

### **General considerations:**

**Reagent information:** All reactions were carried out under air atmosphere in screw cap reaction tubes. All the solvents were bought from Sigma-Aldrich and Merck in sealed bottle and were used as received. Copper acetate monohydrate was obtained from S.D. Fine-Chem Limited. Anilines were bought from Aldrich and Alfa-Aesar. For column chromatography, silica (100–200 mesh) from SRL. A gradient elution-using pet-ether and ethyl acetate were performed, based on Merck aluminium TLC sheets (silica gel 60 F<sub>254</sub>).

**Analytical Information:** All isolated compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy and mass spectrometry (MS). Copies of the <sup>1</sup>H NMR and <sup>13</sup>C NMR can be found in the supporting information. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument. All <sup>1</sup>H NMR experiments were reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All <sup>13</sup>C NMR spectra were reported in ppm relative to deuteriochloroform (77.23 ppm). Mass spectra (HRMS) were recorded on an Agilent TOF/6500 series Q-TOF mass spectrometer. FTIR (Fourier Transform Infrared) spectroscopy data was recorded for the synthesized products using Jasco FTIR-6600 spectrophotometer.

### **General procedure for copper-catalyzed *o*-thiocyanation of aromatic of amines:**

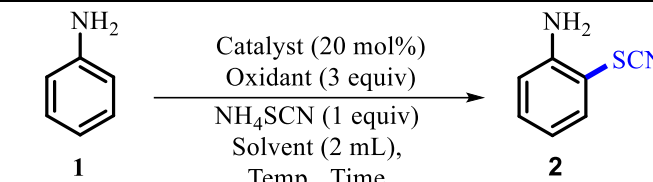
In this experiment, an oven-dried screw cap reaction tube was employed. Inside the reaction tube, a magnetic stir bar was placed to ensure efficient mixing. The tube was then charged with aniline (0.25 mmol), Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (20 mol%), TBHP (3 equiv) (70 % in water), NH<sub>4</sub>SCN (1 equiv) and acetonitrile (2 mL) under air atmosphere. To initiate the reaction, the screw cap was securely closed, and the reaction tube was subjected to vigorous stirring. To maintain optimal conditions, a preheated oil bath was utilized, maintaining a constant temperature of 110 °C for a duration of 2 hours. Upon completion, the mixture was diluted with EtOAc (25 mL) and filtered with a celite pad. Then, the EtOAc layer was concentrated using a rotary evaporator followed by column chromatography using silica (100–200 mesh size) and petroleum ether/ethyl acetate as the eluent.

### **General procedure for scale-up reaction:**

An oven dried round bottom flask was charged with the amine compound (456 μL or 5 mmol), Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (798 mg or 20 mol%), TBHP (1445 μL or 3 equiv) (70 % in water), NH<sub>4</sub>SCN (380 mg or 1 equiv) were dissolved in 40 mL of acetonitrile which was then reflux at 110 °C

in a pre-heated oil bath for 2 h, leading to the formation of dark green colour solution. Then, the reaction mixture was allowed to cool down to room temperature. Upon completion, the mixture was diluted with EtOAc and filtered. The filtrate was washed with distilled water. The EtOAc layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under a vacuum. The crude mixture was purified by column chromatography using silica (100–200 mesh size) and petroleum ether/ethyl acetate as the eluent.

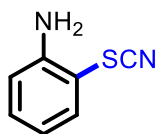
### Optimization of reaction conditions

					
Entry	Catalyst	Oxidant	Solvent	Time (h)	Isolated Yield (%)
1	CuCl	TBHP	EtOH	2	35%
2	CuBr	TBHP	EtOH	2	23%
3	CuI	TBHP	EtOH	2	10%
4	CuO	TBHP	EtOH	2	n.d
5	CuSO <sub>4</sub>	TBHP	EtOH	2	50%
6	CuSO <sub>4</sub> .5H <sub>2</sub> O	TBHP	EtOH	2	45%
7	Cu(OTf) <sub>2</sub>	TBHP	EtOH	2	55%
8	CuCl <sub>2</sub> .2H <sub>2</sub> O	TBHP	EtOH	2	47%
9	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	EtOH	2	60%
10	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	DTBP	EtOH	2	n.d
11	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	EtOH	2	n.d
12	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	EtOH	2	n.d
13	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	DCP	EtOH	2	45%
14	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	Bz <sub>2</sub> O <sub>2</sub>	EtOH	2	n.d
15	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	EtOH	2	n.d
16	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	Tert-butyl per benzoate	EtOH	2	20%
17	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	Cumene hydroperoxide	EtOH	2	n.d
18	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	MeOH	2	65%
19	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	<i>i</i> -PrOH	2	59%
20	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	<i>t</i> -BuOH	2	53%
21	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	<i>t</i> -AmOH	2	46%
22	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	H <sub>2</sub> O	2	n.d
23	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	DMF	2	n.d
24	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	DMSO	2	n.d
25	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	DMA	2	n.d
26	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	NMP	2	n.d
27	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	Chloro benzene	2	n.d

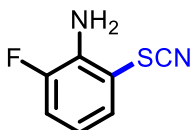
28	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	THF	2	n.d
29	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	1,4 dioxane	2	n.d
30	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	Toluene	2	20%
31	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	MeCN	2	80%
32	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	TBHP	DCE	2	25%
33	-	TBHP	MeCN	2	n.d
34	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	-	MeCN	2	n.d

Reaction conditions: Compound 1 (0.25 mmol), Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (20 mol%), TBHP (3 equiv), NH<sub>4</sub>SCN (1 equiv), MeCN (2 mL), 110 °C, 2 h, n.d means not detected

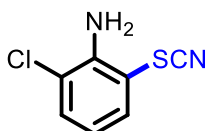
### Characterization data of synthesized compounds:



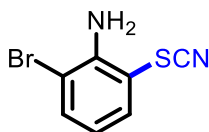
**2-thiocyanatoaniline (Table 2, 2a):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.4, brown solid (30 mg, isolated yield: 80%), mp: 49-51 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 5.55 (s, 2H), 7.12 – 7.18 (m, 1H), 7.30 – 7.36 (m, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.27, 151.59, 131.31, 126.06, 122.38, 120.98, 119.01. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>S ([M+H]<sup>+</sup>) is 151.0324 and found 151.0319. **IR** (neat, cm<sup>-1</sup>): 3322, 3205, 2053, 1263, 748.



**2-fluoro-6-thiocyanatoaniline (Table 2, 2b):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.48, brown solid (25 mg, isolated yield: 59%), mp: 33-34 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.06 (s, 2H), 6.94 – 7.01 (m, 2H), 7.25 – 7.30 (m, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.90, 137.66, 129.93, 119.87, 117.47, 111.86, 109.62. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -135.36. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>6</sub>FN<sub>2</sub>S ([M+H]<sup>+</sup>) is 169.0235 and found 169.0235. **IR** (neat, cm<sup>-1</sup>): 3357, 3322, 2059, 1267 741.

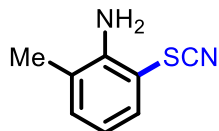


**2-chloro-6-thiocyanatoaniline (Table 2, 2c):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.44, brown solid (27.70 mg, isolated yield: 60%), mp: 51-52 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.03 (s, 2H), 6.98 (t, *J* = 7.9, 7.9 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 150.13, 137.91, 135.47, 116.28, 114.63, 111.22, 108.77. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>6</sub>ClN<sub>2</sub>S ([M+H]<sup>+</sup>) is 184.9940 and found 184.9940. **IR** (neat, cm<sup>-1</sup>): 3453, 3359, 2061, 1263, 744.

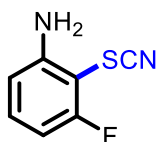


**2-bromo-6-thiocyanatoaniline (Table 2, 2d):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.4, light brown solid (35.30 mg, isolated yield: 62%), mp: 57-59 °C; **<sup>1</sup>H NMR** (400 MHz,

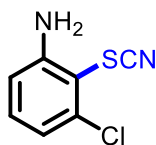
CDCl<sub>3</sub>)  $\delta$  5.95 (s, 2H), 6.96 – 7.04 (m, 1H), 7.53 (dd,  $J$  = 8.1, 11.7 Hz, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.65, 137.04, 133.42, 116.35, 111.96, 110.19, 109.29. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>6</sub>BrN<sub>2</sub>S ([M+H]<sup>+</sup>) is 228.9435 and found 228.9438. **IR** (neat, cm<sup>-1</sup>): 3434, 3351, 2059, 1261, 852.



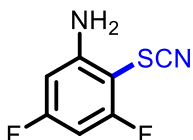
**2-methyl-6-thiocyanatoaniline (Table 2, 2e):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.36, red solid (24.80 mg, isolated yield: 60%), mp: 69-71 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.47 (s, 3H), 5.81 (s, 2H), 6.95 (t,  $J$  = 6.9, 6.9 Hz, 1H), 7.04 (d,  $J$  = 7.3 Hz, 1H), 7.35 (d,  $J$  = 7.9 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.67, 150.99, 131.06, 128.73, 126.86, 122.13, 118.44, 18.57. **HRMS (ESI)** calcd. For C<sub>8</sub>H<sub>9</sub>N<sub>2</sub>S ([M+H]<sup>+</sup>) is 165.0486 and found 165.0487. **IR** (neat, cm<sup>-1</sup>): 3336, 3207, 2053, 1257, 746.



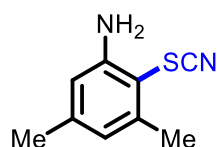
**3-fluoro-2-thiocyanatoaniline (Table 2, 2f):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.48, light brown solid (26.95 mg, isolated yield: 64%), mp: 37-39 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.06 (s, 2H), 6.74 – 6.80 (m, 1H), 7.16 (ddd,  $J$  = 1.0, 2.1, 8.4 Hz, 1H), 7.24 (dd,  $J$  = 2.1, 10.4 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.32, 149.90, 137.66, 129.93, 120.08, 117.47, 111.86. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>)  $\delta$  -113.20. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>6</sub>FN<sub>2</sub>S ([M+H]<sup>+</sup>) is 169.0235 and found 169.0235. **IR** (neat, cm<sup>-1</sup>): 3357, 3322, 2059, 1267, 741.



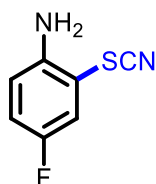
**3-chloro-2-thiocyanatoaniline (Table 2, 2g):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.33, brown solid (30.50 mg, isolated yield: 66%), mp: 56-58 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.92 (s, 2H), 6.57 (dt,  $J$  = 2.0, 2.0, 8.5 Hz, 1H), 6.77 (t,  $J$  = 2.0, 2.0 Hz, 1H), 7.41 (dd,  $J$  = 1.9, 8.5 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.24, 143.30, 134.34, 115.20, 111.93, 110.80, 83.68. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>6</sub>ClN<sub>2</sub>S ([M+H]<sup>+</sup>) is 184.9940 and found 184.9940. **IR** (neat, cm<sup>-1</sup>): 3453, 3359, 2061, 1263, 744.



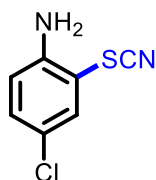
**3,5-difluoro-2-thiocyanatoaniline (Table 2, 2h):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.44, yellow solid (30.10 mg, isolated yield: 65%), mp: 46-48 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 4.22 (s, 2H), 6.21 (d, *J* = 1.5 Hz, 1H), 6.23 (d, *J* = 1.5 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 152.38, 149.95, 137.66, 129.91, 120.08, 117.49, 111.78. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -117.22, -108.85. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>5</sub>F<sub>2</sub>N<sub>2</sub>S ([M+H]<sup>+</sup>) is 187.0141 and found 187.0143. **IR** (neat, cm<sup>-1</sup>): 3357, 3322, 2059, 1267, 741.



**3,5-dimethyl-2-thiocyanatoaniline (Table 2, 2i):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.43, dark red solid (26.73 mg, isolated yield: 60%), mp: 123-124 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.31 (d, *J* = 3.3 Hz, 6H), 5.48 (s, 2H), 6.71 (s, 1H), 7.13 (s, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 147.27, 140.72, 133.53, 122.83, 114.19, 112.51, 110.93, 18.44, 13.98. **HRMS (ESI)** calcd. for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>S ([M+H]<sup>+</sup>) is 179.0642 and found 179.0637. **IR** (neat, cm<sup>-1</sup>): 3336, 3207, 2053, 1257, 746.

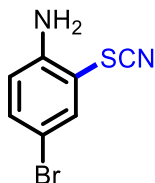


**4-fluoro-2-thiocyanatoaniline (Table 2, 2j):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.44, brown solid (29.40 mg, isolated yield: 70%), mp: 42-44 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 5.22 (s, 2H), 6.96 (td, *J* = 2.6, 9.0, 9.0 Hz, 1H), 7.23 (dd, *J* = 2.7, 8.1 Hz, 1H), 7.39 (dd, *J* = 4.7, 8.8 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.36, 119.80, 119.70, 113.90, 113.66, 107.83, 107.56. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -126.87. **HRMS (ESI)** calcd. for C<sub>7</sub>H<sub>6</sub>FN<sub>2</sub>S ([M+H]<sup>+</sup>) is 169.0235 and found 169.0236. **IR** (neat, cm<sup>-1</sup>): 3357, 3322, 2059, 1267, 741.

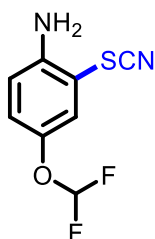


**4-chloro-2-thiocyanatoaniline (Table 2, 2k):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.37, white solid (34.50 mg, isolated yield: 75%), mp: 70-72 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 5.54 (s, 2H), 7.38 (dd, *J* = 8.6, 13.9 Hz, 2H), 7.48 (d, *J* = 2.1 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.50, 133.95, 132.77, 119.79, 116.58, 111.90, 109.99. **HRMS (ESI)** calcd.

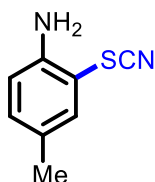
For  $C_7H_6ClN_2S$  ( $[M+H]^+$ ) is 184.9940 and found 184.9937. **IR** (neat,  $cm^{-1}$ ): 3453, 3359, 2061, 1263, 744.



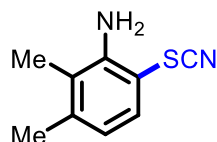
**4-bromo-2-thiocyanatoaniline (Table 2, 2l):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.42, yellow solid (38.50 mg, isolated yield: 67%), mp: 76-78 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  5.46 (s, 2H), 7.24 (s, 1H), 7.42 (dd,  $J = 1.6, 8.6$  Hz, 1H), 7.55 (s, 1H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  145.50, 133.95, 132.77, 119.79, 116.58, 111.90, 109.99. **HRMS (ESI)** calcd. For  $C_7H_6BrN_2S$  ( $[M+H]^+$ ) is 228.9435 and found 228.9434. **IR** (neat,  $cm^{-1}$ ): 3434, 3351, 2059, 1261, 852.



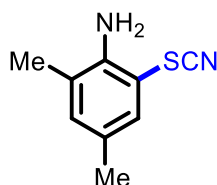
**4-(difluoromethoxy)-2-thiocyanatoaniline (Table 2, 2m):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.44, brown liquid (32.80 mg, isolated yield: 61%);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  5.73 (s, 2H), 6.56 (d,  $J = 74.0$  Hz, 1H), 7.09 (d,  $J = 7.3$  Hz, 1H), 7.37 (s, 1H), 7.47 (d,  $J = 8.7$  Hz, 1H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  151.39, 138.48, 137.24, 116.95, 115.95, 111.12, 110.48, 97.51.  **$^{19}F$  NMR** (377 MHz,  $CDCl_3$ )  $\delta$  -80.10. **HRMS (ESI)** calcd. for  $C_8H_7F_2N_2OS$  ( $[M+H]^+$ ) is 217.0247 and found 217.0242. **IR** (neat)  $cm^{-1}$ : 3356, 2970, 2160, 1373, 732.



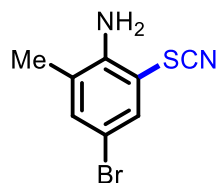
**4-methyl-2-thiocyanatoaniline (Table 2, 2n):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.375, red solid (31.65 mg, isolated yield: 77%) mp: 79-81 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  2.32 (s, 3H), 5.50 (s, 2H), 7.03 (dd,  $J = 1.8, 8.0$  Hz, 1H), 7.29 – 7.38 (m, 2H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  149.77, 132.15, 129.51, 127.19, 121.01, 120.04, 118.77, 21.27. **HRMS (ESI)** calcd. For  $C_8H_9N_2S$  ( $[M+H]^+$ ) is 165.0486 and found 165.0487. **IR** (neat,  $cm^{-1}$ ): 3336, 3207, 2053, 1257, 746.



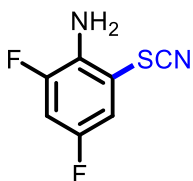
**2,3-dimethyl-6-thiocyanatoaniline (entry 2, 2o):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.43, dark red solid (25.57 mg, isolated yield: 57%), mp: 75-77 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.26 (s, 3H), 2.41 (s, 3H), 5.46 (s, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.34, 139.07, 129.32, 122.90, 120.77, 117.88, 115.61, 29.74, 21.45. **HRMS (ESI)** calcd. for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>S ([M+H]<sup>+</sup>) is 179.0642 and found 179.0637. **IR** (neat, cm<sup>-1</sup>): 3336, 3207, 2053, 1257, 746.



**2,4-dimethyl-6-thiocyanatoaniline (Table 2, 2p):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.44, brown solid (26.30 mg, isolated yield: 59%), mp: 78-80 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.27 (s, 3H), 2.41 (s, 3H), 5.87 (s, 2H), 6.85 (s, 1H), 7.14 (s, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.84, 131.81, 131.14, 130.98, 128.87, 128.17, 118.43, 21.20, 18.50. **HRMS (ESI)** calcd. for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>S ([M+H]<sup>+</sup>) is 179.0642 and found 179.0642. **IR** (neat, cm<sup>-1</sup>): 3336, 3207, 2053, 1257, 746.

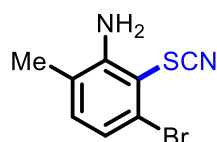


**4-bromo-2-methyl-6-thiocyanatoaniline (Table 2, 2q):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf :0.35, light yellow solid (37.65 mg, isolated yield: 62%), mp: 84-86 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 2.43 (s, 3H), 6.14 (s, 2H), 7.14 (s, 1H), 7.44 (d, *J* = 2.1 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 152.32, 149.90, 137.66, 129.93, 119.87, 117.47, 111.86, 29.85. **HRMS (ESI)** calcd. for C<sub>8</sub>H<sub>8</sub>BrN<sub>2</sub>S ([M+H]<sup>+</sup>) is 242.9591 and found 242.9588. **IR** (neat, cm<sup>-1</sup>): 3336, 3207, 2053, 1257, 746.

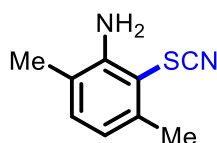




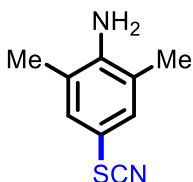
**2,4-difluoro-6-thiocyanatoaniline (entry 2, 2r):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.4, brown solid (28 mg, isolated yield: 60%), mp: 48-49 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.06 (s, 2H), 6.78 (t,  $J = 8.7, 8.7$  Hz, 1H), 7.15 – 7.25 (m, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.37, 149.94, 137.66, 129.94, 120.10, 117.48, 111.79.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -130.74, -123.89. **HRMS (ESI)** calcd. For  $\text{C}_7\text{H}_5\text{F}_2\text{N}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ) is 187.0141 and found 187.0144. **IR** (neat,  $\text{cm}^{-1}$ ): 3357, 3322, 2059, 1267, 741.



