

## Supporting Information

For

### **A solvent-free mechanochemical electrophilic C-H thiocyanation of indoles and imidazo[1,2-*a*]pyridines using a cost-effective combination of *N*-chlorosuccinimide-NaSCN, and tandem C-C, C-S bond formation**

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## Experimental Section

### Experimental procedure for the synthesis of NTS<sup>1</sup>

*N*-Thiocyanatosuccinimide (NTS) was synthesized using the reported literature.<sup>1</sup> In dry dichloromethane (4 mL), *N*-bromosuccinimide (1.78 g, 10 mmol, 1.0 equiv) and NaSCN (1.22 g, 15 mmol, 1.5 equiv) were mixed under N<sub>2</sub> atmosphere. The reaction mixture was stirred in the dark at room temperature for 3 h. After completion of the reaction, the reaction mixture was filtered and the filtrate was concentrated under vacuum to afford sufficiently pure NTS as a white solid (1.24 g, 80% yield). The reagent was utilized without further purification.

### Experimental procedure for the synthesis of trifluoromethylthioethers

In a 5 mL stainless steel jar with a 10 mm SS ball in it, **2a** (94 mg, 0.5 mmol) or **2ad** (112 mg, 0.5 mmol), TMSCF<sub>3</sub> (74 μL, 0.5 mmol), Cs<sub>2</sub>CO<sub>3</sub> (325 mg, 1 mmol), and silica gel (60-120 mesh, 300 mg) were taken, the jar was placed in a RETSCH mixer-mill MM400 instrument and a frequency of 30 Hz was set. The reaction slurry was milled at the same frequency for 3 h. After the completion of the reaction, the slurry was charged to a column for purification and was eluted with ethyl acetate-petroleum ether to afford products **5a** (109 mg) or **5c** (121 mg) with 94% or 91% isolated yields, respectively.

### Experimental procedure for the synthesis of 5-sulfenyl tetrazoles

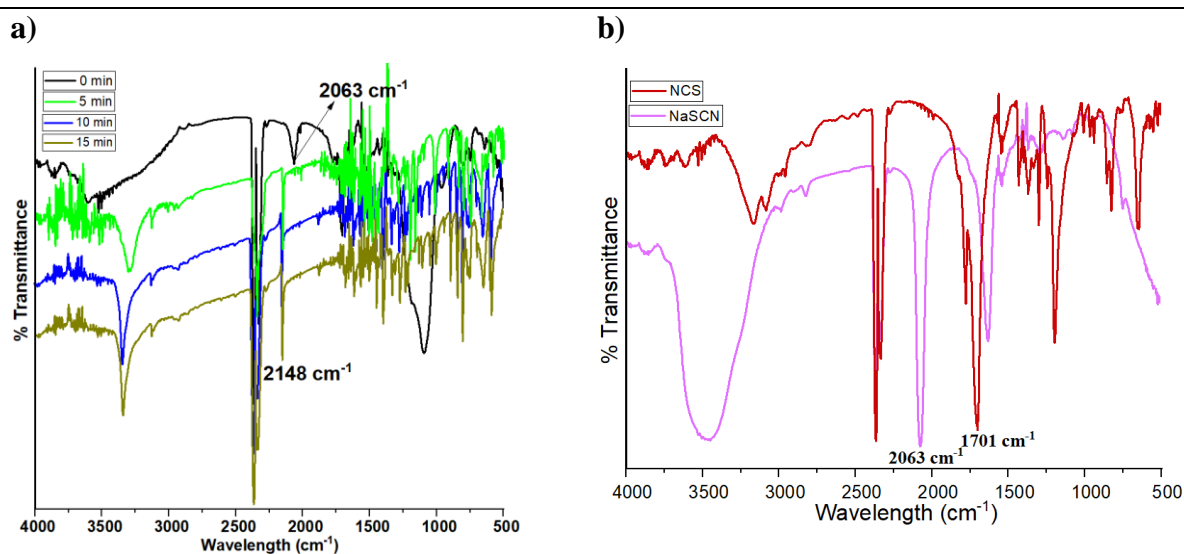
A mixture of **2a** (94 mg, 0.5 mmol) or **2ad** (112 mg, 0.5 mmol), NaN<sub>3</sub> (39 mg, 0.6 mmol), CeCl<sub>3</sub>·7H<sub>2</sub>O (25 mg, 0.1 mmol), and silica gel (60-120 mesh, 300 mg) was taken in a 5 mL stainless steel jar containing a 10 mm SS ball in it. The reaction mixture was milled at a frequency of 30 Hz for 2 h in a RETSCH mixer-mill MM400 instrument. The solid reaction

slurry was charged to the column for purification and a mixture of chloroform-methanol was used as eluent to obtain products **5b** (104 mg) or **5d** (123 mg) with 90% or 92% yields, respectively.

**Table S1.** Optimization of the milling parameters

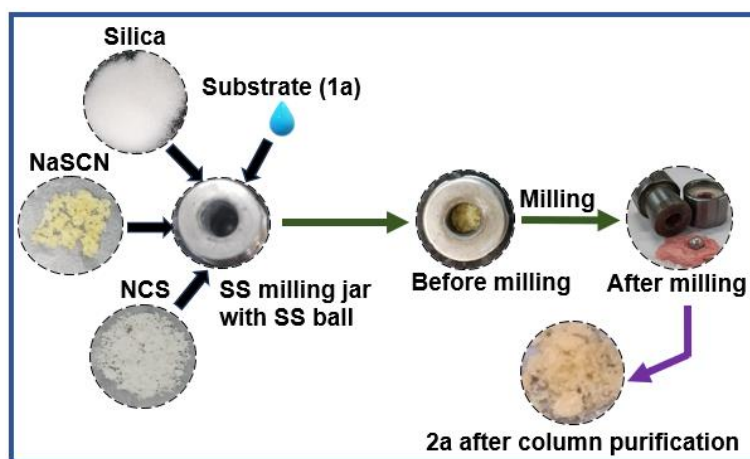
Entry	Jar type	Ball size (no. of balls)	Operating frequency (Hz)	Time (min)	Isolated yield of 2a (%)
1	SS	10 mm (1)	25	30	89
2	SS	<b>10 mm (1)</b>	<b>30</b>	<b>15</b>	<b>95</b>
3	Zirconia	10 mm (1)	30	15	92
4	Teflon	10 mm (1)	30	15	90
5	SS	7 mm (1)	30	15	82 <sup>b</sup>
6	SS	5 mm (2)	30	15	63 <sup>b</sup>

<sup>a</sup>1 mmol of **1a** was milled with 1.1 mmol of NaSCN, 1 mmol of NCS, and 300 mg silica gel (60-120 mesh) in a RETSCH mixer mill (MM 400) using a 5 mL jar. <sup>b</sup>Some amount of unreacted starting material (**1a**) was also recovered.



**Figure S1.** Monitoring of the reaction mixture in solid state by time-scale infrared spectroscopy. The consumption of the peak at  $2063\text{ cm}^{-1}$  just after 5 min indicates the formation

of NTS and the gradual increase of a new peak at  $2148\text{ cm}^{-1}$  indicates the formation of **2a** in solid-state.



**Figure S2.** Images of the reaction mixture before and after the milling reaction.

**Table S2.** Comparison of different thiocyanation reactions with our mechanochemical method

Entry	Method	-SCN source	Media	Catalyst (mol %)/ Oxidant (equiv)	Condition	Yield (%)	E-factor <sup>a</sup>	Eco-score <sup>a</sup>	Cost in USD <sup>b</sup> (per gram)	Ref
<b>Indoles</b>										
1.	Solution phase	NH <sub>4</sub> SCN	Methanol	CeBr <sub>3</sub> (20)/ H <sub>2</sub> O <sub>2</sub> (3.5)	Stirring, rt, 6 h	1-99	14	55	24	2
2.	Solution phase	NH <sub>4</sub> SCN	THF	Rose Bengal (1)	Visible light, rt, 24 h	73-95	31	59	32	3
3.	Solution phase	<i>N</i> -thiocyanato-saccharin	THF	-	Stirring, rt, 6 h	73-98	18	40	13	4
4.	Solution phase	KSCN	DMSO	Cu(OTf) <sub>2</sub> (20)/TMEDA (20)/BF <sub>3</sub> .Et <sub>2</sub> O (2)	Heating, 80 °C, 12 h	62-94	17	36	20	5
5.	Solution phase	KSCN	Ethanol: Water	PdCl <sub>2</sub> (5)/NBS (1.5)	Heating, 90°C, 2 h	68-97	29	35	37 <sup>c</sup>	6

**Imidazo[1,2-*a*]pyridines**

6.	Solution phase	NH <sub>4</sub> SCN	CH <sub>3</sub> CN	Eosin Y (5)	Visible light, rt, 12 h	54-93	18	57	214	7
7.	Electrochemical method	NH <sub>4</sub> SCN	CH <sub>3</sub> CN	I <sub>2</sub> (20)	Stirring, rt, 6 h	66-88	48	47	205	8
8.	<b>Solid phase milling</b>	<b>NaSCN + NCS</b>	<b>Silica gel</b>	-	<b>Mixer-milling, 15 min</b>	<b>71-97</b>	<b>3</b>	<b>86</b>	<b>4.75</b>	<b>Current work</b>

<sup>a</sup>E-factor and Eco-scale score are calculated according to reference 9. <sup>b</sup>The approximate costs for **2a** (or **4a**) are estimated based on the cost of raw materials only, and the work-up and isolation steps are not considered. The standard pack sizes of Sigma-Aldrich or TCI in INR, and converted to USD by a factor 83. <sup>c</sup>Cost calculations are done considering **1w** as the substrate.

**For a typical E-factor calculation**

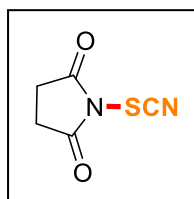
Parameters	Values	Remarks
% Yield	95	Calculated for <b>2a</b>
Wt. of generated waste (mg)	461	
Wt. of end product (mg)	178	
<b>E-factor = Wt. of generated waste/Wt. of end product</b>	<b>3</b>	

**For a typical Ecoscale score calculation**

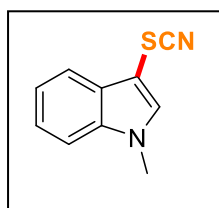
Parameters	Penalty points	Remarks
% Yield = (100-% Yield)/2	2	Calculated for <b>2a</b>
Price of reaction component	0	Inexpensive (<10US\$)
Technical setup	2	Unconventional activation technique (Ball milling)
Temperature/Time	0	Room temperature reaction/<1 h
Workup and purification	10	Classical chromatography (Purification)
<b>Sum of penalty points</b>	<b>14</b>	
<b>Ecoscale score =</b> <b>(100-Sum of penalty points)</b>	<b>86</b>	



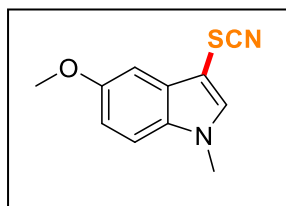
## Spectral Characterization



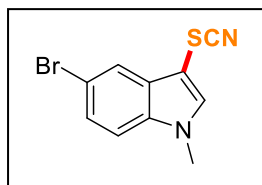
1-Thiocyanatopyrrolidine-2,5-dione (**NTS**).<sup>1,10</sup> Yellow solid, 127 mg (82%); mp. 134-135 °C (lit. mp. 135-136 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 2.73 (s, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 178.04, 126.87, 29.57; HRMS (ESI-TOF): *m/z* calcd for C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>S [M + H]<sup>+</sup>, 157.0072; found, 157.0070.



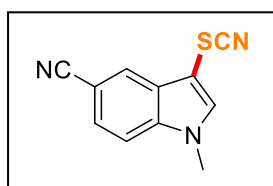
1-Methyl-3-thiocyanato-1*H*-indole (**2a**).<sup>2</sup> Grey solid, 178 mg (95%); mp. 83-84 °C (lit. mp. 84-86 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.78 (d, *J* = 7.4 Hz, 1H), 7.37-7.29 (m, 4H), 3.78 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 137.15, 135.05, 128.45, 123.41, 121.58, 118.91, 111.87, 110.19, 89.83, 33.39; IR (KBr):  $\tilde{\nu}$  2949, 2927, 2148, 1687, 1608, 1519, 1516, 1460, 1338, 1244, 1157 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 189.0486; found, 189.0484.



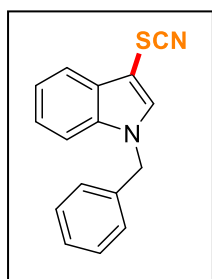
5-Methoxy-1-methyl-3-thiocyanato-1*H*-indole (**2b**).<sup>11</sup> Brown solid, 211 mg (97%); mp. 124-125 °C (lit. mp. 125-126 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.40 (s, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.23 (s, 1H), 7.03 (d, *J* = 9.1 Hz, 1H), 3.98 (s, 3H), 3.82 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 155.70, 135.25, 132.16, 129.25, 114.06, 111.94, 111.18, 99.95, 88.88, 55.82, 33.54; IR (KBr):  $\tilde{\nu}$  3111, 3005, 2951, 2829, 2150, 1624, 1577, 1510, 1489, 1450, 1421, 1352, 1290, 1246, 1220, 1178 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>OS [M + H]<sup>+</sup>, 219.0592; found, 219.0591.



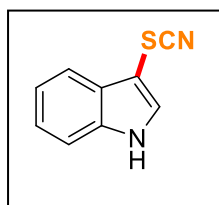
5-Bromo-1-methyl-3-thiocyanato-1*H*-indole (**2c**).<sup>11</sup> White solid, 249 mg (94%); mp. 55-56 °C (lit. mp. 56-57 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.88 (d, *J* = 2.0 Hz, 1H), 7.39-7.37 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 136.12, 135.87, 130.08, 126.52, 121.55, 115.27, 111.78, 111.44, 89.71, 33.65; IR (KBr):  $\tilde{\nu}$  3101, 2920, 2850, 2144, 1658, 1544, 1508, 1462, 1330, 1267, 1242, 1165, 1141 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>10</sub>H<sub>7</sub>BrN<sub>2</sub>S [M + H]<sup>+</sup>, 266.9592 (for <sup>79</sup>Br) and 268.9571 (for <sup>81</sup>Br); found, 266.9590 (for <sup>79</sup>Br) and 268.9589 (for <sup>81</sup>Br).



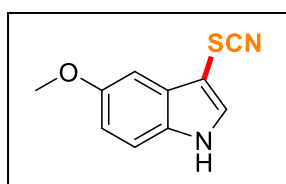
1-Methyl-3-thiocyanato-1*H*-indole-5-carbonitrile (**2d**). White solid, 193 mg (91%); mp. 125-126 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 8.21 (d, *J* = 7.1 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 139.75, 139.10, 128.02, 126.15, 123.96, 120.26, 113.25, 112.38, 104.10, 90.89, 33.96; IR (KBr):  $\tilde{\nu}$  3115, 2956, 2927, 2850, 2216, 2160, 1774, 1691, 1610, 1516, 1473, 1340, 1286, 1247, 1197, 1139 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>11</sub>H<sub>7</sub>N<sub>3</sub>S [M + H]<sup>+</sup>, 214.0439; found, 214.0437.



1-Benzyl-3-thiocyanato-1*H*-indole (**2e**).<sup>3</sup> Pink solid, 256 mg (97%); mp. 85-86 °C (lit. mp. 84-86 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.82 (d, *J* = 8.8 Hz, 1H), 7.42 (s, 1H), 7.36-7.30 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.29 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 136.76, 135.65, 134.28, 129.03, 128.62, 128.25, 127.10, 123.60, 121.78, 119.07, 111.72, 110.68, 90.83, 50.69; IR (KBr):  $\tilde{\nu}$  3118, 3028, 2935, 2150, 1543, 1510, 1496, 1452, 1438, 1386, 1354, 1336, 1253, 1199, 1159 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 265.0799; found, 265.0798.

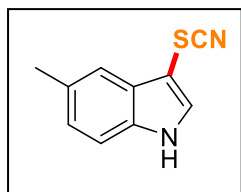


3-Thiocyanato-1*H*-indole (**2f**).<sup>2</sup> Yellow solid, 158 mg (91%); mp. 72-73 °C (lit. mp. 72-74 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.71 (bs, 1H), 7.80-7.75 (m, 1H), 7.48 (s, 1H), 7.43-7.40 (m, 1H), 7.32-7.28 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 136.03, 130.99, 127.69, 123.90, 121.92, 118.77, 112.09, 111.91, 92.29; IR (KBr):  $\tilde{\nu}$  3340, 3294, 2926, 2831, 2158, 1656, 1543, 1508, 1456, 1419, 1338, 1236 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>9</sub>H<sub>6</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 175.0330; found, 175.0333.

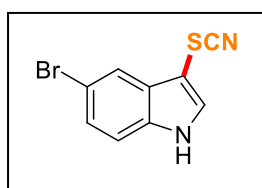


5-Methoxy-3-thiocyanato-1*H*-indole (**2g**).<sup>2</sup> White solid, 194 mg (95%); mp. 119-120 °C (lit. mp. 119-121 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.69 (bs, 1H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4

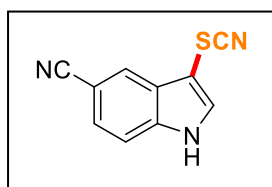
Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 155.76, 131.41, 130.84, 128.51, 114.54, 113.03, 112.01, 99.82, 91.49, 55.85; IR (KBr):  $\tilde{\nu}$  3309, 3136, 2960, 2927, 2152, 1541, 1508, 1489, 1340, 1292, 1203, 1203, 1165, 1014  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{10}\text{H}_8\text{N}_2\text{OS}$   $[\text{M} + \text{H}]^+$ , 205.0436; found, 205.0432.



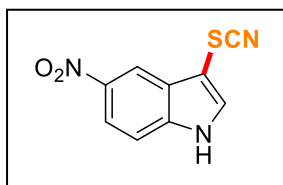
5-Methyl-3-thiocyanato-1H-indole (**2h**).<sup>3</sup> Brown solid, 177 mg (94%); mp. 88-89 °C (lit. mp. 88-90 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.66 (bs, 1H), 7.56 (s, 1H), 7.39 (d,  $J = 3.0$  Hz, 1H), 7.28 (d,  $J = 8.4$  Hz, 1H), 7.11 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.5$  Hz, 1H), 2.49 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 134.31, 131.49, 131.02, 127.88, 125.49, 118.20, 112.23, 111.78, 91.22, 21.50; IR (KBr):  $\tilde{\nu}$  3307, 3118, 2912, 2852, 2150, 1676, 1579, 1489, 1440, 1413, 1336, 1242, 1224  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{10}\text{H}_8\text{N}_2\text{S}$   $[\text{M} + \text{H}]^+$ , 189.0486; found, 189.0482.



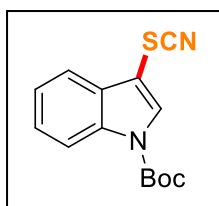
5-Bromo-3-thiocyanato-1H-indole (**2i**).<sup>2</sup> White solid, 223 mg (89%); mp. 127-128 °C (lit. mp. 127-129 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.81 (bs, 1H), 7.90 (s, 1H), 7.49 (d,  $J = 3.0$  Hz, 1H), 7.36 (dd,  $J_1 = 8.7$  Hz,  $J_2 = 2.0$  Hz, 1H), 7.27 (d,  $J = 8.6$  Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 134.69, 132.10, 129.39, 127.04, 121.45, 115.45, 113.60, 111.55, 92.10; IR (KBr):  $\tilde{\nu}$  3334, 3111, 2916, 2150, 1654, 1544, 1508, 1460, 1332, 1296, 1107  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_9\text{H}_5\text{BrN}_2\text{S}$   $[\text{M} + \text{H}]^+$ , 252.9435 (for  $^{79}\text{Br}$ ) and 254.9415 (for  $^{81}\text{Br}$ ); found, 252.9433 (for  $^{79}\text{Br}$ ) and 254.9412 (for  $^{81}\text{Br}$ ).



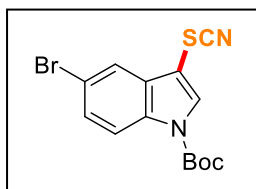
3-Thiocyanato-1H-indole-5-carbonitrile (**2j**).<sup>12</sup> White solid, 171 mg (86%); mp. 215-217 °C (lit. mp. 217-218 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 8.22 (s, 1H), 8.20 (d,  $J = 2.1$  Hz, 1H), 7.71 (d,  $J = 8.5$  Hz, 1H), 7.64 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.7$  Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  (ppm) 138.50, 136.21, 127.73, 126.22, 120.36, 114.68, 112.49, 103.94, 92.0; IR (KBr):  $\tilde{\nu}$  3280, 3109, 2927, 2852, 2225, 2154, 1689, 1618, 1544, 1508, 1467, 1427, 1340, 1247, 1159  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{10}\text{H}_5\text{N}_3\text{S}$   $[\text{M} + \text{H}]^+$ , 200.0282; found, 200.0276.



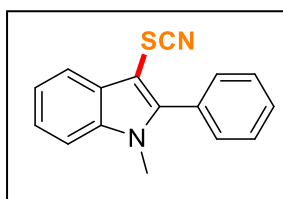
5-Nitro-3-thiocyanato-1*H*-indole (**2k**).<sup>2</sup> Yellow solid, 175 mg (80%); mp. 126-127 °C (lit. mp. 126-128 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.60 (s, 1H), 8.16-8.09 (m, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 7.37-7.33 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 138.77, 137.72, 127.29, 123.98, 118.71, 117.78, 111.80, 111.01, 105.18; IR (KBr):  $\tilde{\nu}$  3284, 3116, 2931, 2859, 2156, 1688, 1621, 1550, 1512, 1468, 1429, 1365, 1247, 1145 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>9</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>S [M + H]<sup>+</sup>, 220.0181; found, 220.0178.



*tert*-Butyl 3-thiocyanato-1*H*-indole-1-carboxylate (**2l**).<sup>2</sup> Colourless liquid, 233 mg (85%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.18 (d, *J* = 8.1 Hz, 1H), 7.94 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.44-7.37 (m, 2H), 1.67 (s, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 148.50, 135.42, 131.72, 129.10, 126.06, 124.08, 119.14, 115.71, 110.12, 99.16, 85.47, 28.11; IR (KBr):  $\tilde{\nu}$  2983, 2926, 2851, 2157, 1749, 1532, 1428, 1365, 1221, 1147 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S [M + H]<sup>+</sup>, 275.0854; found, 275.0848.

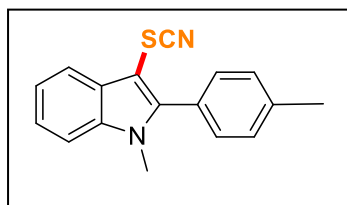


*tert*-Butyl 5-bromo-3-thiocyanato-1*H*-indole-1-carboxylate (**2m**). White solid, 252 mg (72%); mp. 131-132 °C (lit. mp. 131-133 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.05 (d, *J* = 9.0 Hz, 1H), 7.93 (s, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.51 (dd, *J*<sub>1</sub> = 8.9 Hz, *J*<sub>2</sub> = 2.2 Hz, 1H), 1.66 (s, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 144.07, 134.17, 132.86, 130.79, 129.12, 121.86, 117.68, 117.20, 109.73, 98.44, 86.03, 28.06; IR (KBr):  $\tilde{\nu}$  3136, 3003, 2972, 2935, 2158, 1750, 1527, 1446, 1352, 1260, 1220, 1147, 1068 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>14</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>2</sub>S [M + H]<sup>+</sup>, 352.9959 (for <sup>79</sup>Br) and 354.9939 (for <sup>81</sup>Br); found, 352.9957 (for <sup>79</sup>Br) and 354.9937 (for <sup>81</sup>Br).

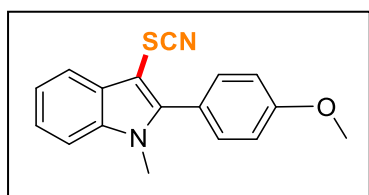


1-Methyl-2-phenyl-3-thiocyanato-1*H*-indole (**2n**).<sup>13</sup> White solid, 222 mg (84%); mp. 79-80 °C (lit. mp. 83-84 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.85 (d, *J* = 7.4 Hz, 1H), 7.59-7.53 (m, 3H), 7.49-7.48 (m, 2H), 7.42 (dd, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 1.8 Hz, 1H), 7.39-7.34 (m, 2H), 3.69 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 146.43, 137.18, 130.63, 129.60,

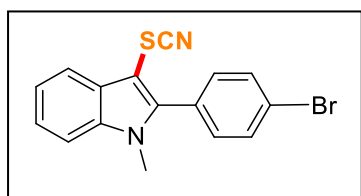
129.11, 128.75, 128.47, 123.58, 121.97, 118.93, 112.18, 110.32, 89.48, 31.75; IR (KBr):  $\tilde{\nu}$  3047, 2974, 2936, 2154, 1600, 1533, 1446, 1337, 1255, 1228, 1152, 1071  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}$   $[\text{M} + \text{H}]^+$ , 265.0799; found, 265.0800.



1-Methyl-3-thiocyanato-2-(*p*-tolyl)-1*H*-indole (**2o**).<sup>14</sup> Brown solid, 245 mg (88%); mp. 81-83 °C (lit. mp. 83-85 °C); <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.82 (d,  $J = 7.1$  Hz, 1H), 7.40 (d,  $J = 7.3$  Hz, 2H), 7.38-7.36 (m, 3H), 7.34 (d,  $J = 7.4$  Hz, 2H), 3.68 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 146.68, 139.78, 137.19, 130.53, 129.50, 128.55, 126.15, 123.48, 121.93, 118.91, 112.28, 110.27, 89.29, 31.73, 21.50; IR (KBr):  $\tilde{\nu}$  3024, 2978, 2914, 2152, 1604, 1537, 1462, 1337, 1265, 1237, 1157, 1079  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}$   $[\text{M} + \text{H}]^+$ , 279.0956; found, 279.0956.

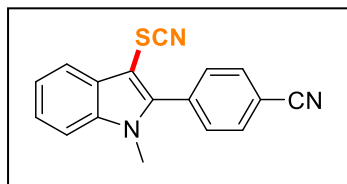


2-(4-Methoxyphenyl)-1-methyl-3-thiocyanato-1*H*-indole (**2p**).<sup>14</sup> Brown solid, 267 mg (91%); mp. 129-131 °C (lit. mp. 133-135 °C); <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.79 (d,  $J = 7.4$  Hz, 1H), 7.42 (d,  $J = 8.6$  Hz, 2H), 7.37-7.35 (m, 3H), 7.10 (d,  $J = 8.7$  Hz, 2H), 3.90 (s, 3H), 3.76 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 160.49, 137.10, 135.02, 131.91, 128.44, 123.34, 121.51, 121.05, 118.82, 114.19, 112.31, 110.17, 89.70, 55.36, 31.63; IR (KBr):  $\tilde{\nu}$  3052, 2981, 2937, 2147, 1610, 1542, 1497, 1339, 1245, 1162, 1085  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{OS}$   $[\text{M} + \text{H}]^+$ , 295.0905; found, 295.0903.



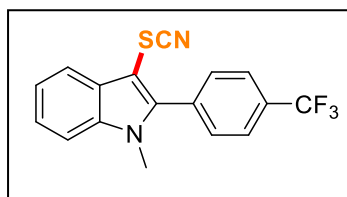
2-(4-Bromophenyl)-1-methyl-3-thiocyanato-1*H*-indole (**2q**). White solid, 279 mg (82%); mp. 52-54 °C; <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.83 (d,  $J = 7.3$  Hz, 1H), 7.71 (d,  $J = 8.4$  Hz, 2H), 7.42-7.38 (m, 3H), 7.35 (d,  $J = 8.5$  Hz, 2H), 3.68 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 145.10, 137.27, 132.18, 132.14, 128.44, 128.02, 124.31, 123.91, 122.21, 119.07, 111.93, 110.37, 90.01, 31.80; IR (KBr):  $\tilde{\nu}$  3049, 2995, 2947, 2156, 1630, 1528, 1467, 1322, 1247, 1167, 1075  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for

$C_{16}H_{11}BrN_2S$   $[M + H]^+$ , 342.9905 (for  $^{79}Br$ ) and 344.9884 (for  $^{81}Br$ ); found, 342.9902 (for  $^{79}Br$ ) and 344.9881 (for  $^{81}Br$ ).



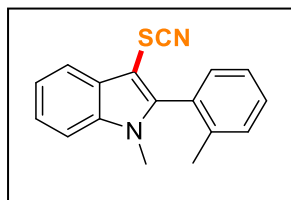
4-(1-Methyl-3-thiocyanato-1*H*-indol-2-yl)benzonitrile (**2r**).

White solid, 231 mg (80%); mp. 99-100 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.81 (d,  $J = 8.4$  Hz, 2H), 7.69-7.65 (m, 3H), 7.37 (d,  $J = 7.4$  Hz, 2H), 7.27-7.26 (m, 1H), 3.69 (s, 3H);  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 136.81, 134.46, 133.92, 132.27, 131.08, 125.54, 123.87, 120.91, 118.74, 118.57, 112.08, 109.94, 105.11, 31.77; IR (KBr):  $\tilde{\nu}$  3070, 2997, 2939, 2223, 2151, 1602, 1531, 1467, 1331, 1265, 1169, 1065  $cm^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $C_{17}H_{11}N_3S$   $[M + H]^+$ , 290.0752; found, 289.0749.



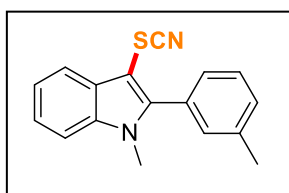
1-Methyl-3-thiocyanato-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**2s**).

Yellow solid, 193 mg (78%); mp. 130-132 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.91-7.86 (m, 3H), 7.67 (d,  $J = 8.0$  Hz, 2H), 7.50-7.40 (m, 3H), 3.75 (s, 3H);  $^{19}F$  NMR (470 MHz,  $CDCl_3$ ):  $\delta$  (ppm) -63.82 (s);  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 144.52, 137.34, 132.81, 131.62 (q,  $J = 32.5$  Hz), 131.13, 128.37, 125.79 (q,  $J = 3.8$  Hz), 124.86, 124.24 (q,  $J = 227.5$  Hz), 122.57, 119.15, 111.76, 110.45, 90.50, 31.90; IR (KBr):  $\tilde{\nu}$  3112, 2959, 2915, 2151, 1621, 1544, 1479, 1327, 1235, 1242, 1162, 1144  $cm^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $C_{17}H_{11}F_3N_2S$   $[M + H]^+$ , 333.0673; found, 333.0672.

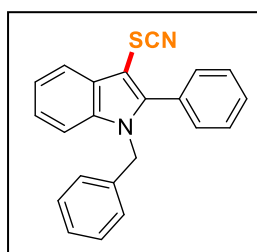


1-Methyl-3-thiocyanato-2-(*o*-tolyl)-1*H*-indole (**2t**).

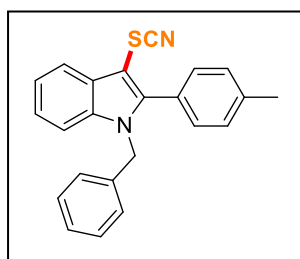
Brown solid, 230 mg (83%); mp. 65-67 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.84 (d,  $J = 7.6$  Hz, 1H), 7.48-7.34 (m, 6H), 7.27 (d,  $J = 8.1$  Hz, 1H), 3.53 (s, 3H), 2.13 (s, 3H);  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 146.50, 138.34, 136.98, 130.98, 130.44, 130.14, 128.90, 128.34, 126.10, 123.35, 121.88, 118.88, 111.78, 110.25, 89.66, 31.11, 19.72; IR (KBr):  $\tilde{\nu}$  3022, 2975, 2912, 2157, 1607, 1541, 1469, 1328, 1261, 1236, 1169, 1065  $cm^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $C_{17}H_{14}N_2S$   $[M + H]^+$ , 279.0956; found, 279.0953.



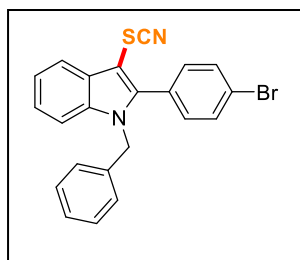
1-Methyl-3-thiocyanato-2-(*m*-tolyl)-1*H*-indole (**2u**). Yellow solid, 225 mg (81%); mp. 69-71 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.83 (d, *J* = 7.1 Hz, 1H), 7.47-7.34 (m, 6H), 7.26 (d, *J* = 8.3 Hz, 1H), 3.68 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 146.70, 138.56, 137.18, 131.19, 130.41, 129.07, 128.63, 128.51, 127.74, 123.51, 121.94, 118.93, 112.23, 110.28, 89.38, 31.74, 21.50; IR (KBr):  $\tilde{\nu}$  3020, 2978, 2915, 2152, 1609, 1544, 1472, 1334, 1264, 1239, 1170, 1062 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 279.0956; found, 279.0954.



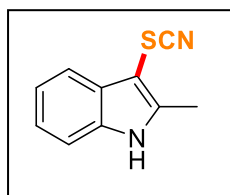
1-Benzyl-2-phenyl-3-thiocyanato-1*H*-indole (**2v**). Brown solid, 292 mg (86%); mp. 105-107 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.91 (d, *J* = 7.8 Hz, 1H), 7.56-7.50 (m, 3H), 7.45-7.44 (m, 2H), 7.39-7.36 (m, 1H), 7.32-7.27 (m, 5H), 6.97 (d, *J* = 7.8 Hz, 2H), 5.34 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 146.69, 136.77, 136.71, 130.53, 129.77, 129.06, 128.91, 128.79, 128.69, 127.67, 125.99, 123.84, 122.18, 119.11, 112.10, 111.29, 90.56, 48.54; IR (KBr):  $\tilde{\nu}$  3041, 3014, 2941, 2153, 1601, 1547, 1462, 1344, 1268, 1154, 1052 cm<sup>-1</sup>; IR (KBr):  $\tilde{\nu}$  3047, 3018, 2149, 1602, 1547, 1465, 1347, 1268, 1156, 1065 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 341.1112; found, 341.1109.



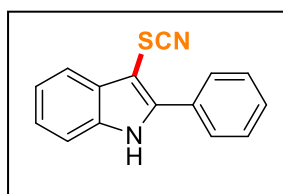
1-Benzyl-3-thiocyanato-2-(*p*-tolyl)-1*H*-indole (**2w**). Brown solid, 315 mg (89%); mp. 139-140 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.81 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.23-7.18 (m, 8H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.24 (s, 2H), 2.38 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 146.92, 139.33, 136.80, 136.73, 130.39, 129.52, 128.73, 127.62, 126.03, 125.97, 124.79, 123.70, 122.11, 119.03, 112.18, 111.27, 90.28, 48.49, 21.47; IR (KBr):  $\tilde{\nu}$  3027, 2921, 2151, 1601, 1562, 1460, 1342, 1258, 1161, 1057 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 355.1269; found, 355.1266.



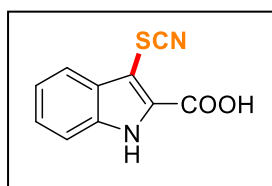
1-Benzyl-2-(4-bromophenyl)-3-thiocyanato-1*H*-indole (**2x**). Brown solid, 343 mg (82%); mp. 120-122 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.86 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.36-7.32 (m, 1H), 7.30-7.26 (m, 7H), 6.90 (d, *J* = 8.1 Hz, 2H), 5.28 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 145.33, 136.90, 136.51, 132.13, 132.04, 129.64, 129.02, 128.80, 127.94, 127.82, 125.87, 124.47, 124.16, 122.39, 119.21, 111.80, 111.27, 48.55; IR (KBr):  $\tilde{\nu}$  3028, 2917, 2153, 1602, 1564, 1463, 1343, 1252, 1167, 1059 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>22</sub>H<sub>15</sub>BrN<sub>2</sub>S [M + H]<sup>+</sup>, 419.0218 (for <sup>79</sup>Br) and 421.0197 (for <sup>81</sup>Br); found, 419.0217 (for <sup>79</sup>Br) and 421.0196 (for <sup>81</sup>Br).



2-Methyl-3-thiocyanato-1*H*-indole (**2y**).<sup>2</sup> Brown solid, 177 mg (94%); mp. 101-103 °C (lit. mp. 102-104 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.56 (bs, 1H), 7.70 (dd, *J*<sub>1</sub> = 7.0 Hz, *J*<sub>2</sub> = 1.9 Hz, 1H), 7.34 (dd, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 1.9 Hz, 1H), 7.29-7.24 (m, 2H), 2.56 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 141.96, 135.10, 128.72, 123.01, 121.59, 118.12, 111.96, 111.18, 89.09, 12.09; IR (KBr):  $\tilde{\nu}$  3327, 3062, 2920, 2852, 2146, 1585, 1543, 1456, 1413, 1298, 1234 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 189.0486; found, 189.0481.



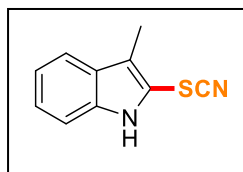
2-Phenyl-3-thiocyanato-1*H*-indole (**2z**).<sup>14</sup> Yellow solid, 202 mg (81%); mp. 70-71 °C (lit. mp. 70-71 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.79 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.54-7.46 (m, 3H), 7.44-7.39 (m, 1H), 7.33-7.29 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 143.13, 135.44, 130.03, 129.71, 129.59, 129.11, 128.63, 124.08, 122.11, 119.05, 111.94, 111.65, 89.09; IR (KBr):  $\tilde{\nu}$  3443, 3048, 2922, 2857, 2155, 1641, 1543, 1456, 1292, 1239 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 251.0643; found, 251.0641.



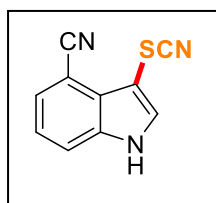
3-Thiocyanato-1*H*-indole-2-carboxylic acid (**2aa**).<sup>2</sup> White solid, 166 mg (76%); mp. 190-194 °C (lit. mp. 192-196 °C); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 12.66 (bs, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 168.1, 145.3, 136.9, 136.5, 132.1, 132.0, 129.6, 129.0, 128.8, 127.9, 127.8, 125.9, 124.5, 124.2, 122.4, 119.2, 111.8, 111.3, 48.6.



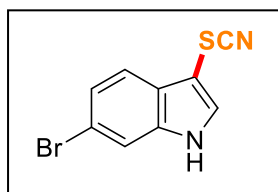
NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 161.77, 136.37, 130.52, 127.93, 126.18, 122.37, 119.82, 114.09, 111.95, 96.45; IR (KBr):  $\tilde{\nu}$  3300, 2953, 2927, 2856, 2164, 1654, 1525, 1508, 1460, 1431, 1334, 1255 cm<sup>-1</sup>; HRMS (ESI-TOF):  $m/z$  calcd for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S [M + H]<sup>+</sup>, 219.0228; found, 219.0224.



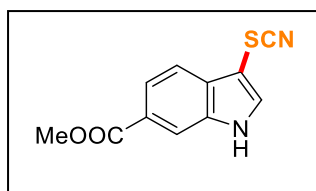
3-Methyl-2-thiocyanato-1*H*-indole (**2ab**).<sup>4</sup> Brown solid, 171 mg (91%); mp. 84-86 °C (lit. mp. 86-87 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.24 (bs, 1H), 7.56 (d,  $J$  = 8.1 Hz, 1H), 7.35-7.28 (m, 2H), 7.16 (t,  $J$  = 8.1 Hz, 1H), 2.44 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 137.53, 127.91, 125.13, 122.28, 120.51, 119.88, 111.28, 109.35, 109.26, 9.47; IR (KBr):  $\tilde{\nu}$  3396, 2954, 2924, 2848, 2152, 1560, 1508, 1438, 1342, 1273 cm<sup>-1</sup>; HRMS (ESI-TOF):  $m/z$  calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 189.0486; found, 189.0481.



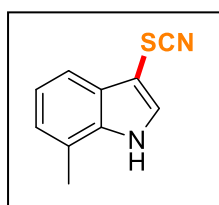
3-Thiocyanato-1*H*-indole-4-carbonitrile (**2ac**).<sup>5</sup> Yellow solid, 175 mg (88%); mp. 176-177 °C (lit. mp. 177-178 °C); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 11.07 (s, 1H), 8.28 (s, 1H), 7.88 (d,  $J$  = 8.5 Hz, 1H), 7.74 (d,  $J$  = 8.3 Hz, 1H), 7.41 (t,  $J$  = 8.5 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 137.62, 137.17, 128.55, 126.69, 123.42, 118.86, 117.93, 113.09, 101.12, 90.38; IR (KBr):  $\tilde{\nu}$  3301, 3112, 2959, 2915, 2220, 1766, 1714, 1540, 1479, 1346, 1284, 1244, 1194, 1140 cm<sup>-1</sup>; HRMS (ESI-TOF):  $m/z$  calcd for C<sub>10</sub>H<sub>5</sub>N<sub>3</sub>S [M + H]<sup>+</sup>, 200.0282; found, 200.0280.



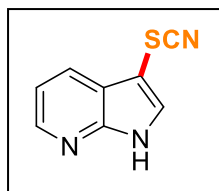
6-Bromo-3-thiocyanato-1*H*-indole (**2ad**).<sup>3</sup> White solid, 211 mg (84%); mp. 138-141 °C (lit. mp. 139-142 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.70 (bs, 1H), 7.63 (d,  $J$  = 8.4 Hz, 1H), 7.57 (s, 1H), 7.48 (d,  $J$  = 2.9 Hz, 1H), 7.38 (dd,  $J_1$  = 8.6 Hz,  $J_2$  = 1.9 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 136.76, 131.46, 126.59, 125.40, 120.10, 117.62, 115.07, 111.52, 93.08; IR (KBr):  $\tilde{\nu}$  3342, 3111, 2146, 1614, 1564, 1500, 1444, 1392, 1328, 1269, 1211 cm<sup>-1</sup>; HRMS (ESI-TOF):  $m/z$  calcd for C<sub>9</sub>H<sub>5</sub>BrN<sub>2</sub>S [M + H]<sup>+</sup>, 252.9435 (for <sup>79</sup>Br) and 254.9415 (for <sup>81</sup>Br); found, 252.9432 (for <sup>79</sup>Br) and 254.9412 (for <sup>81</sup>Br).



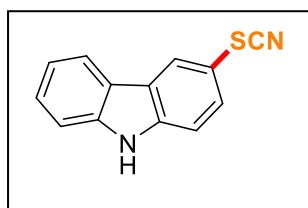
Methyl 3-thiocyanato-1*H*-indole-6-carboxylate (**2ae**).<sup>13</sup> White solid, 188 mg (81%); mp. 200-202 °C (lit. mp. 202-204 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.95 (bs, 1H), 8.20 (s, 1H), 7.98 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 3.1 Hz, 1H), 3.95 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 167.44, 135.46, 133.73, 131.26, 125.97, 122.94, 118.71, 114.41, 111.22, 95.53, 52.30; IR (KBr):  $\tilde{\nu}$  3302, 3147, 2924, 2854, 2150, 1693, 1570, 1508, 1490, 1435, 1406, 1319, 1236, 1207, 1114, 1082 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S [M + H]<sup>+</sup>, 233.0385; found, 233.0369.



7-Methyl-3-thiocyanato-1*H*-indole (**2af**).<sup>2</sup> Brown solid, 165 mg (88%); mp. 157-159 °C (lit. mp. 159-161 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.67 (bs, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 2.9 Hz, 1H), 7.30-7.24 (m, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 2.51 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 135.62, 130.61, 127.33, 124.41, 122.10, 121.36, 116.43, 111.94, 92.71, 16.35; IR (KBr):  $\tilde{\nu}$  3317, 3101, 2926, 2856, 2156, 1498, 1420, 1126 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>S [M + H]<sup>+</sup>, 189.0486; found, 189.0484.

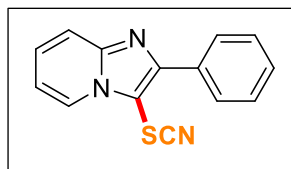


3-Thiocyanato-1*H*-pyrrolo[2,3-*b*]pyridine (**2ag**).<sup>13</sup> White solid, 124 mg (71%); mp. 197-199 °C (lit. mp. 203-206 °C); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 12.59 (bs, 1H), 8.40 (d, *J* = 4.8 Hz, 1H), 8.17 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.31 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 3.4 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 148.83, 144.98, 134.46, 126.97, 120.30, 117.83, 112.61, 89.50; IR (KBr):  $\tilde{\nu}$  3319, 3108, 2924, 2861, 2159, 1603, 1586, 1508, 1499, 1433, 1345, 1281, 1122 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>8</sub>H<sub>5</sub>N<sub>3</sub>S [M + H]<sup>+</sup>, 176.0282; found, 176.0285.

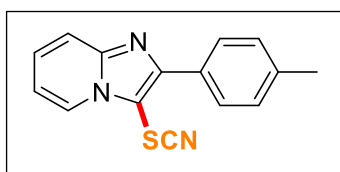


3-Thiocyanato-9*H*-carbazole (**2ah**).<sup>15</sup> Yellow solid, 208 mg (93%); mp. 88-89 °C (lit. mp. 89-90 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.32 (bs, 1H), 8.23 (d, *J* = 2.1 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.53 (dd, *J*<sub>1</sub> = 8.5 Hz, *J*<sub>2</sub> = 2.3 Hz, 1H), 7.48-7.39 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 140.18, 139.90, 129.63, 127.12, 125.29, 124.83, 122.15, 120.62, 120.44, 112.59, 112.28, 112.17, 111.04; IR (KBr):  $\tilde{\nu}$  3417,

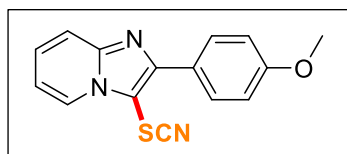
3082, 2924, 2854, 2148, 1595, 1448, 1317, 1276, 1242, 1197  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{S}$   $[\text{M} + \text{H}]^+$ , 225.0486; found, 225.0481.



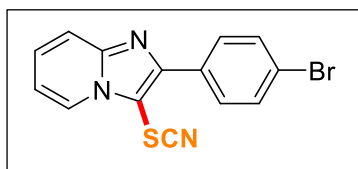
2-Phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4a**).<sup>16</sup> Red solid, 111 mg (88%); mp. 108-110 °C (lit. mp. 110-112 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.13 (t,  $J = 7.8$  Hz, 3H), 7.65 (d,  $J = 9.2$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 2H), 7.38 (t,  $J = 7.4$  Hz, 1H), 7.26 (d,  $J = 7.8$  Hz, 1H), 6.94 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 143.77, 139.86, 132.55, 128.58, 128.29, 127.53, 124.9, 122.73, 117.72, 112.95, 105.74; IR (KBr): 3076, 2221, 1654, 1463, 1346, 1240  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{14}\text{H}_9\text{N}_3\text{S}$   $[\text{M} + \text{H}]^+$ , 253.0595; found, 253.0592.



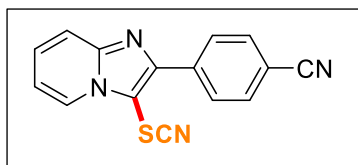
3-Thiocyanato-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (**4b**).<sup>16</sup> Red solid, 113 mg (85%); mp. 109-111 °C (lit. mp. 110-112 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.56 (d,  $J = 7.2$  Hz, 1H), 8.14 (d,  $J = 8.1$  Hz, 2H), 7.88 (d,  $J = 9.0$  Hz, 1H), 7.76 (d,  $J = 9.0$  Hz, 1H), 7.58 (t,  $J = 7.2$  Hz, 1H), 7.46 (d,  $J = 8.1$  Hz, 2H), 2.53 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 143.65, 138.21, 129.30, 129.09, 128.70, 127.93, 127.40, 124.81, 122.65, 117.56, 112.87, 108.16, 21.36; IR (KBr): 3061, 2154, 1634, 1523, 1464, 1340, 1120  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{N}_3\text{S}$   $[\text{M} + \text{H}]^+$ , 266.0752; found, 266.0751.



