

## *Supporting Information*

### **Magnesium-promoted nickel-catalysed chlorination of aryl halides and triflates under mild conditions**

Tian-Yu Zhang, Muhammad Bilal, Tian-Zhang Wang, Chao-Peng Zhang, and Yu-Feng Liang\*

School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

Email: yfliang@sdu.edu.cn

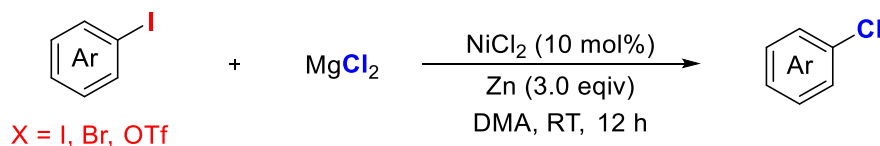
#### **Table of Contents**

<b>1. General remarks .....</b>	<b>S2</b>
<b>2. General procedure.....</b>	<b>S2</b>
<b>3. Optimization of the reaction conditions.....</b>	<b>S3</b>
<b>4. Characterization data.....</b>	<b>S3</b>
<b>5. Studies of Ni<sup>II</sup> complex .....</b>	<b>S20</b>
<b>6. Gram scale chlorination of bromiodobenzene .....</b>	<b>S22</b>
<b>7. Reaction kinetics .....</b>	<b>S22</b>
<b>8. References.....</b>	<b>S24</b>
<b>9. NMR Spectra.....</b>	<b>S26</b>

## 1. General remarks

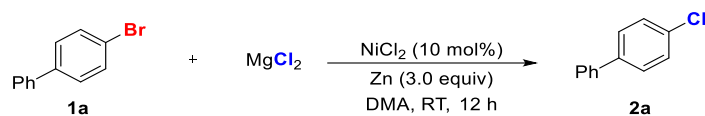
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR data were obtained on AVANCE III Bruker 400 or 500 MHz nuclear resonance spectrometers unless otherwise noted. Chemical shifts (in ppm) were referenced to tetramethylsilane (TMS) ( $\delta = 0.00$  ppm) in  $\text{CDCl}_3$  or dimethyl sulfoxide ( $\delta = 2.50$  ppm) in  $\text{DMSO-d}_6$  as an internal standard. The data of  $^1\text{H}$  NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant ( $J$  values) in Hz and integration.  $^{13}\text{C}$  NMR spectra were obtained by the same NMR spectrometers and were calibrated with  $\text{CDCl}_3$  ( $\delta = 77.00$  ppm) or  $\text{DMSO-d}_6$  ( $\delta = 39.50$  ppm). Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) unless otherwise noted. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI) mode.

## 2. General procedure



To a 15 mL Schlenk tube was added sequentially  $\text{NiCl}_2$  (2.6 mg, 0.02 mmol), Zn powder (39.2 mg, 0.60 mmol) and  $\text{MgCl}_2$  (57.1 mg, 0.6 mmol). Then aryl halides (0.2 mmol) was added. DMA (1.0 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature under  $\text{N}_2$ . The crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (2.0 mL  $\times$  3). The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The residue was purified by flash chromatography to afford aryl chlorides.

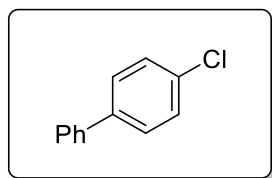
### 3. Optimization of the reaction conditions



Entry	Variation of optimal conditions	Yield of <b>2a</b> <sup>b</sup>
1	none	91% (89%)
2	NaCl instead of MgCl <sub>2</sub>	0
3	KCl instead of MgCl <sub>2</sub>	0
4	ZnCl <sub>2</sub> instead of MgCl <sub>2</sub>	trace
5	CaCl <sub>2</sub> instead of MgCl <sub>2</sub>	0
6	FeCl <sub>2</sub> instead of MgCl <sub>2</sub>	trace
7	CuCl <sub>2</sub> instead of MgCl <sub>2</sub>	trace
8	Et <sub>3</sub> BnNCl instead of MgCl <sub>2</sub>	trace
9	<sup>n</sup> Bu <sub>4</sub> NCl instead of MgCl <sub>2</sub>	trace
10	with MgSO <sub>4</sub> and NaCl instead of MgCl <sub>2</sub>	0
11	with 1.0 equiv of NiCl <sub>2</sub> in the absence of MgCl <sub>2</sub>	0
12	NiBr <sub>2</sub> instead of NiCl <sub>2</sub>	87%
13	NiI <sub>2</sub> instead of NiCl <sub>2</sub>	81% <sup>c</sup>
14	Ni(acac) <sub>2</sub> instead of NiCl <sub>2</sub>	85%
15	Ni(COD) <sub>2</sub> instead of NiCl <sub>2</sub> and Zn	86%
16	with 1,10-phenanthroline as ligand	90%
17	with 2,2'-bipyridine as ligand	89%
18	DMF instead of DMA	71%
19	THF instead of DMA	0
20	H <sub>2</sub> O instead of DMA	0
21	MeCN instead of DMA	0
22	without NiCl <sub>2</sub>	0
23	Mn instead of Zn	trace
24	without Zn	0

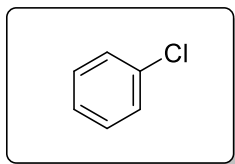
<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), MgCl<sub>2</sub> (0.6 mmol), NiCl<sub>2</sub> (10 mol%), Zn (0.6 mmol) and DMA (1.0 mL), at RT for 12 h under N<sub>2</sub>. <sup>b</sup>GC yields (isolated yield in parentheses). <sup>c</sup>The iodination byproduct was not detected.

### 4. Characterization data

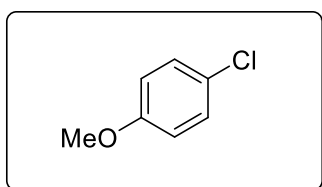


**4-Chloro-1,1'-biphenyl (2a)**.<sup>1</sup> The representative procedure was followed using 4-bromobiphenyl (**1a**) (46.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2a** (30.9 mg, 82%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.53 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.43 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 (dd, *J* = 8.4, 6.3 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.01, 139.67,

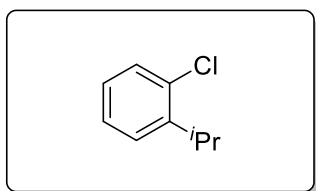
133.39, 128.95, 128.93, 128.44, 127.64, 127.03; **MS** (EI)  $m/z$  (relative intensity): 188 ( $M^+$ , 100), 152 (35), 153 (20).



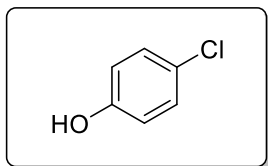
**Chlorobenzene (2b).**<sup>1</sup> The representative procedure was followed using bromobenzene (**1b**) (31.4 mg, 0.20 mmol). The yield was obtained *via* GC-MS (99%); **MS** (EI)  $m/z$  (relative intensity): 112.0 ( $M^+$ , 100), 77 (50), 51 (15).



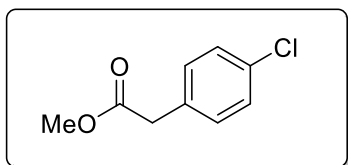
**1-Chloro-4-methoxybenzene (2c).**<sup>2</sup> The representative procedure was followed using 4-bromoanisole (**1c**) (37.4 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2c** (27.9 mg, 98%) as a colorless oil; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.31 – 7.15 (m, 2H), 6.88 – 6.76 (m, 2H), 3.77 (s, 3H), **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  158.18, 129.33, 125.50, 115.17, 55.50; **MS** (EI)  $m/z$  (relative intensity): 142 ( $M^+$ , 100), 127 (60), 99 (55).



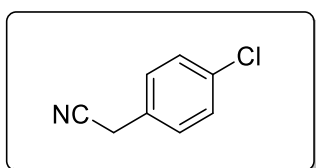
**1-Chloro-2-isopropylbenzene (2d).**<sup>3</sup> The representative procedure was followed using 1-bromo-2-(1-methylethyl)benzene (**1d**) (39.8 mg, 0.20 mmol). The yield was obtained *via* GC-MS (91%); **MS** (EI)  $m/z$  (relative intensity): 154 ( $M^+$ , 30), 139 (100), 103 (60), 77 (20).



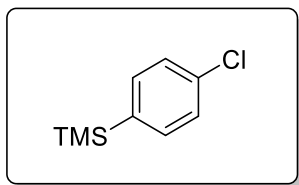
**4-Chlorophenol (2e).**<sup>4</sup> The representative procedure was followed using 4-bromophenol (**1e**) (34.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2e** (23.4 mg, 91%) as a white solid; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.23 – 7.16 (m, 2H), 6.80 – 6.74 (m, 2H), 5.10 (s, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  153.97, 129.60, 125.77, 116.69; **MS (EI) *m/z*** (relative intensity): 128 (**M<sup>+</sup>**, 100), 65 (50), 39 (20).



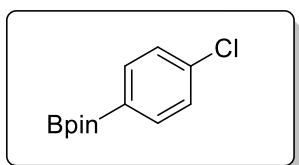
**Methyl 2-(4-chlorophenyl)acetate (2f).**<sup>5</sup> The representative procedure was followed using methyl 4-bromophenylacetate (**1f**) (45.8 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2f** (35.8 mg, 97%) as a colorless oil; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.35 – 7.25 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 3H), 3.59 (s, 3H), **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  171.68, 133.08, 132.42, 130.70, 128.74, 52.21, 40.44; **MS (EI) *m/z*** (relative intensity): 184 (**M<sup>+</sup>**, 25), 125 (100), 89 (25).



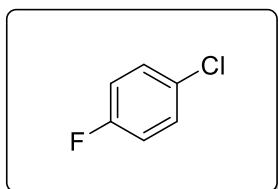
**2-(4-Chlorophenyl)acetonitrile (2g).**<sup>6</sup> The representative procedure was followed using 4-bromophenylacetonitrile (**1g**) (39.2 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2g** (27.9 mg, 92%) as a colorless oil; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.36 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.23 (m, 2H), 3.74 (s, 2H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  134.16, 129.36, 129.32, 128.37, 117.51, 23.16; **MS (EI) *m/z*** (relative intensity): 116 (**M<sup>+</sup>**, 100), 89 (15).



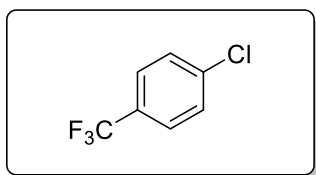
**(4-Chlorophenyl)trimethylsilane (2h).**<sup>7</sup> The representative procedure was followed using 4-bromophenylacetonitrile (**1h**) (45.8 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2h** (33.2 mg, 90%) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 – 7.28 (m, 2H), 7.26 – 7.16 (m, 2H), 0.15 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.91, 136.26, 135.86, 129.13, 0.00; MS (EI) *m/z* (relative intensity): 184 (**M**<sup>+</sup>, 45), 171 (95), 169 (100), 91 (40).



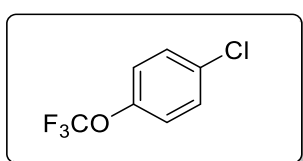
**2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i).**<sup>8</sup> The representative procedure was followed using 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1i**) (56.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2i** (44.4 mg, 93%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 1.26 (s, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.54, 136.14, 128.01, 84.02, 24.87; MS (EI) *m/z* (relative intensity): 238 (**M**<sup>+</sup>, 45), 223 (100), 152 (70), 85 (30), 58 (20).



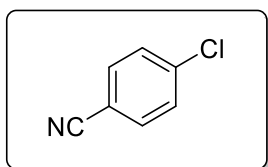
**1-Chloro-4-fluorobenzene (2j).**<sup>9</sup> The representative procedure was followed using 1-bromo-4-fluorobenzene (**1j**) (35.0 mg, 0.20 mmol). The yield was obtained *via* GC-MS (81%); MS (EI) *m/z* (relative intensity): 130 (**M**<sup>+</sup>, 100), 95 (60), 75 (25), 50 (10).



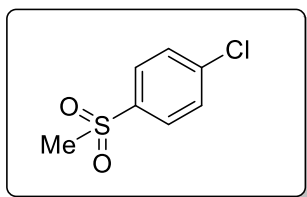
**1-Chloro-4-(trifluoromethyl)benzene (2k).**<sup>10</sup> The representative procedure was followed using 1-bromo-4-(trifluoromethyl)benzene (**1k**) (45.0 mg, 0.20 mmol). The yield was obtained *via* GC-MS (93%); **MS** (EI) *m/z* (relative intensity): 180 (**M**<sup>+</sup>, 100), 161 (40), 145 (45), 130 (25), 75 (20).



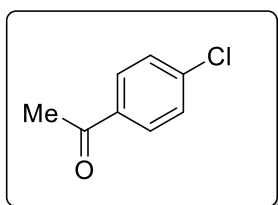
**4-(Trifluoromethoxy)chlorobenzene (2l).**<sup>11</sup> The representative procedure was followed using 4-(trifluoromethoxy)bromobenzene (**2l**) (48.2 mg, 0.20 mmol). The yield was obtained *via* GC-MS (70%); **MS** (EI) *m/z* (relative intensity): 196 (**M**<sup>+</sup>, 100), 127 (35), 101 (10), 99 (30), 69 (10).



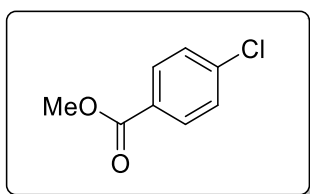
**4-Chlorobenzonitrile (2m).**<sup>6</sup> The representative procedure was followed using 4-bromobenzonitrile (**1m**) (36.4 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2m** (22.3 mg, 81%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 – 7.55 (m, 2H), 7.53 – 7.39 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.58, 133.43, 129.73, 118.05, 110.76; **MS** (EI) *m/z* (relative intensity): 137 (**M**<sup>+</sup>, 100), 102 (30), 75 (10), 50 (10).



**1-Chloro-4-(methylsulfonyl)benzene (2n).**<sup>12</sup> The representative procedure was followed using 1-bromo-4-(methylsulfonyl)benzene (**1n**) (47.0 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2n** (29.7 mg, 78%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.55 (m, 2H), 7.53 – 7.39 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.46, 139.06, 129.72, 128.93, 44.54; MS (EI) *m/z* (relative intensity): 190 (**M**<sup>+</sup>, 70), 111 (100), 75 (75), 50 (30).



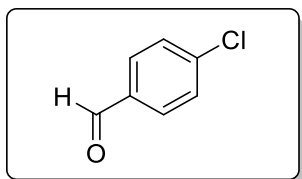
**1-(4-Chlorophenyl)ethan-1-one (2o).**<sup>13</sup> The representative procedure was followed using 1-(4-bromophenyl)ethan-1-one (**1o**) (39.8 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2o** (22.3 mg, 72%) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 – 7.86 (m, 2H), 7.46 – 7.39 (m, 2H), 2.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.88, 139.55, 135.37, 129.75, 128.89, 26.61; MS (EI) *m/z* (relative intensity): 139 (**M**<sup>+</sup>, 100), 111 (40), 75 (20), 43 (15).



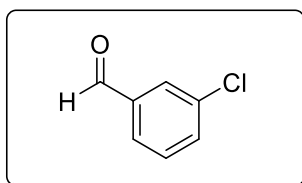
**Methyl 4-chlorobenzoate (2p).**<sup>14</sup> The representative procedure was followed using Methyl 4-bromobenzoate (**1p**) (43.0 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2p** (27.3 mg, 80%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 – 7.61 (m, 2H), 7.26 (dd, *J* = 5.9, 4.7 Hz, 2H), 3.79 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.81, 139.13, 130.82, 128.51, 51.98; MS



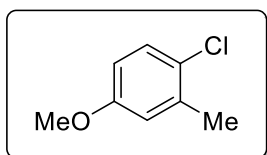
(EI)  $m/z$  (relative intensity): 183 ( $M^+$ , 100), 155 (30), 158 (30).



**4-Chlorobenzaldehyde (2q).**<sup>15</sup> The representative procedure was followed using 4-bromobenzaldehyde (**1q**) (37.0 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2q** (22.5 mg, 80%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.91 (d,  $J = 11.9$  Hz, 1H), 7.89 – 7.63 (m, 2H), 7.40 (d,  $J = 8.5$  Hz, 2H),  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.70, 140.71, 134.72, 130.80, 129.33; **MS** (EI)  $m/z$  (relative intensity): 139 ( $M^+$ , 100), 111 (65), 75 (50), 50 (50).

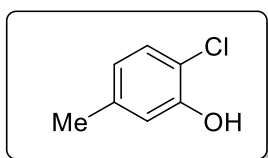


**3-Chlorobenzaldehyde (2r).**<sup>16</sup> The representative procedure was followed using 3-bromobenzaldehyde (**1r**) (37.0 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2r** (26.1 mg, 93%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.98 (d,  $J = 5.8$  Hz, 1H), 7.91 – 7.83 (m, 1H), 7.77 (ddd,  $J = 6.0, 4.4, 1.2$  Hz, 1H), 7.65 – 7.57 (m, 1H), 7.49 (dd,  $J = 7.7, 5.5$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.81, 137.83, 135.45, 134.36, 130.37, 129.26, 127.96; **MS** (EI)  $m/z$  (relative intensity): 140 ( $M^+$ , 80), 111 (55), 75 (30).

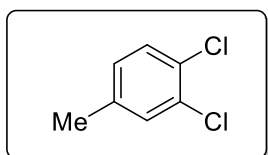


**1-Chloro-4-methoxy-2-methylbenzene (2s).**<sup>17</sup> The representative procedure was followed using 1-bromo-4-methoxy-2-methylbenzene (**1s**) (40.2 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2s** (29.8 mg, 95%) as a

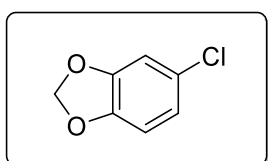
white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (d,  $J = 8.7$  Hz, 1H), 6.82 (d,  $J = 2.7$  Hz, 1H), 6.72 (dd,  $J = 8.7, 2.7$  Hz, 1H), 3.81 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.21, 136.96, 129.59, 125.81, 116.49, 112.54, 55.37, 20.29;  $\text{MS}$  (EI)  $m/z$  (relative intensity): 158 ( $\text{M}^+$ , 30), 156 (100), 121 (40), 113 (40), 91 (30).



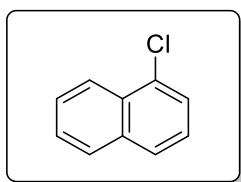
**2-Chloro-5-methylphenol (2t).**<sup>18</sup> The representative procedure was followed using 2-bromo-5-methylphenol (**1t**) (37.4 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2t** (27.8 mg, 98%) as a white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (d,  $J = 8.2$  Hz, 1H), 6.84 (d,  $J = 2.0$  Hz, 1H), 6.68 (dd,  $J = 8.2, 2.0$  Hz, 1H), 5.47 (s, 1H), 2.30 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.94, 138.73, 128.48, 128.41, 122.17, 116.76, 21.02;  $\text{MS}$  (EI)  $m/z$  (relative intensity): 142 ( $\text{M}^+$ , 50), 107 (100), 77 (25), 51 (5).



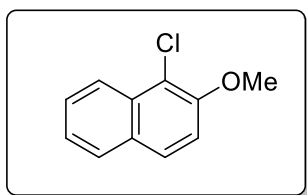
**1,2-Dichloro-4-methoxybenzene (2u).**<sup>17</sup> The representative procedure was followed using 1-bromo-2-chloro-4-methoxybenzene (**1u**) (41.1 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2u** (25.0 mg, 78%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.27 (m, 2H), 7.06 – 6.99 (m, 1H), 2.33 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.04, 132.02, 130.96, 130.07, 129.32, 128.55, 20.65;  $\text{MS}$  (EI)  $m/z$  (relative intensity): 160 ( $\text{M}^+$ , 50), 125 (100), 89 (20).



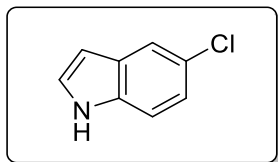
**5-Chloro-1,3-benzodioxole (2v).**<sup>19</sup> The representative procedure was followed using 4-bromo-1,2-(methylenedioxy)benzene (**1v**) (40.2 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2v** (22.5 mg, 72%) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.85 – 6.80 (m, 2H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.99 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.35, 146.47, 126.28, 121.30, 109.63, 108.88, 101.67; MS (EI) *m/z* (relative intensity): 156 (**M**<sup>+</sup>, 80), 155 (100), 98 (10).



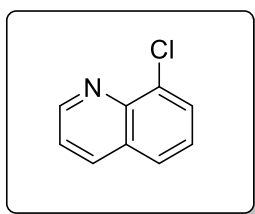
**1-Chloronaphthalene (2w).**<sup>20</sup> The representative procedure was followed using 1-bromonaphthalene (**1w**) (50.8 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2w** (32.5 mg, 92%) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.50 (m, 3H), 7.43 – 7.33 (m, 1H), 7.24 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 134.56, 131.94, 130.81, 128.26, 127.21, 127.09, 126.73, 126.20, 125.77, 124.44; MS (EI) *m/z* (relative intensity): 162 (**M**<sup>+</sup>, 100), 127 (35), 126 (15).



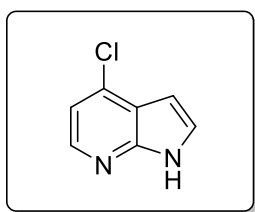
**1-Chloro-2-methoxynaphthalene (2x).**<sup>21</sup> The representative procedure was followed using 1-bromo-2-methoxynaphthalene (**1x**) (47.4 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2x** (21.6 mg, 56%) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 8.6 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.60 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.43 (ddd, *J* = 8.1, 6.9, 1.0 Hz, 1H), 7.34 – 7.30 (m, 1H), 4.06 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.59, 131.91, 129.55, 128.02, 127.98, 127.47, 124.34, 123.48, 113.75, 57.01; MS (EI) *m/z* (relative intensity): 192 (**M**<sup>+</sup>, 100), 177 (35), 151 (25), 149 (85).



