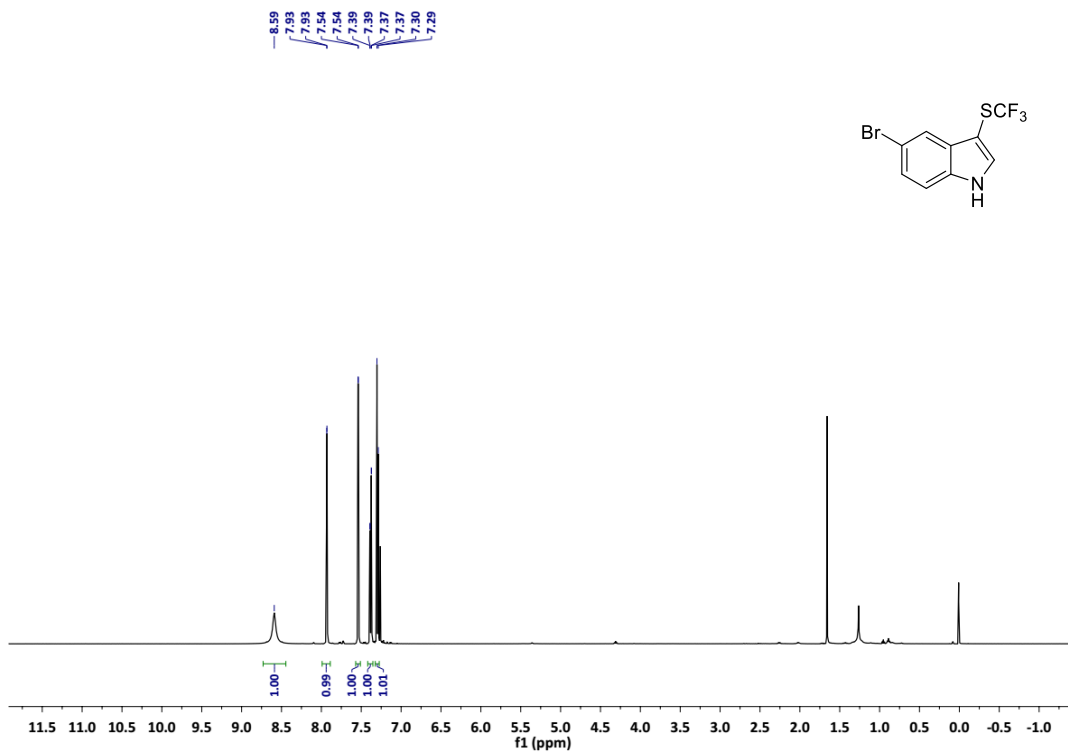
¹H NMR spectrum (500 MHz, CDCl₃) of **3h**



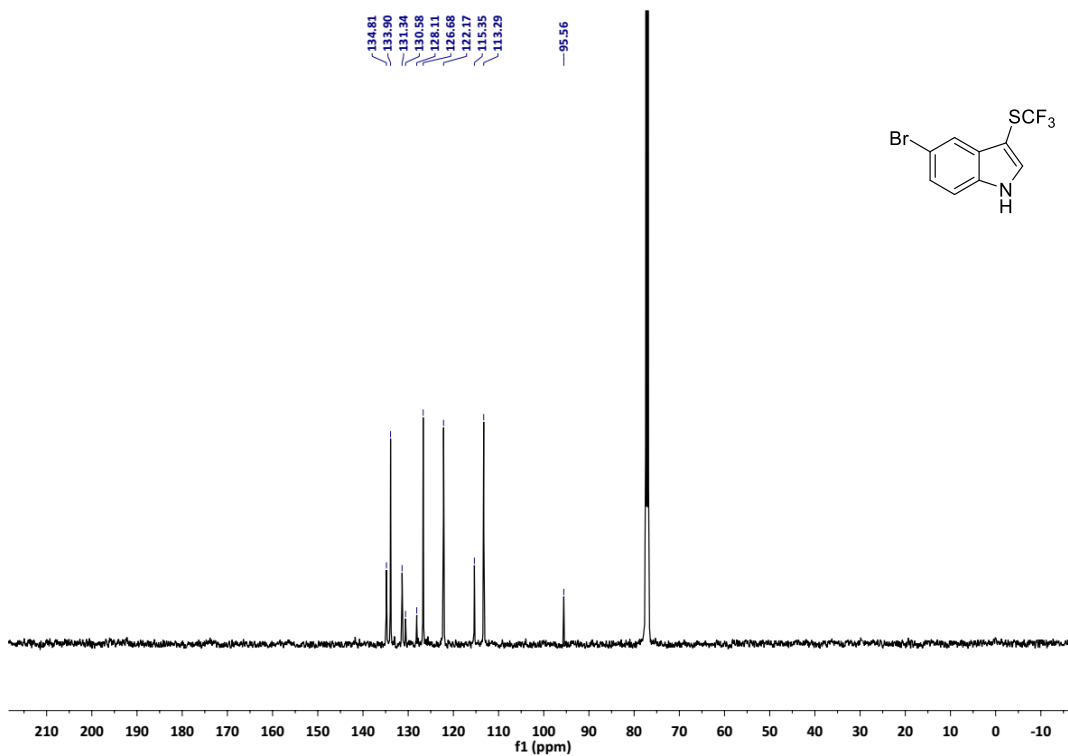
¹³C NMR spectrum (125 MHz, CDCl₃) of **3h**



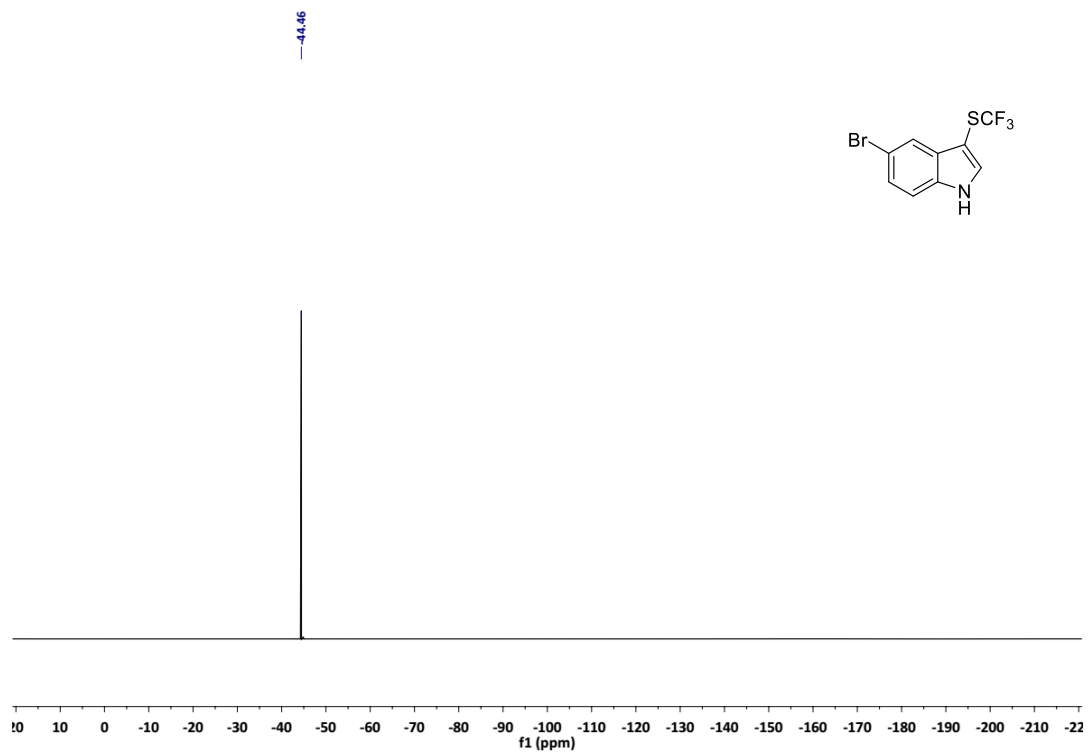
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3h**



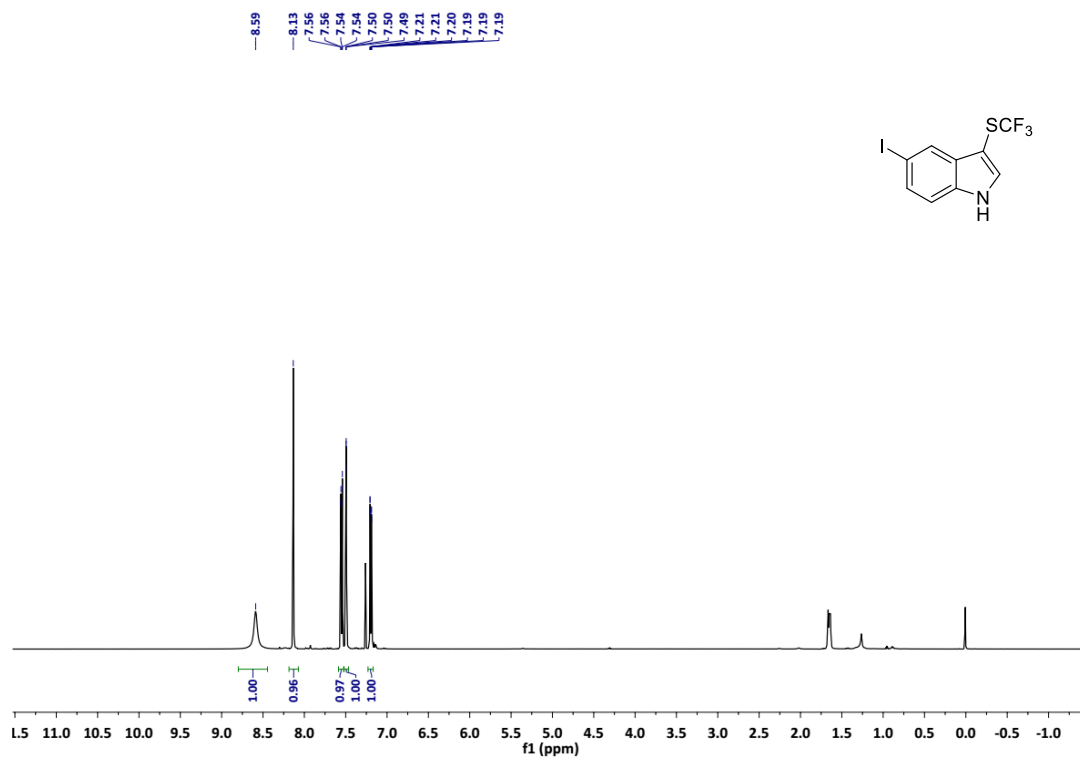
¹H NMR spectrum (500 MHz, CDCl₃) of **3i**



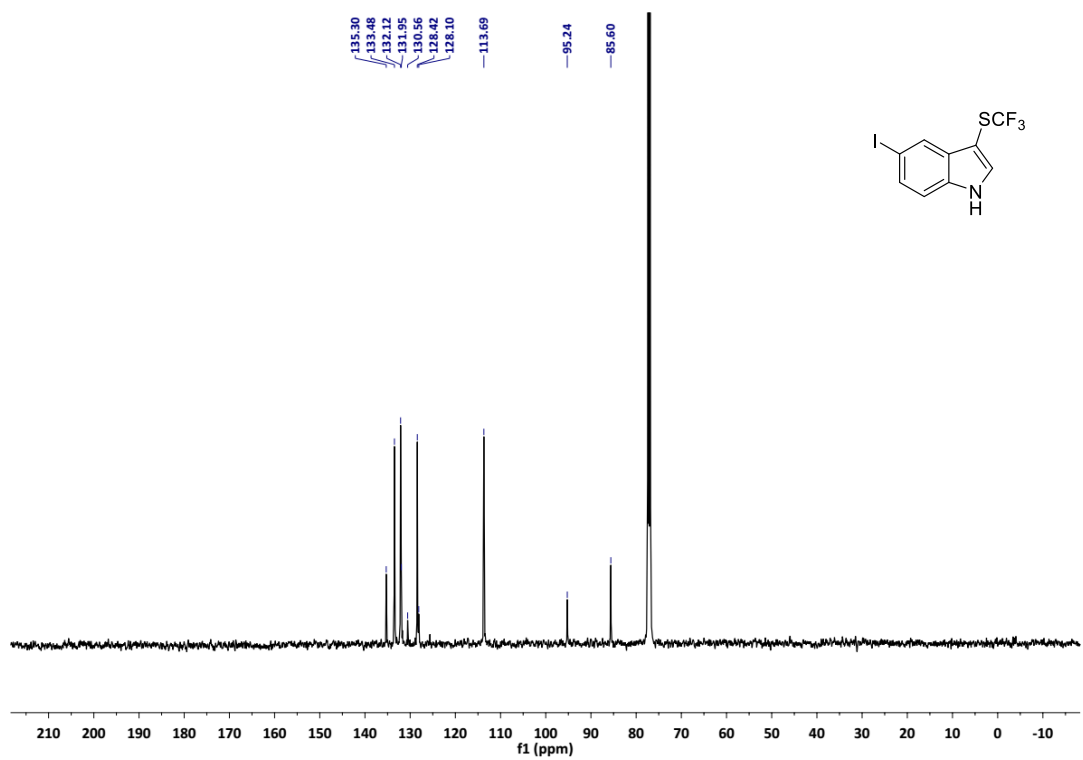
¹³C NMR spectrum (125 MHz, CDCl₃) of **3i**