**3-bromo-6-methyl-2-thiocyanatoaniline (Table 2, 2s):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.35, red solid (36 mg, isolated yield: 59%), mp: 88-90 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.42 (s, 3H), 5.43 (s, 2H), 6.94 (d,  $J = 7.9$  Hz, 1H), 7.08 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.65, 137.04, 133.42, 116.35, 111.96, 110.19, 109.29, 29.83. **HRMS (ESI)** calcd. for  $\text{C}_8\text{H}_8\text{BrN}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ) is 242.9591 and found 242.9588. **IR** (neat,  $\text{cm}^{-1}$ ): 3336, 3207, 2053, 1257, 746.



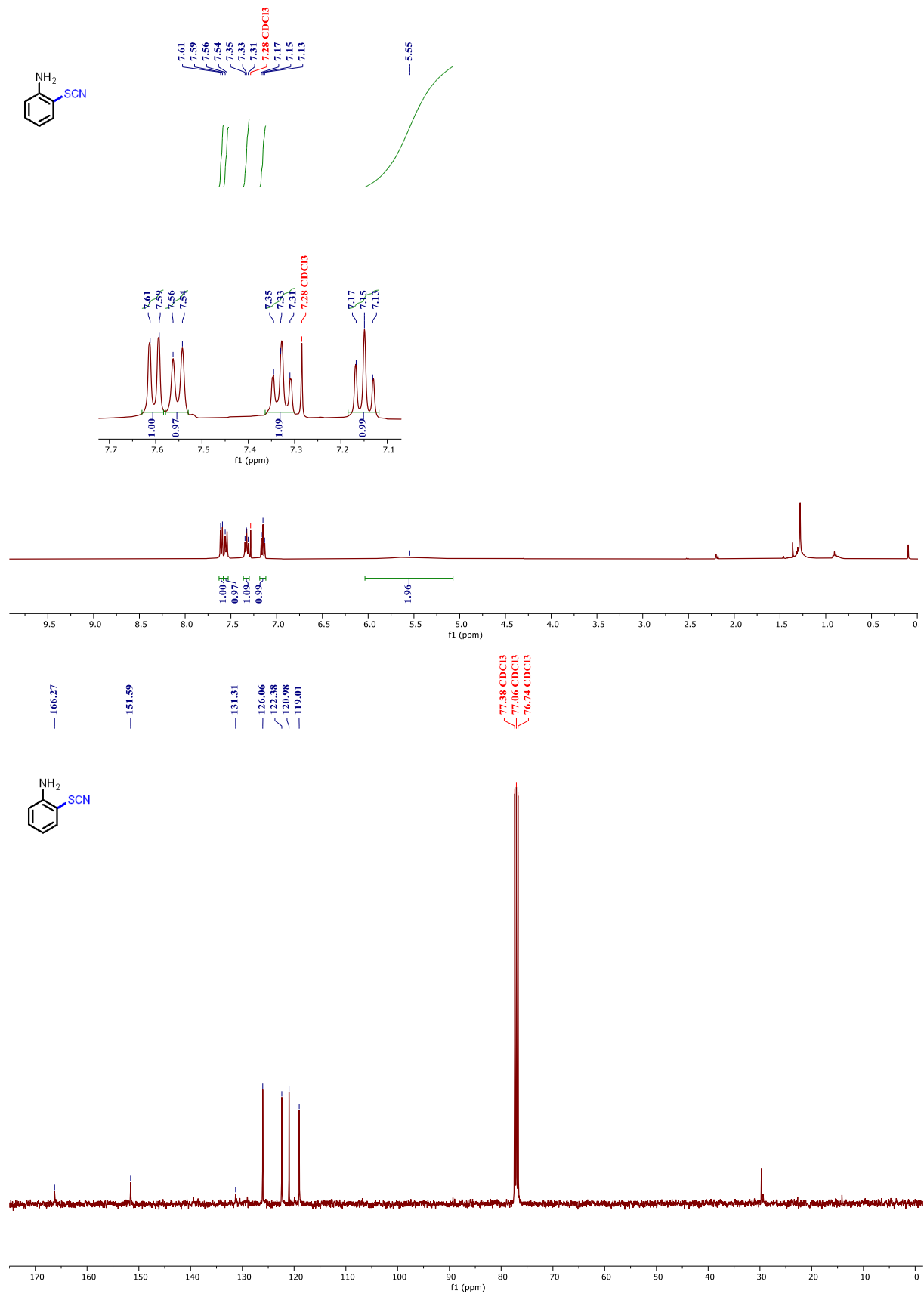
**3,6-dimethyl-2-thiocyanatoaniline (Table 2, 2t):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.4, dark red solid (28.85 mg, isolated yield: 65%), mp: 79-80 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3H), 2.41 (s, 3H), 5.99 (s, 2H), 6.74 (d,  $J = 7.5$  Hz, 1H), 6.94 (d,  $J = 7.5$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.74, 150.64, 131.30, 128.29, 126.95, 125.84, 122.57, 21.12, 18.32. **HRMS (ESI)** calcd. for  $\text{C}_9\text{H}_{11}\text{N}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ) is 179.0642 and found 179.0638. **IR** (neat,  $\text{cm}^{-1}$ ): 3336, 3207, 2053, 1257, 746.



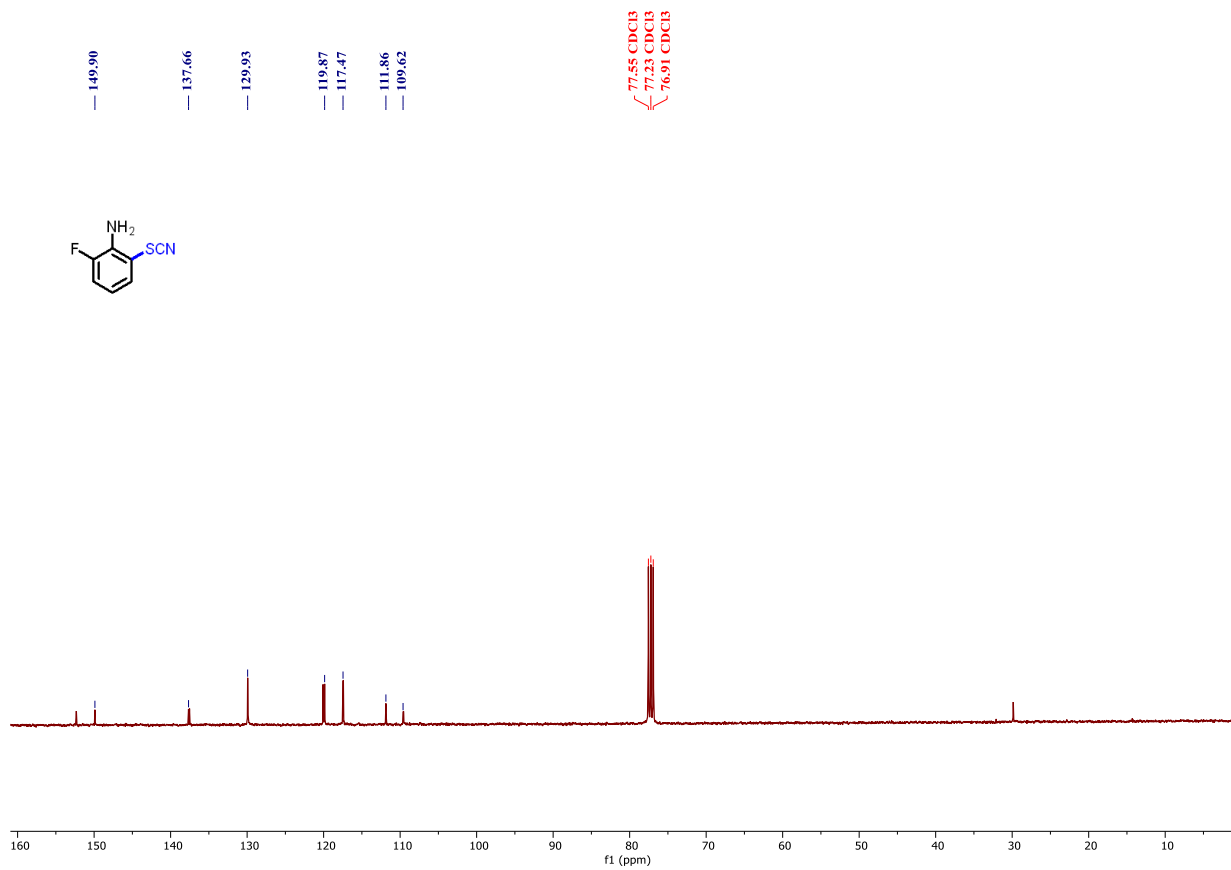
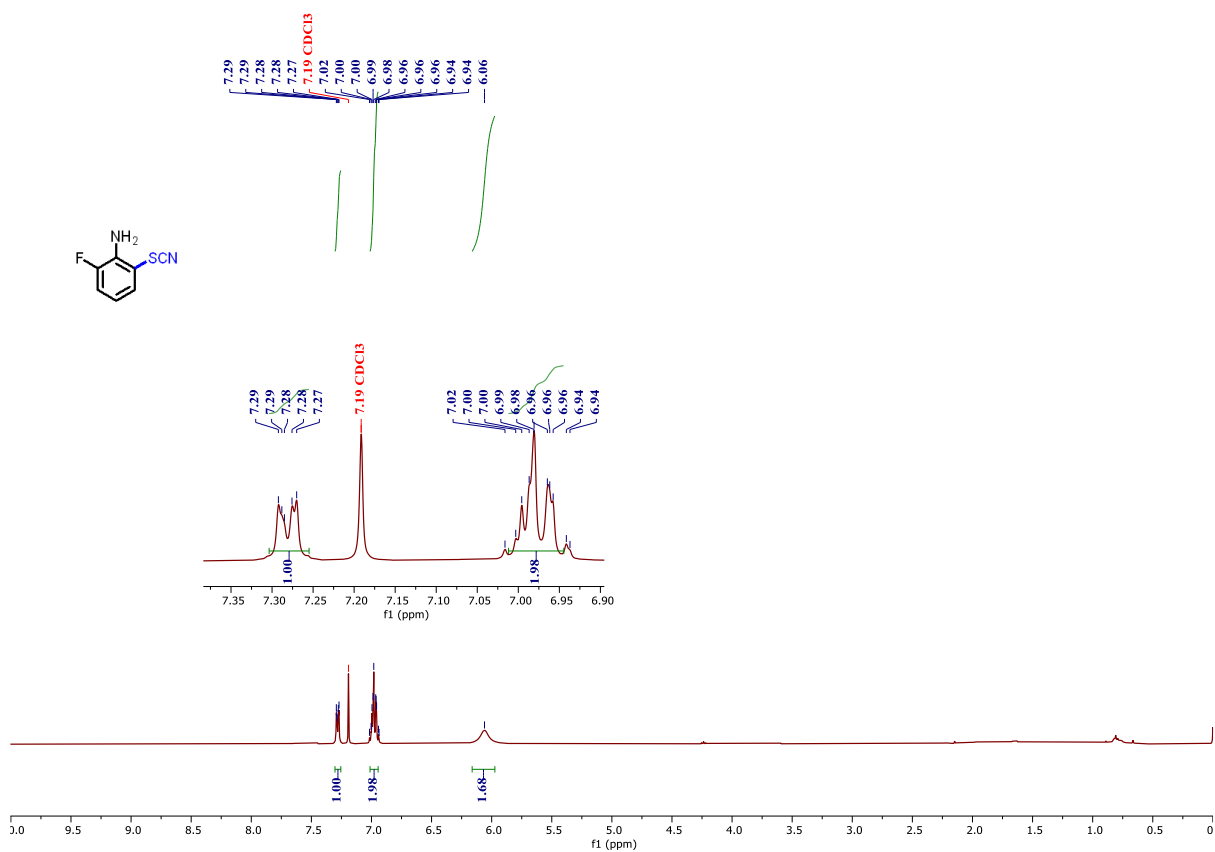
**2,6-dimethyl-4-thiocyanatoaniline (Table 2, 2u):** eluent petroleum ether / ethyl acetate (4:1, v/v), Rf: 0.4, red solid (31.10 mg, isolated yield: 70%), mp: 82-83 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.16 (s, 6H), 3.72 (s, 2H), 7.16 (s, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.39, 132.98, 123.32, 112.88, 108.64, 17.60. **HRMS (ESI)** calcd. for  $\text{C}_9\text{H}_{11}\text{N}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ) is 179.0642 and found 179.0638. **IR** (neat,  $\text{cm}^{-1}$ ): 3336, 3207, 2053, 1257, 746.

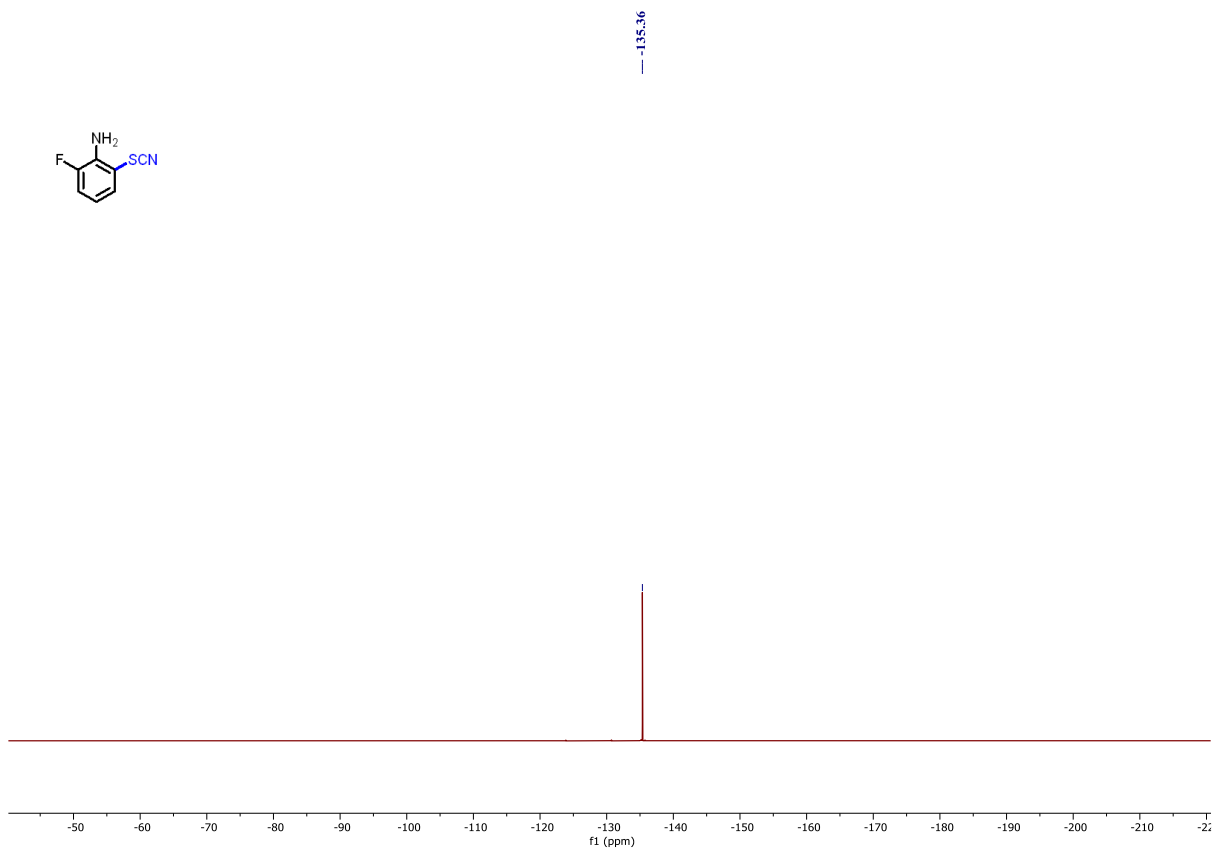
# NMR Data:

(Table 2, entry 2a)

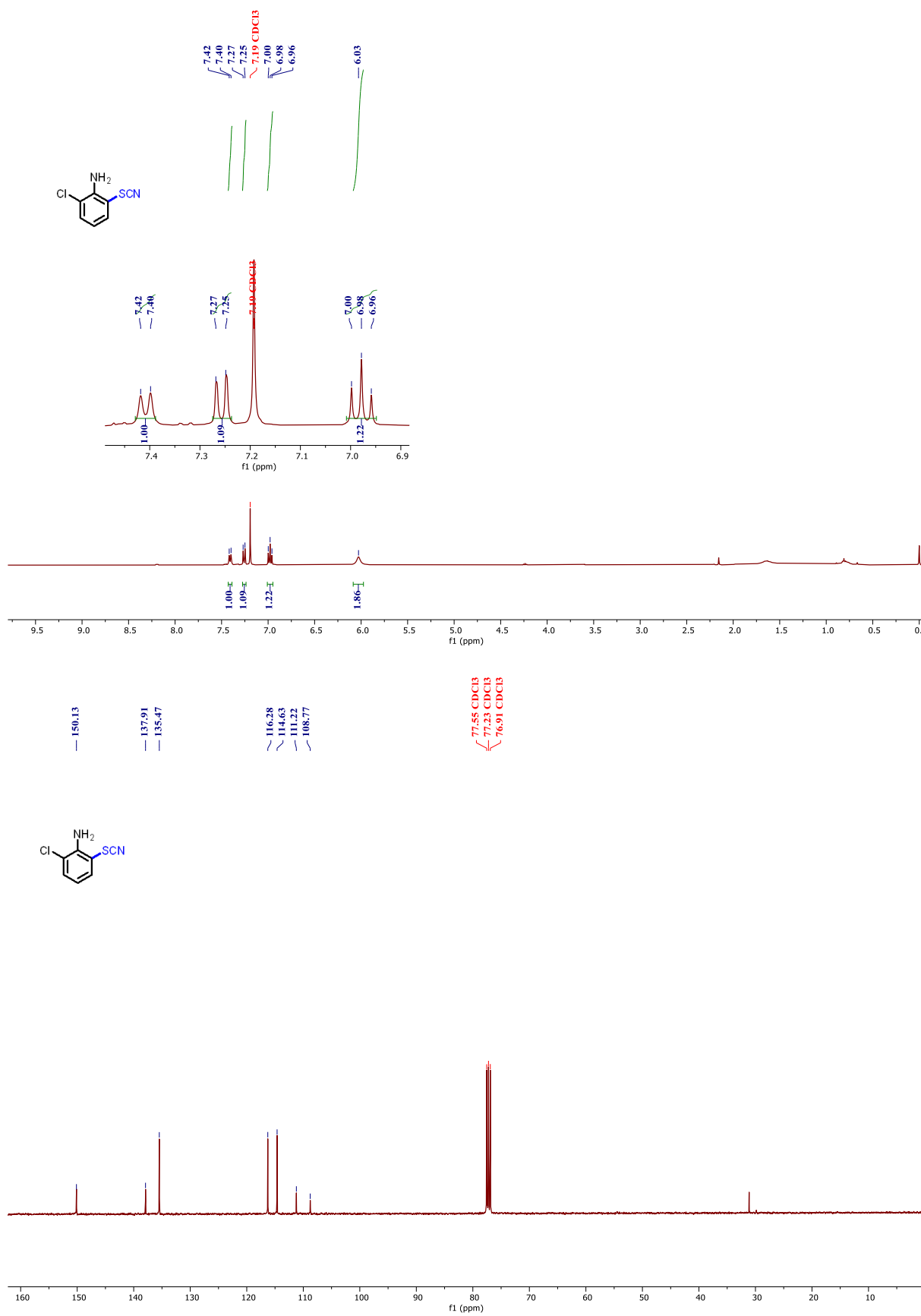


(Table 2, entry 2b)