**5-Chloroindole (2y).**<sup>22</sup> The representative procedure was followed using 5-iodoindole (**1y**) (39.2 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2y** (23.3 mg, 77%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (s, 1H), 7.75 (s, 1H), 7.32 – 7.24 (m, 2H), 7.21 (s, 1H), 6.64 – 6.54 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 134.26, 129.06, 125.91, 125.49, 122.36, 120.19, 112.31, 102.40; MS (EI) *m/z* (relative intensity): 151 (M<sup>+</sup>, 100), 116 (20), 89 (25).

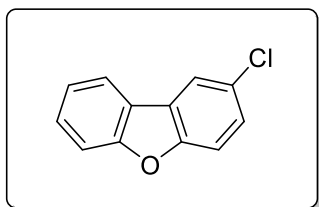


**8-Chloroquinoline (2z).**<sup>23</sup> The representative procedure was followed using 8-bromoquinoline (**1z**) (41.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2z** (17.0 mg, 52%) as a yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.06 – 9.00 (m, 1H), 8.15 (ddd, *J* = 7.3, 5.5, 1.6 Hz, 1H), 7.82 (ddd, *J* = 7.4, 4.9, 1.2 Hz, 1H), 7.77 – 7.66 (m, 1H), 7.47 – 7.41 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.97, 144.44, 136.51, 133.45, 129.59, 126.98, 126.48, 121.90; MS (EI) *m/z* (relative intensity): 163 (M<sup>+</sup>, 100), 128 (40), 101 (20).

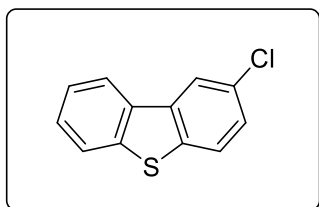


**4-Chloro-1H-pyrrolo[2,3-*b*]pyridine (2a').**<sup>24</sup> The representative procedure was followed using 4-bromo-1H-pyrrolo[2,3-*b*]pyridine (**1a'**) (39.2 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2a'** (17.6 mg, 58%) as a grey solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.39 (s, 1H), 8.23 (d, *J* = 5.2 Hz, 1H),

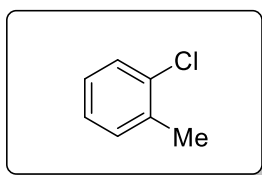
7.42 (d,  $J = 3.5$  Hz, 1H), 7.15 (d,  $J = 5.2$  Hz, 1H), 6.63 (d,  $J = 3.5$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.05, 142.51, 136.59, 125.81, 120.04, 116.03, 99.47; MS (EI)  $m/z$  (relative intensity): 152 ( $\text{M}^+$ , 100), 117 (60), 90 (25), 63 (40).



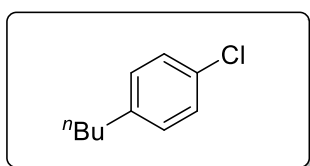
**2-Chlorodibenzo[b,d]furan (2b')**.<sup>25</sup> The representative procedure was followed using 2-bromodibenzo[b,d]furan (**1b'**) (49.4 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2b'** (33.7 mg, 83%) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.77 (m, 2H), 7.49 – 7.43 (m, 1H), 7.40 – 7.35 (m, 2H), 7.34 – 7.21 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 154.4, 128.2, 127.8, 127.1, 125.6, 123.3, 123.0, 120.8, 120.5, 112.6, 111.8; MS (EI)  $m/z$  (relative intensity): 202 ( $\text{M}^+$ , 100), 139 (40), 101 (10), 69 (10).



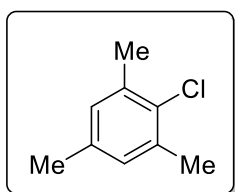
**2-Chlorodibenzo[b,d]thiophene (2c')**.<sup>26</sup> The representative procedure was followed using 2-bromodibenzo[b,d]thiophene (**1c'**) (52.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2c'** (29.3 mg, 67%) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 – 8.00 (m, 2H), 7.79 – 7.75 (m, 1H), 7.68 – 7.61 (m, 1H), 7.46 – 7.32 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 137.3, 136.9, 134.4, 130.6, 127.3, 126.9, 124.6, 123.7, 122.9, 121.7, 121.5; MS (EI)  $m/z$  (relative intensity): 218 ( $\text{M}^+$ , 100), 183 (15), 139 (30), 109 (10), 91 (15),.



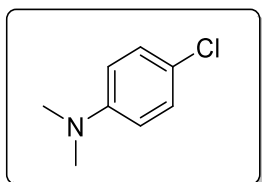
**1-Chloro-2-methylbenzene (4c).**<sup>27</sup> The representative procedure was followed using 1-iodo-2-methylbenzene (**3c**) (43.6 mg, 0.20 mmol). The yield was obtained *via* GC-MS (95%); **MS** (EI) *m/z* (relative intensity): 126 (**M**<sup>+</sup>, 30), 91 (100), 89 (20), 63 (15).



**1-Butyl-4-chlorobenzene (4d).**<sup>28</sup> The representative procedure was followed using 1-butyl-4-iodidobenzene (**3d**) (42.6 mg, 0.20 mmol). The yield was obtained *via* GC-MS (98%); **MS** (EI) *m/z* (relative intensity): 168 (**M**<sup>+</sup>, 25), 125 (100), 91 (20), 89 (10).

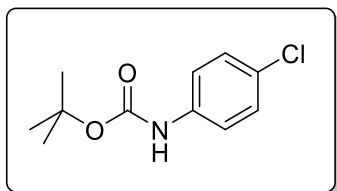


**2-Chloro-1,3,5-trimethylbenzene (4e).**<sup>29</sup> The representative procedure was followed using 2-iodo-1,3,5-trimethylbenzene (**3e**) (49.2 mg, 0.20 mmol). The yield was obtained *via* GC-MS (98%); **MS** (EI) *m/z* (relative intensity): 154 (**M**<sup>+</sup>, 30), 119 (100), 91 (20), 77 (15).

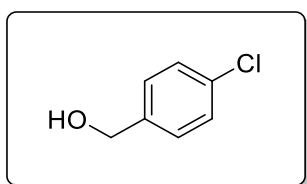


**4-Chloro-*N,N*-dimethylaniline (4f).**<sup>30</sup> The representative procedure was followed using 4-iodo-*N,N*-dimethylaniline (**3f**) (49.4 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **2f** (29.3 mg, 94%) as a pale amber molten

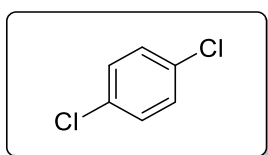
solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 6.91 (m, 2H), 6.79 – 6.39 (m, 2H), 2.81 (s, 6H),  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.23, 128.83, 121.45, 113.71, 40.67; **MS** (EI)  $m/z$  (relative intensity): 154 ( $\text{M}^+$ , 100), 139 (15), 119 (15), 118 (20), 77 (15).



**Tert-butyl (4-chlorophenyl)carbamate (4g).**<sup>31</sup> The representative procedure was followed using *tert*-butyl (4-iodophenyl)carbamate (**3g**) (63.8 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **4g** (40.1 mg, 88%) as a white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.8$  Hz, 2H), 7.25 (d,  $J = 8.8$  Hz, 2H), 1.53 (s, 9H), 1.50 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.00, 128.93, 127.96, 119.76, 80.86, 28.32; **MS** (EI)  $m/z$  (relative intensity): 227 ( $\text{M}^+$ , 10), 171 (35), 127 (40), 57 (100), 59 (20).

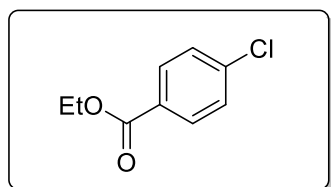


**4-Chlorobenzyl alcohol (4i).**<sup>32</sup> The representative procedure was followed using 4-iodobenzyl alcohol (**3i**) (46.8 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **4i** (27.4 mg, 96%) as a white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.29 (m, 2H), 7.27 (d,  $J = 8.3$  Hz, 2H), 4.63 (s, 2H), 2.14 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.24, 133.33, 128.69, 128.31, 64.50; **MS** (EI)  $m/z$  (relative intensity): 142 ( $\text{M}^+$ , 70), 113 (20), 107 (95), 77 (100).

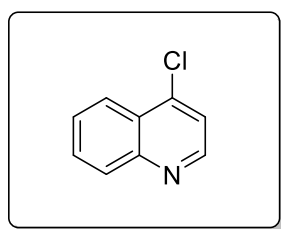


**1,4-Dichlorobenzene (4k).**<sup>9</sup> The representative procedure was followed using 1-chloro-4-iodobenzene (**3k**) (47.7 mg, 0.20 mmol). Isolation by column chromatography

(petroleum ether) yielded **4k** (28.5 mg, 97%) as a white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (s, 4H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.57, 129.82; MS (EI)  $m/z$  (relative intensity): 146 ( $\text{M}^+$ , 100), 113 (10), 111 (35), 75 (25), 50 (15).

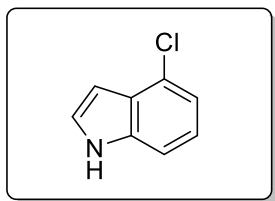


**Ethyl 4-chlorobenzoate (4o).**<sup>33</sup> The representative procedure was followed using ethyl 4-iodobenzoate (**3o**) (55.2 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **4o** (28.8 mg, 78%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.5$  Hz, 2H), 7.42 (d,  $J = 8.5$  Hz, 2H), 4.39 (q,  $J = 7.1$  Hz, 2H), 1.40 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.73, 139.23, 130.93, 128.97, 128.64, 61.19, 14.28; MS (EI)  $m/z$  (relative intensity): 184 ( $\text{M}^+$ , 15), 156 (30), 139 (100), 111 (30), 75 (20).

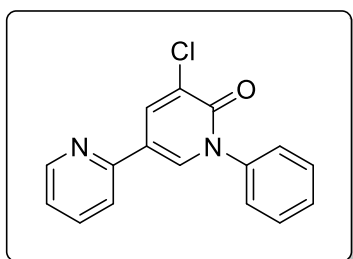


**4-Chloroquinoline (4q).**<sup>23</sup> The representative procedure was followed using ethyl 4-iodoquinoline (**3q**) (51.1 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **4q** (30.1 mg, 92%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.7$  Hz, 1H), 8.25 (dd,  $J = 8.4, 1.1$  Hz, 1H), 8.15 (d,  $J = 8.4$  Hz, 1H), 7.79 (ddd,  $J = 8.4, 7.0, 1.3$  Hz, 1H), 7.70 – 7.62 (m, 1H), 7.51 (d,  $J = 4.7$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.80, 148.96, 142.86, 130.53, 129.73, 127.72, 126.54, 124.20, 121.30; MS (EI)  $m/z$  (relative intensity): 163 ( $\text{M}^+$ , 100), 128 (40), 127 (20), 101 (15), 100 (10).

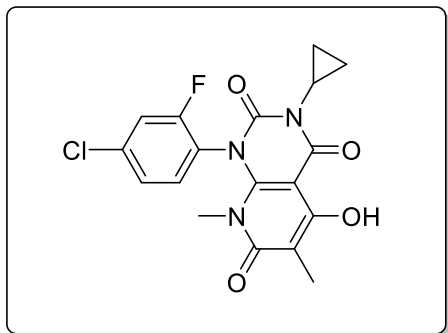




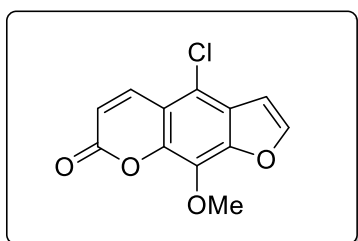
**4-Chloro-1H-indole (4r).**<sup>22</sup> The representative procedure was followed using ethyl 4-iodo-1H-indole (**3r**) (48.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **4r** (27.9 mg, 86%) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (s, 1H), 7.27 (d,  $J$  = 7.3 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.14 – 7.08 (m, 2H), 6.65 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.47, 126.78, 126.10, 124.79, 122.65, 119.63, 109.76, 101.35; MS (EI)  $m/z$  (relative intensity): 151 (M<sup>+</sup>, 100), 116 (20), 89 (25).



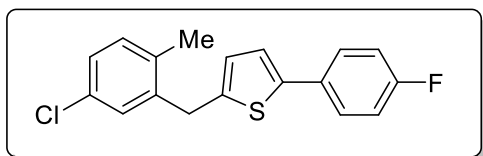
**5'-Chloro-1'-phenyl-[2,3'-bipyridin]-6'(1'H)-one (5a).**<sup>17</sup> The representative procedure was followed using 5'-bromo-1'-phenyl-[2,3'-bipyridin]-6'(1'H)-one (**5a'**) (65.4 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **5a** (46.0 mg, 82%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (d,  $J$  = 4.3 Hz, 1H), 8.22 (d,  $J$  = 2.4 Hz, 1H), 8.07 (d,  $J$  = 2.4 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.50 – 7.32 (m, 6H), 7.14 (dd,  $J$  = 6.9, 4.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.33, 152.32, 149.81, 140.78, 137.13, 136.31, 135.61, 129.45, 129.02, 127.13, 126.51, 122.26, 118.53, 118.05.



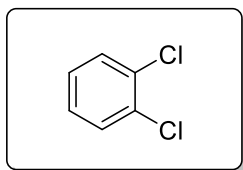
**1-(4-Chloro-2-fluorophenyl)-3-cyclopropyl-5-hydroxy-6,8-dimethylpyrido[2,3-d]pyrimidine-2,4,7(1H,3H,8H)-trione (5b).**<sup>17</sup> The representative procedure was followed using 3-cyclopropyl-1-(2-fluoro-4-iodophenyl)-5-hydroxy-6,8-dimethylpyrido[2,3-d]pyrimidine-2,4,7(1H,3H,8H)-trione (**5b'**) (96.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **5b** (60.7 mg, 78%) as a white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.90 (s, 1H), 7.25 – 7.09 (m, 3H), 2.82 (s, 3H), 1.95 (d, *J* = 12.5 Hz, 3H), 1.27 – 1.05 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.62, 163.79, 160.80, 157.04, 153.91, 148.39, 131.86, 129.36, 125.33, 117.26, 117.06, 103.28, 34.51, 29.69, 25.37, 8.42, 8.36, 8.21.



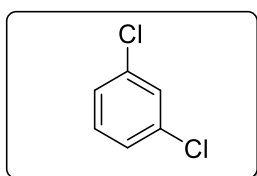
**4-chloro-9-methoxy-7H-furo[3,2-g]chromen-7-one (5c).**<sup>17</sup> The representative procedure was followed using 4-bromo-9-methoxy-7H-furo[3,2-g]chromen-7-one (**5c'**) (58.8 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **5c** (40.0 mg, 60%) as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.6 (d, *J* = 10.0 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.46 (d, *J* = 10.0 Hz, 1H), 4.28 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.6, 149.8, 146.9, 143.7, 140.2, 131.9, 125.6, 116.2, 115.6, 114.3, 105.8, 61.5.



**2-(5-Chloro-2-methylbenzyl)-5-(4-fluorophenyl)thiophene (5d).**<sup>17</sup> The representative procedure was followed using 2-(4-fluorophenyl)-5-(5-iodo-2-methylbenzyl)thiophene (**5d'**) (81.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **5d** (52.6 mg, 83%) as a white solid; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.46 – 7.35 (m, 3H), 7.20 – 7.02 (m, 2H), 7.01 – 6.79 (m, 4H), 4.06 – 3.95 (m, 2H), 2.28 – 2.17 (m, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  142.31, 141.85, 140.61, 138.13, 136.08, 135.99, 132.38, 131.68, 130.47, 129.30, 127.23, 127.15, 126.20, 122.74, 115.86, 115.64, 33.70, 19.12.

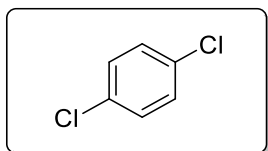


**1,2-Dichlorobenzene (7a).**<sup>9</sup> The representative procedure was followed using 1-bromo-2-iodobenzene (**6a**) (56.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **7a** (23.2 mg, 79%) as a colorless oil; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.46 – 7.25 (m, 2H), 7.18 – 7.00 (m, 2H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  132.59, 130.55, 127.73; **MS (EI) *m/z*** (relative intensity): 147 (**M<sup>+</sup>**, 10), 146 (100), 111 (35), 75 (20).

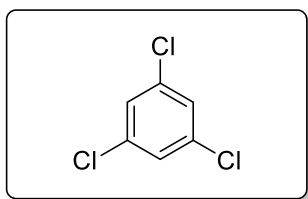


**1,3-Dichlorobenzene (7b).**<sup>34</sup> The representative procedure was followed using 1-bromo-3-iodobenzene (**6b**) (56.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **7b** (24.4 mg, 83%) as a colorless oil; **<sup>1</sup>H NMR (400 MHz,**

$\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 1.5$  Hz, 1H), 7.28 – 7.23 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.05, 130.47, 128.76, 126.91; MS (EI)  $m/z$  (relative intensity): 147 ( $\text{M}^+$ , 10), 146 (100), 111 (35), 75 (20).



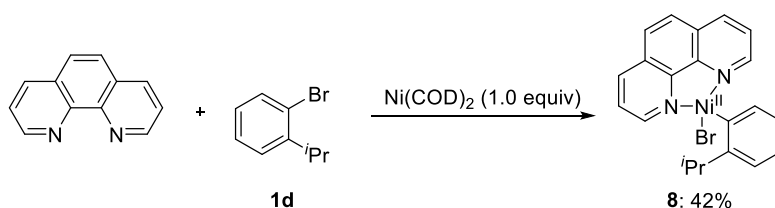
**1,4-Dichlorobenzene (7c).**<sup>9</sup> The representative procedure was followed using 1-bromo-4-iodobenzene (**6b**) (56.6 mg, 0.20 mmol). Isolation by column chromatography (petroleum ether) yielded **7c** (25.1 mg, 86%) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.57, 129.82; MS (EI)  $m/z$  (relative intensity): 146 ( $\text{M}^+$ , 100), 113 (10), 111 (35), 75 (25), 50 (15).



**1,3,5-Trichlorobenzene (7d).**<sup>35</sup> The representative procedure was followed using 1-bromo-3-chloro-5-iodobenzene (**6d**) (3.15 g, 10.0 mmol). Isolation by column chromatography (petroleum ether) yielded **7d** (1.48 g, 82%) as a white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.31, 135.56, 127.20; MS (EI)  $m/z$  (relative intensity): 181 ( $\text{M}^+$ , 10), 180 (100), 145 (25), 74 (20).

## 4. Studies of $\text{Ni}^{\text{II}}$ complex

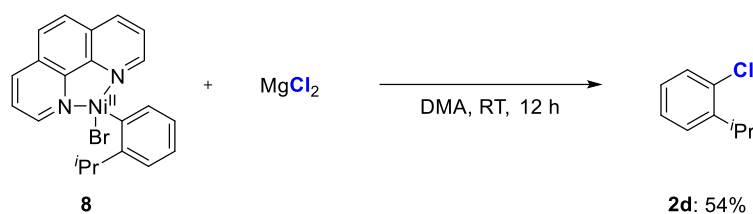
### 4.1 Preparation of $\text{Ar-Ni}^{\text{II}}(\text{1,10-phen})\text{Br}$ :



In a nitrogen-filled glove box,  $\text{Ni}(\text{COD})_2$  (1.00 g, 3.6 mmol), 1,10-phenanthroline

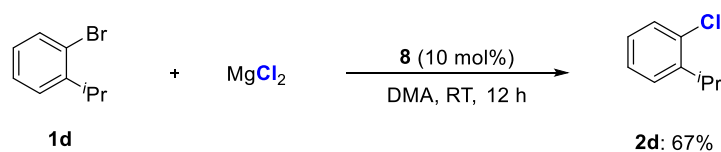
(0.778 g, 4.3 mmol), and THF (144 mL) were added to a dry round bottom flask. The resulting mixture was then stirred at RT for 20 h. After this time, 2-bromocumene (695  $\mu$ L, 4.3 mmol) was added, and reaction was stirred in the glovebox at RT for 2 h. The resulting solution was concentrated in vacuo, and the resulting dark red solid was triturated with pentanes to remove residual cyclooctadiene and aryl halide to afford complex **8** in 42% yield.<sup>14</sup> (S. Biswas and D. J. Weix, *J. Am. Chem. Soc.*, 2013, **135**, 16192-16197)

#### 4.2 Reaction of Ni<sup>II</sup> complex with MgCl<sub>2</sub>



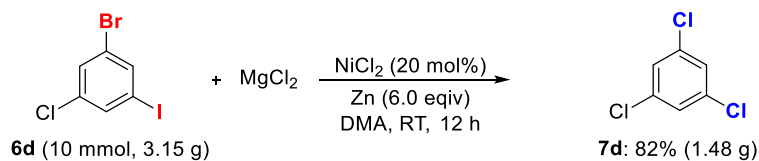
To a 15 mL Schlenk tube was added sequentially complex **8** (87.2 mg, 0.2 mmol) and MgCl<sub>2</sub> (57.1 mg, 0.6 mmol). Then DMA (1.0 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature under N<sub>2</sub>. The yield of **2d** was obtained *via* GC-MS (54%).

#### 4.3 Ni<sup>II</sup> complex catalyzed chlorination



To a 15 mL Schlenk tube was added sequentially complex **8** (8.7 mg, 0.02 mmol) and MgCl<sub>2</sub> (57.1 mg, 0.6 mmol). Then 2-bromocumene (0.2 mmol) and DMA (1.0 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature under N<sub>2</sub>. The yield of **2d** was obtained *via* GC-MS (67%).