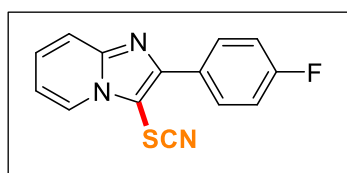
2-(4-Methoxyphenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4c**).<sup>16</sup> White solid, 122 mg (87%); mp. 101-103 °C (lit. mp. 102-104 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.10 (d,  $J = 9.0$  Hz, 3H), 7.65 (d,  $J = 9.0$  Hz, 1H), 7.29-7.24 (m, 1H), 7.04 (d,  $J = 8.9$  Hz, 2H), 6.94 (t,  $J = 7.0$  Hz, 1H), 3.89 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 159.70, 152.72, 143.64, 139.73, 128.82, 125.10, 124.71, 122.59, 117.42, 114.01, 112.77, 104.83, 55.31; IR (KBr): 3081, 2130, 1627, 1459, 1365, 1279, 1153, 1029  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{N}_3\text{OS}$   $[\text{M} + \text{H}]^+$ , 282.0701; found, 282.0700.



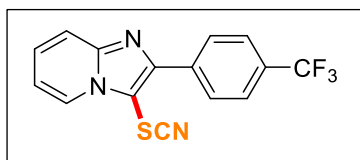
2-(4-Bromophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4d**).<sup>16</sup> Yellow solid, 129 mg (78%); mp. 175-176 °C (lit. mp. 175-177 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.42 (d, *J* = 7.0 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 151.90, 147.99, 131.99, 130.91, 130.24, 128.26, 124.42, 124.02, 118.34, 114.63, 107.78, 94.82; IR (KBr): 3018, 2142, 1603, 1466, 1414, 1298, 1231, 1164, 1106, 1048 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>14</sub>H<sub>8</sub>BrN<sub>3</sub>S [M + H]<sup>+</sup>, 329.9701; found, 329.9697.



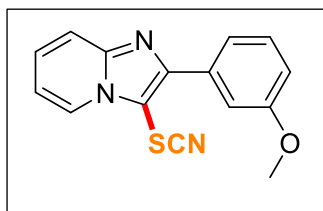
4-(3-Thiocyanatoimidazo[1,2-*a*]pyridine-2-yl)benzonitrile (**4e**).<sup>7</sup> White solid, 123 mg (91%); mp. 141-144 °C (lit. mp. 142-144 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.46 (d, *J* = 6.9 Hz, 1H), 8.19 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 3H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 177.74, 150.61, 148.04, 136.28, 132.50, 129.24, 128.67, 124.45, 118.53, 115.08, 112.93, 107.39, 95.98; IR (KBr): 3076, 2221, 1754, 1654, 1463, 1325, 1270 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>15</sub>H<sub>8</sub>N<sub>4</sub>S [M + H]<sup>+</sup>, 277.0548; found, 277.0545.



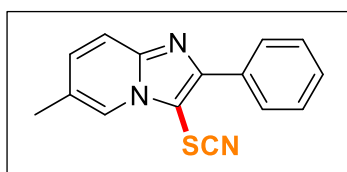
2-(4-Fluorophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4f**).<sup>7</sup> White solid, 120 mg (89%); mp. 101-103 °C (lit. mp. 102-104 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.42 (d, *J* = 6.5 Hz, 1H), 8.04-8.02 (m, 2H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.50 (m, *J* = 7.0 Hz, 1H), 7.19 (t, *J* = 8.8 Hz, 2H), 7.11 (t, *J* = 9.4 Hz, 1H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ (ppm) -111.06 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 163.50 (d, *J* = 249.5 Hz), 152.10, 147.91, 130.66 (d, *J* = 8.2 Hz), 128.14 (d, *J* = 3.8 Hz), 124.38, 118.21, 115.84 (d, *J* = 21.5 Hz), 114.49, 107.94, 94.49; IR (KBr): 3061, 2143, 1634, 1464, 1340, 1288, 1192 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>14</sub>H<sub>8</sub>FN<sub>3</sub>S [M + H]<sup>+</sup>, 270.0501; found, 270.0501.



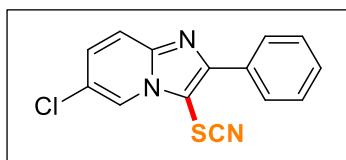
3-Thiocyanato-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (**4g**).<sup>8</sup> White solid, 116 mg (73%); mp. 145-147 °C (lit. mp. 146-148 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.44 (d, *J* = 7.5 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 3H), 7.48 (t, *J* = 8.9 Hz, 1H), 7.14 (t, *J* = 3.5 Hz, 1H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ (ppm) -62.58 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 151.32, 148.03, 135.44, 131.27 (q, *J* = 32.5 Hz), 129.03, 128.40, 125.70 (q, *J* = 3.8 Hz), 125.07 (q, *J* = 287.5 Hz), 124.44, 118.14, 114.84, 107.61, 95.60; IR (KBr): 2358, 2152, 1622, 1480, 1414, 1326, 1231, 1164, 1106, 1048 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>15</sub>H<sub>8</sub>F<sub>3</sub>N<sub>3</sub>S [M + H]<sup>+</sup>, 320.0469; found, 320.0467.



2-(3-Methoxyphenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4h**). White solid, 116 mg (83%); mp. 100-102 °C; (lit. mp. 102-104 °C); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 8.46 (d, *J* = 6.9 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 (s, 1H), 7.45 (t, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 6.9 Hz, 1H), 7.01 (dd, *J*<sub>1</sub> = 8.3 Hz, *J*<sub>2</sub> = 2.9 Hz, 1H), 3.84 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 172.33, 159.94, 143.08, 137.87, 133.30, 130.41, 127.26, 124.28, 119.72, 117.06, 114.74, 114.54, 112.80, 105.98, 55.64; IR (KBr): 3072, 2130, 1627, 1460, 1260, 1211, 1030 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>OS [M + H]<sup>+</sup>, 282.0701; found, 282.0702.



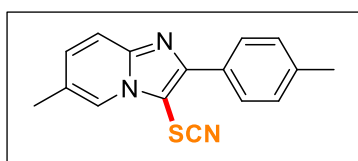
6-Methyl-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4i**).<sup>8</sup> White solid, 118 mg (89%); mp. 151-153 °C (lit. mp. 152-154 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.25 (s, 1H), 8.00 (d, *J* = 9.6 Hz, 2H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.54-7.47 (m, 3H), 2.49 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 151.79, 146.10, 132.07, 130.97, 129.78, 128.89, 128.87, 125.40, 122.35, 117.20, 107.96, 94.99, 18.53; IR (KBr): 2949, 2154, 1640, 1374, 1230, 1110 cm<sup>-1</sup>. HRMS (ESI-TOF): *m/z* calcd for C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>S [M + H]<sup>+</sup>, 266.0752; found, 266.0756.



6-Chloro-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4j**).

White solid, 108 mg (76%); mp. 180-183 °C (lit. mp. 183-184 °C);

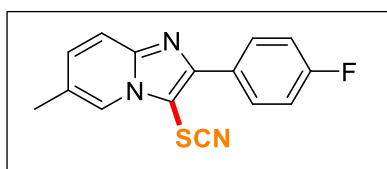
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.15 (s, 1H), 7.91 (d,  $J = 7.0$  Hz, 2H), 7.81 (s, 1H), 7.55 (d,  $J = 9.5$  Hz, 1H), 7.42 (t,  $J = 7.5$  Hz, 2H), 7.33 (t,  $J = 7.5$  Hz, 1H), 7.12 (dd,  $J_1 = 2.0$  Hz,  $J_2 = 10.0$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 139.32, 136.05, 130.95, 127.74, 124.78, 123.92, 121.94, 118.86, 118.0, 112.05, 111.71, 92.52; IR (KBr): 3018, 2156, 1519, 1493, 1466, 1443  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{14}\text{H}_8\text{ClN}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ , 286.0206; found, 286.0205.



6-Methyl-3-thiocyanato-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (**4k**).

White solid, 128 mg (92%); mp. 162-164 °C (lit. mp. 164-165

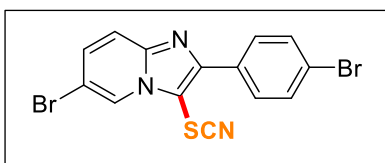
°C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.04 (d,  $J = 5.8$  Hz, 2H), 7.90 (s, 1H), 7.55 (d,  $J = 9.1$  Hz, 1H), 7.30 (t,  $J = 8.1$  Hz, 2H), 7.10 (d,  $J = 7.4$  Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 142.76, 139.67, 137.98, 129.85, 129.25, 127.93, 127.28, 123.78, 122.66, 120.34, 116.88, 104.93, 21.35, 18.39; IR (KBr): 2962, 2154, 1640, 1613, 1507, 1462, 1180  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ , 280.0908; found, 280.0909.



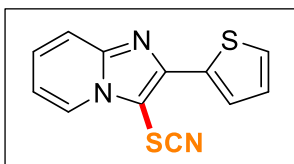
2-(4-Fluorophenyl)-6-methyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4l**). White solid, 128 mg (91%); mp. 146-148°C

(lit. mp. 147-150 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm)

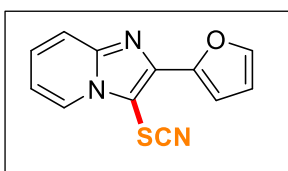
8.09-8.04 (m, 2H), 7.82 (s, 1H), 7.48 (d,  $J = 9.2$  Hz, 1H), 7.11 (t,  $J = 10.7$  Hz, 2H), 7.05 (d,  $J = 9.3$  Hz, 1H), 2.34 (s, 3H);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -113.54 (s, 1F);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.63 (d,  $J = 250.0$  Hz), 142.74, 138.66, 129.11 (d,  $J = 8.0$  Hz), 128.86 (d,  $J = 3.2$  Hz), 128.16, 126.04, 122.84, 120.34, 116.86, 115.45 (d,  $J = 21.5$  Hz), 104.92, 18.34; IR (KBr): 2962, 2154, 1640, 1620, 1487, 1462, 1300  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{10}\text{FN}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ , 284.0658; found, 284.0657.



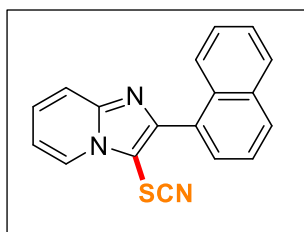
6-Bromo-2-(4-bromophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4m**). White solid, 183 mg (90%); mp. 191-194 °C (lit. mp. 190-196 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.55 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.64 (t, *J* = 7.9 Hz, 3H), 7.53 (d, *J* = 9.5 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 152.34, 146.45, 132.11, 131.92, 130.45, 130.20, 124.64, 124.36, 118.92, 109.60, 107.37, 95.57; IR (KBr): 2962, 2144, 1634, 1513, 1507, 1462, 1321 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>14</sub>H<sub>7</sub>Br<sub>2</sub>N<sub>3</sub>S [M + H]<sup>+</sup>, 407.8804 (for <sup>79</sup>Br), 409.8785 (for <sup>79</sup>Br & <sup>81</sup>Br), and 411.8760 (for <sup>81</sup>Br); found, 407.8808 (for <sup>79</sup>Br), 409.8789 (for <sup>79</sup>Br & <sup>81</sup>Br) and 411.8765 (for <sup>81</sup>Br).



3-Thiocyanato-2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine (**4n**).<sup>8</sup> White solid, 109 mg (85%); mp. 139-141 °C (lit. mp. 140-142 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.01 (d, *J* = 6.9 Hz, 1H), 7.74 (d, *J* = 2.8 Hz, 1H), 7.57 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 4.1 Hz, 1H), 7.19 (t, *J* = 8.4 Hz, 1H), 7.12 (t, *J* = 2.4 Hz, 1H) 6.87 (t, *J* = 7.3 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 143.71, 139.64, 135.80, 135.55, 127.77, 126.0, 125.29, 125.05, 122.53, 117.40, 113.0, 104.58; IR (KBr): 3074, 2343, 2143, 1734, 1643, 1488, 1223 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>12</sub>H<sub>7</sub>FN<sub>3</sub>S [M + H]<sup>+</sup>, 258.0160; found, 258.0159.



2-(Furan-2-yl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4o**).<sup>16</sup> White solid, 107 mg (89%); mp. 174-175 °C (lit. mp. 174-176 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.08 (d, *J* = 7.1 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.58 (s, 1H), 7.26 (d, *J* = 9.2 Hz, 1H), 7.01 (d, *J* = 3.5 Hz, 1H), 6.94 (t, *J* = 6.9 Hz, 1H), 6.56 (s, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 147.36, 143.98, 142.81, 137.52, 132.93, 125.14, 122.59, 117.68, 113.15, 111.51, 108.75, 104.92; IR (KBr): 2959, 2156, 1633, 1512, 1494, 1429, 1321 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>12</sub>H<sub>7</sub>N<sub>3</sub>OS [M + H]<sup>+</sup>, 242.0288; found, 242.0286.



2-(Naphthalen-1-yl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (**4p**).<sup>7</sup>

Yellow solid, 133 mg (87%); mp. 117-119 °C (lit. mp. 118-120 °C);

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.50 (d, *J* = 7.0 Hz, 1H), 8.04 (d, *J* = 7.3 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H),

7.83 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 6.1 Hz, 1H), 7.60 (d, *J* = 8.0

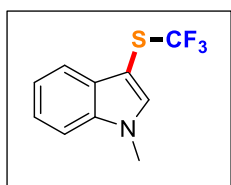
Hz, 1H), 7.50 (dd, *J*<sub>1</sub> = 9.8 Hz, *J*<sub>2</sub> = 12.7 Hz, 3H), 7.19 (t, *J* = 6.4 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125

MHz, CDCl<sub>3</sub>): δ (ppm) 153.91, 148.03, 133.81, 131.88, 129.97, 129.21, 129.14, 128.42, 128.03,

126.95, 126.23, 125.75, 125.07, 124.57, 118.52, 114.61, 108.17, 97.69; IR (KBr): 3076, 2360,

2334, 2221, 2143, 1643, 1463 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>18</sub>H<sub>11</sub>N<sub>3</sub>S [M + H]<sup>+</sup>,

302.0752; found, 302.0754.



1-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (**5a**).<sup>17</sup> Colourless liquid,

109 mg (94%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.50 (d, *J* = 8.0 Hz,

1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz,

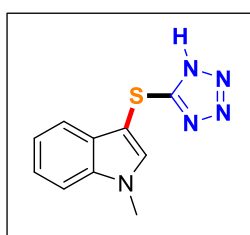
1H), 6.97 (s, 1H), 3.71 (s, 3H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ (ppm) -

44.94 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 137.21, 136.95, 130.22, 129.35 (q, *J* =

308.0 Hz), 122.94, 121.53, 119.40, 109.89, 93.00, 33.30; IR (KBr): 2929, 2847, 1659, 1561,

1454, 1380, 1335, 1264, 1248, 1214, 1129 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>10</sub>H<sub>8</sub>F<sub>3</sub>NS

[M + H]<sup>+</sup>, 232.0408; found, 232.0407.



3-((1*H*-Tetrazol-5-yl)thio)-1-methyl-1*H*-indole (**5b**).<sup>11</sup> White solid, 104

mg (90%); mp. 178-179 °C (lit. mp. 180-181 °C); <sup>1</sup>H NMR (500 MHz,

CDCl<sub>3</sub>): δ (ppm) 7.57 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 8.4

Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H);

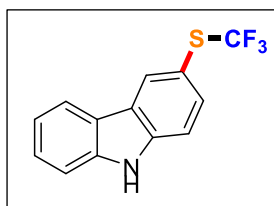
<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 156.52, 137.47, 135.94,

128.85, 123.28, 121.42, 118.88, 110.23, 93.86, 33.39; IR (KBr): 3394, 3112, 2921, 2852, 1506,

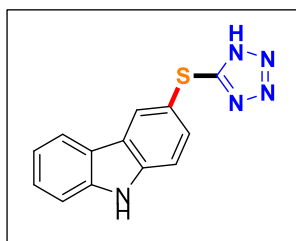
1497, 1460, 1335, 1317, 1243, 1155, 1128, 1109 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for

C<sub>10</sub>H<sub>9</sub>N<sub>5</sub>S [M + H]<sup>+</sup>, 232.0657; found, 232.0655.





3-((Trifluoromethyl)thio)-9H-carbazole (**5c**).<sup>18</sup> White solid, 121 mg (91%); mp. 145-146 °C (lit. mp. 146-147 °C); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 11.49 (s, 1H), 8.31 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.53-7.49 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H); <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) -43.35 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 140.63, 140.30, 133.66, 131.14 (q, *J* = 308.0 Hz), 125.80, 124.42, 123.61, 122.25, 120.94, 119.55, 112.37, 111.69, 110.56; IR (KBr): 3410, 3387, 2926, 2843, 1658, 1598, 1561, 1463, 1451, 1432, 1335, 1266, 1248, 1206, 1132 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>13</sub>H<sub>8</sub>F<sub>3</sub>NS [M + H]<sup>+</sup>, 268.0408; found, 268.0405.



3-((1H-Tetrazol-5-yl)thio)-9H-carbazole (**5d**).<sup>19</sup> White solid, 123 mg (92%); mp. 165-168 °C (lit. mp. 170-171 °C); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 11.60 (bs, 1H), 8.45 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.61-7.52 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 155.52, 140.66, 140.61, 131.64, 127.14, 126.81, 124.05, 122.22, 121.10, 119.70, 116.49, 112.80, 111.75; IR (KBr): 3397, 3118, 2924, 2858, 1512, 1502, 1469, 1356, 1321, 1251, 1147, 1132, 1121 cm<sup>-1</sup>; HRMS (ESI-TOF): *m/z* calcd for C<sub>13</sub>H<sub>9</sub>N<sub>5</sub>S [M + H]<sup>+</sup>, 268.0657; found, 268.0654.

## References

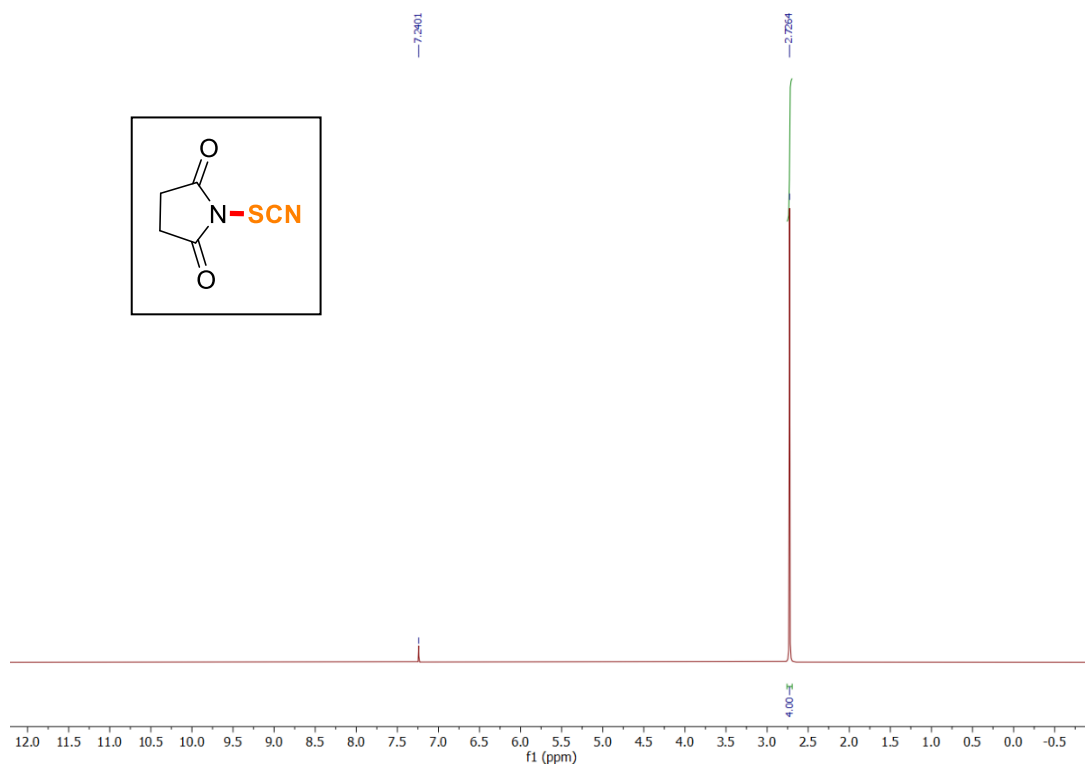
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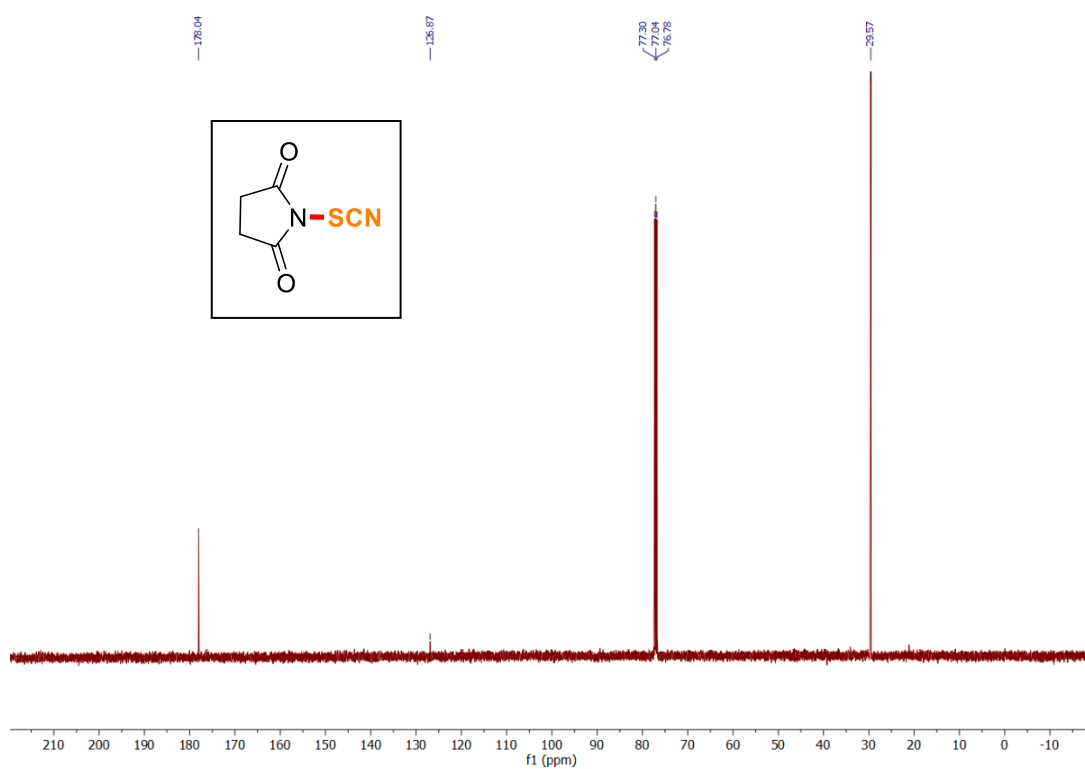
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## Copies of NMR spectra

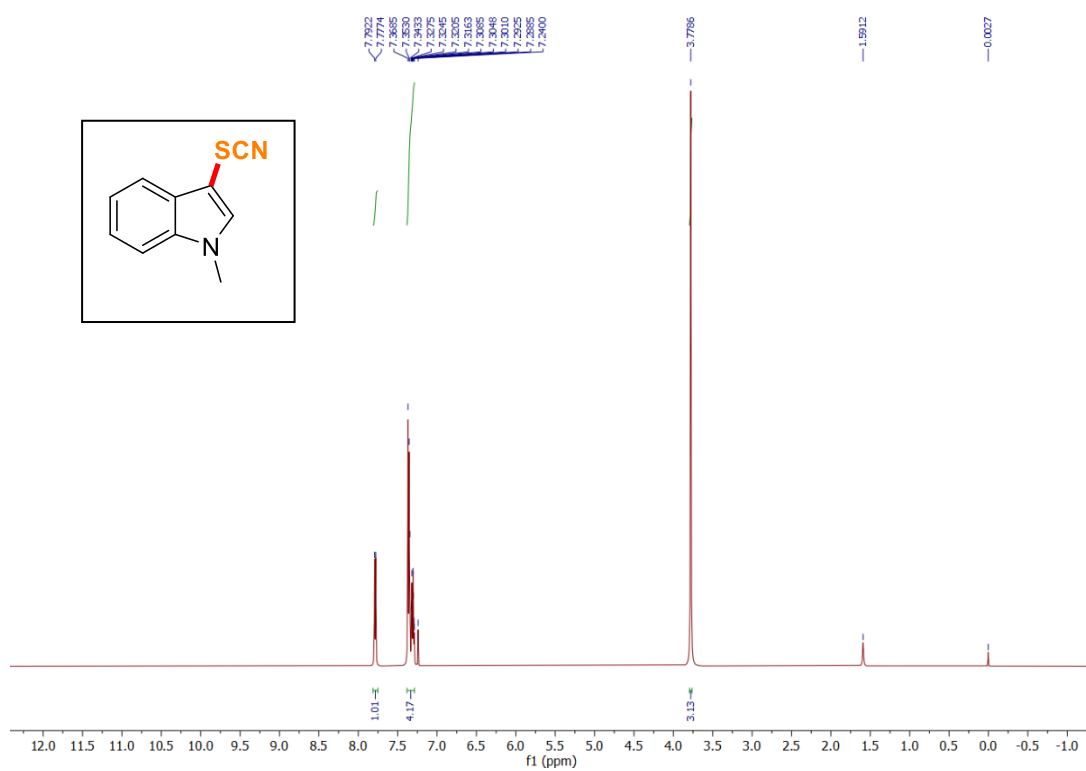
$^1\text{H}$  NMR spectrum of compound NTS, ( $\text{CDCl}_3$ , 500 MHz).



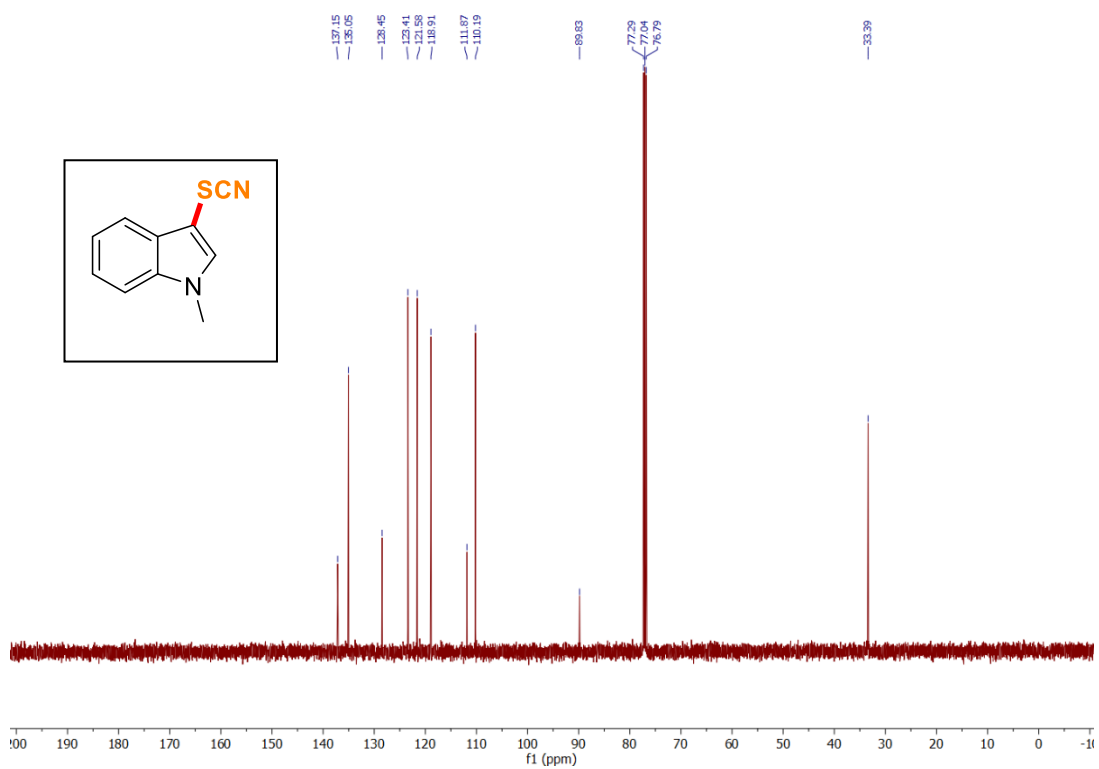
$^{13}\text{C}$  NMR spectrum of compound NTS, ( $\text{CDCl}_3$ , 125 MHz).



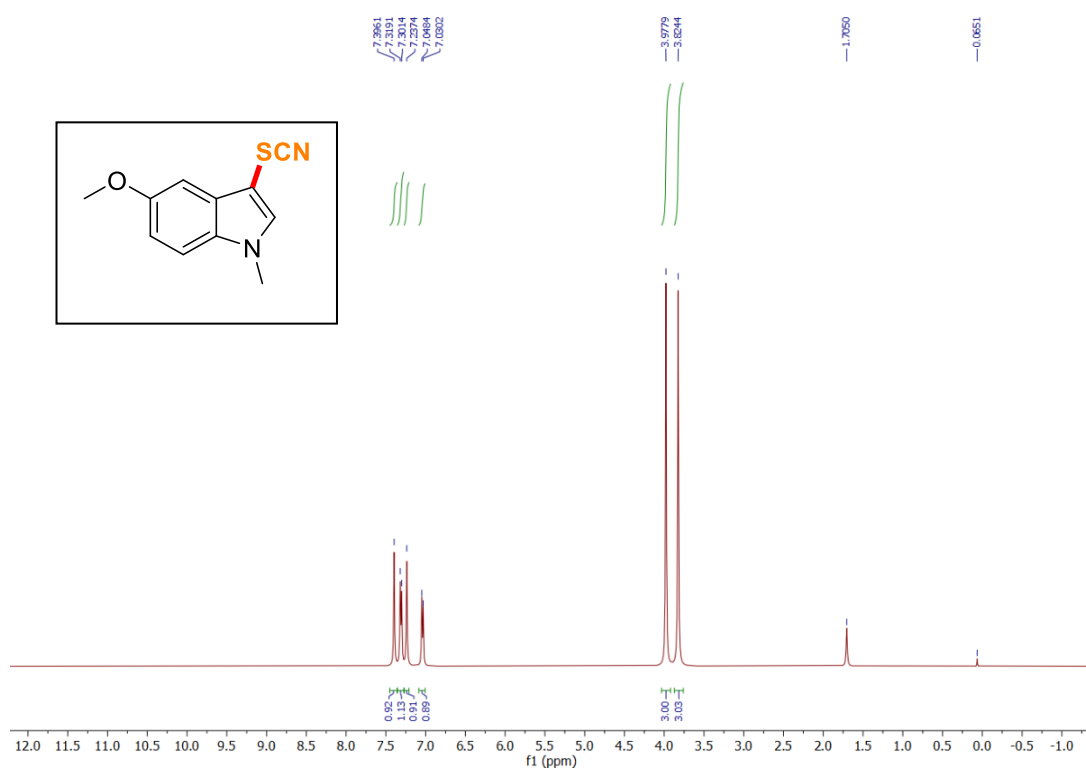
$^1\text{H}$  NMR spectrum of compound **2a**, ( $\text{CDCl}_3$ , 500 MHz).



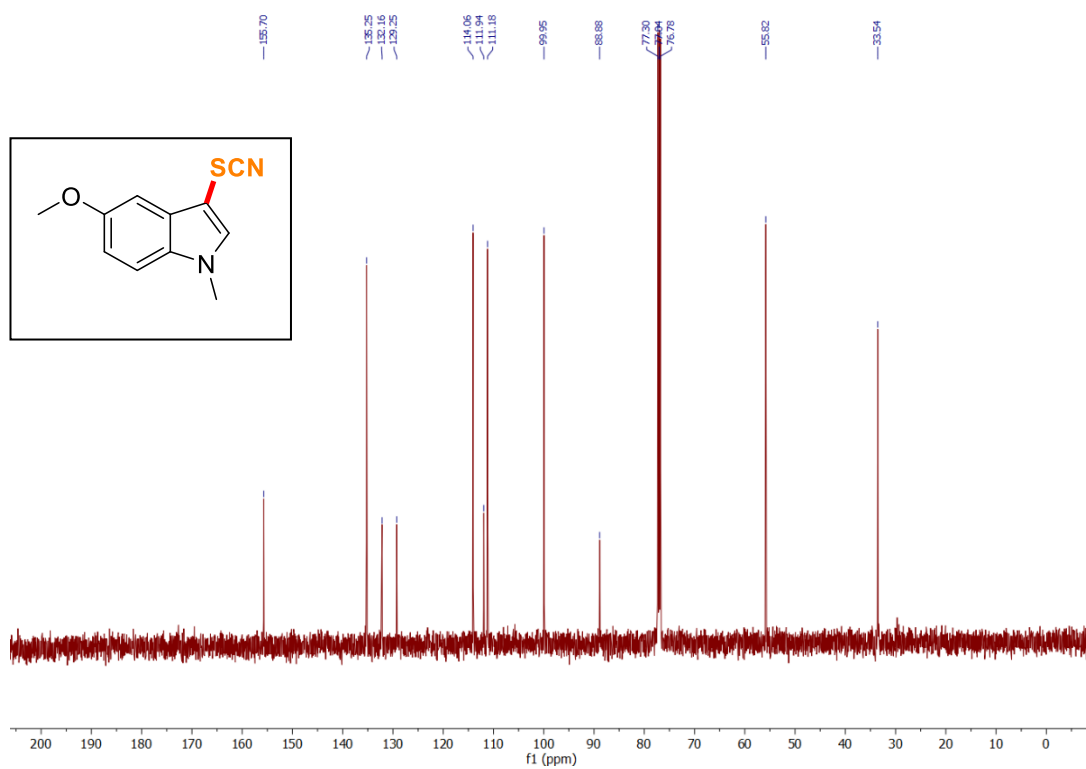
$^{13}\text{C}$  NMR spectrum of compound **2a**, ( $\text{CDCl}_3$ , 125 MHz).



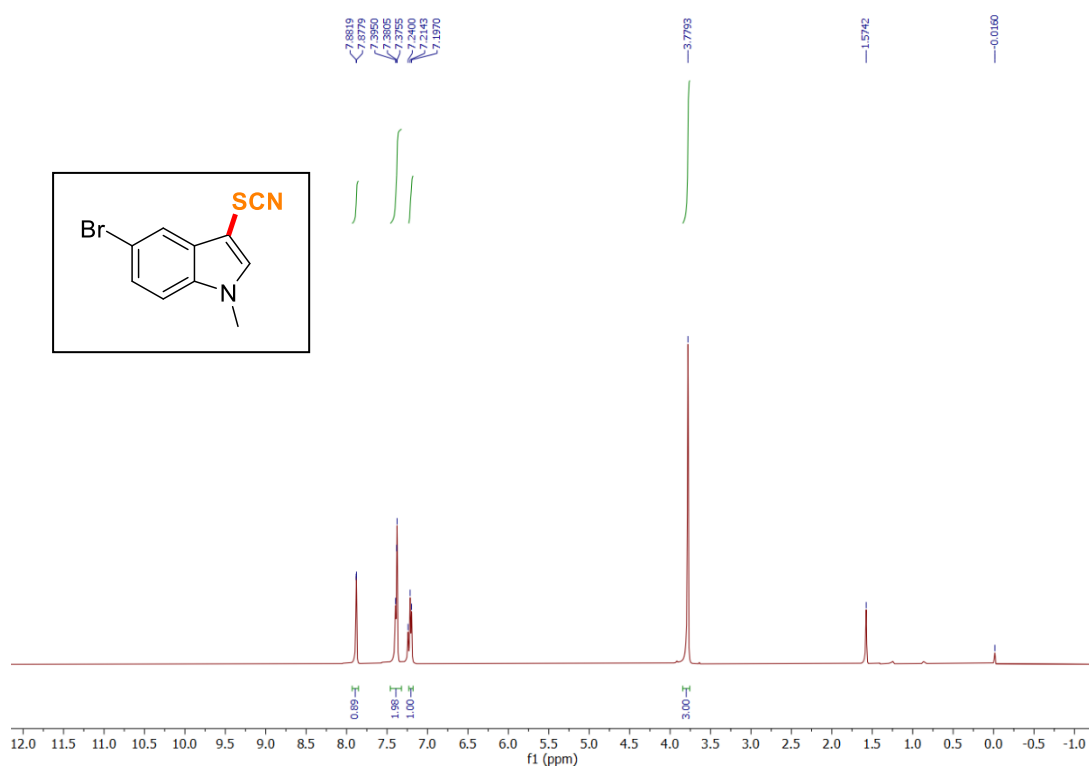
$^1\text{H}$  NMR spectrum of compound **2b**, ( $\text{CDCl}_3$ , 500 MHz).



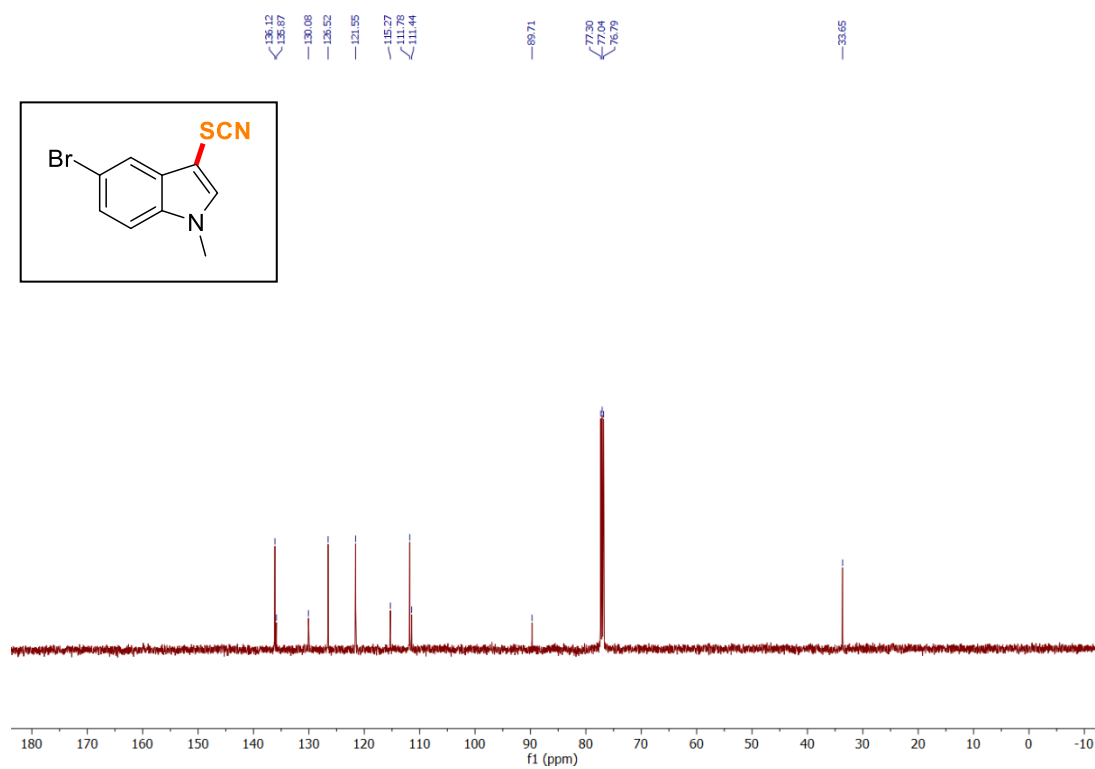
$^{13}\text{C}$  NMR spectrum of compound **2b**, ( $\text{CDCl}_3$ , 125 MHz).



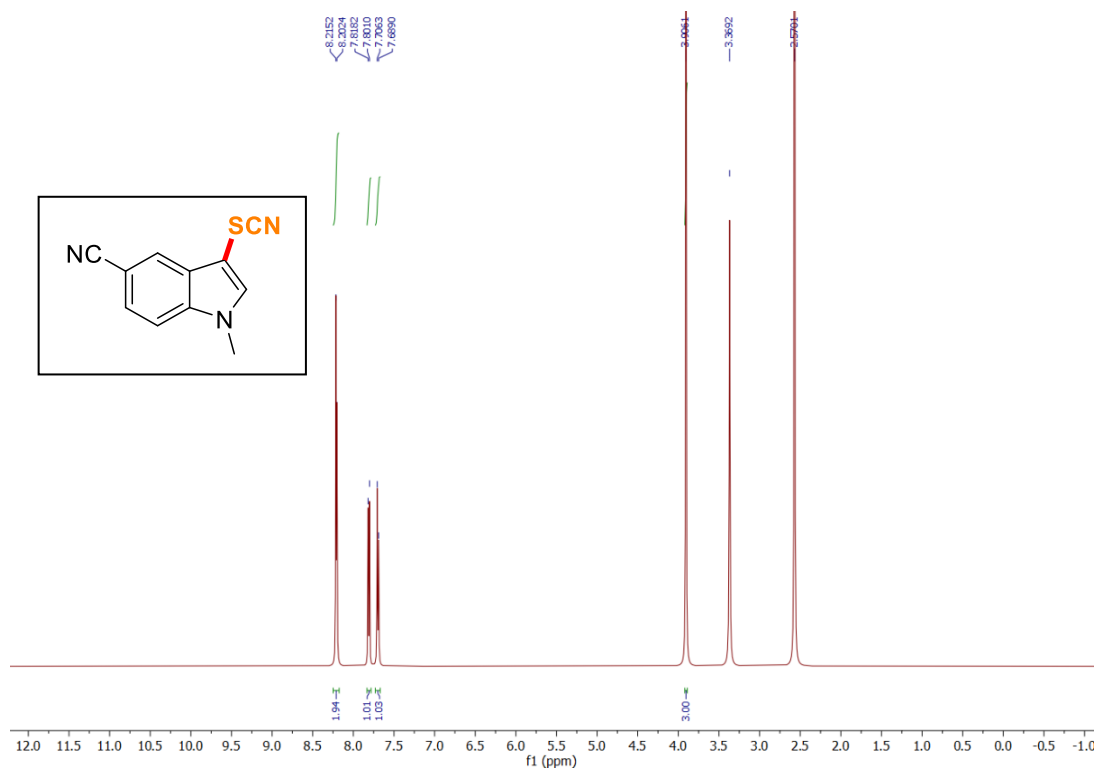
$^1\text{H}$  NMR spectrum of compound **2c**, ( $\text{CDCl}_3$ , 500 MHz).



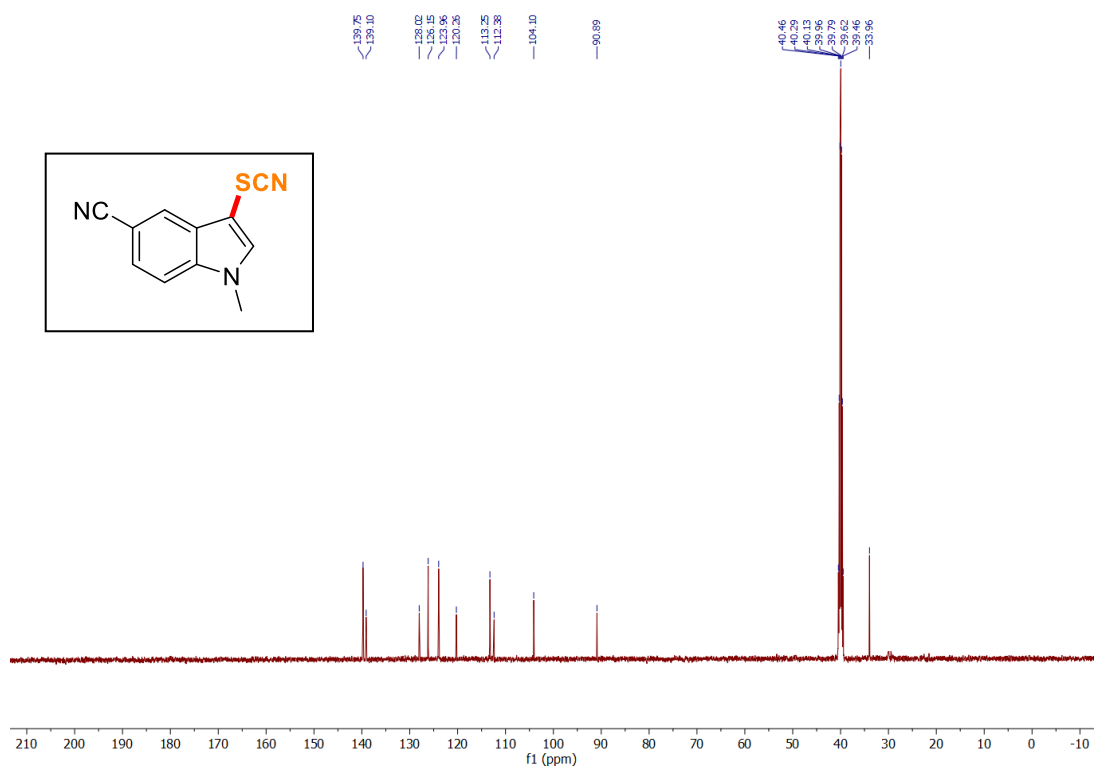
$^{13}\text{C}$  NMR spectrum of compound **2c**, ( $\text{CDCl}_3$ , 125 MHz).



$^1\text{H}$  NMR spectrum of compound **2d**, ( $\text{DMSO-}d_6$ , 500 MHz).

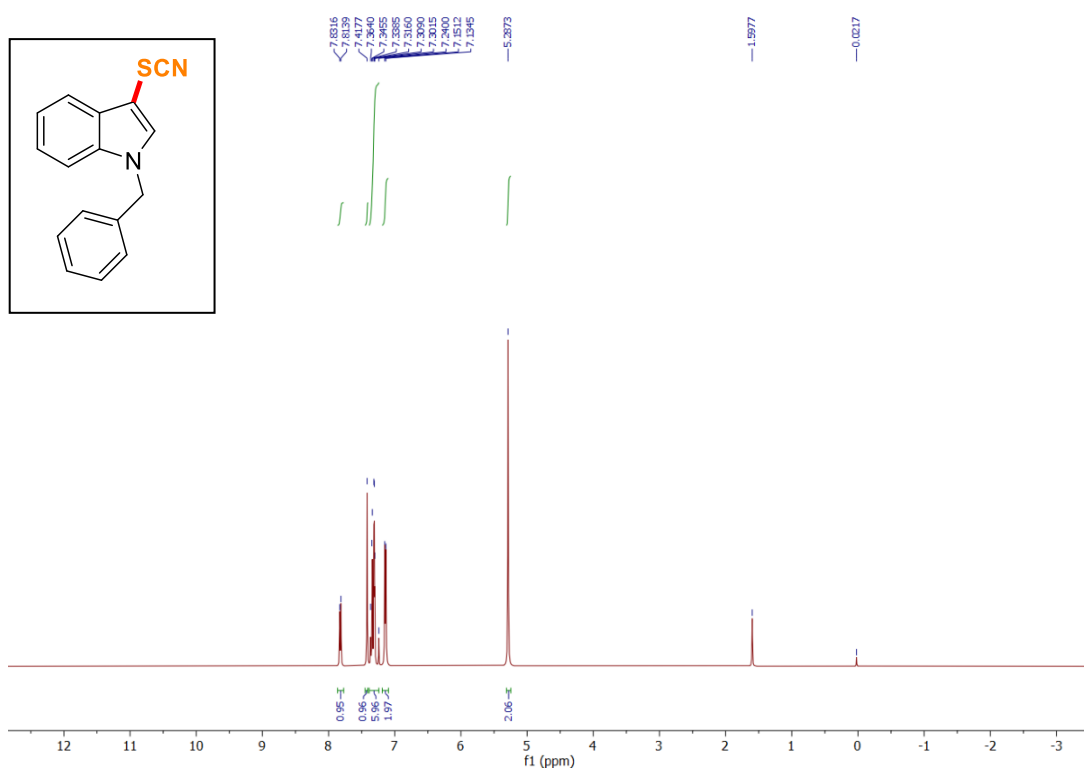


$^{13}\text{C}$  NMR spectrum of compound **2d**, ( $\text{DMSO-}d_6$ , 125 MHz).