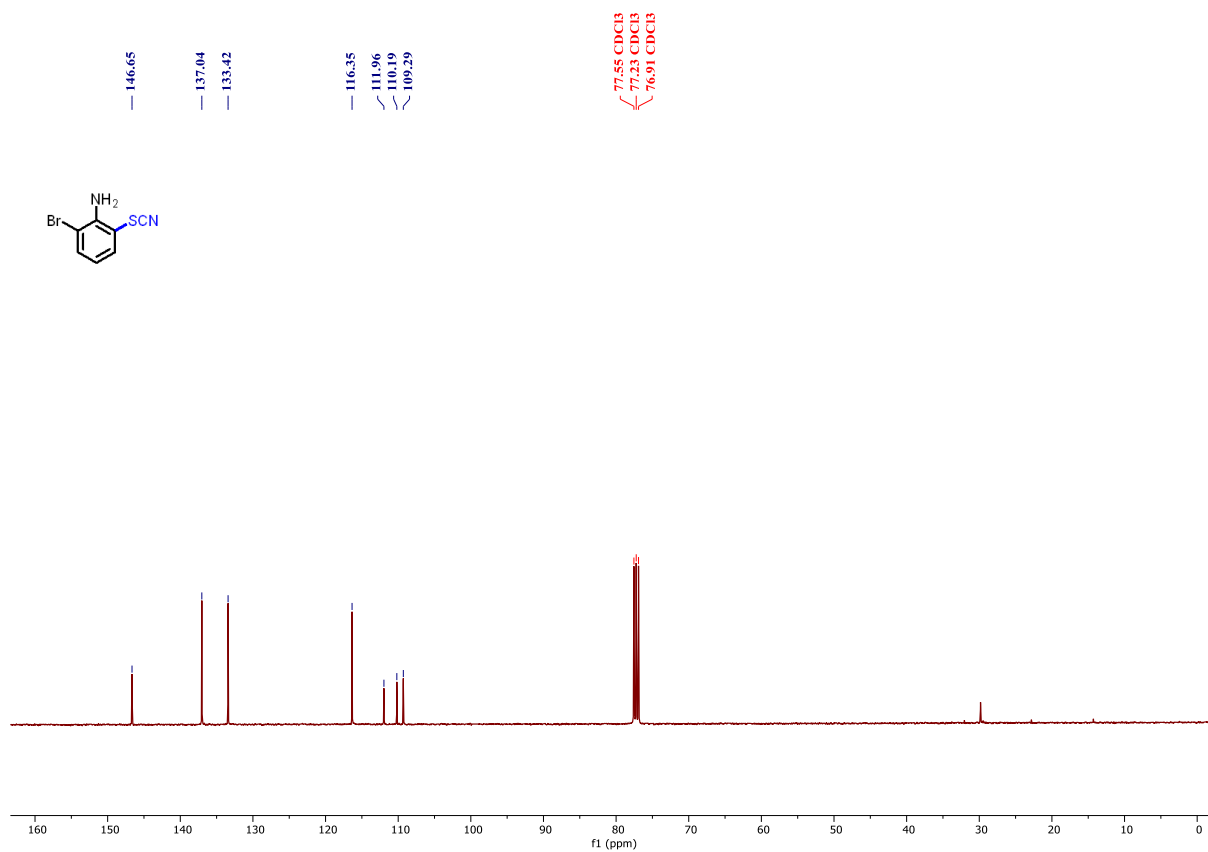
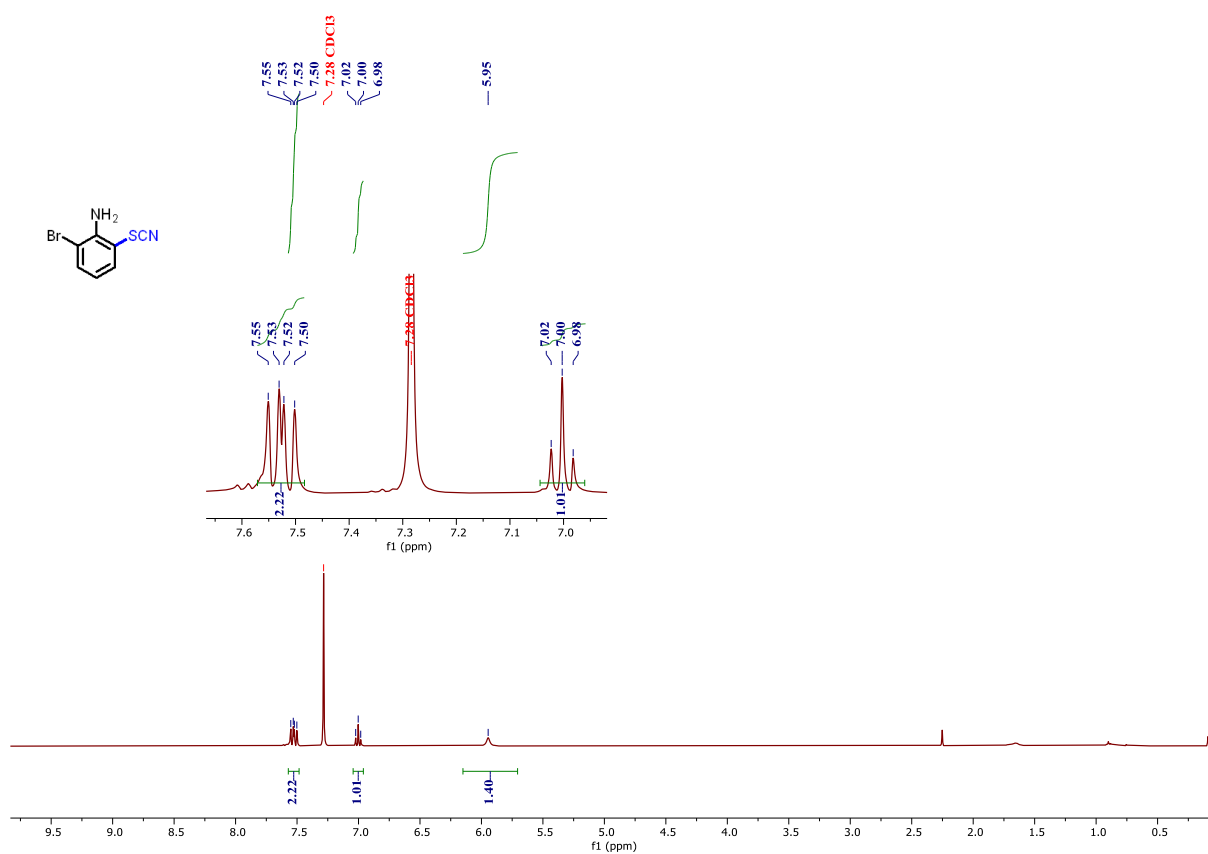




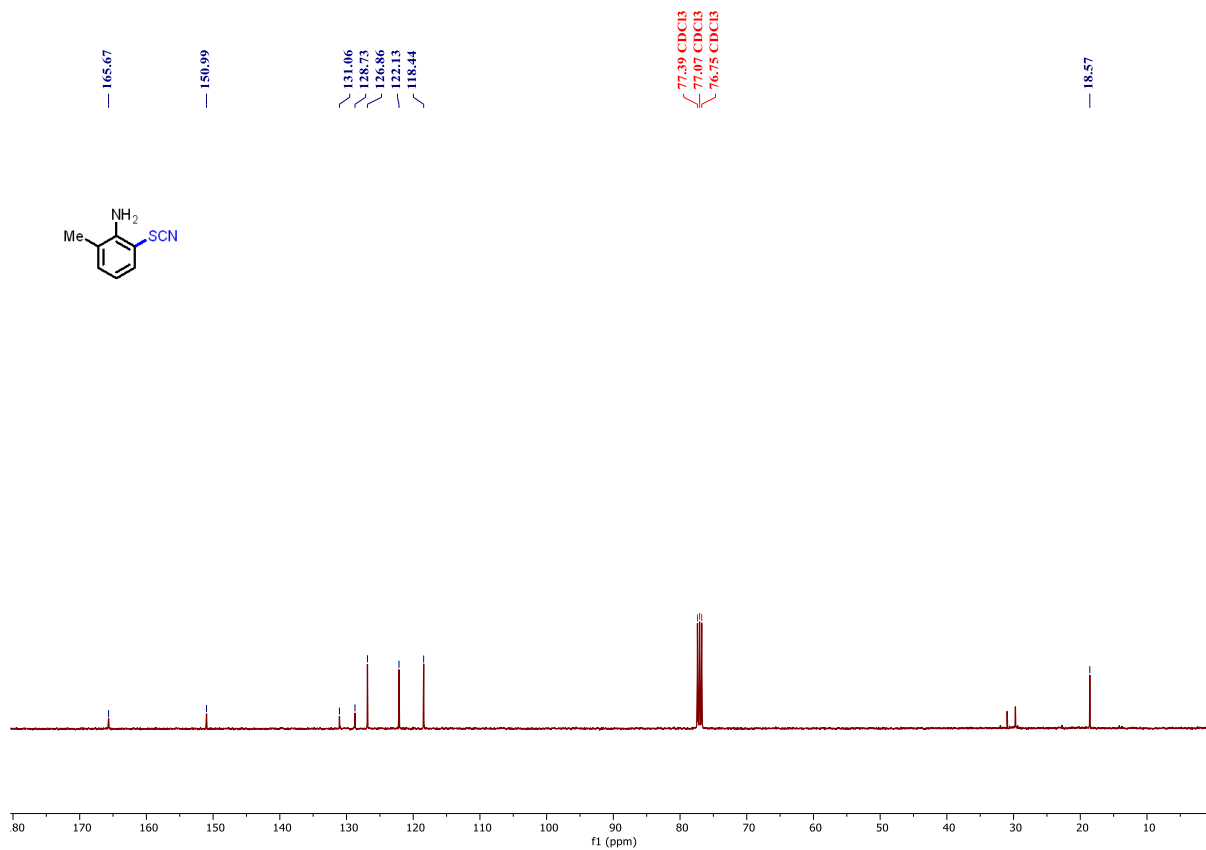
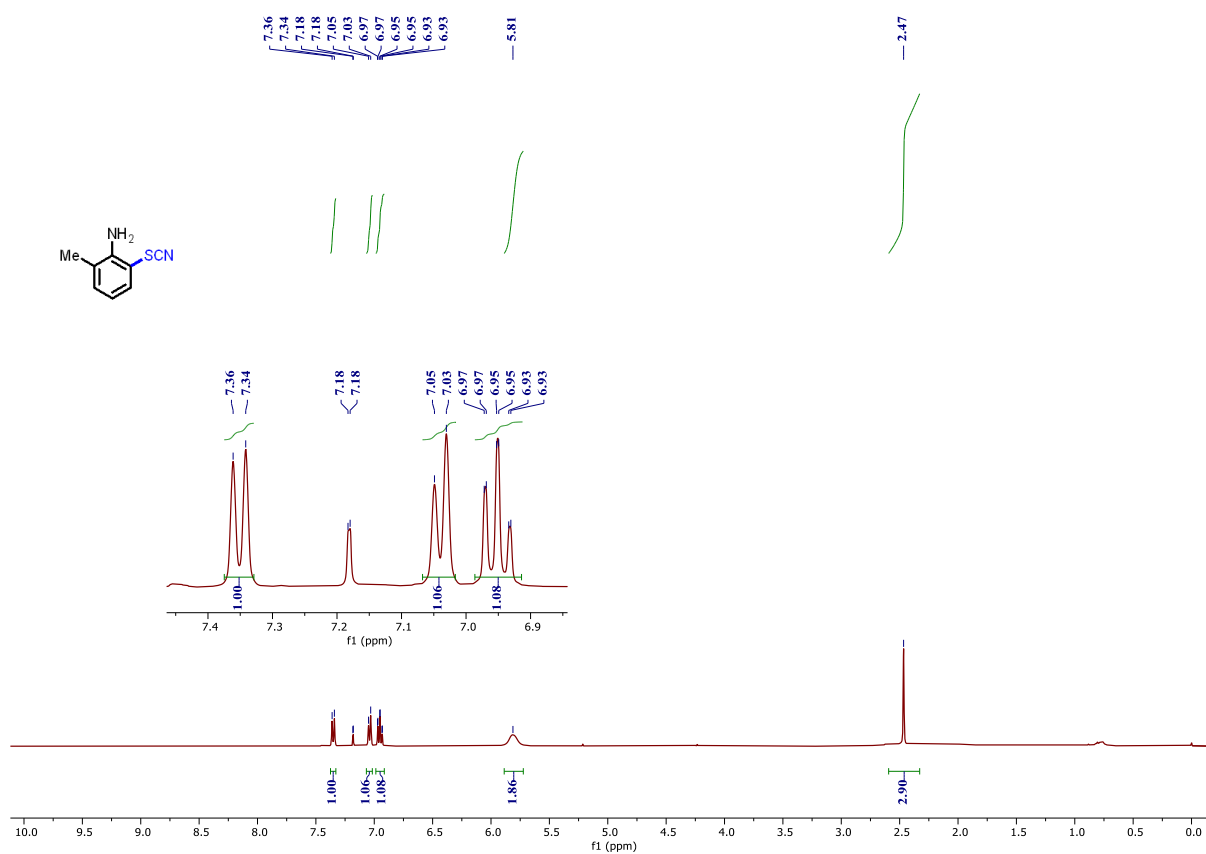
(Table 2, entry 2c)



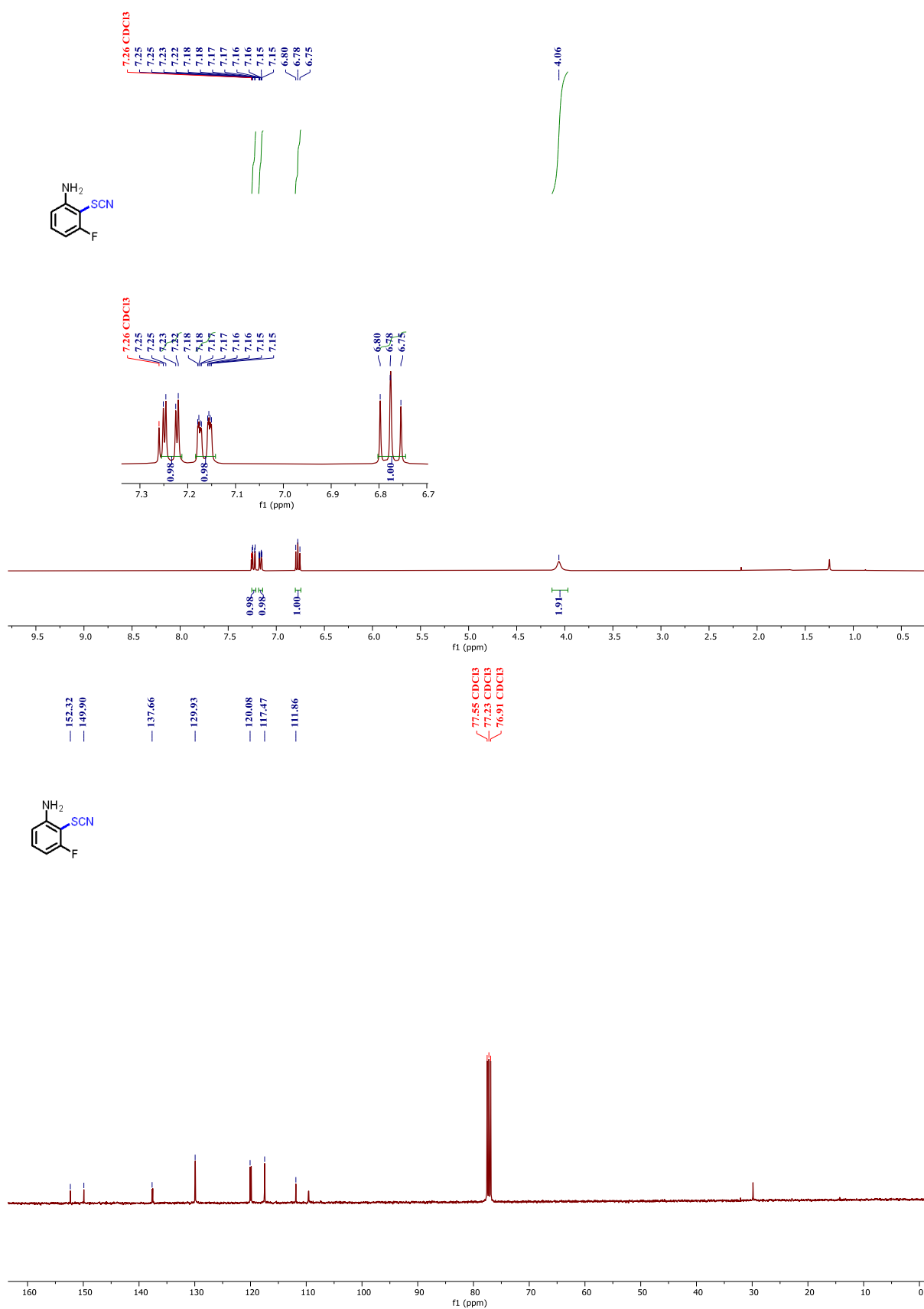
(Table 2, entry 2d)



(Table 2, entry 2e)



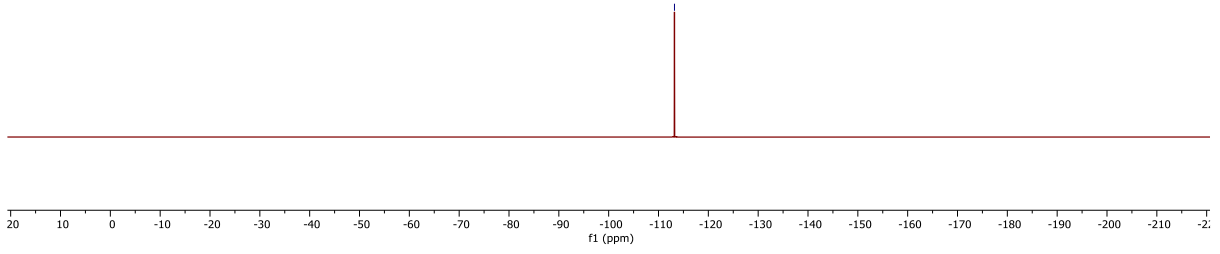
(Table 2, entry 2f)