## 5. Gram scale chlorination of bromiodobenzene

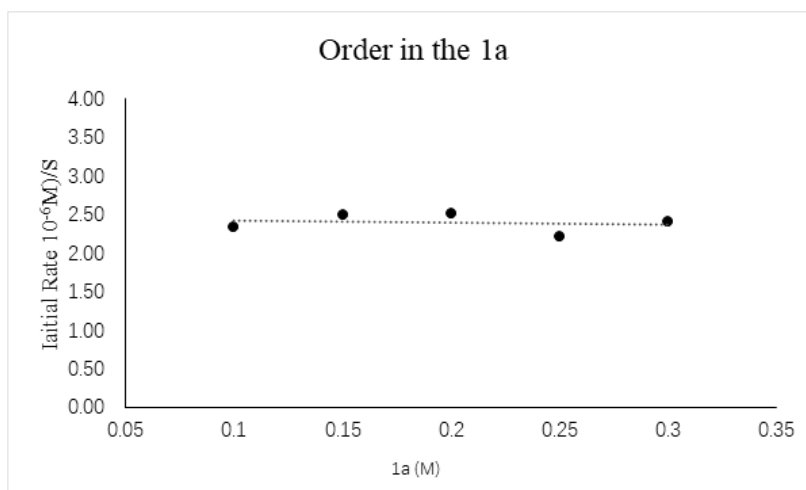


To a 100 mL Schlenk flask was added sequentially  $\text{NiCl}_2$  (260 mg, 2 mmol), Zn power (3.92 g, 60 mmol) and  $\text{MgCl}_2$  (5.71 g, 60 mmol). Then 1-bromo-3-chloro-5-iodobenzene (3.15 g, 10 mmol) and DMA (50 mL) was subsequently added *via* syringe. The resulting solution was stirred for 12 h at room temperature under  $\text{N}_2$ . The crude reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (20 mL  $\times$  3). The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The residue was purified by flash chromatography to afford 1,3,5-trichlorobenzene **7d** (1.48 g, 82% yield).

## 6. Reaction kinetics

### a) Order in **1a**

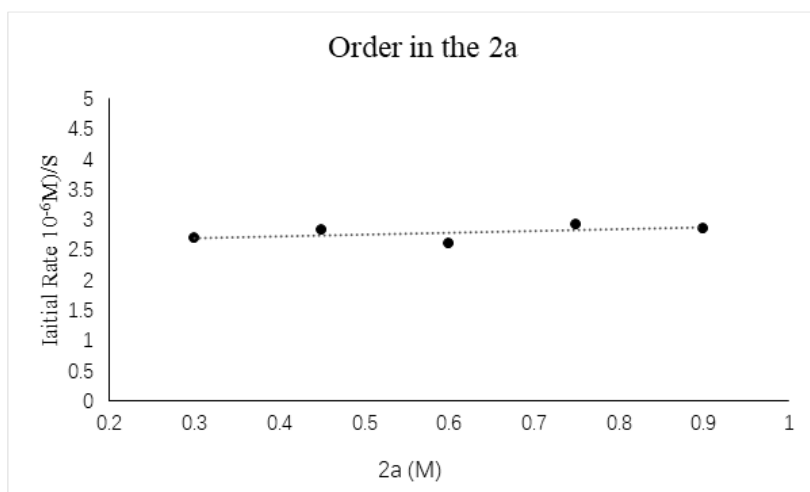
The order in **1a** was determined by obtaining the initial rate of the **2a** formation at differing amount of **1a**.



### b) Order in $\text{MgCl}_2$

The order in  $\text{MgCl}_2$  was determined by obtaining the initial rate of the **2a** formation at differing amount of  $\text{MgCl}_2$ .

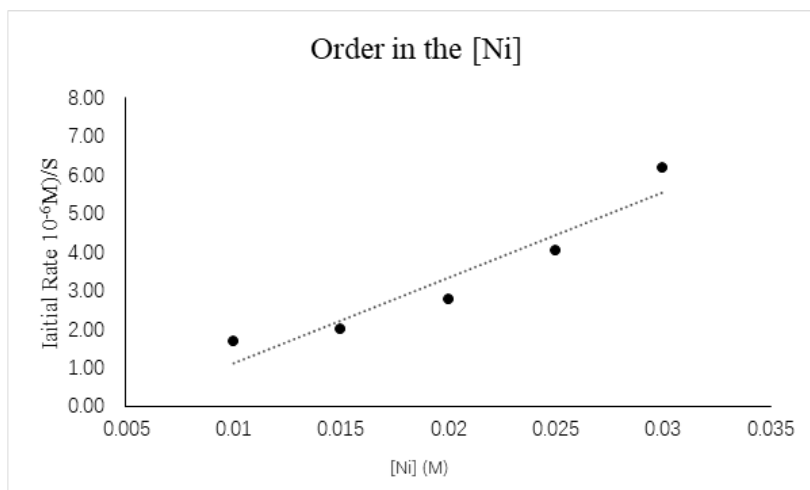
MgCl <sub>2</sub> (M)	2a (10 <sup>-2</sup> M)	Initial Rate (10 <sup>-6</sup> M/s)
0.30	1.94	2.69
0.45	2.04	2.83
0.60	1.88	2.61
0.75	2.10	2.92
0.90	2.06	2.86



### c) Order in NiCl<sub>2</sub>

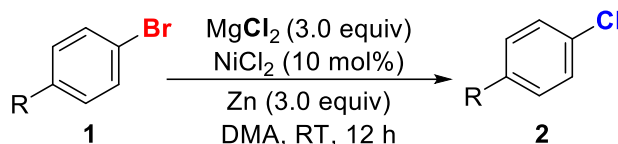
The order in NiCl<sub>2</sub> was determined by obtaining the initial rate of the **2a** formation at differing amount of NiCl<sub>2</sub>.

NiCl <sub>2</sub> (M)	2a (10 <sup>-2</sup> M)	Initial Rate (10 <sup>-6</sup> M/s)
0.01	1.22	1.69
0.015	1.44	2.00
0.02	2.00	2.78
0.025	2.90	4.03
0.030	4.46	6.19



#### d) Hammett studies

The Hammett plot was determined by obtaining the initial rate of the formation of corresponding **2** with different substrate **1**.



R	yield	<b>2</b> (10 <sup>-2</sup> M)	Initial Rate (10 <sup>-6</sup> M/s)
OMe	23%	4.6	6.39
Ph	17%	3.4	4.72
H	15%	3.0	4.17
CO <sub>2</sub> Me	9%	1.8	2.50
CN	6%	1.2	1.67

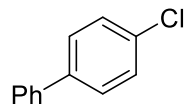
## 7. Reference

- 1) W.-J. Kang, Y. Zhang, B. Li and H. Guo, *Nat. Commun.*, 2024, **15**, 655.
- 2) M. Wasa, K. M. Engle, D. W. Lin, E. J. Yoo and J.-Q. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 19598–19601.
- 3) Y. Lin, J. Jin, C. Wang, J.-P. Wan and Y. Liu, *J. Org. Chem.*, 2021, **86**, 12378–12385.
- 4) H.-J. Xu, Y.-F. Liang, Z.-Y. Cai, H.-X. Qi, C.-Y. Yang and Y.-S. Feng, *J. Org. Chem.*, 2011, **76**, 2296–2300.
- 5) K. D. Hesp, R. J. Lundgren and M. Stradiotto, *J. Am. Chem. Soc.*, 2011, **133**, 5194–5197.
- 6) B. J. Shields and A. G. Doyle, *J. Am. Chem. Soc.*, 2016, **138**, 12719–12722.
- 7) M. J. Harper, E. J. Emmett, J. F. Bower and C. A. Russell, *J. Am. Chem. Soc.*, 2017, **139**, 12386–12389.
- 8) P. K. Verma, S. Mandal and K. Geetharani, *ACS Catal.*, 2018, **8**, 4049–4054.
- 9) L. Gu, T. Lu, M. Zhang, L. Tou and Y. Zhang, *Adv. Synth. Catal.*, 2013, **355**, 1077–1082.
- 10) D. A. Everson, B. A. Jones, D. J. Weix, *J. Am. Chem. Soc.*, 2012, **134**, 6146–6159.



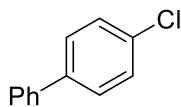
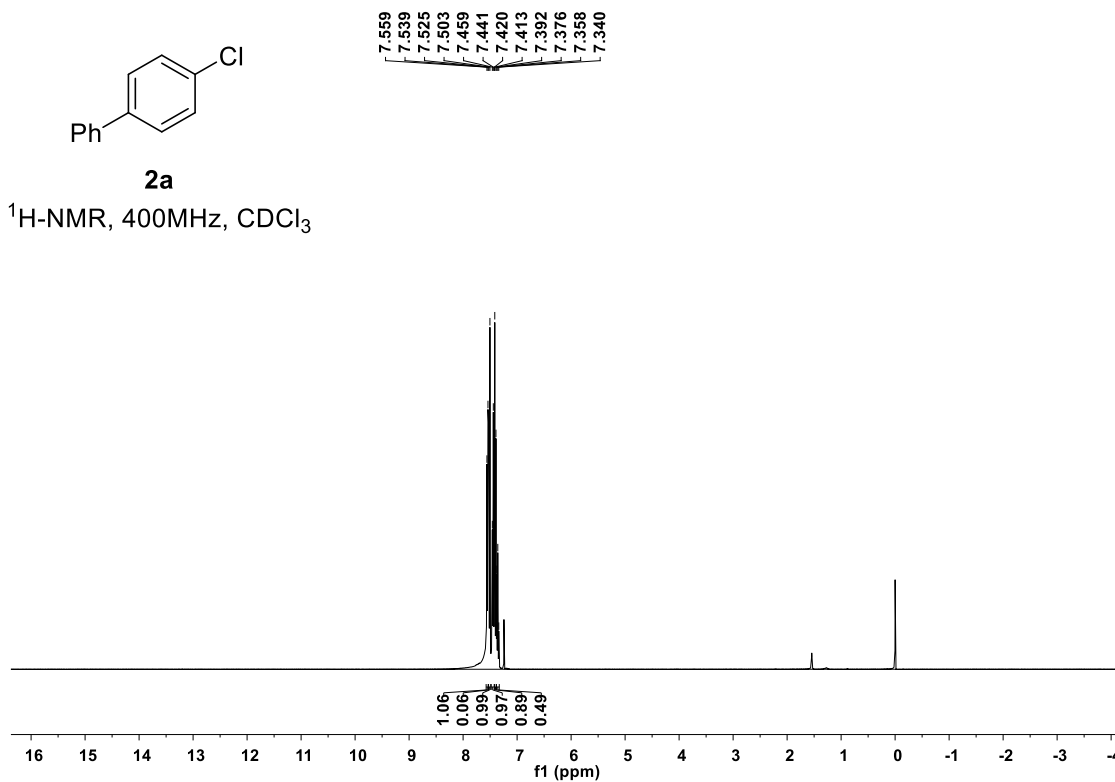
- 11) S. Zhang, B.-S. Kim, C. Wu, J. Mao and P. J. Walsh, *Nat. Commun.*, 2017, **8**, 14641.
- 12) G. Yuan, J. Zheng, X. Gao, X. Li, L. Huang, H. Chen and H. Jiang, *Chem. Commun.*, 2012, **48**, 7513–7515.
- 13) I. Ghosh, T. Ghosh, J. I. Bardagi and B. König, *Science*, **2014**, *346*, 725–728.
- 14) L. C. Finney, L. J. Mitchell and C. J. Moody, *Green Chem.*, 2018, **20**, 2242–2249.
- 15) J. Zhang, S. Lin, X. Zhu, B. Jiang, Z. Yang and Z. Pan, *Chem. Commun.*, 2012, **48**, 6235–6237.
- 16) N. Jiang and A. J. Ragauskas, *Org. Lett.*, 2005, **7**, 3689–3692.
- 17) S. Song, X. Li, J. Wei, W. Wang, Y. Zhang, L. Ai, Y. Zhu, X. Shi, X. Zhang and N. Jiao, *Nat. Catal.*, 2020, **3**, 107–115.
- 18) Y. K. Bommegowda, N. Mallesha, A. C. Vinayaka and M. P. Sadashiva, *Chem. Lett.*, 2016, **45**, 268–270.
- 19) V. Dichiarante, M. Fagnoni and A. Albini, *Green Chem.*, 2009, **11**, 942–945.
- 20) K. Iizuka, Y. Maegawa, Y. Shimoyama, K. Sakamoto, N. Kayakiri, Y. Goto, Y. Naganawa, S. Tanaka, M. Yoshida, S. Inagaki and Y. Nakajima, *Chem. Eur. J.*, 2024, **30**, e202303159.
- 21) S. Rana, B. Pandey, A. Dey, R. Haque, G. Rajaraman and D. Maiti, *ChemCatChem*, 2016, **8**, 3367–3374.
- 22) L. Jiao and T. Bach, *J. Am. Chem. Soc.*, 2011, **133**, 12990–12993.
- 23) B. Ghosh, T. Antonio, J. Zhen, P. Kharkar, M. E. A. Reith and A. K. Dutta, *J. Med. Chem.*, 2010, **53**, 1023–1037.
- 24) M. Juchun, M. Günther, E. Döring, A. Sievers-Engler, M. Lämmerhofer and S. Laufer, *J. Med. Chem.*, 2017, **60**, 4636–4656.
- 25) S. Maetani, T. Fukuyama and I. Ryu, *Org. Lett.*, 2013, **15**, 2754–2757.
- 26) M. Tobisu, Y. Masuya, K. Baba and N. Chatani, *Chem. Sci.*, 2016, **7**, 2587–2591.
- 27) S. Kawamorita, H. Ohmiya, T. Iwai and M. Sawamura, *Angew. Chem., Int. Ed.*, 2011, **50**, 8363–8366.
- 28) S. T. Keaveney, G. Kundu and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2018, **57**, 12573–12577.
- 29) R. Schmidt, A. Stolle and B. Ondruschka, *Green Chem.*, 2012, **14**, 1673–1679.
- 30) H. Kim, H. Kim, T. H. Lambert and S. Lin, *J. Am. Chem. Soc.*, 2020, **142**, 2087–2092.
- 31) N. A. Isley, S. Dobarco and B. H. Lipshutz, *Green Chem.*, 2014, **16**, 1480–1488.
- 32) S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel and M. Beller, *Nat. Commun.*, 2016, **7**, 12641.
- 33) J. Miao, P. Fang, S. Jagdeep and H. Ge, *Org. Chem. Front.*, 2016, **3**, 243–250.
- 34) L. J. Gooßen, C. Linder, N. Rodríguez, P. P. Lange and A. Fromm, *Chem. Commun.*, 2009, **46**, 7173–7175.
- 35) M. C. Davis, *Synth. Commun.*, 2009, **39**, 1100–1108.

## 8. NMR Spectrum



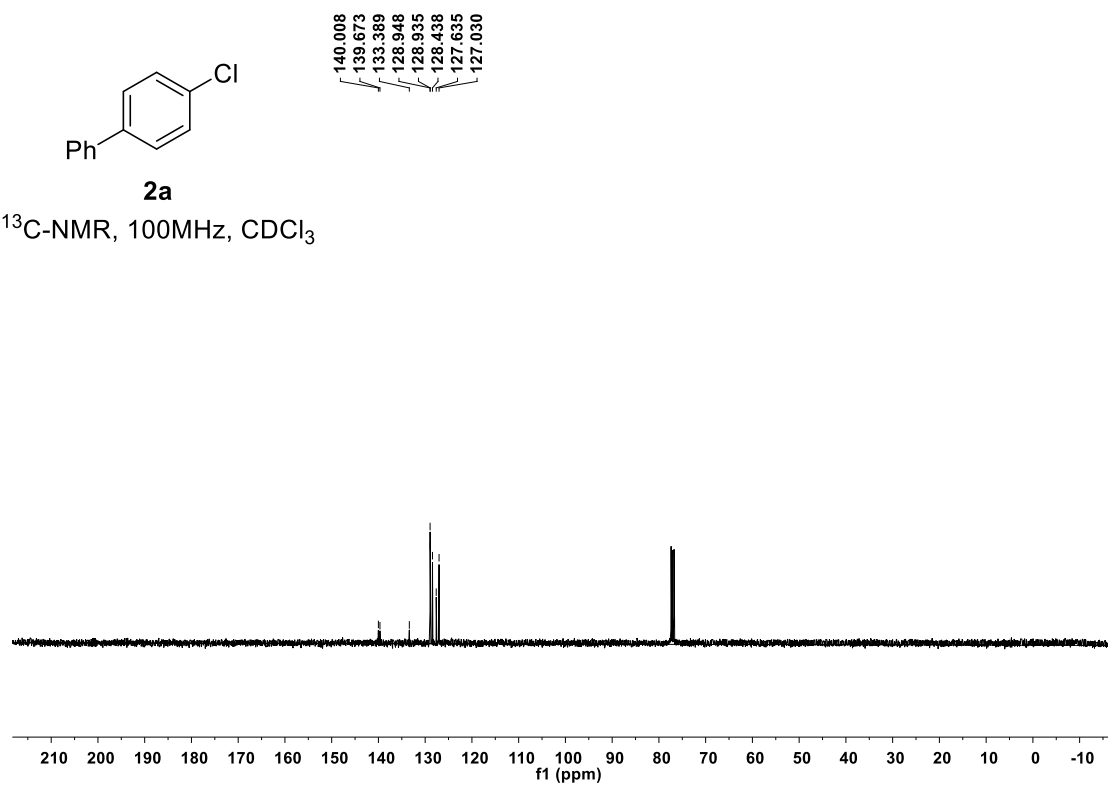
**2a**

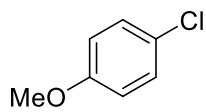
$^1\text{H-NMR}$ , 400MHz,  $\text{CDCl}_3$



**2a**

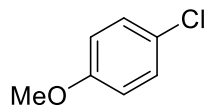
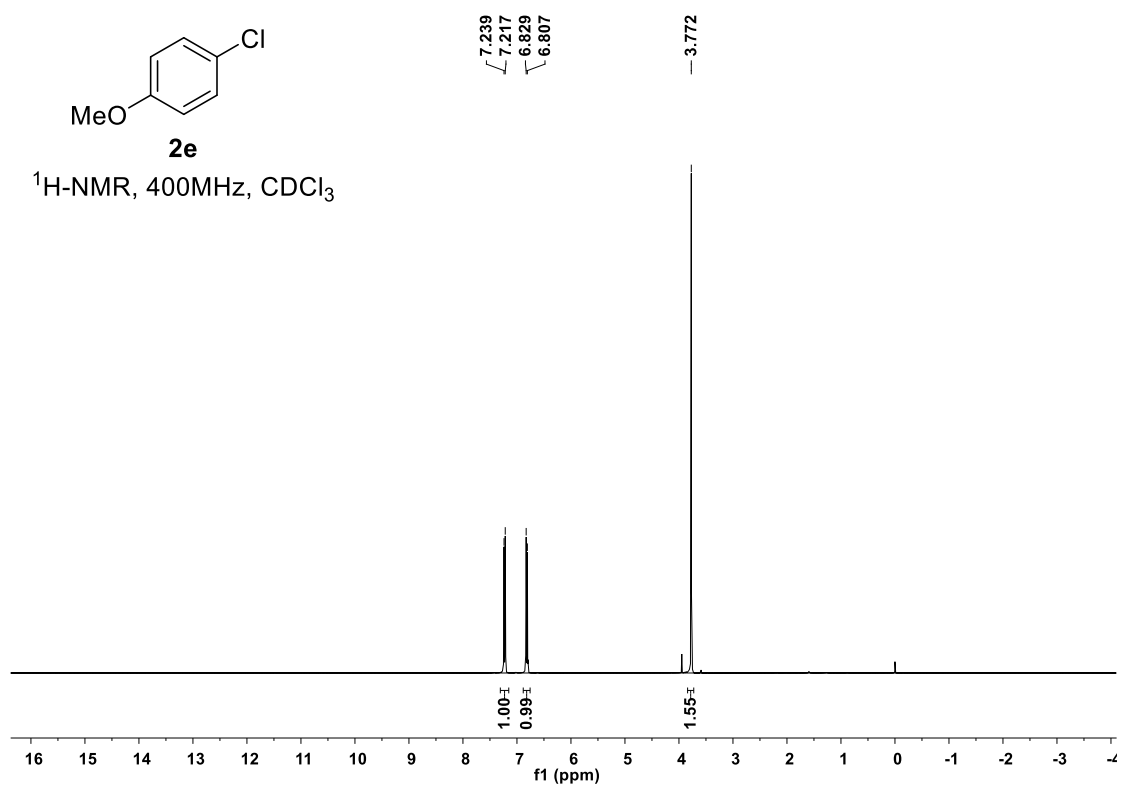
$^{13}\text{C-NMR}$ , 100MHz,  $\text{CDCl}_3$





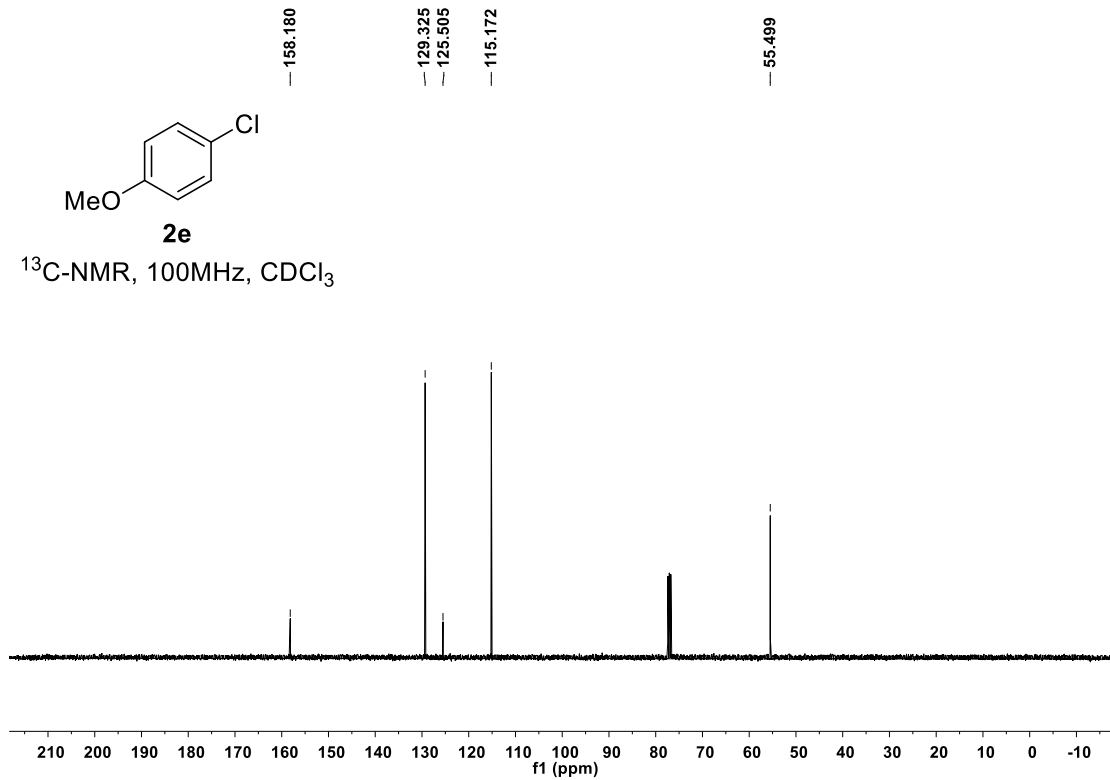
**2e**

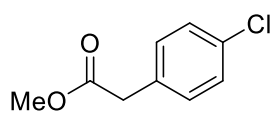
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**2e**