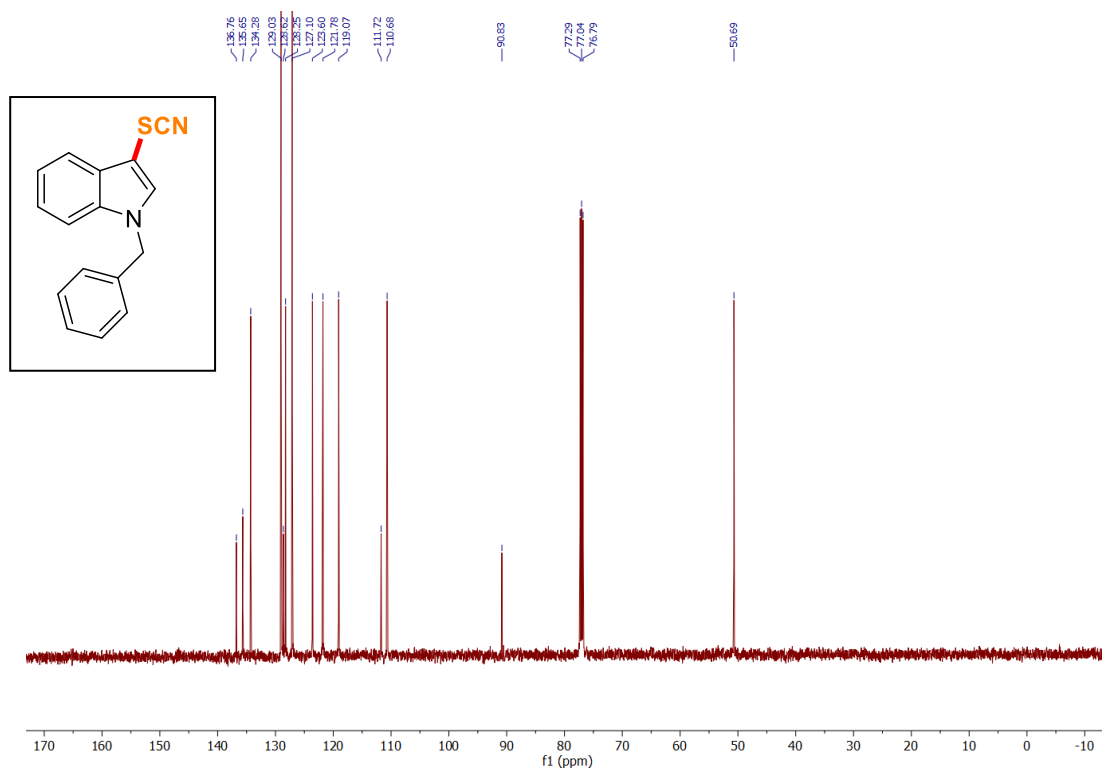




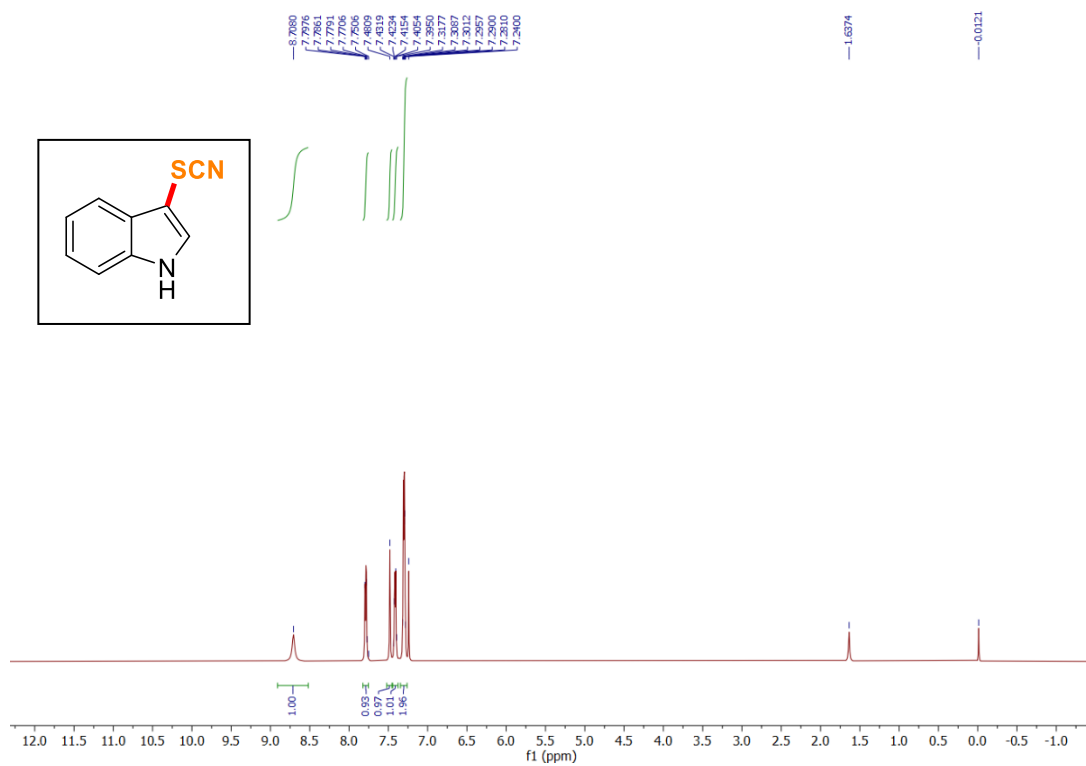
<sup>1</sup>H NMR spectrum of compound **2e**, (CDCl<sub>3</sub>, 500 MHz).



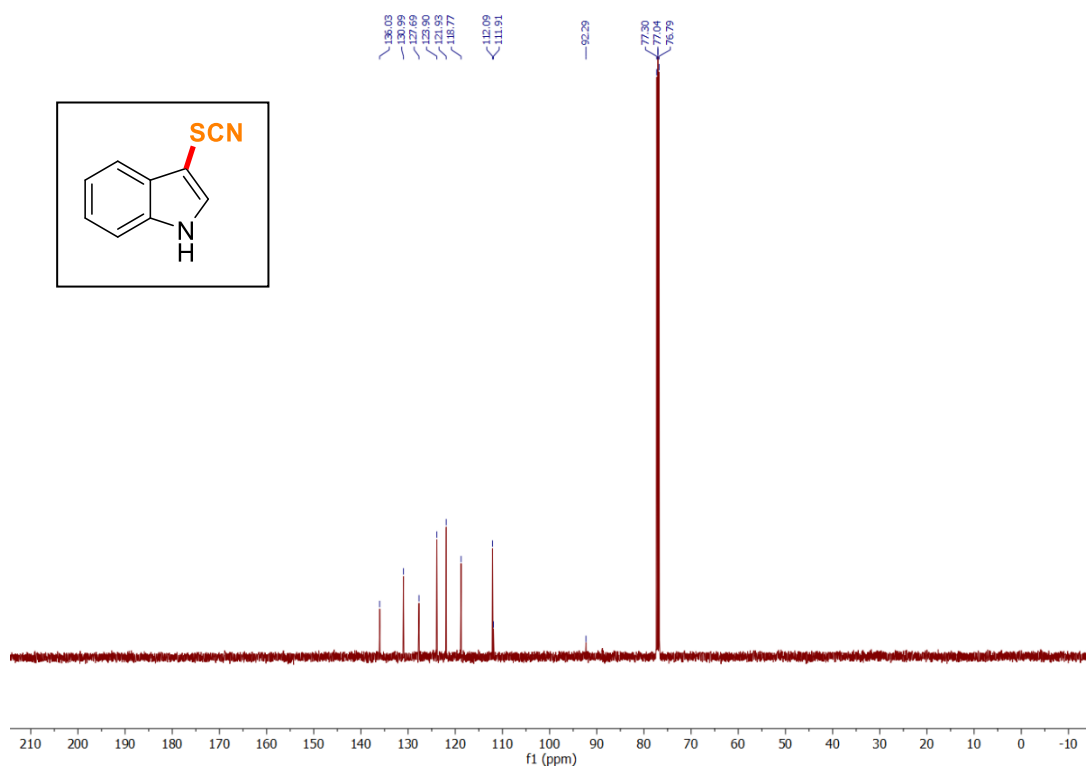
<sup>13</sup>C NMR spectrum of compound **2e**, (CDCl<sub>3</sub>, 125 MHz).



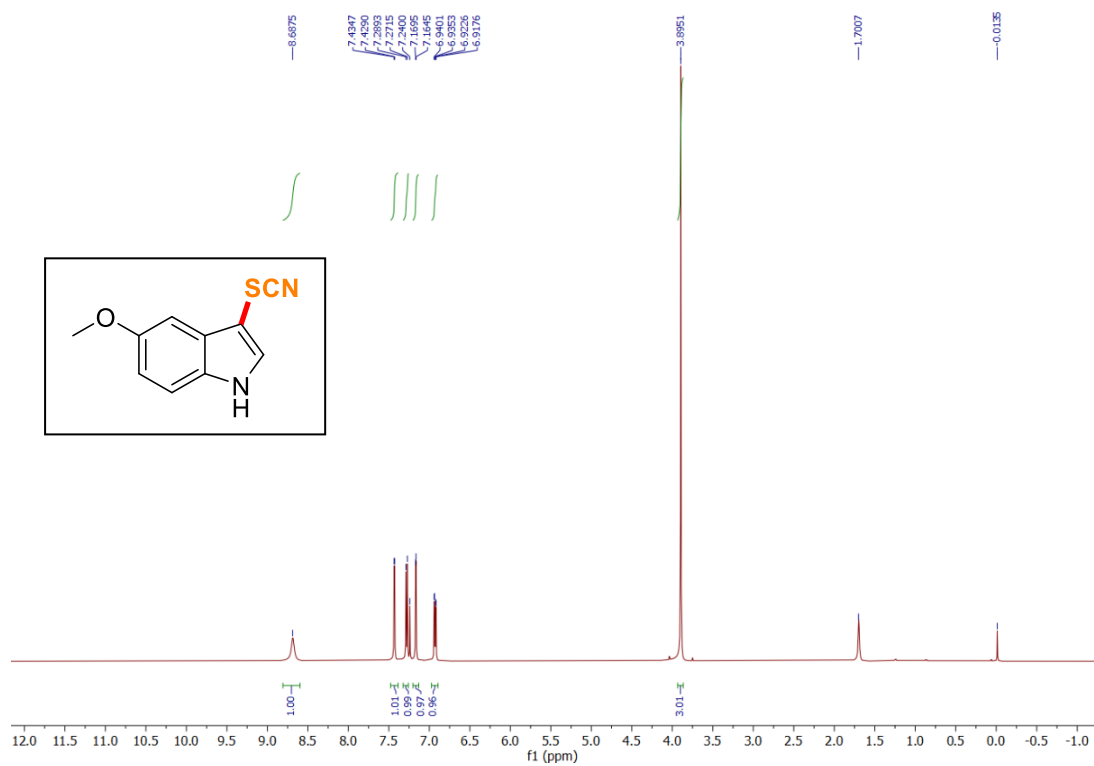
$^1\text{H}$  NMR spectrum of compound **2f**, ( $\text{CDCl}_3$ , 500 MHz).



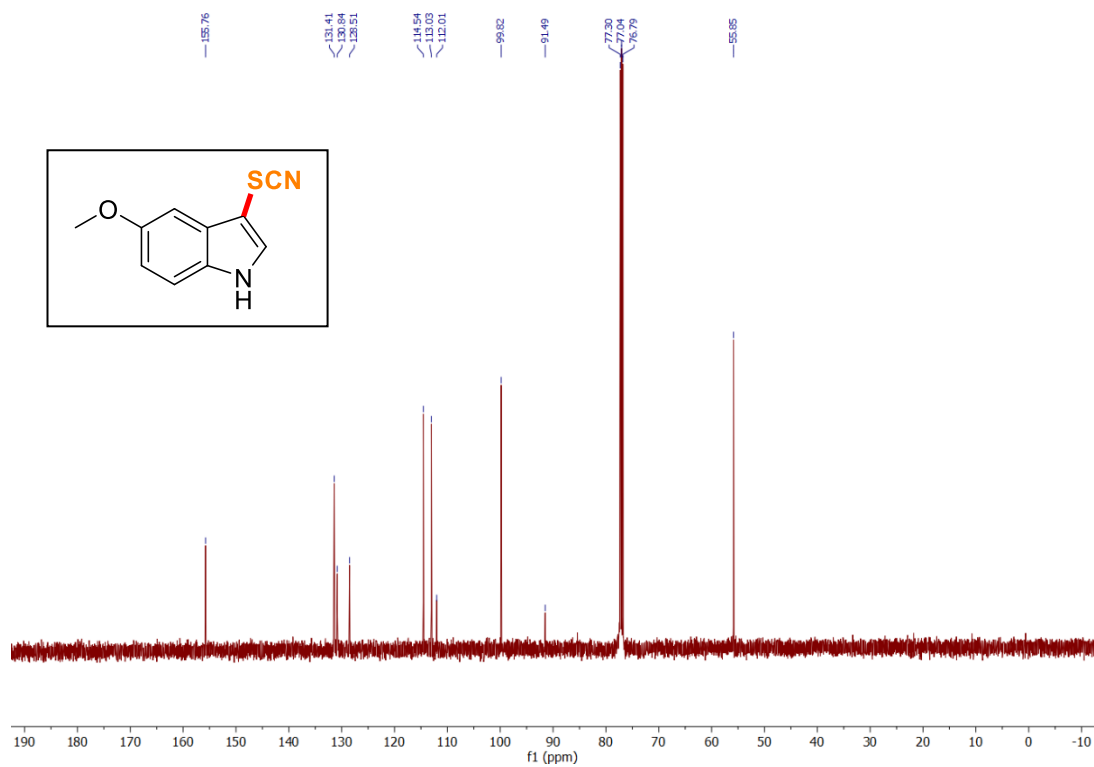
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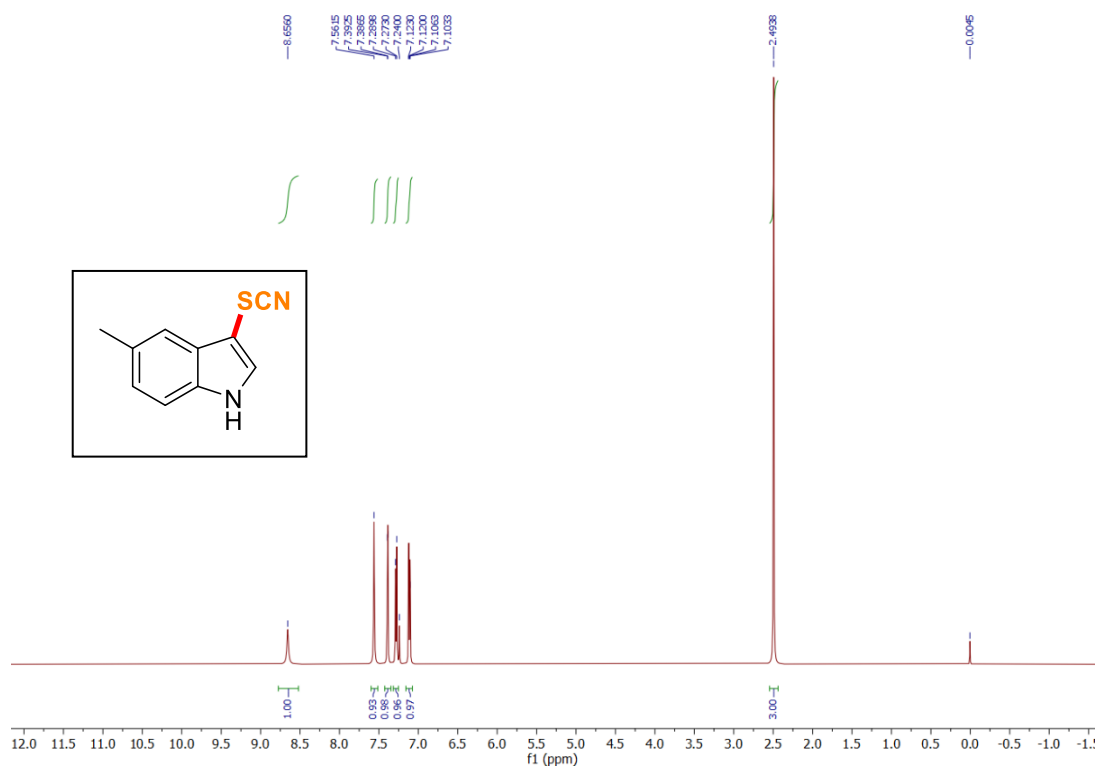
$^1\text{H}$  NMR spectrum of compound **2g**, ( $\text{CDCl}_3$ , 500 MHz).



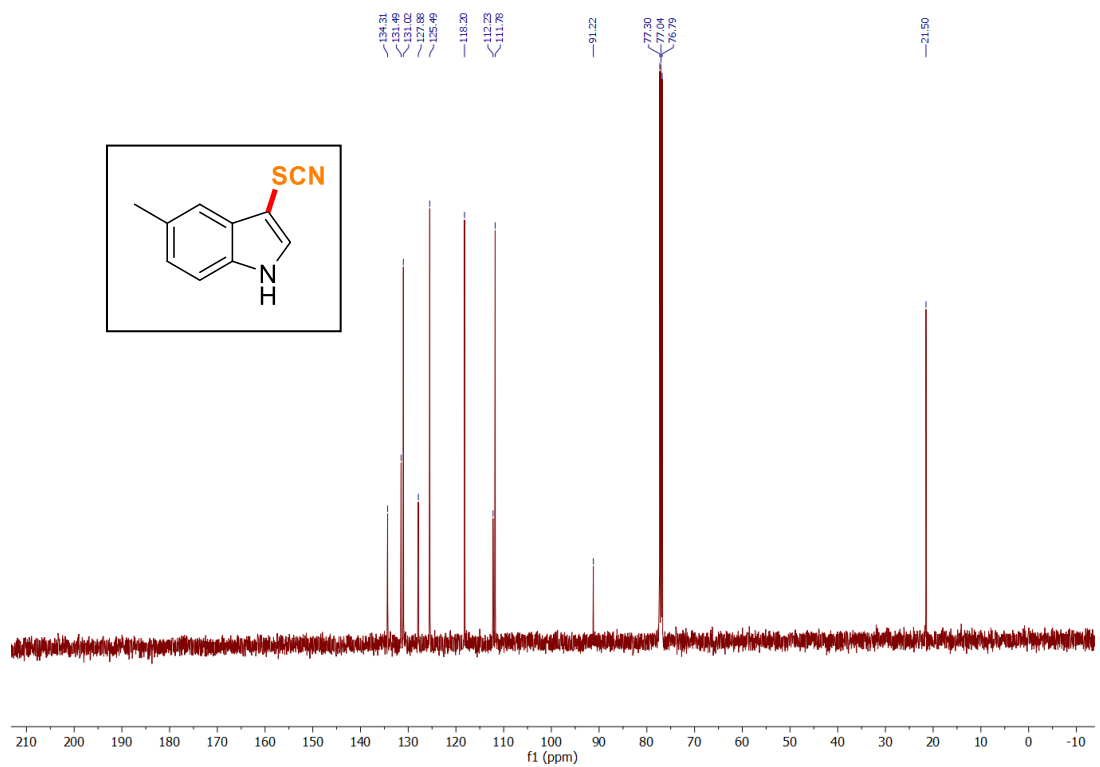
$^{13}\text{C}$  NMR spectrum of compound **2g**, ( $\text{CDCl}_3$ , 125 MHz).



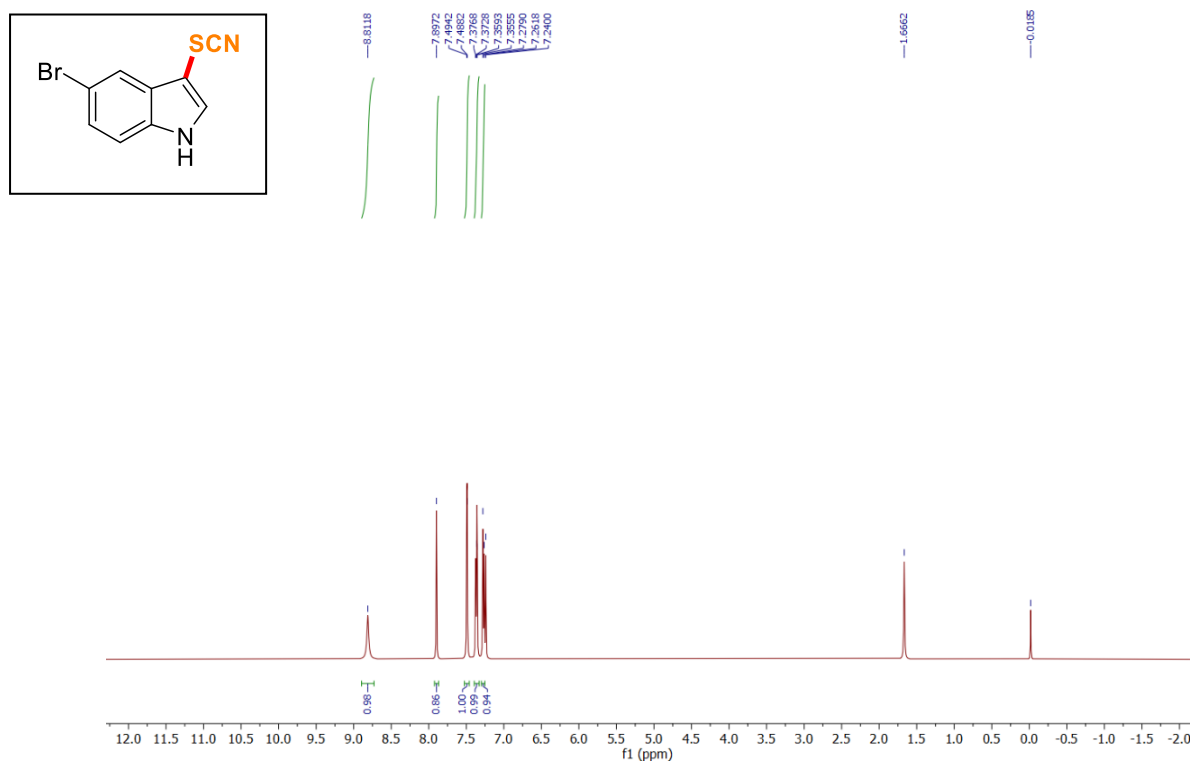
$^1\text{H}$  NMR spectrum of compound **2h**, ( $\text{CDCl}_3$ , 500 MHz).



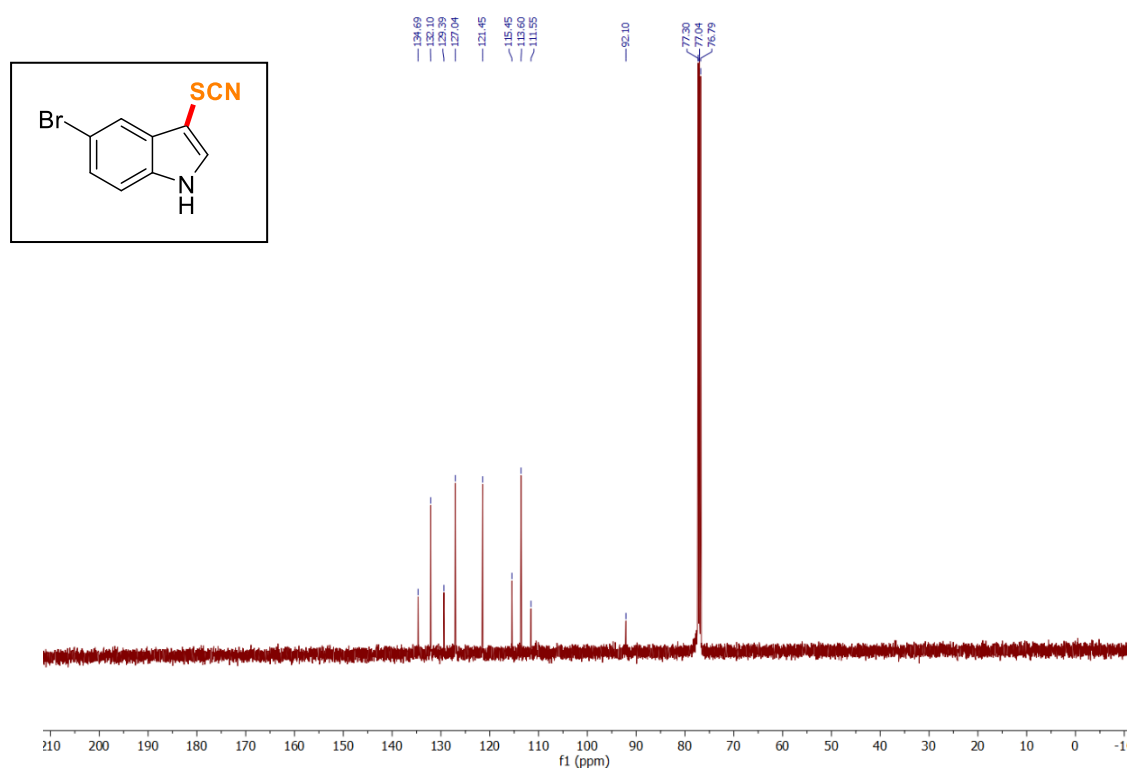
$^{13}\text{C}$  NMR spectrum of compound **2h**, ( $\text{CDCl}_3$ , 125 MHz).



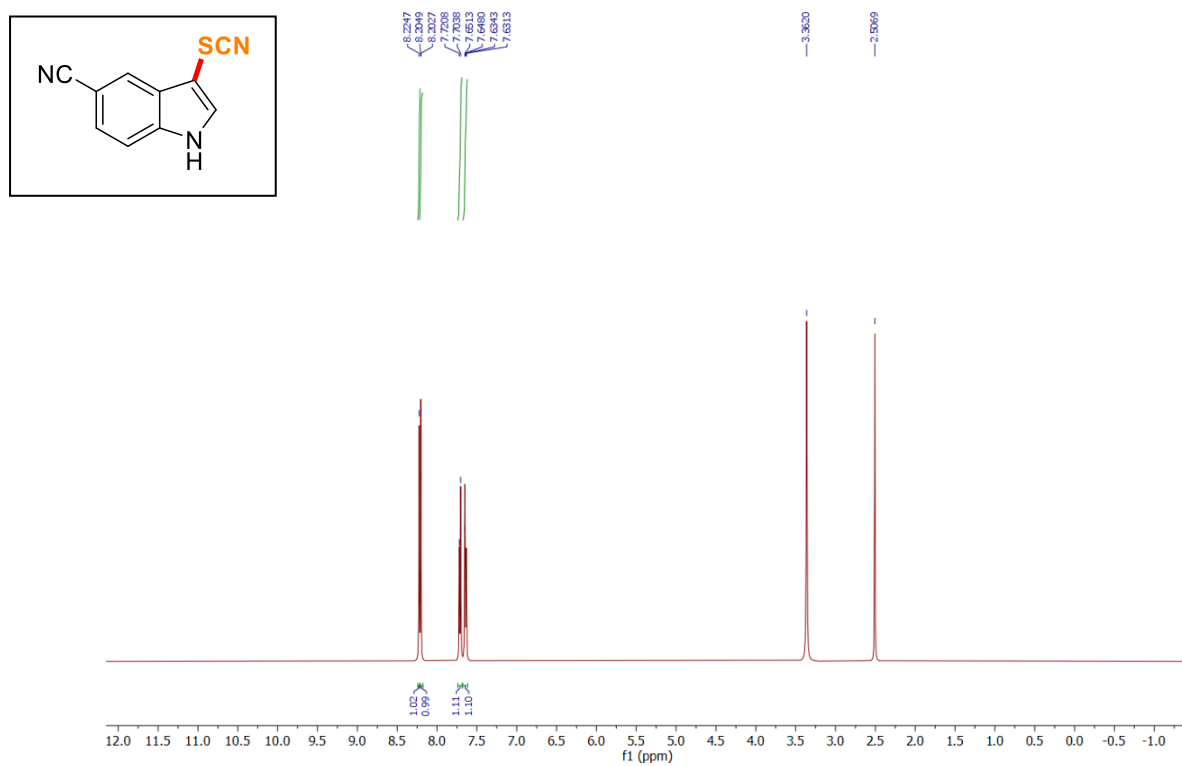
$^1\text{H}$  NMR spectrum of compound **2i**, ( $\text{CDCl}_3$ , 500 MHz).



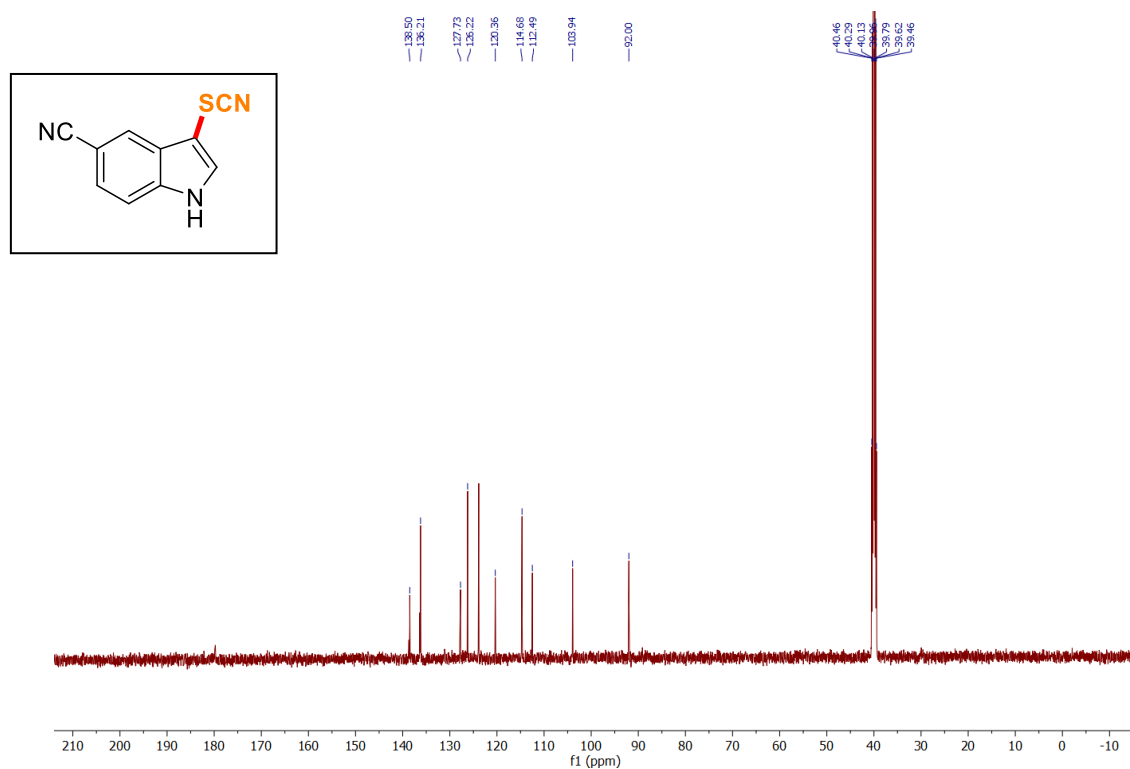
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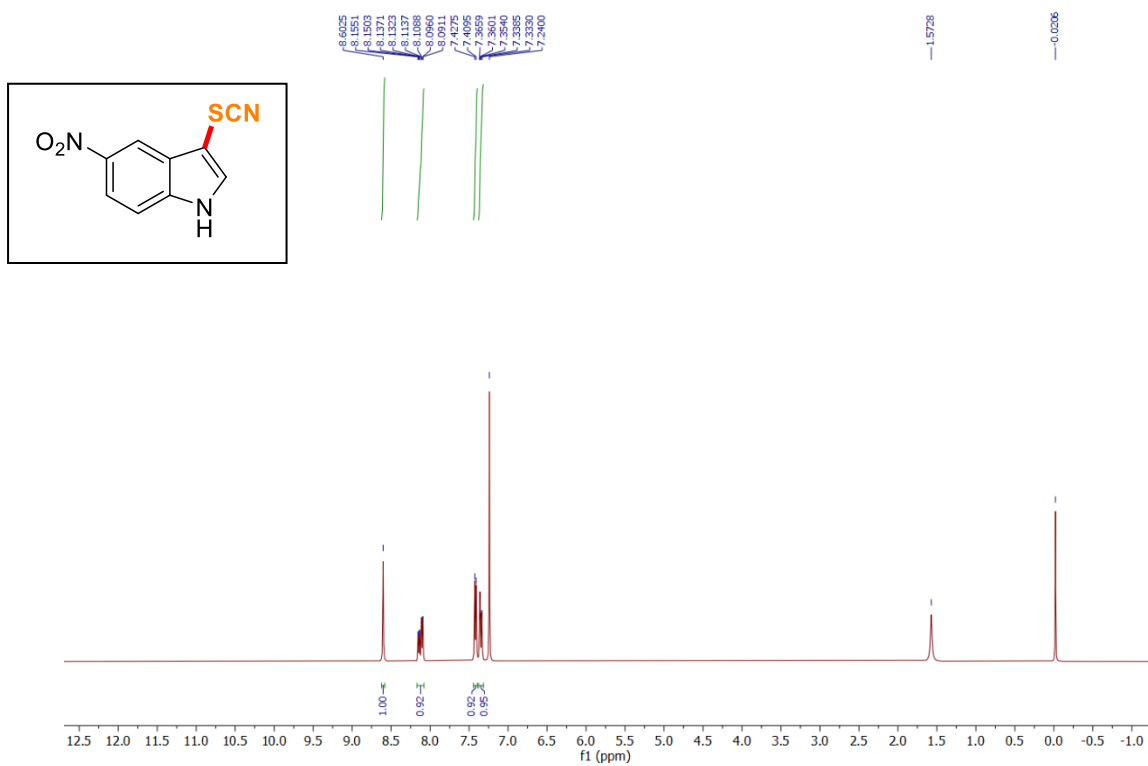
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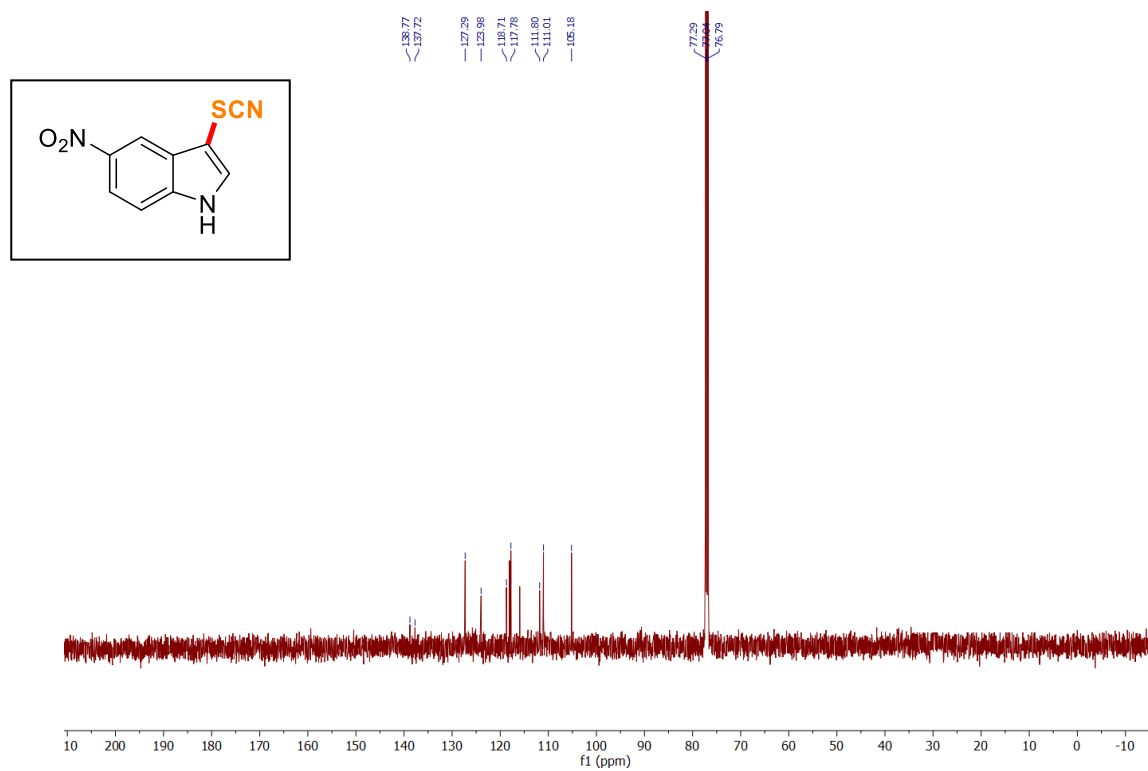
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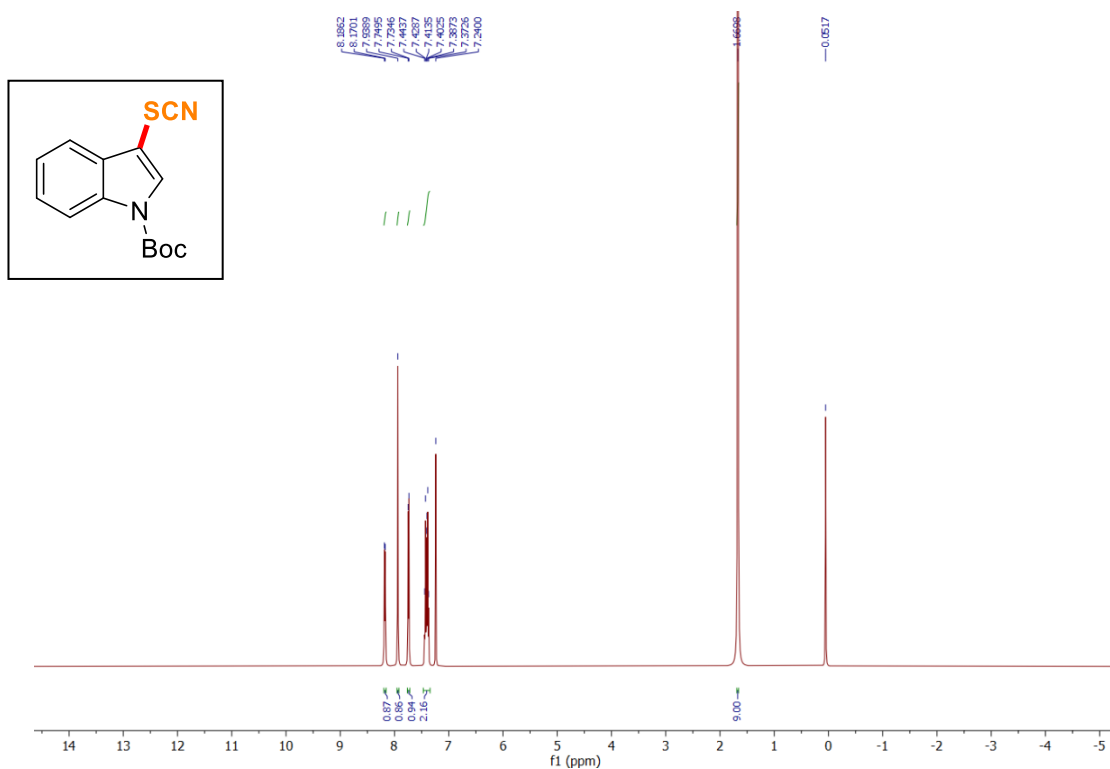
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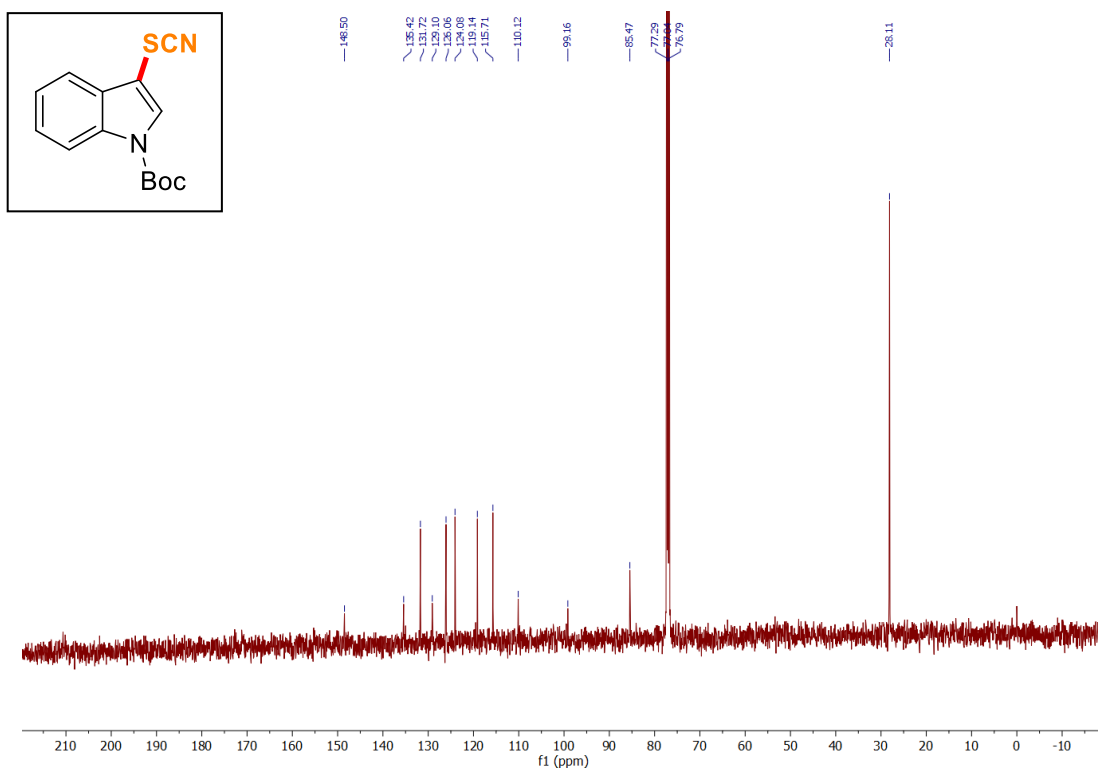
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$^1\text{H}$  NMR spectrum of compound **2l**, ( $\text{CDCl}_3$ , 500 MHz).