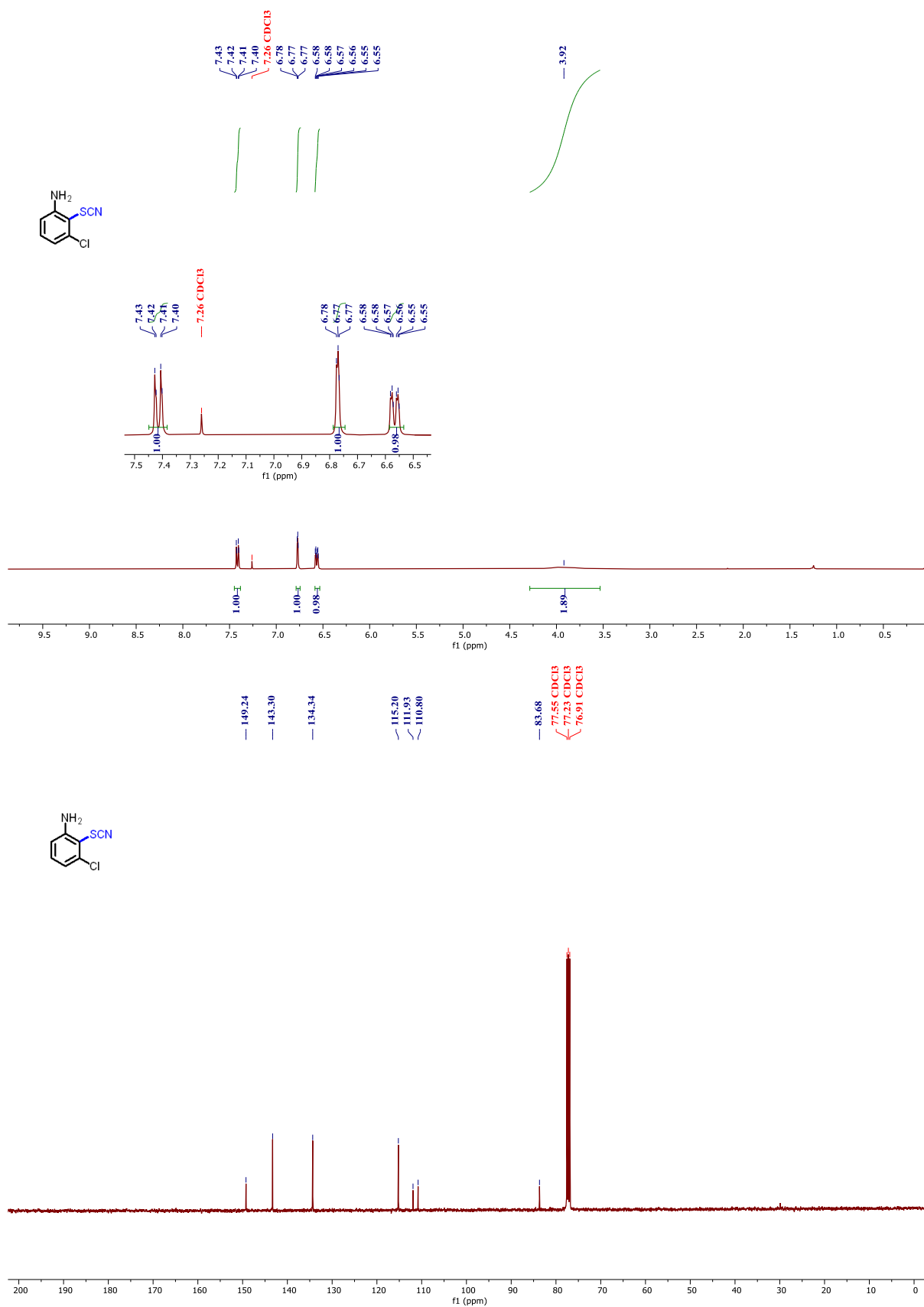




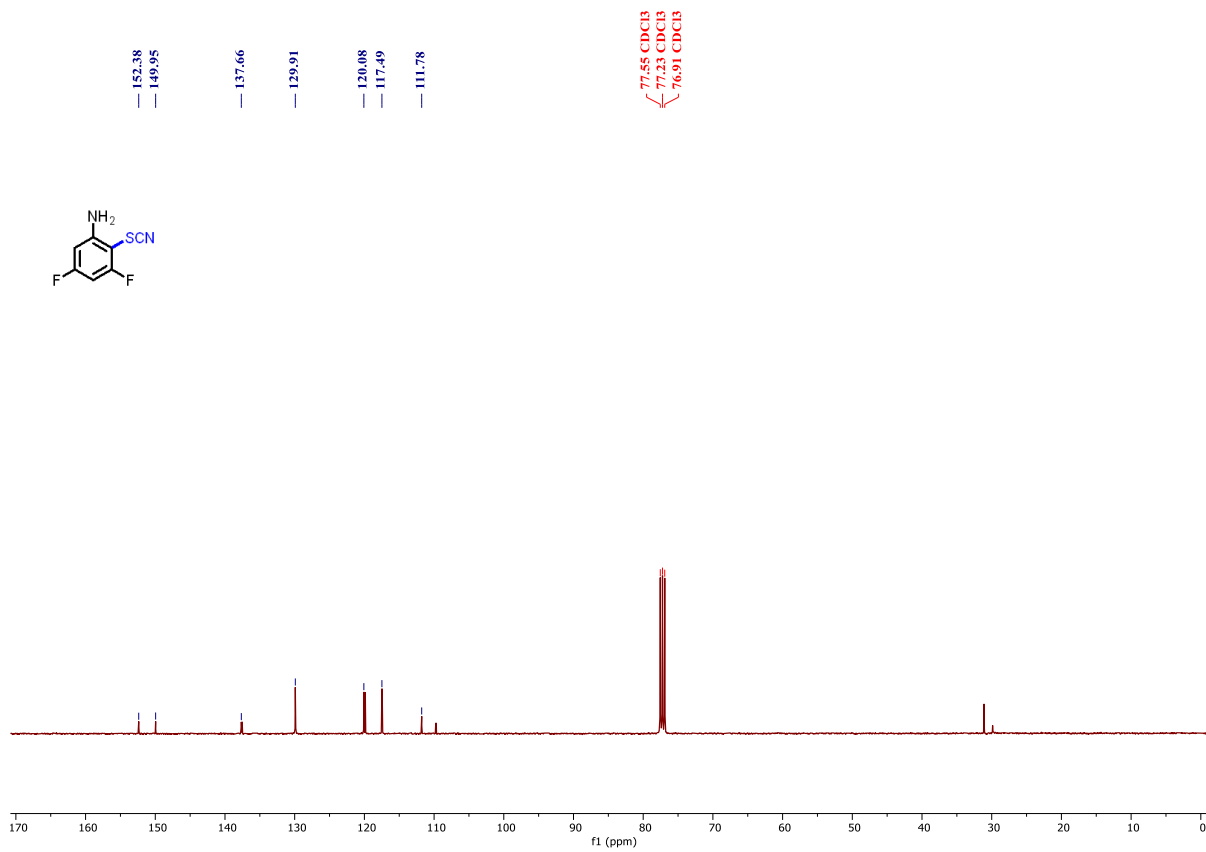
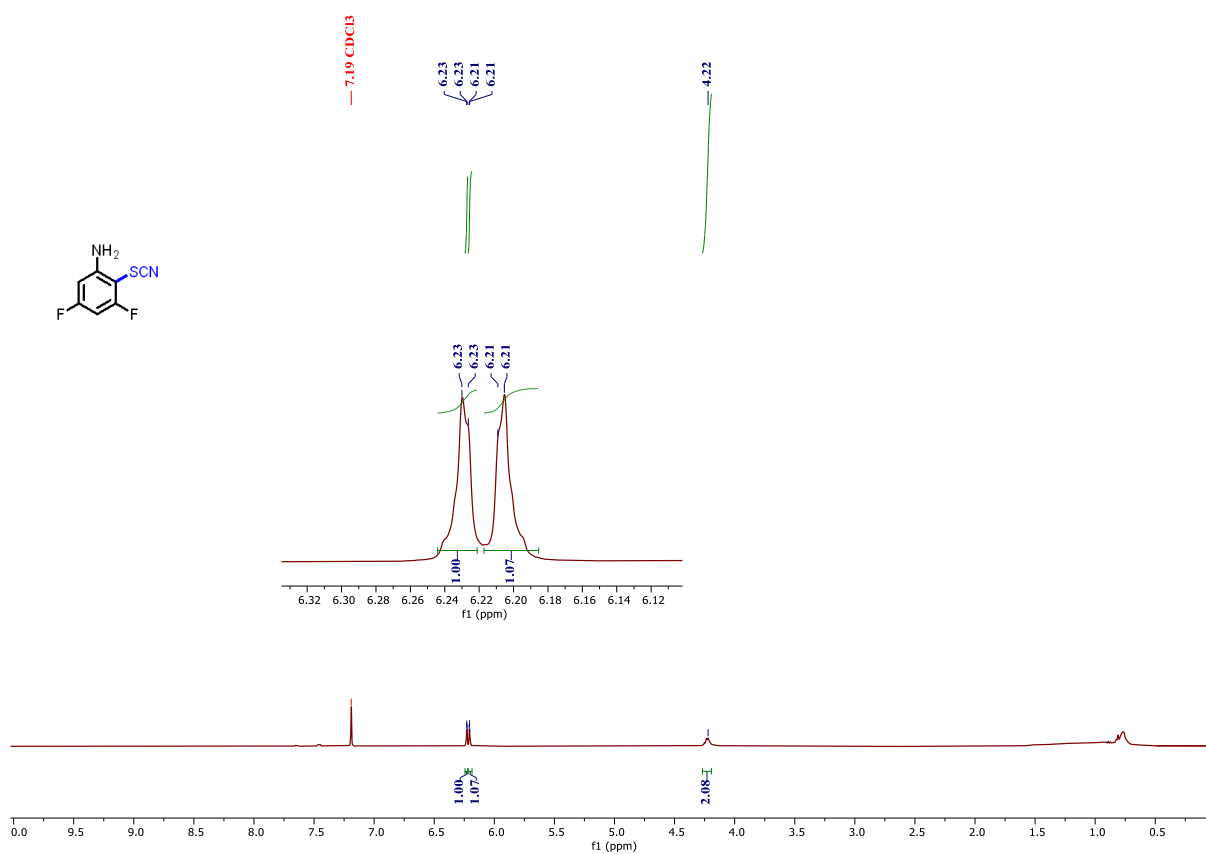
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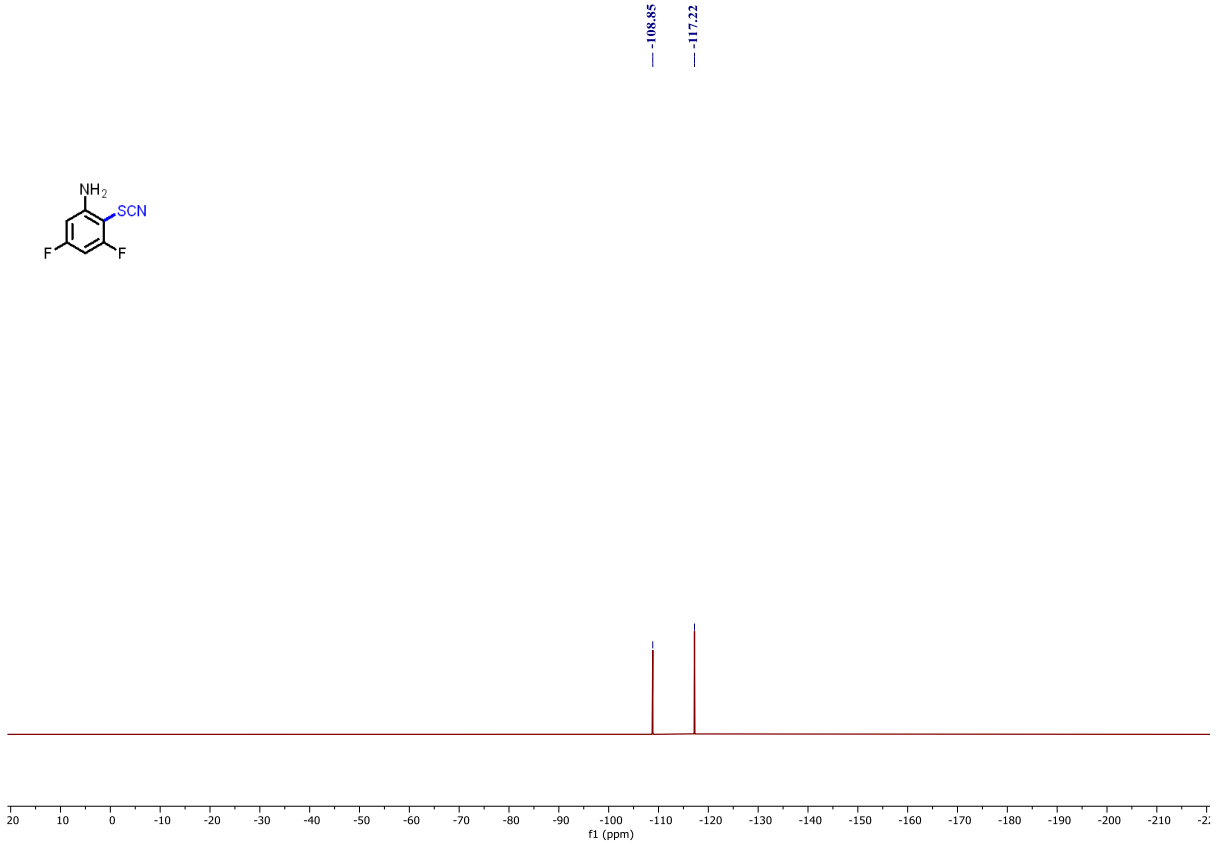
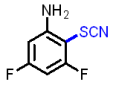


(Table 2, entry 2g)

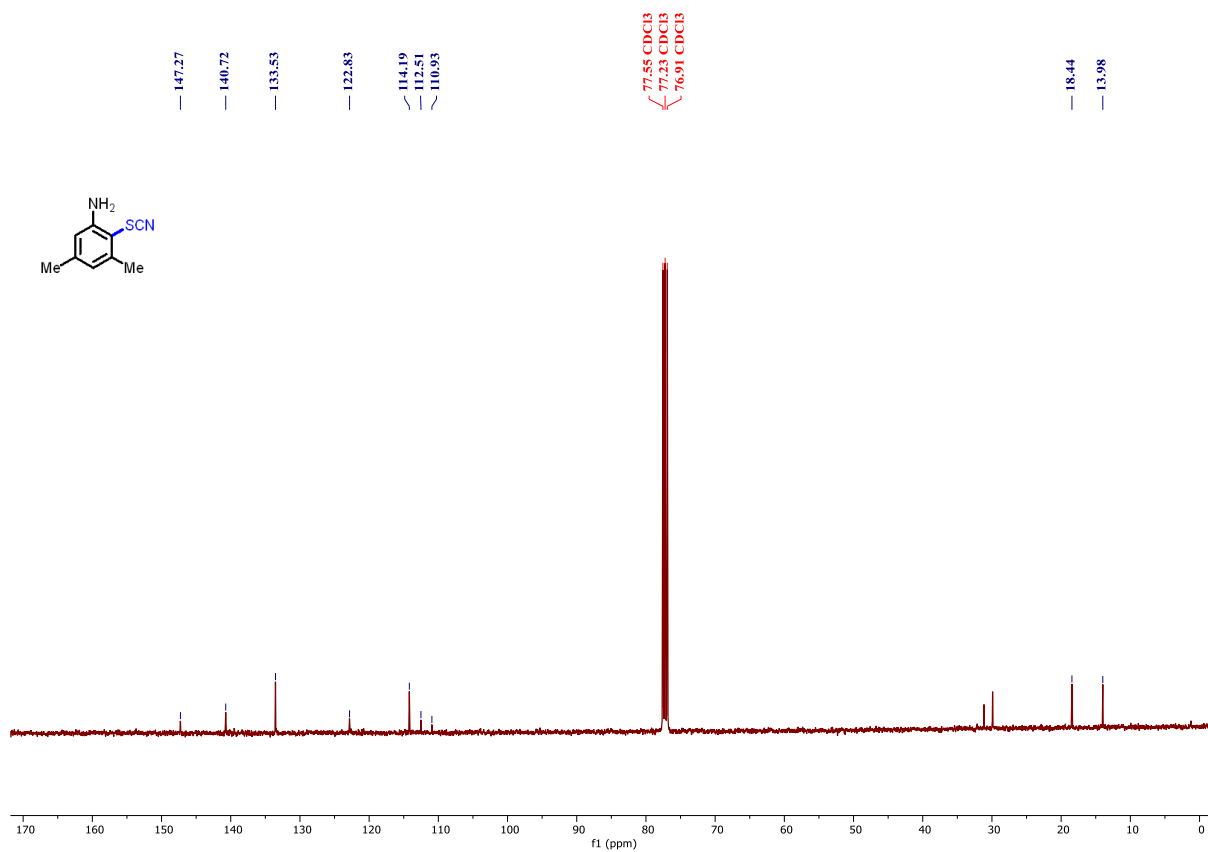
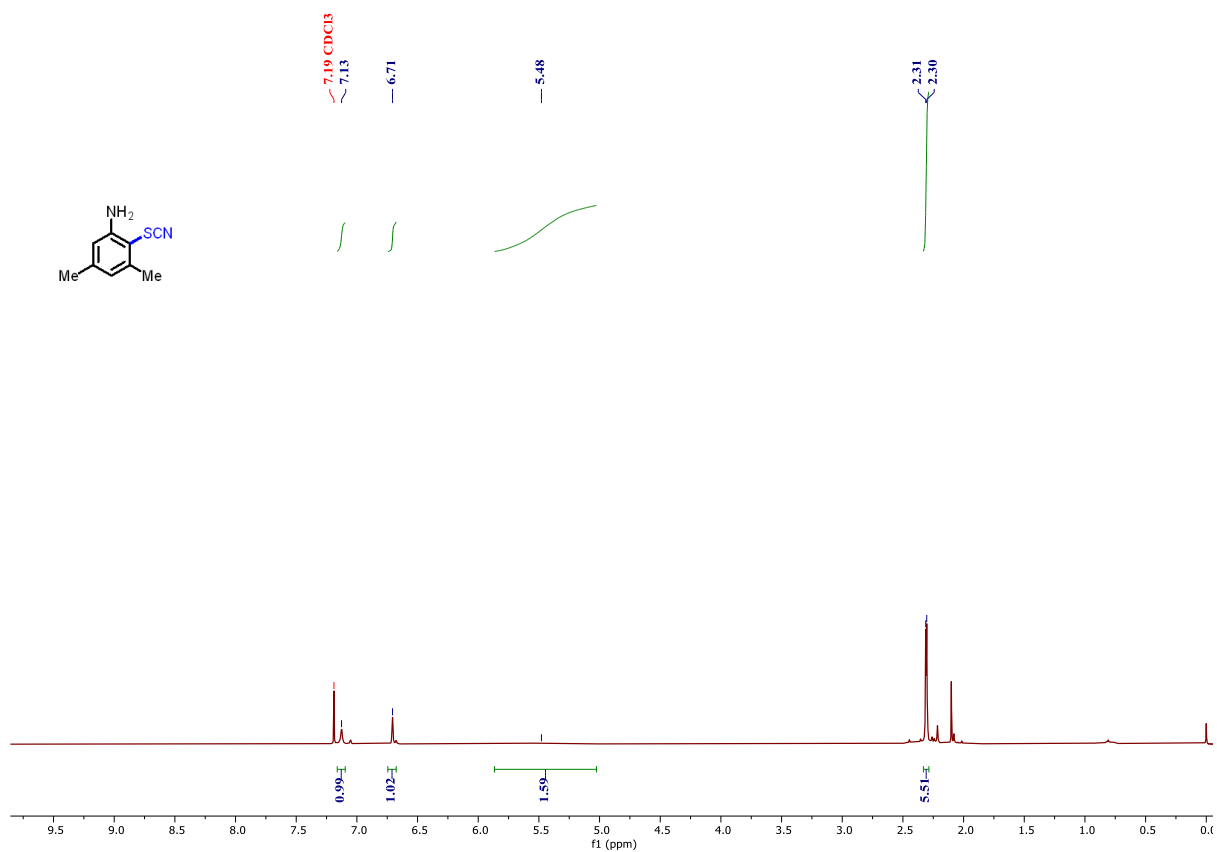