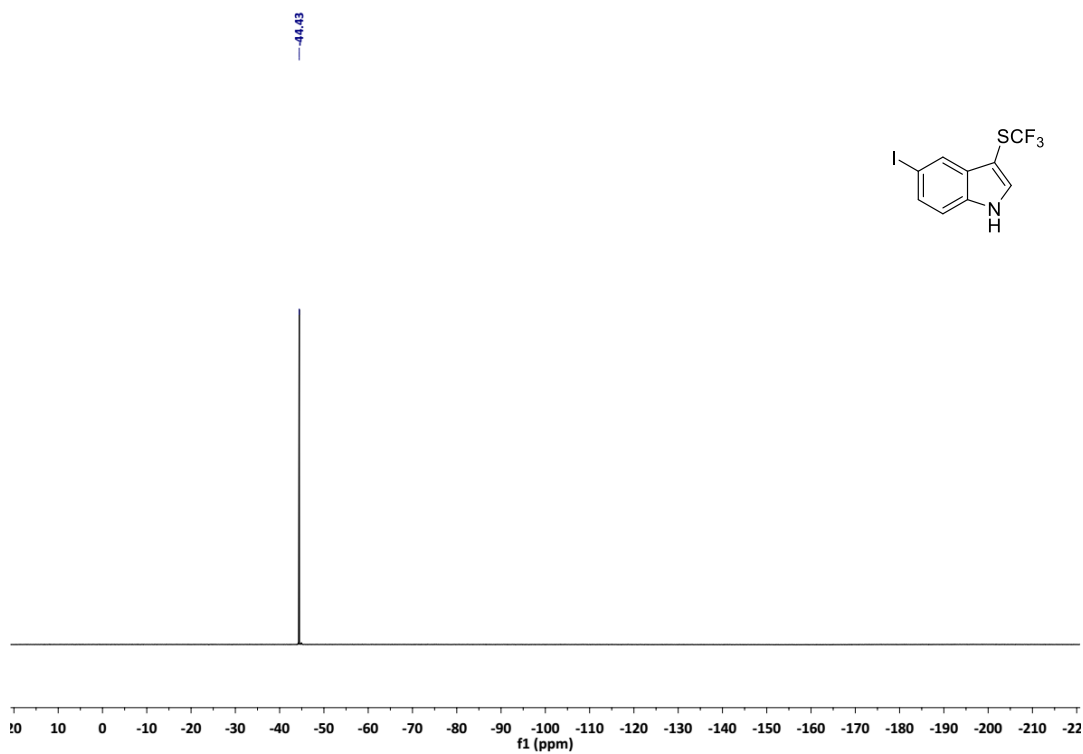
^{19}F NMR spectrum (470 MHz, CDCl_3) of **3i**



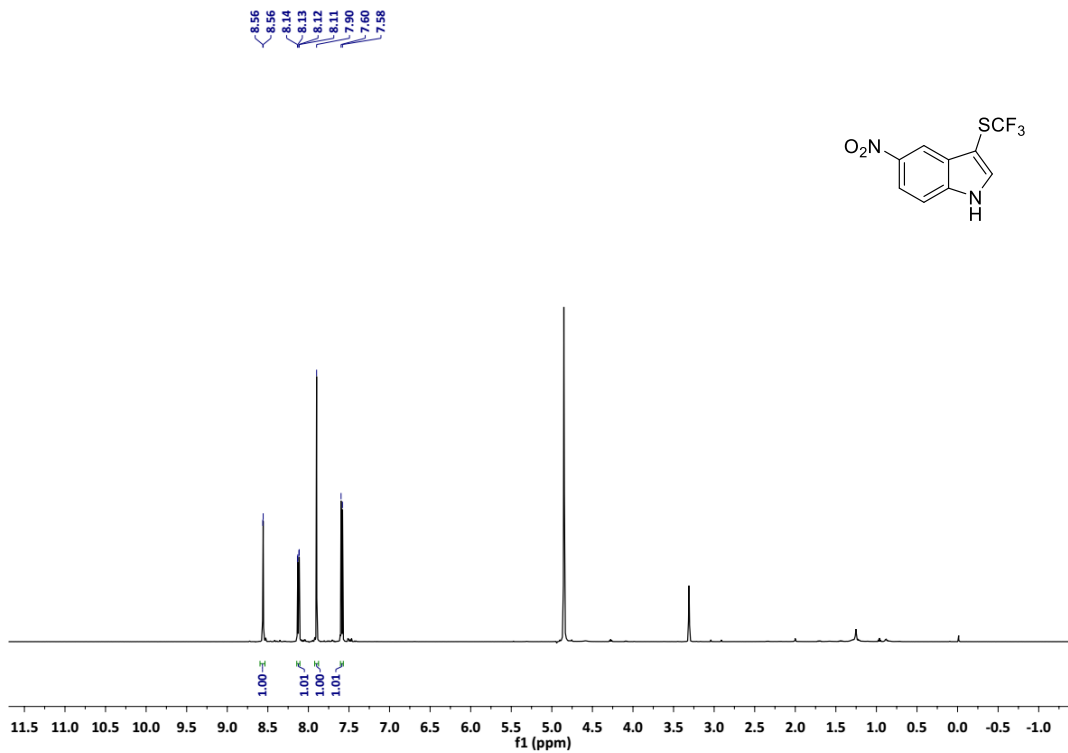
^1H NMR spectrum (500 MHz, CDCl_3) of **3j**



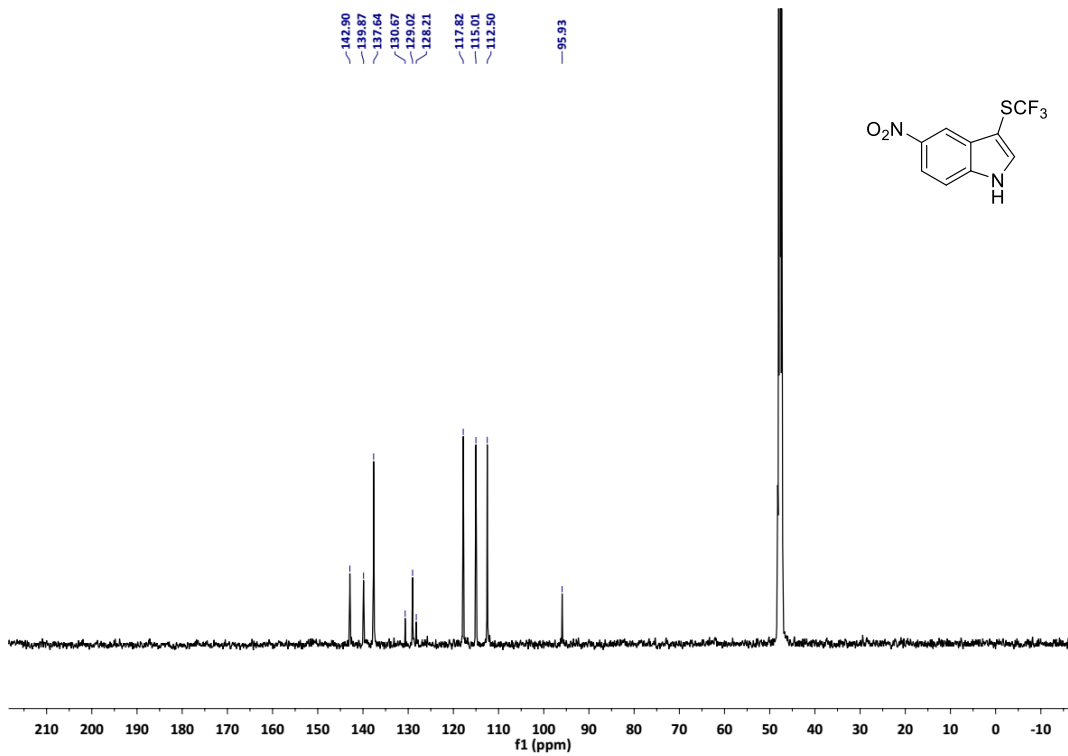
¹³C NMR spectrum (125 MHz, CDCl₃) of **3j**



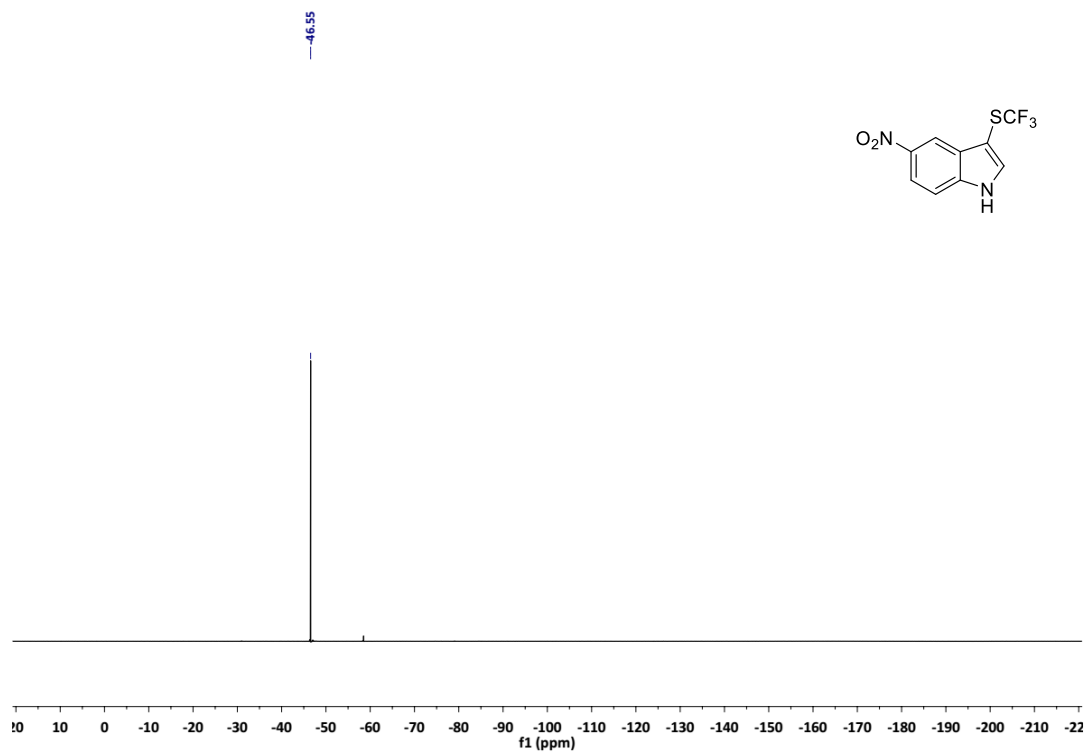
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3j**



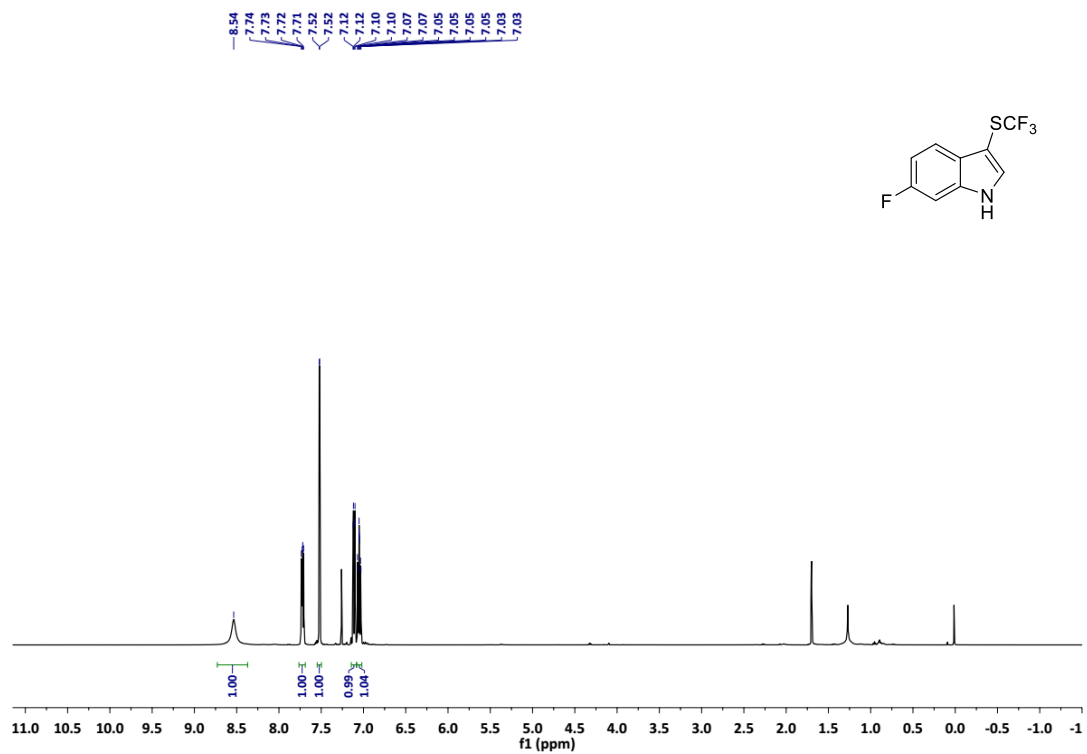
¹H NMR spectrum (500 MHz, CD₃OD) of **3k**