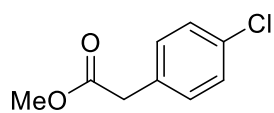
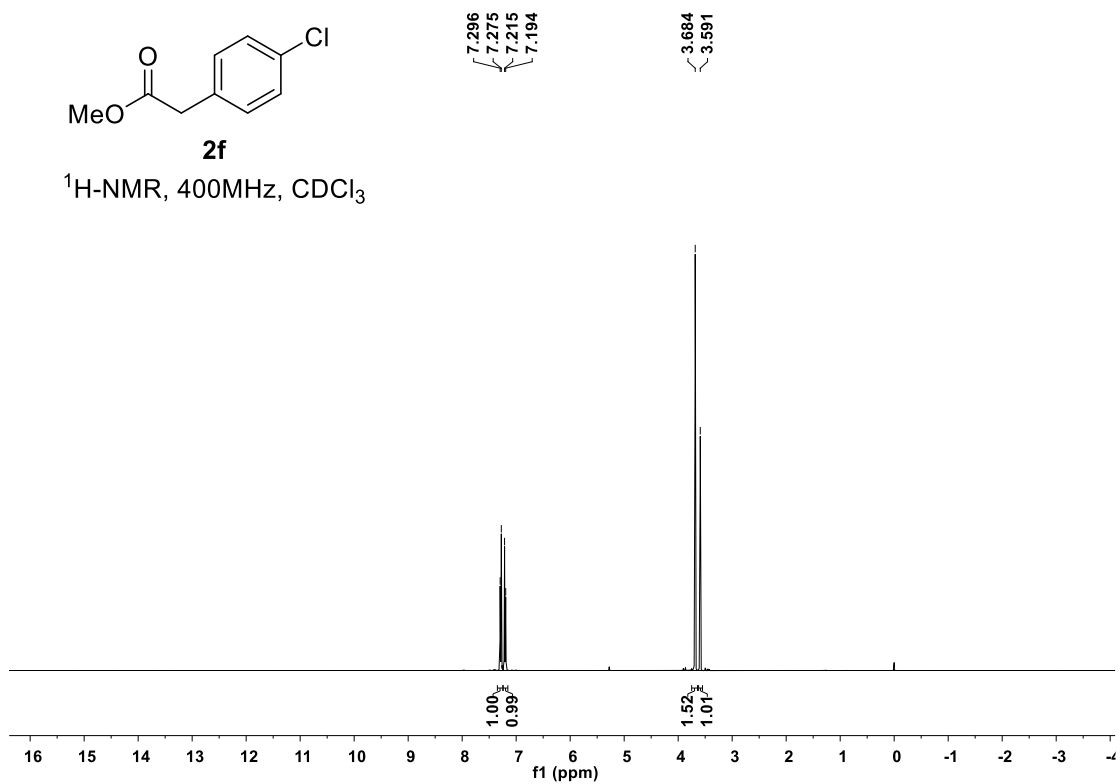
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





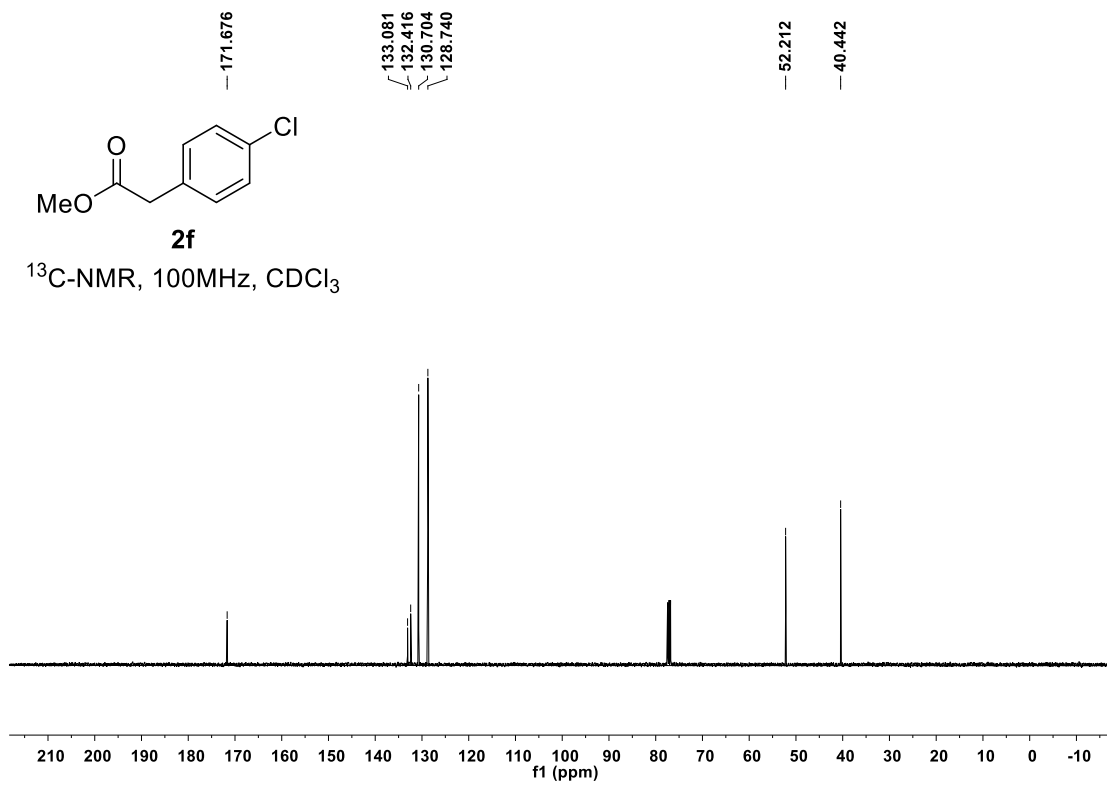
**2f**

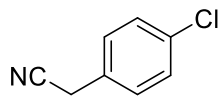
$^1\text{H-NMR}$ , 400MHz,  $\text{CDCl}_3$



**2f**

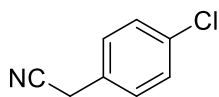
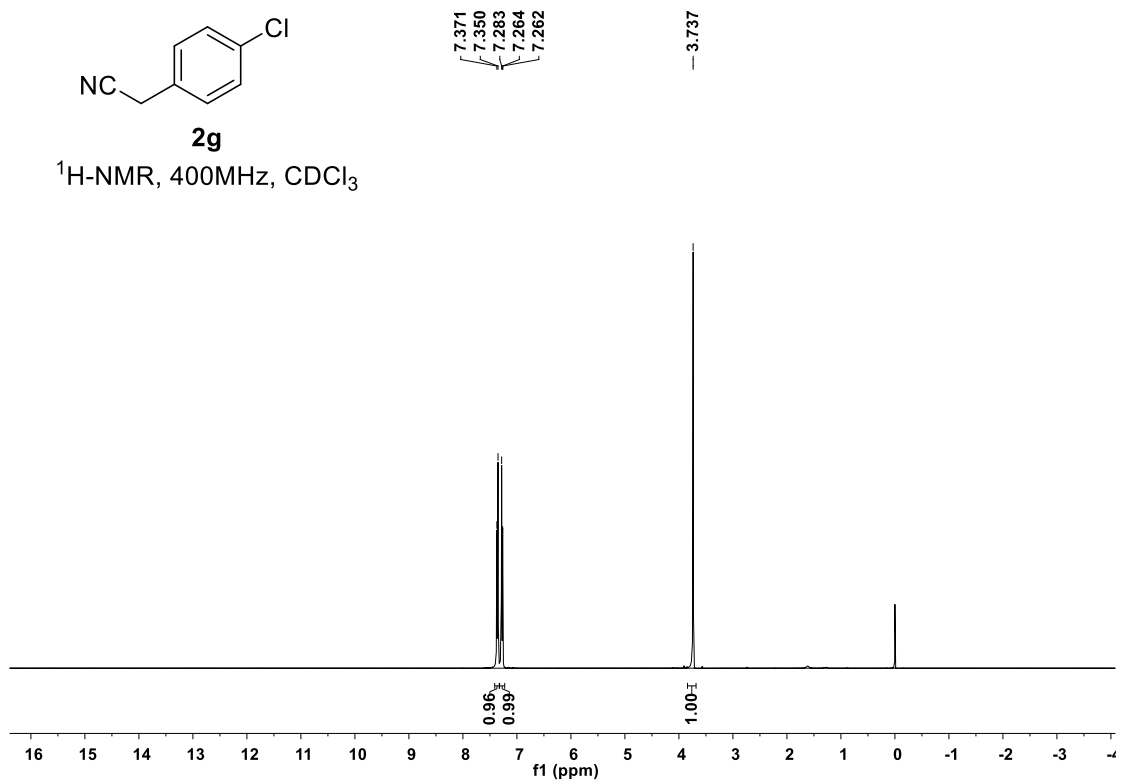
$^{13}\text{C-NMR}$ , 100MHz,  $\text{CDCl}_3$





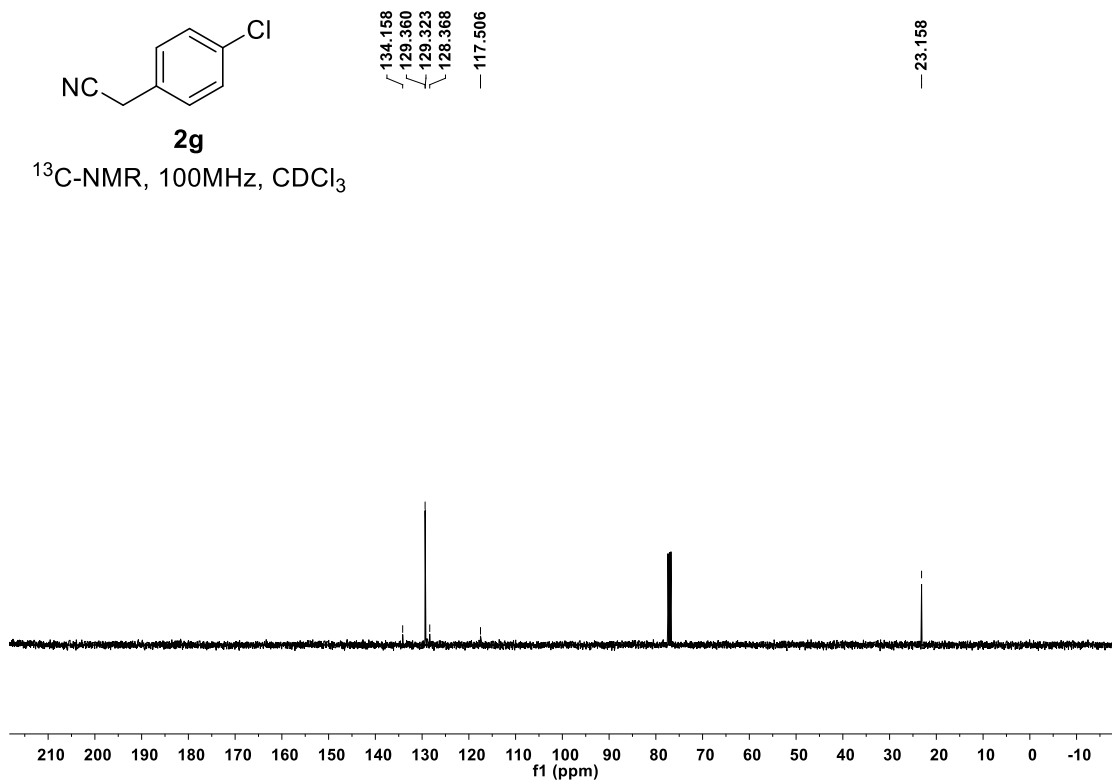
**2g**

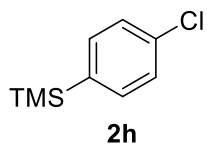
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**2g**

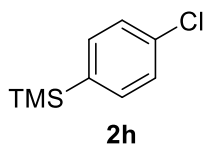
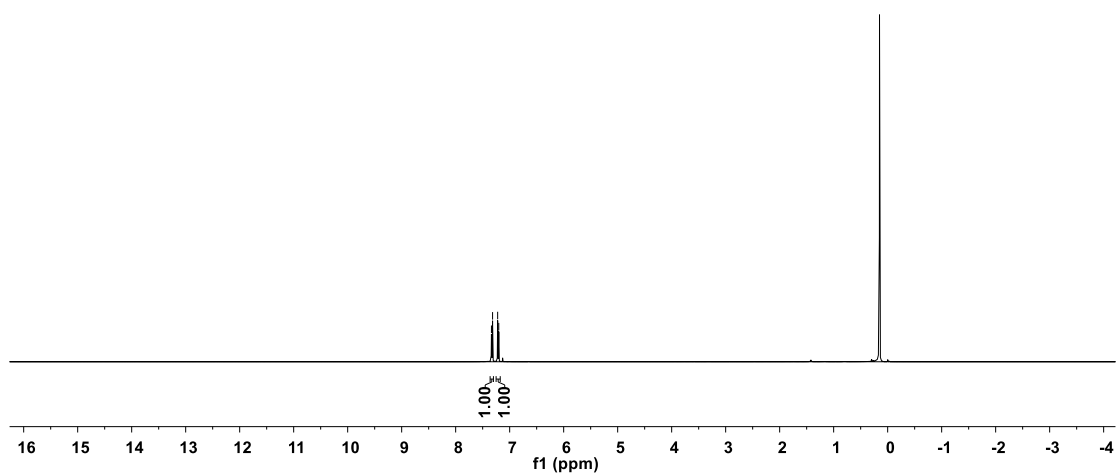
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>

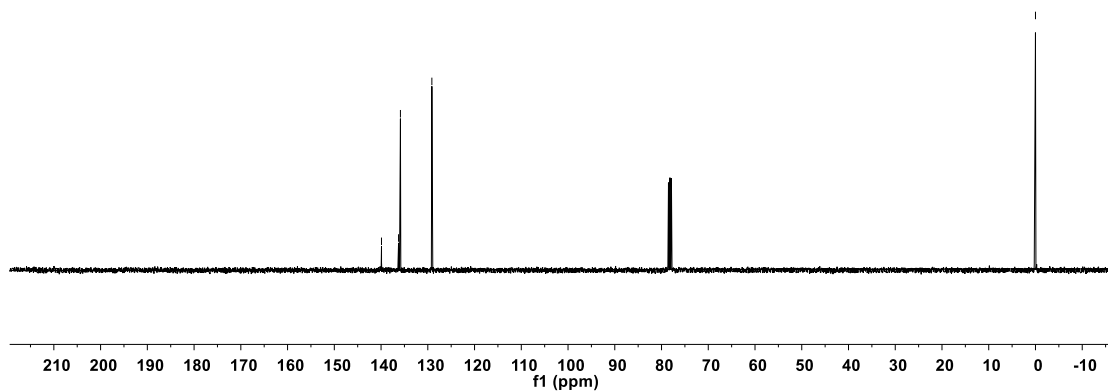
7.337  
7.317  
7.222  
7.202

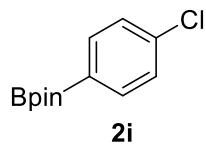


<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>

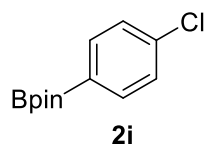
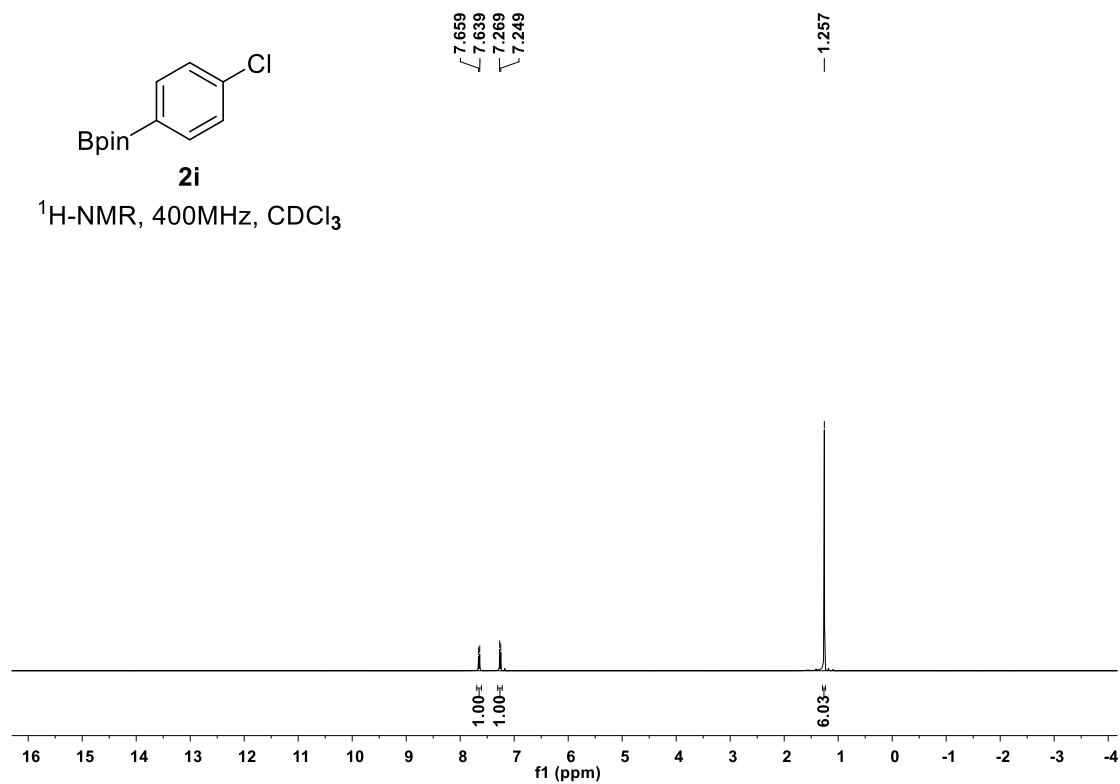
139.908  
136.258  
135.857  
129.131