(Table 2, entry 2h)

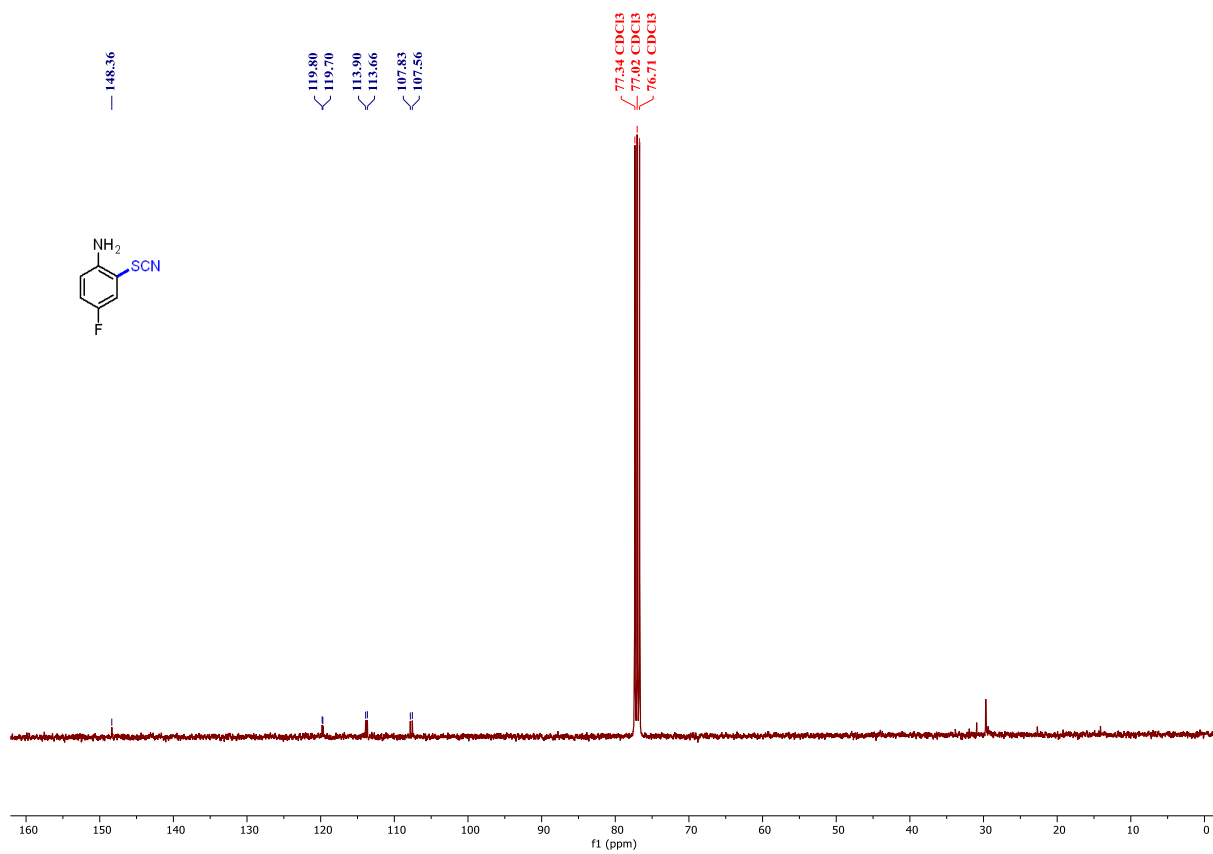
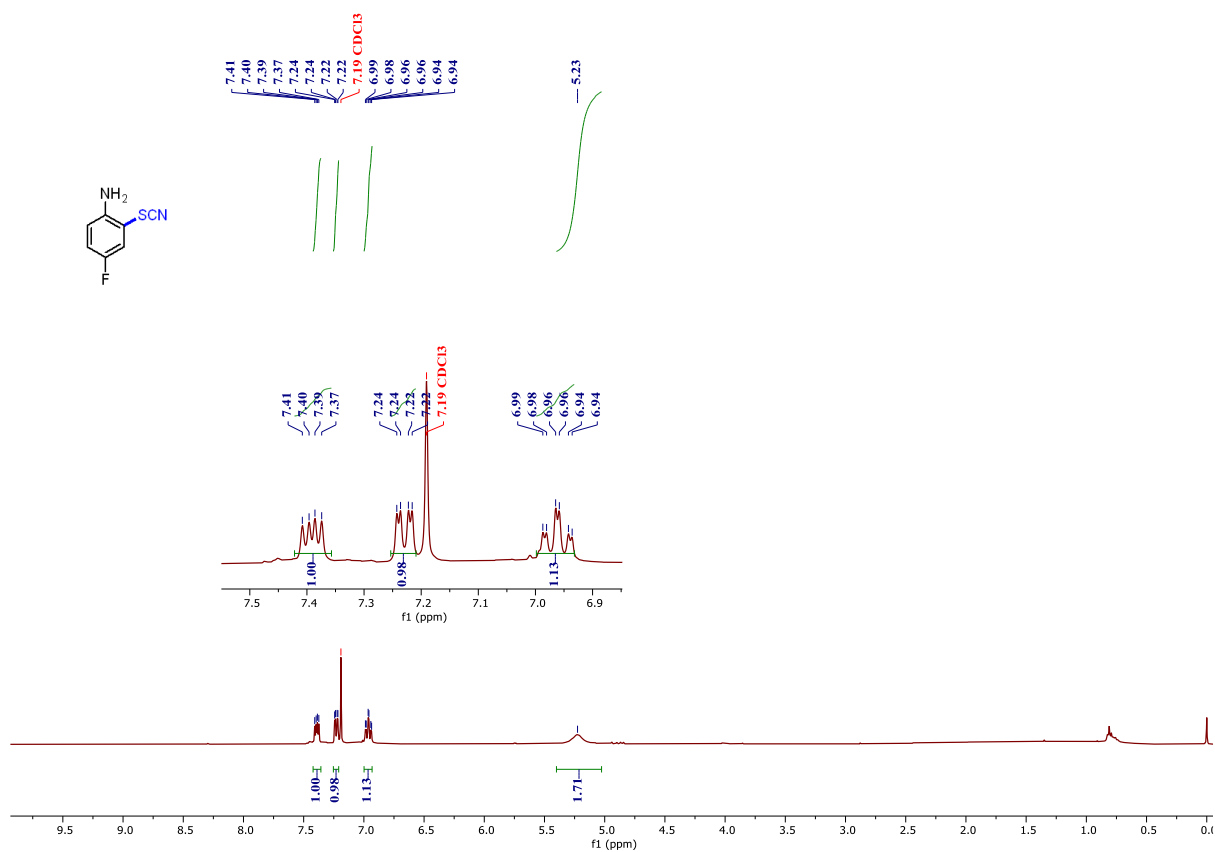


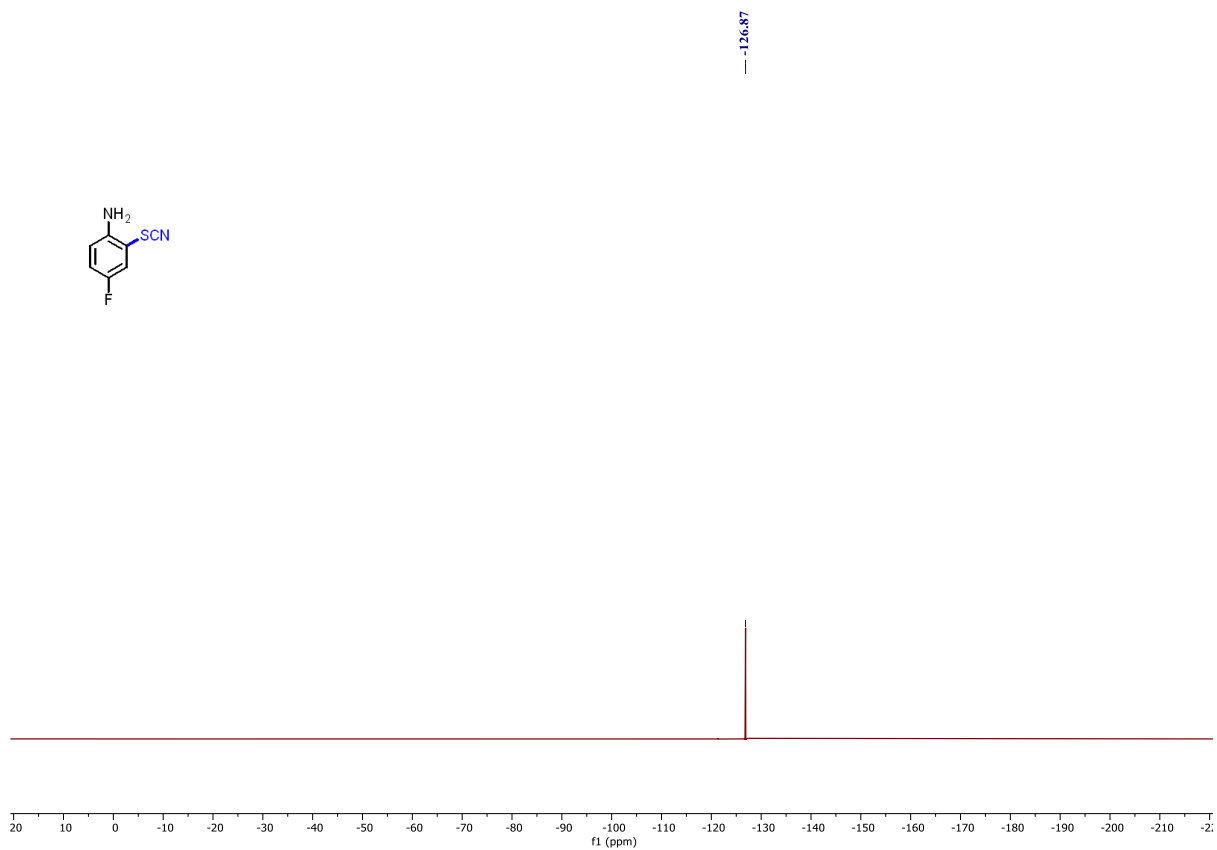


(Table 2, entry 2i)

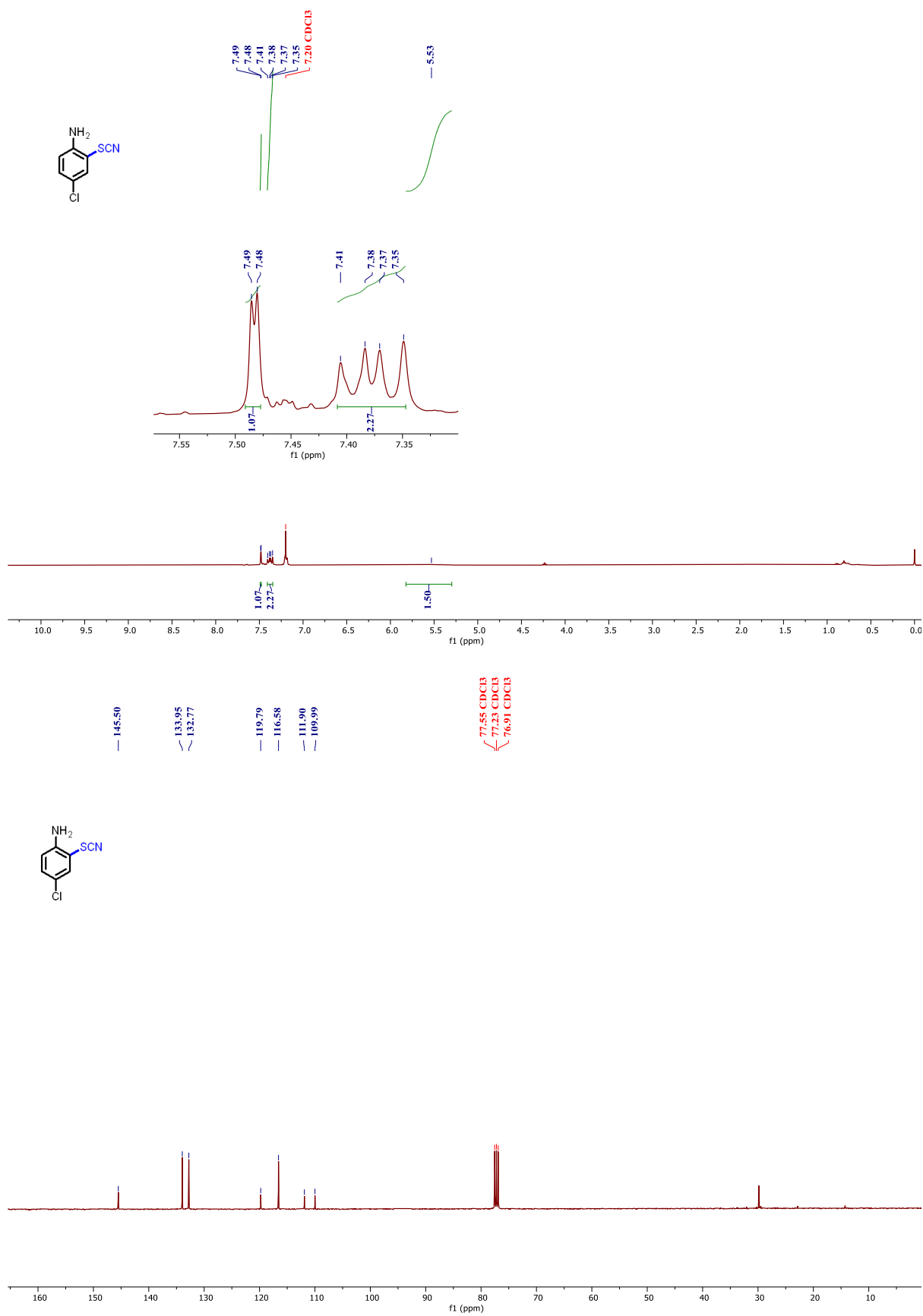


(Table 2, entry 2j)



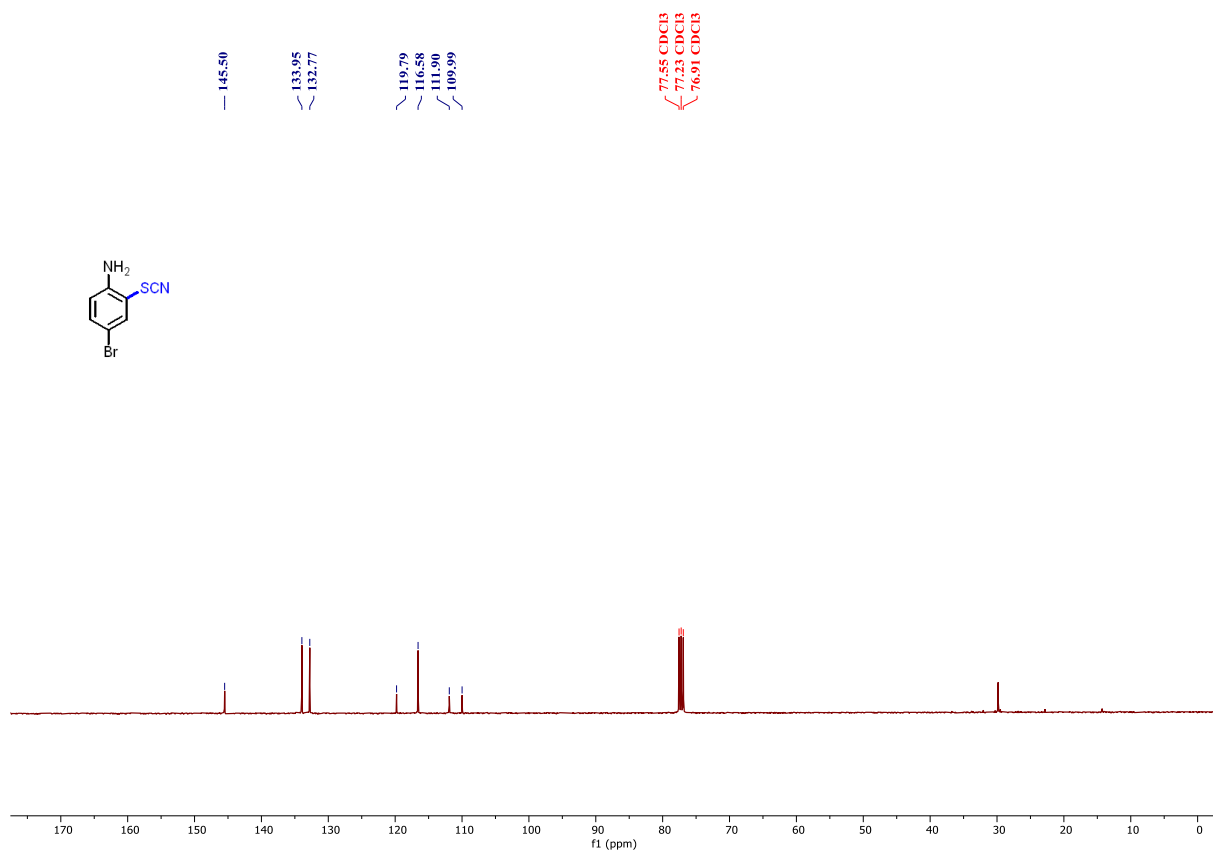
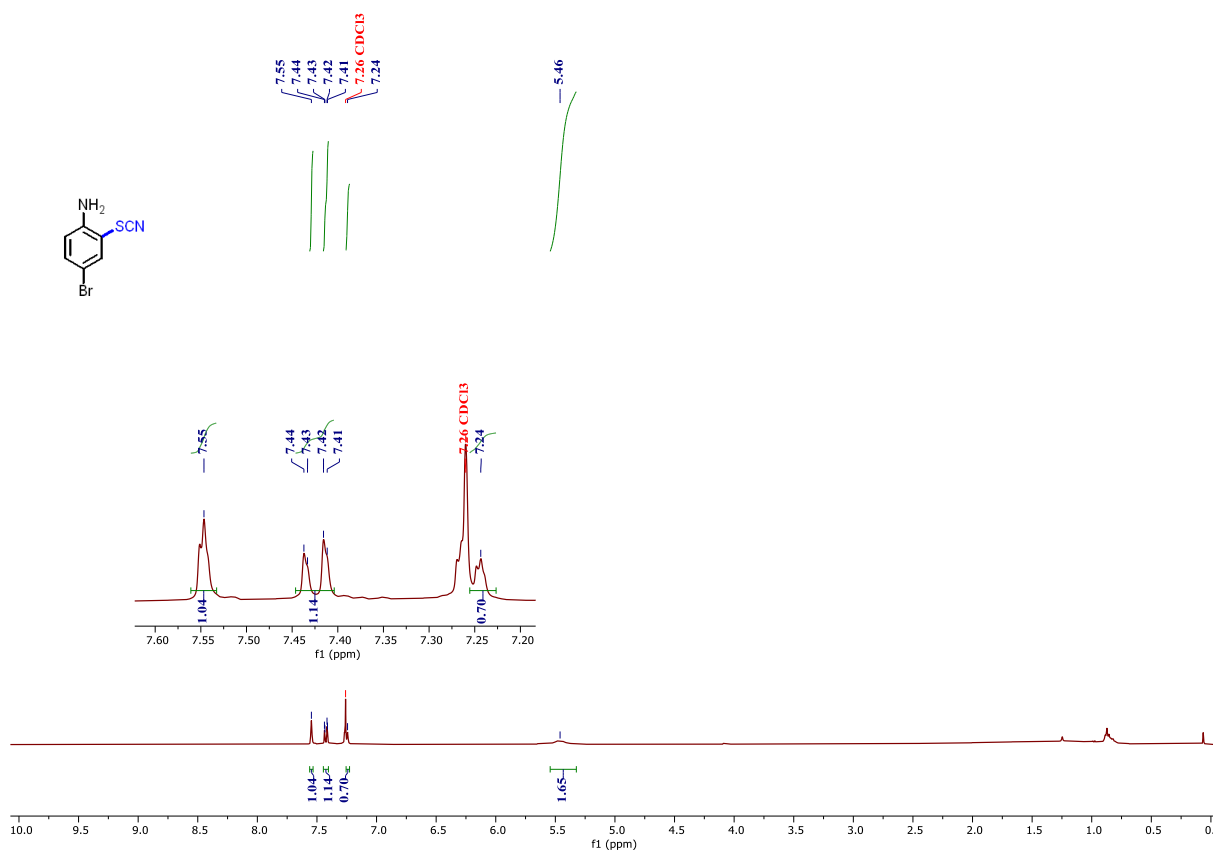