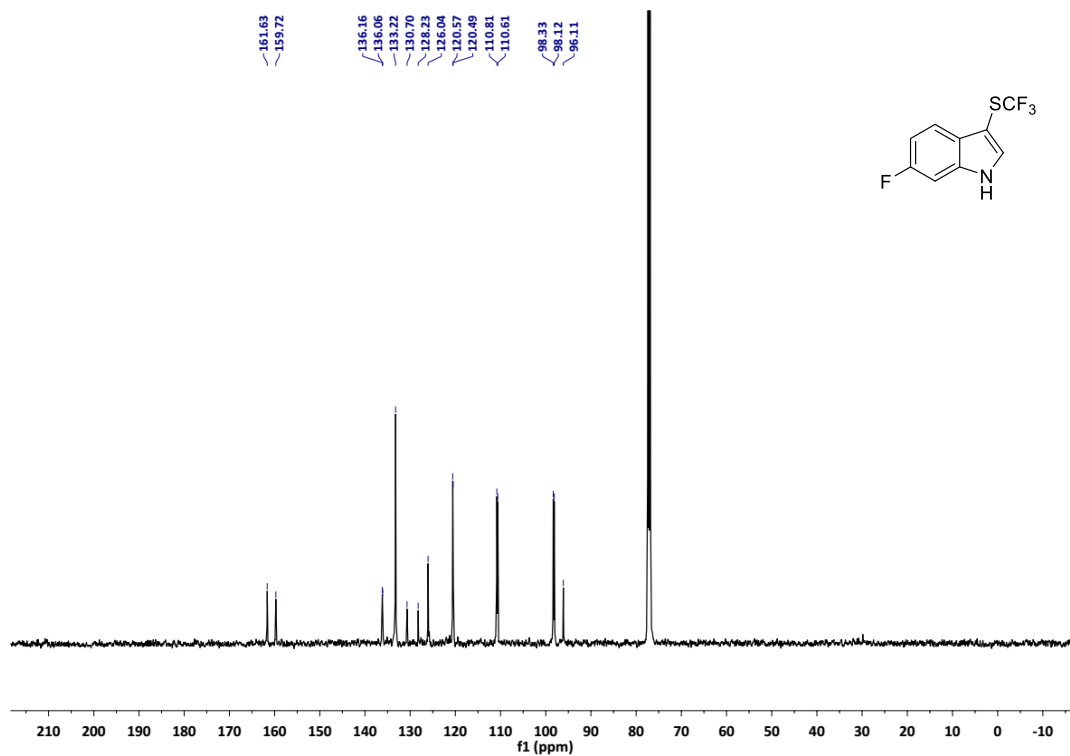
¹³C NMR spectrum (125 MHz, CD₃OD) of **3k**



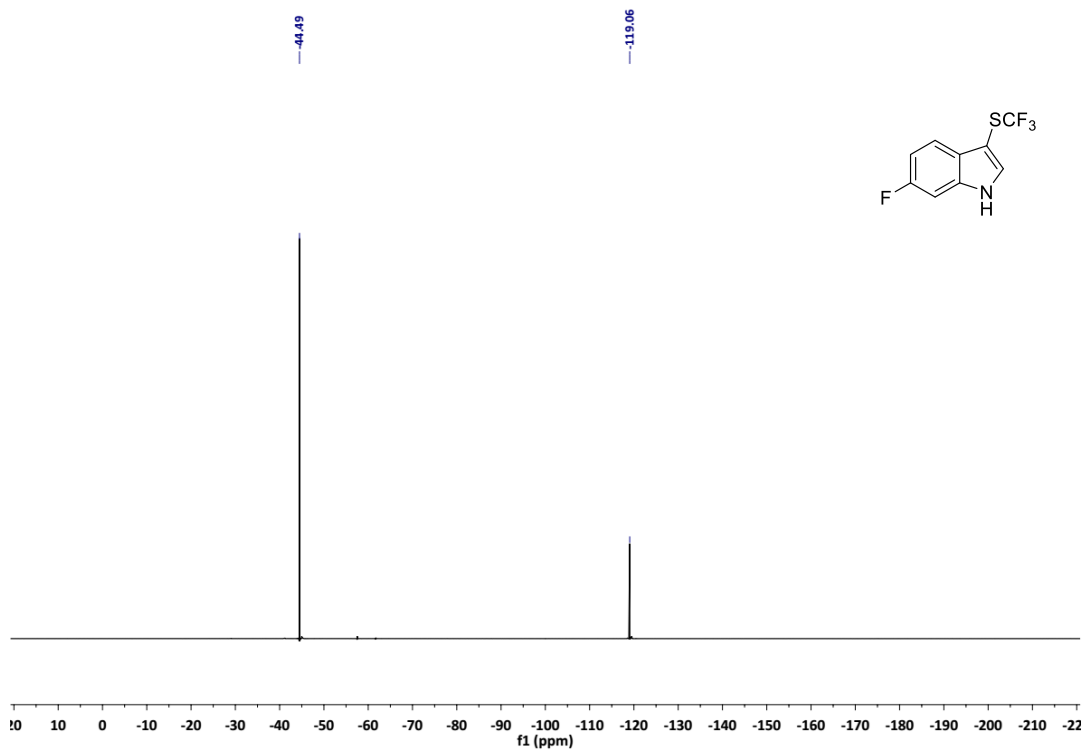
^{19}F NMR spectrum (470 MHz, CD_3OD) of **3k**



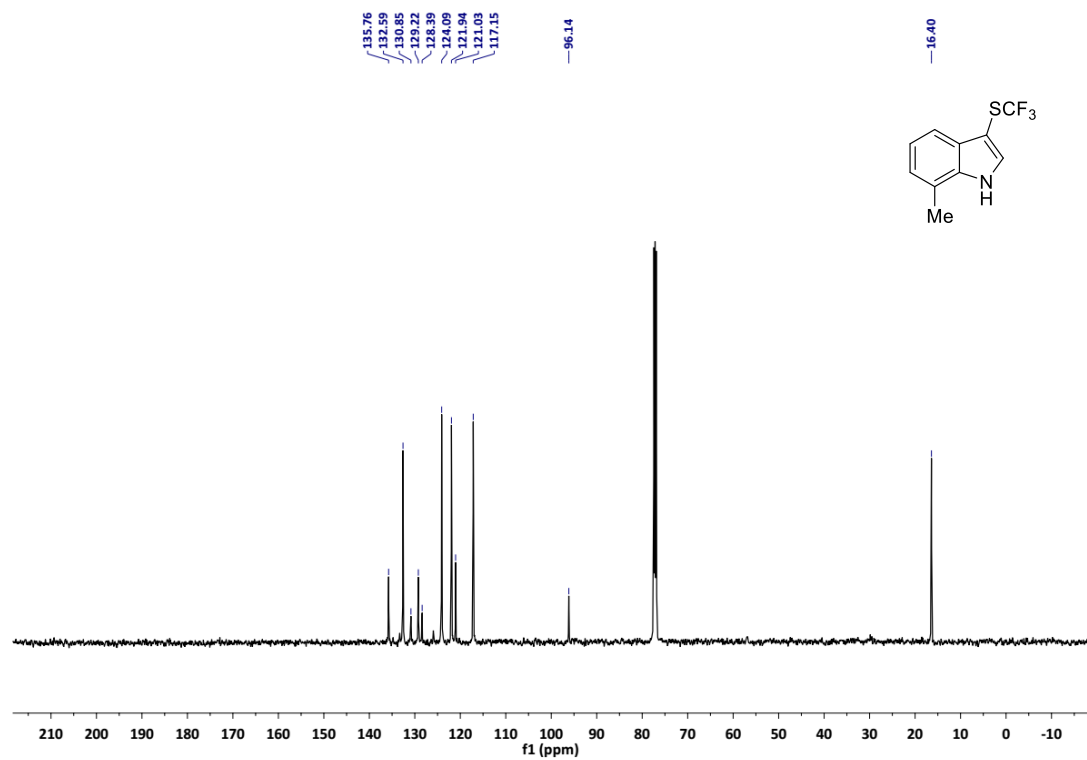
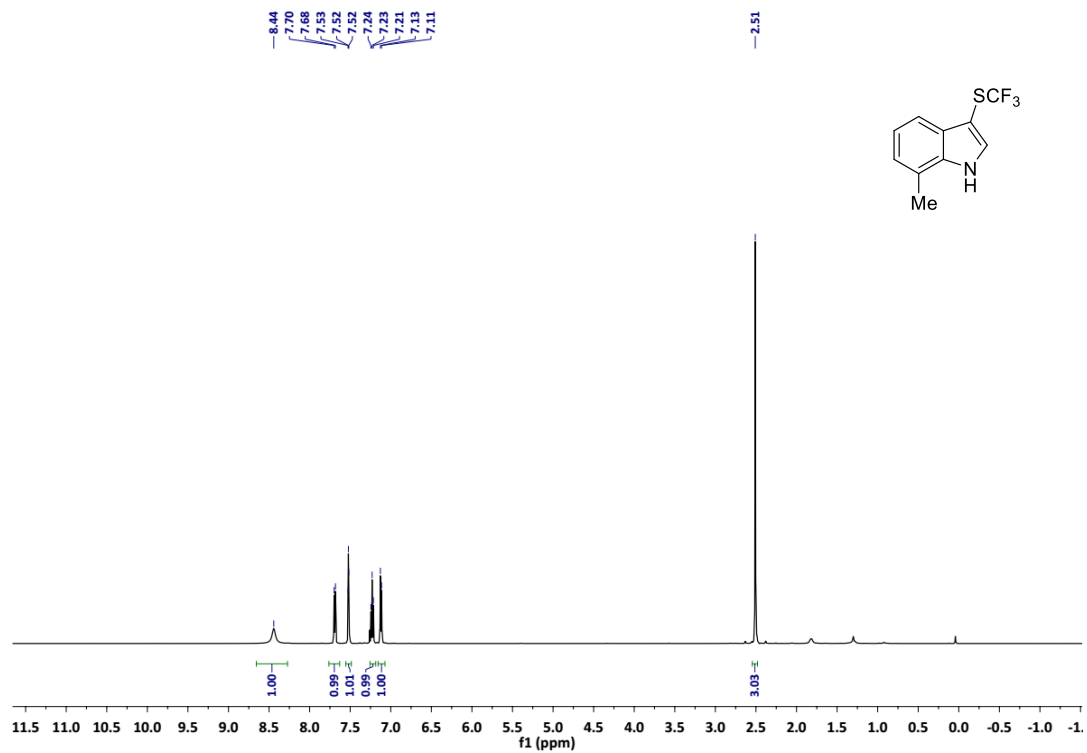
^1H NMR spectrum (500 MHz, CDCl_3) of **3l**