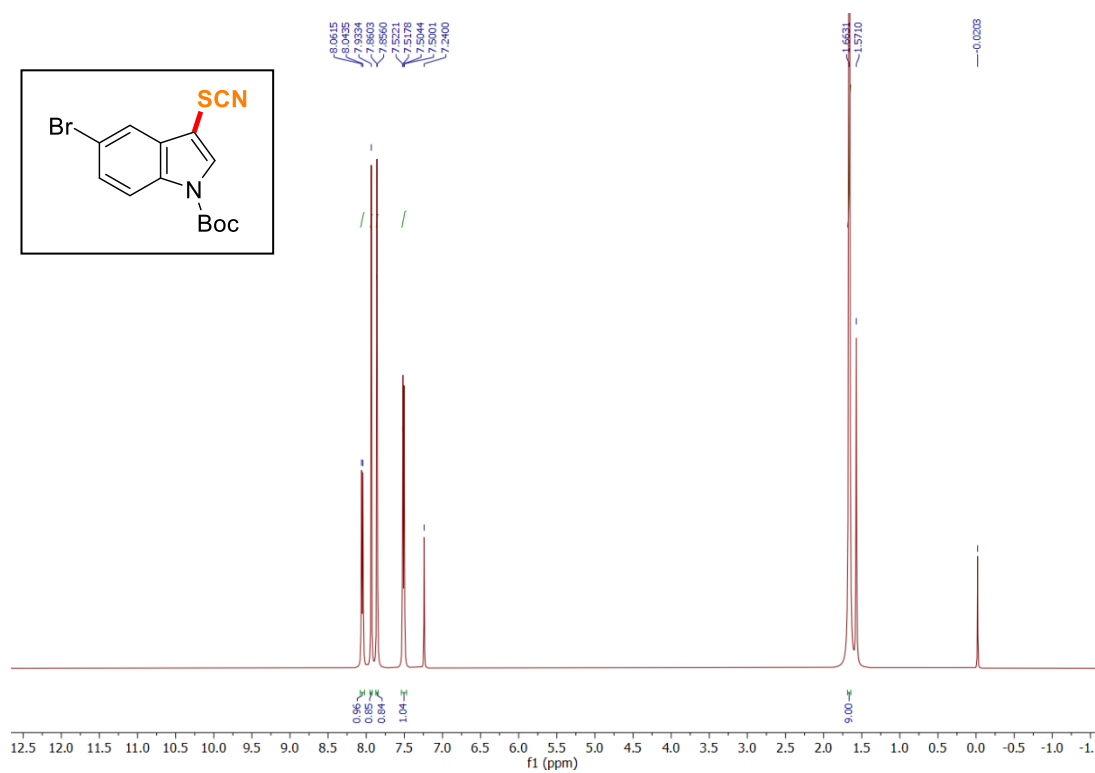


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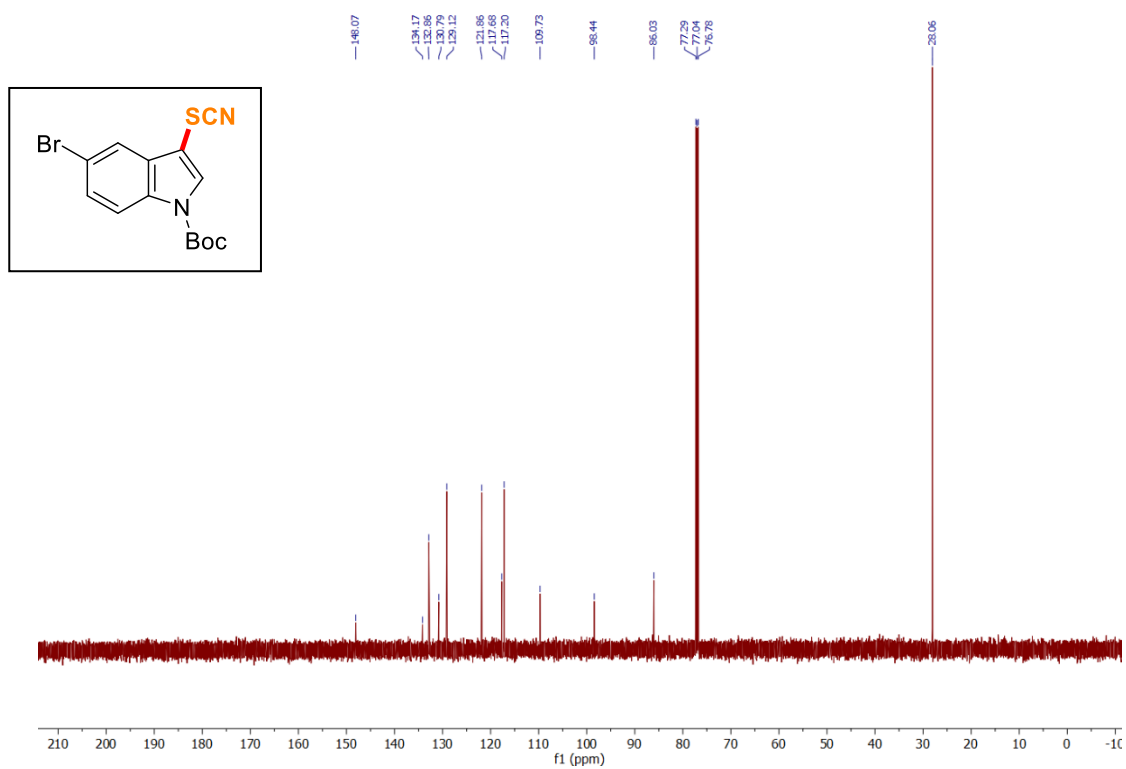




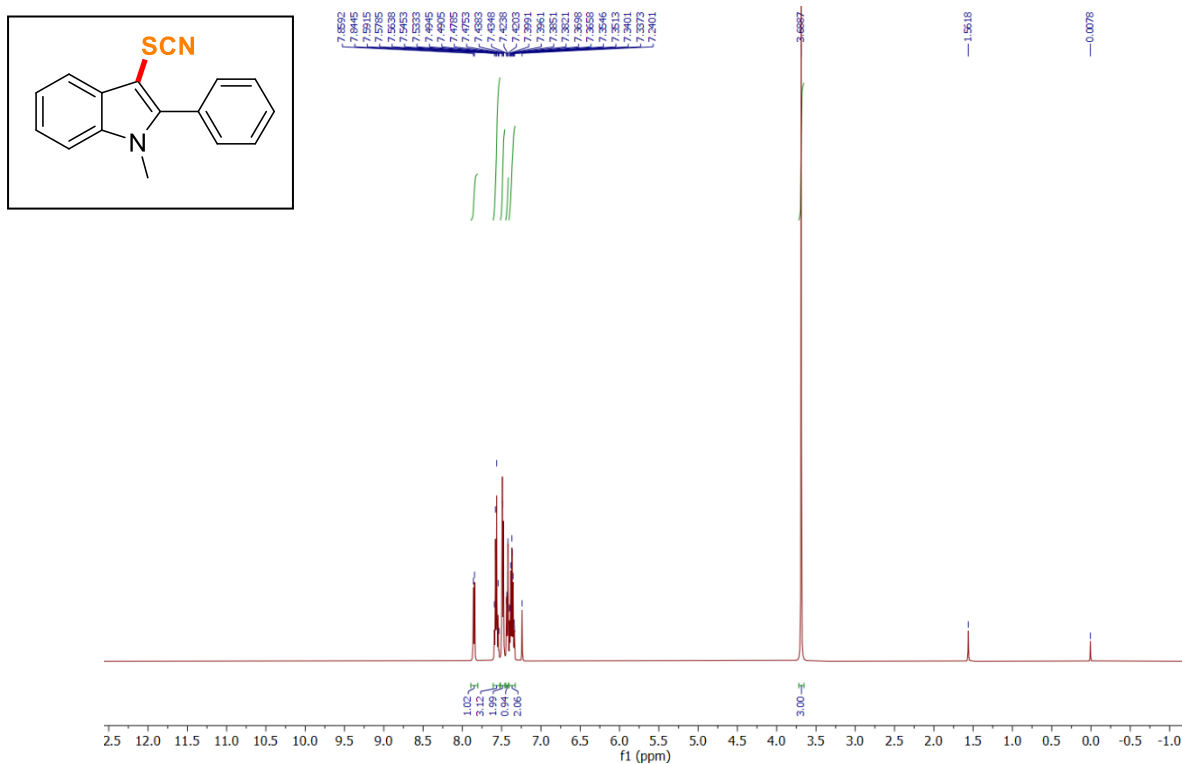
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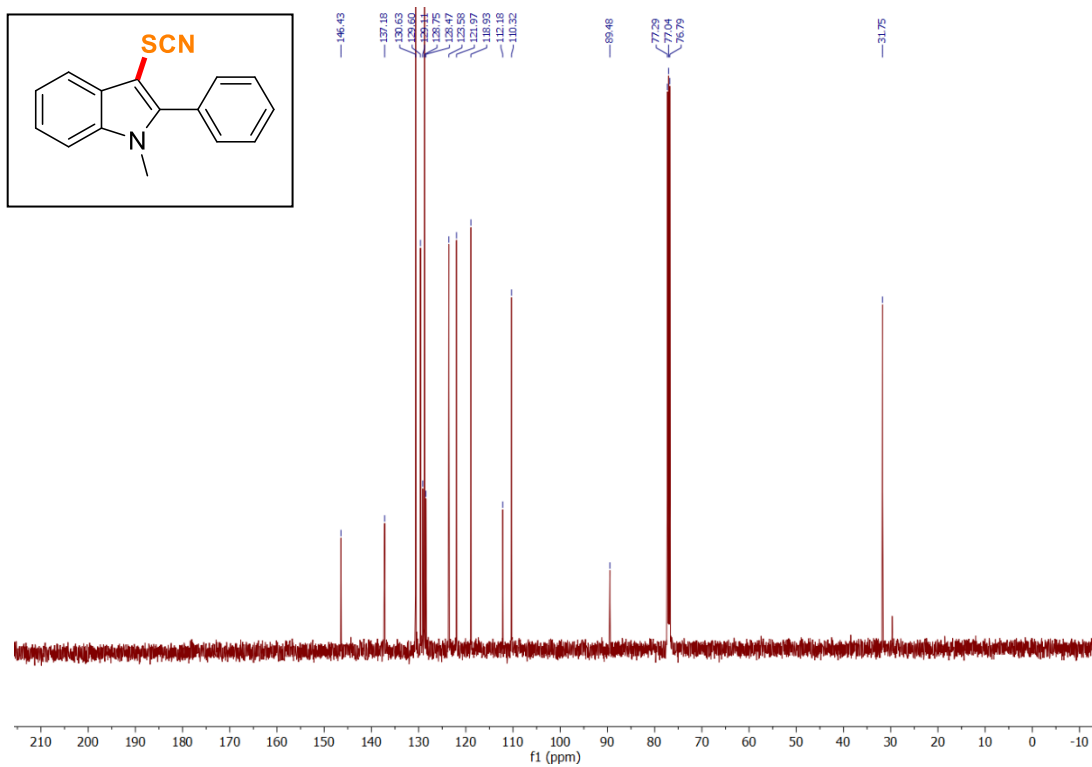
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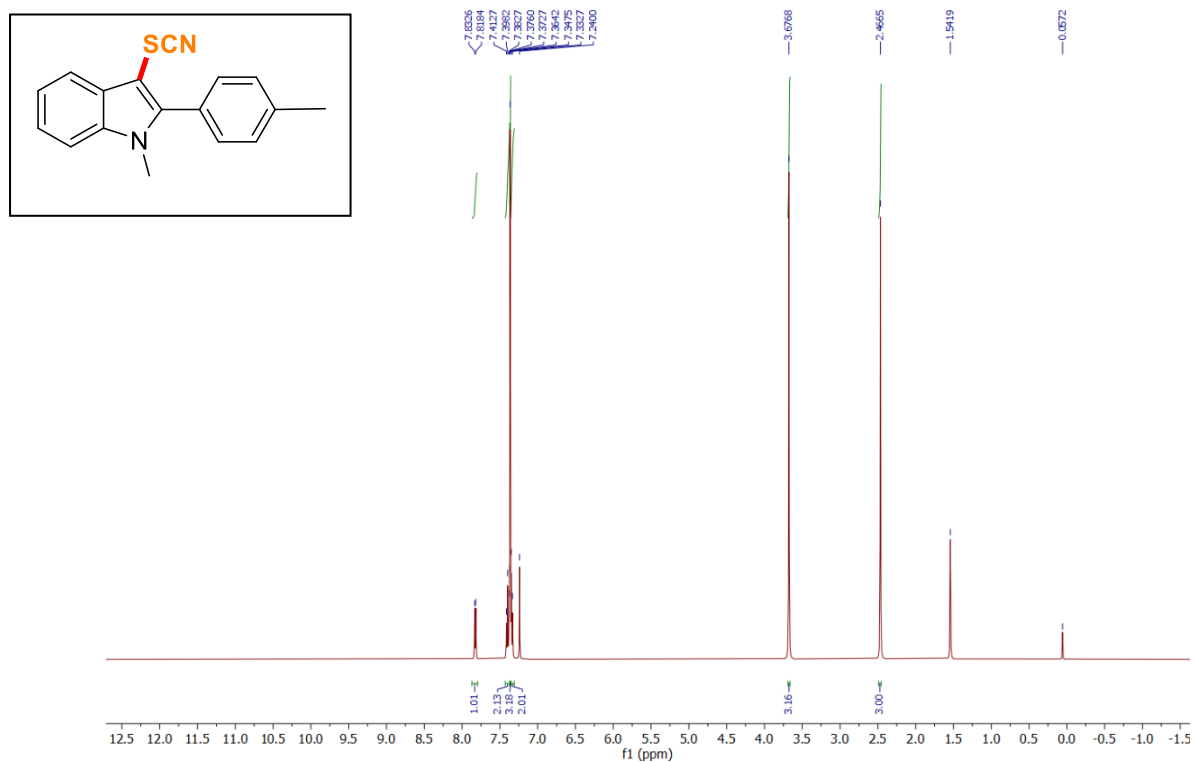
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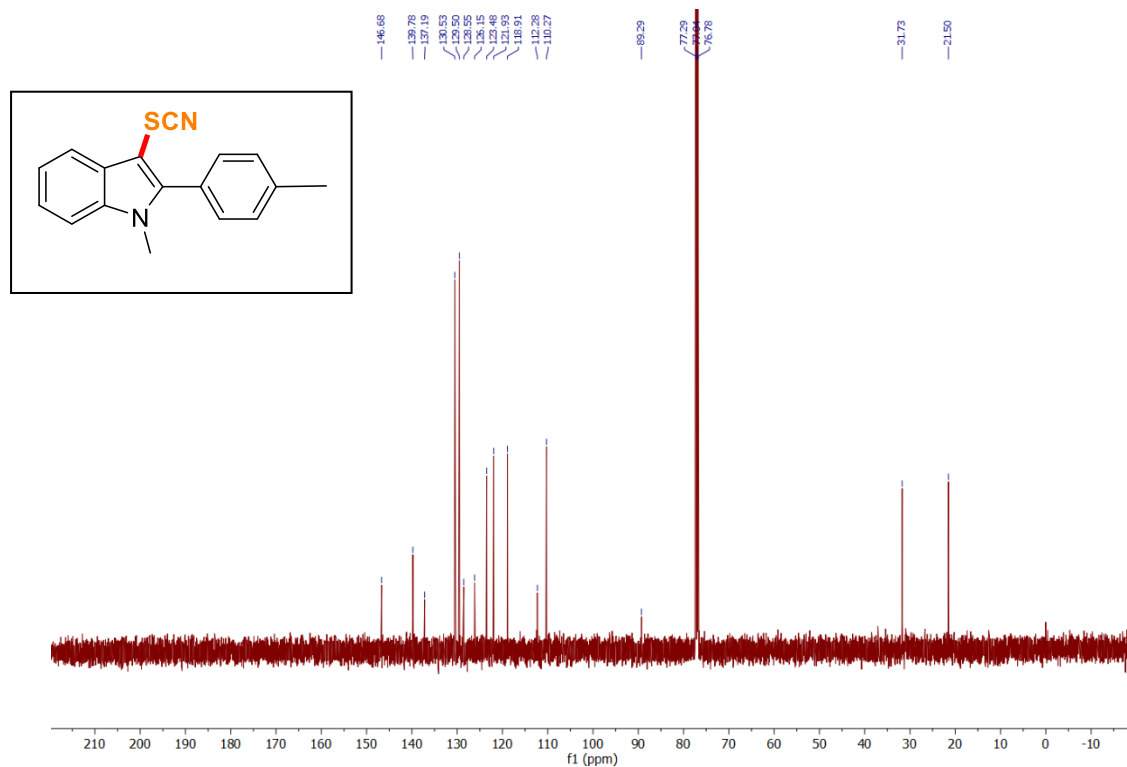
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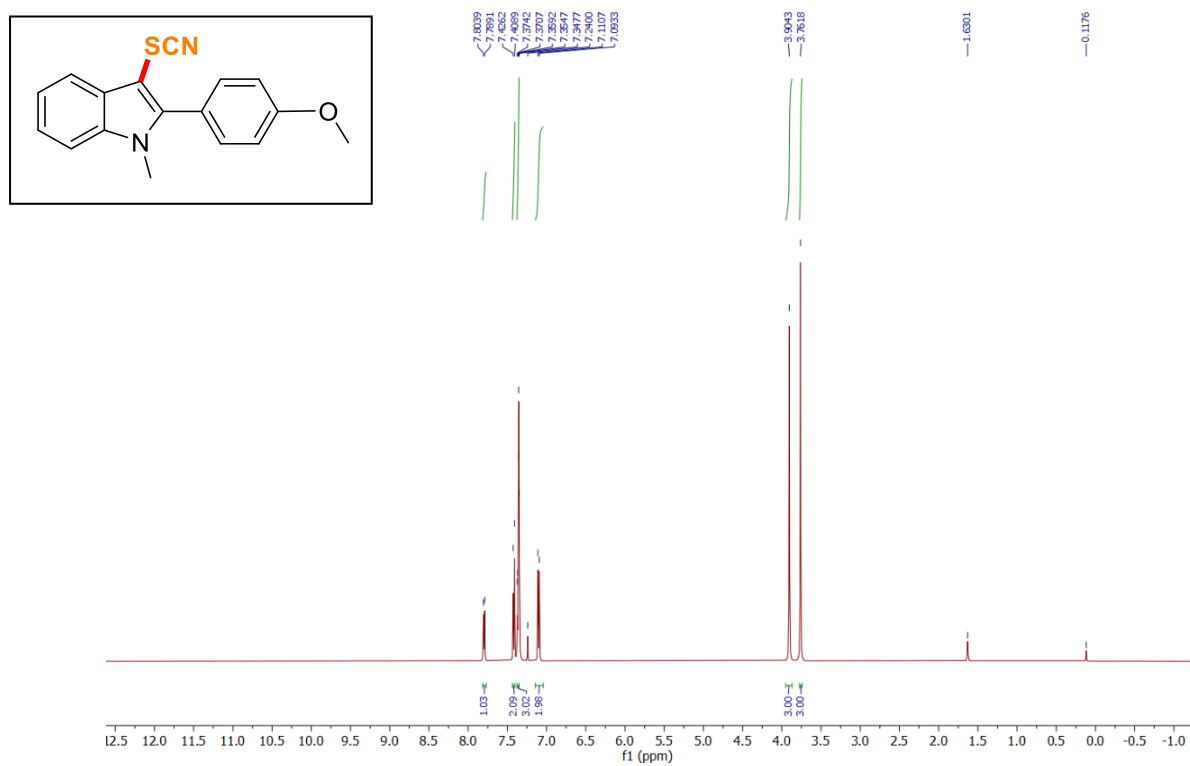
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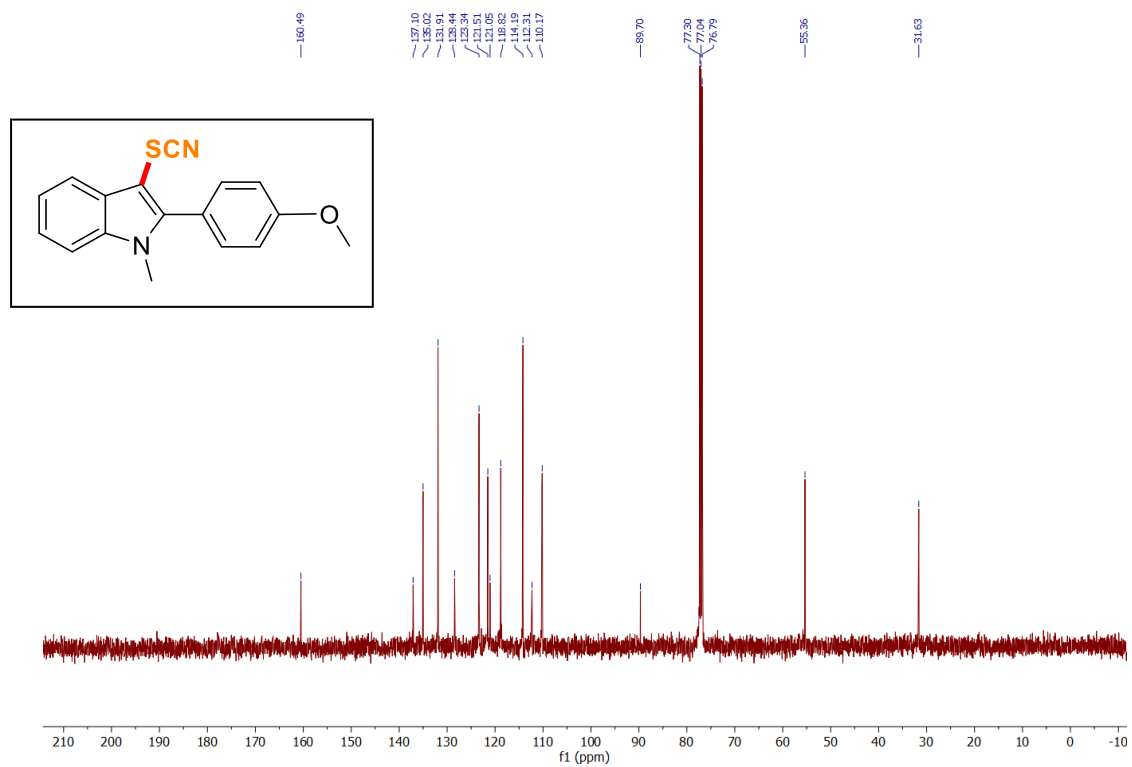
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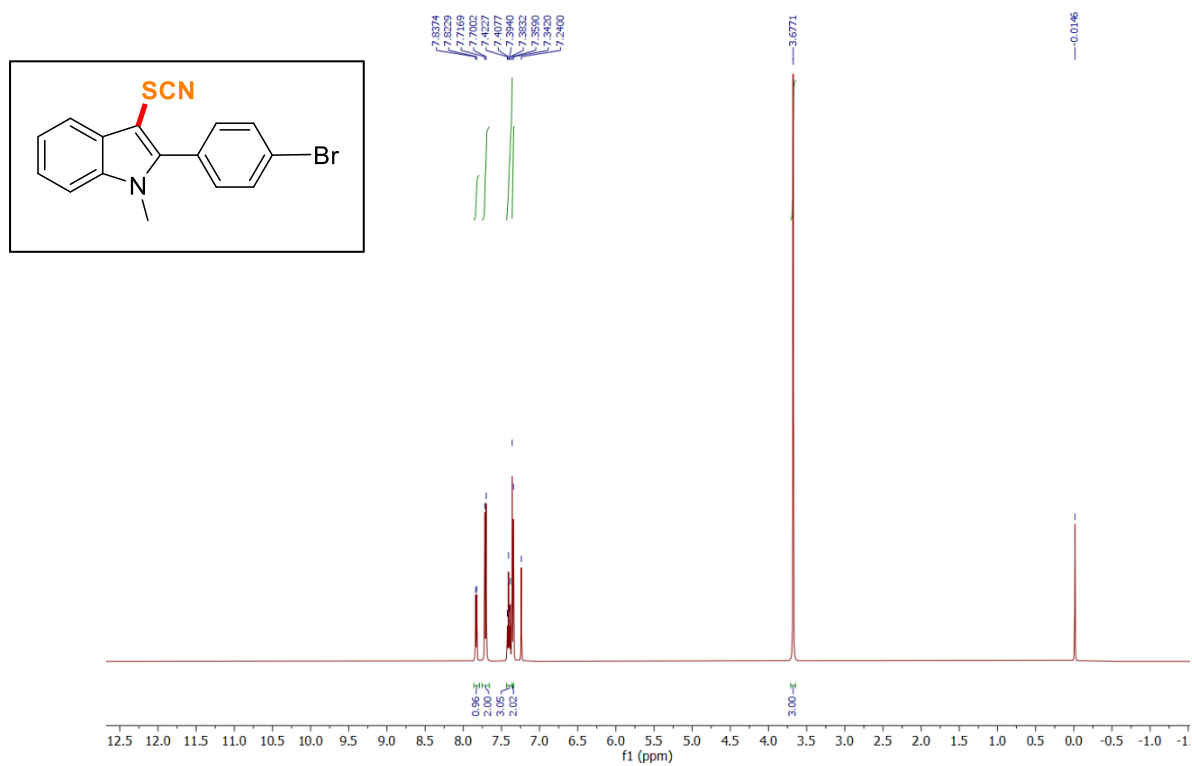
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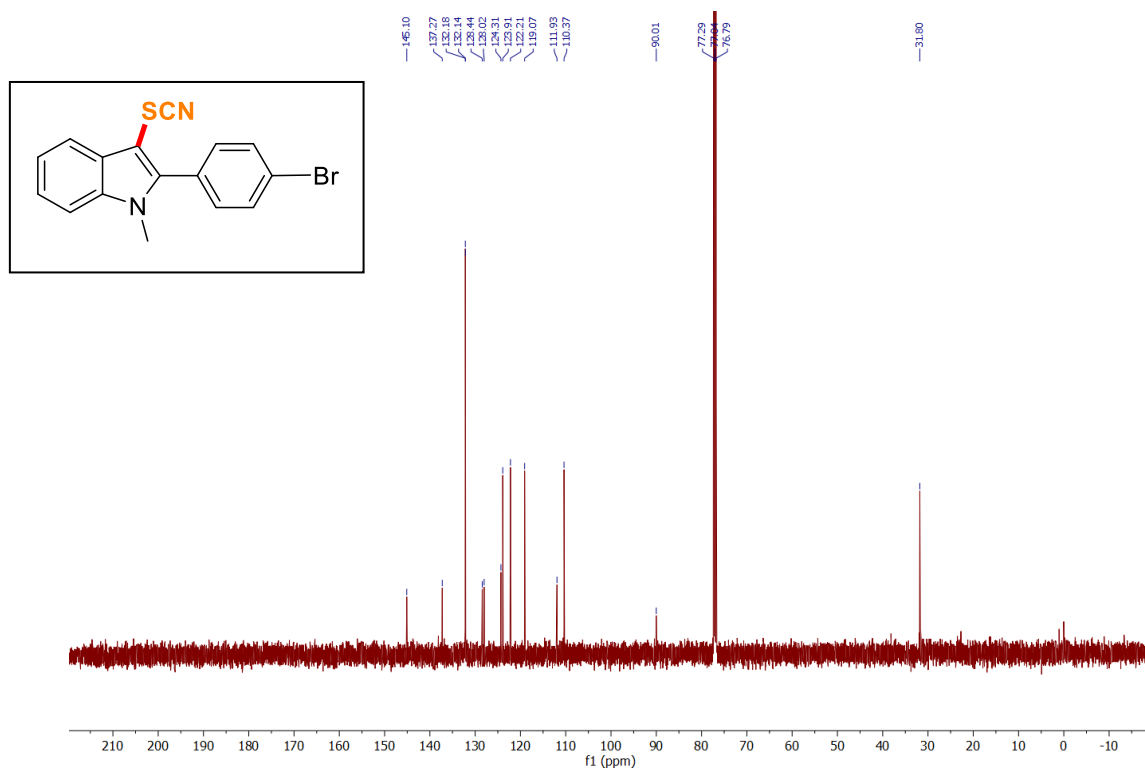
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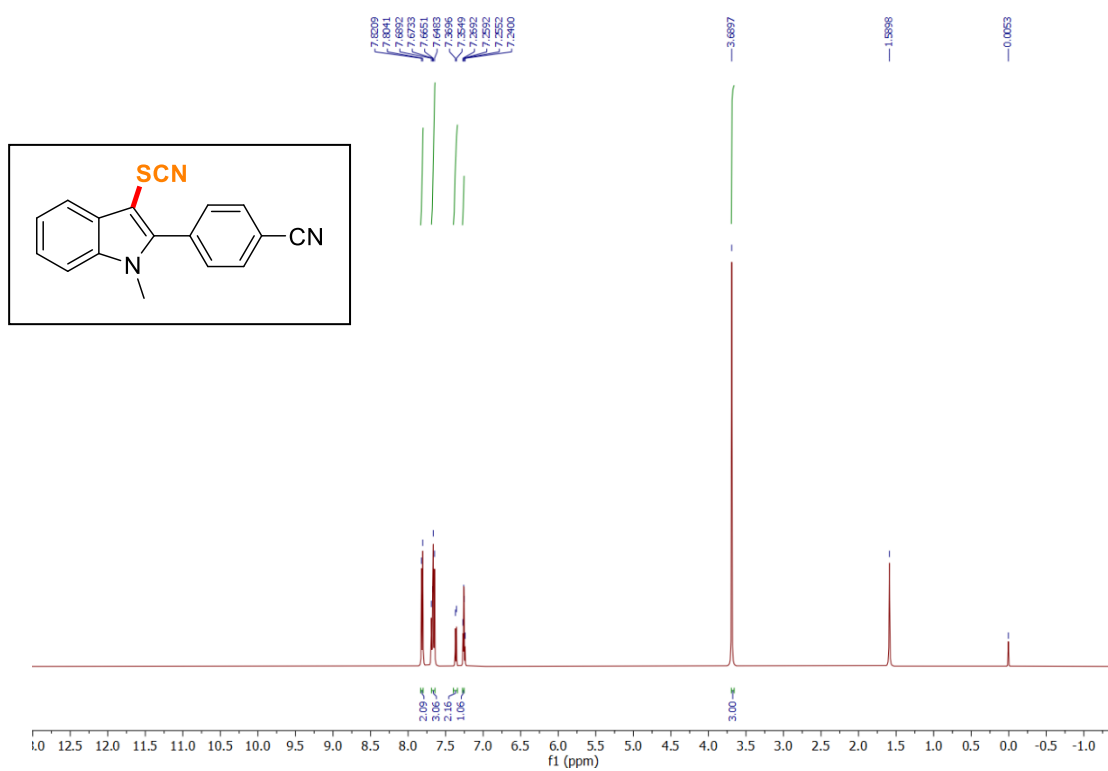
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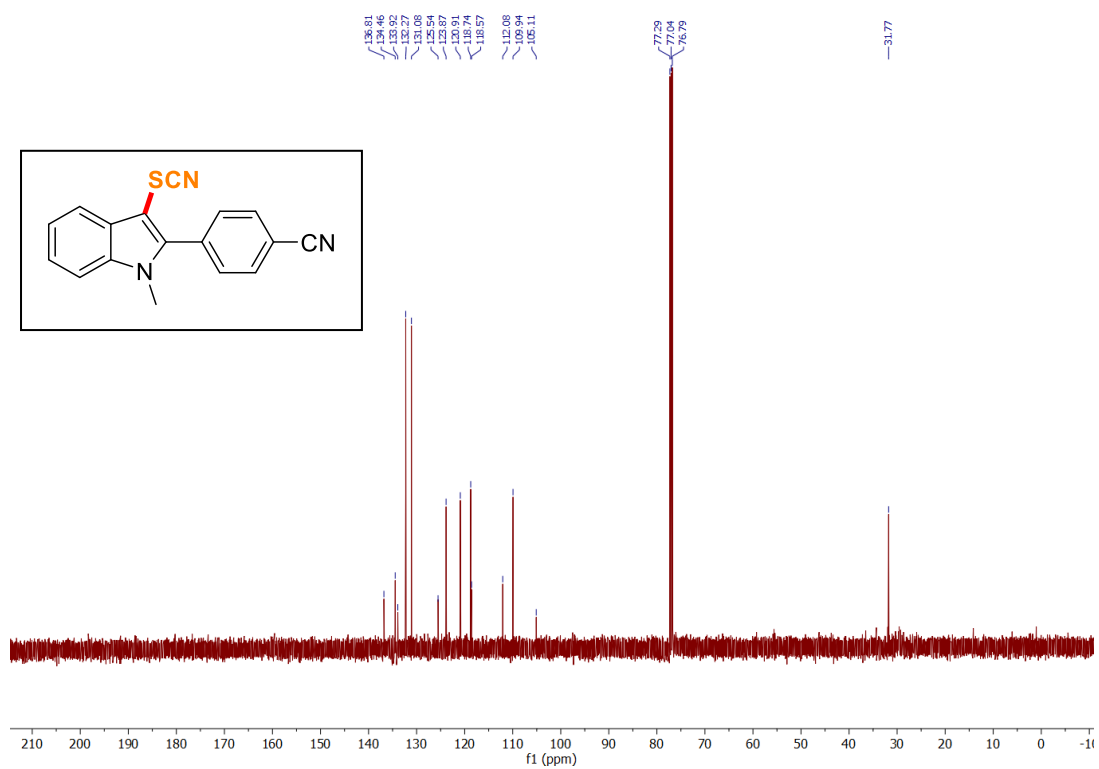
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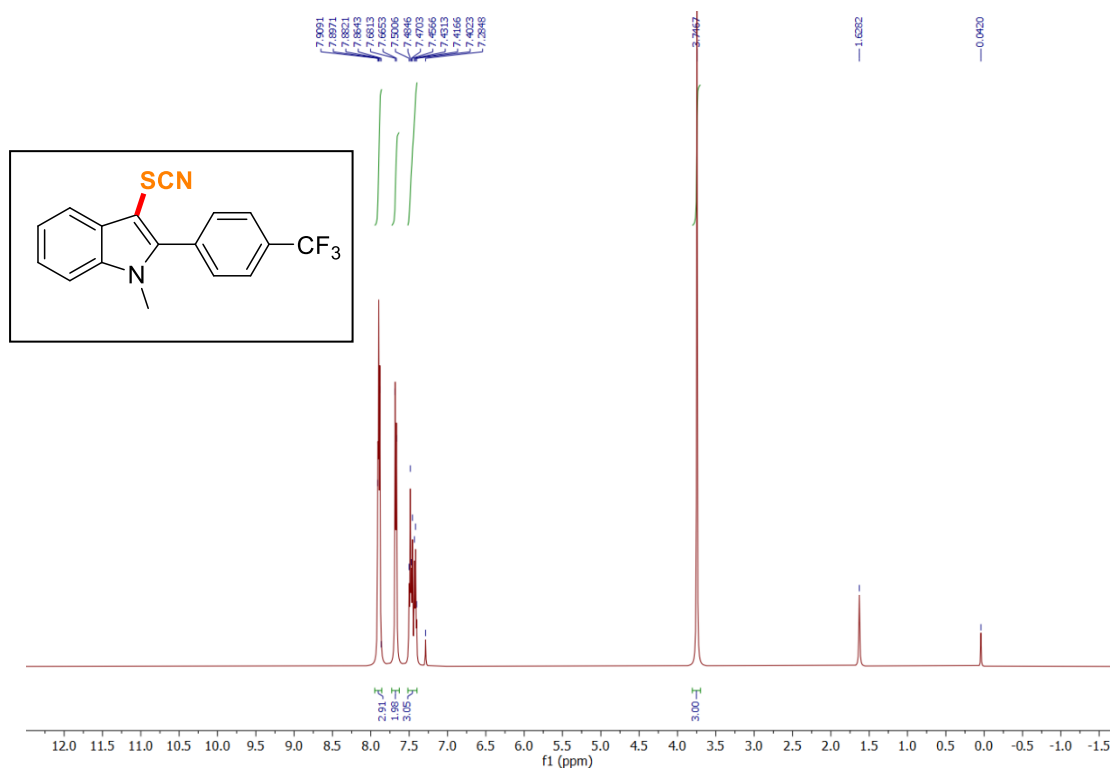
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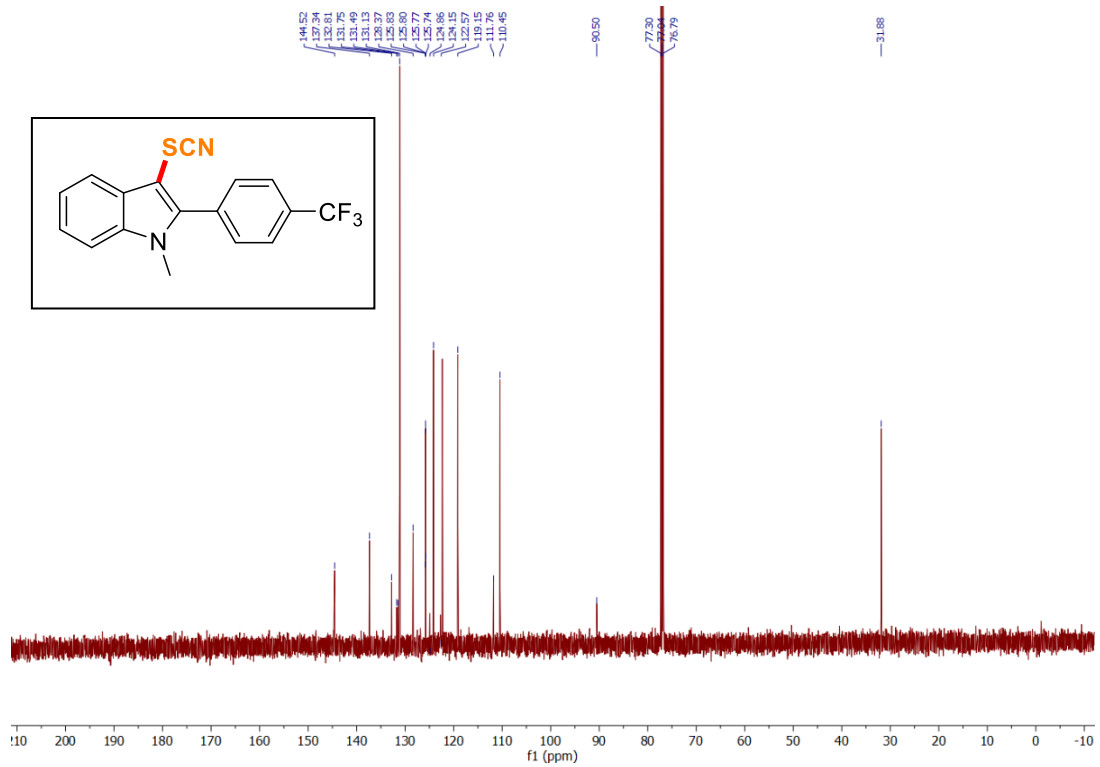
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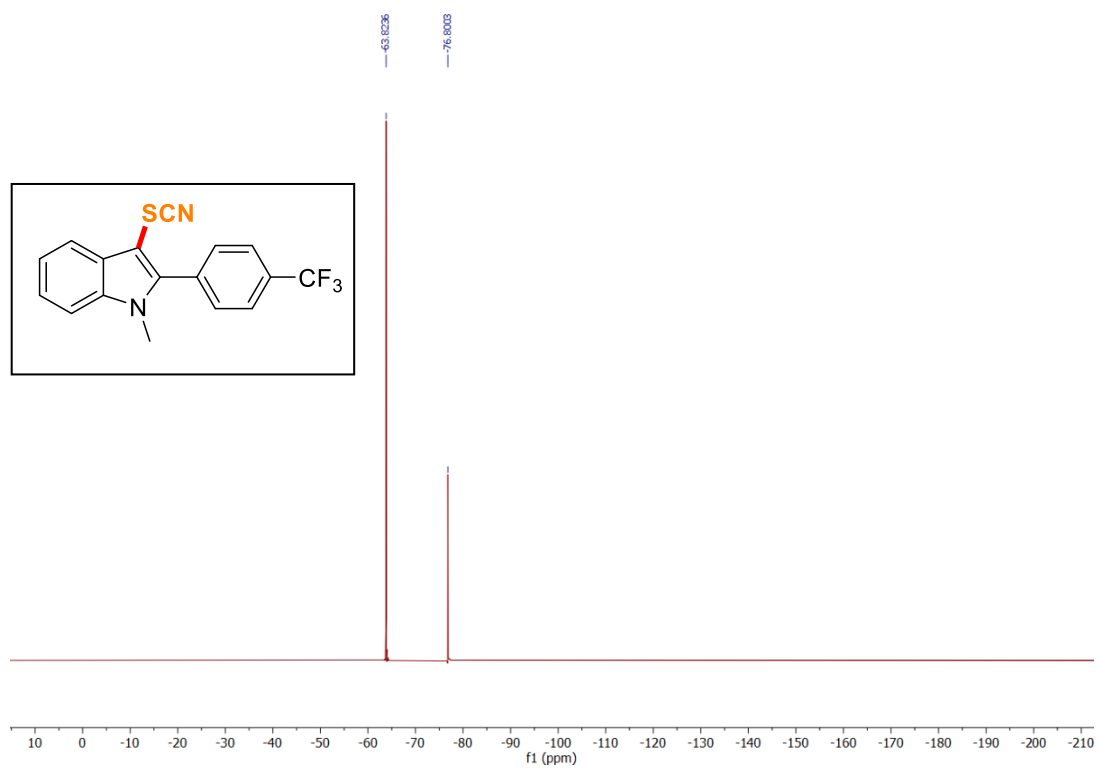
$^1\text{H}$  NMR spectrum of compound **2s**, ( $\text{CDCl}_3$ , 500 MHz).



$^{13}\text{C}$  NMR spectrum of compound **2s**, ( $\text{CDCl}_3$ , 125 MHz).

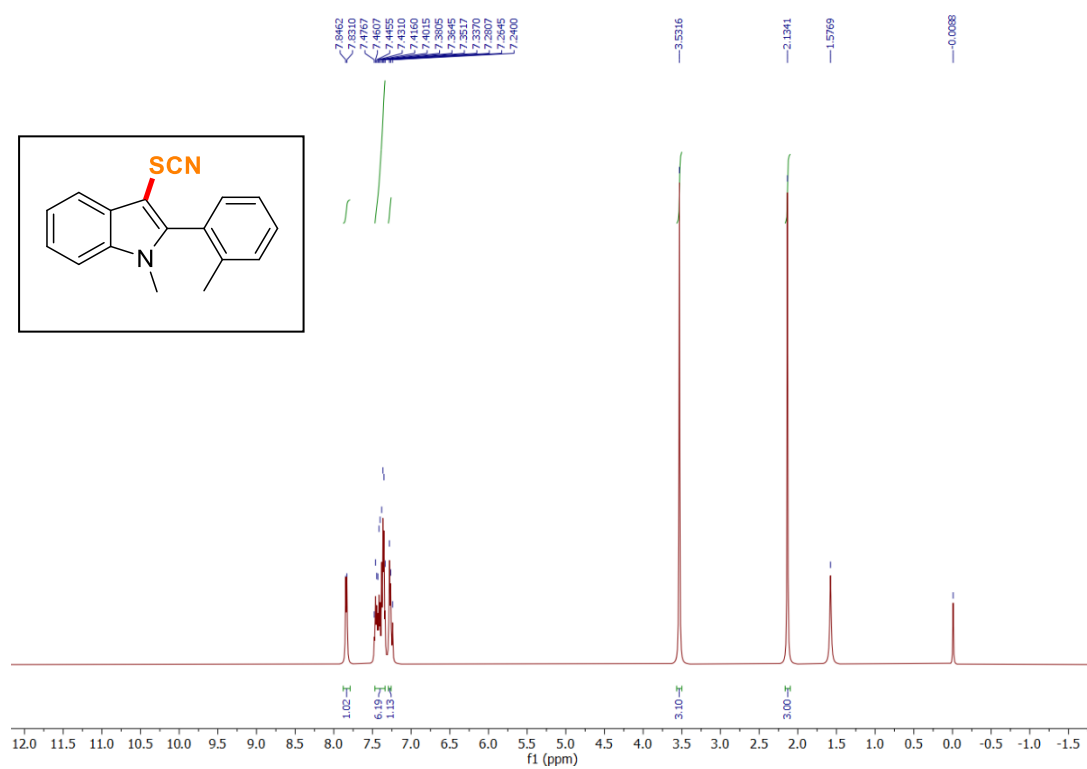


$^{19}\text{F}$  NMR spectrum of compound **2s**, ( $\text{CDCl}_3$ , 470 MHz).