-0.000

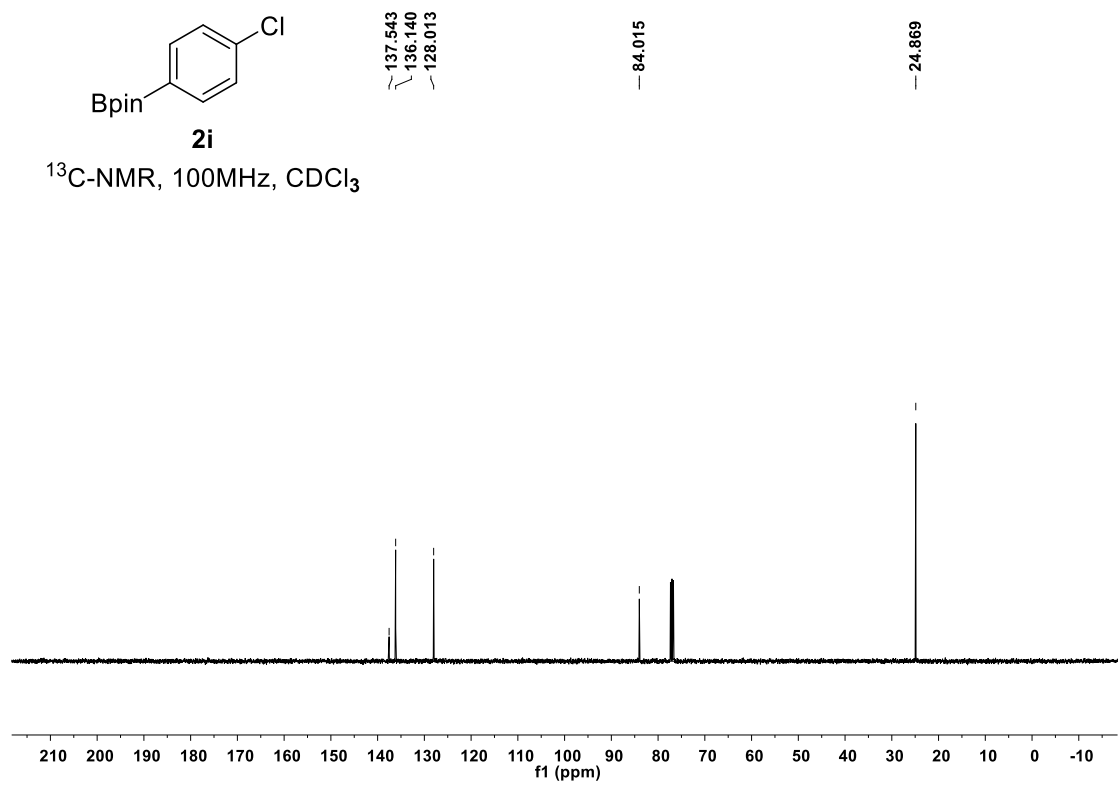


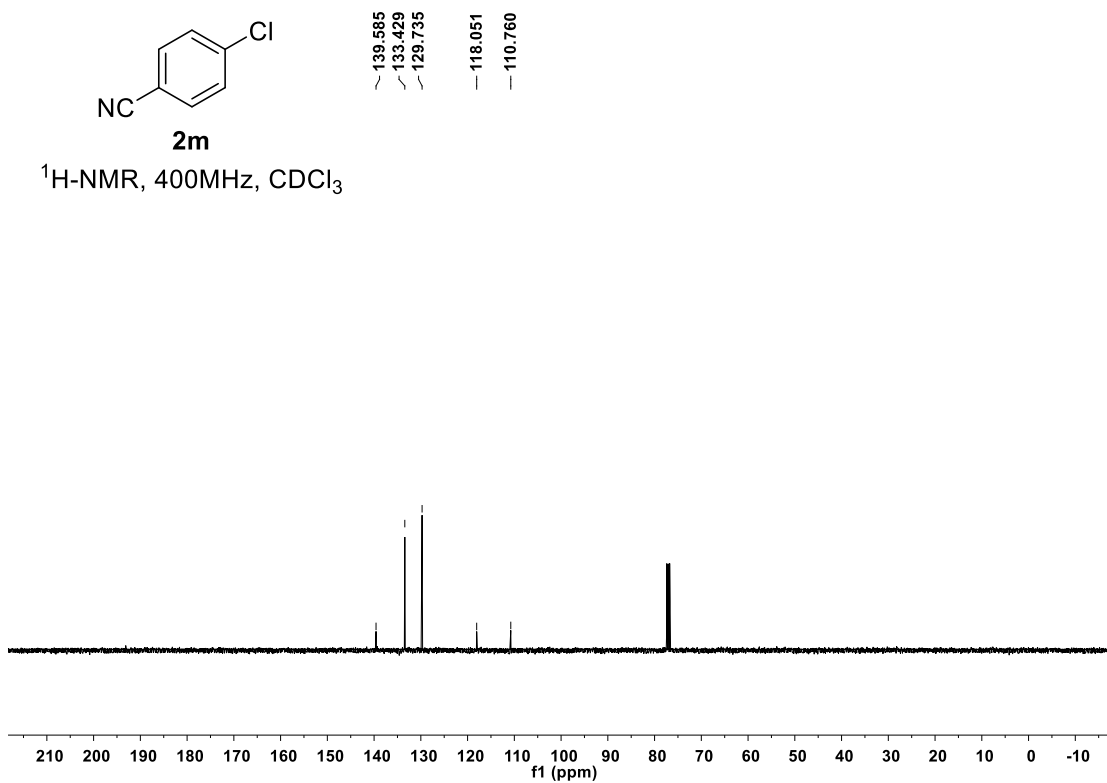
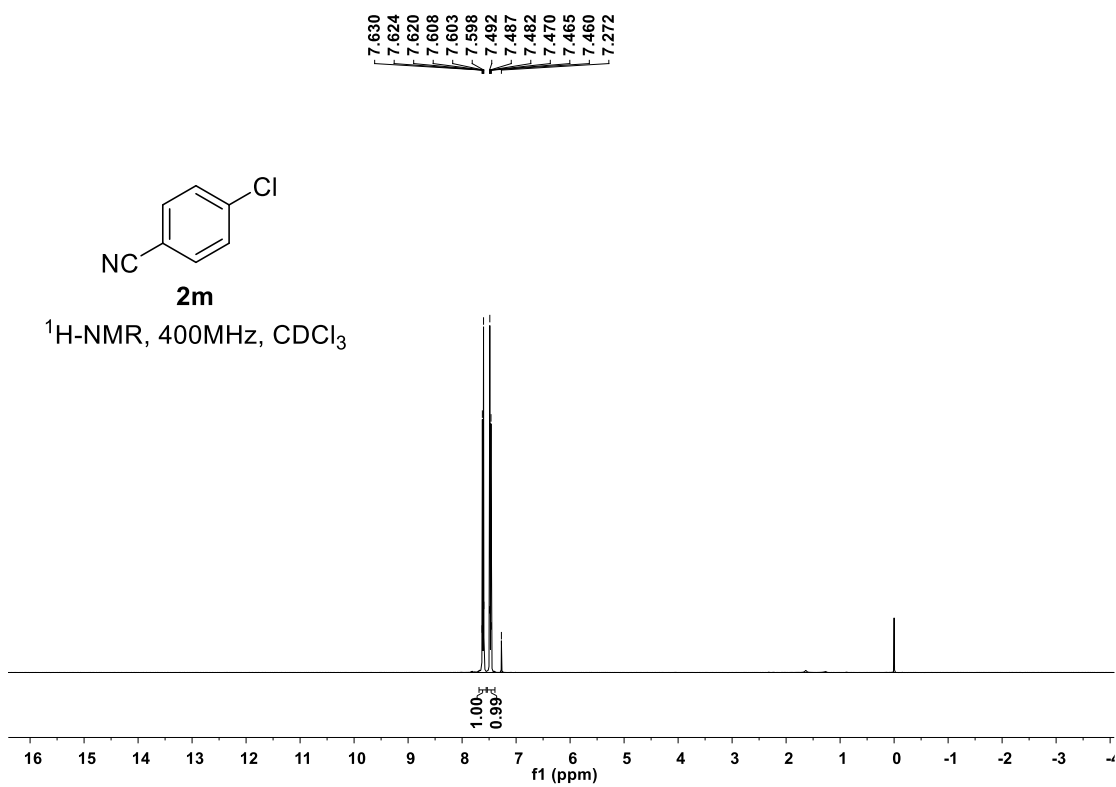


<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>

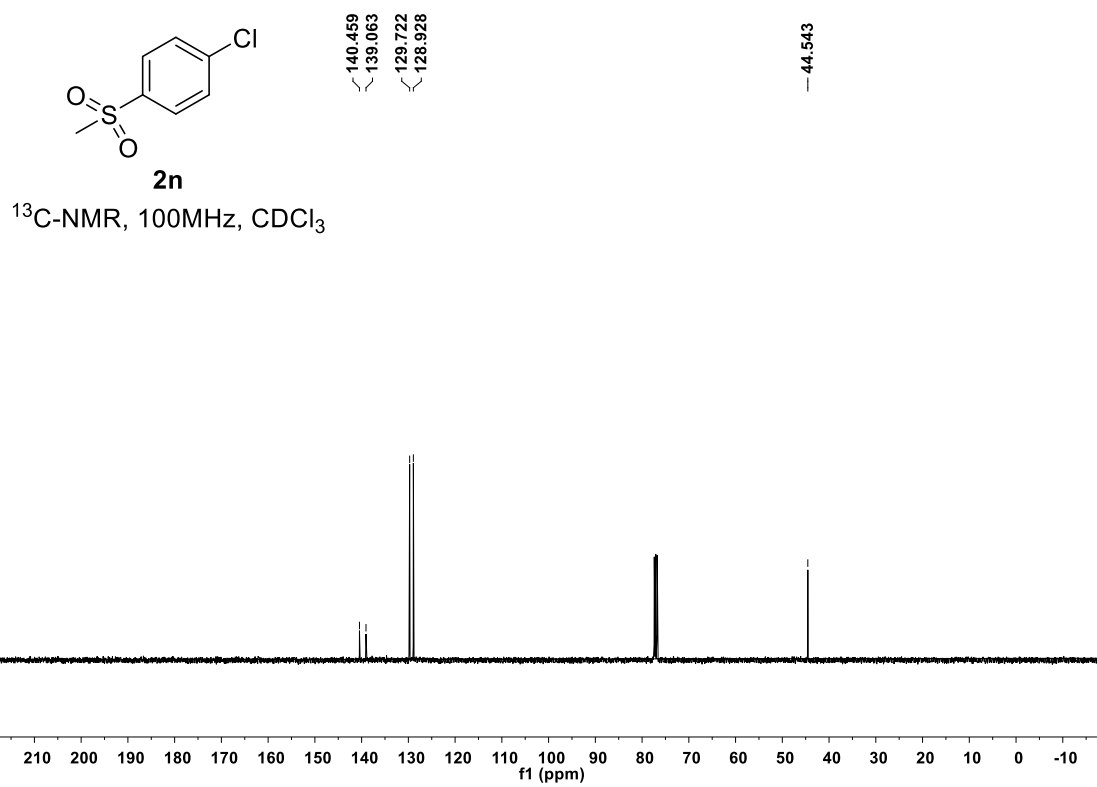
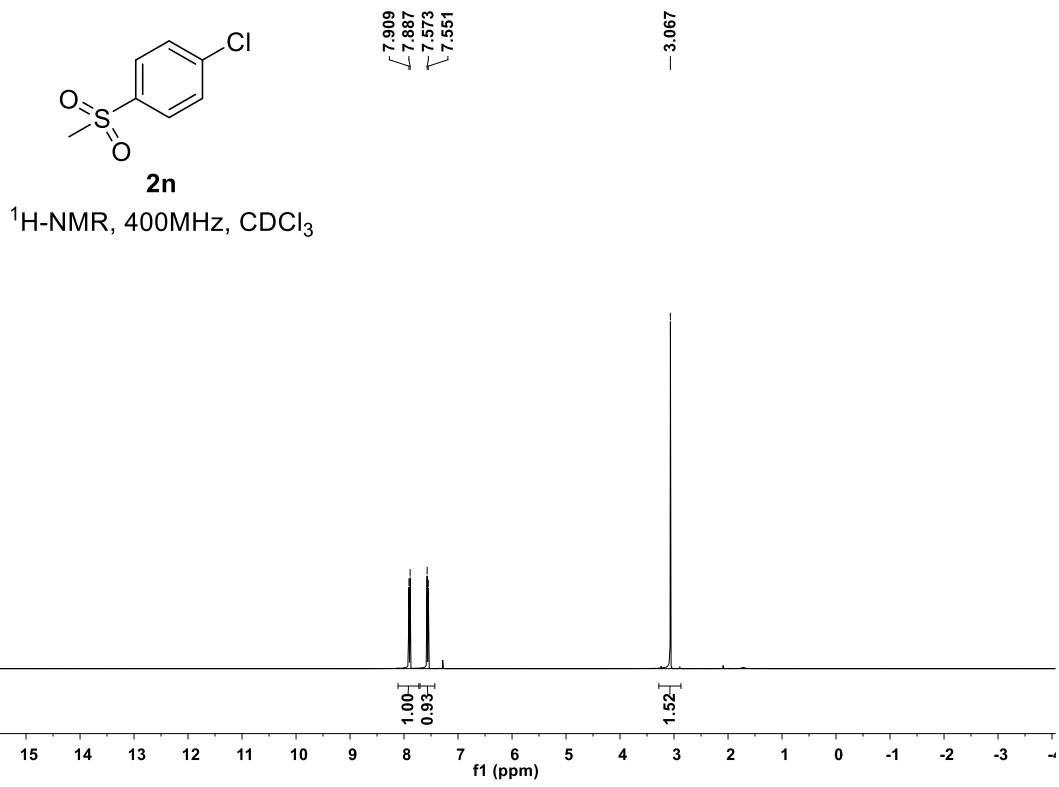


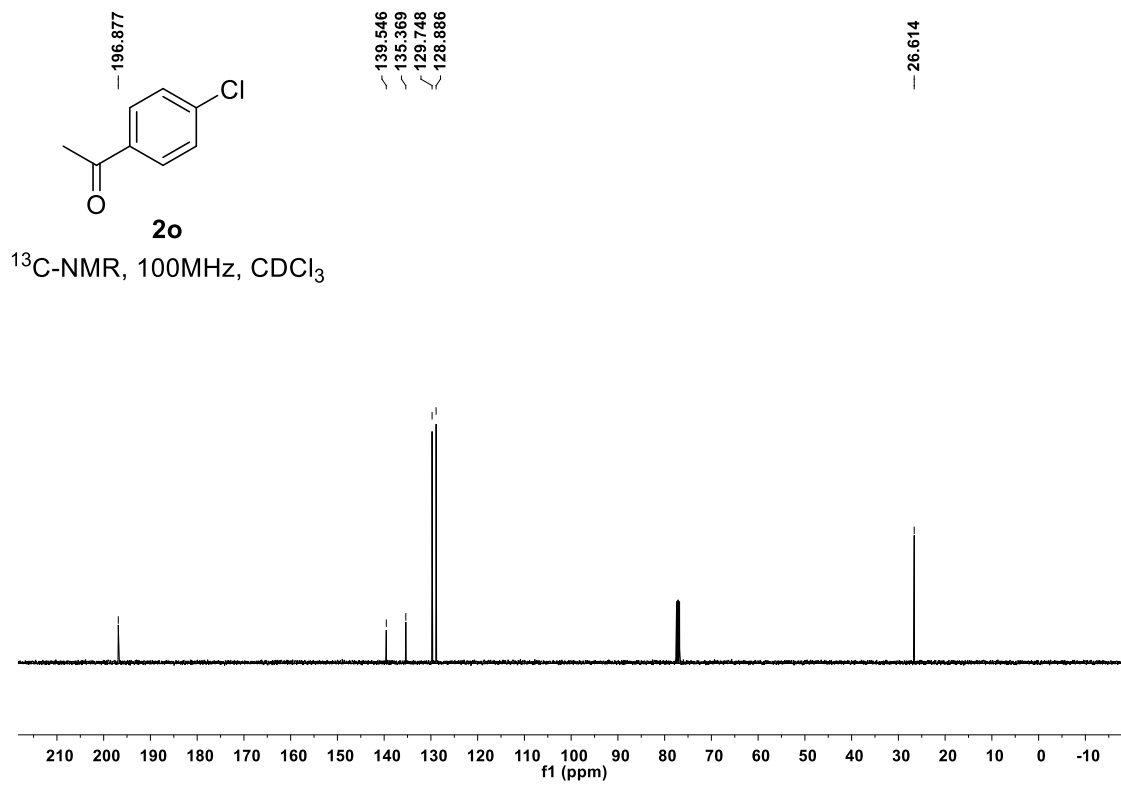
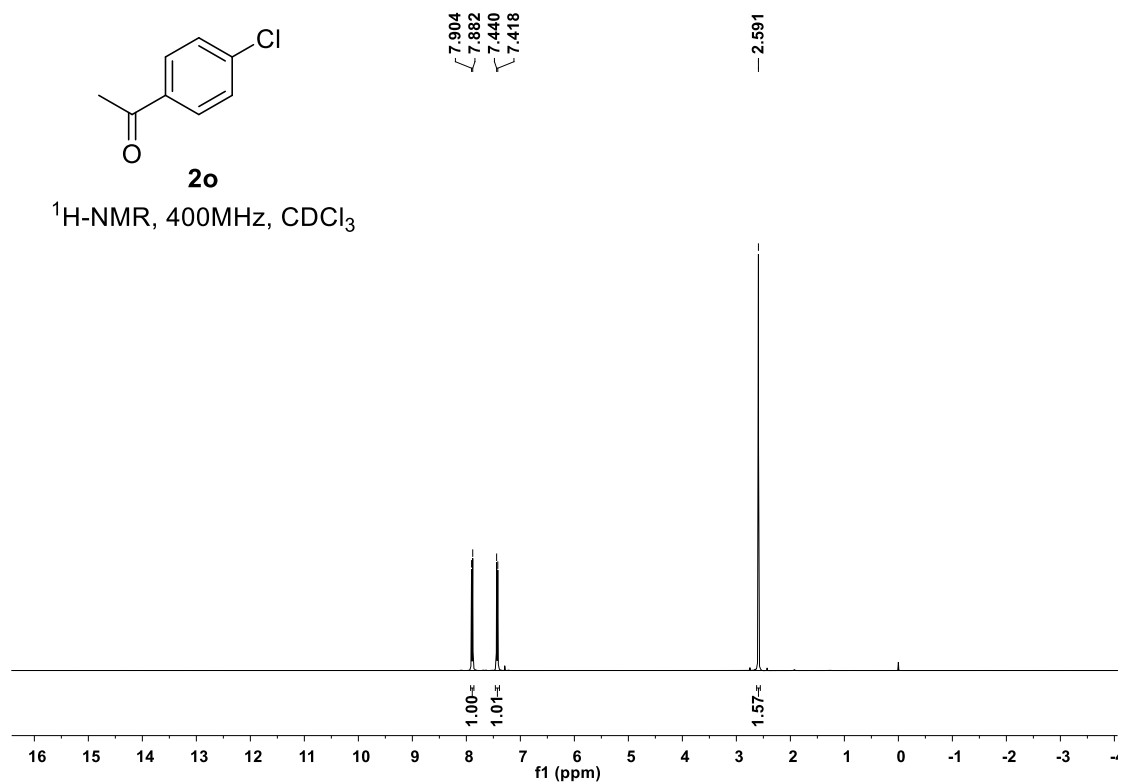
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>

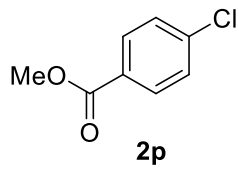




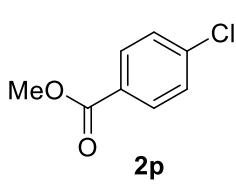
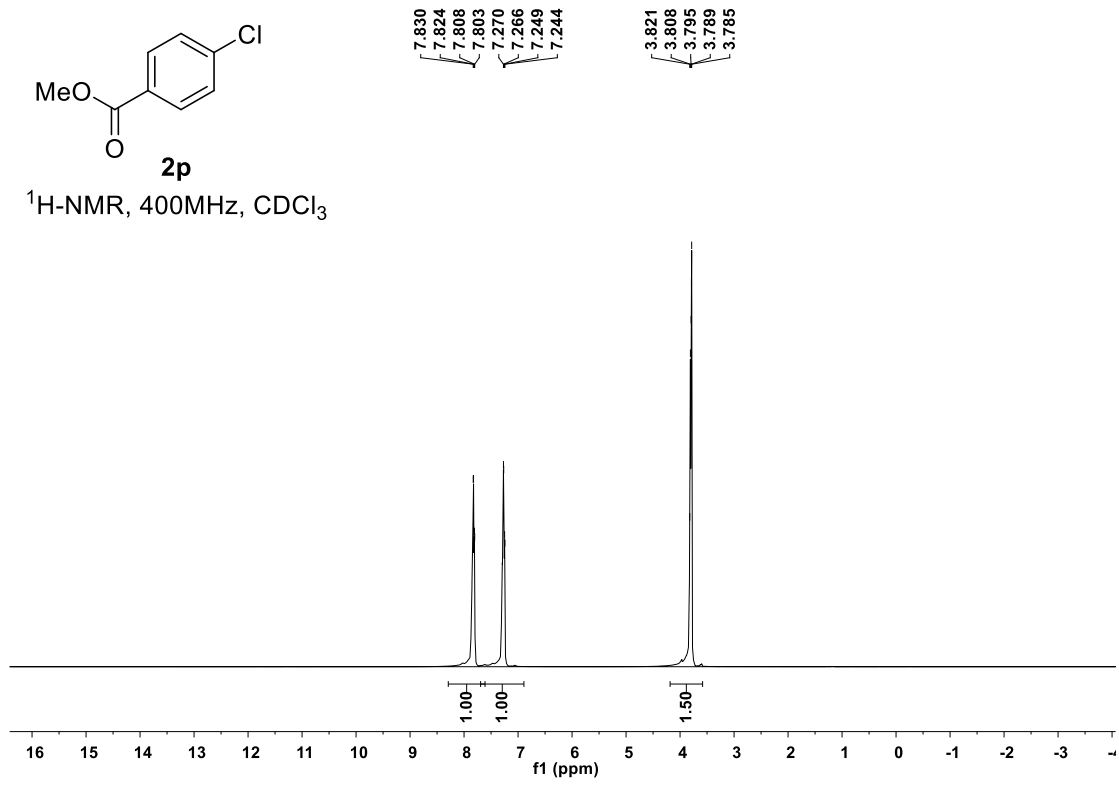