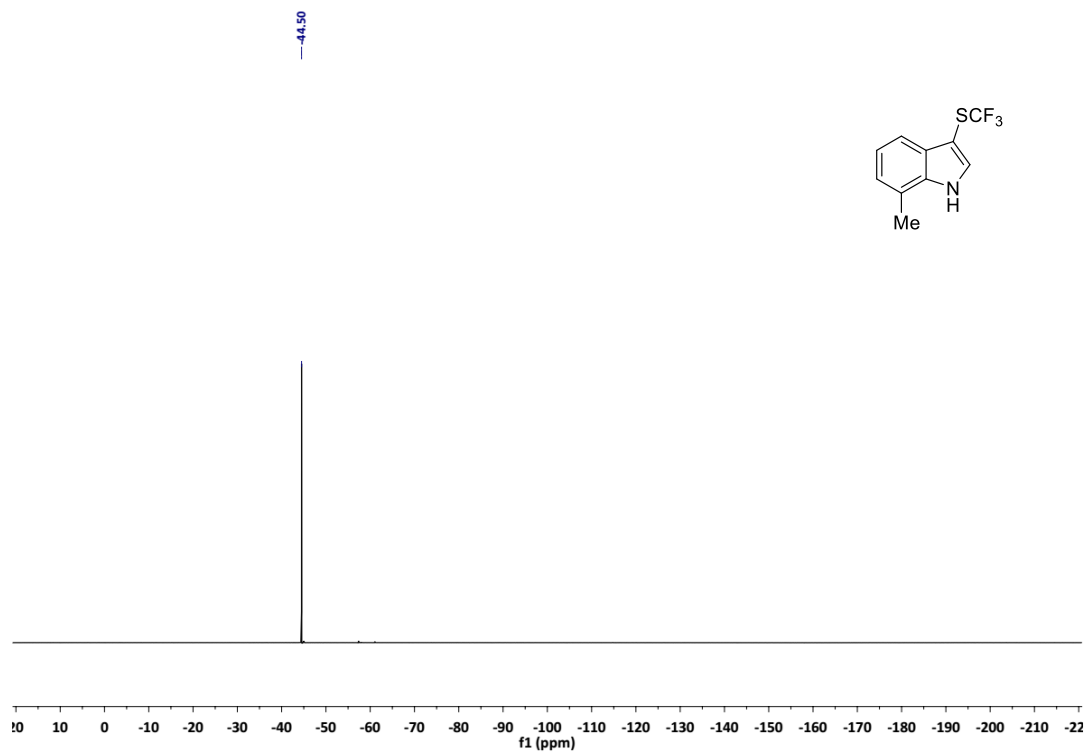


¹³C NMR spectrum (125 MHz, CDCl₃) of **3I**

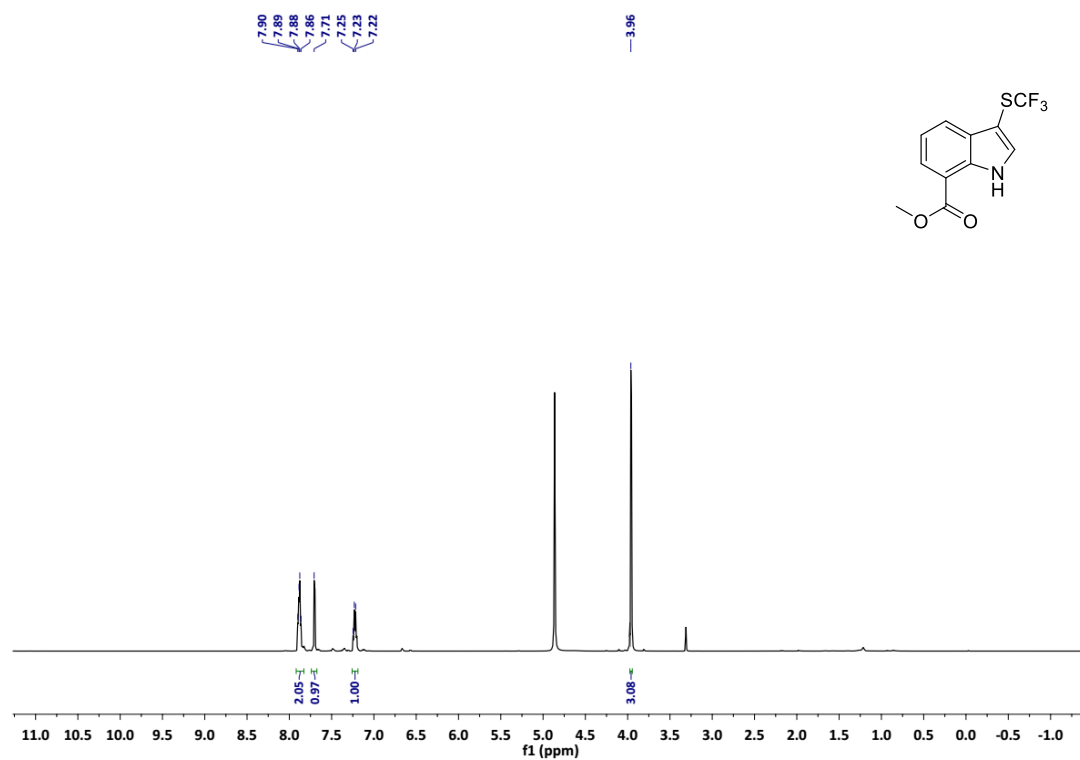


¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3I**

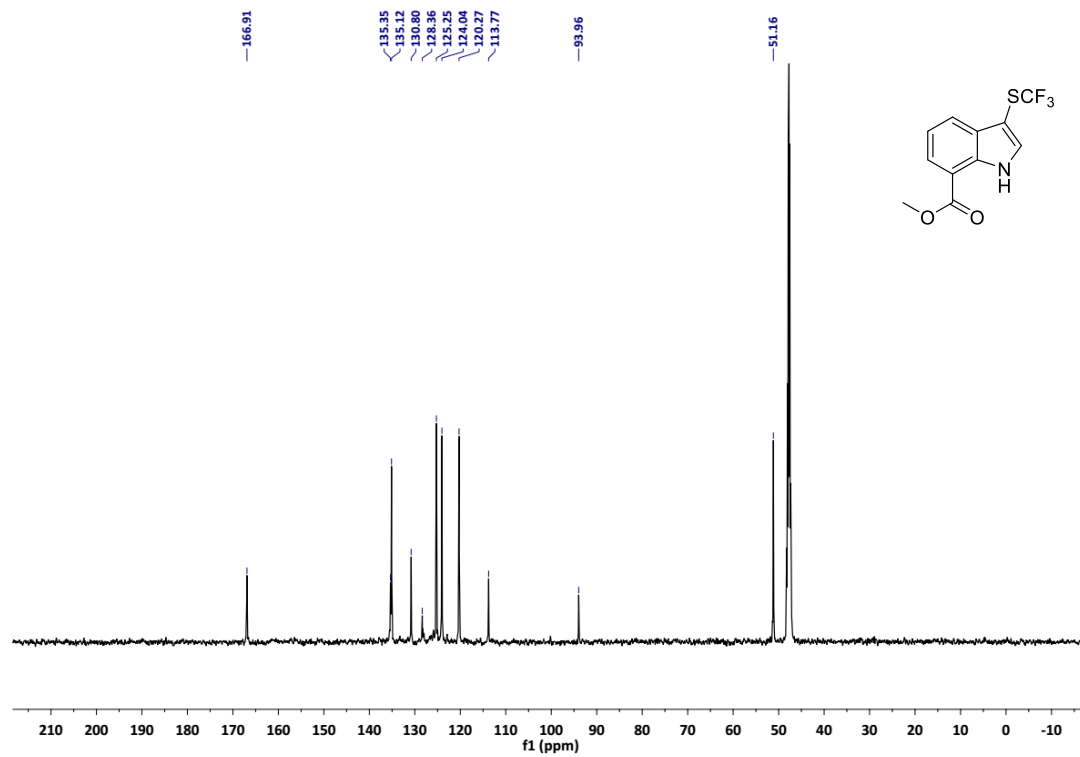




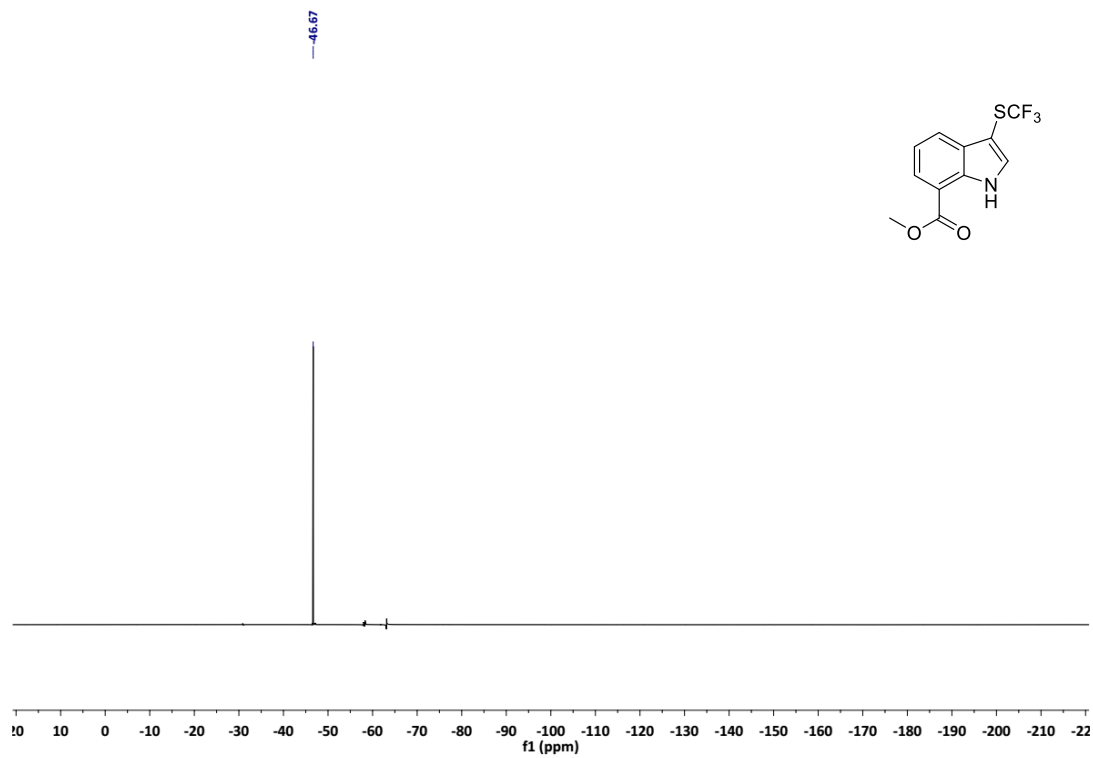
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **3m**



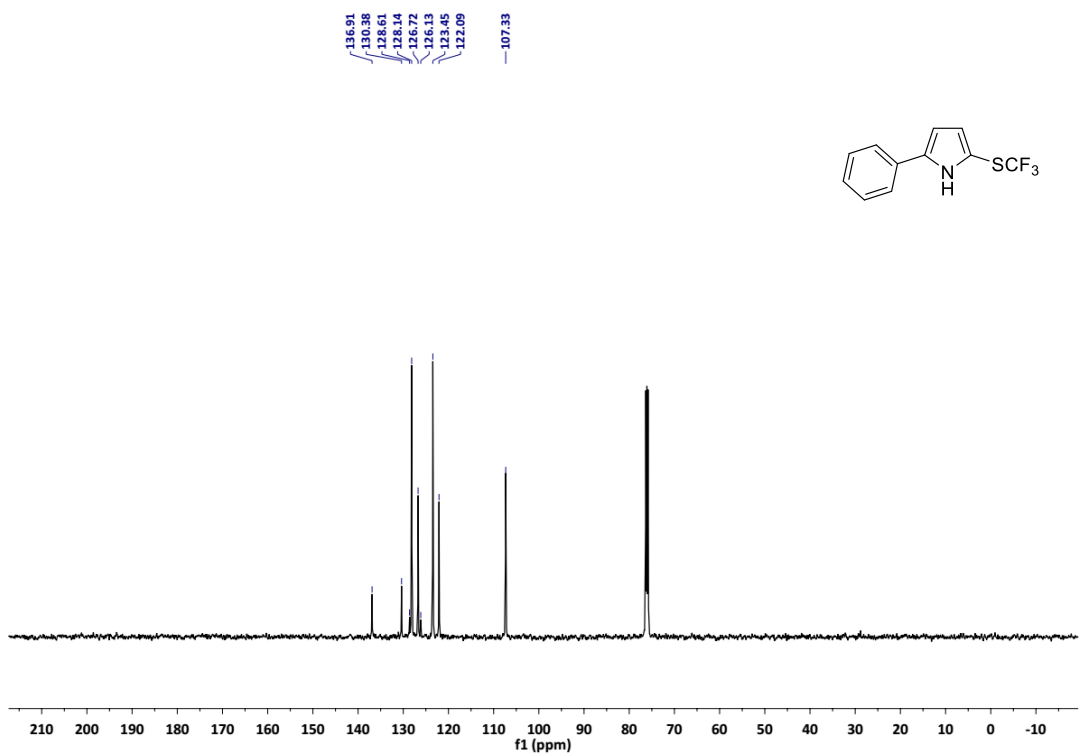
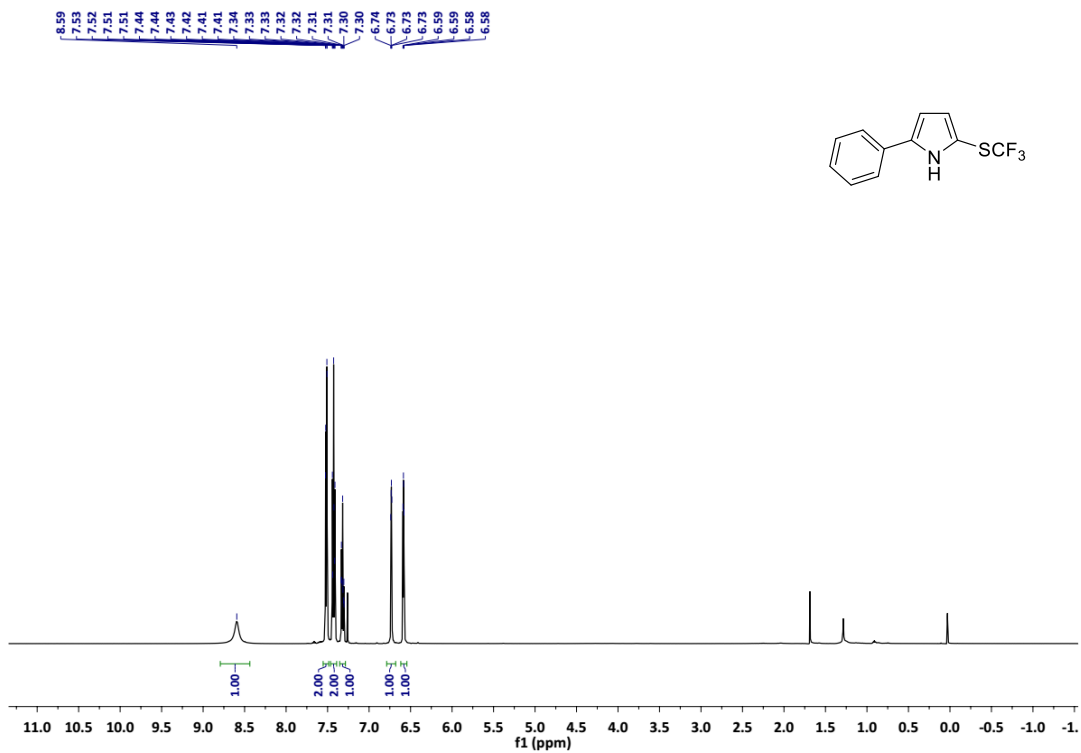
¹H NMR spectrum (500 MHz, CD₃OD) of **3n**