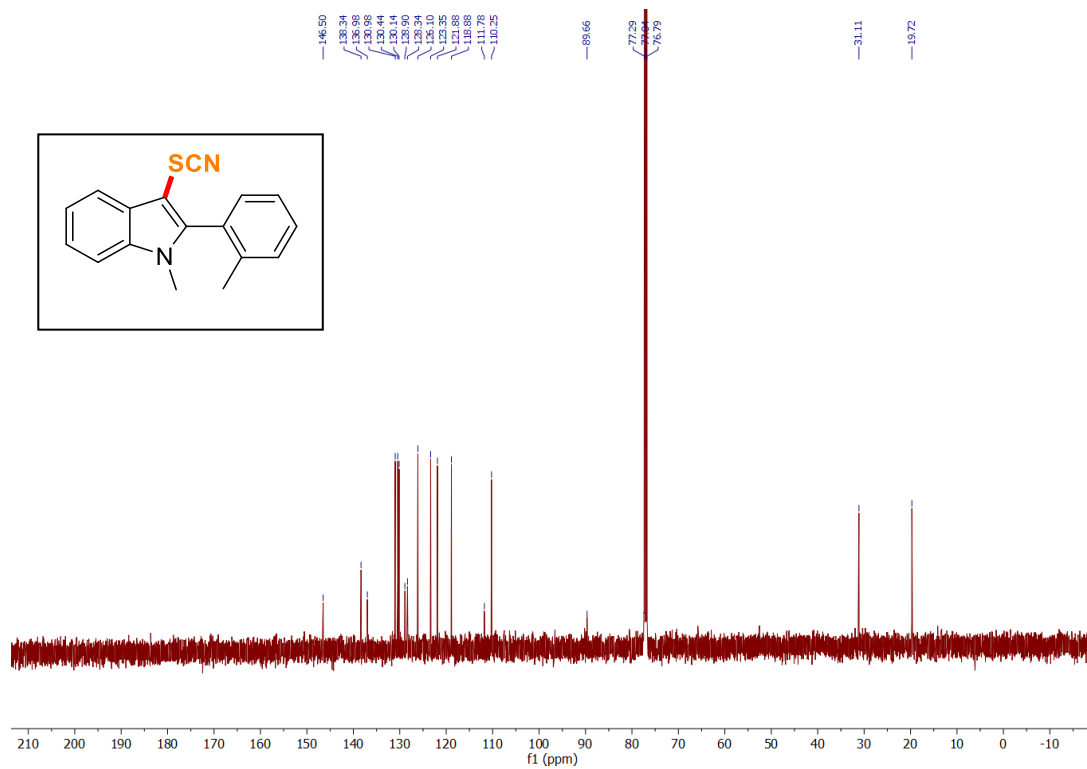




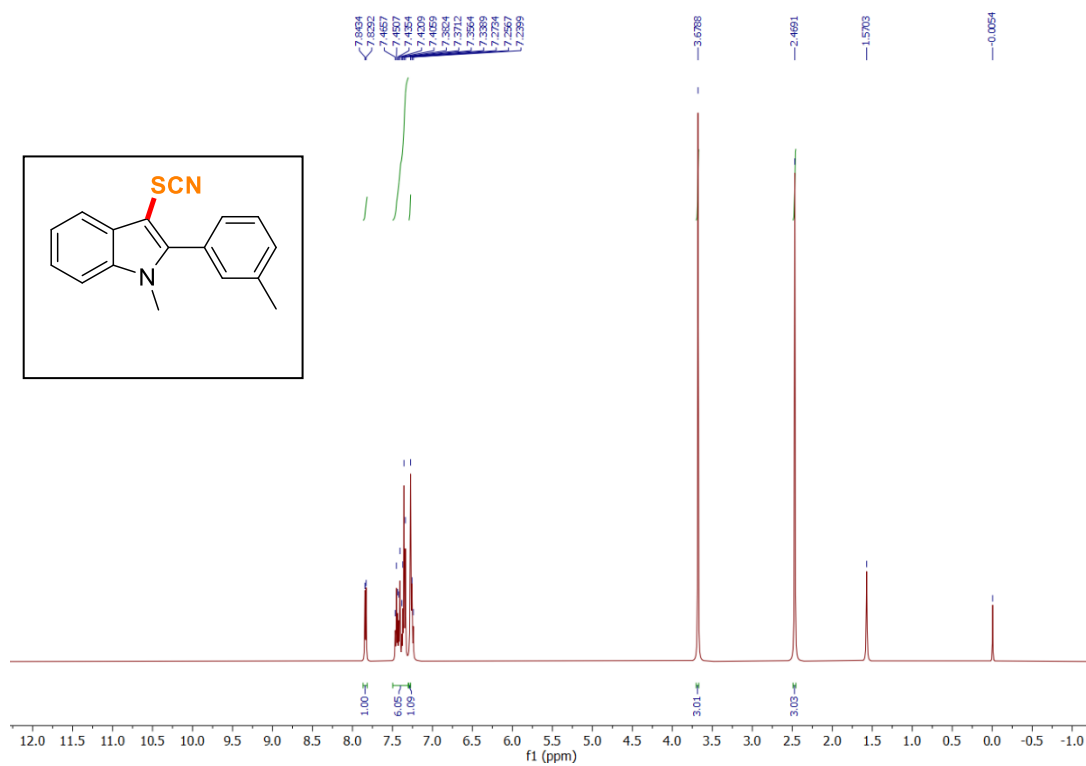
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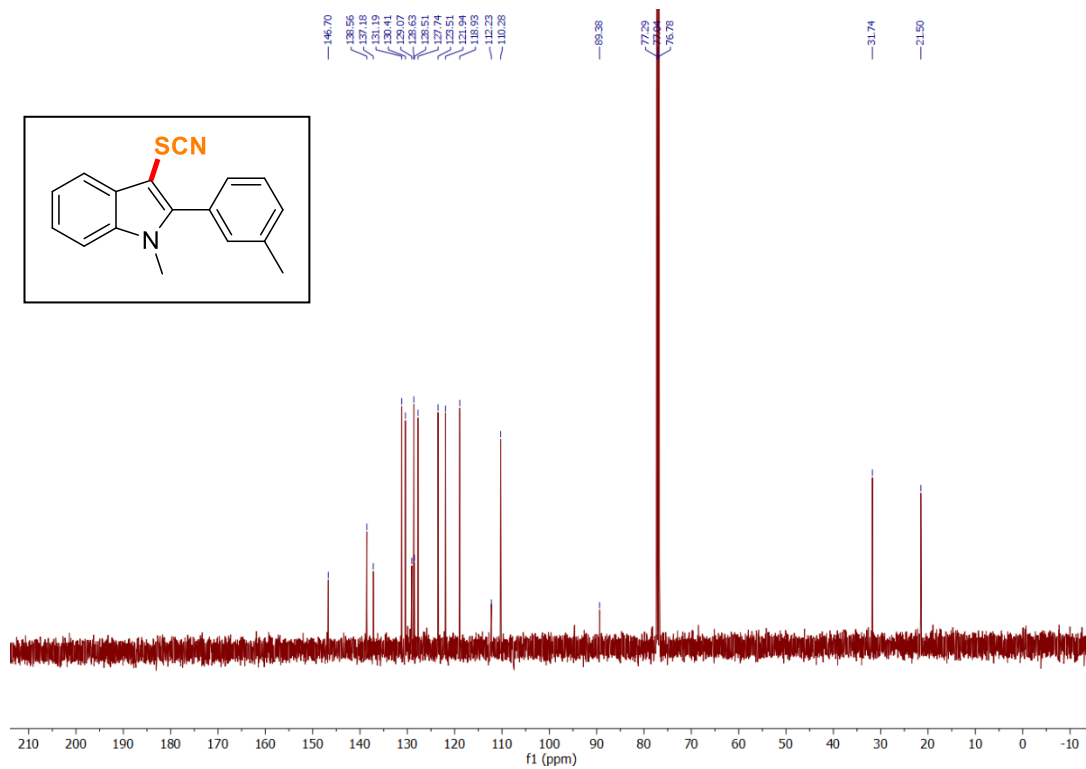
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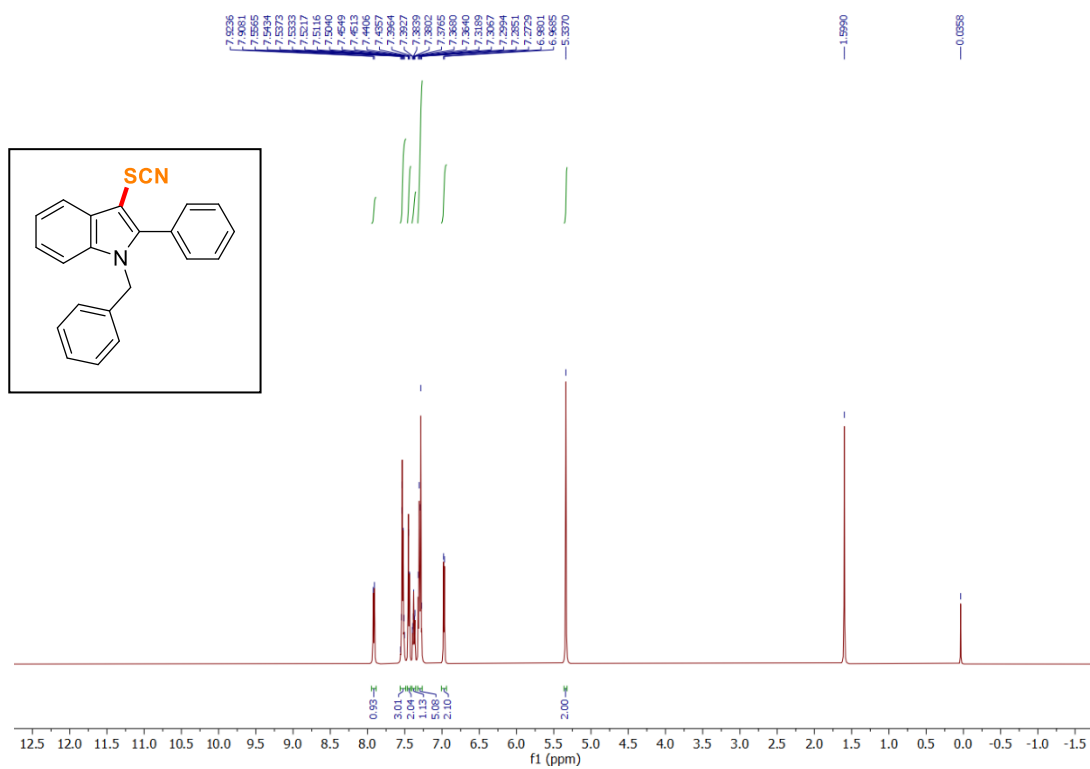
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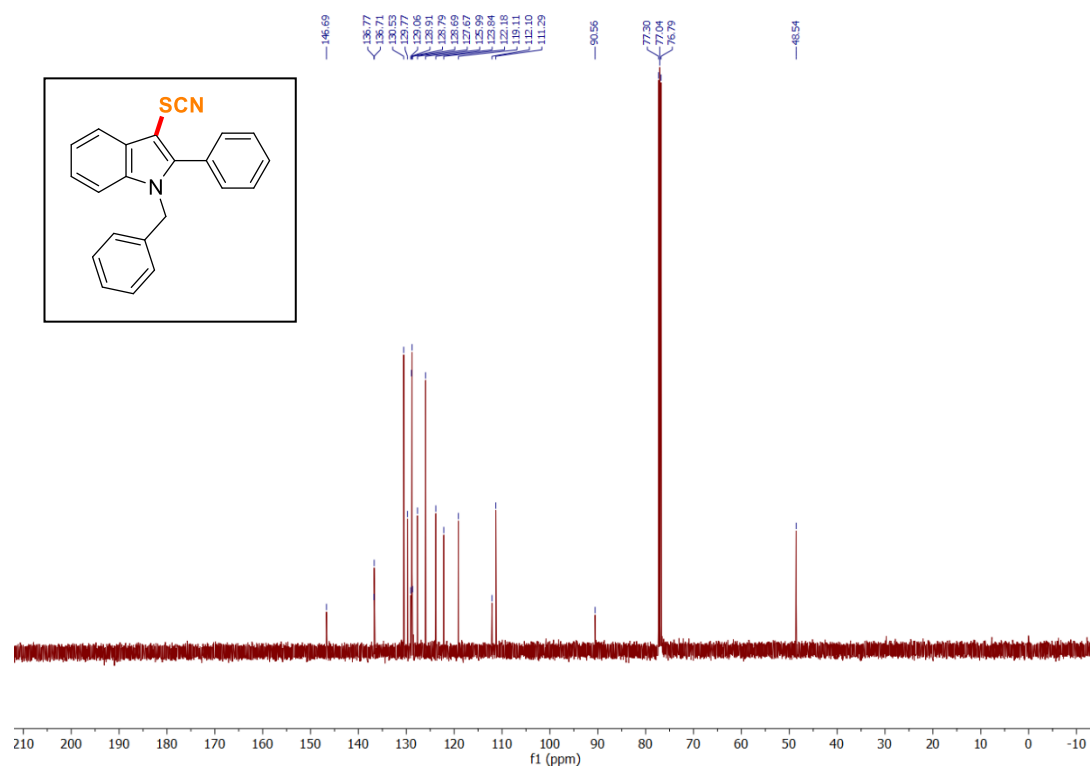
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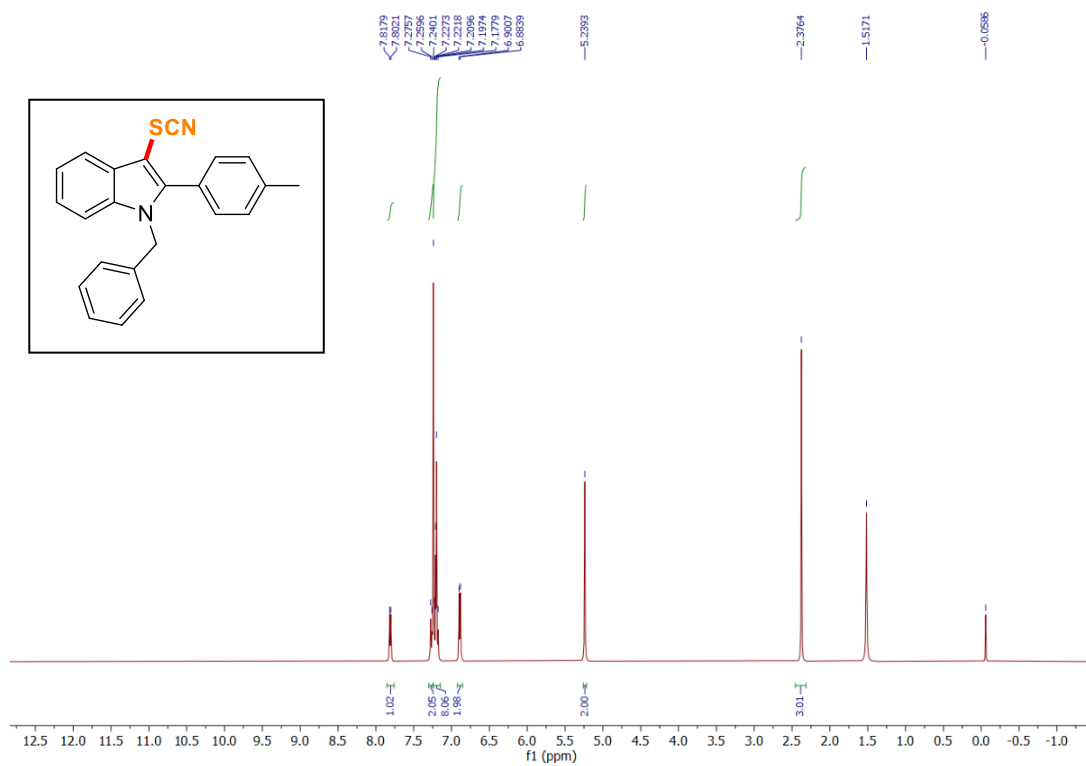
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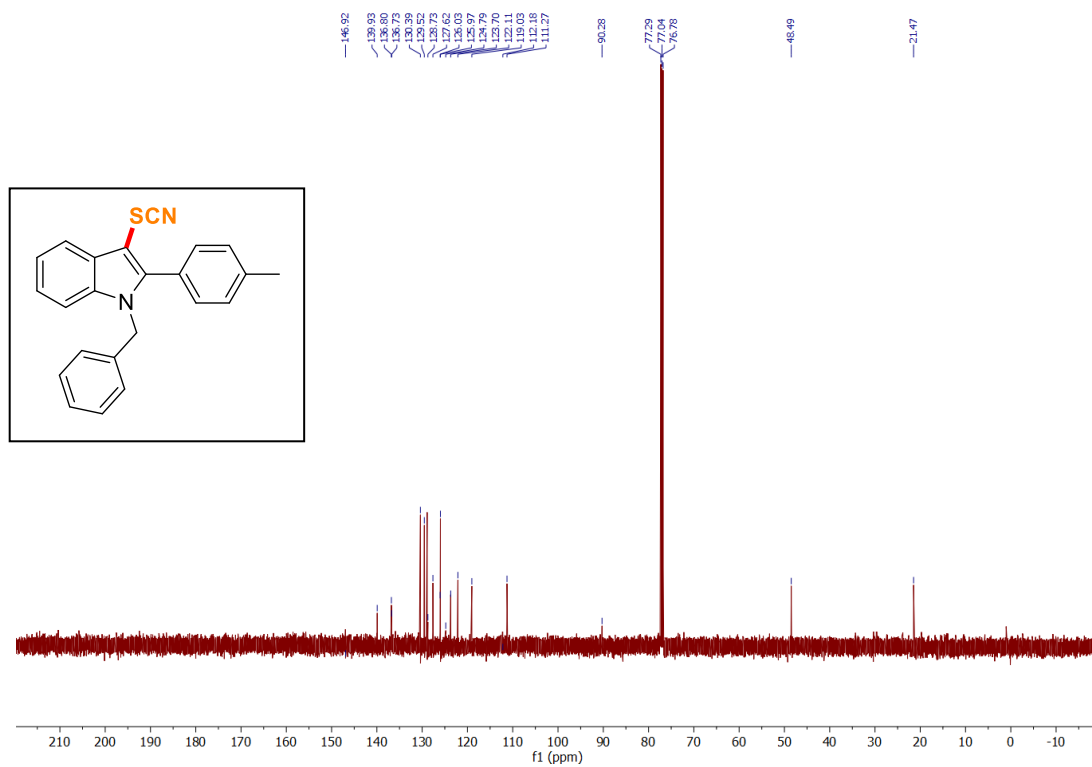
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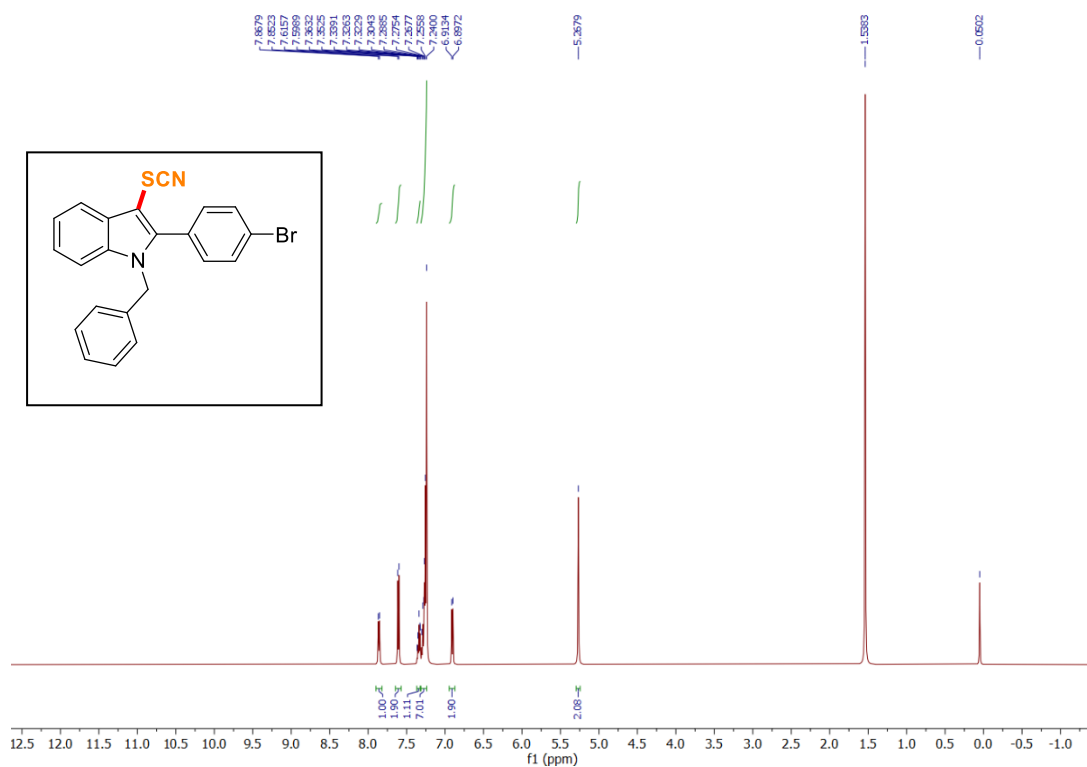
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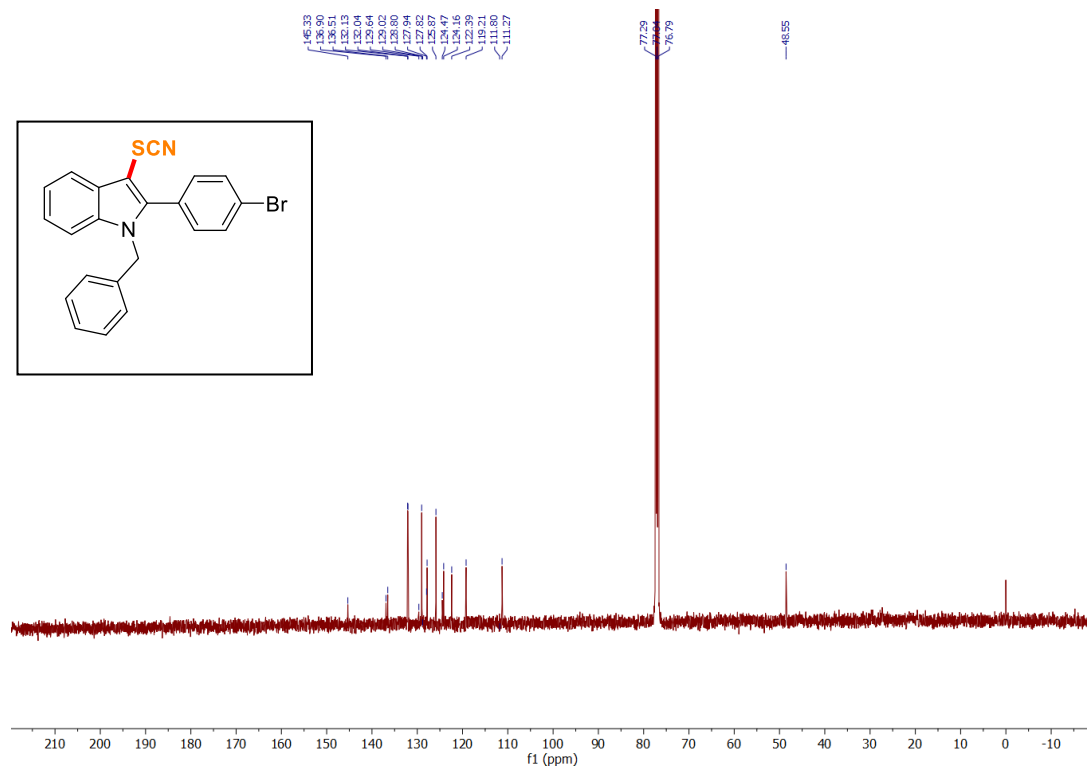
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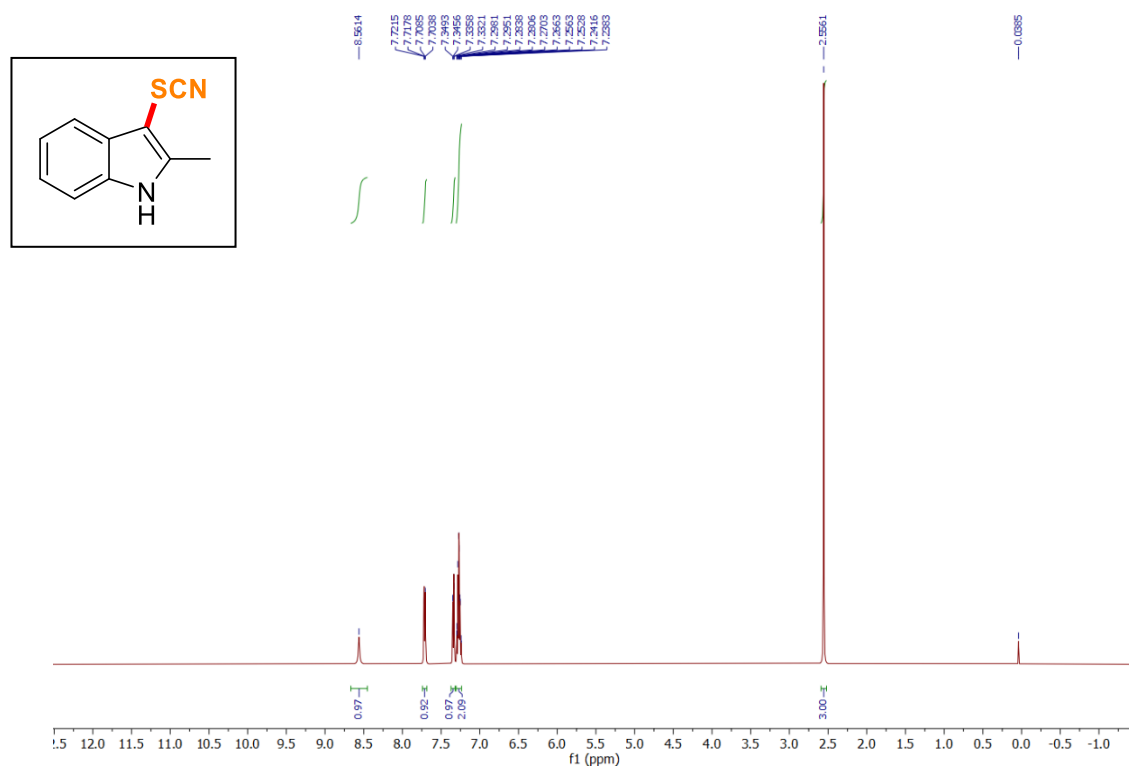
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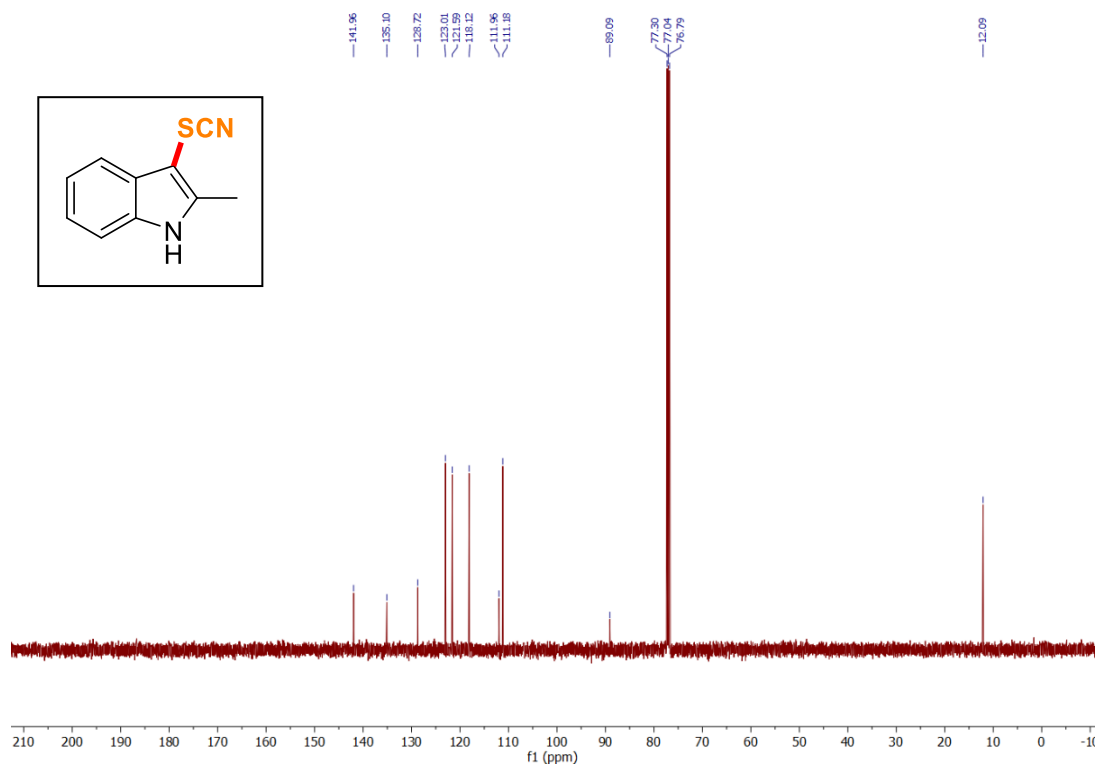
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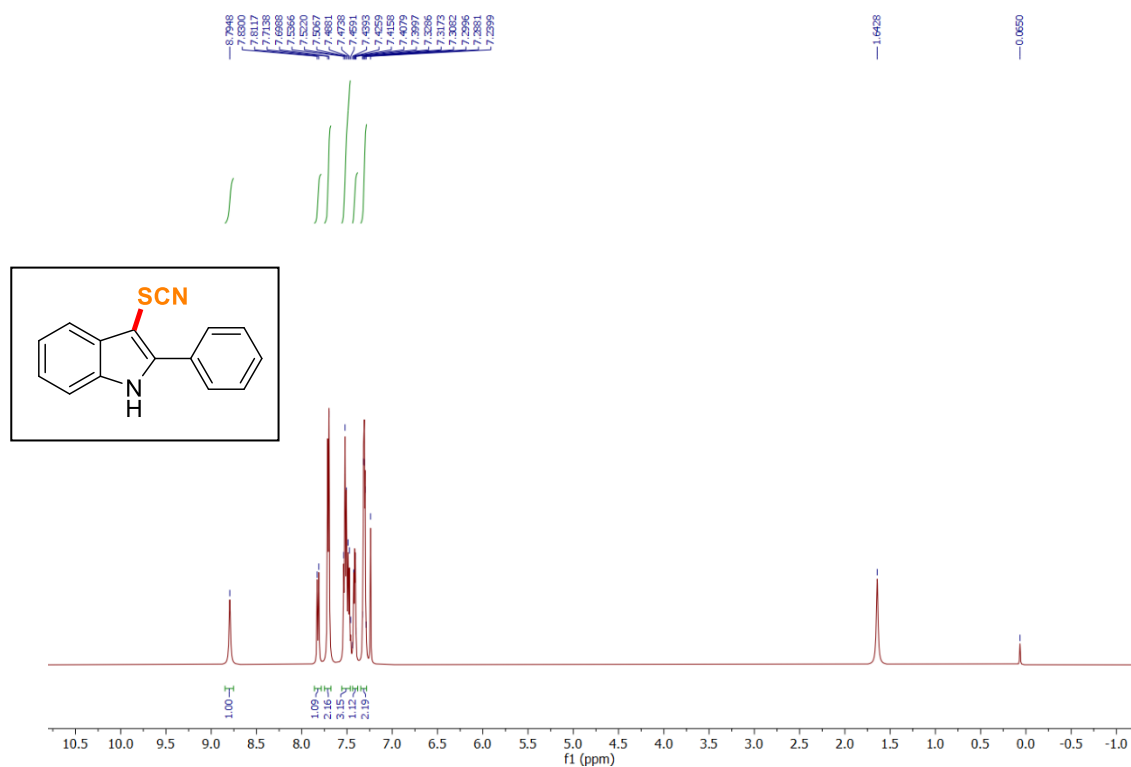
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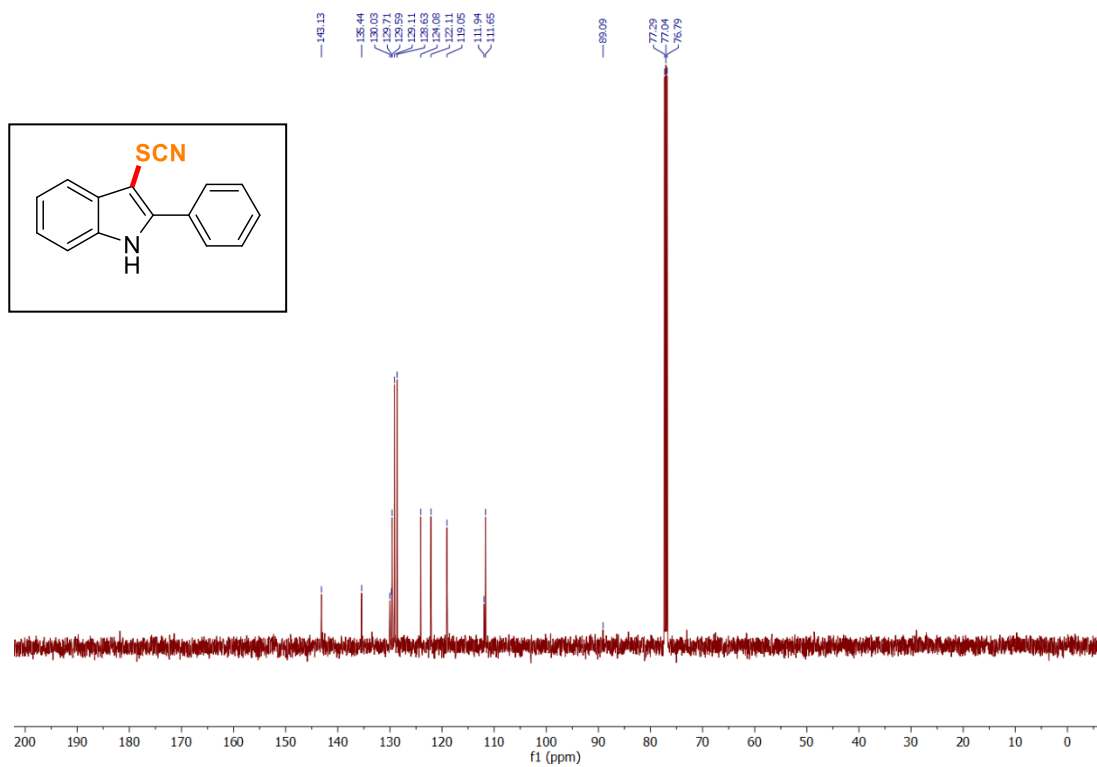
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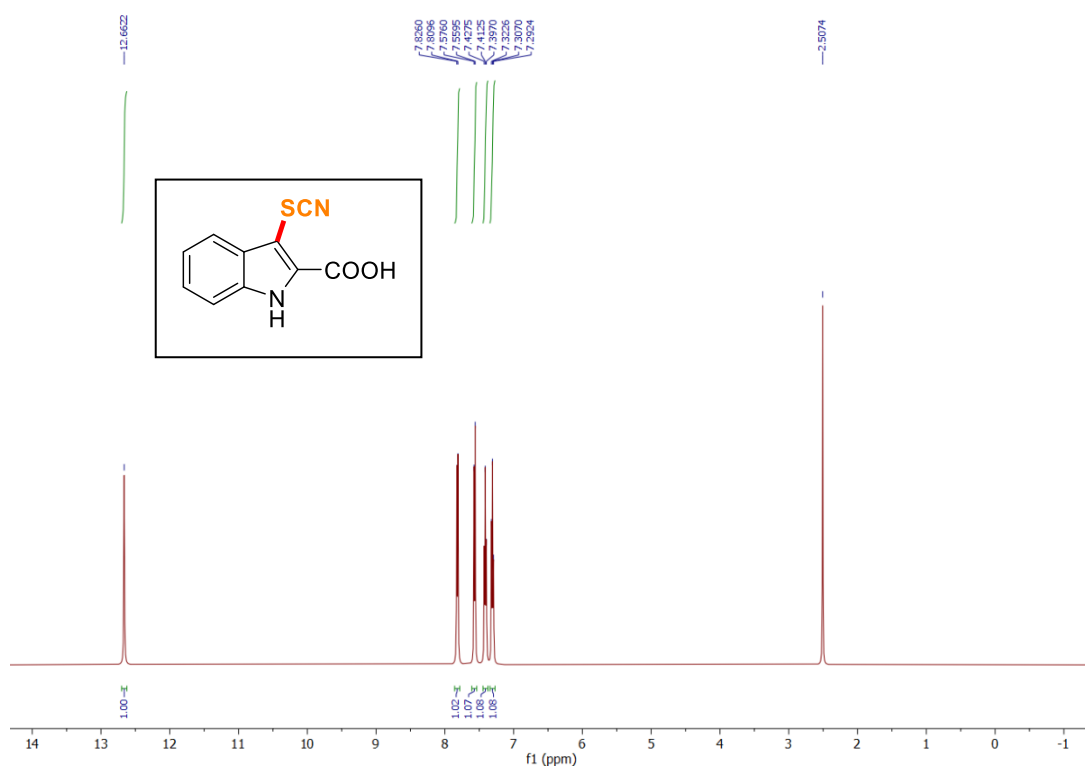
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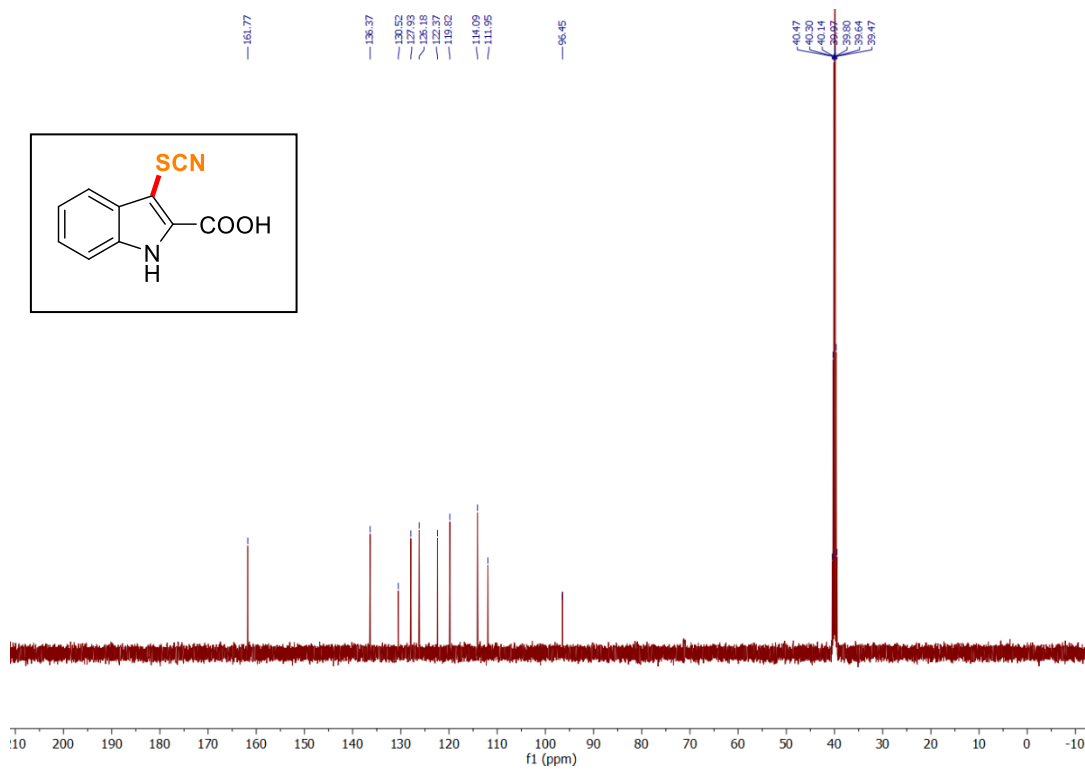
$^{13}\text{C}$  NMR spectrum of compound **2z**, ( $\text{CDCl}_3$ , 125 MHz).



$^1\text{H}$  NMR spectrum of compound **2aa**, (DMSO- $d_6$ , 500 MHz).

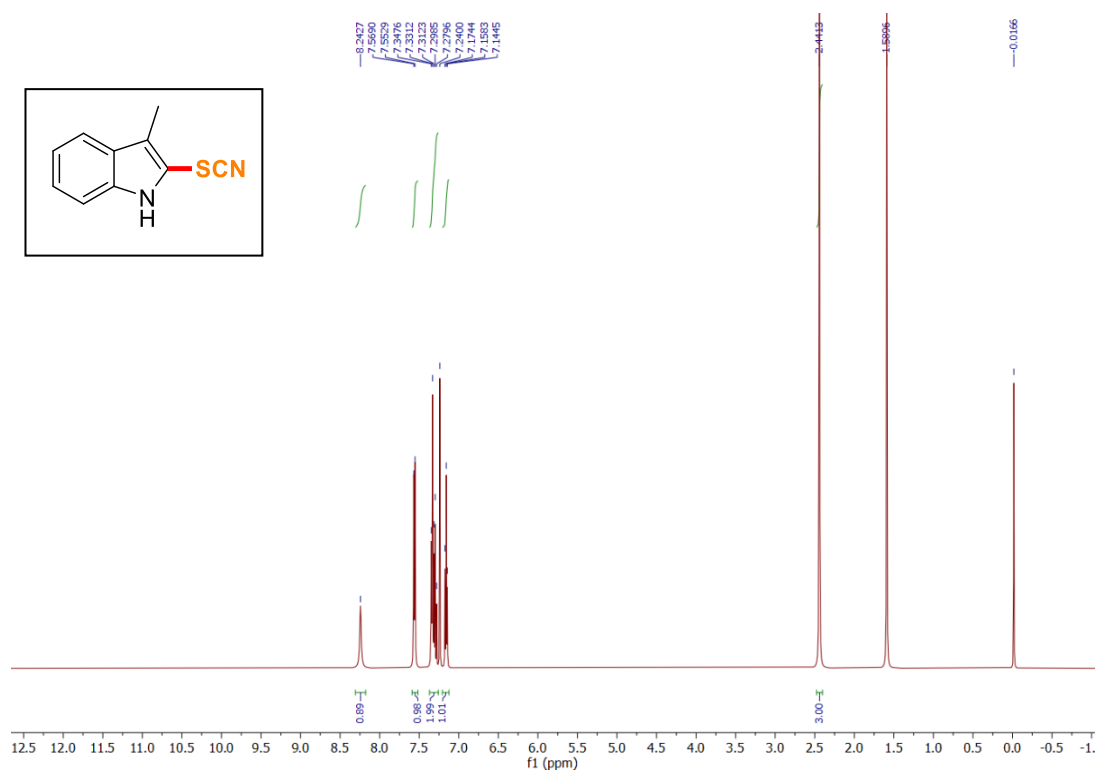


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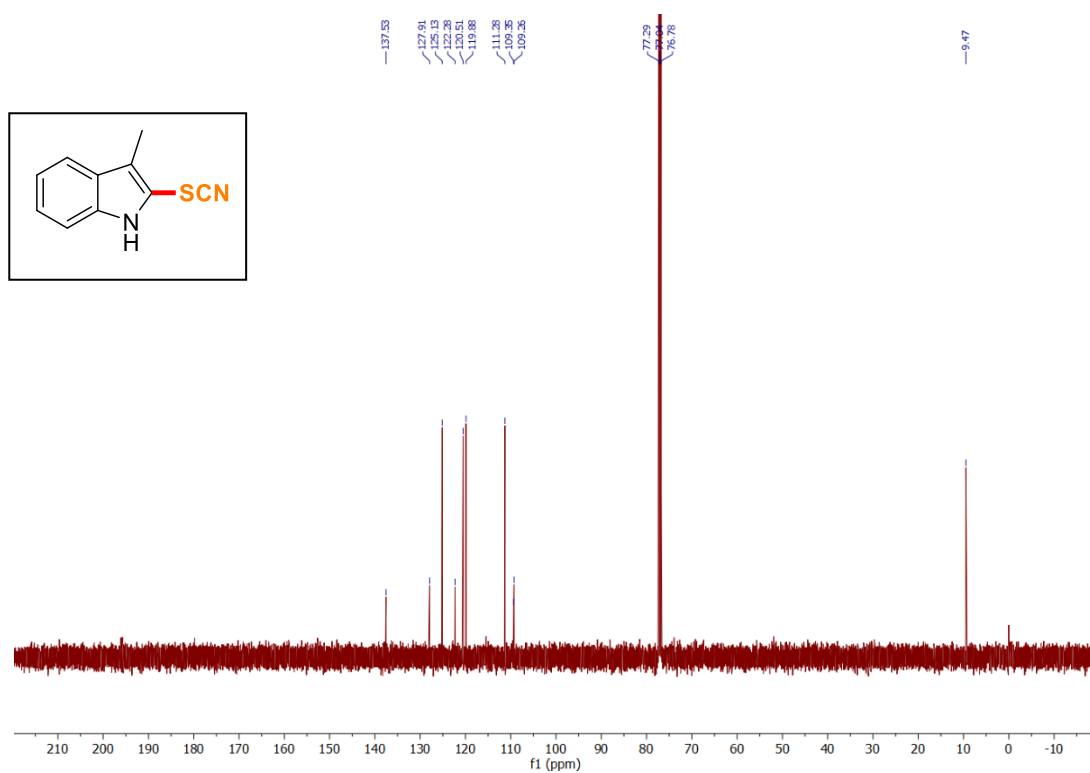




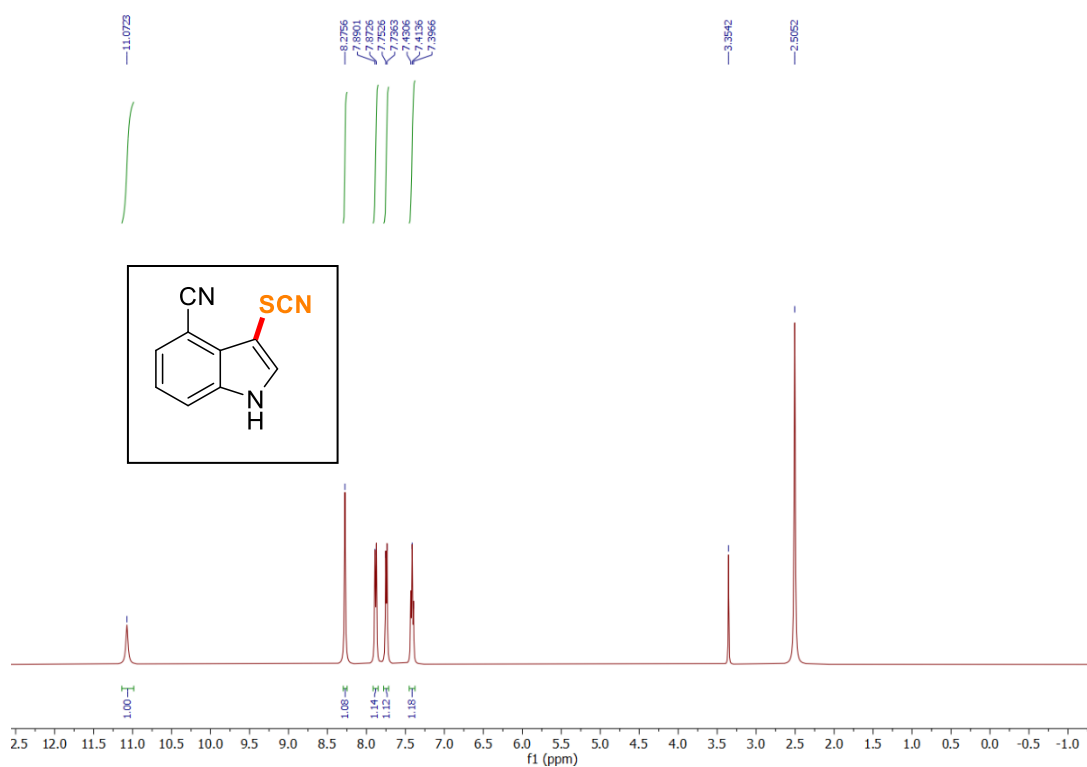
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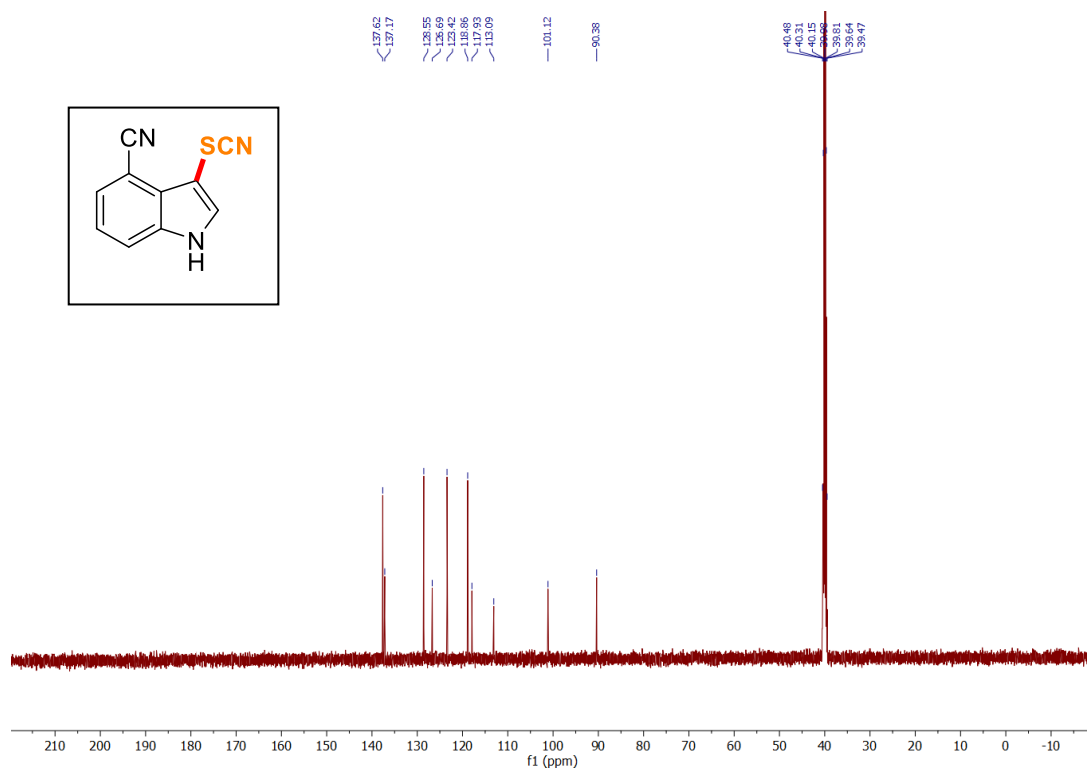
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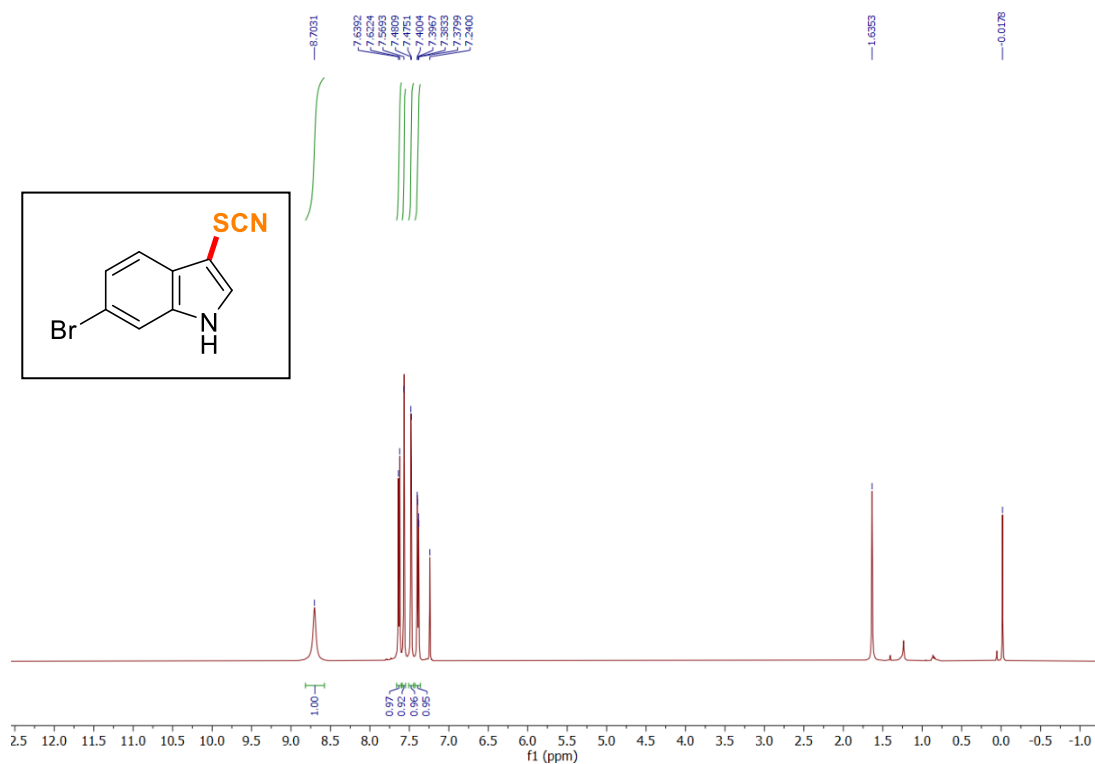
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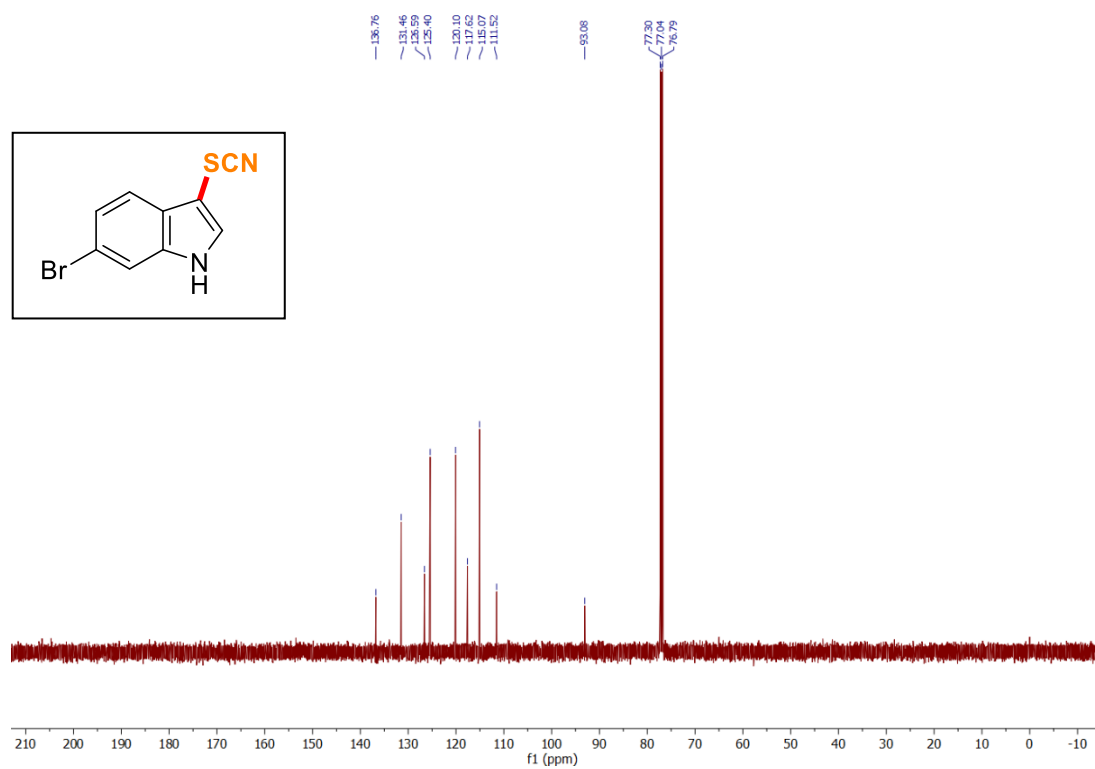
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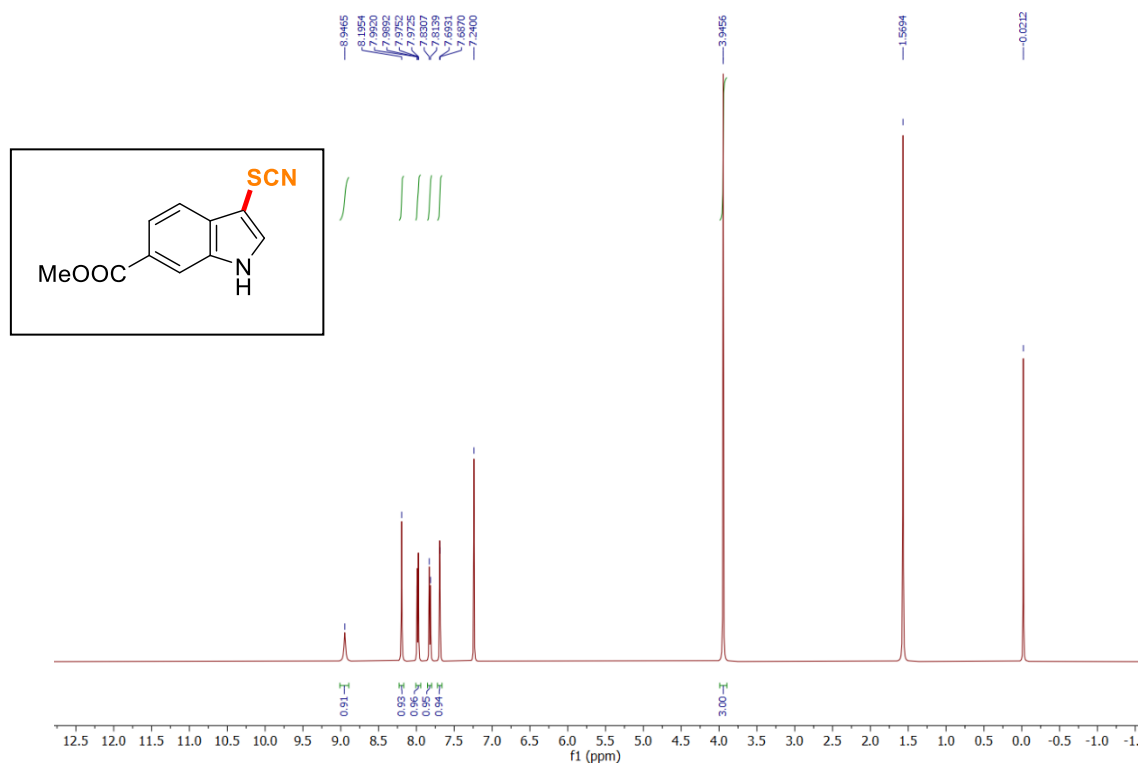
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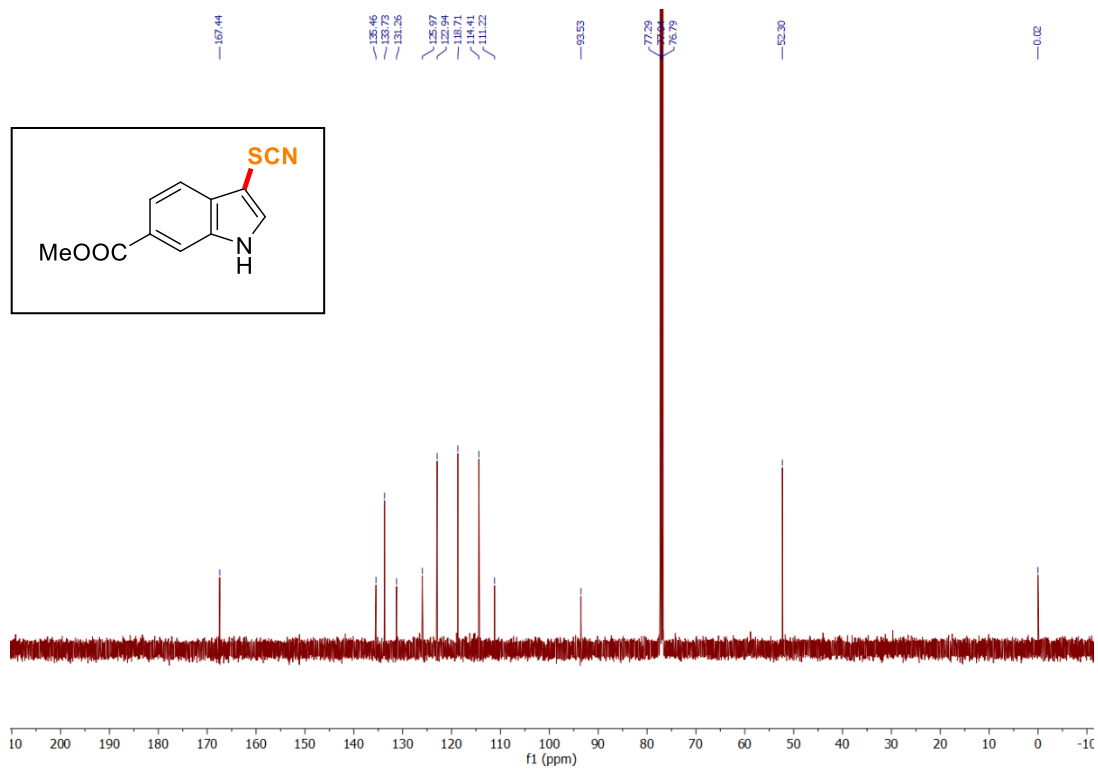
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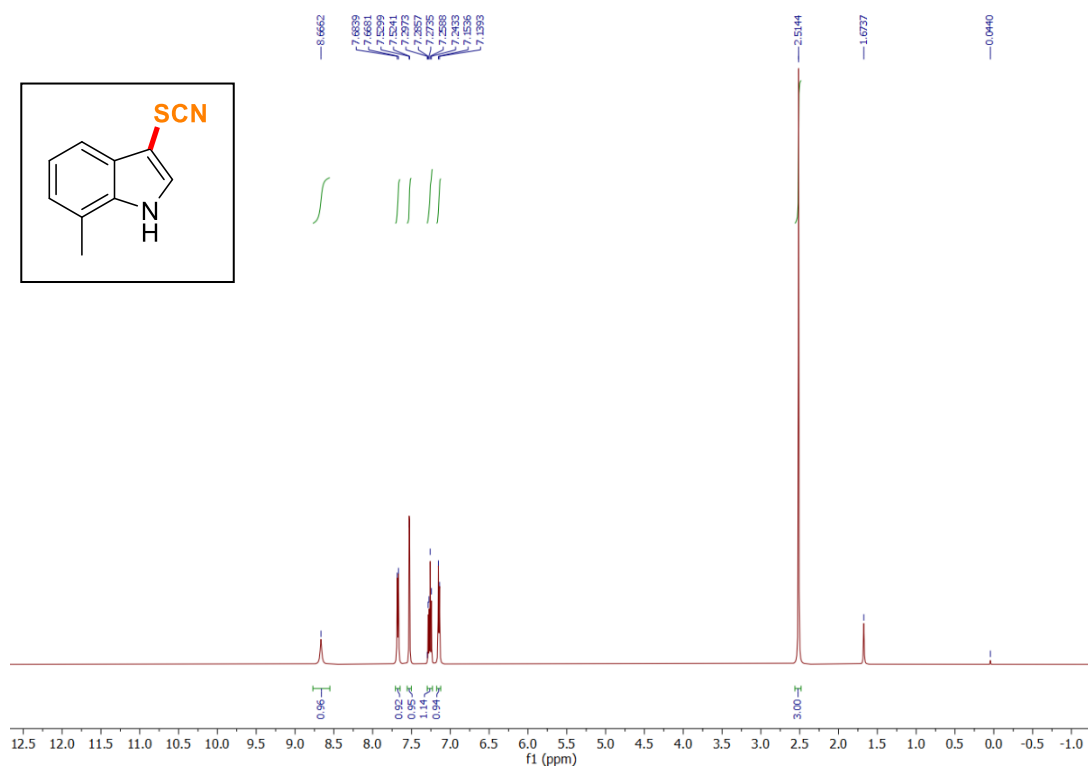
$^1\text{H}$  NMR spectrum of compound **2ae**, ( $\text{CDCl}_3$ , 500 MHz).