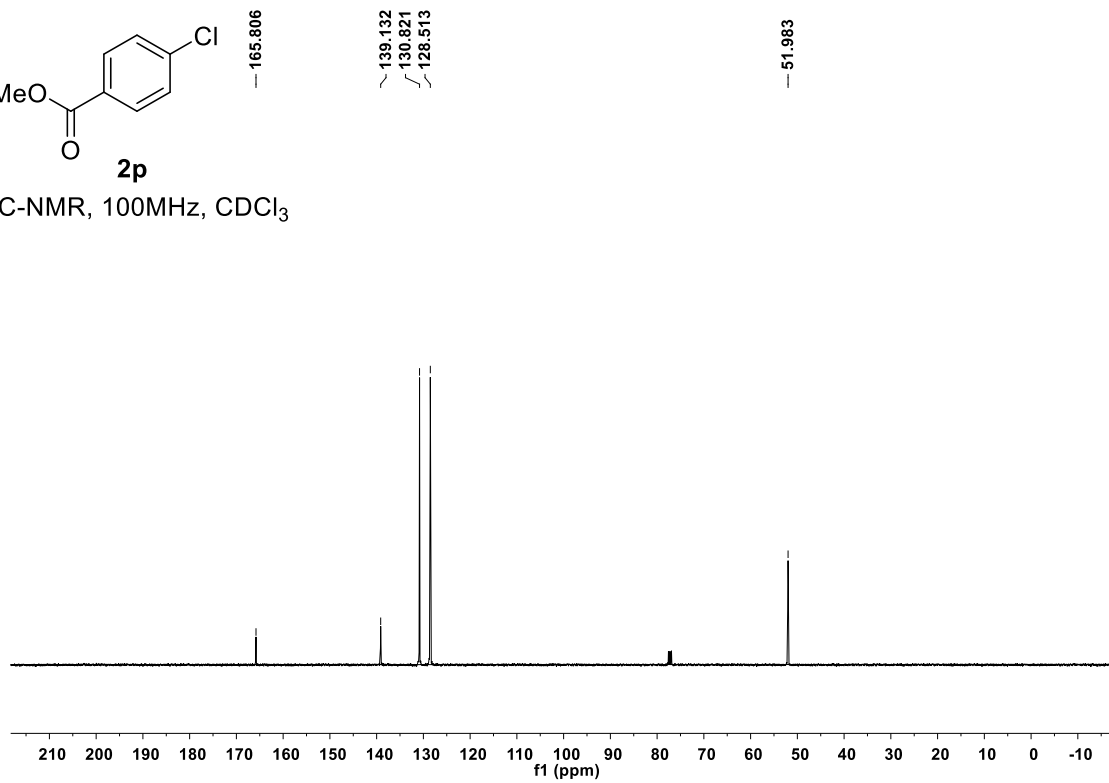


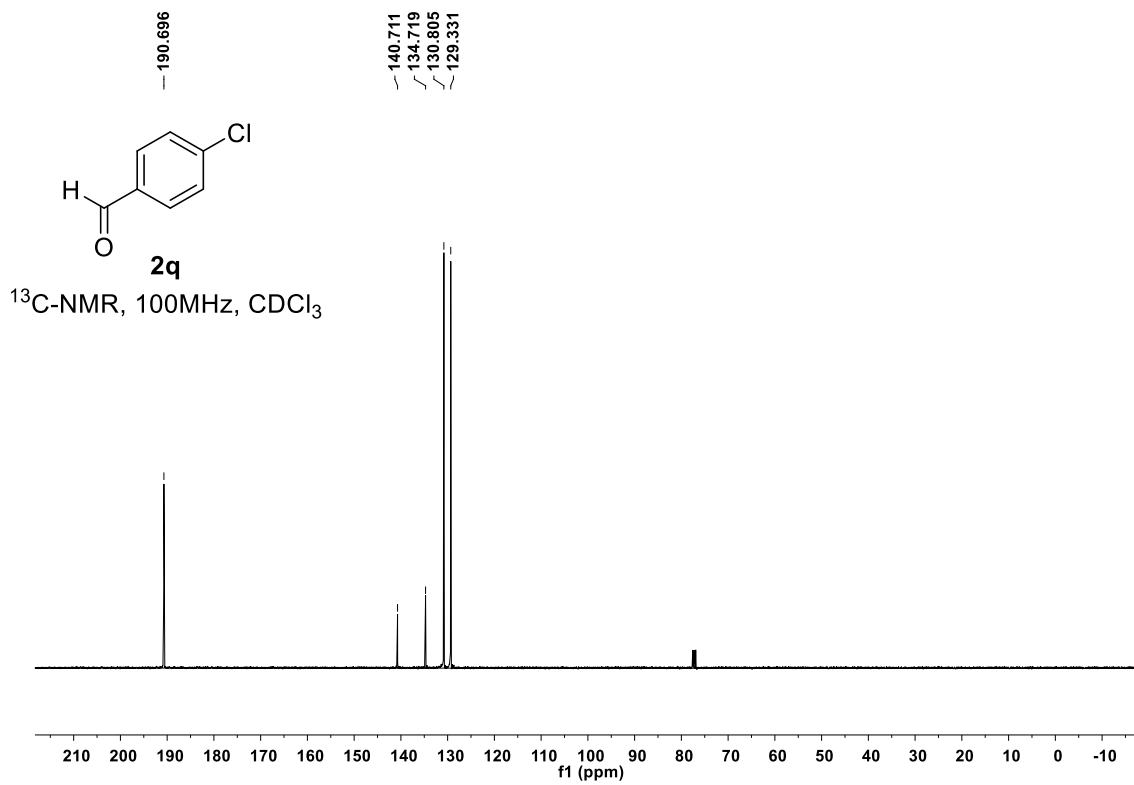
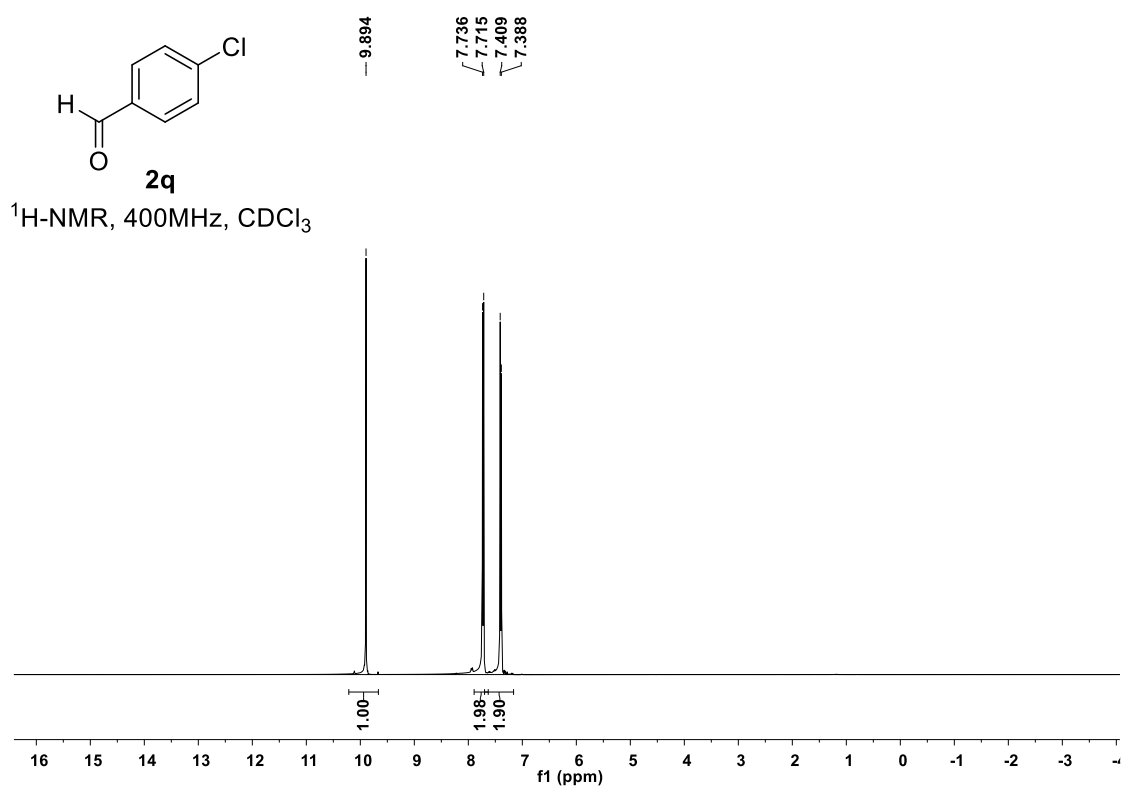


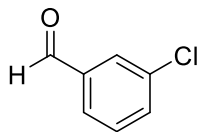
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>

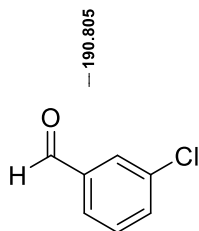
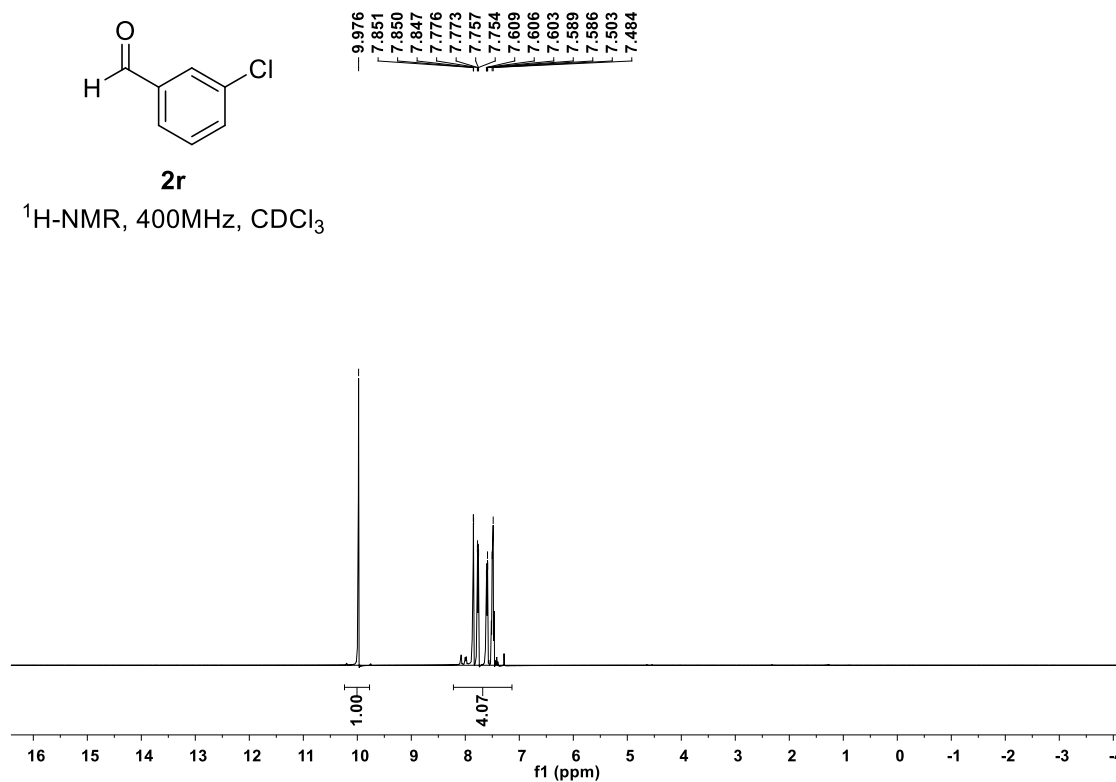






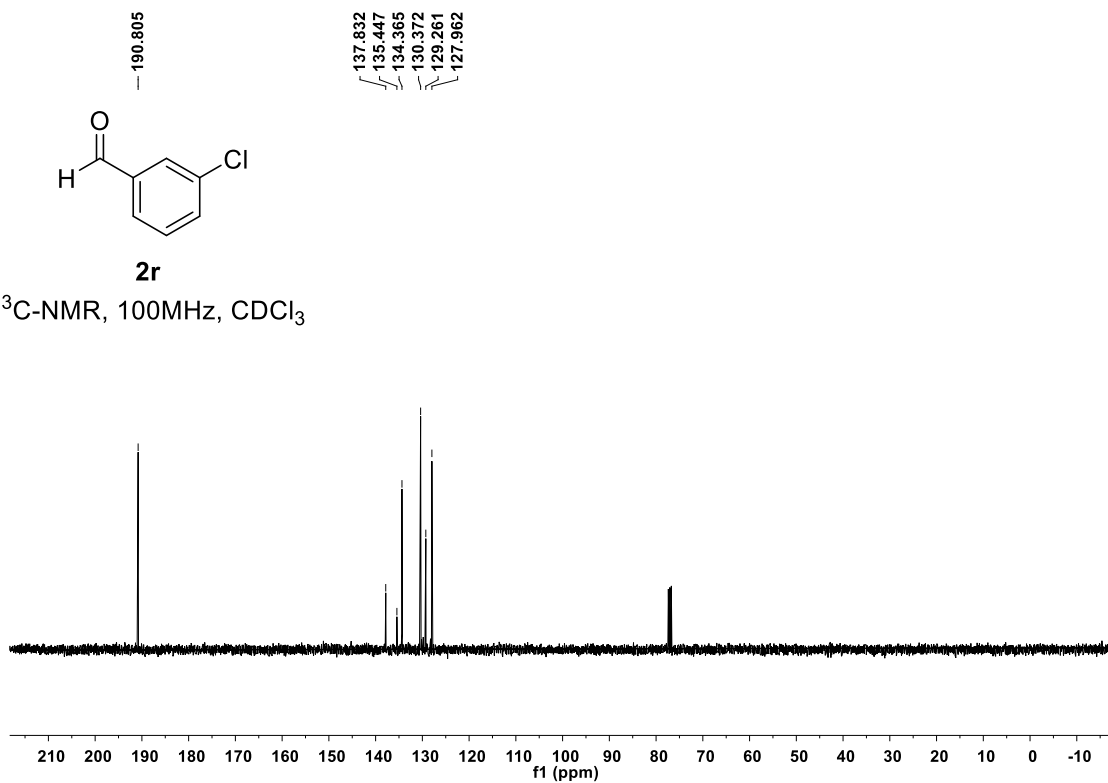
**2r**

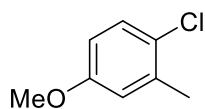
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**2r**

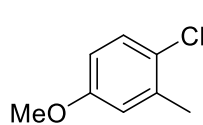
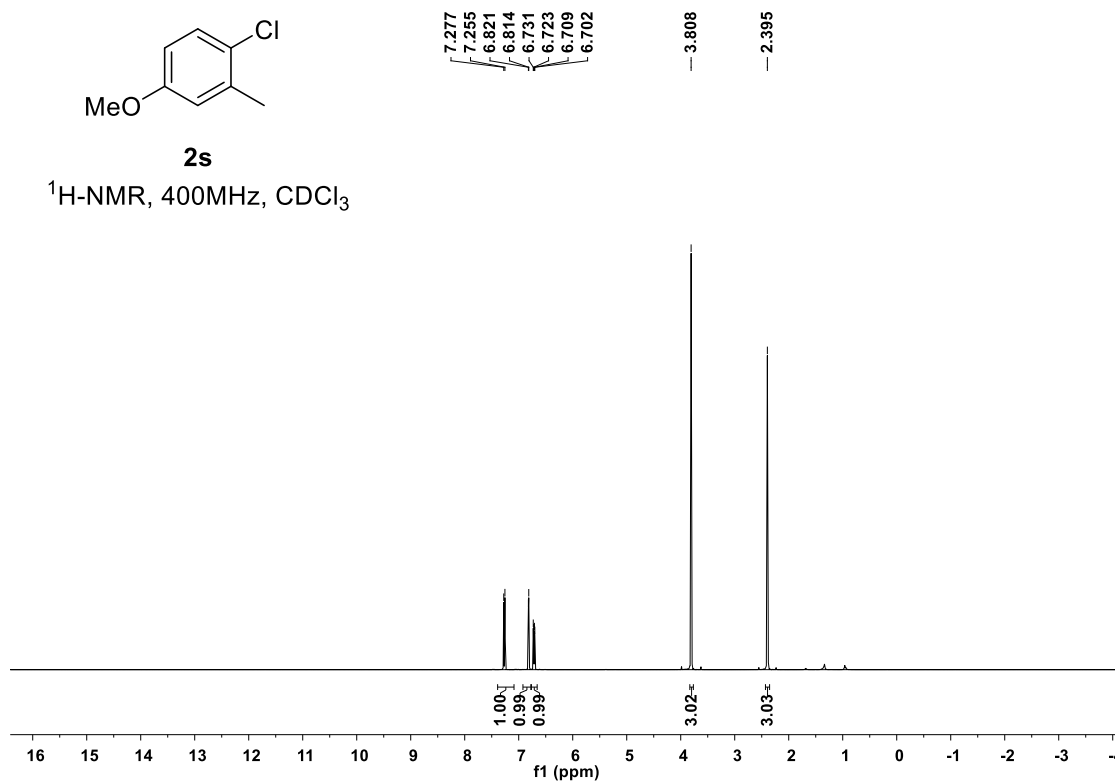
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





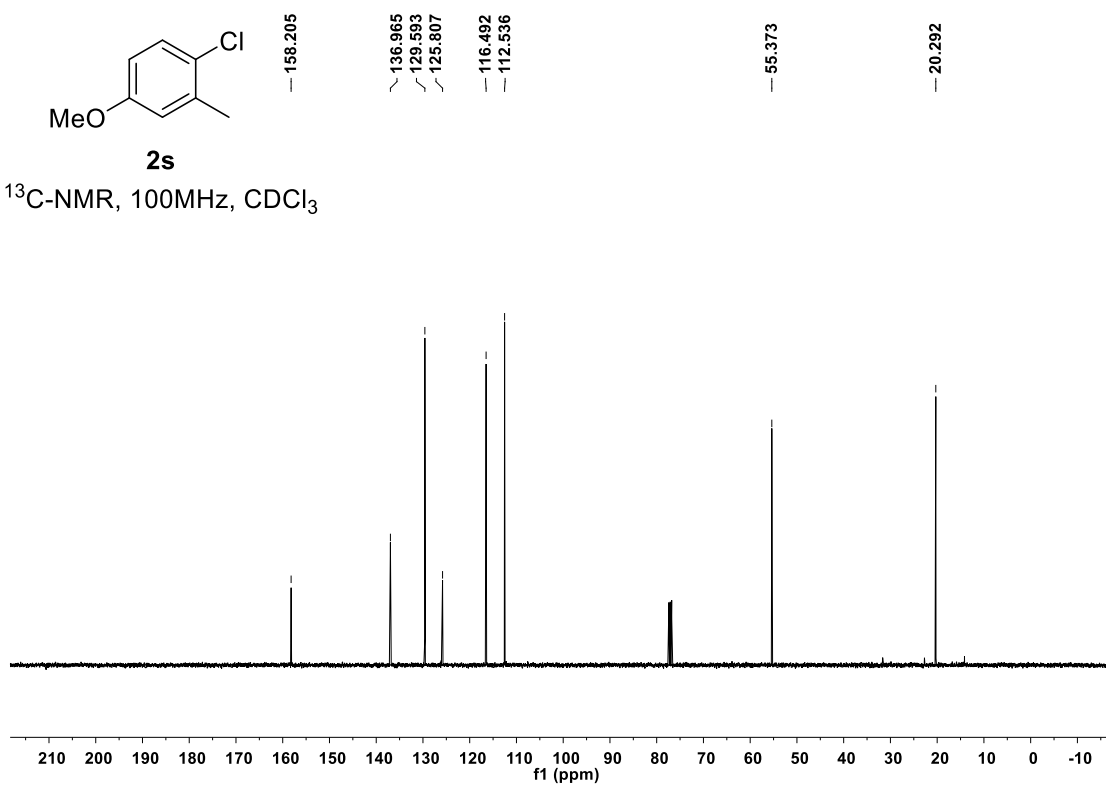
**2s**

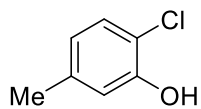
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**2s**

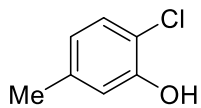
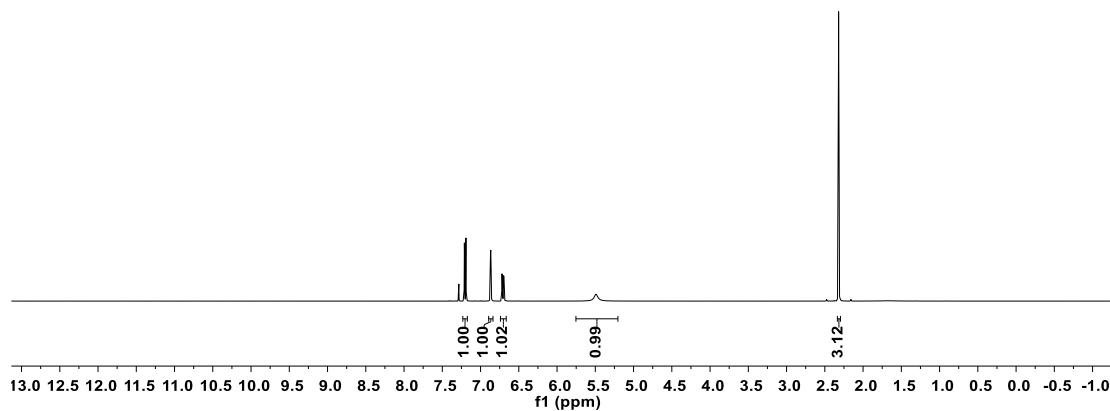
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





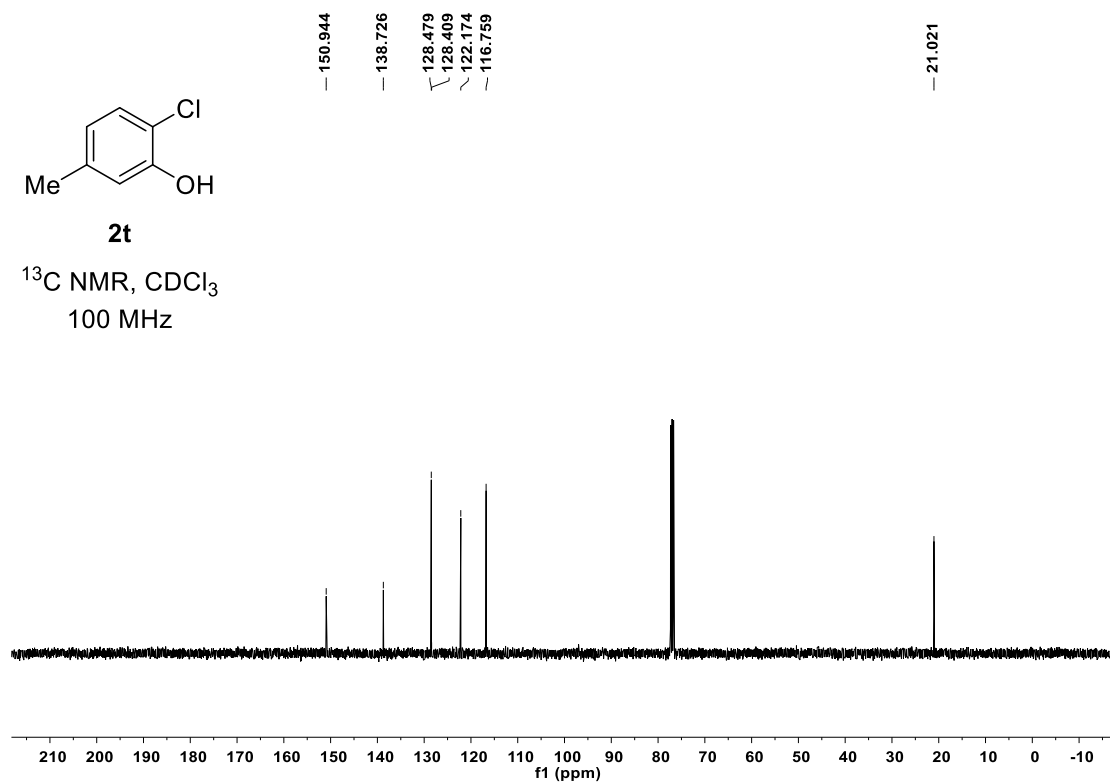
**2t**

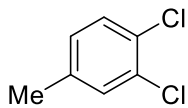
$^1\text{H}$  NMR,  $\text{CDCl}_3$   
400 MHz