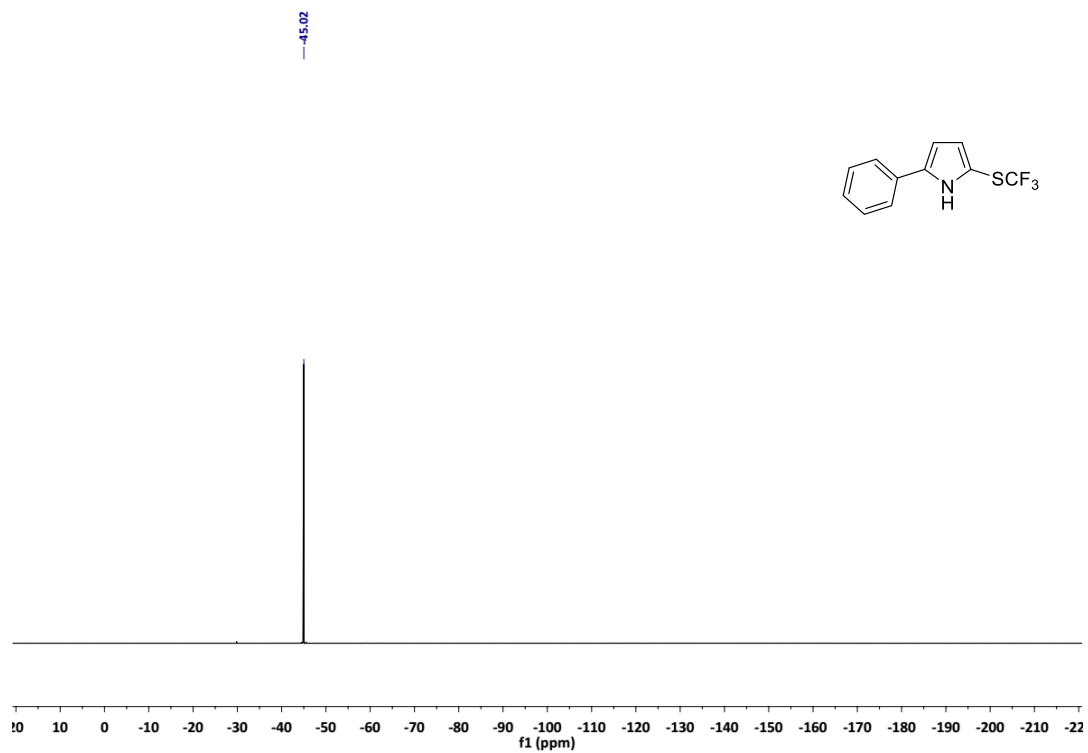


^{13}C NMR spectrum (125 MHz, CD_3OD) of **3n**

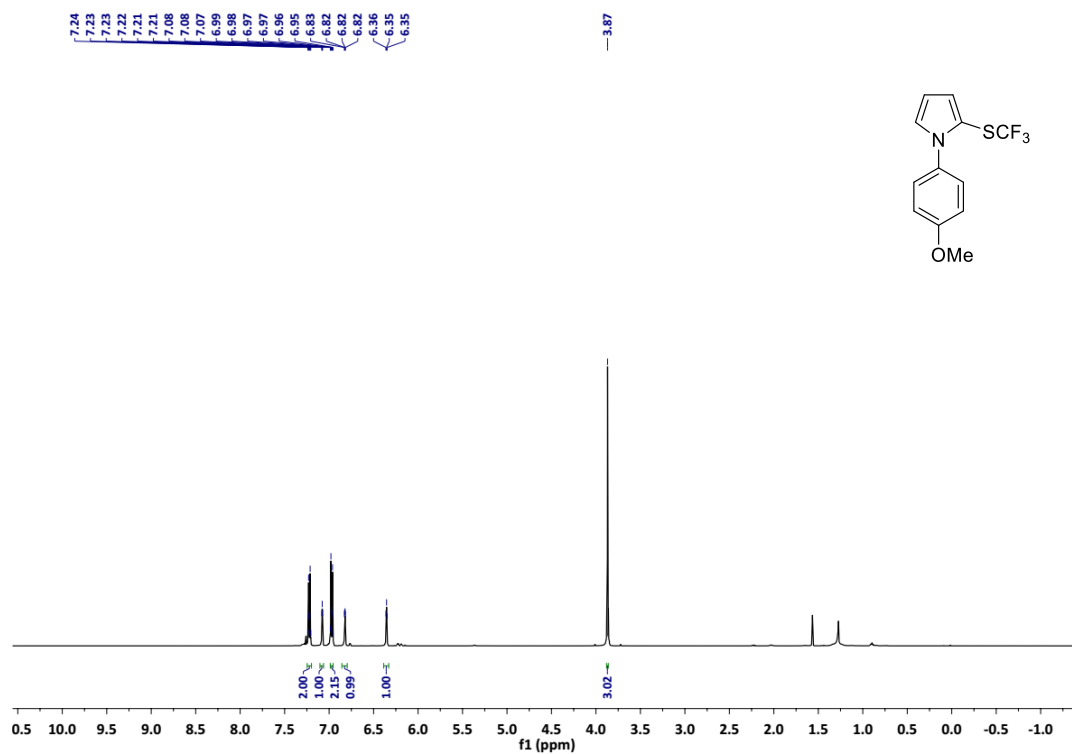


^{19}F NMR spectrum (470 MHz, CD_3OD) of **3n**

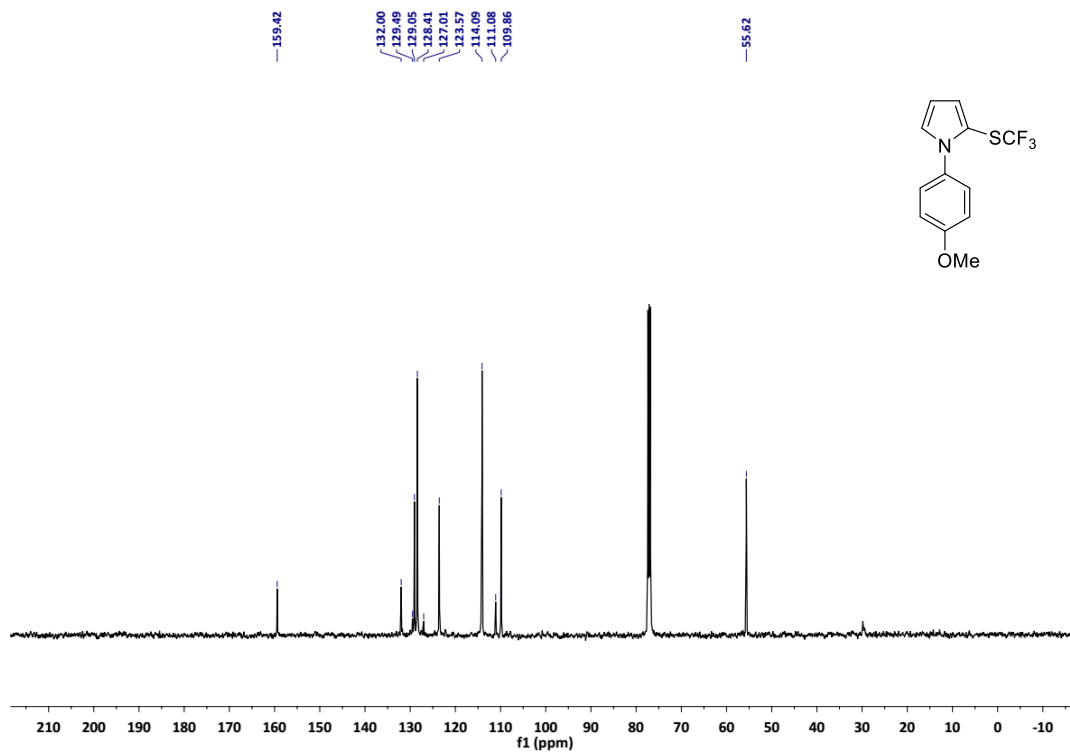




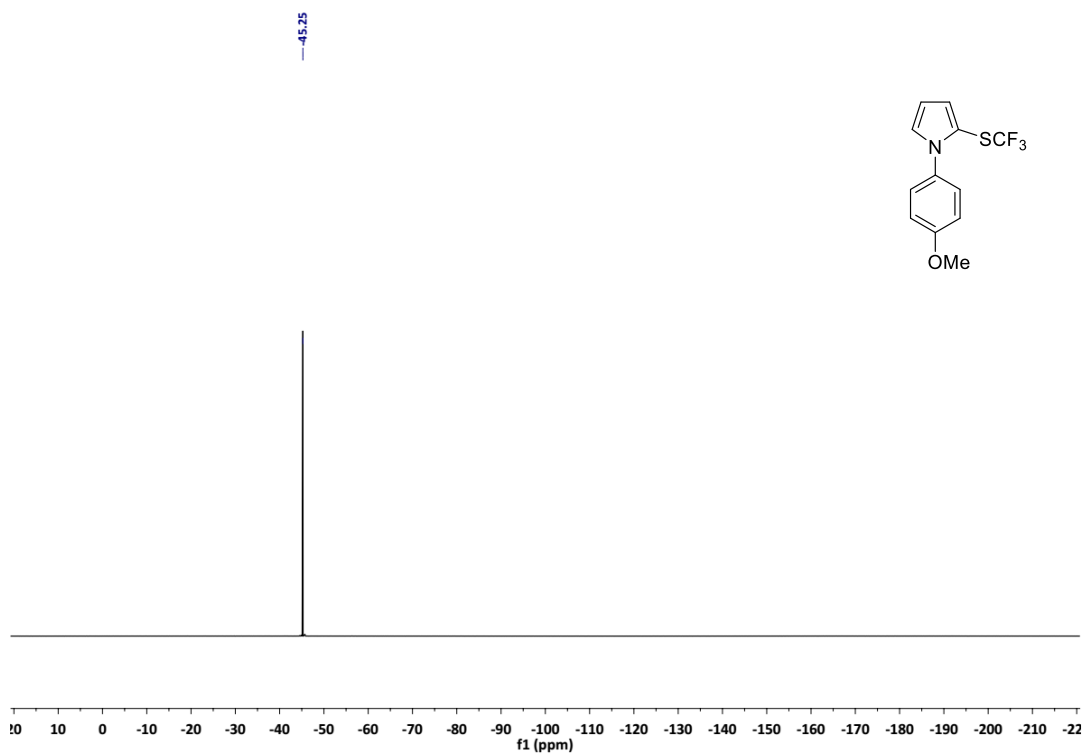
^{19}F NMR spectrum (470 MHz, CDCl_3) of **6a**



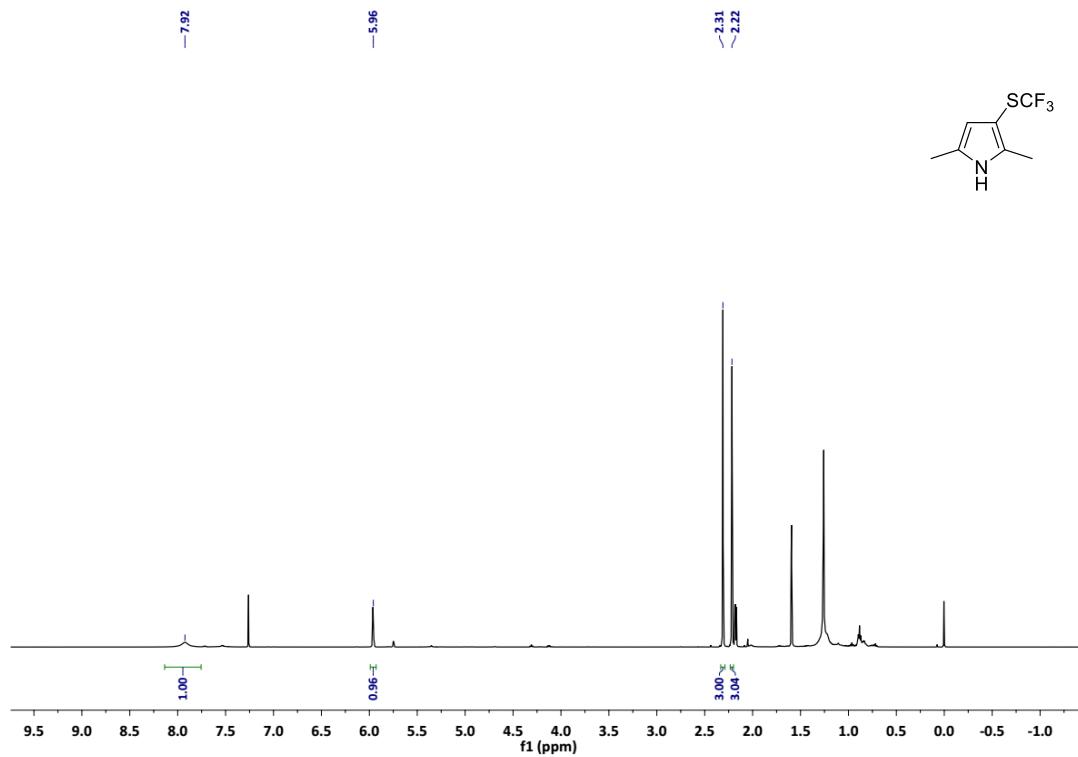
^1H NMR spectrum (500 MHz, CDCl_3) of **6b**



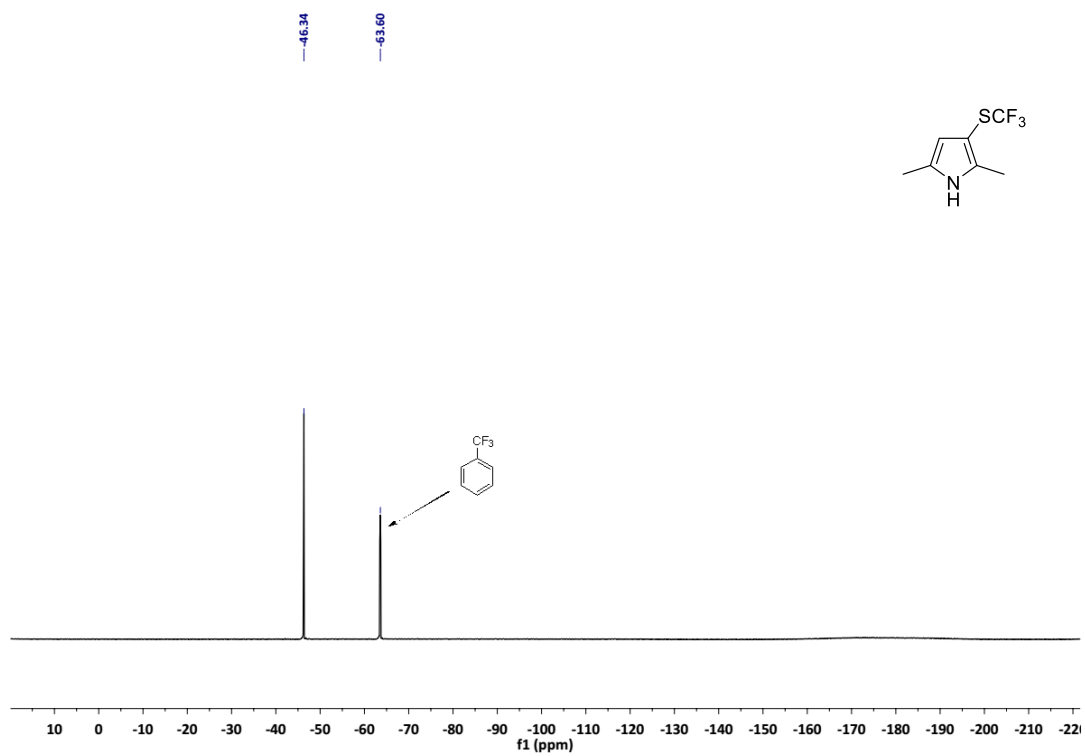
¹³C NMR spectrum (125 MHz, CDCl₃) of **6b**