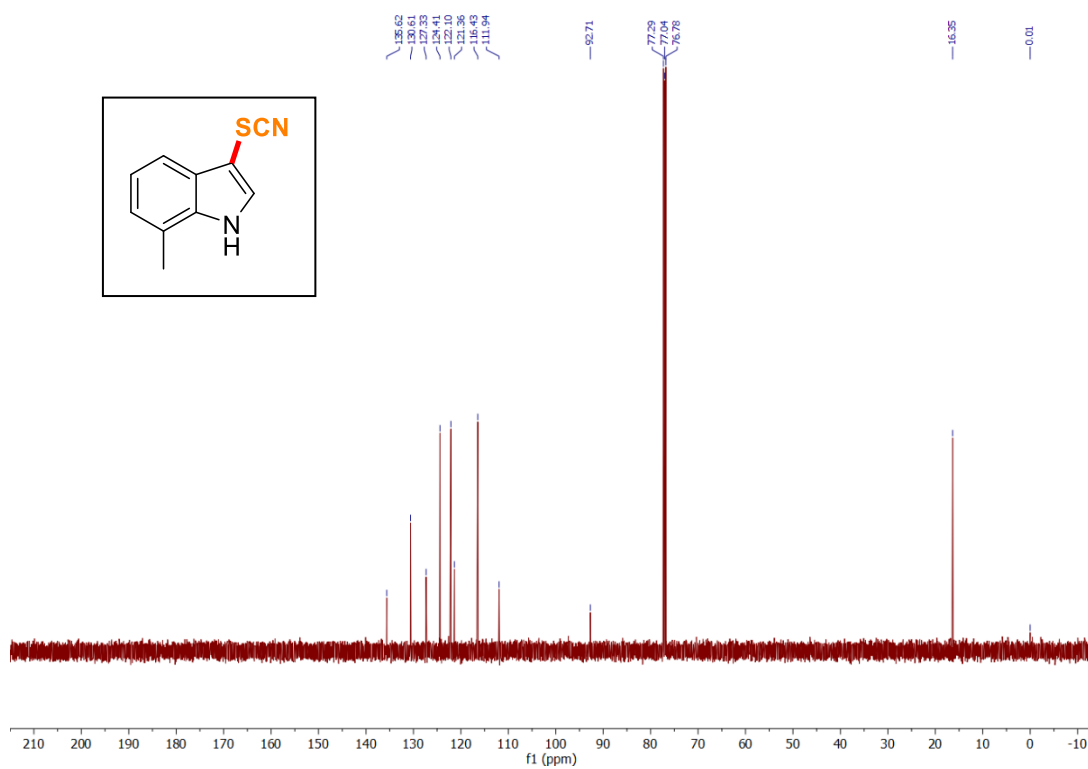
$^{13}\text{C}$  NMR spectrum of compound **2ae**, ( $\text{CDCl}_3$ , 125 MHz).



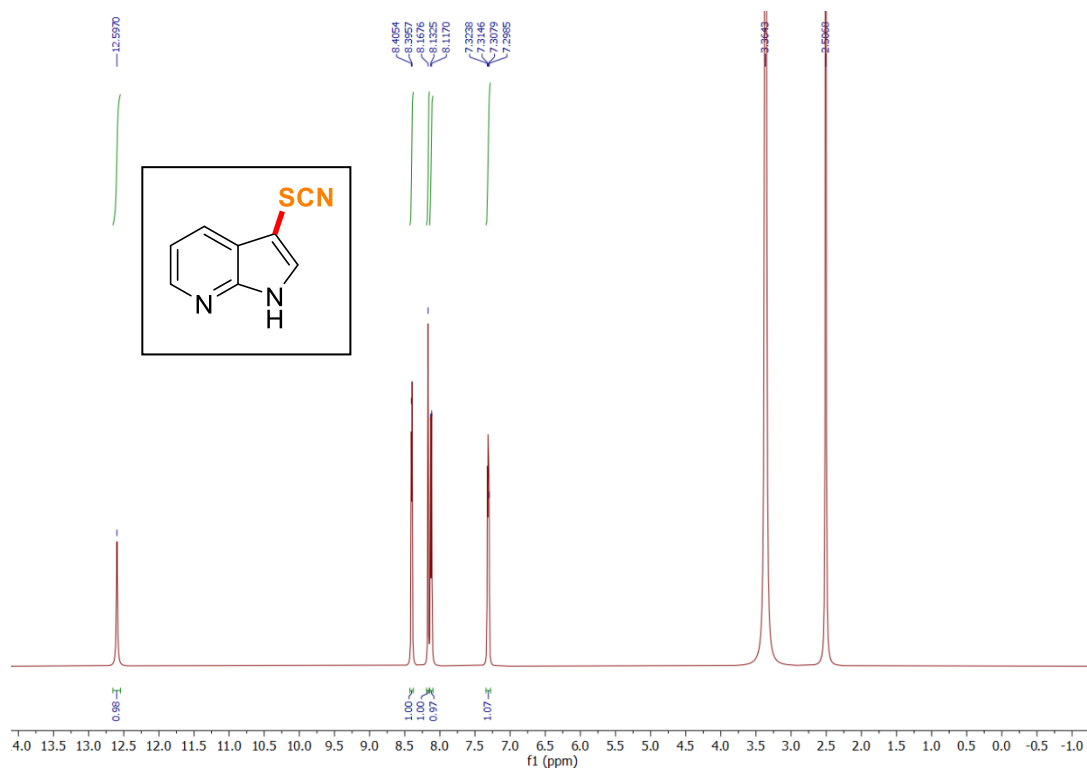
$^1\text{H}$  NMR spectrum of compound **2af**, ( $\text{CDCl}_3$ , 500 MHz).



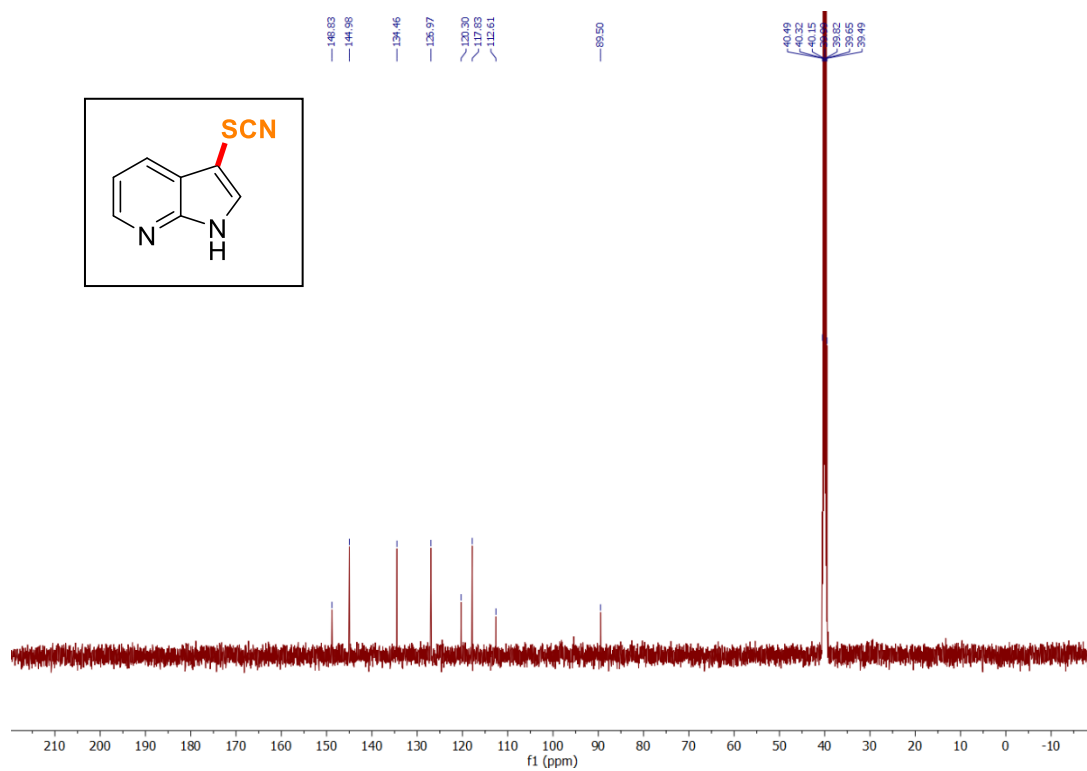
$^{13}\text{C}$  NMR spectrum of compound **2af**, ( $\text{CDCl}_3$ , 125 MHz).



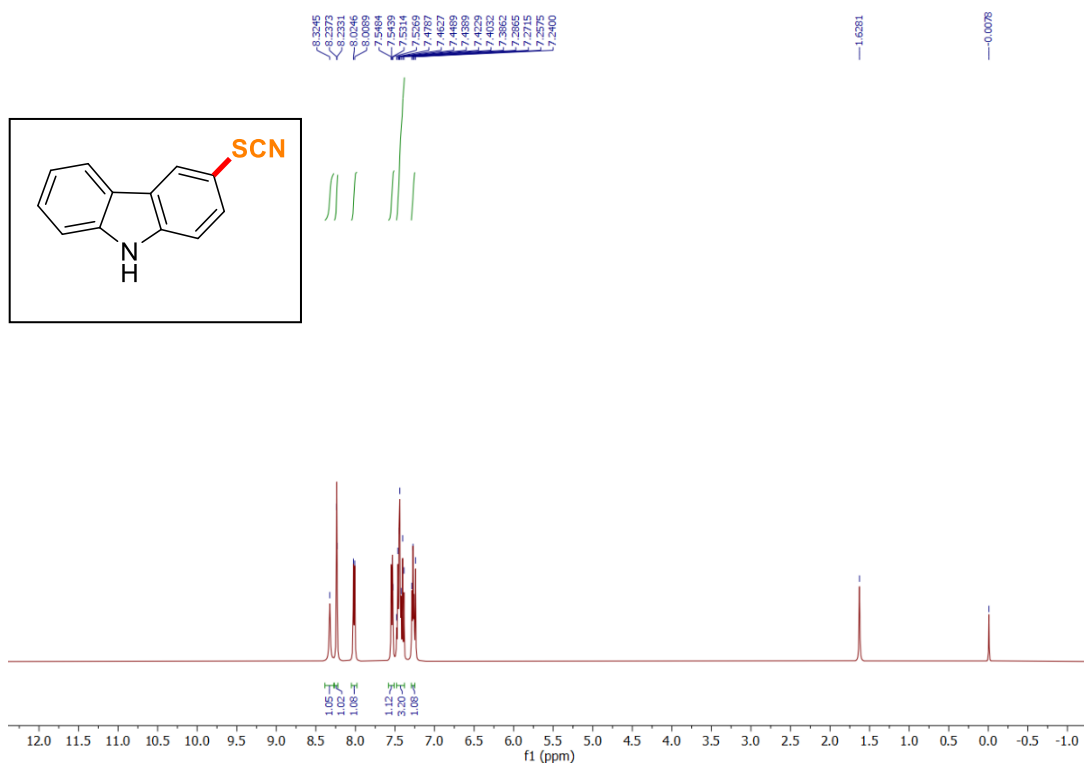
$^1\text{H}$  NMR spectrum of compound **2ag**, (DMSO- $d_6$ , 500 MHz).



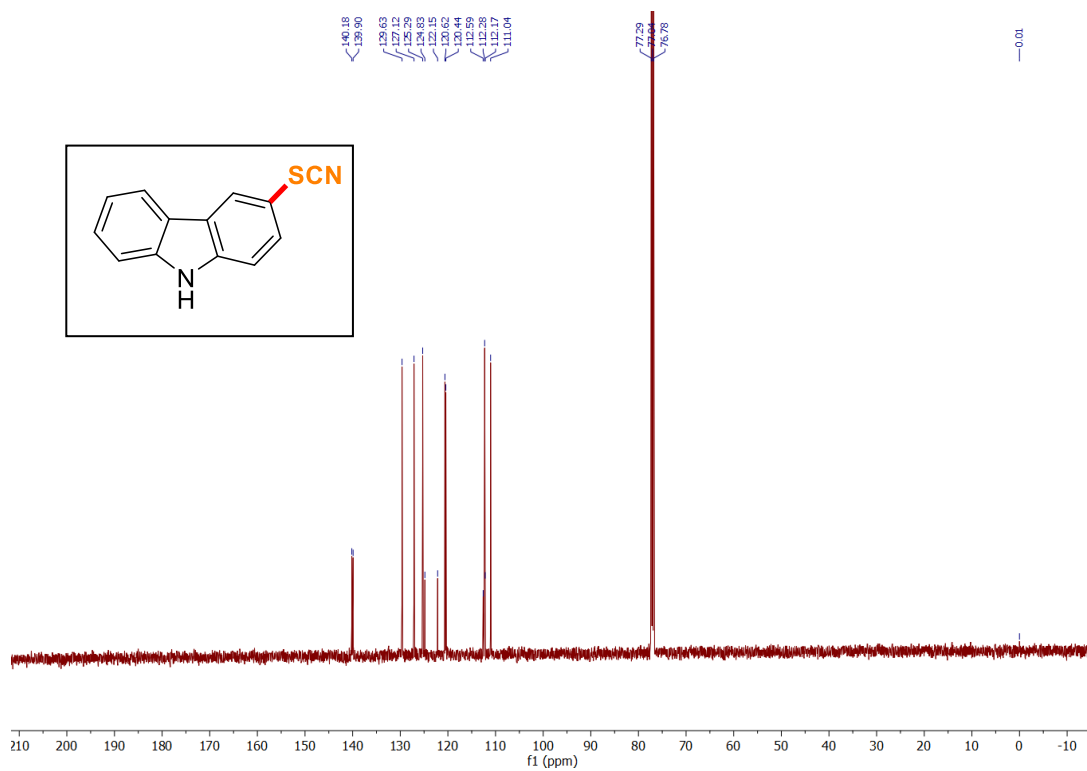
$^{13}\text{C}$  NMR spectrum of compound **2ag**, (DMSO- $d_6$ , 125 MHz).



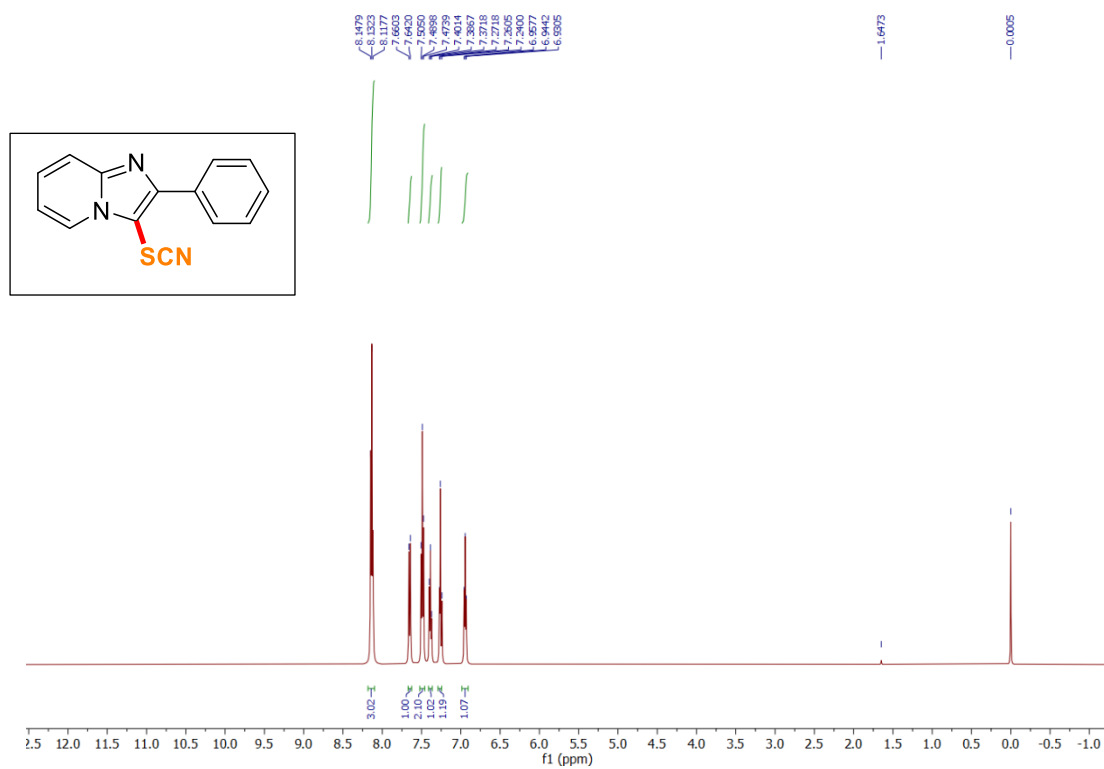
$^1\text{H}$  NMR spectrum of compound **2ah**, ( $\text{CDCl}_3$ , 500 MHz).



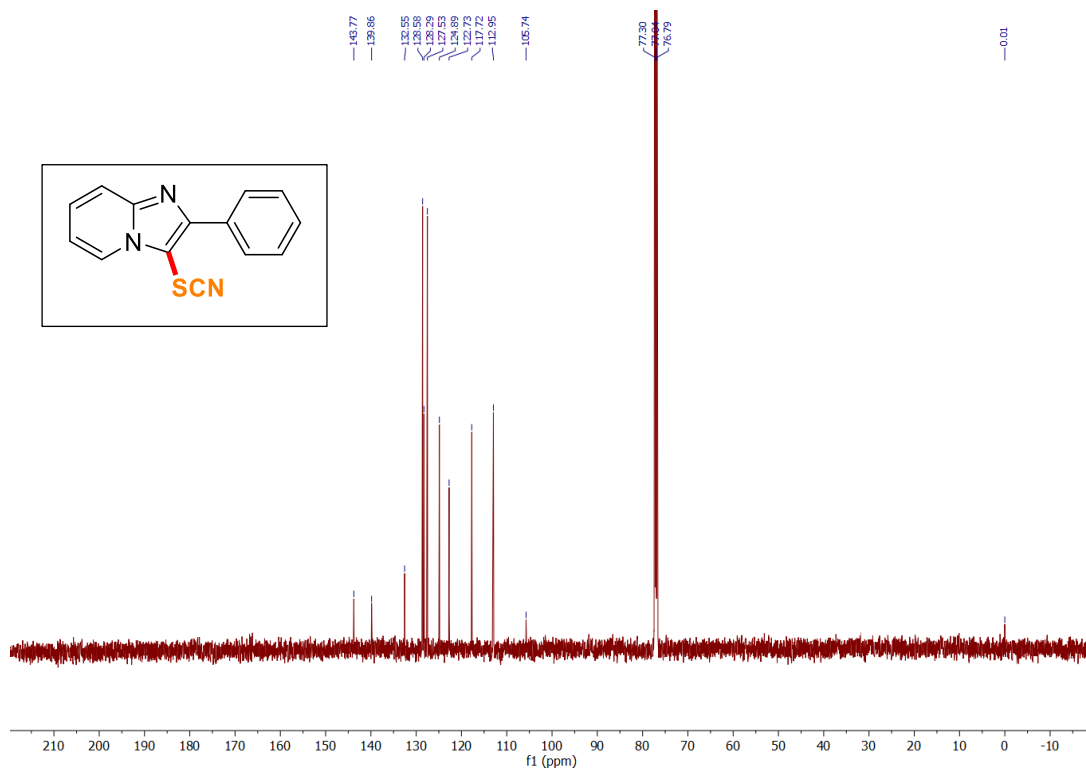
$^{13}\text{C}$  NMR spectrum of compound **2ah**, ( $\text{CDCl}_3$ , 125 MHz).



$^1\text{H}$  NMR spectrum of compound **4a**, ( $\text{CDCl}_3$ , 500 MHz).

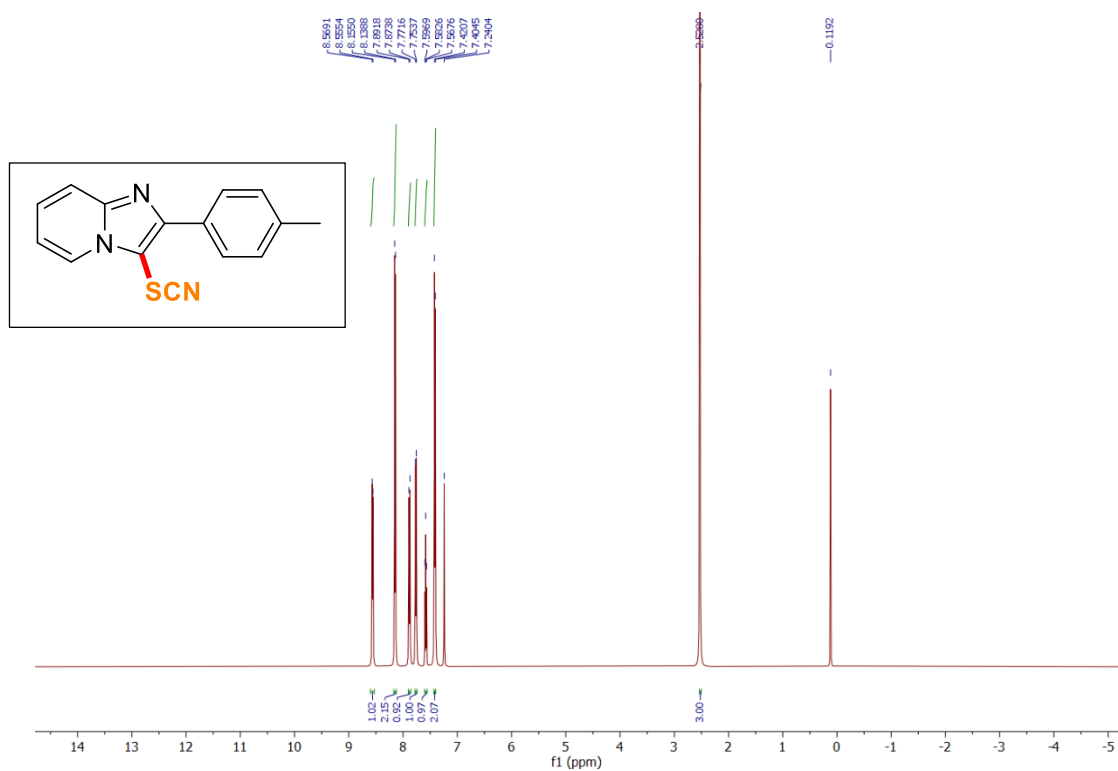


$^{13}\text{C}$  NMR spectrum of compound **4a**, ( $\text{CDCl}_3$ , 125 MHz).

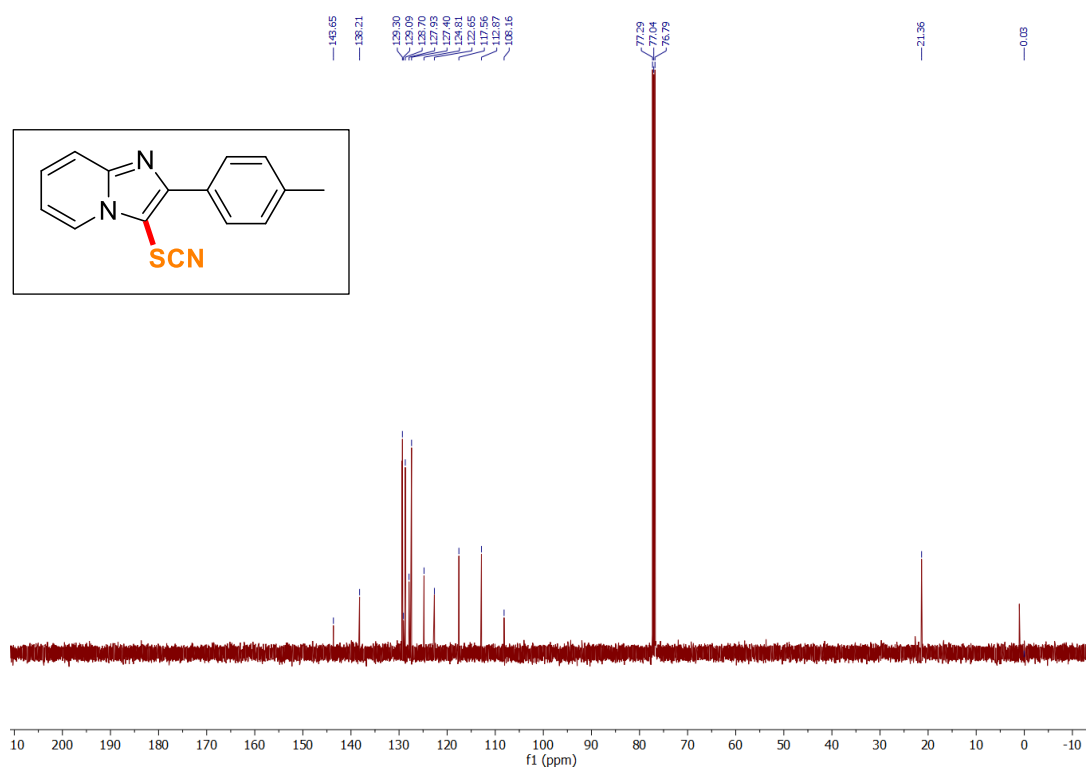




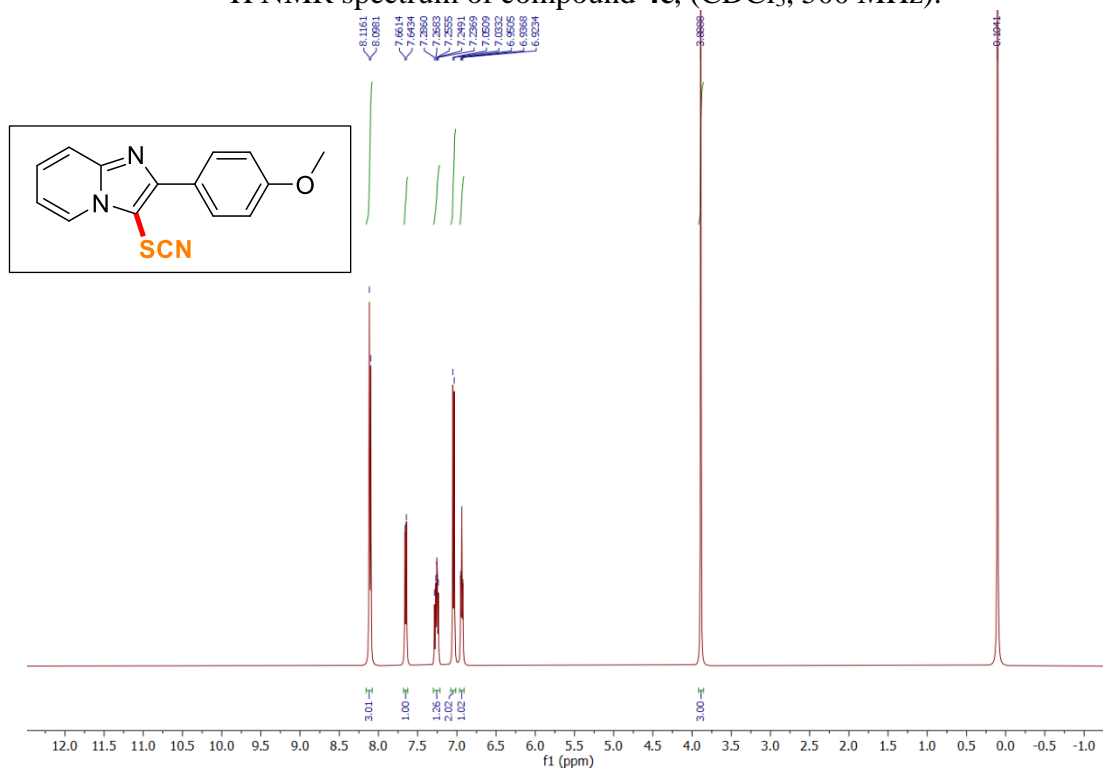
<sup>1</sup>H NMR spectrum of compound **4b**, (CDCl<sub>3</sub>, 500 MHz).



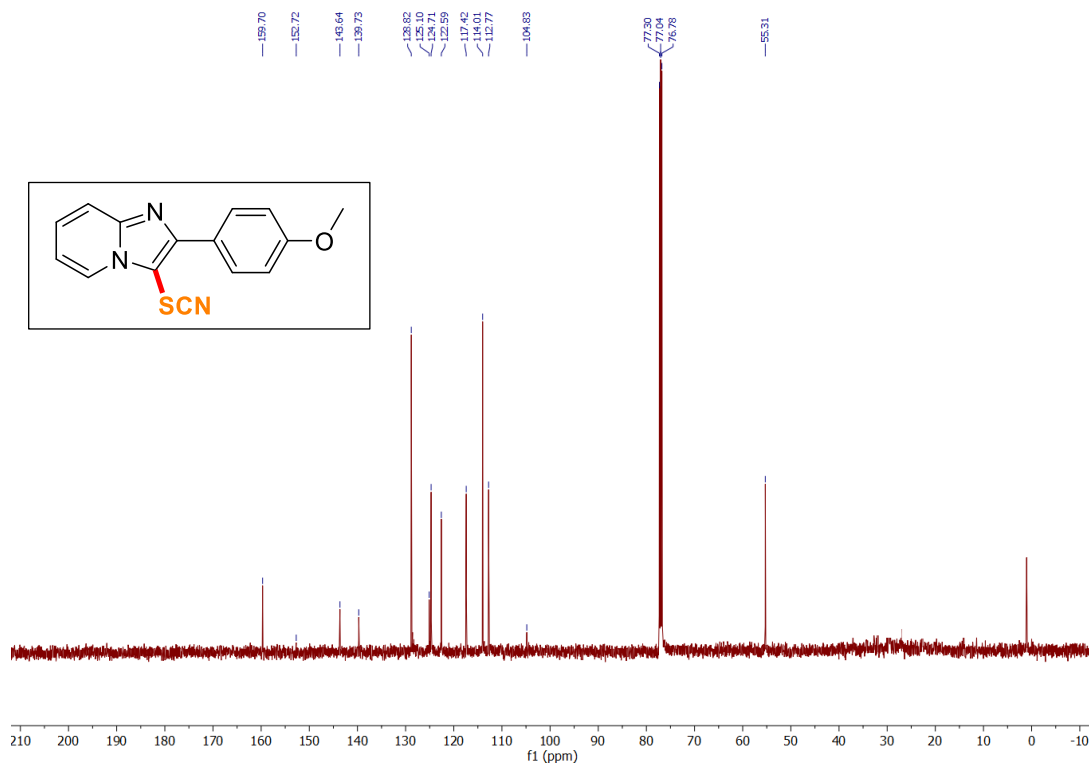
<sup>13</sup>C NMR spectrum of compound **4b**, (CDCl<sub>3</sub>, 125 MHz).



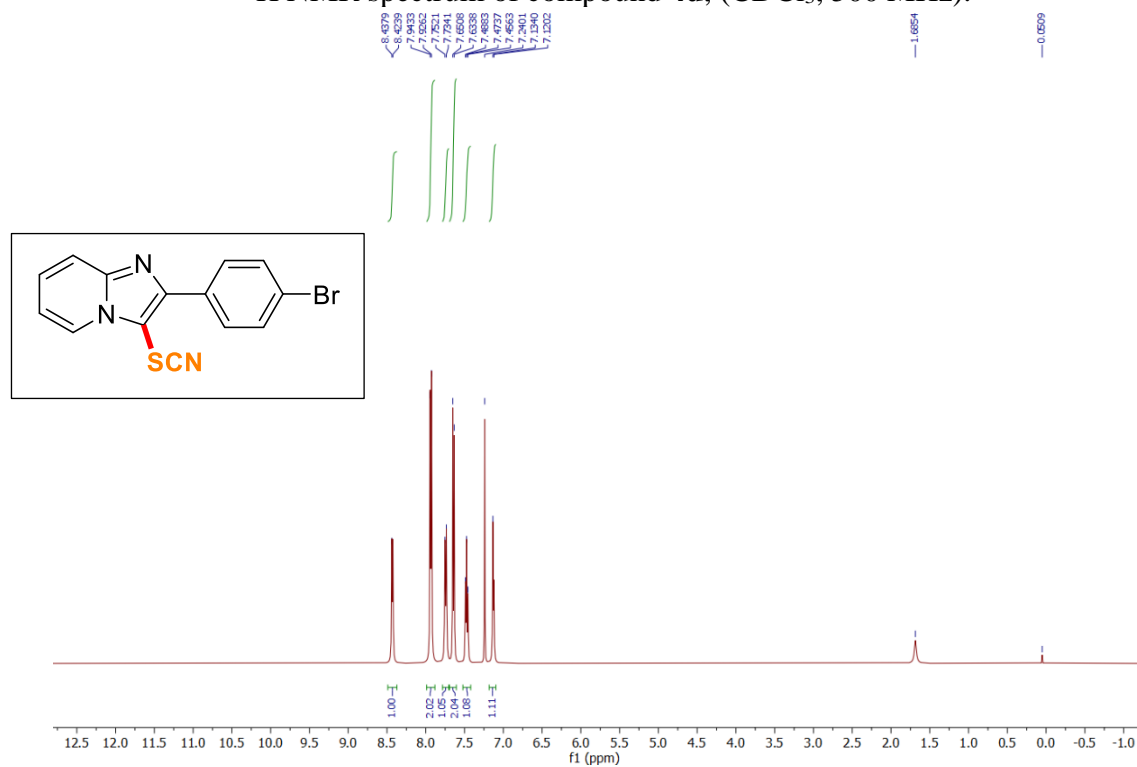
$^1\text{H}$  NMR spectrum of compound **4c**, ( $\text{CDCl}_3$ , 500 MHz).



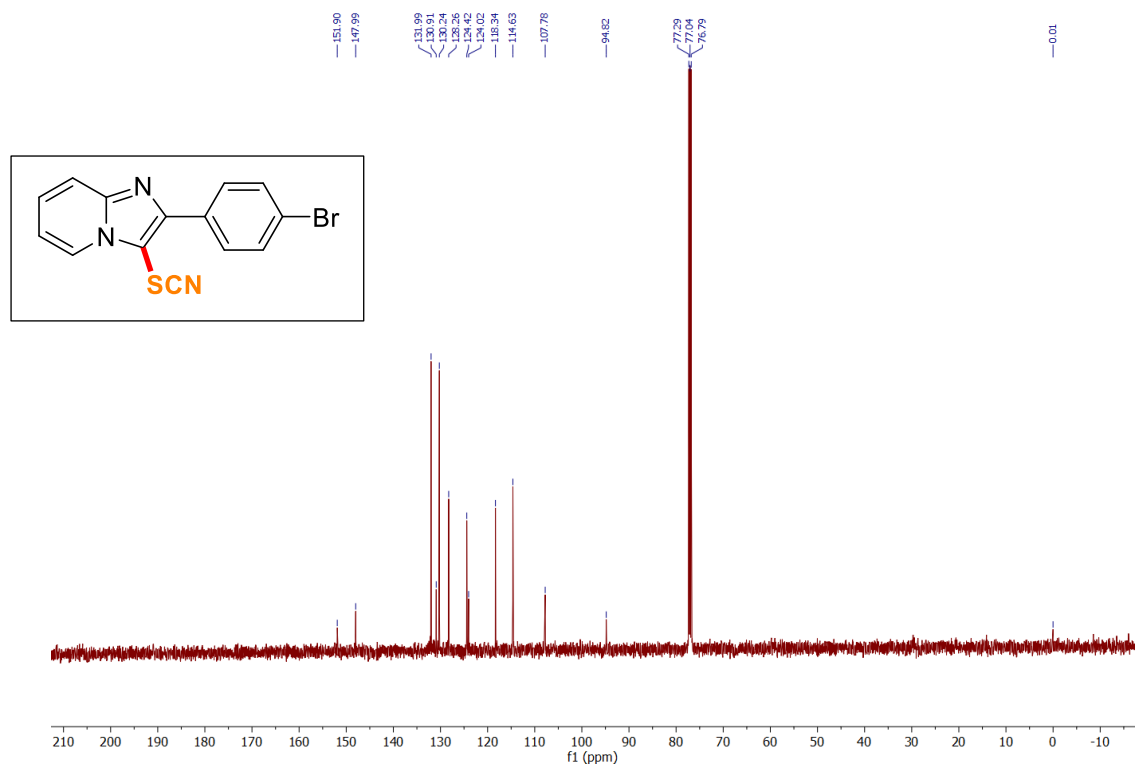
$^{13}\text{C}$  NMR spectrum of compound **4c**, ( $\text{CDCl}_3$ , 125 MHz).



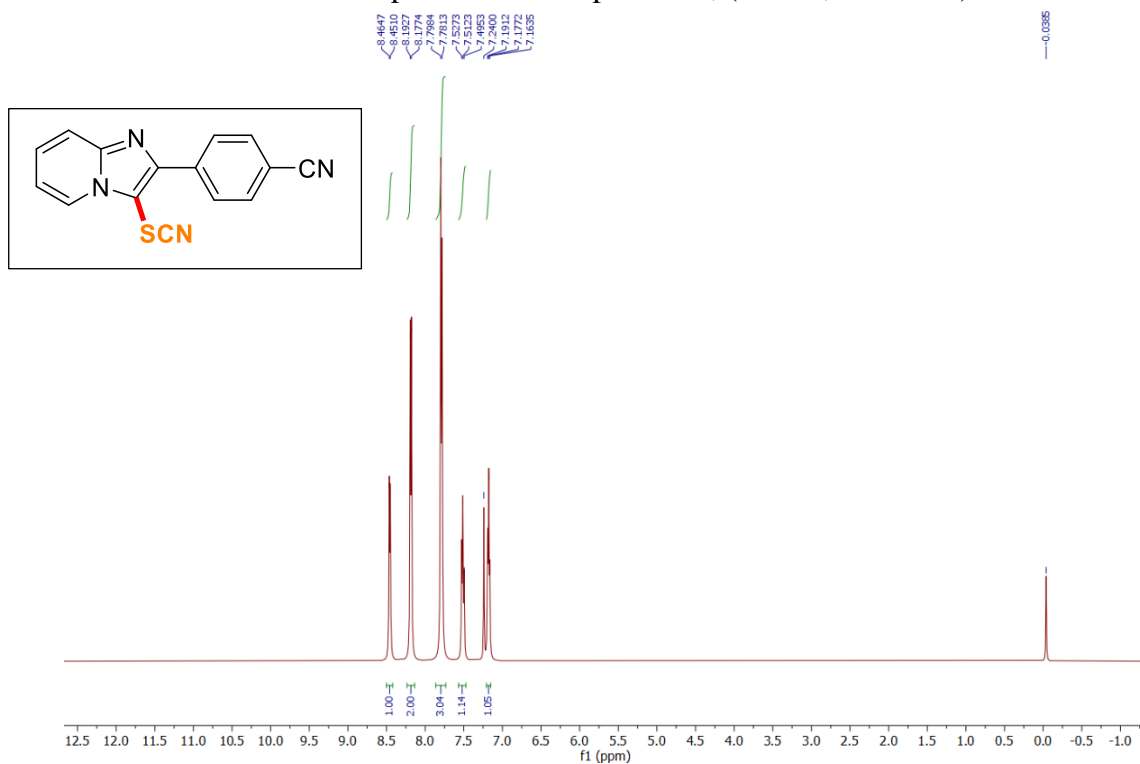
$^1\text{H}$  NMR spectrum of compound **4d**, ( $\text{CDCl}_3$ , 500 MHz).



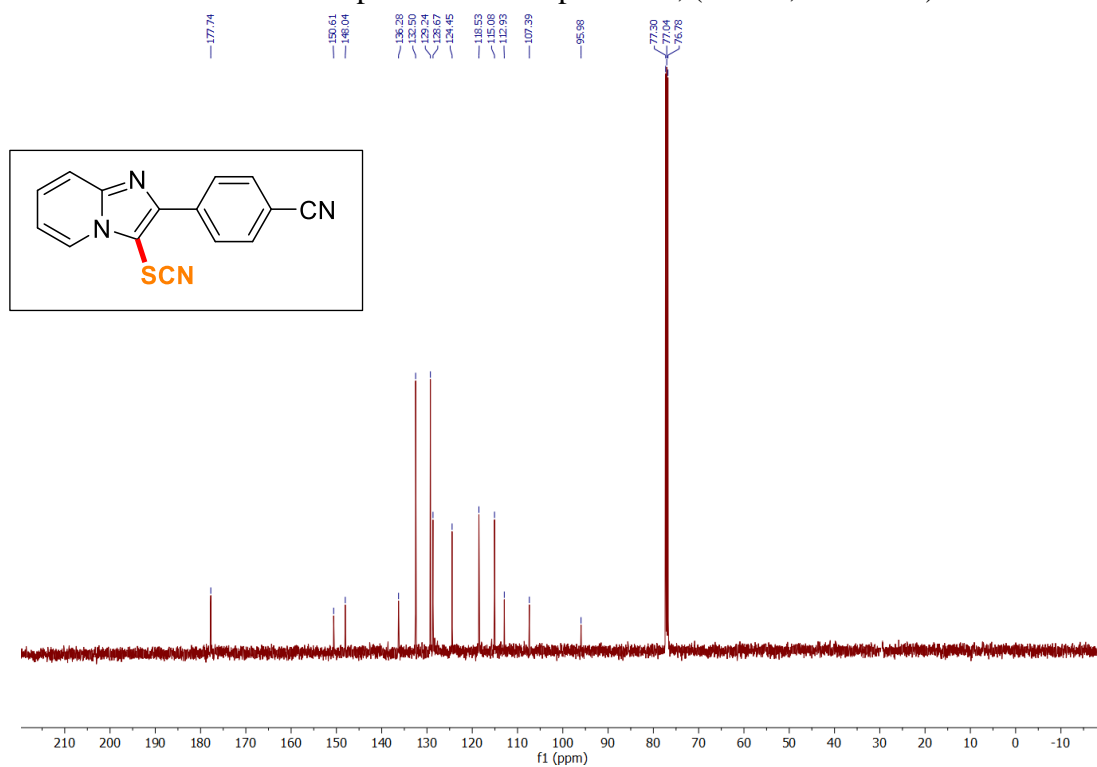
$^{13}\text{C}$  NMR spectrum of compound **4d**, ( $\text{CDCl}_3$ , 125 MHz).