(Table 2, entry 2k)

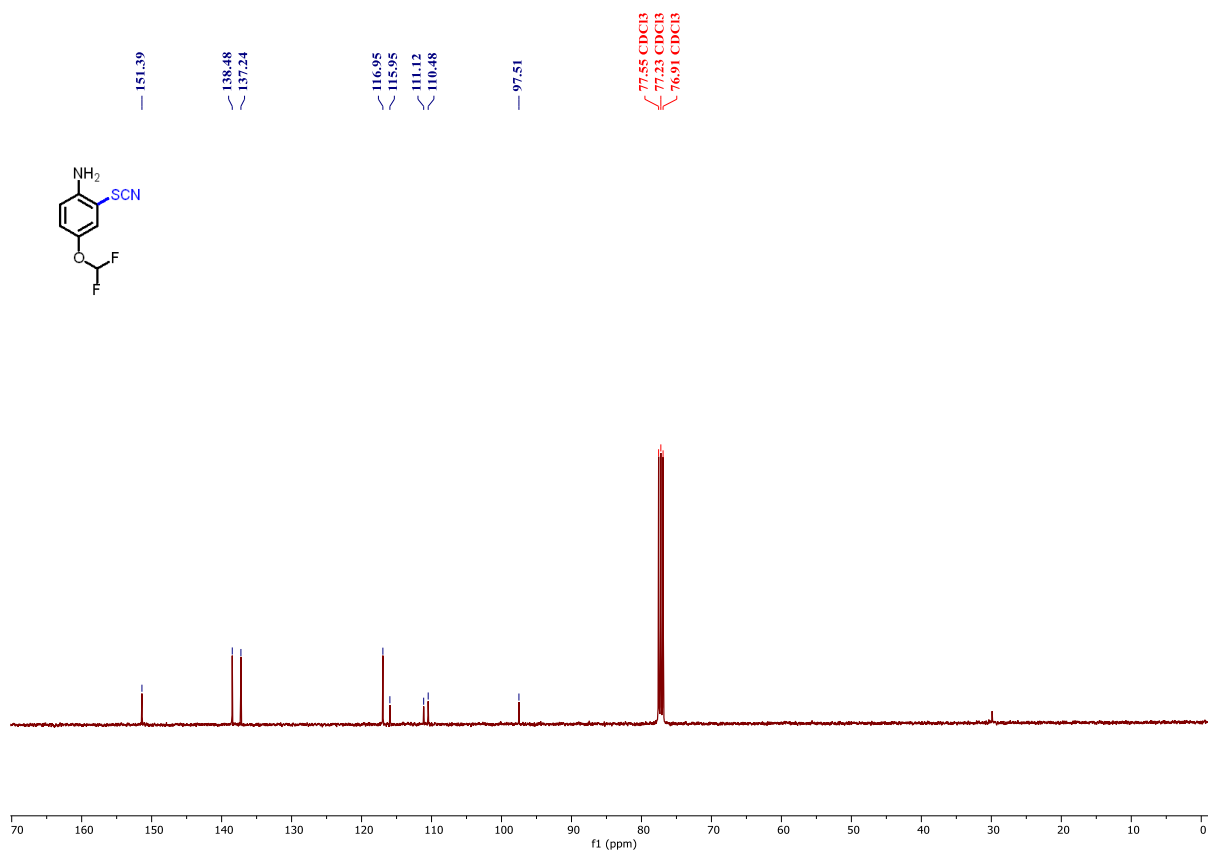
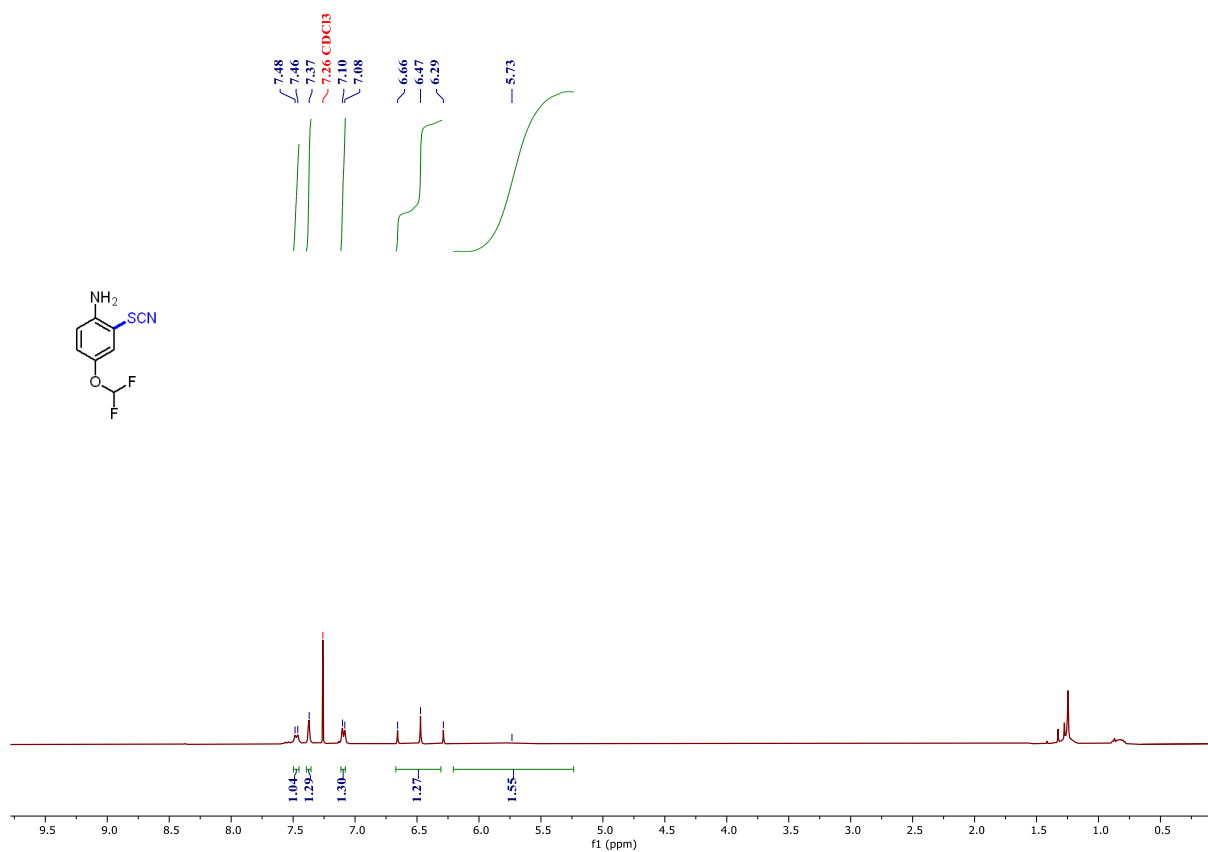


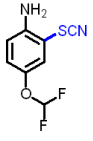


(Table 2, entry 2l)

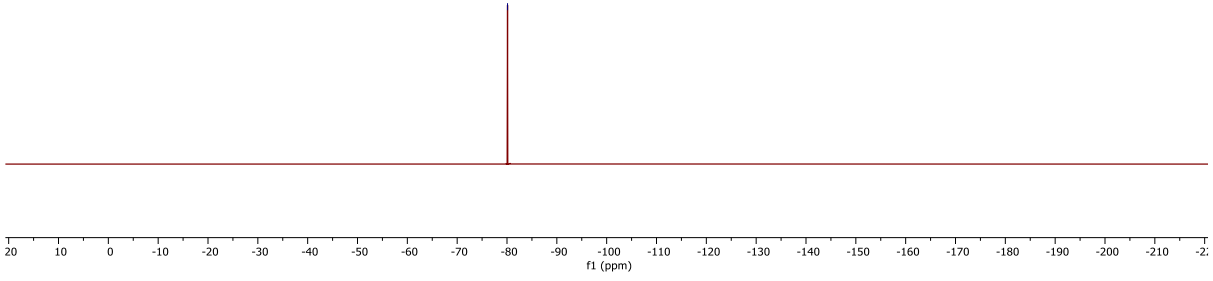


(Table 2, entry 2m)

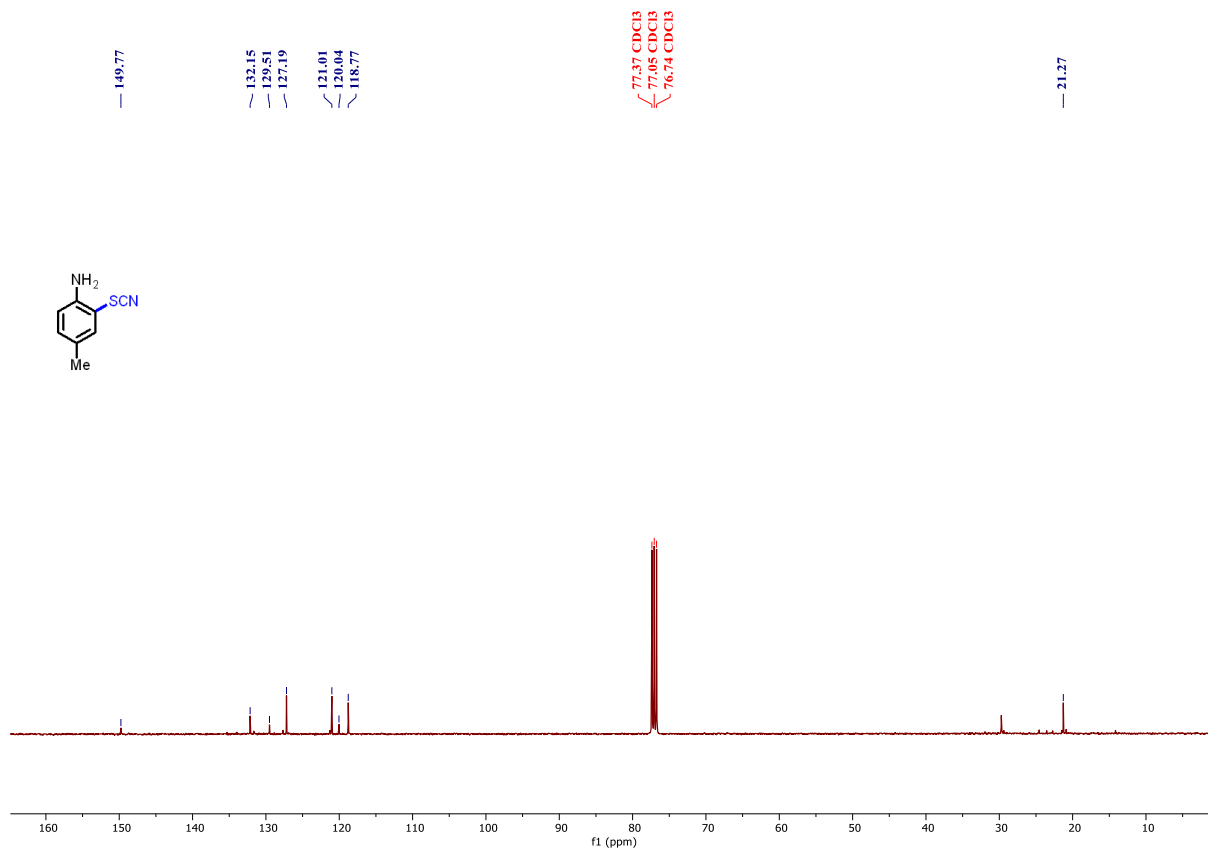
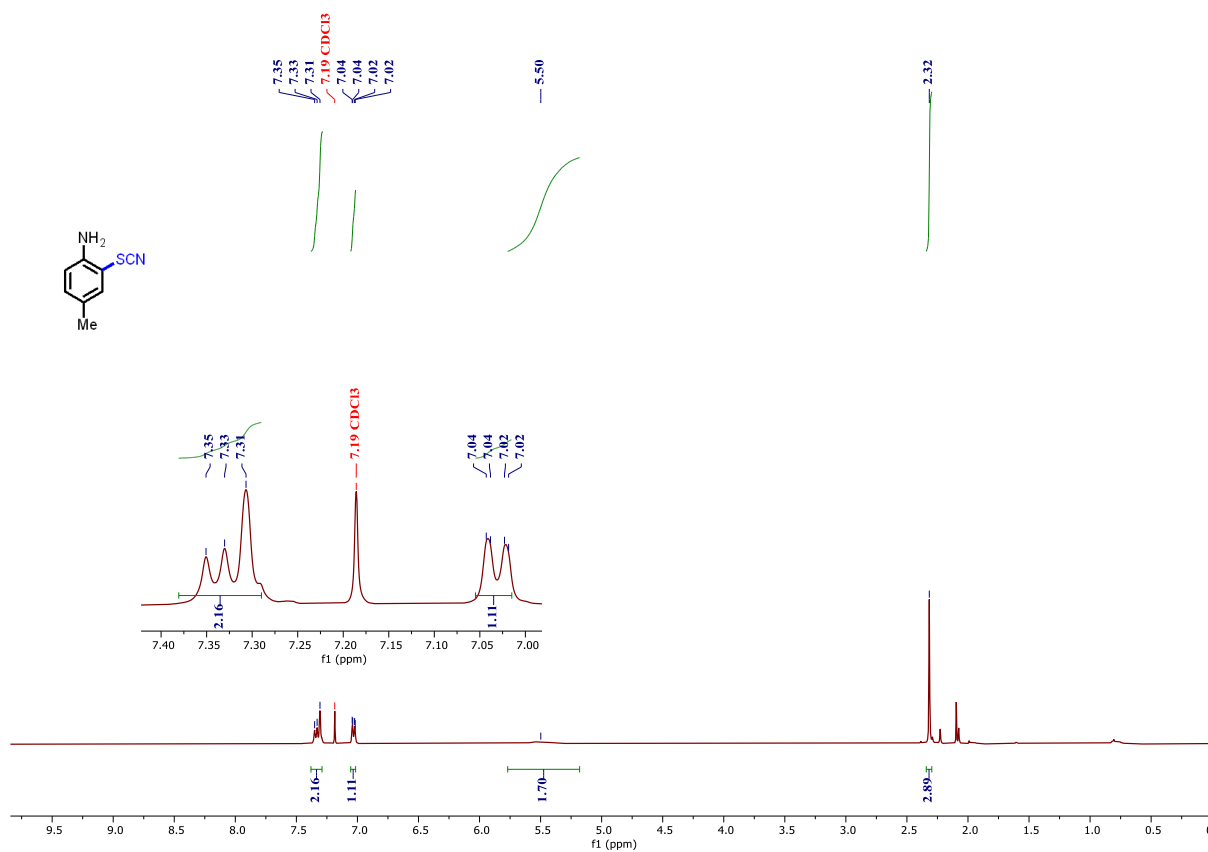