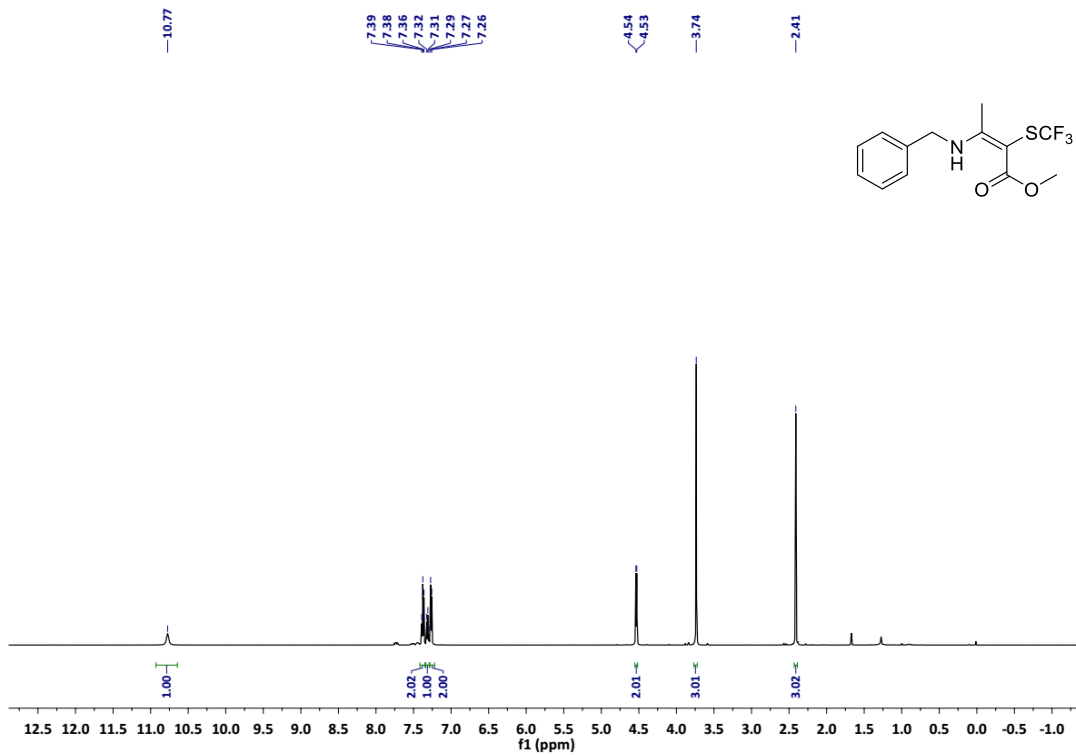
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **6b**



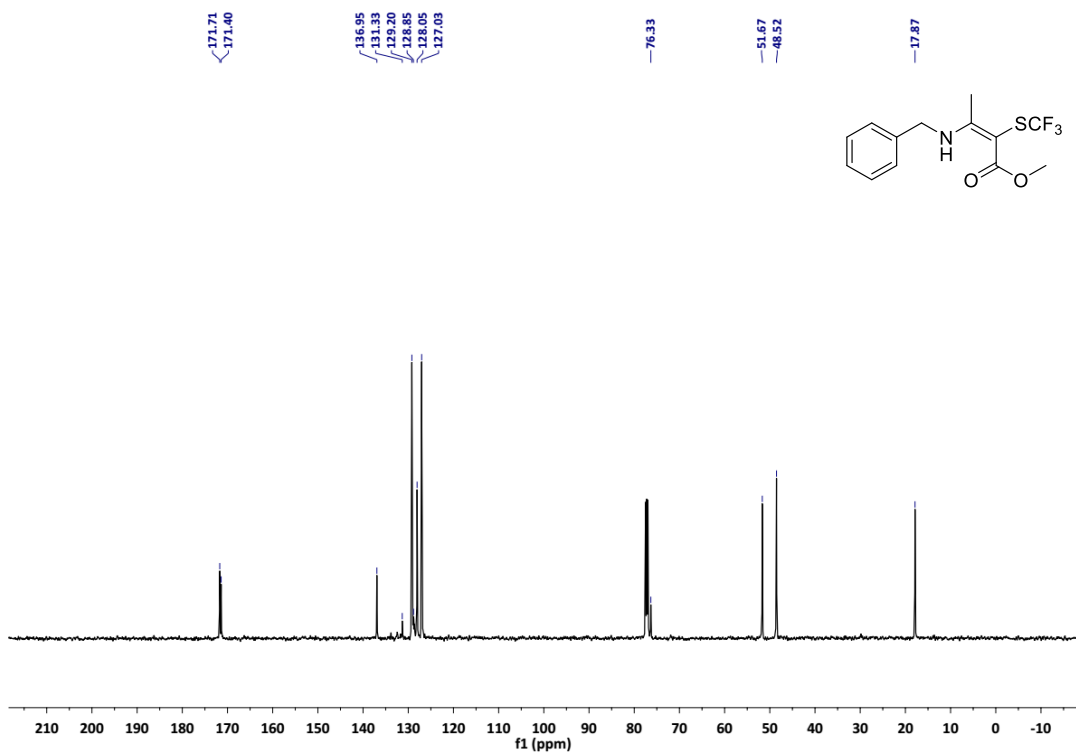
¹H NMR spectrum (500 MHz, CDCl₃) of **6c**



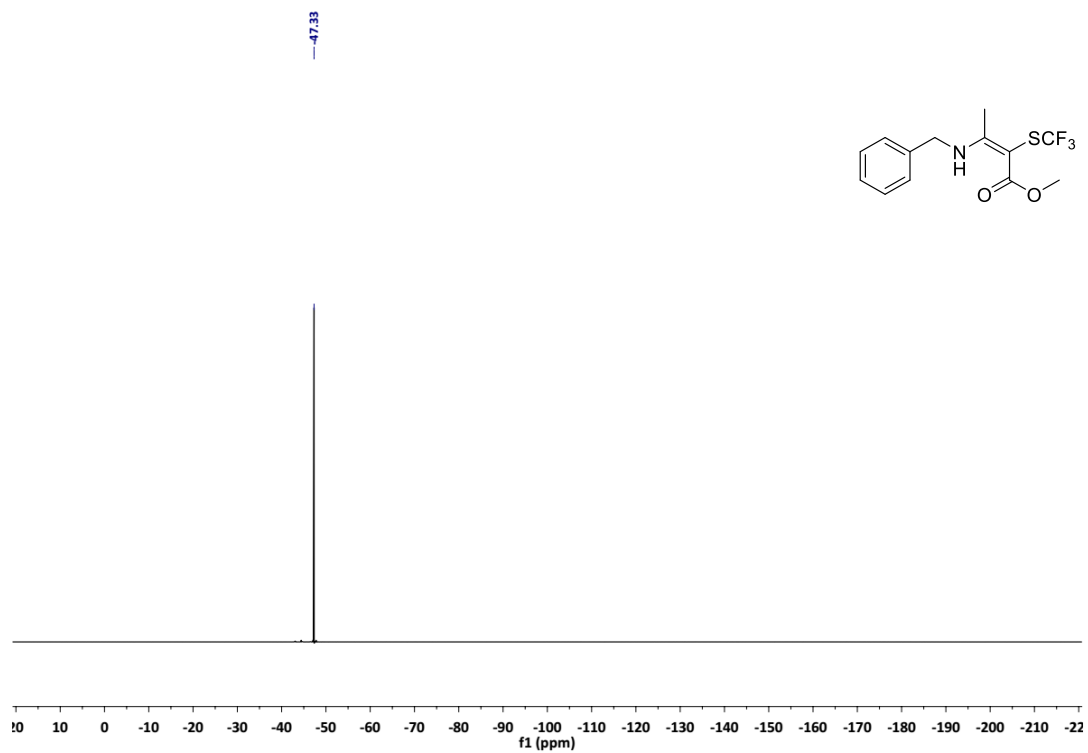
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **6c**



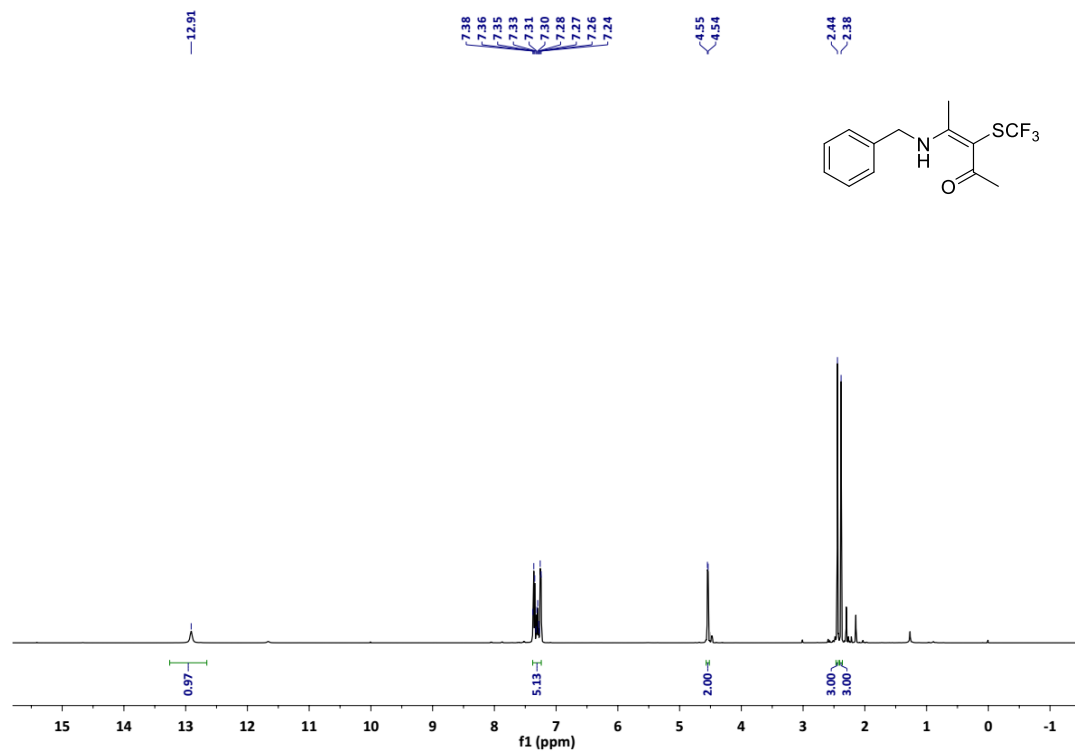
^1H NMR spectrum (500 MHz, CDCl_3) of **7a**