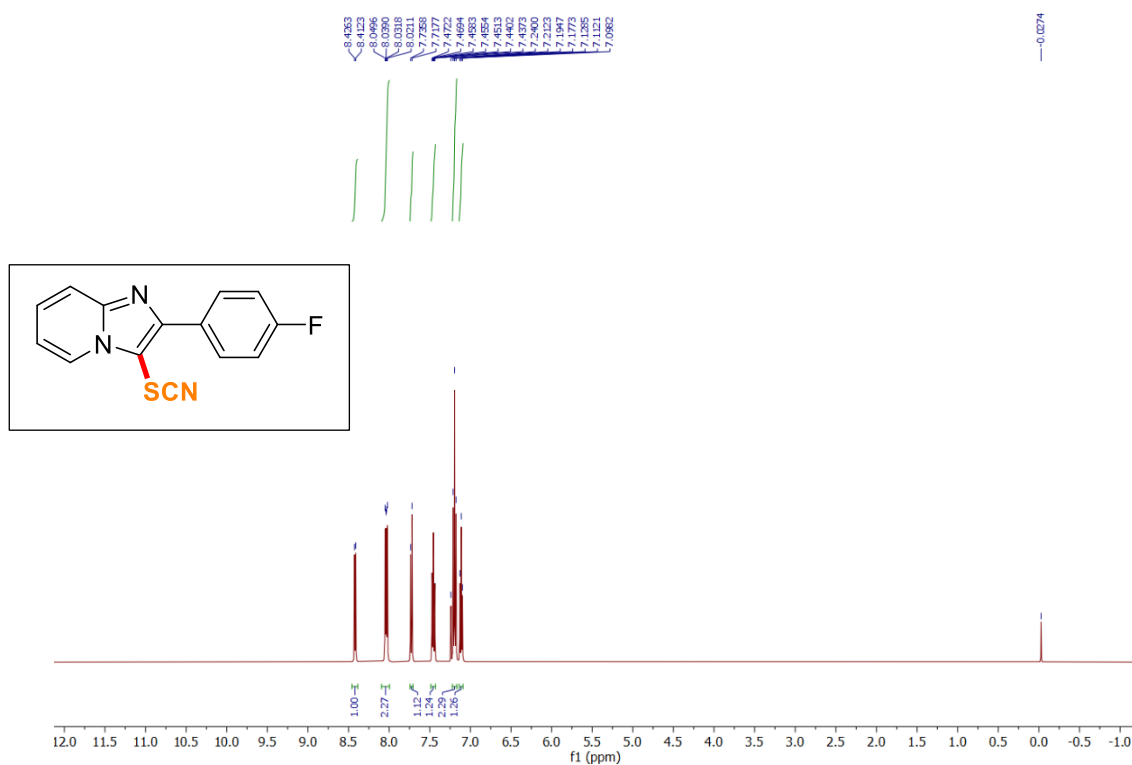
<sup>1</sup>H NMR spectrum of compound **4e**, (CDCl<sub>3</sub>, 500 MHz).



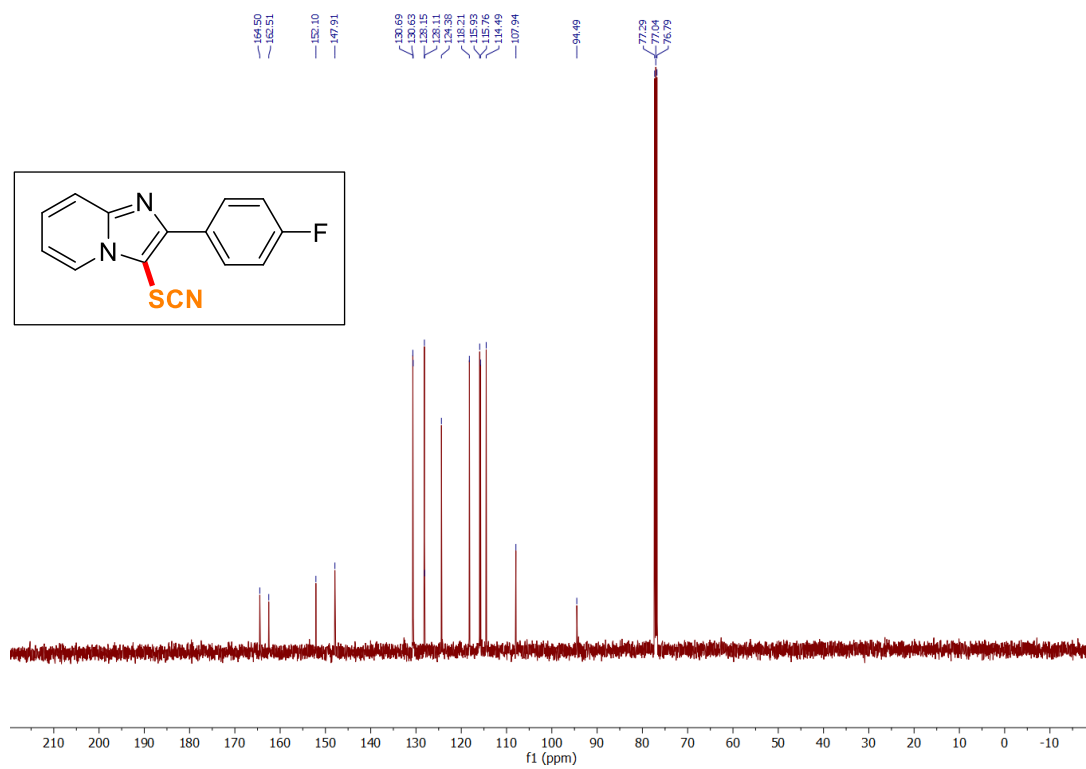
<sup>13</sup>C NMR spectrum of compound **4e**, (CDCl<sub>3</sub>, 125 MHz).



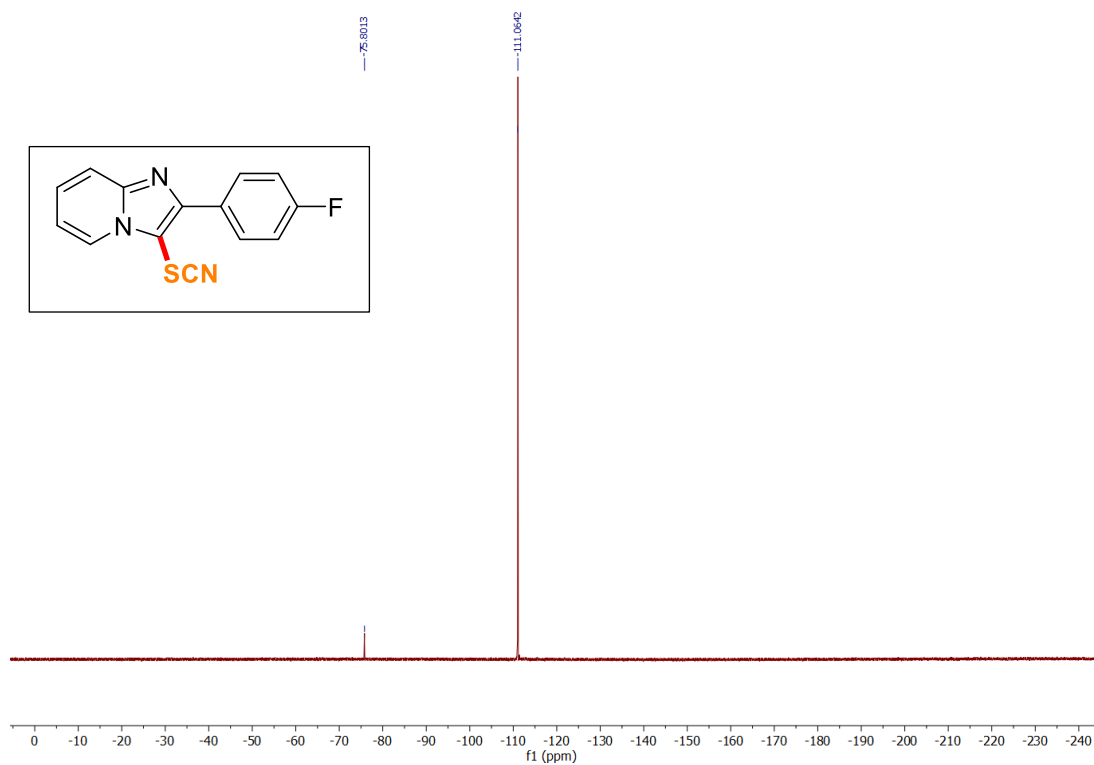
$^1\text{H}$  NMR spectrum of compound **4f**, ( $\text{CDCl}_3$ , 500 MHz).



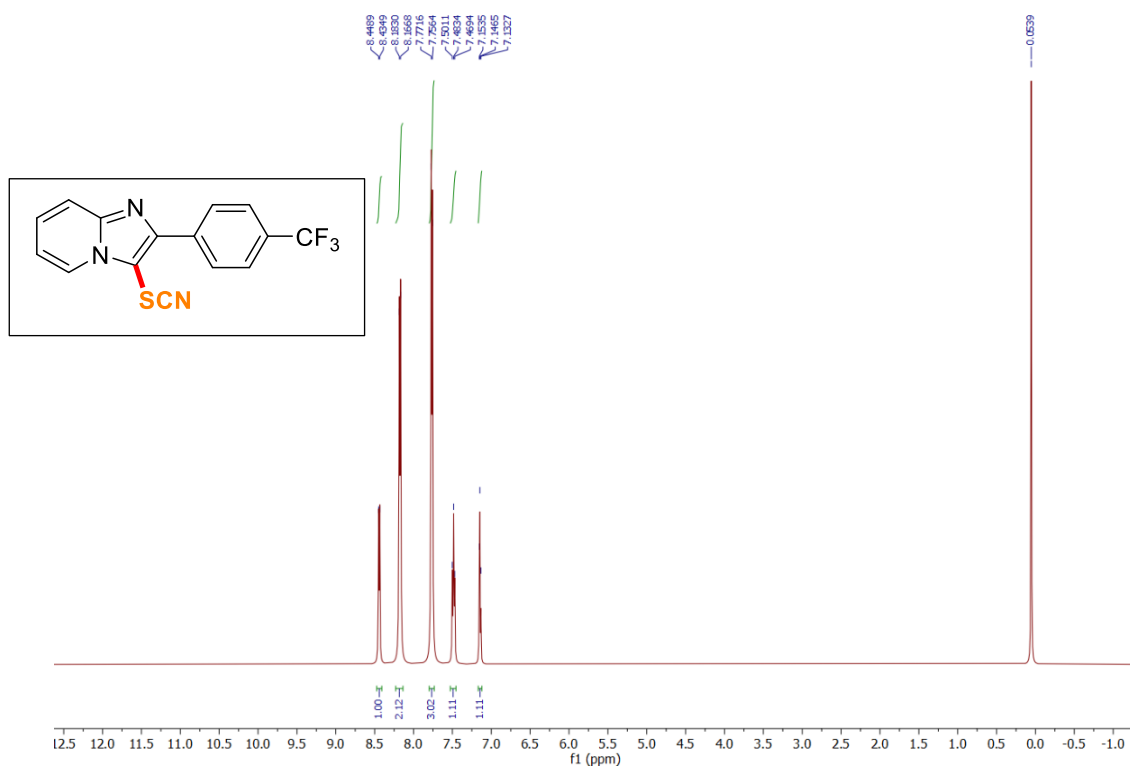
$^{13}\text{C}$  NMR spectrum of compound **4f**, ( $\text{CDCl}_3$ , 125 MHz).



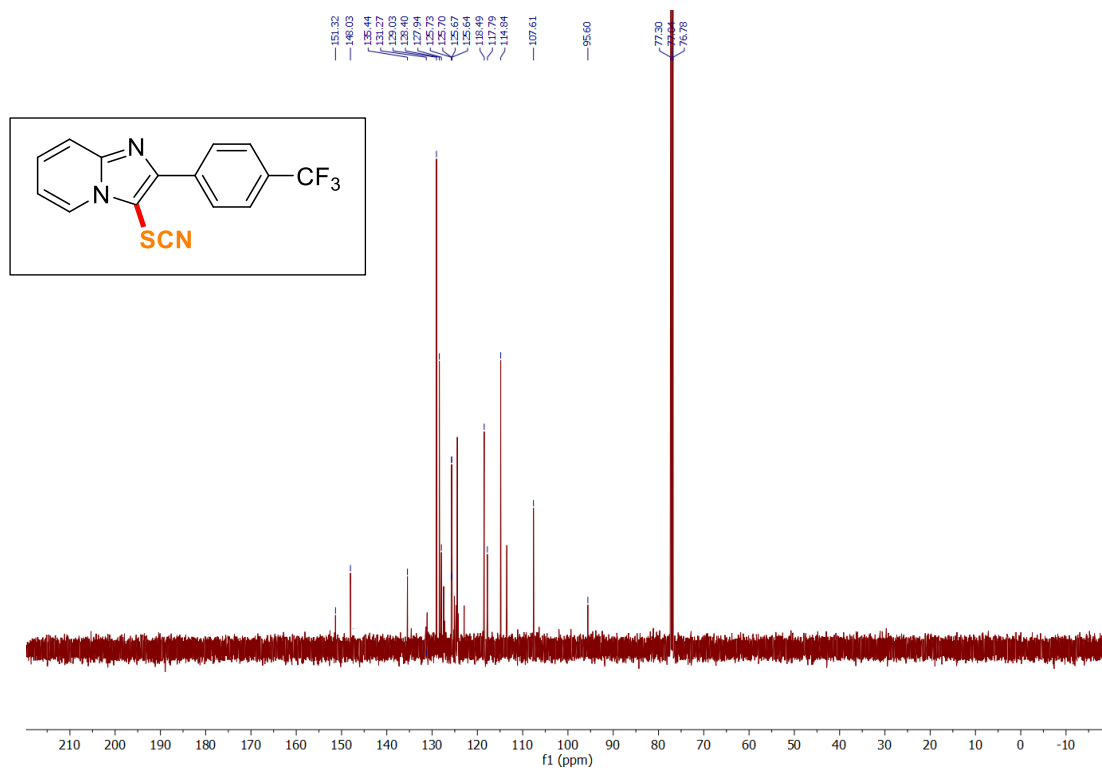
$^{19}\text{F}$  NMR spectrum of compound **4f**, ( $\text{CDCl}_3$ , 470 MHz).



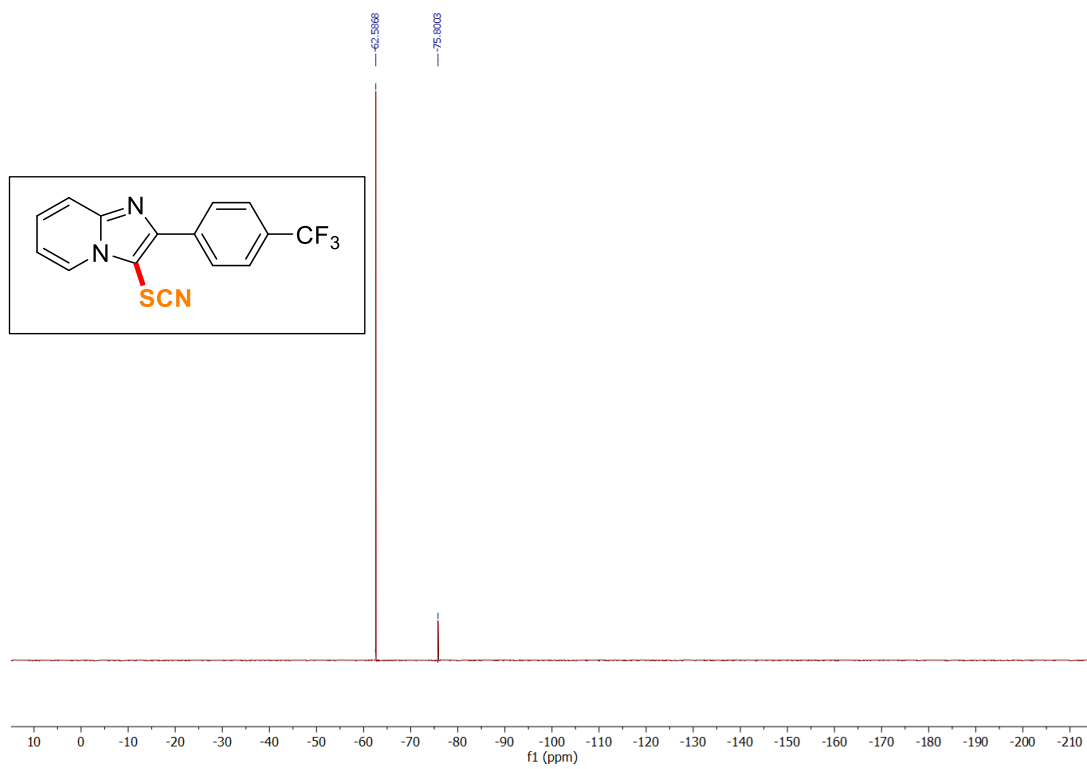
$^1\text{H}$  NMR spectrum of compound **4g**, ( $\text{CDCl}_3$ , 500 MHz).



$^{13}\text{C}$  NMR spectrum of compound **4g**, ( $\text{CDCl}_3$ , 125 MHz).

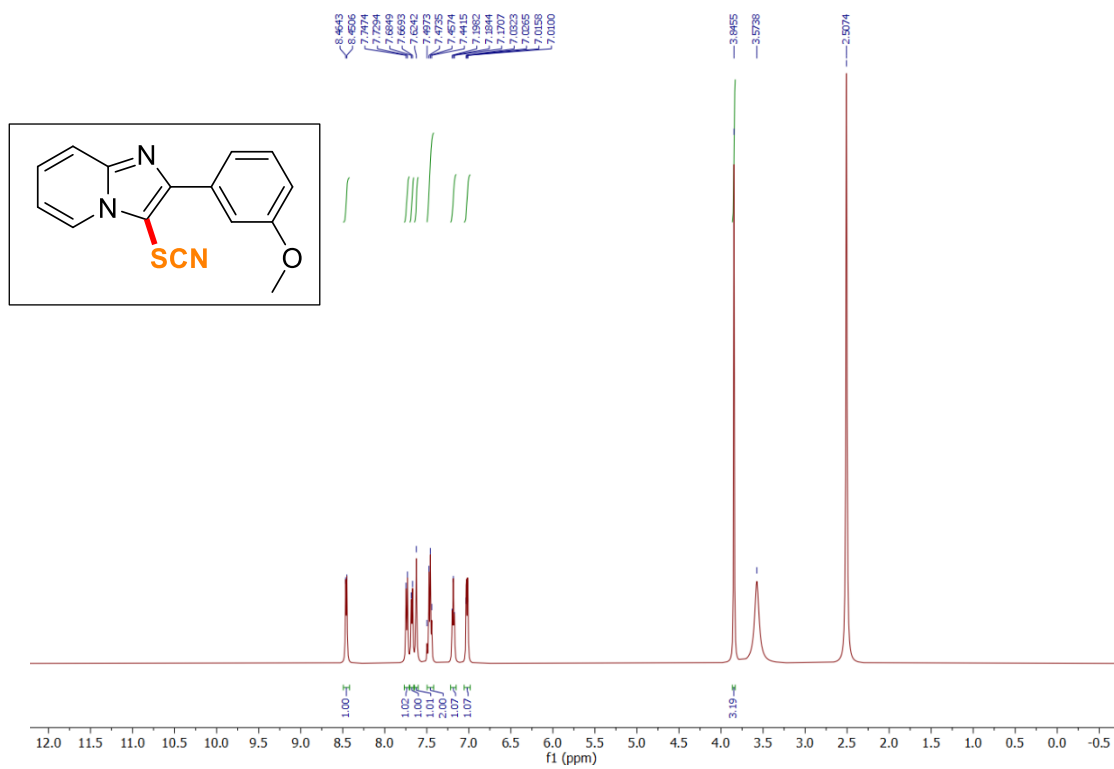


$^{19}\text{F}$  NMR spectrum of compound **4g**, ( $\text{CDCl}_3$ , 470 MHz).

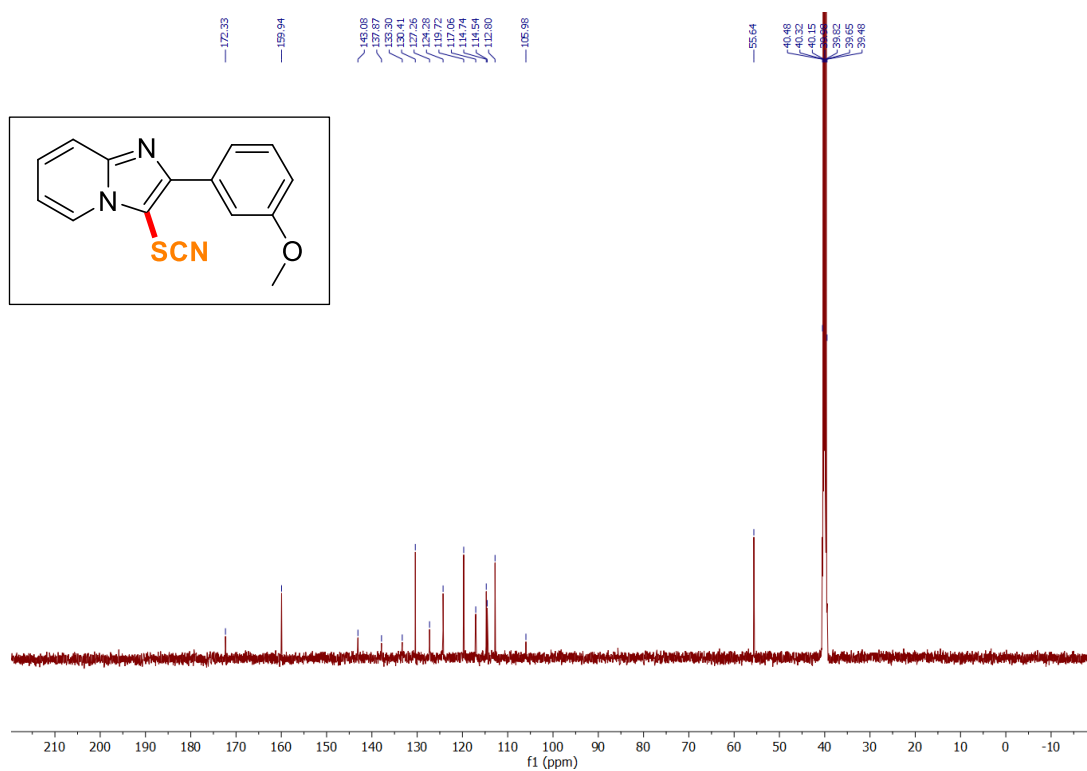




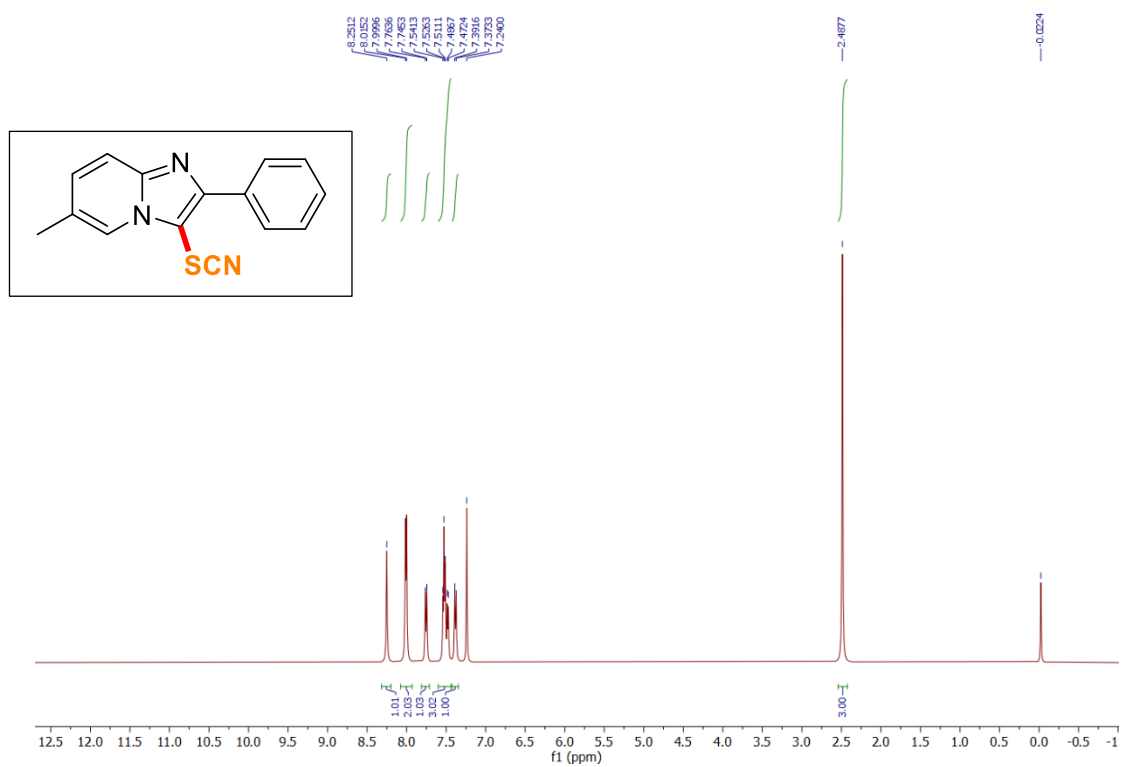
$^1\text{H}$  NMR spectrum of compound **4h**, (DMSO- $d_6$ , 500 MHz).



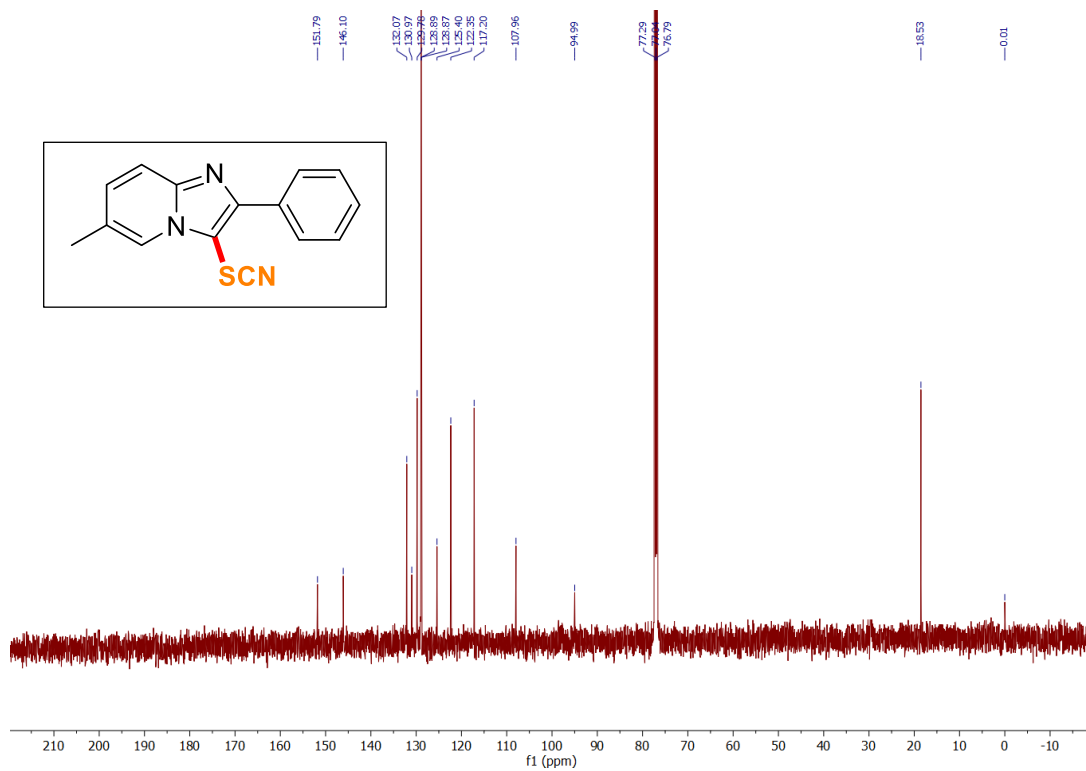
$^{13}\text{C}$  NMR spectrum of compound **4h**, (DMSO- $d_6$ , 125 MHz).



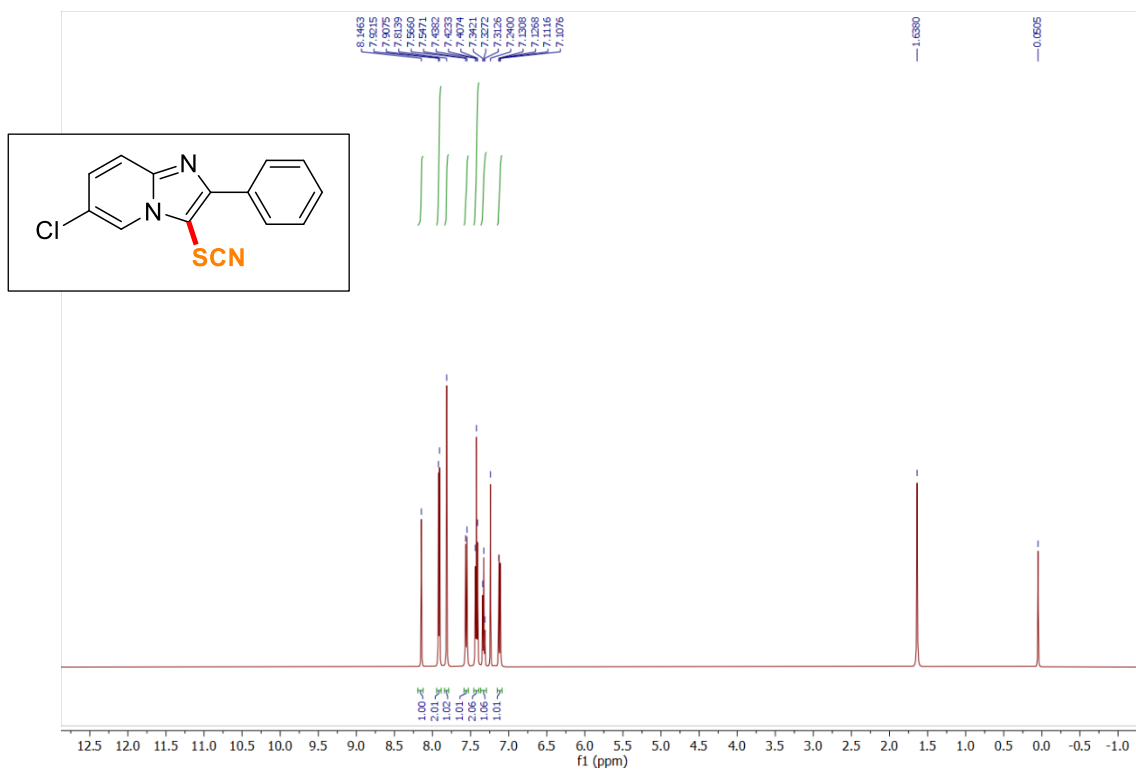
$^1\text{H}$  NMR spectrum of compound **4i**, ( $\text{CDCl}_3$ , 500 MHz).



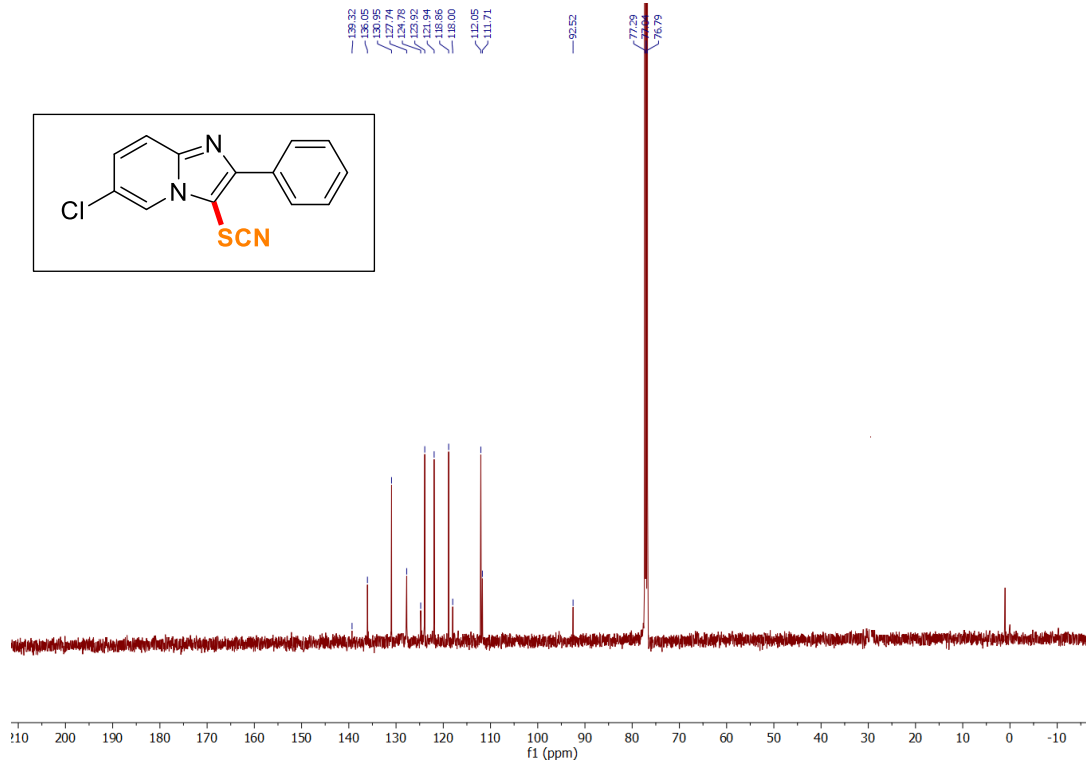
$^{13}\text{C}$  NMR spectrum of compound **4i**, ( $\text{CDCl}_3$ , 125 MHz).



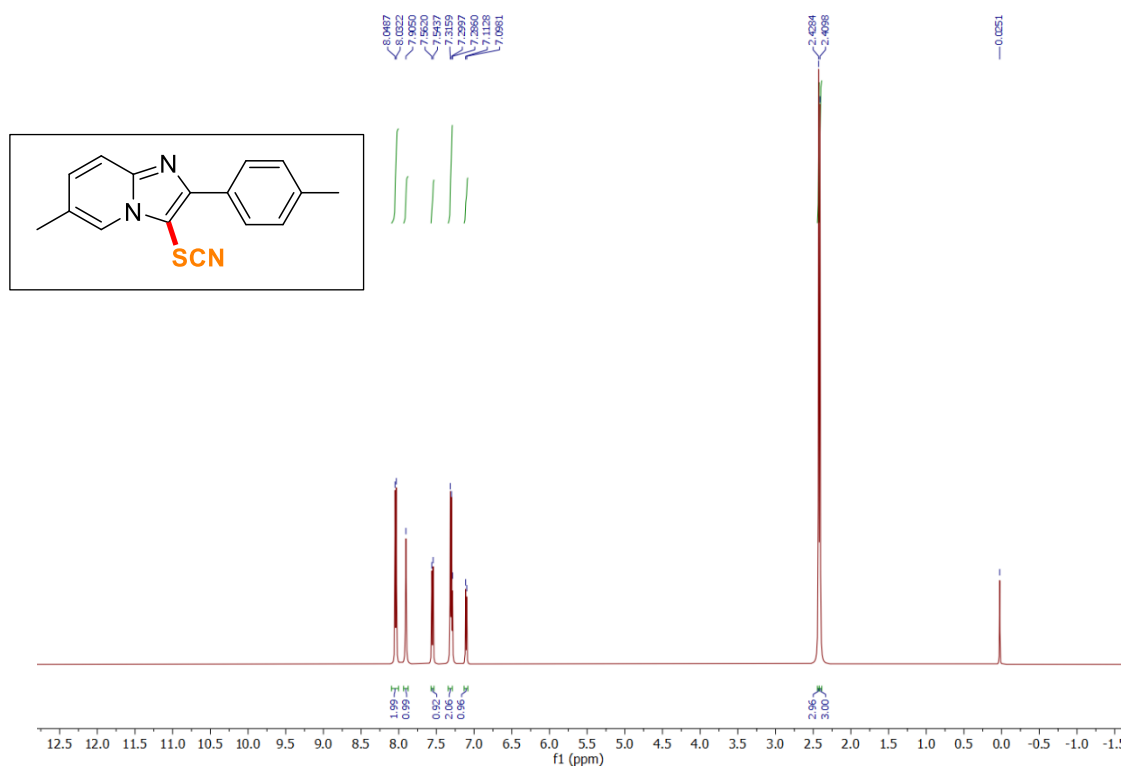
$^1\text{H}$  NMR spectrum of compound **4j**, ( $\text{CDCl}_3$ , 500 MHz).



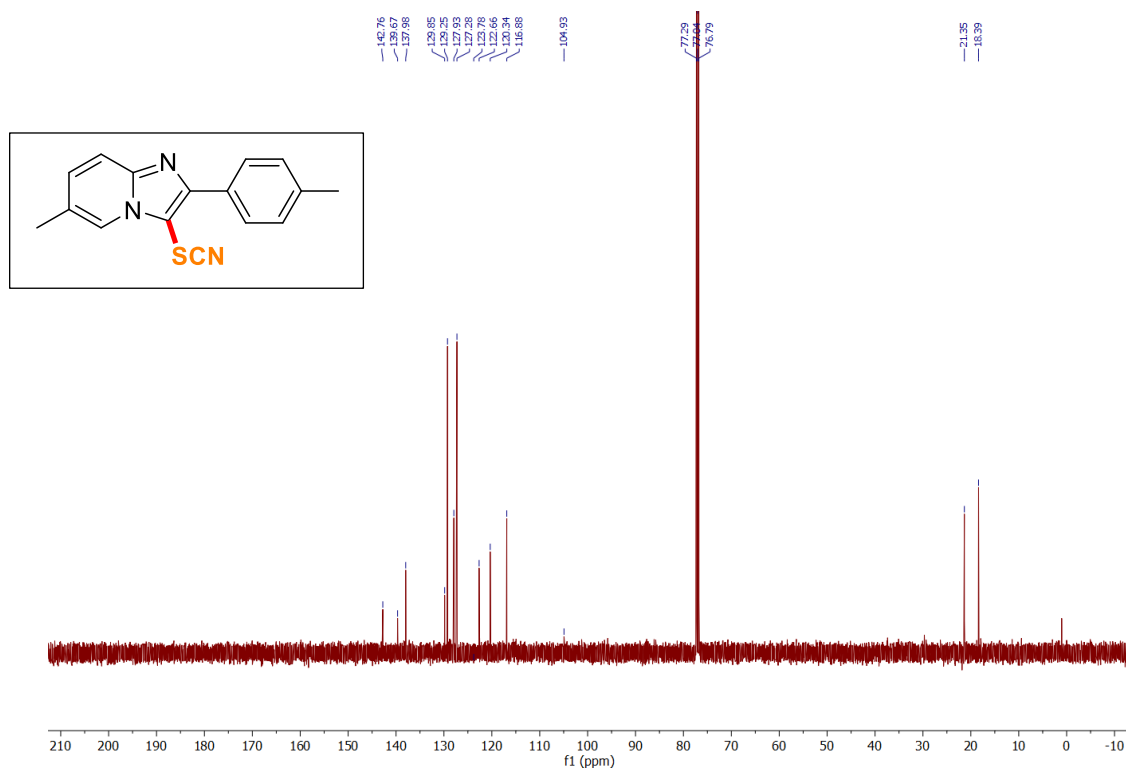
$^{13}\text{C}$  NMR spectrum of compound **4j**, ( $\text{CDCl}_3$ , 125 MHz).



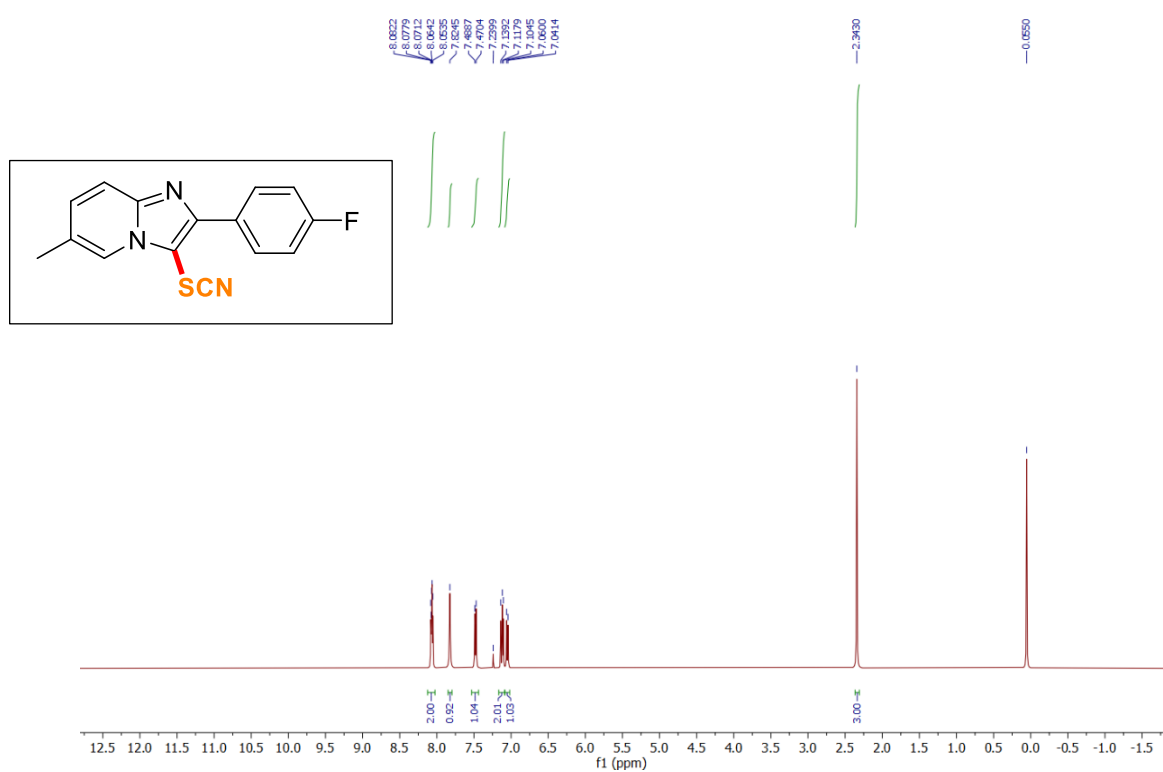
$^1\text{H}$  NMR spectrum of compound **4k**, ( $\text{CDCl}_3$ , 500 MHz).



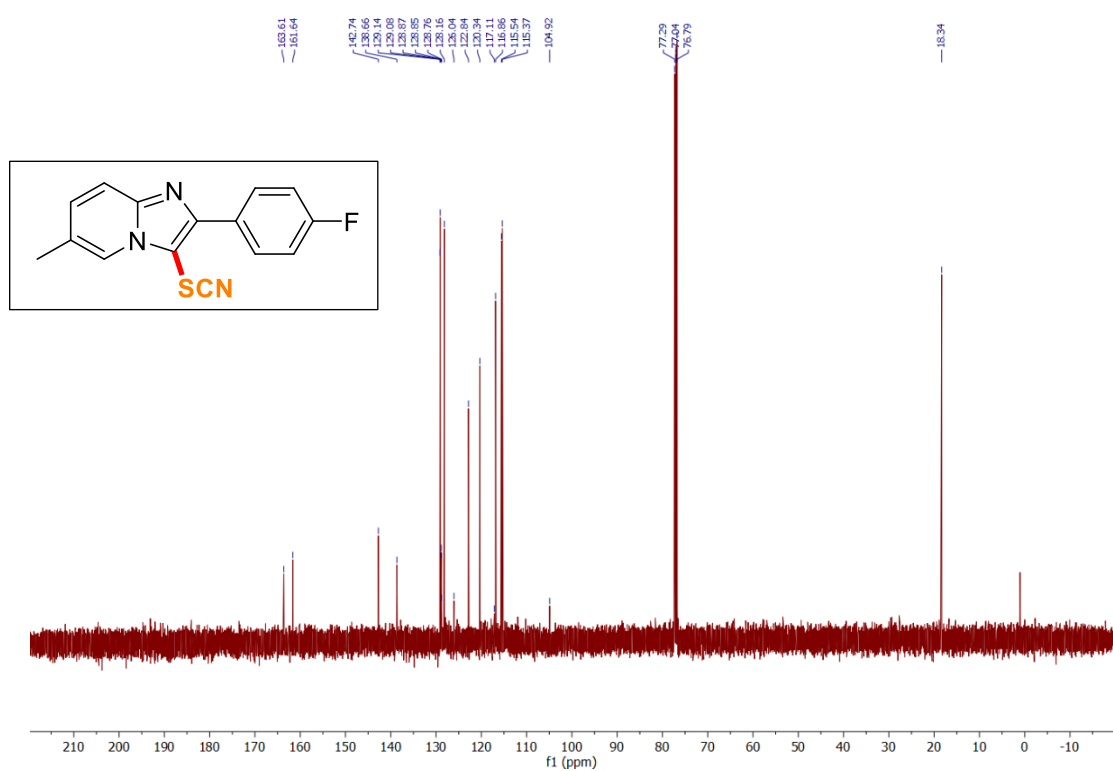
$^{13}\text{C}$  NMR spectrum of compound **4k**, ( $\text{CDCl}_3$ , 125 MHz).



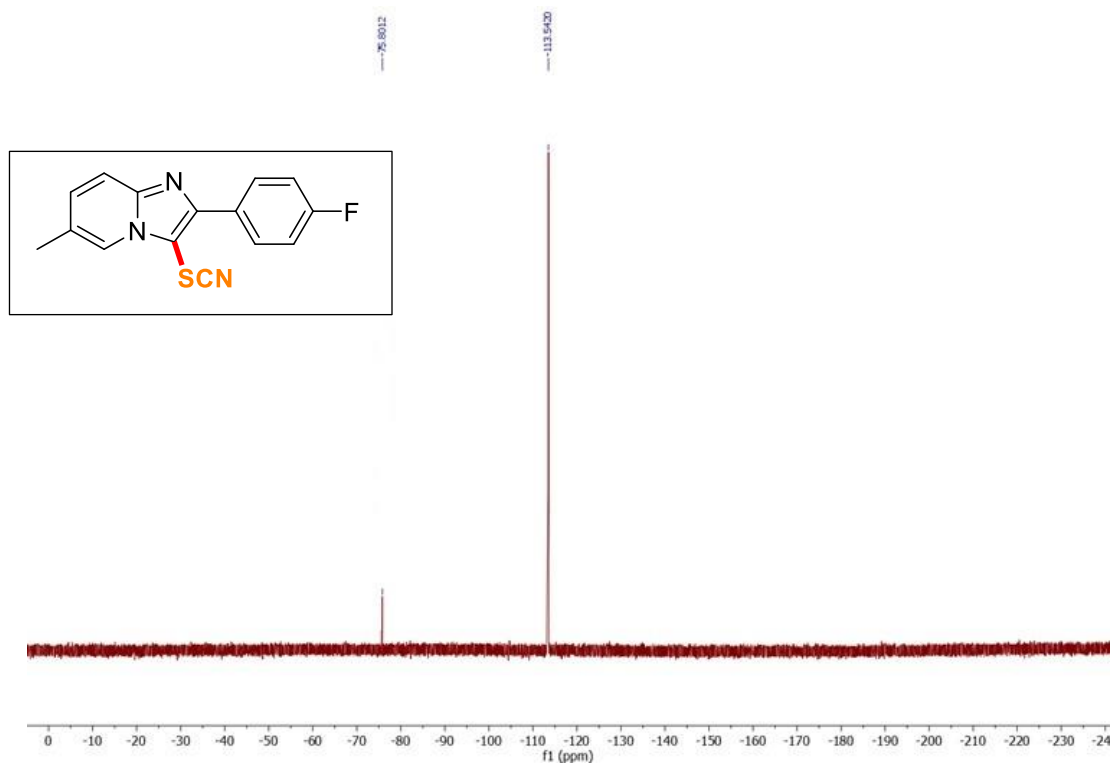
$^1\text{H}$  NMR spectrum of compound **41**, ( $\text{CDCl}_3$ , 500 MHz).