**2t**

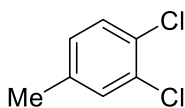
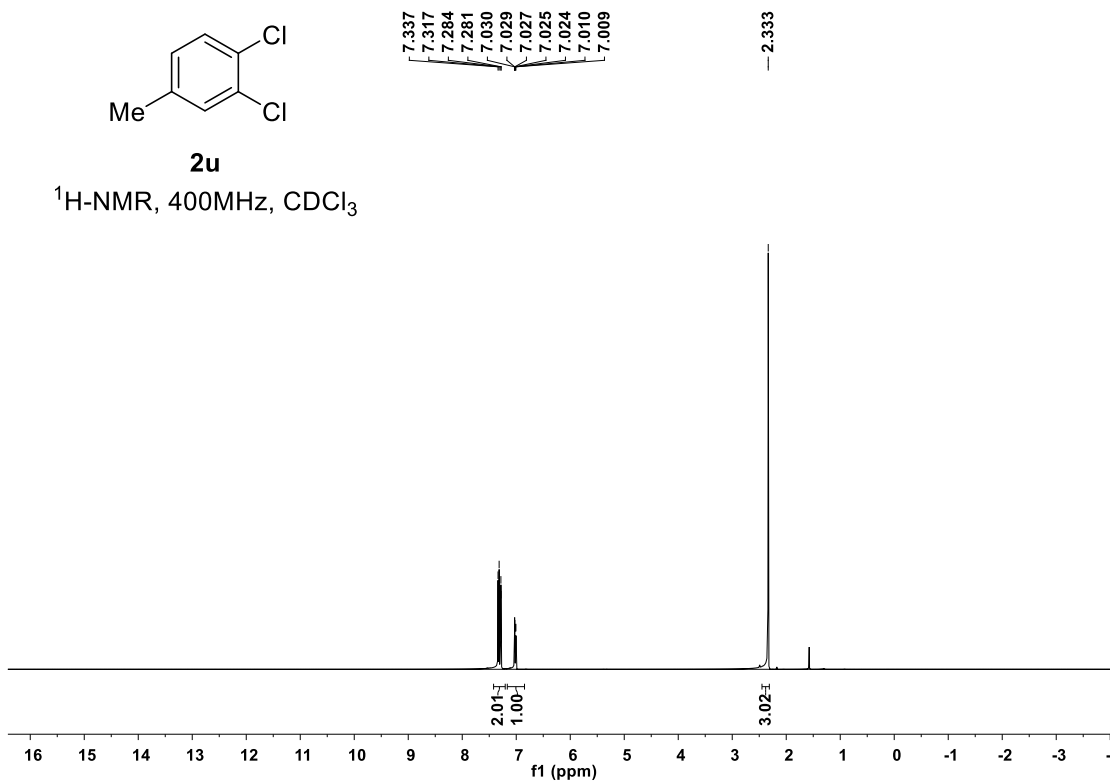
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$   
100 MHz





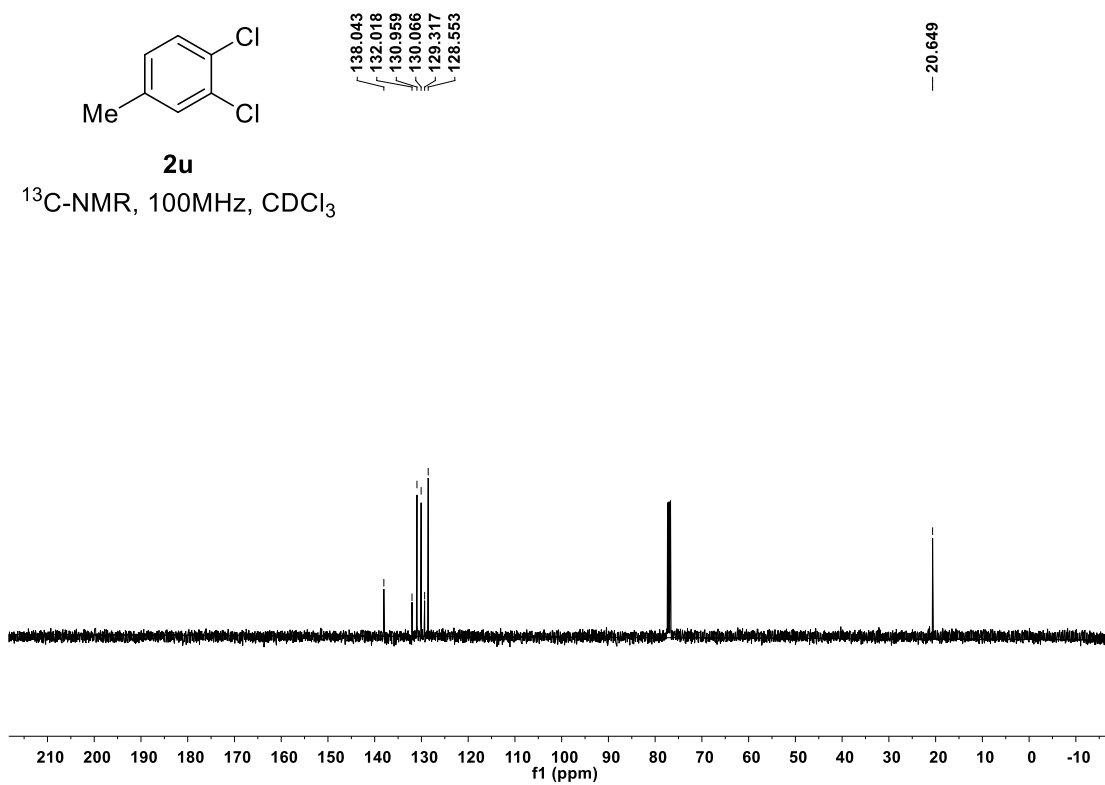
**2u**

<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>

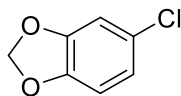


**2u**

<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>

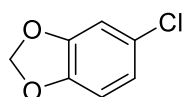
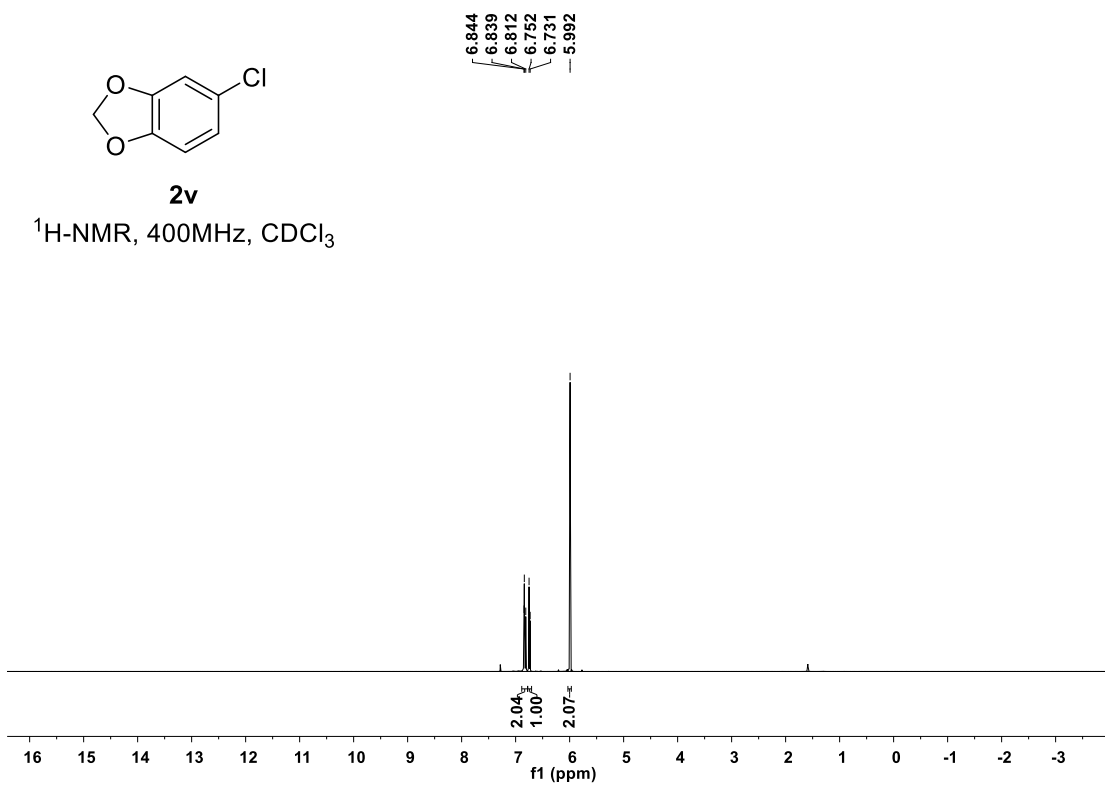






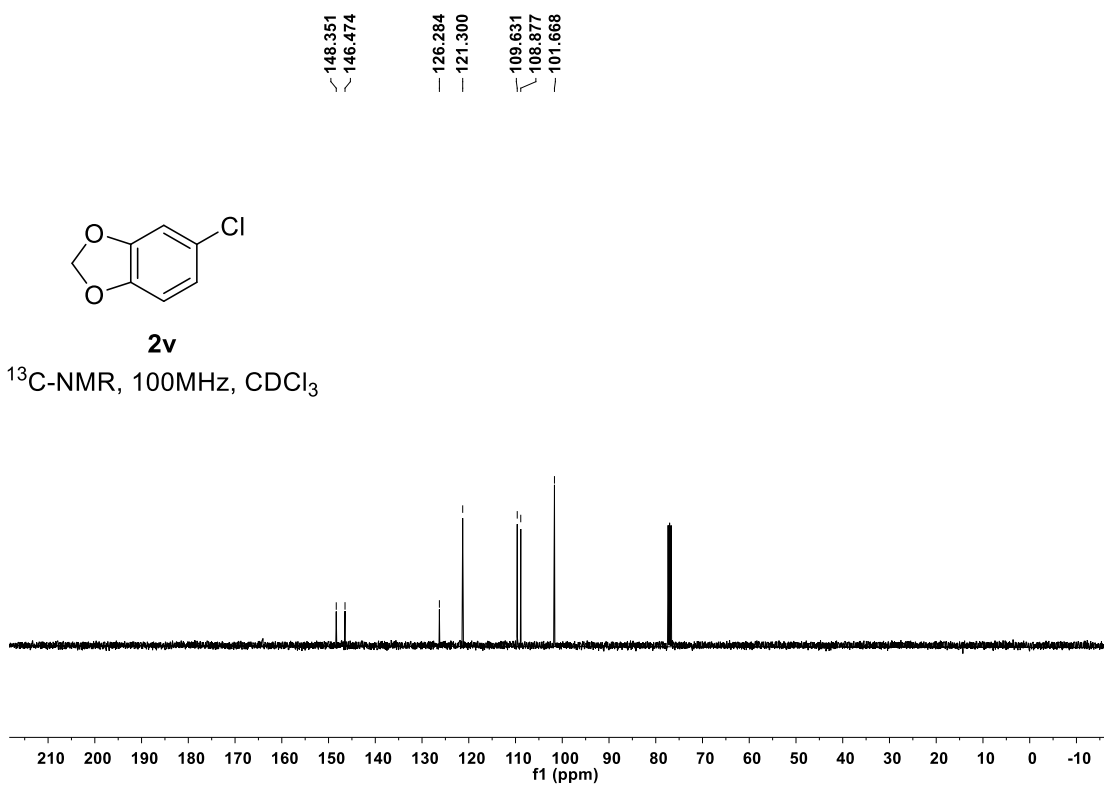
**2v**

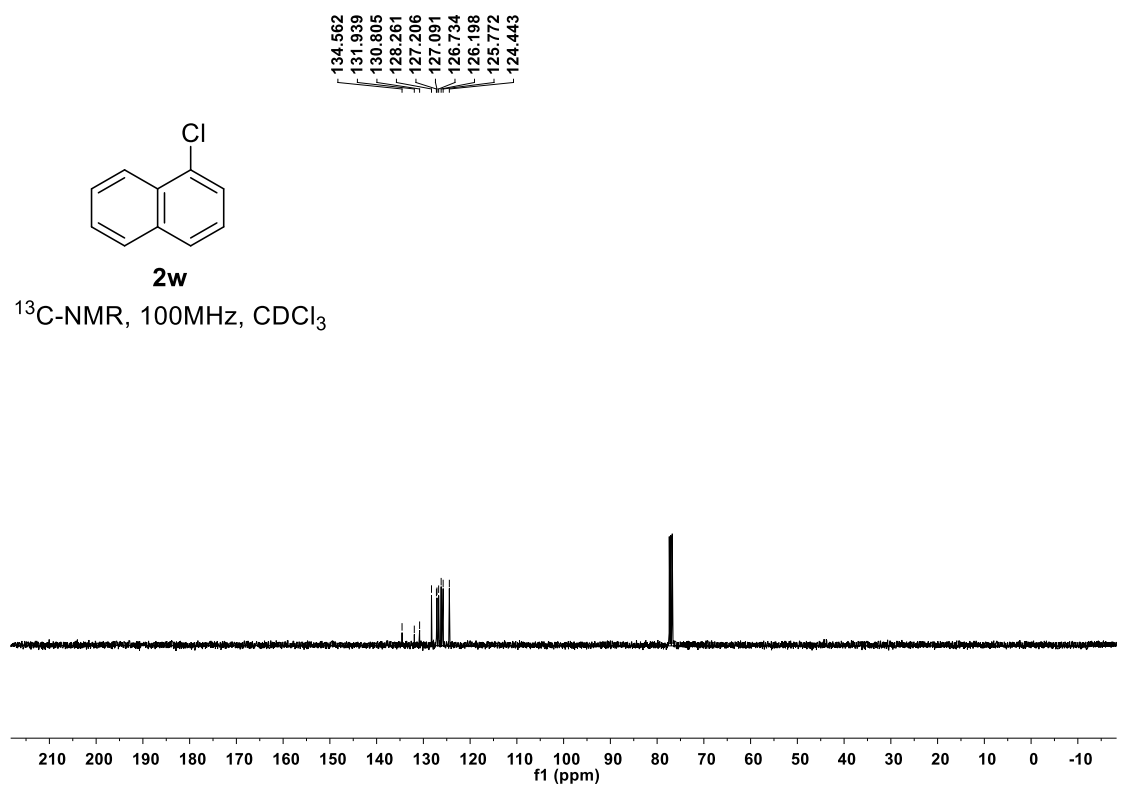
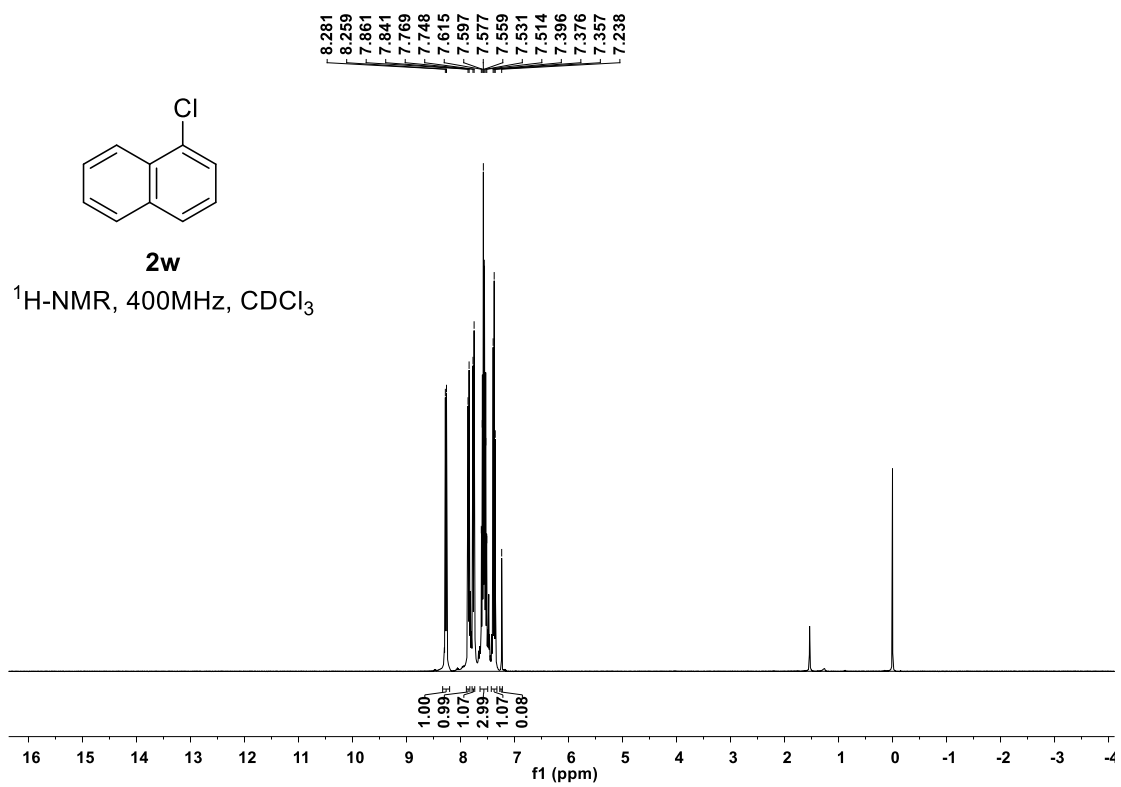
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>

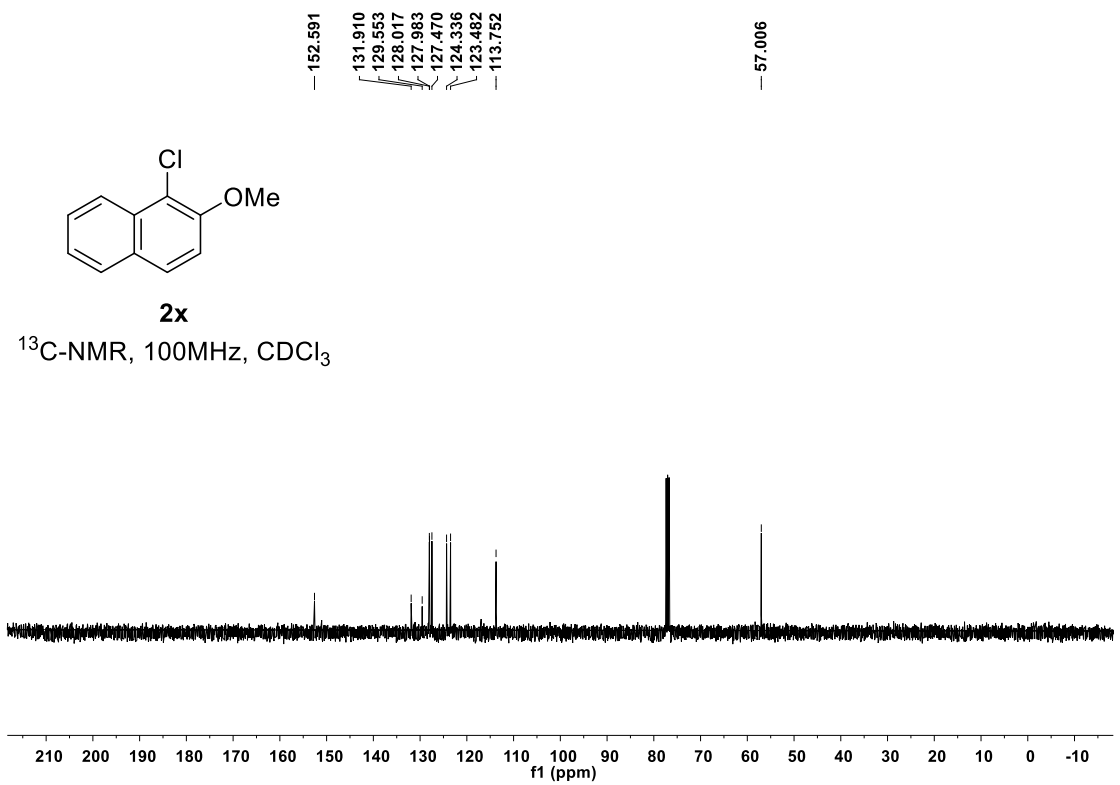
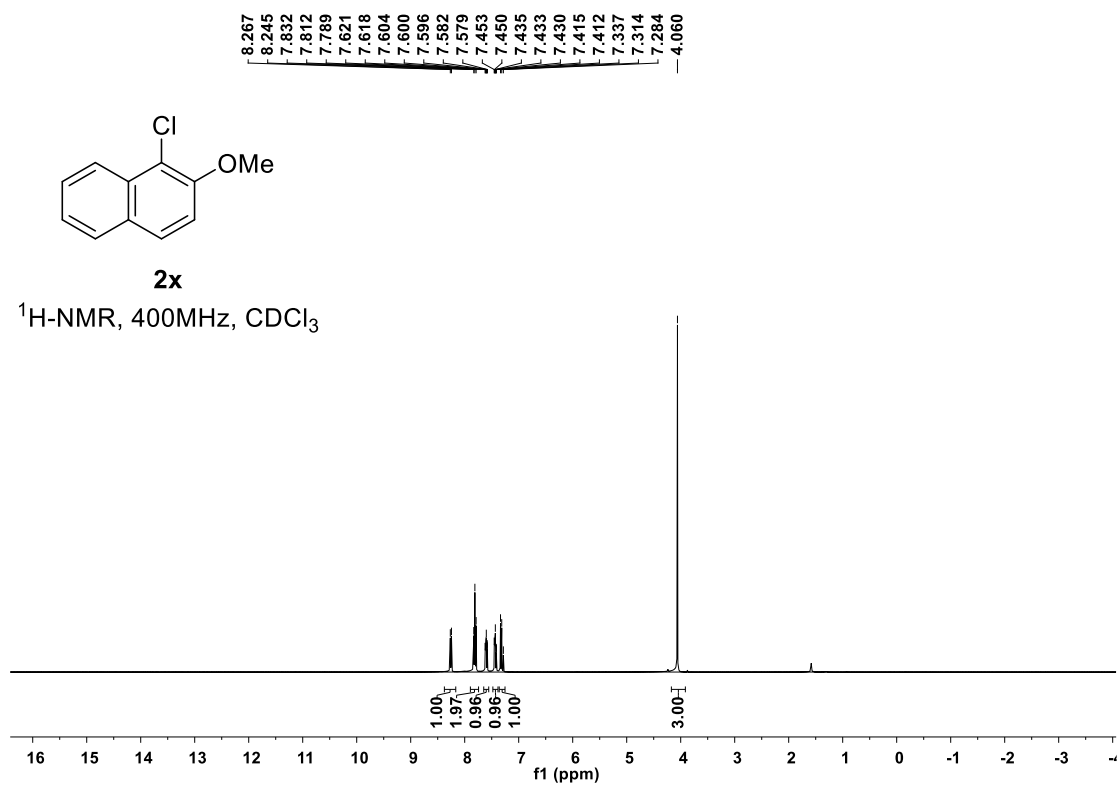