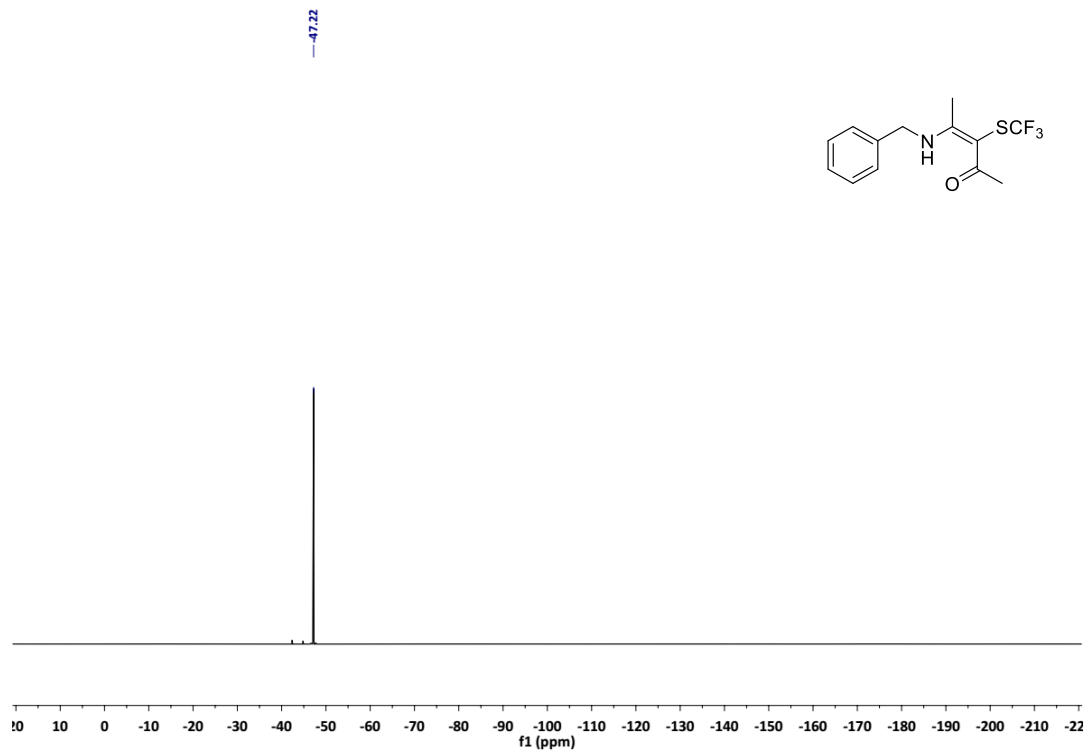
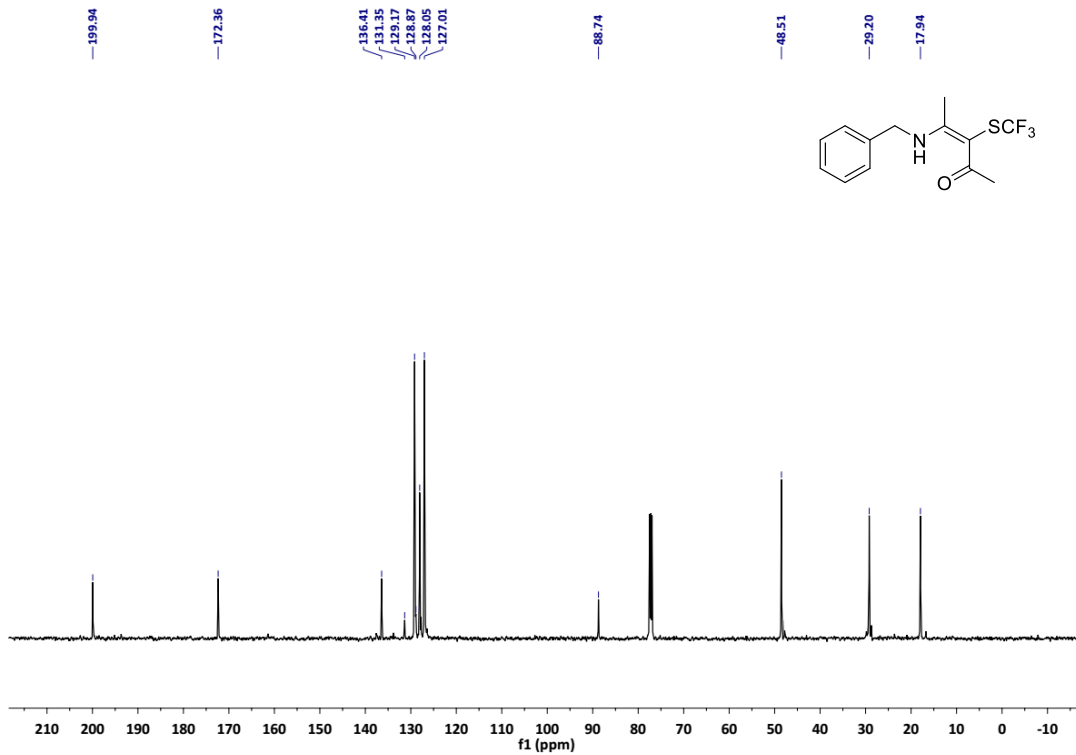
^{13}C NMR spectrum (125 MHz, CDCl_3) of **7a**

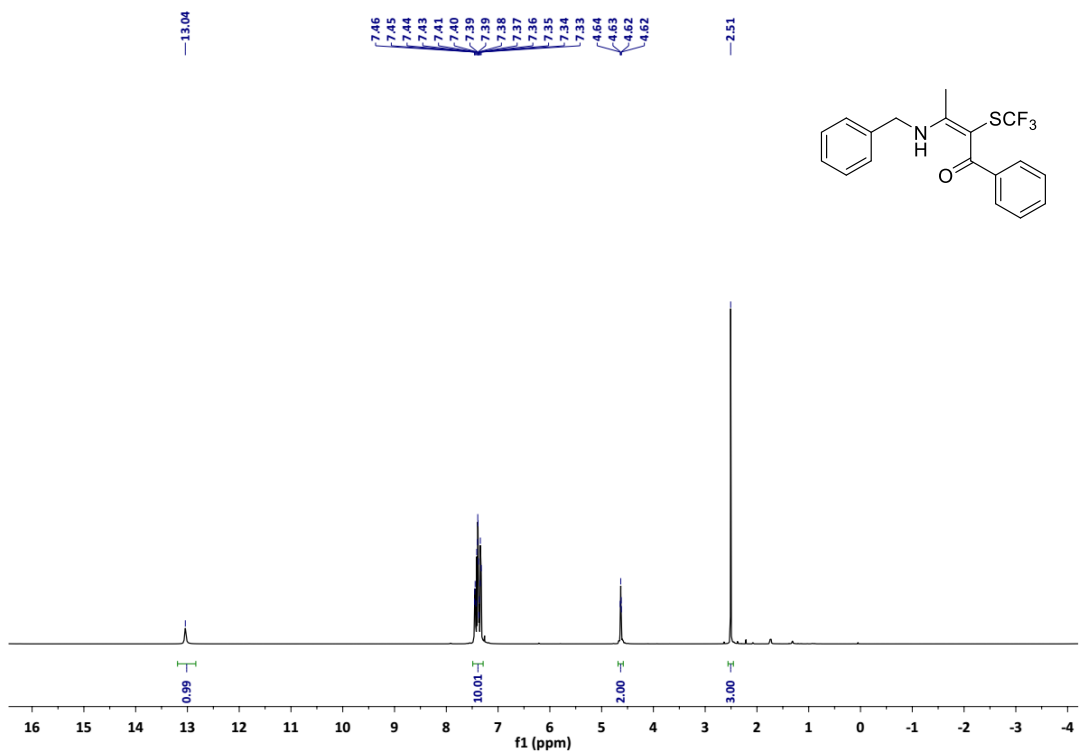


^{19}F NMR spectrum (470 MHz, CDCl_3) of **7a**

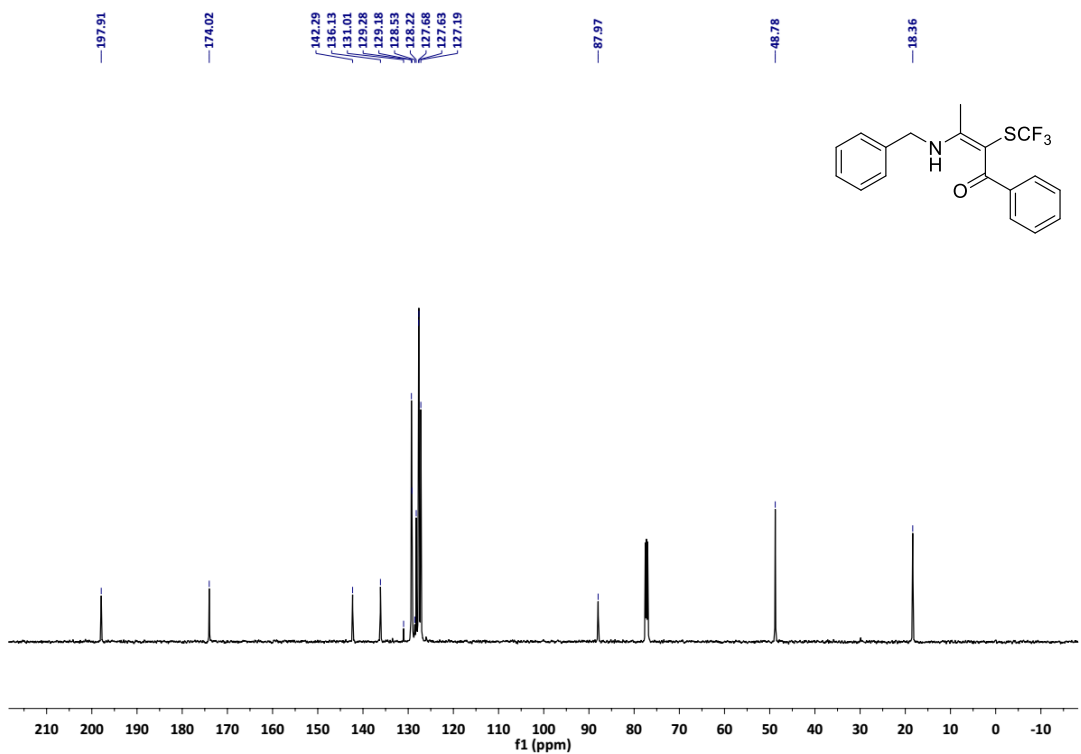


^1H NMR spectrum (500 MHz, CDCl_3) of **7b**

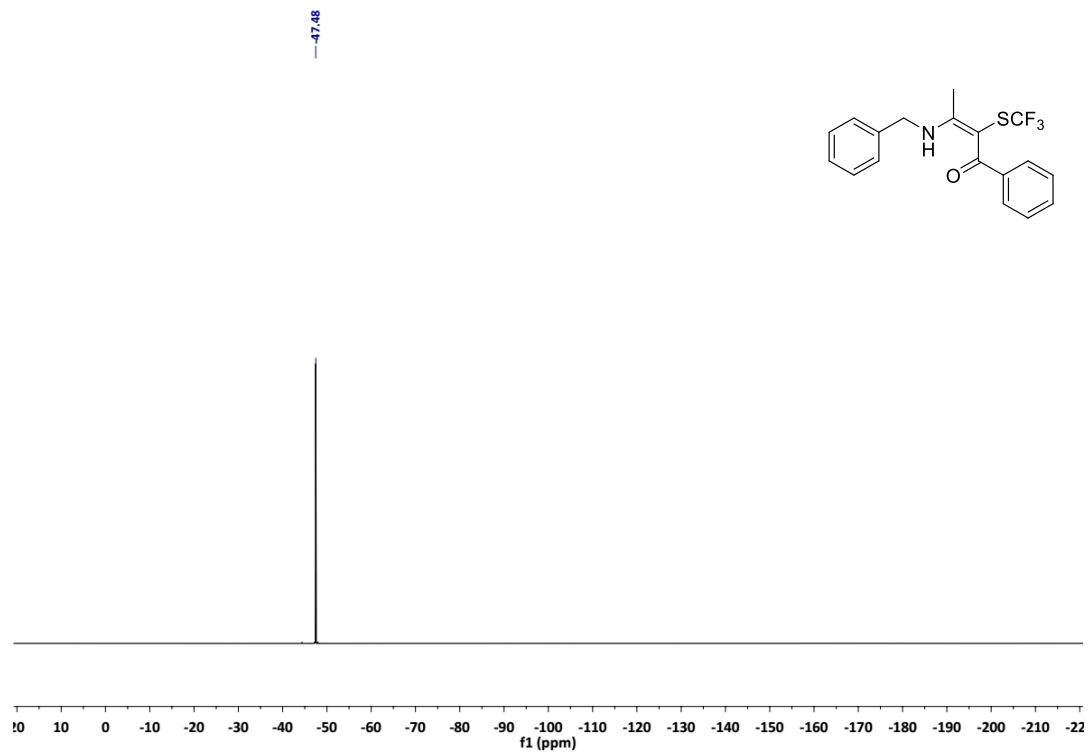




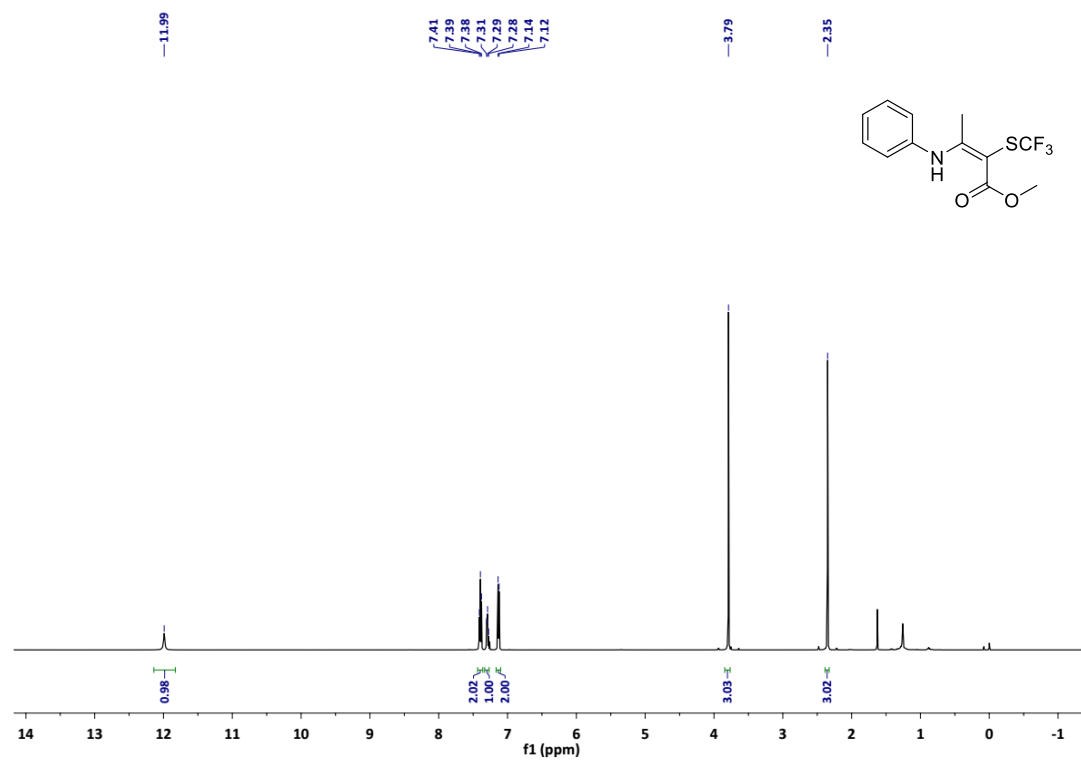
^1H NMR spectrum (500 MHz, CDCl_3) of **7c**