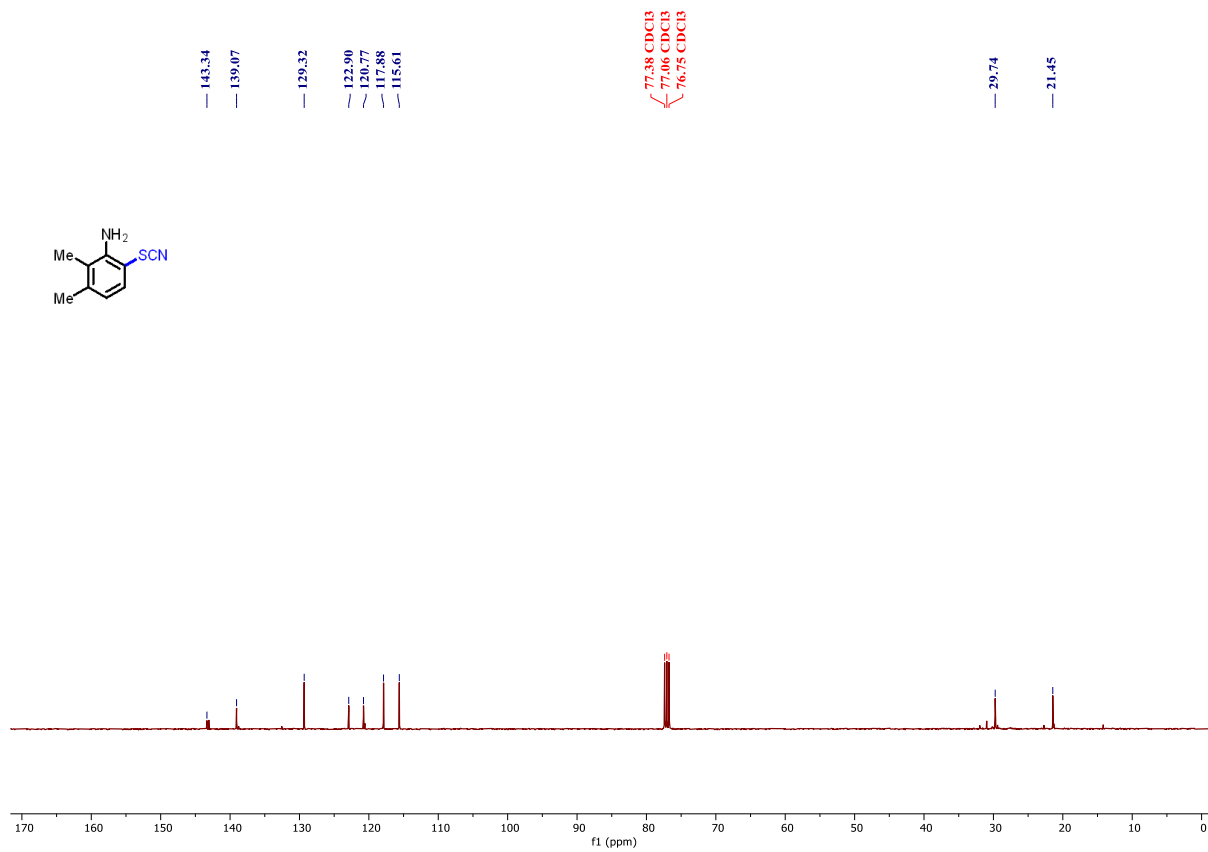
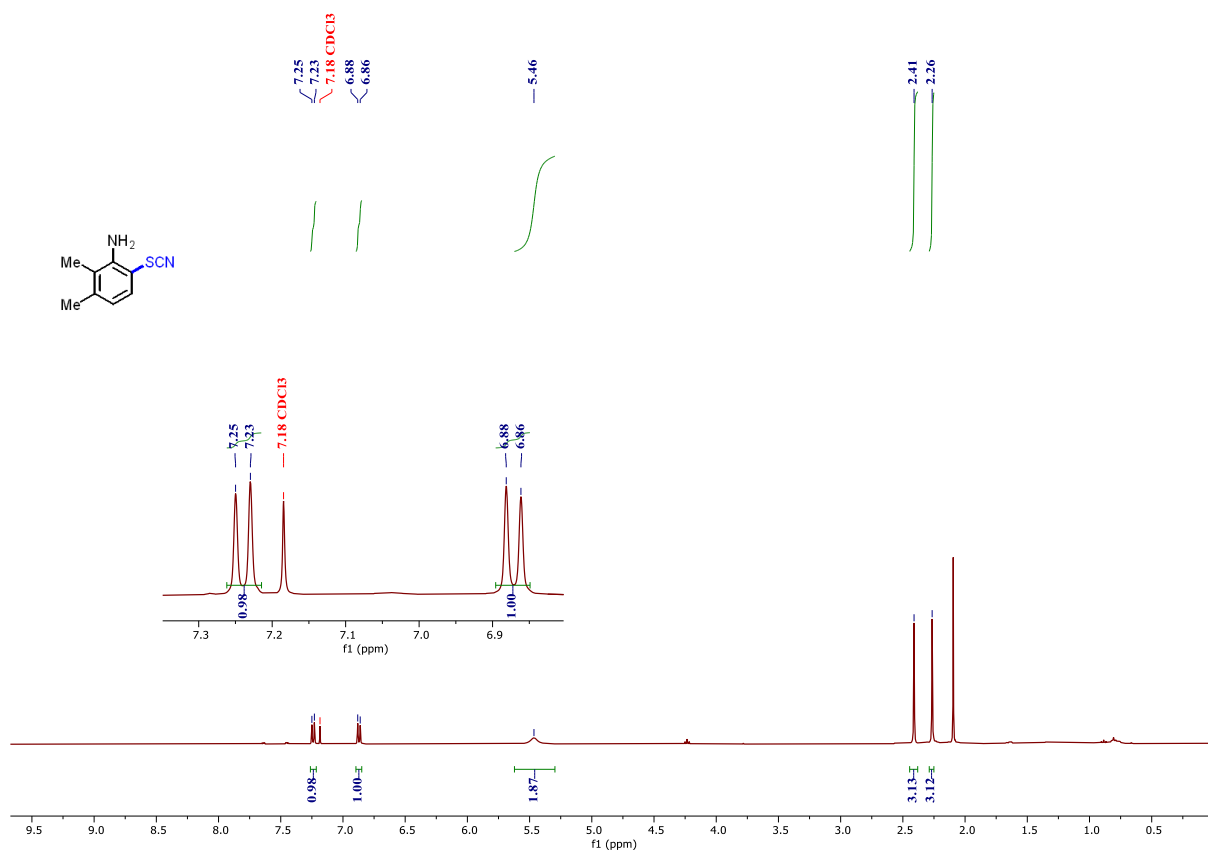
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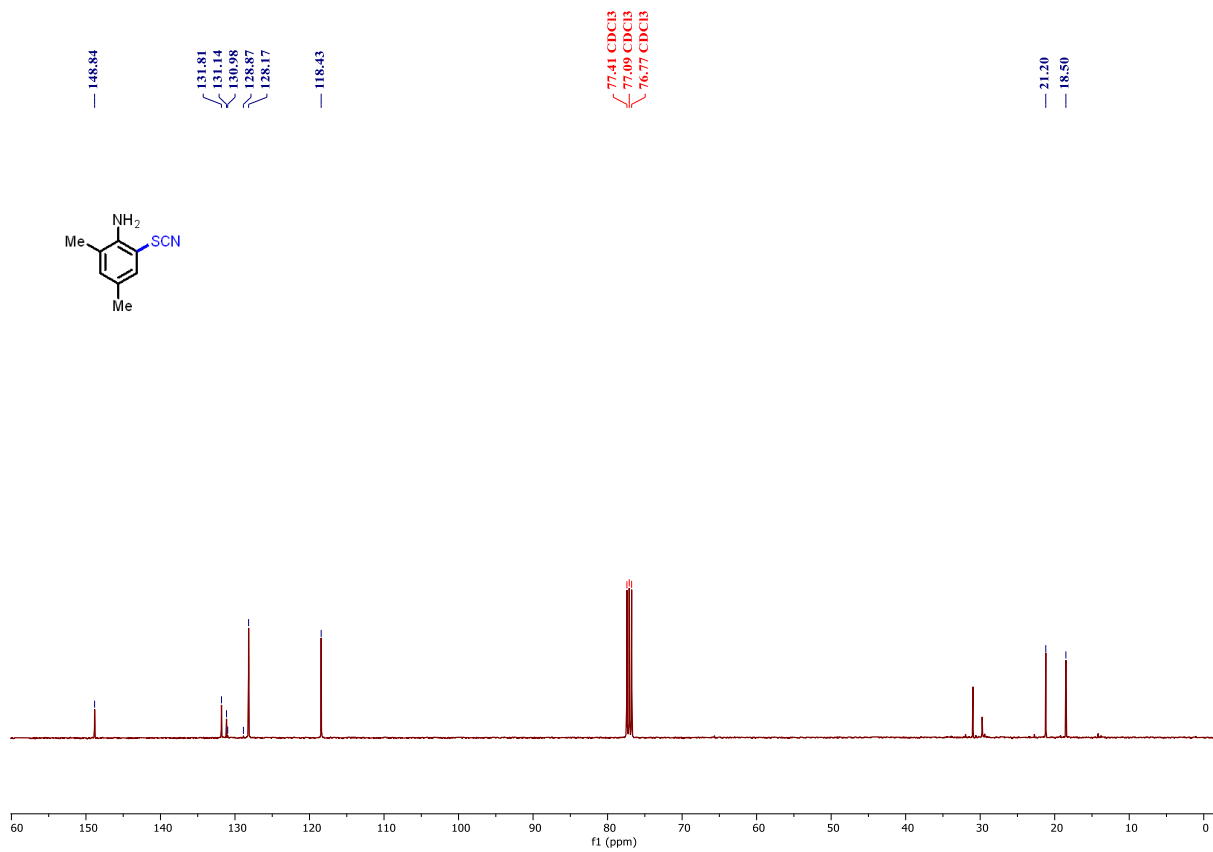
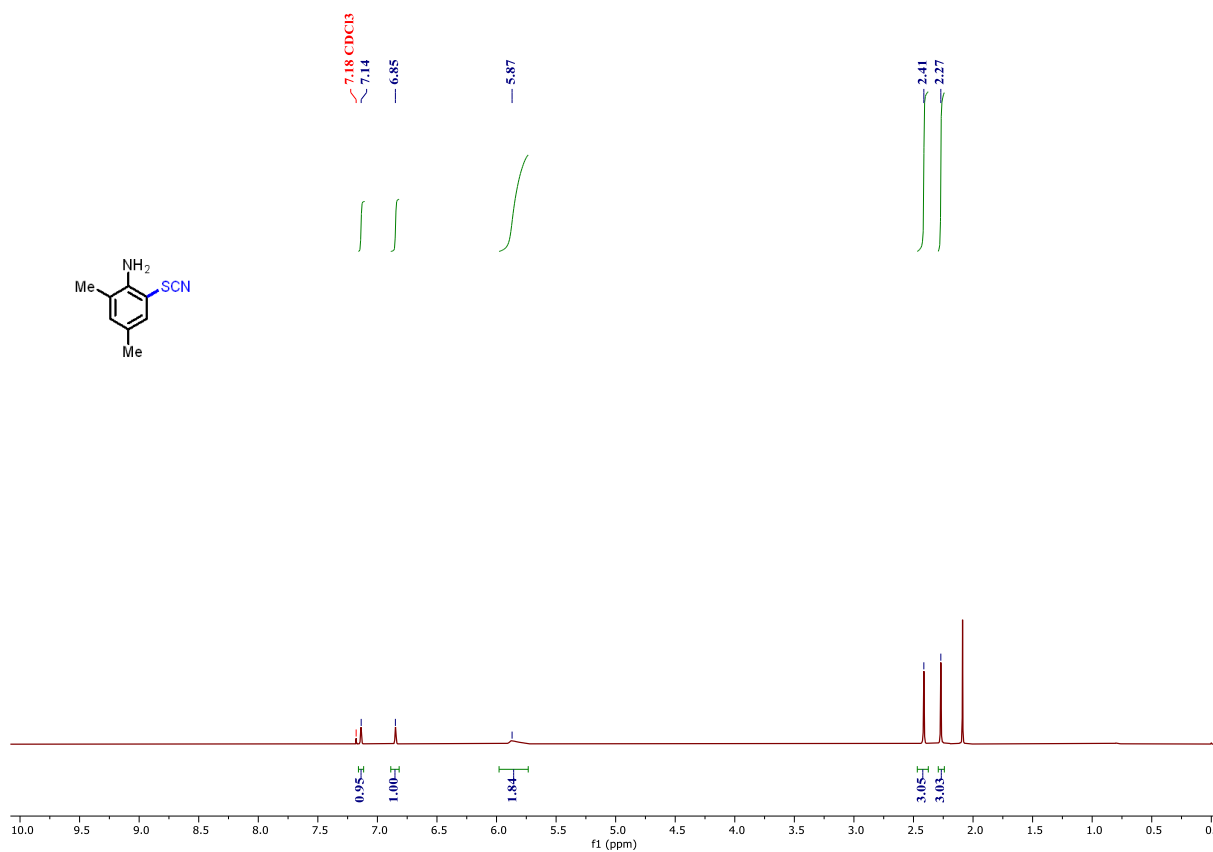
(Table 2, entry 2n)



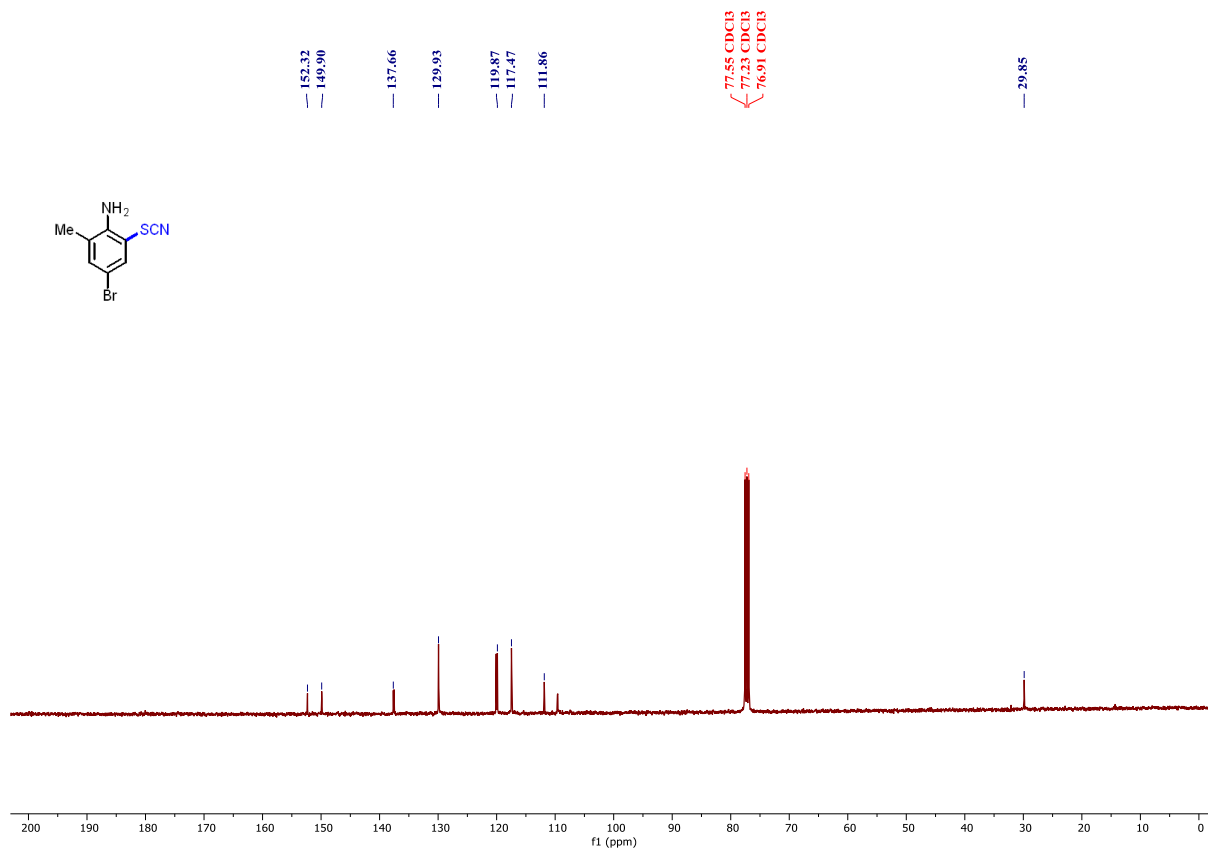
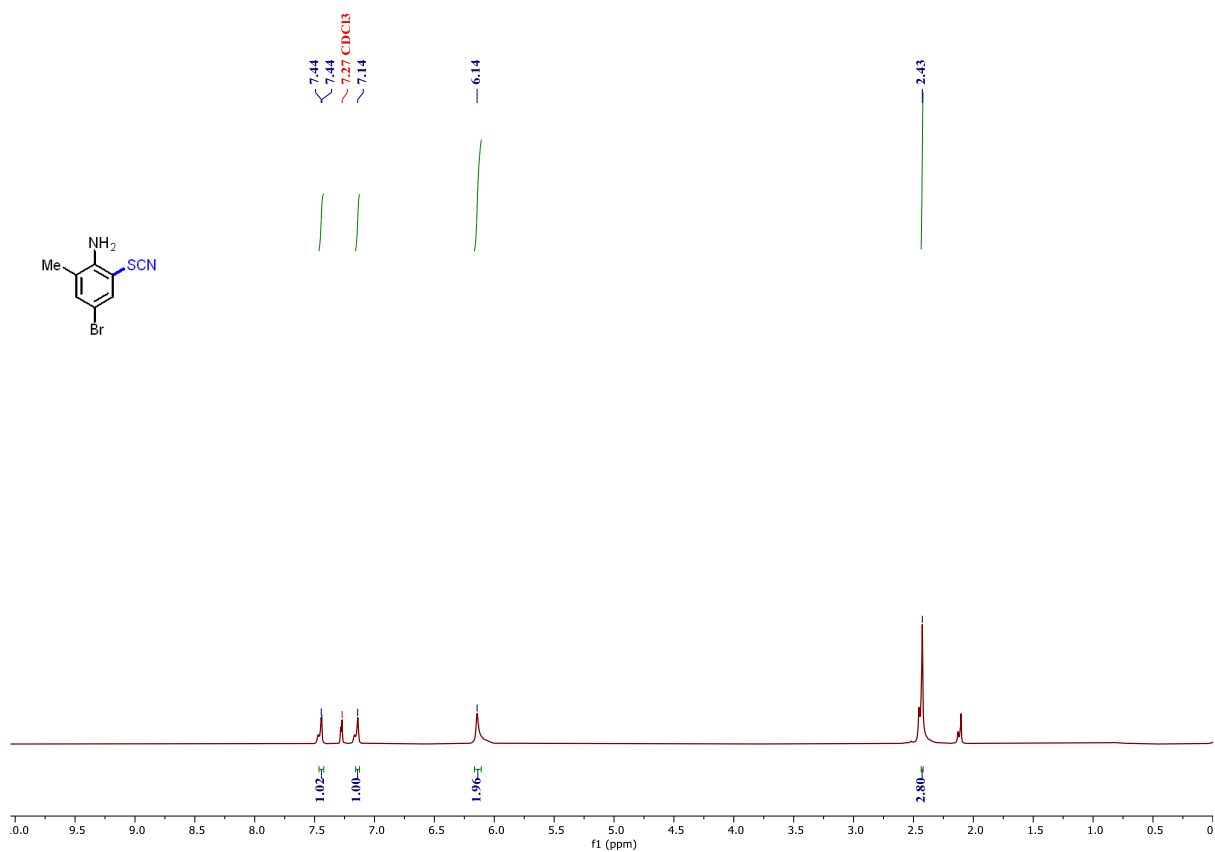
(Table 2, entry 2o)