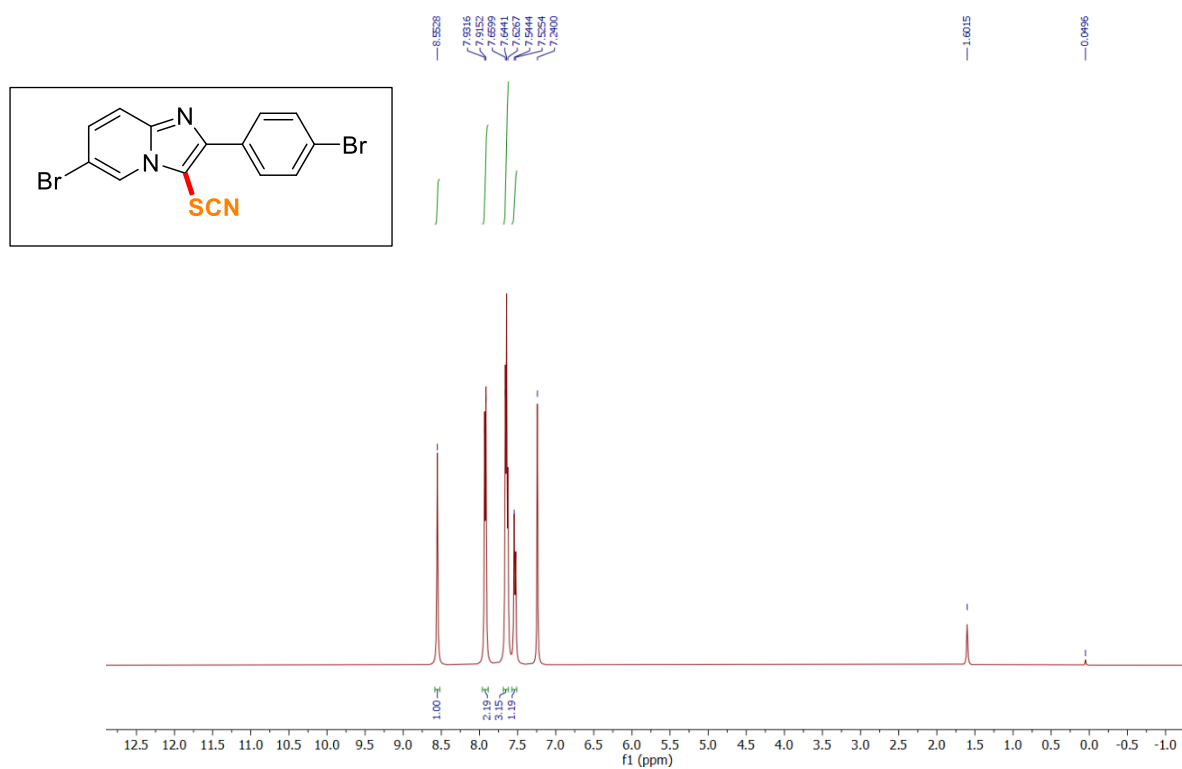
$^{13}\text{C}$  NMR spectrum of compound **41**, ( $\text{CDCl}_3$ , 125 MHz).



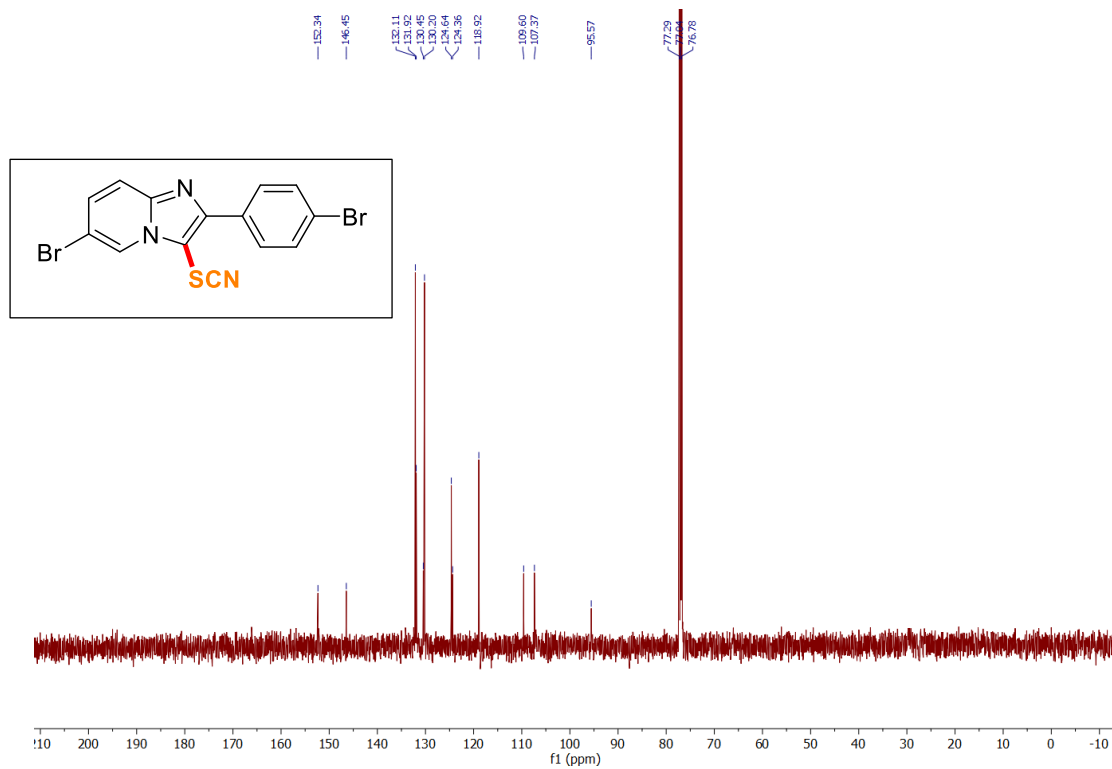
$^{19}\text{F}$  NMR spectrum of compound **41**, ( $\text{CDCl}_3$ , 470 MHz).



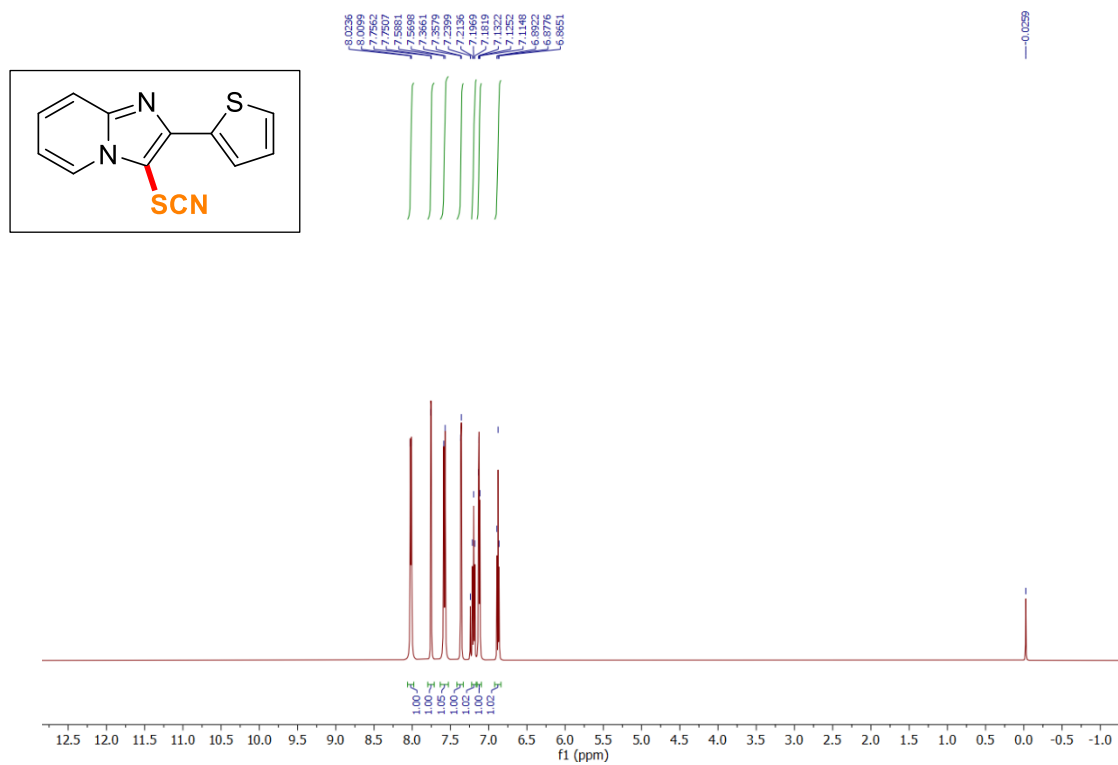
$^1\text{H}$  NMR spectrum of compound **4m**, ( $\text{CDCl}_3$ , 500 MHz).



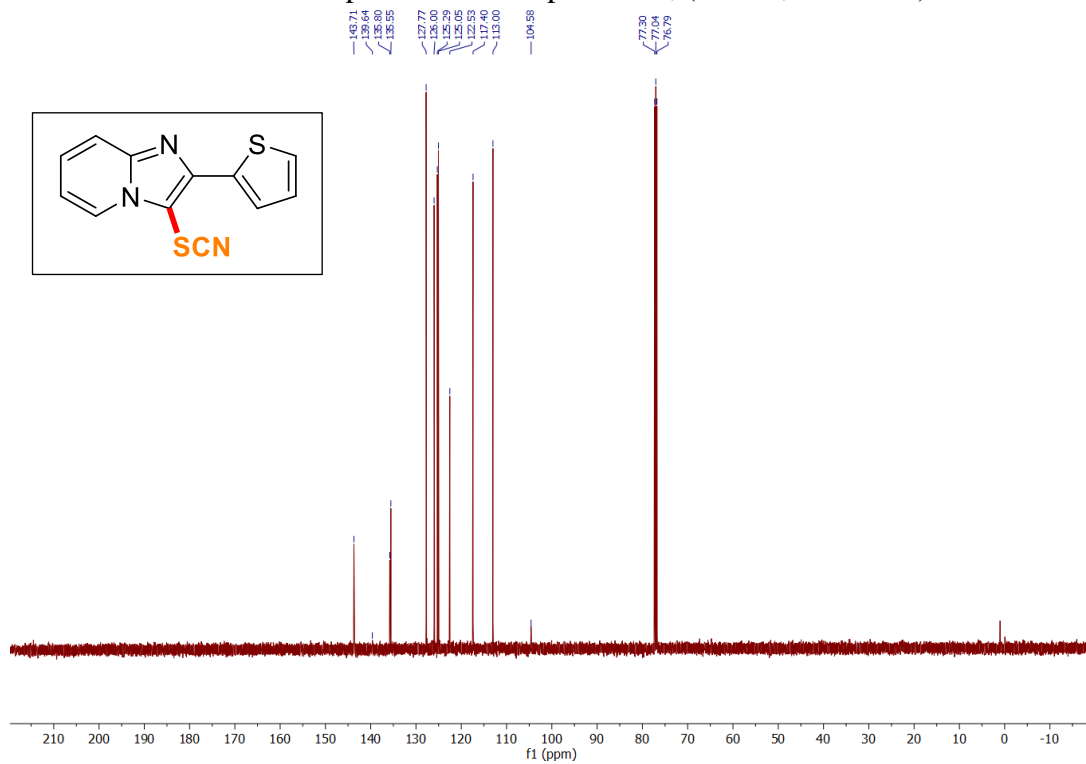
$^{13}\text{C}$  NMR spectrum of compound **4m**, ( $\text{CDCl}_3$ , 125 MHz).



$^1\text{H}$  NMR spectrum of compound **4n**, ( $\text{CDCl}_3$ , 500 MHz).

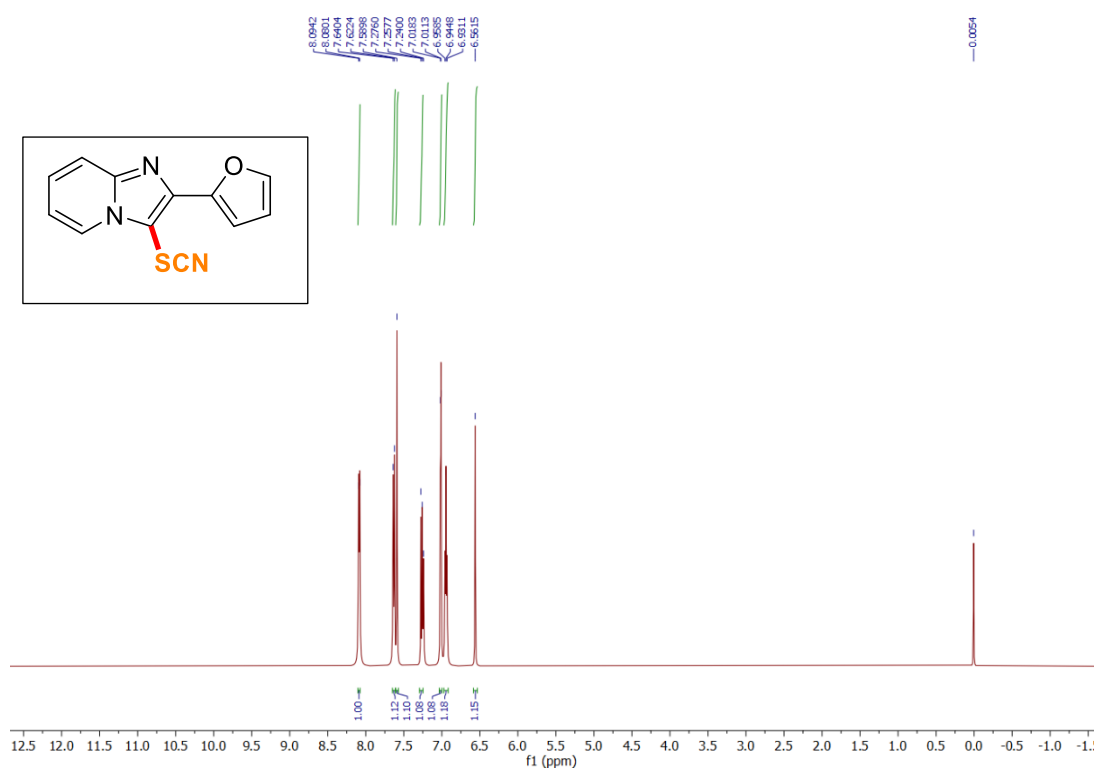


$^{13}\text{C}$  NMR spectrum of compound **4n**, ( $\text{CDCl}_3$ , 125 MHz).

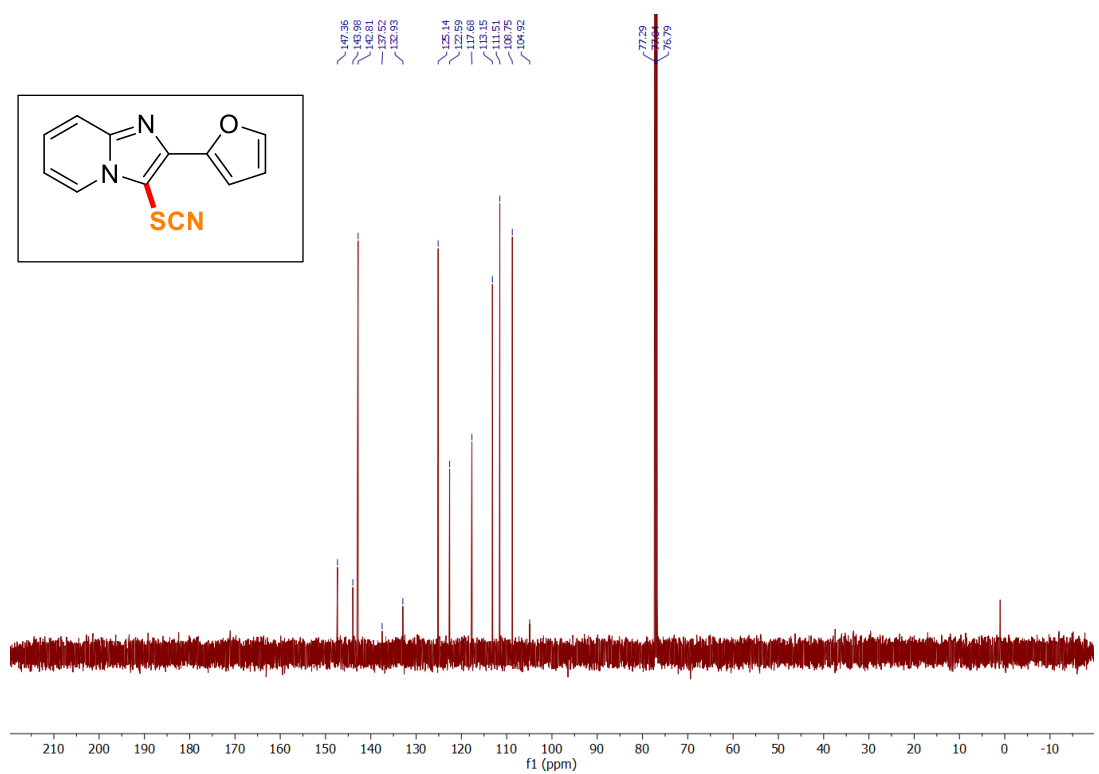




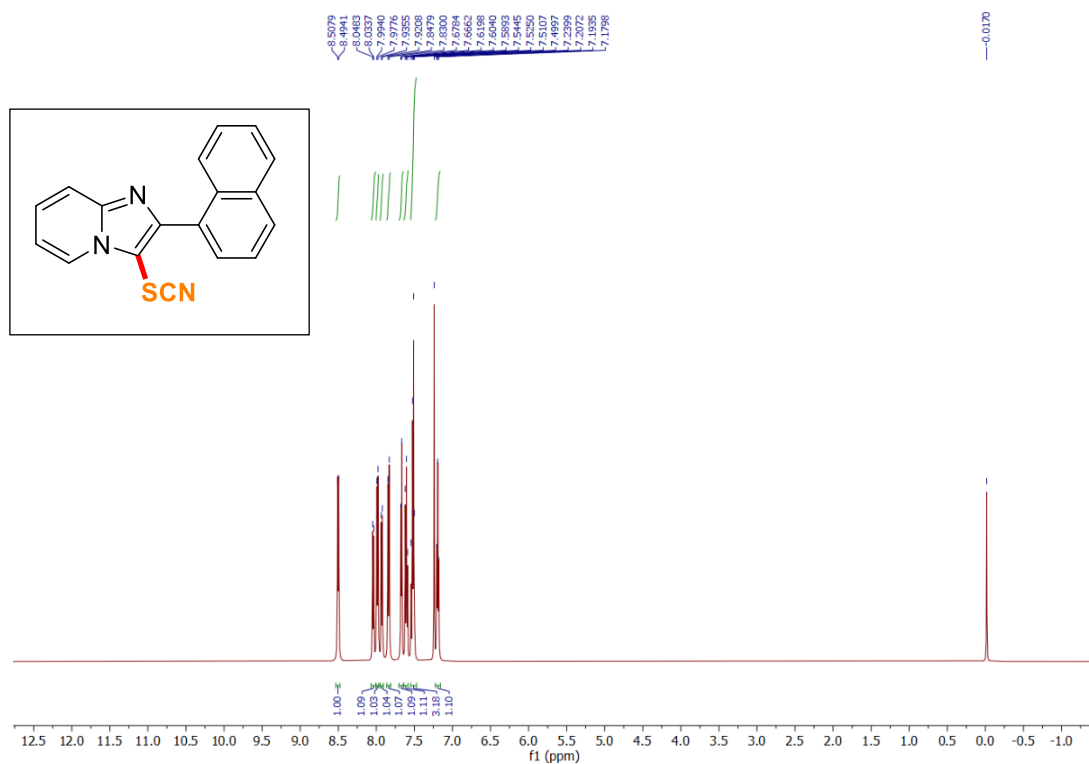
<sup>1</sup>H NMR spectrum of compound **4o**, (CDCl<sub>3</sub>, 500 MHz).



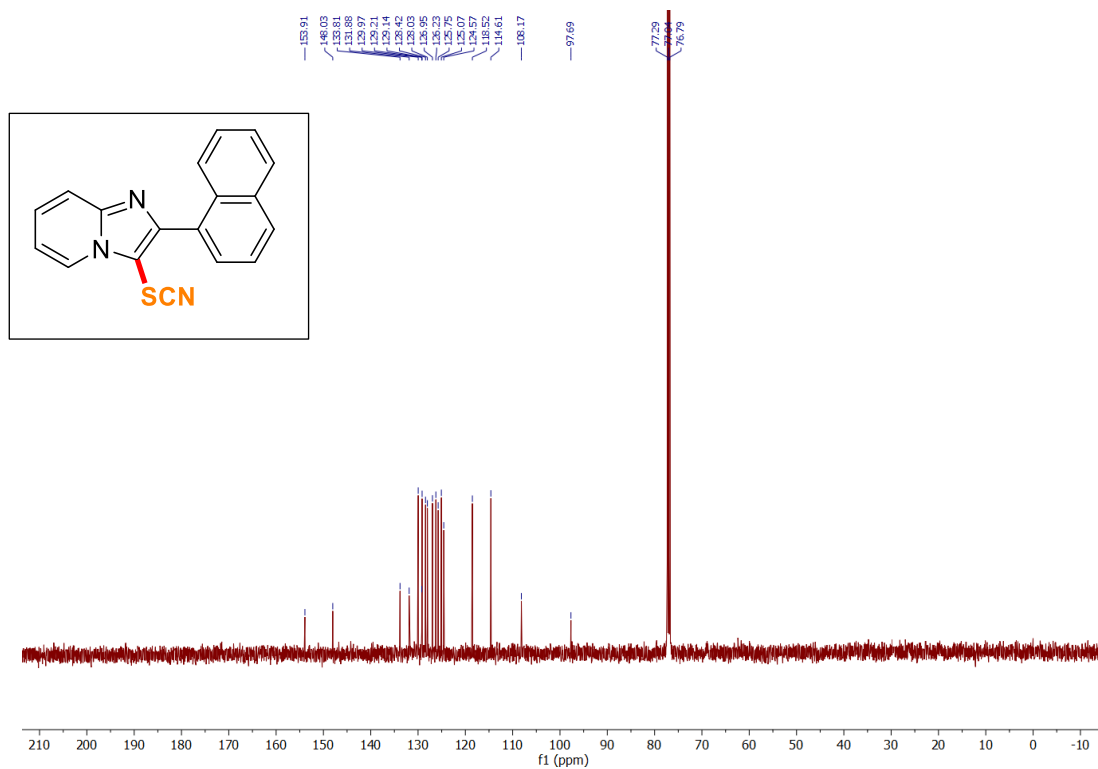
<sup>13</sup>C NMR spectrum of compound **4o**, (CDCl<sub>3</sub>, 125 MHz).



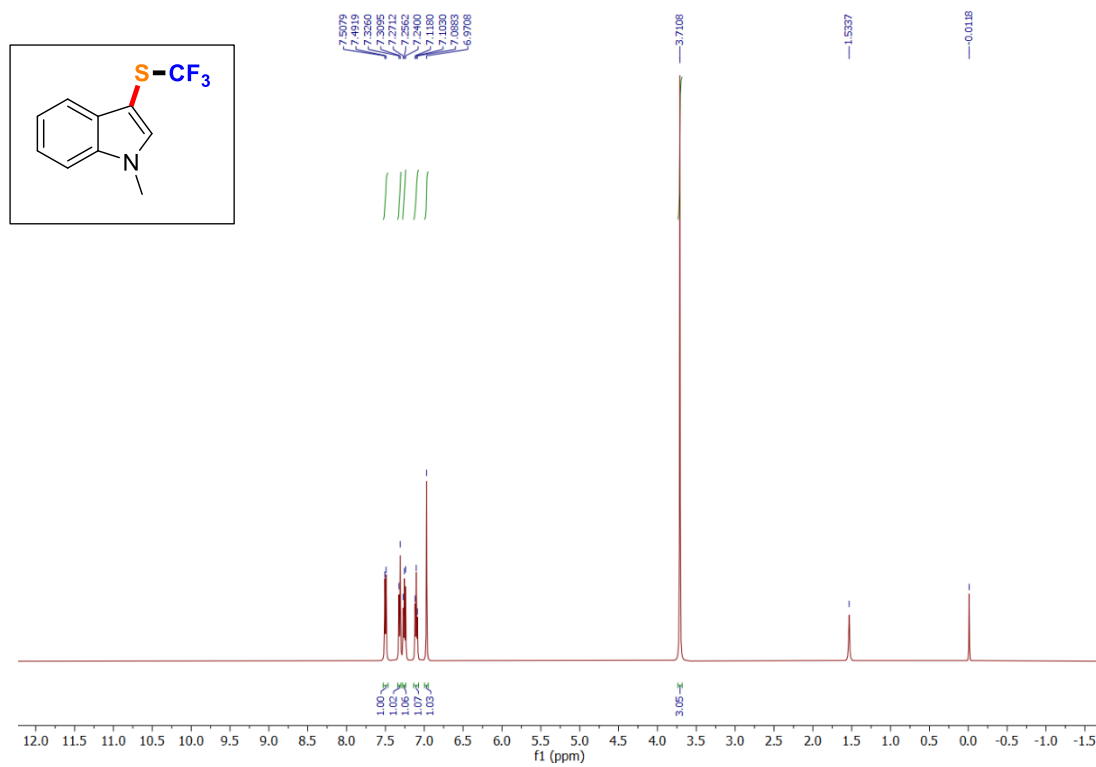
$^1\text{H}$  NMR spectrum of compound **4p**, ( $\text{CDCl}_3$ , 500 MHz).



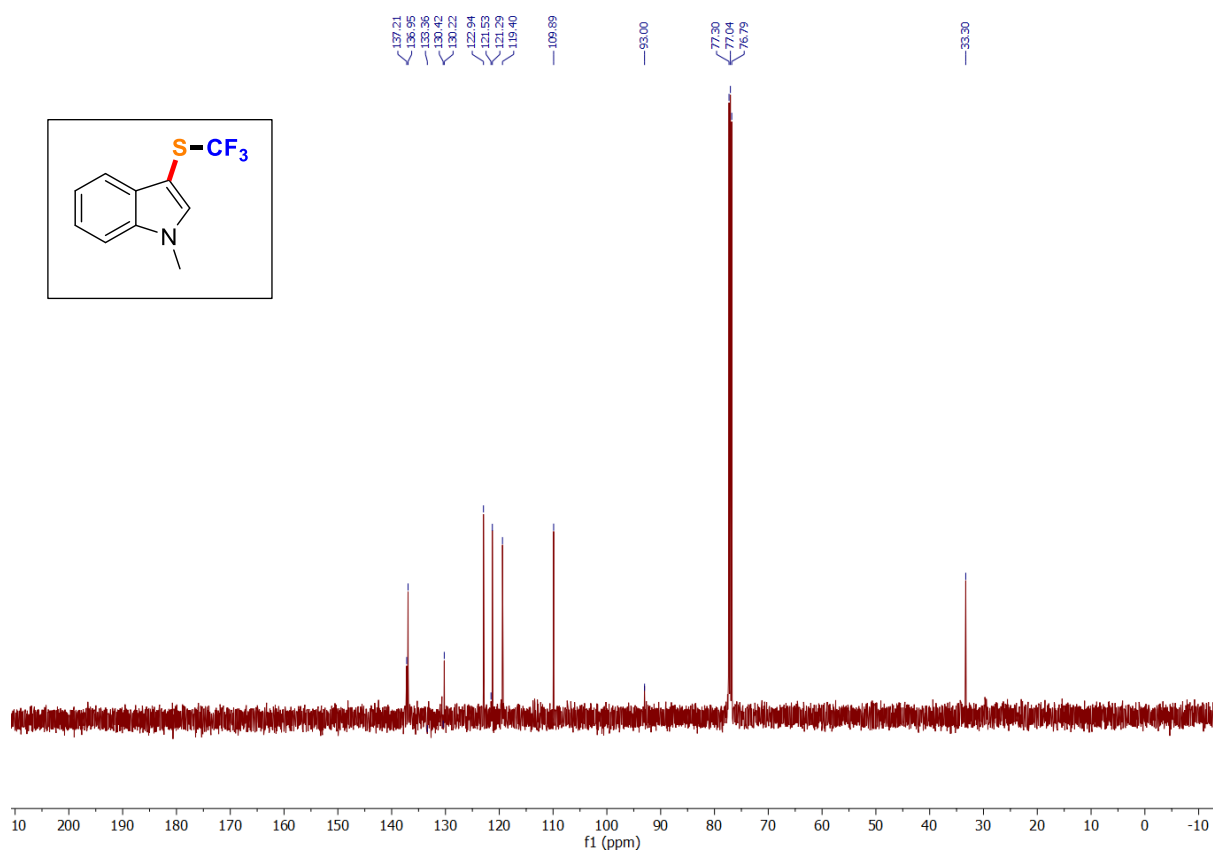
$^{13}\text{C}$  NMR spectrum of compound **4p**, ( $\text{CDCl}_3$ , 125 MHz).



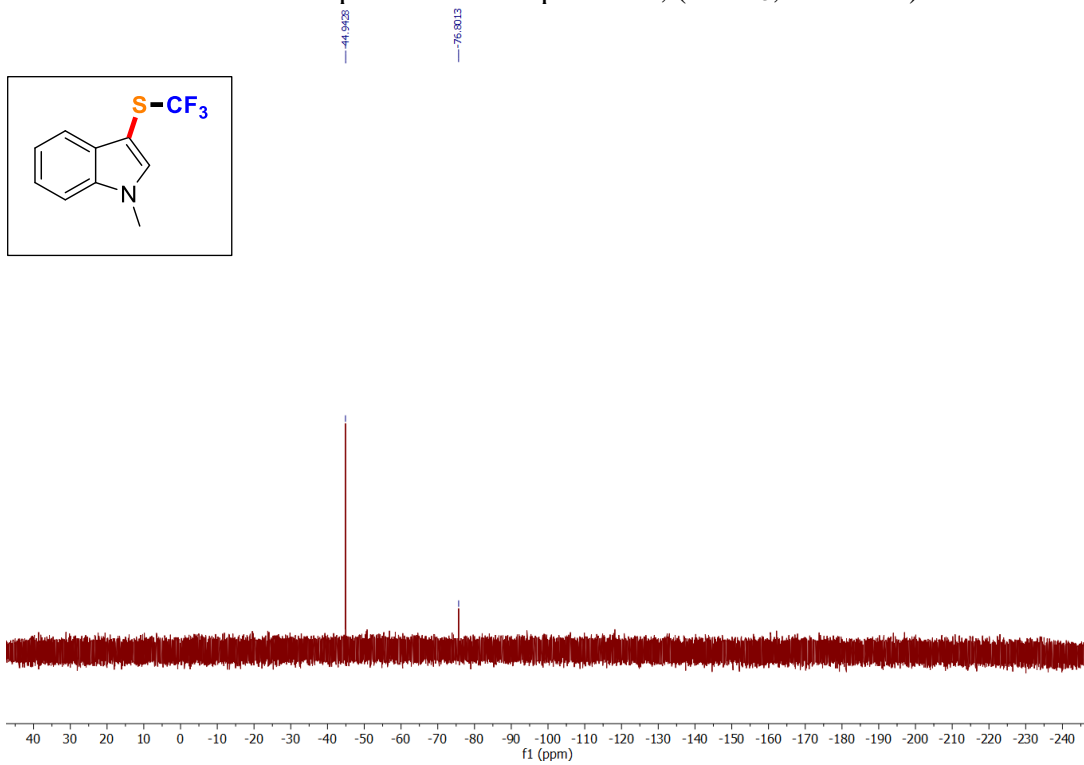
$^1\text{H}$  NMR spectrum of compound **5a**, ( $\text{CDCl}_3$ , 500 MHz).



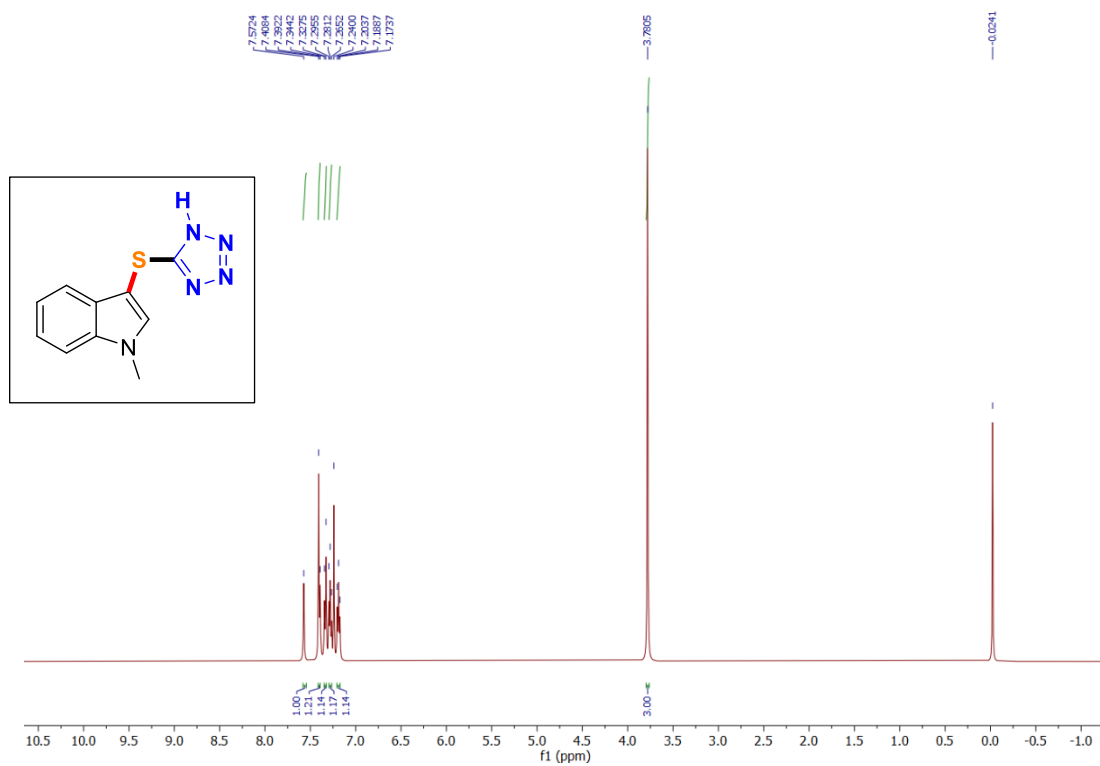
$^{13}\text{C}$  NMR spectrum of compound **5a**, ( $\text{CDCl}_3$ , 125 MHz).



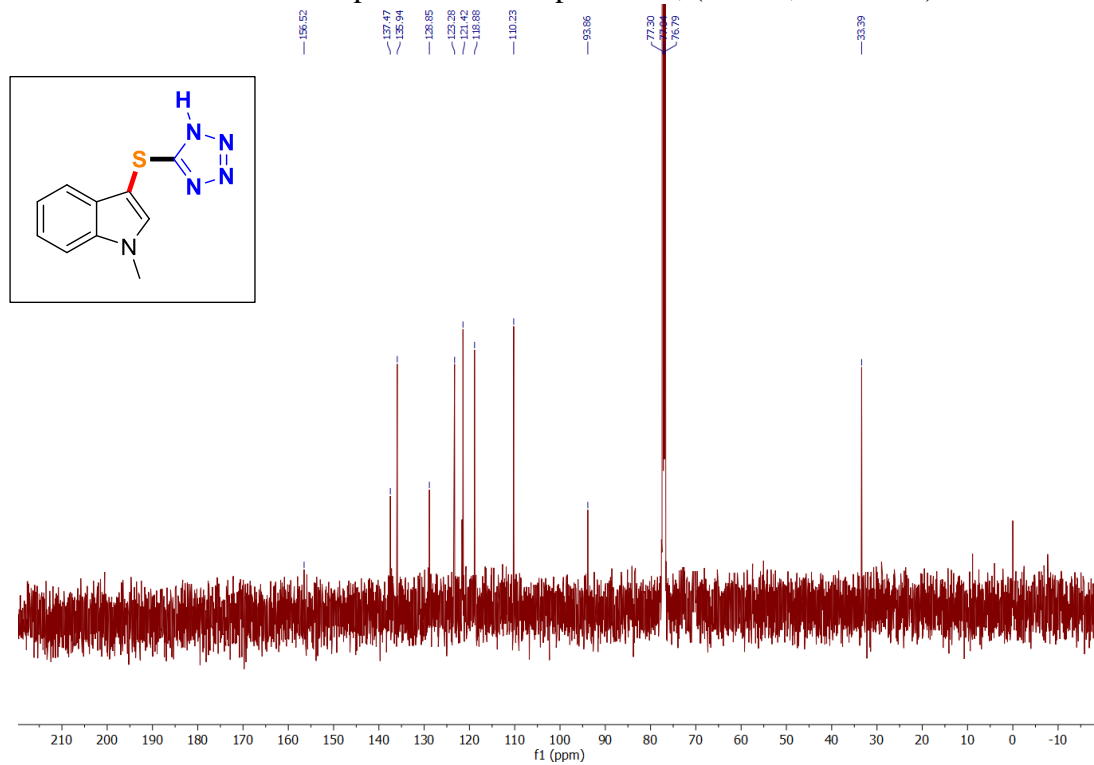
$^{19}\text{F}$  NMR spectrum of compound **5a**, ( $\text{CDCl}_3$ , 470 MHz).



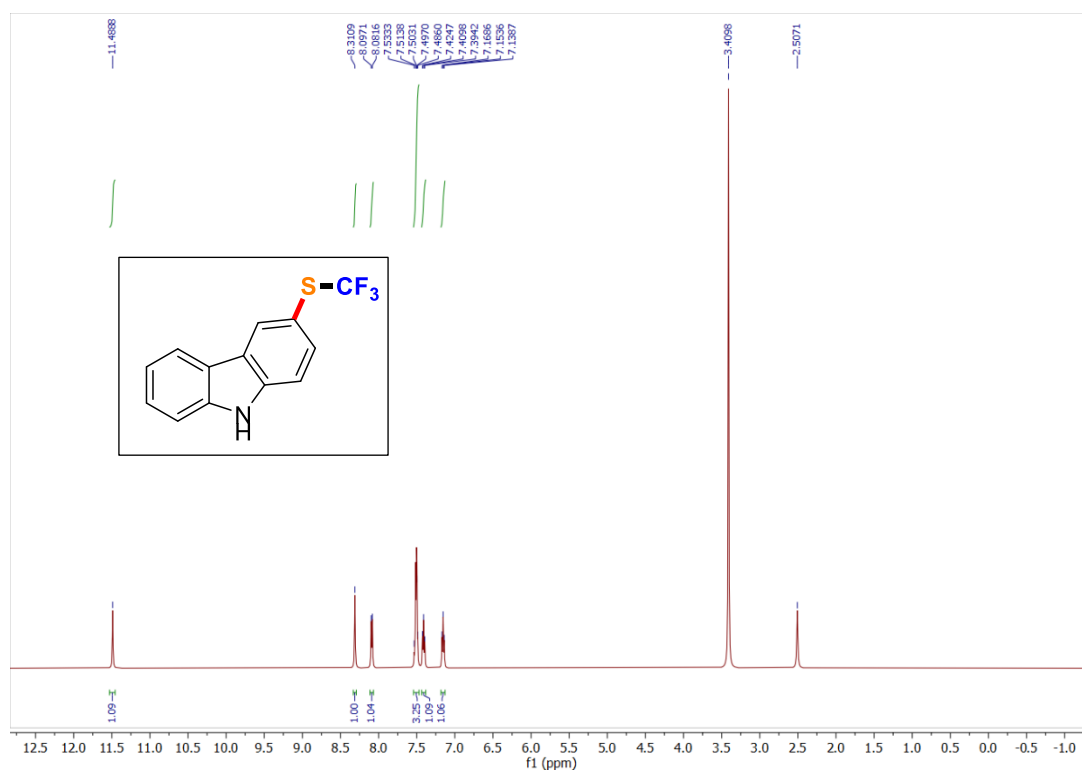
$^1\text{H}$  NMR spectrum of compound **5b**, ( $\text{CDCl}_3$ , 500 MHz).



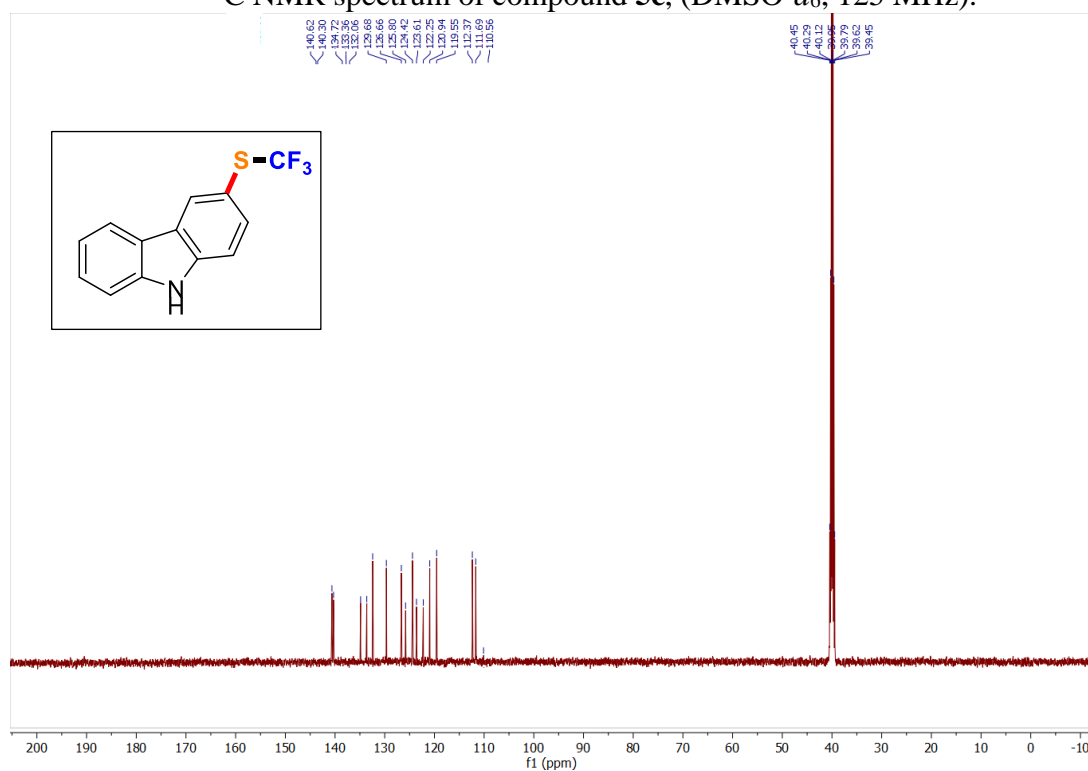
$^{13}\text{C}$  NMR spectrum of compound **5b**, ( $\text{CDCl}_3$ , 125 MHz).



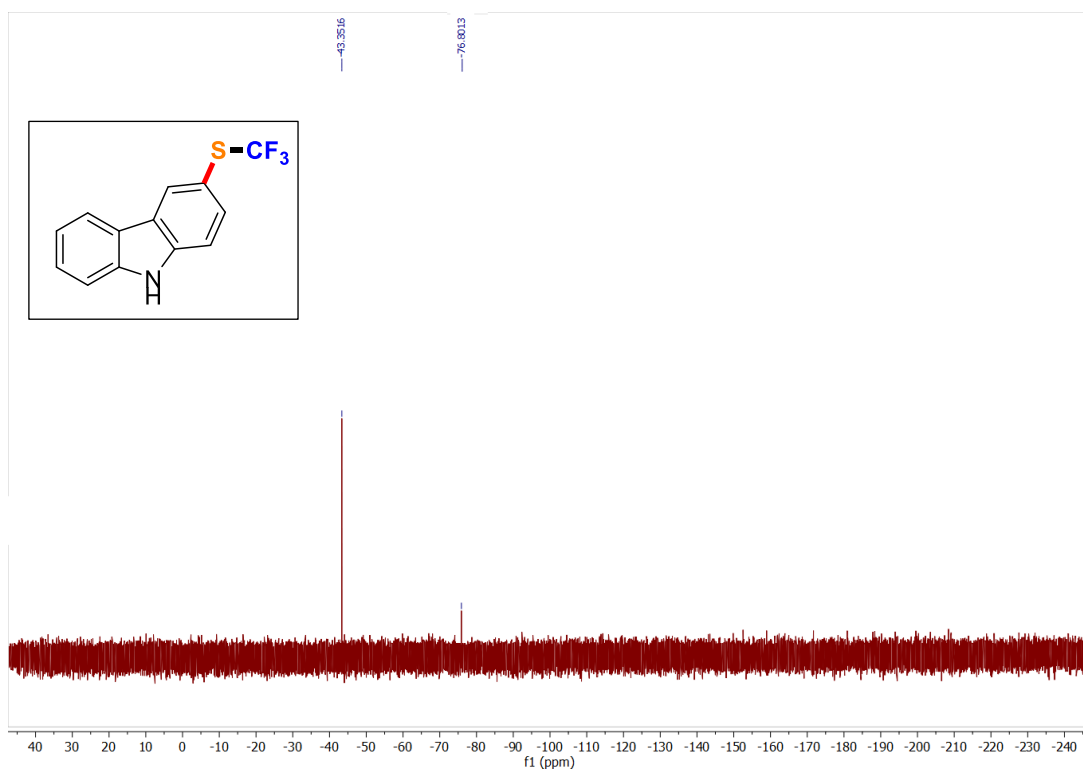
$^1\text{H}$  NMR spectrum of compound **5c**, ( $\text{DMSO-}d_6$ , 500 MHz).



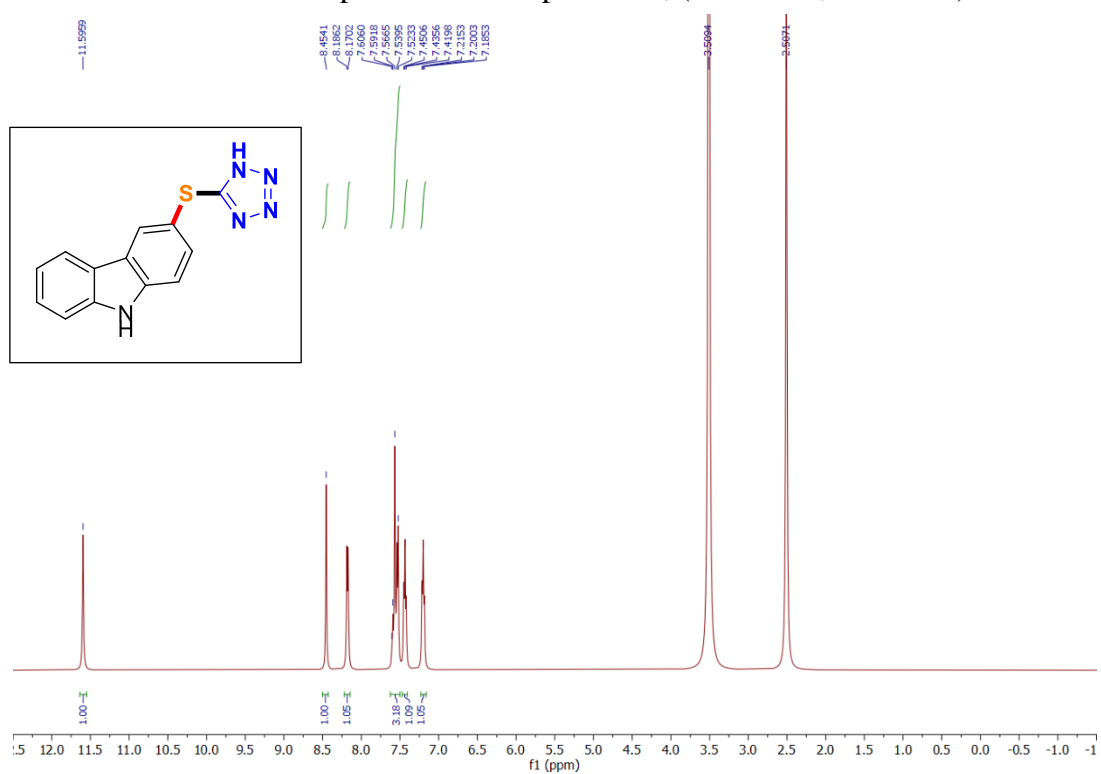
$^{13}\text{C}$  NMR spectrum of compound **5c**, ( $\text{DMSO-}d_6$ , 125 MHz).



$^{19}\text{F}$  NMR spectrum of compound **5c**, ( $\text{DMSO-}d_6$ , 470 MHz).



<sup>1</sup>H NMR spectrum of compound **5d**, (DMSO-*d*<sub>6</sub>, 500 MHz).



<sup>13</sup>C NMR spectrum of compound **5d**, (DMSO-*d*<sub>6</sub>, 125 MHz).