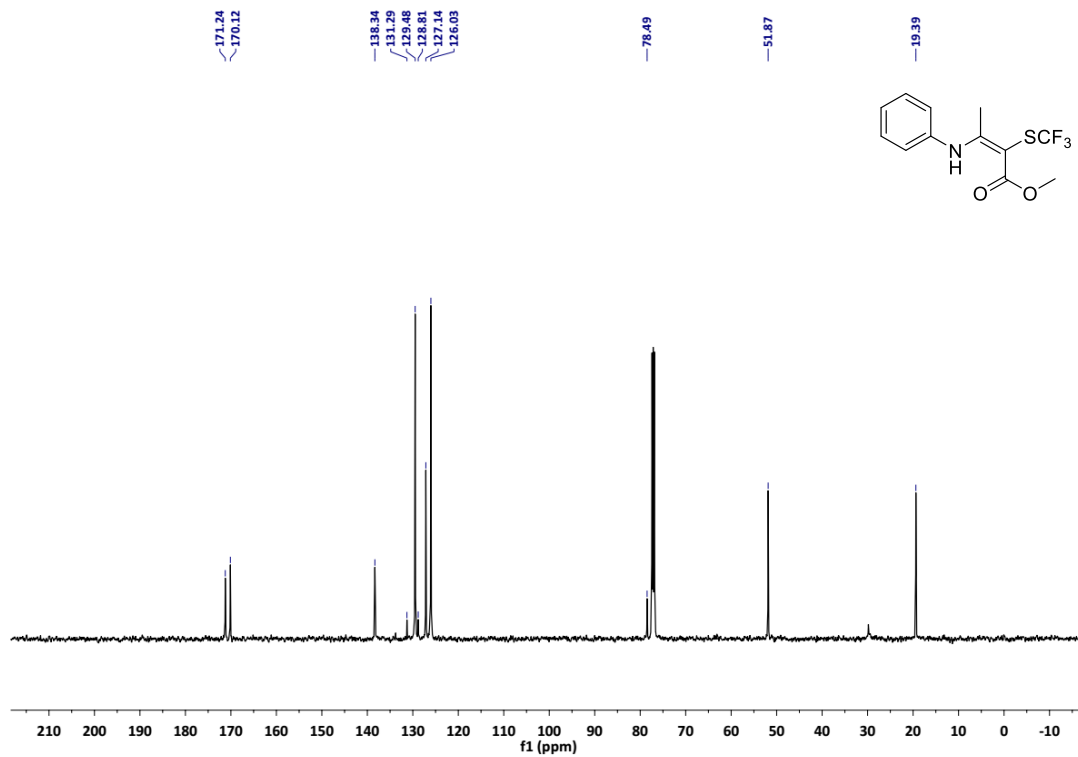
^{13}C NMR spectrum (125 MHz, CDCl_3) of **7c**



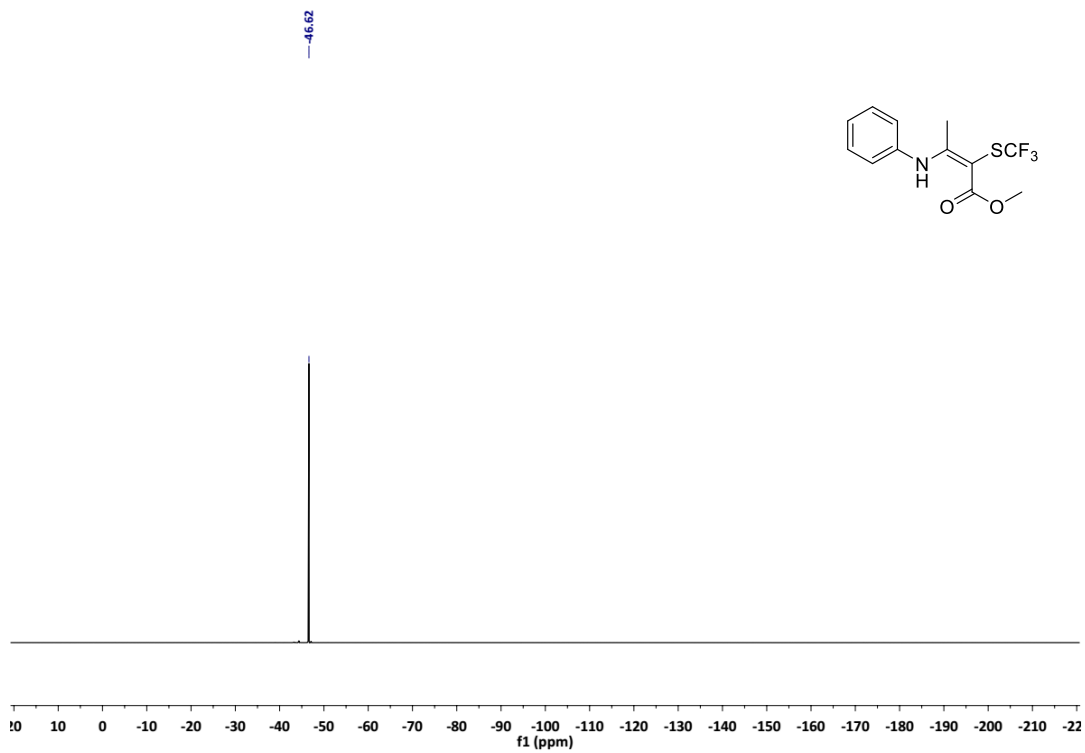
^{19}F NMR spectrum (470 MHz, CDCl_3) of **7c**



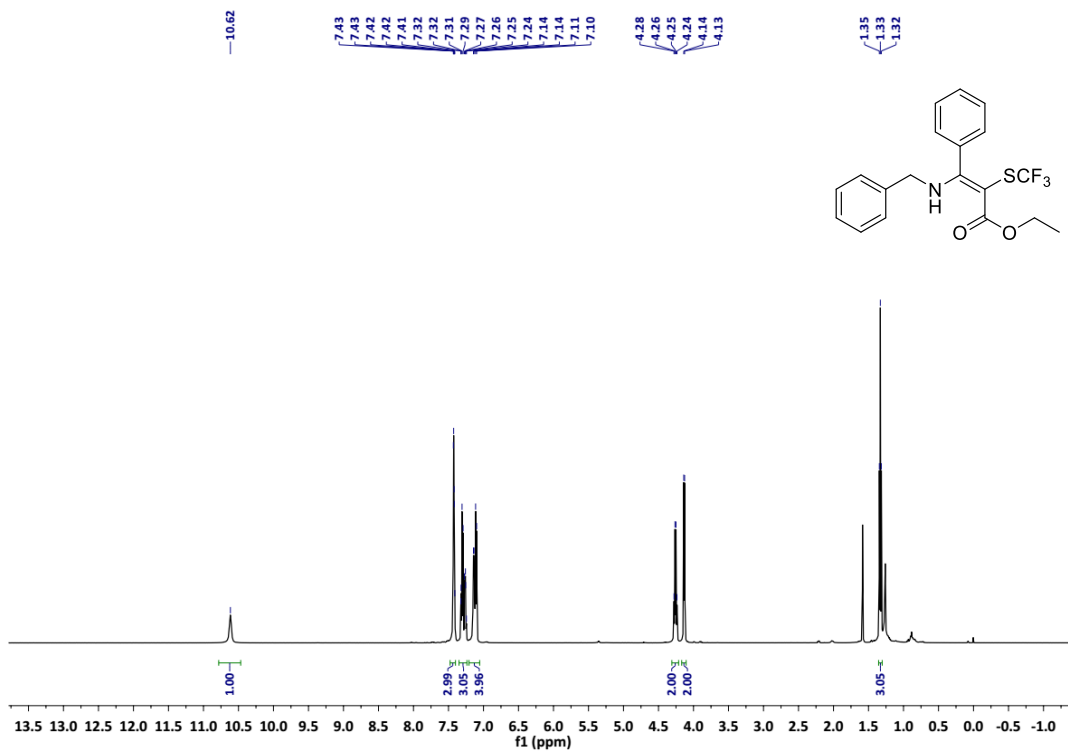
^1H NMR spectrum (500 MHz, CDCl_3) of **7d**



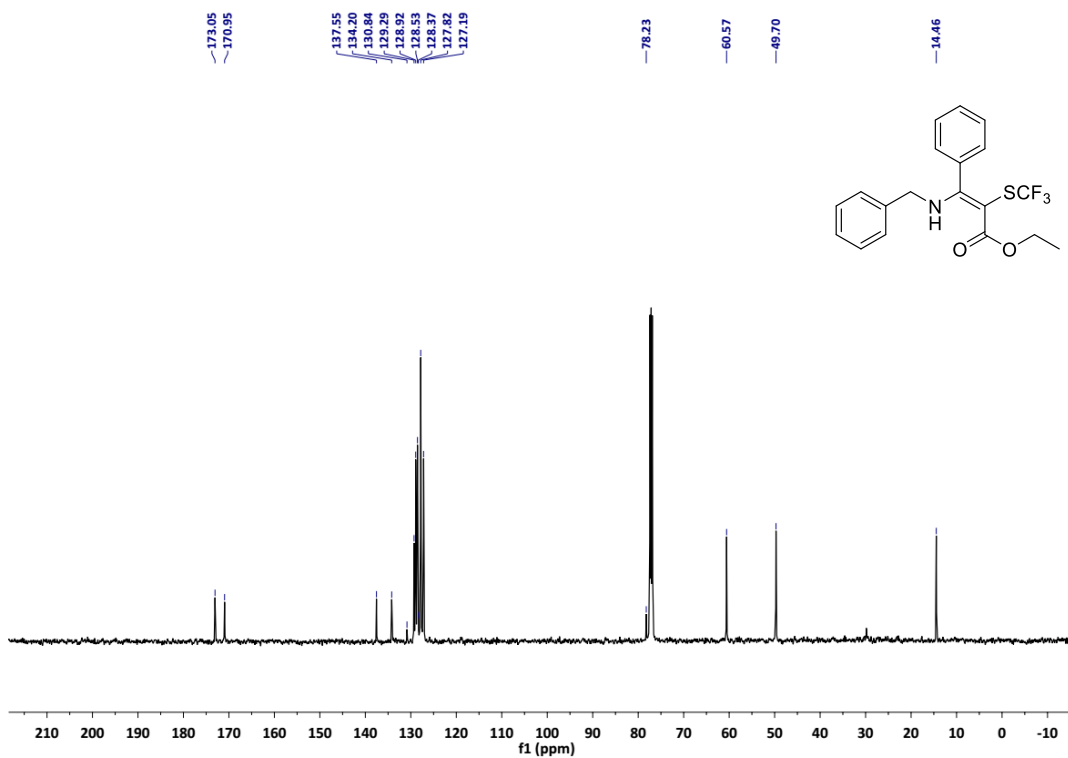
¹³C NMR spectrum (125 MHz, CDCl₃) of **7d**



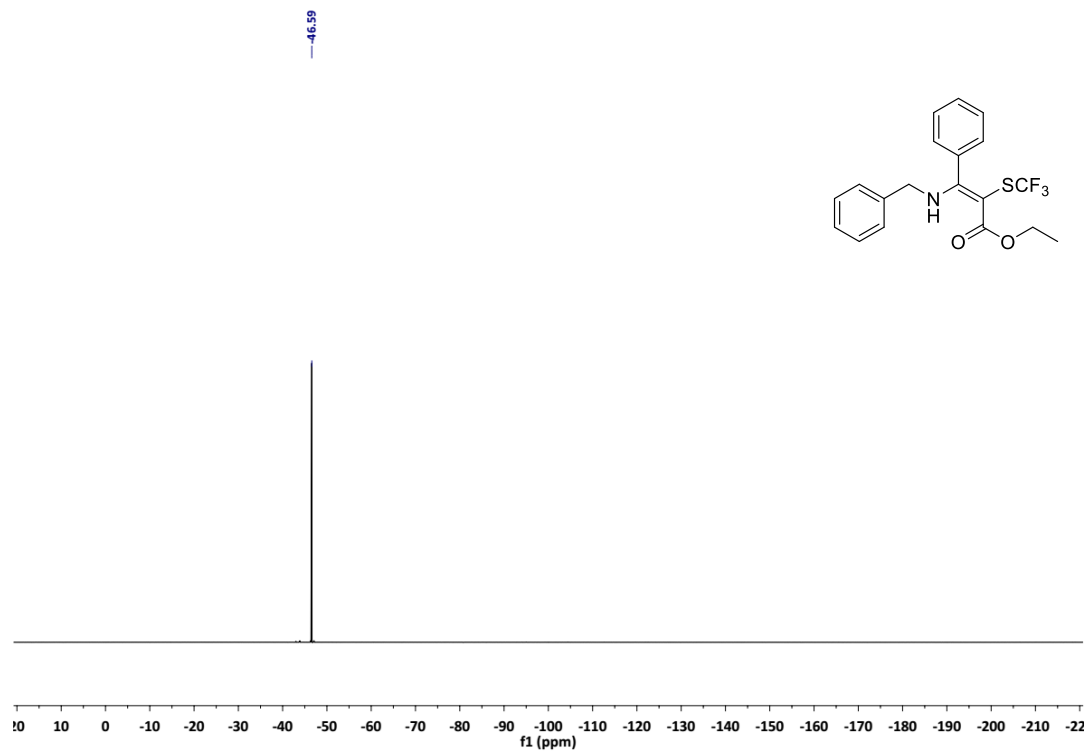
¹⁹F NMR spectrum (470 MHz, CDCl₃) of **7d**



¹H NMR spectrum (500 MHz, CDCl₃) of **7e**



¹³C NMR spectrum (125 MHz, CDCl₃) of **7e**



^{19}F NMR spectrum (470 MHz, CDCl_3) of **7e**