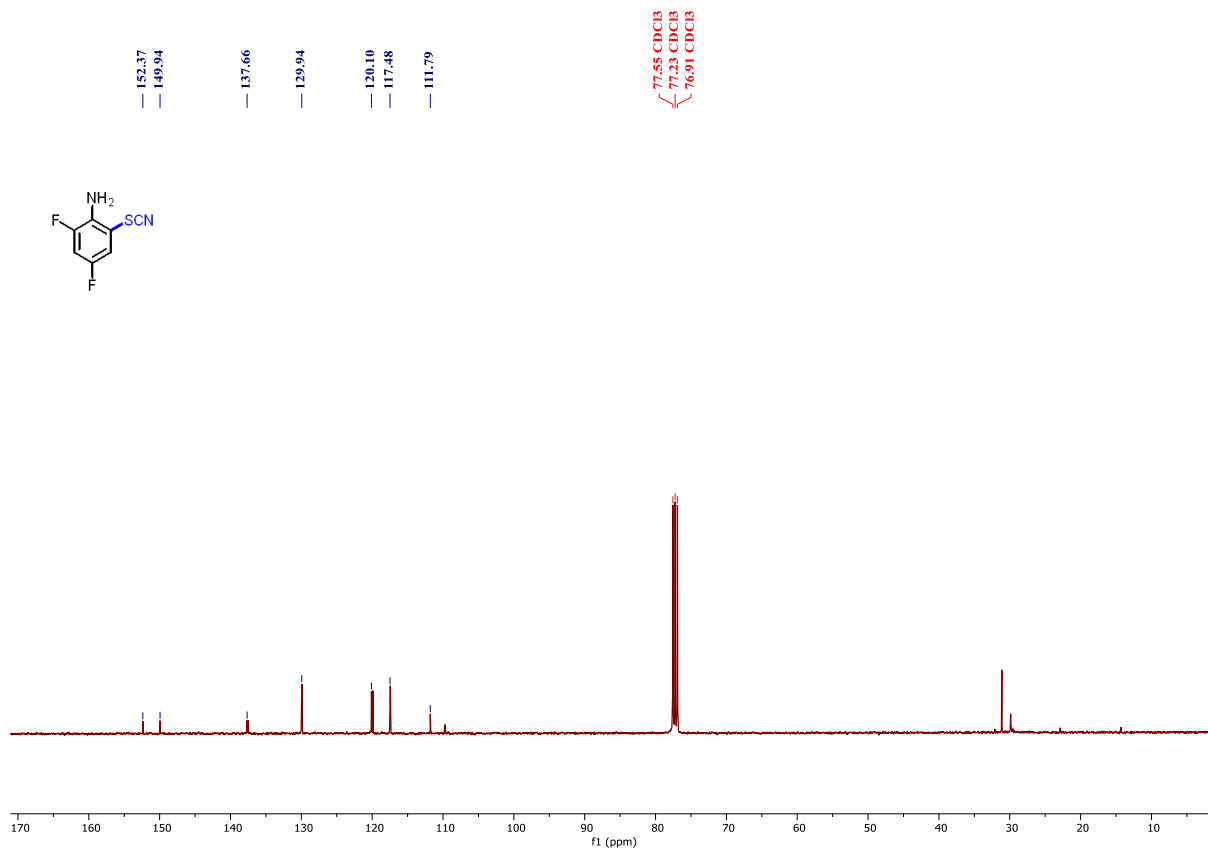
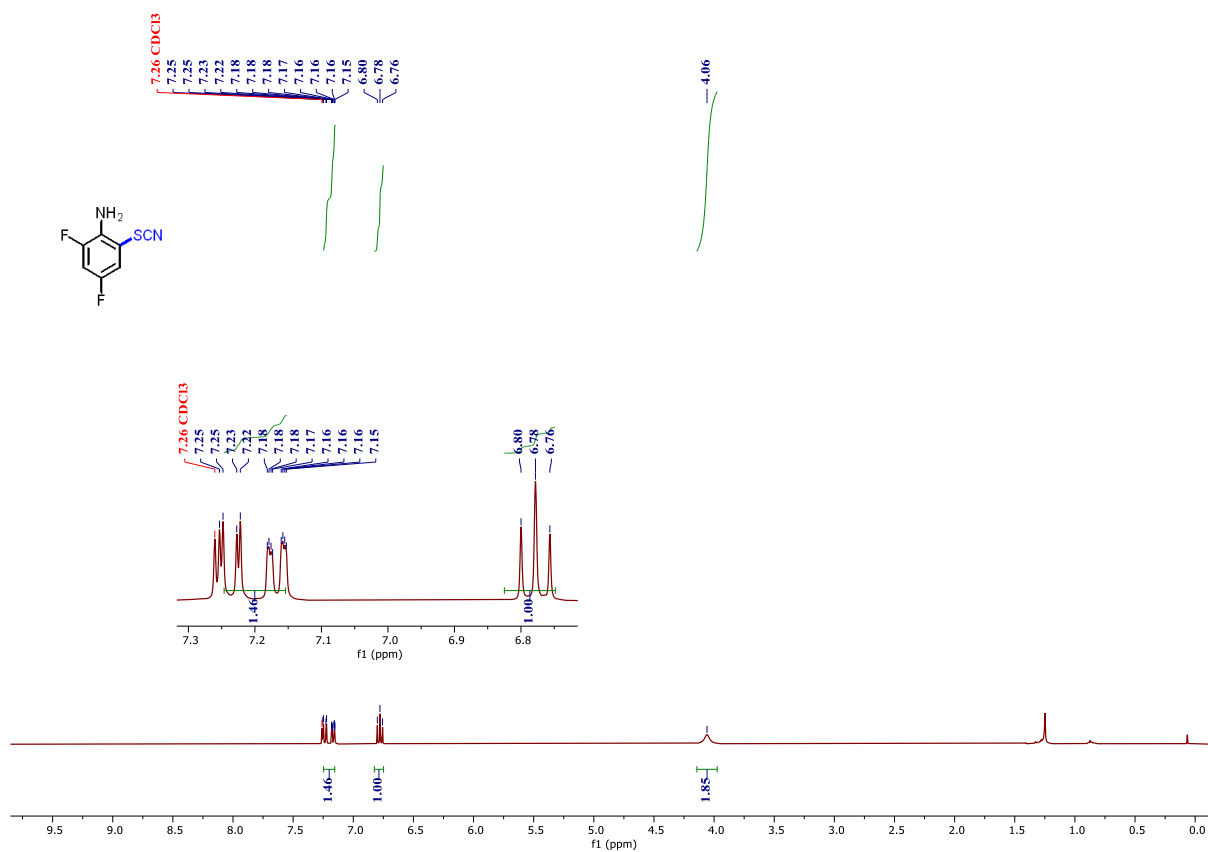
(Table 2, entry 2p)



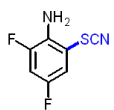
(Table 2, entry 2q)



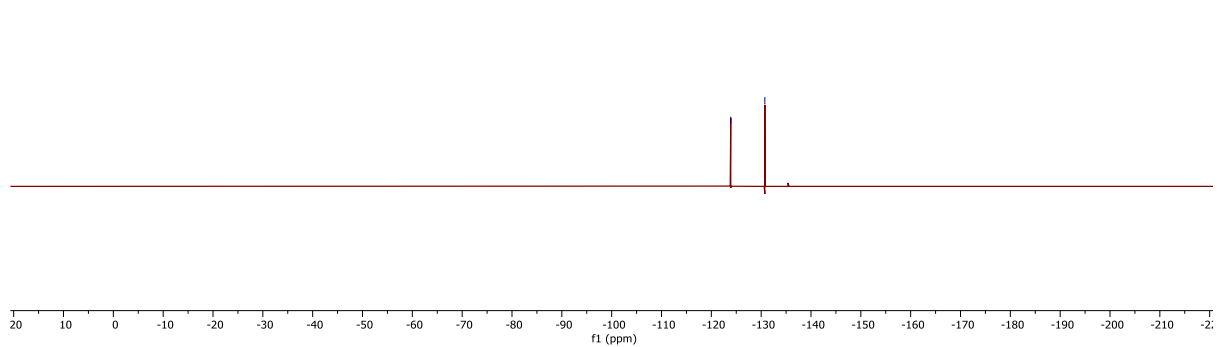
(Table 2, entry 2r)



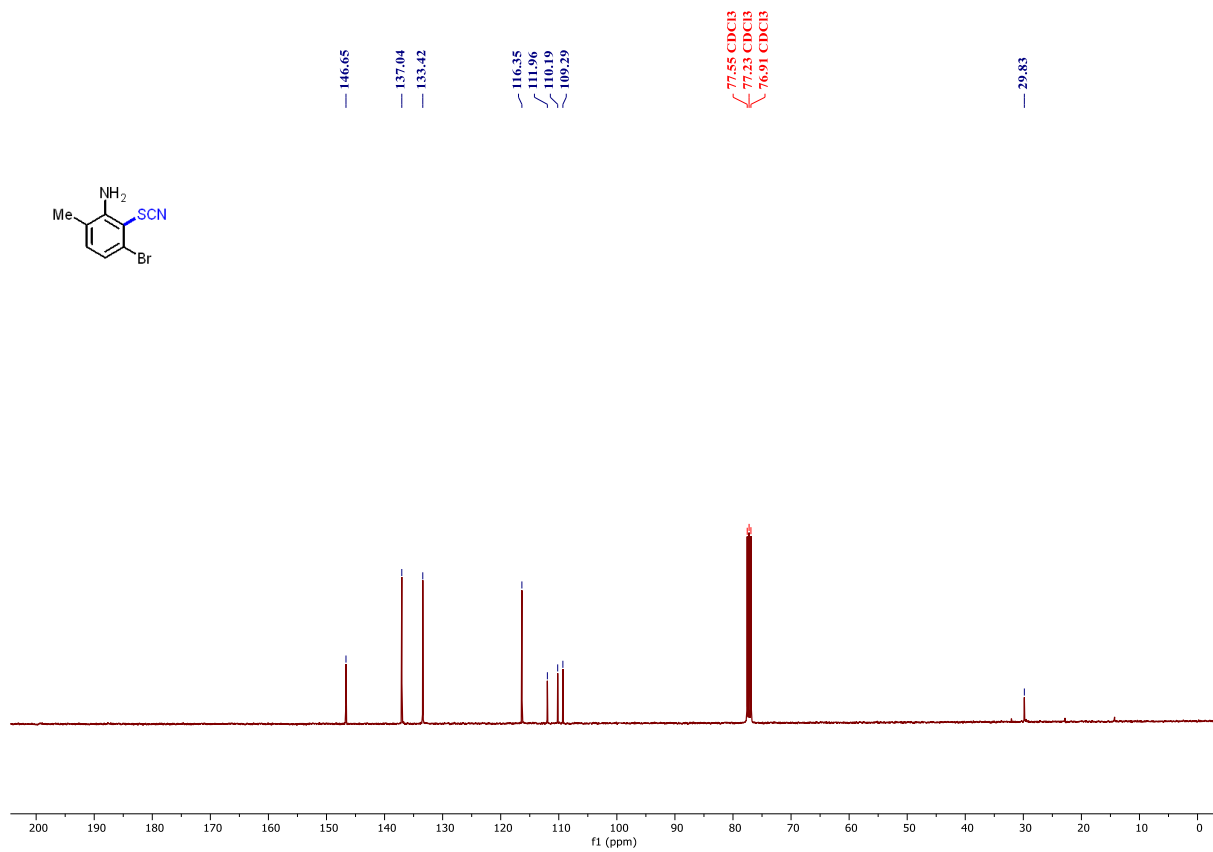
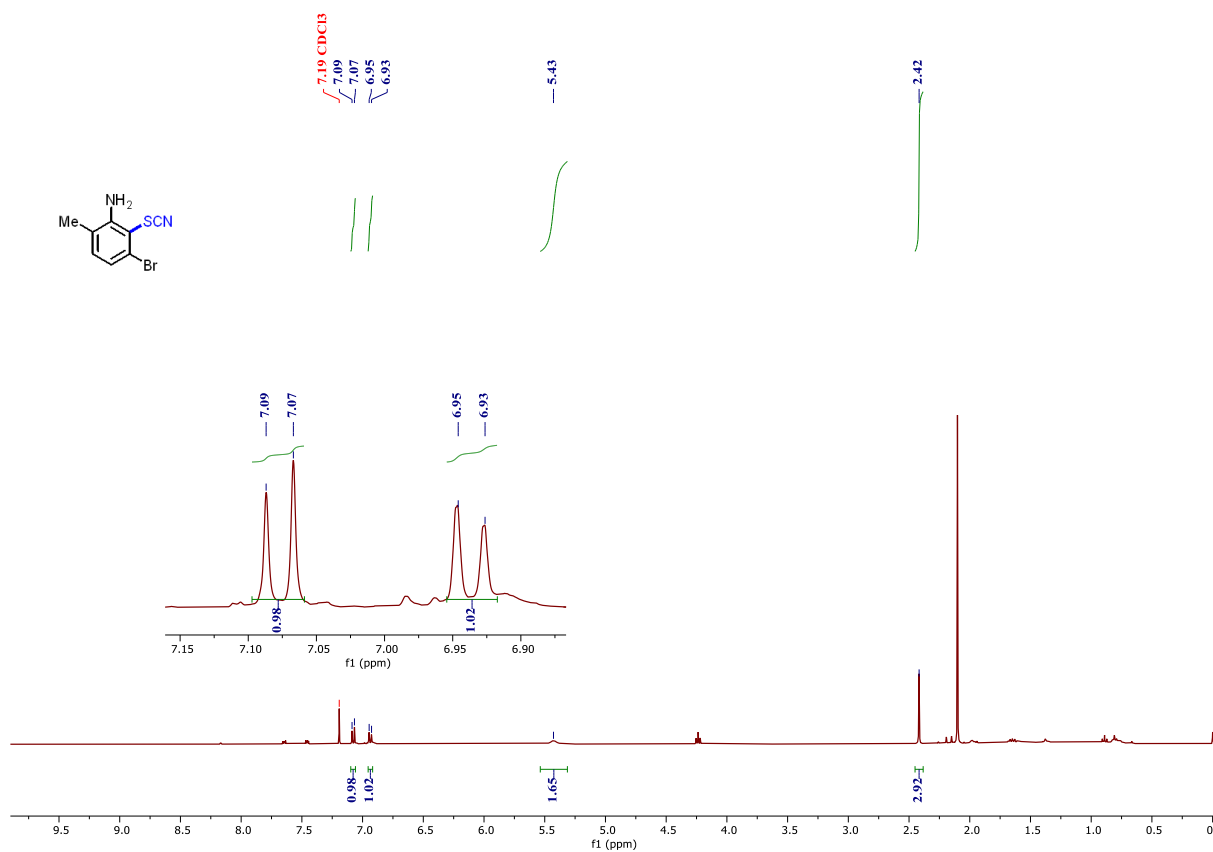




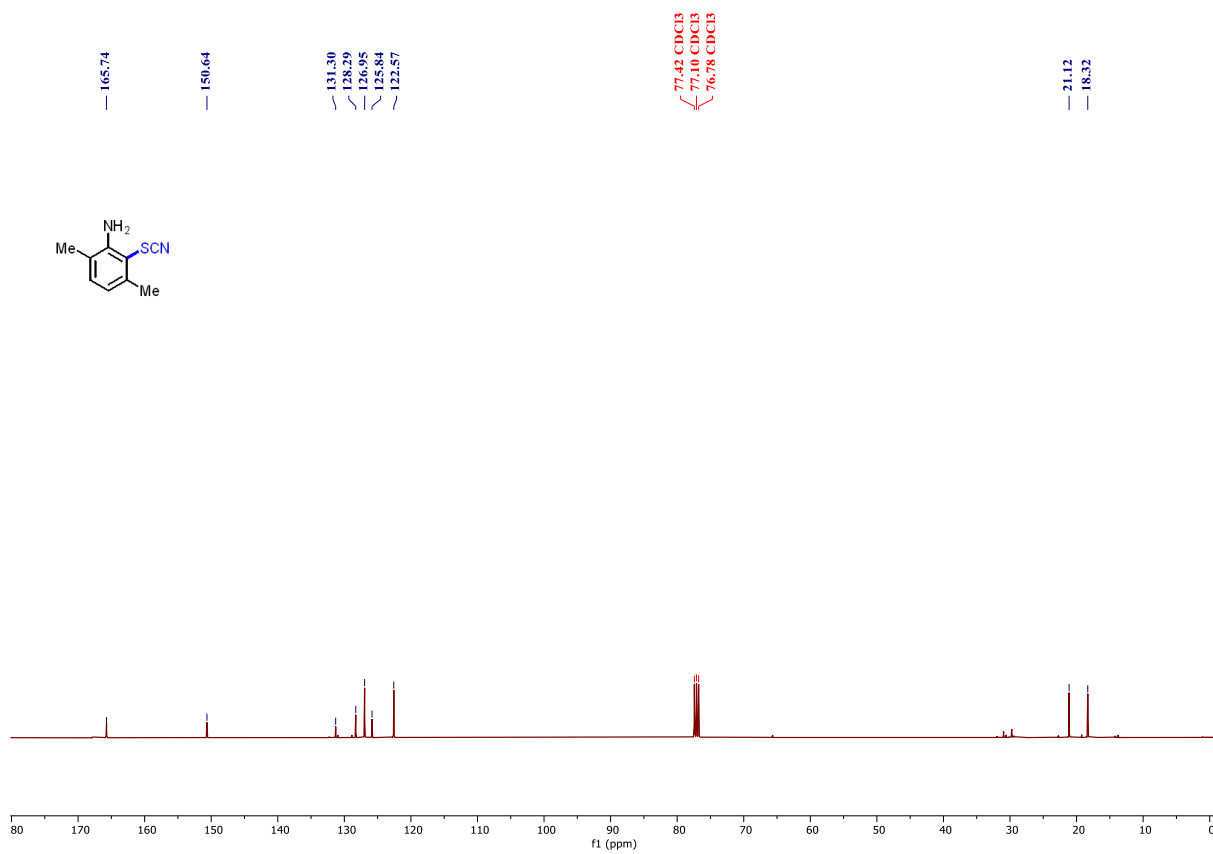
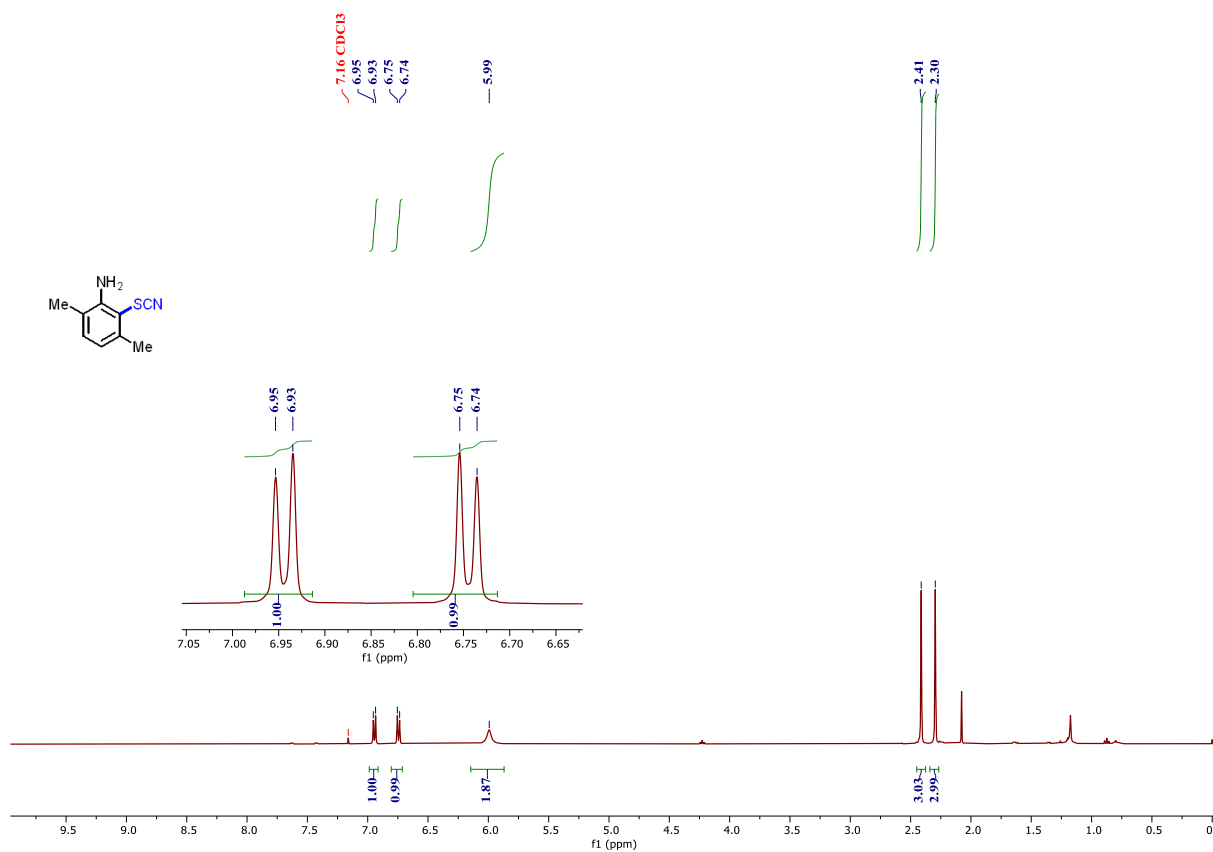
— -123.89  
— -130.74



(Table 2, entry 2s)



(Table 2, entry 2t)



(Table 2, entry 2u)