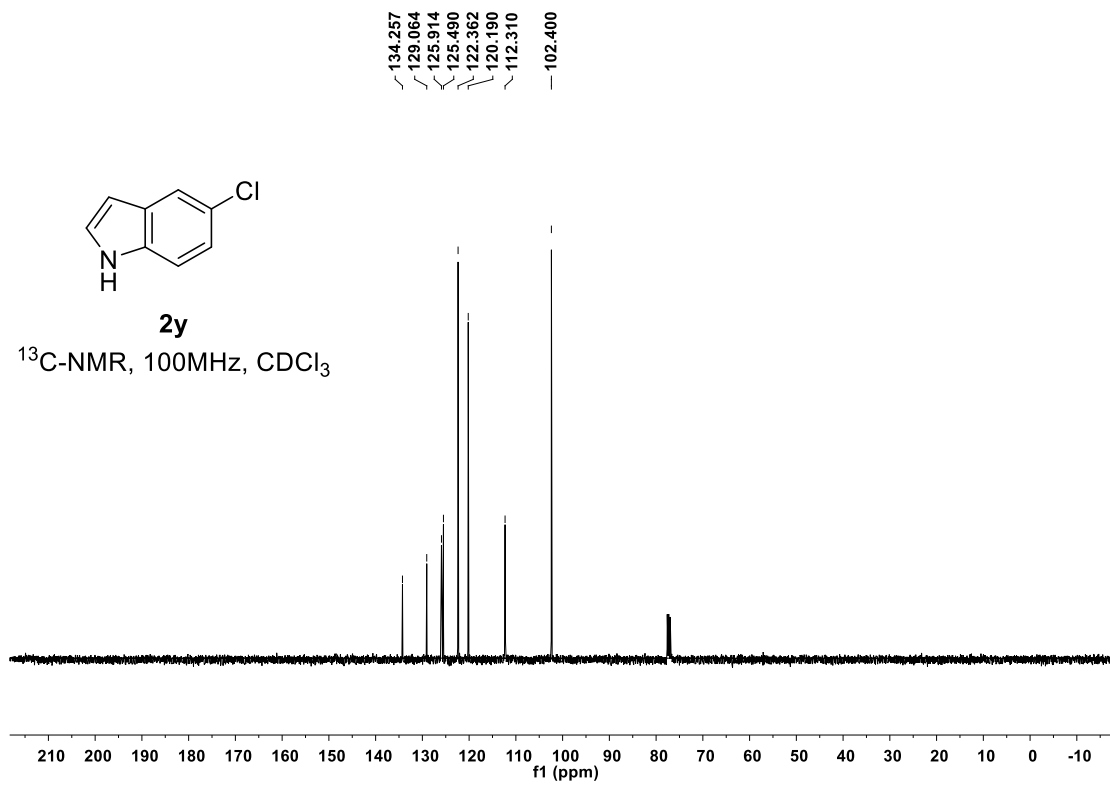
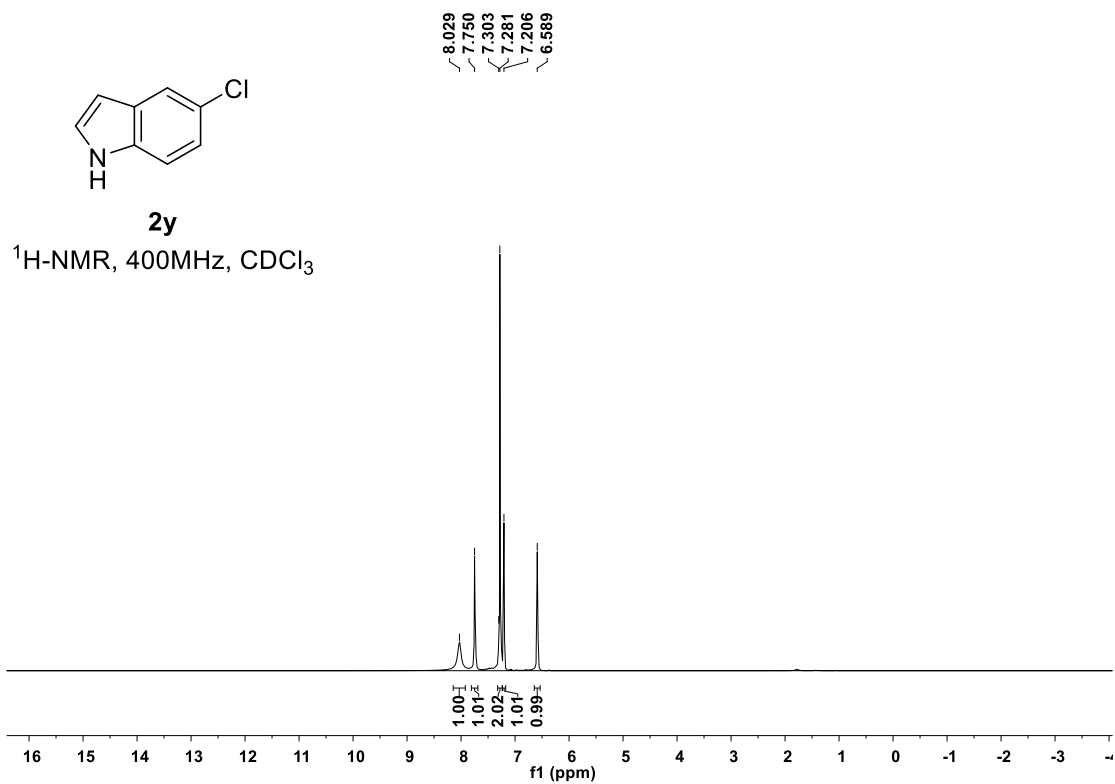
**2v**

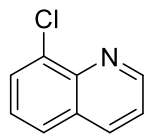
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





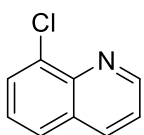
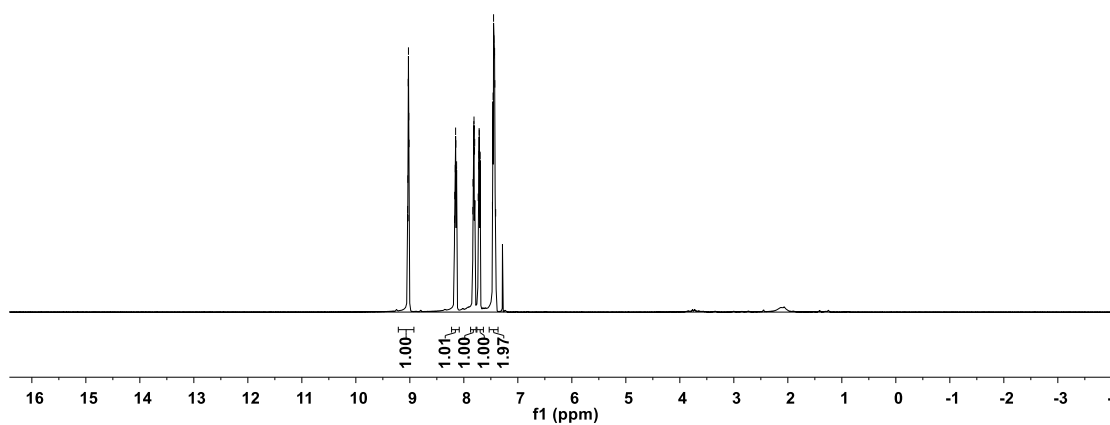






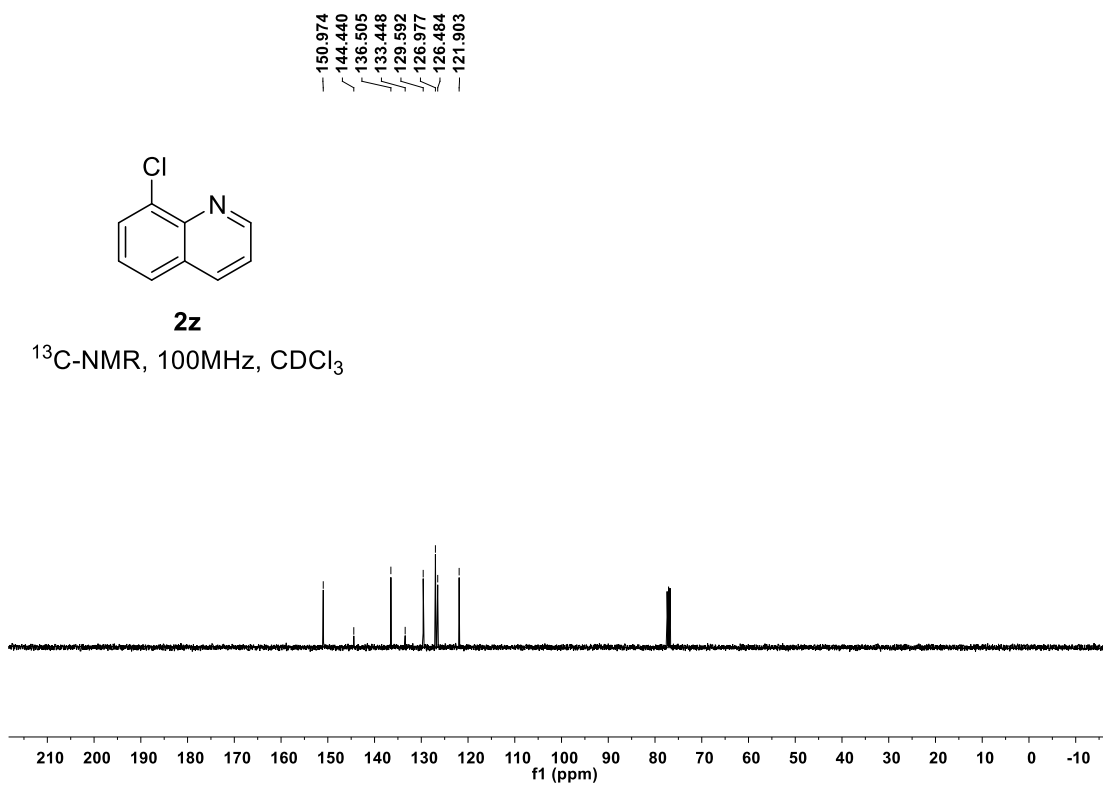
**2z**

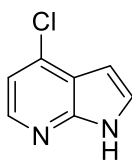
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**2z**

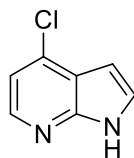
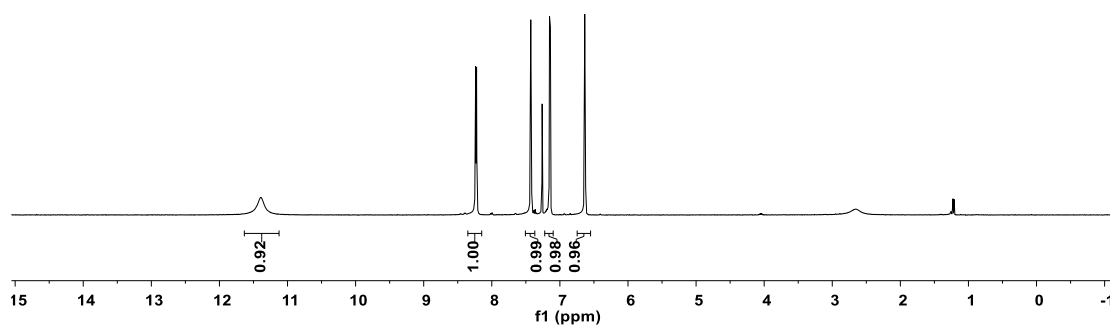
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





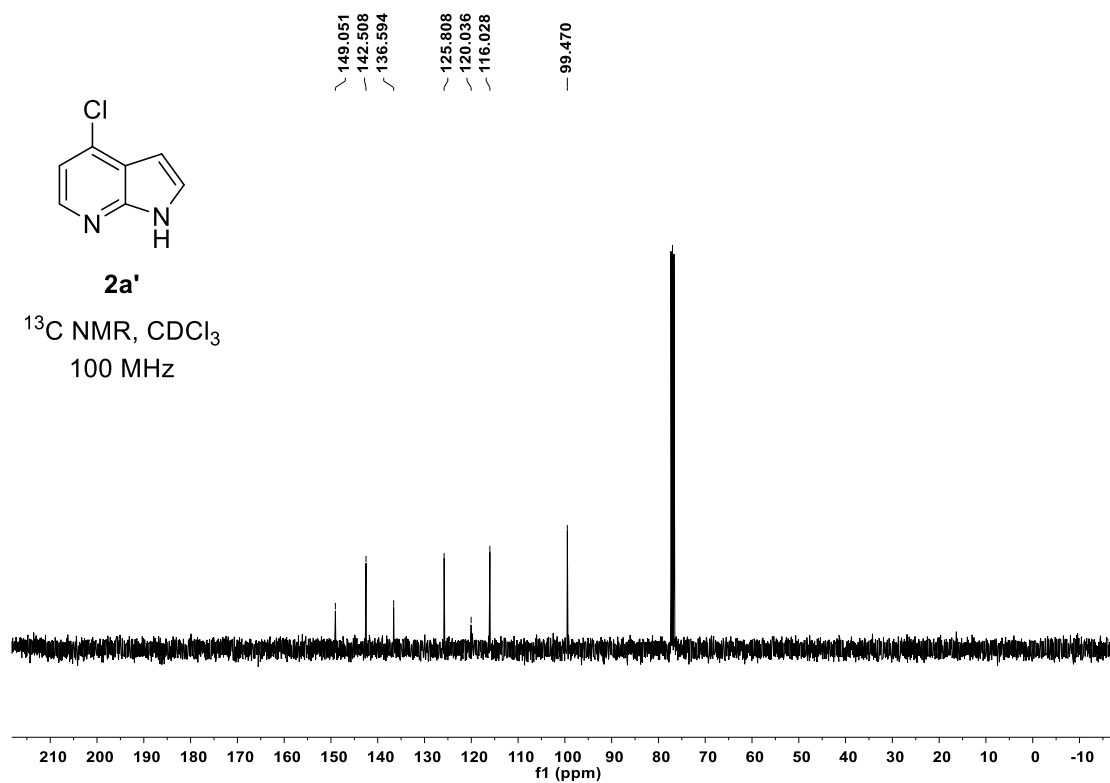
**2a'**

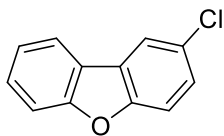
$^1\text{H}$  NMR,  $\text{CDCl}_3$   
400 MHz



**2a'**

$^{13}\text{C}$  NMR,  $\text{CDCl}_3$   
100 MHz

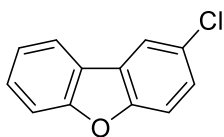
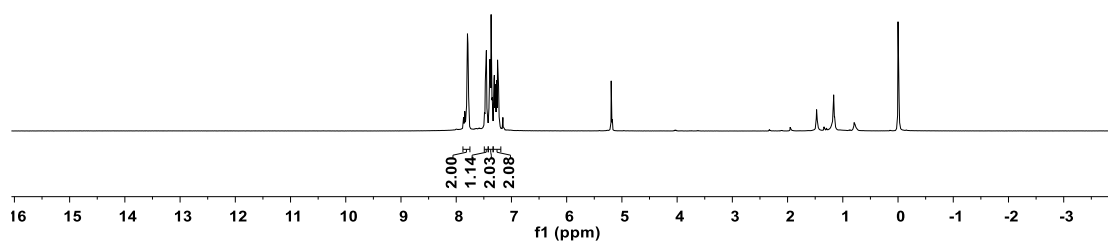




**2b'**

<sup>1</sup>H NMR, CDCl<sub>3</sub>

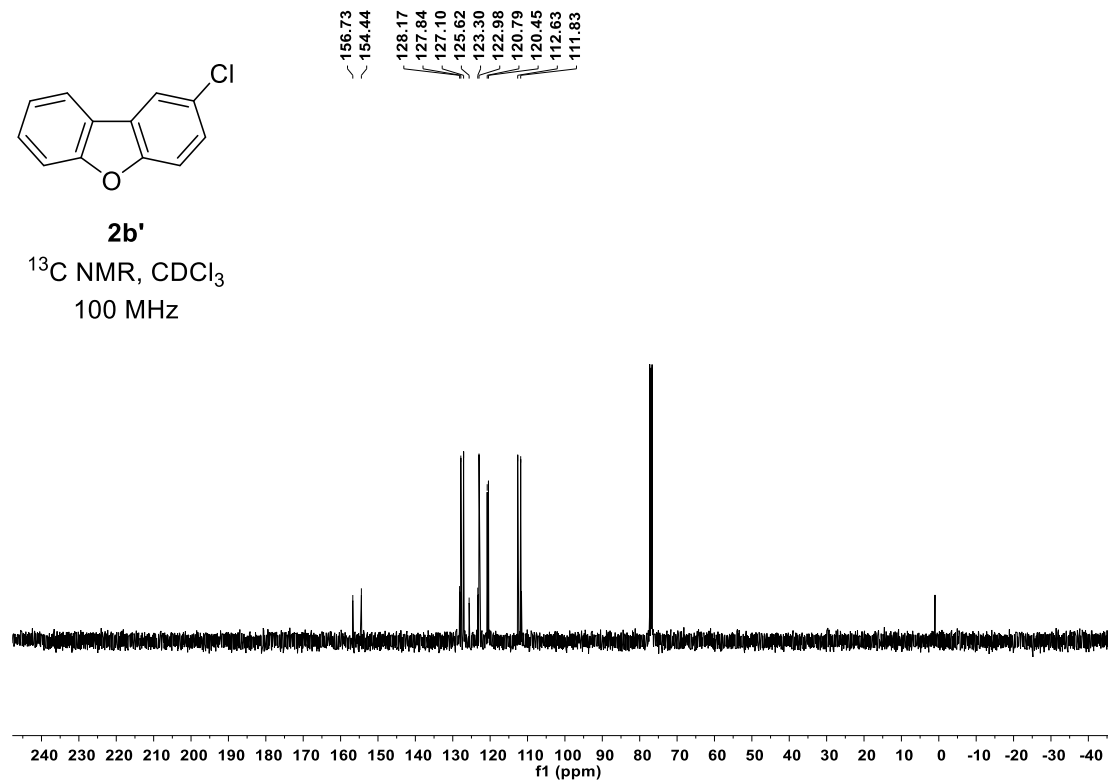
400 MHz

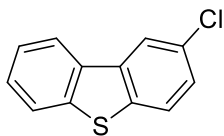


**2b'**

<sup>13</sup>C NMR, CDCl<sub>3</sub>

100 MHz

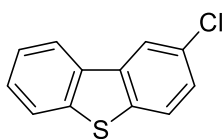
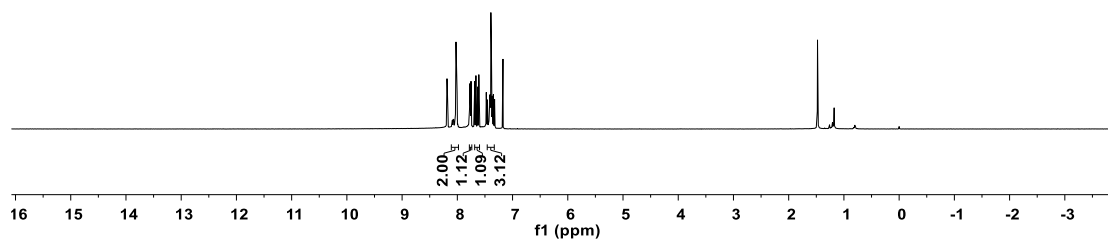




**2c'**

$^1\text{H}$  NMR,  $\text{CDCl}_3$

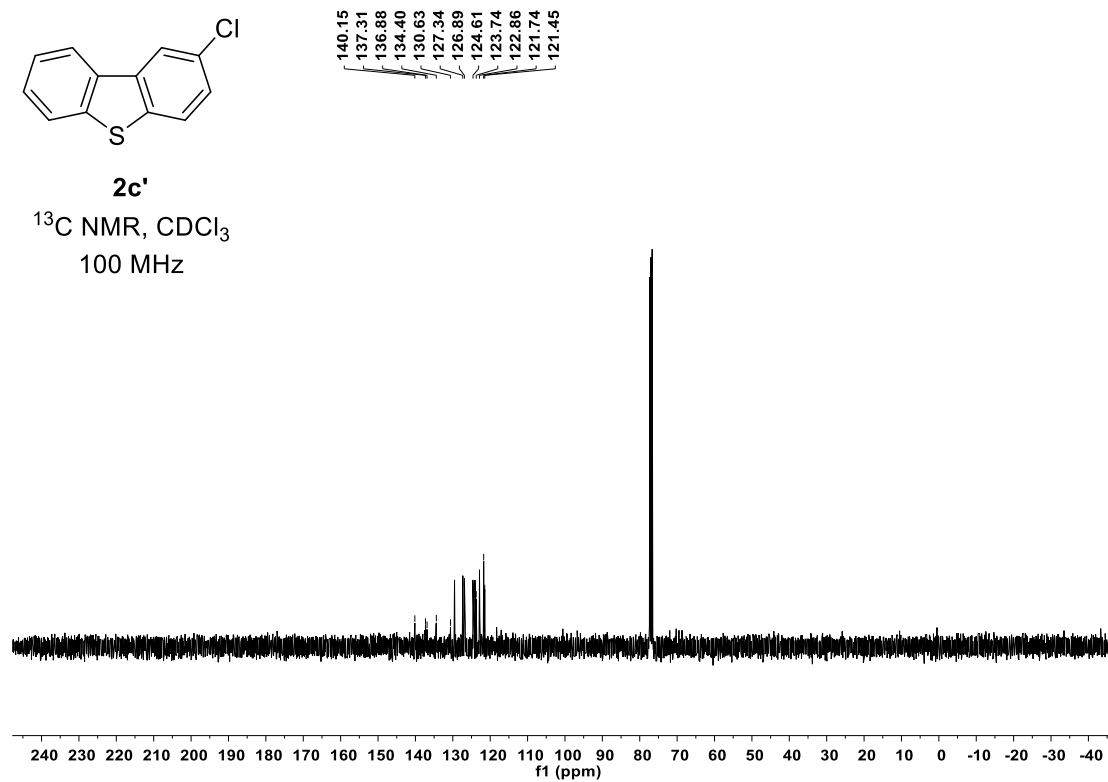
400 MHz



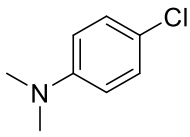
**2c'**

$^{13}\text{C}$  NMR,  $\text{CDCl}_3$

100 MHz

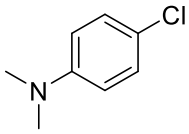
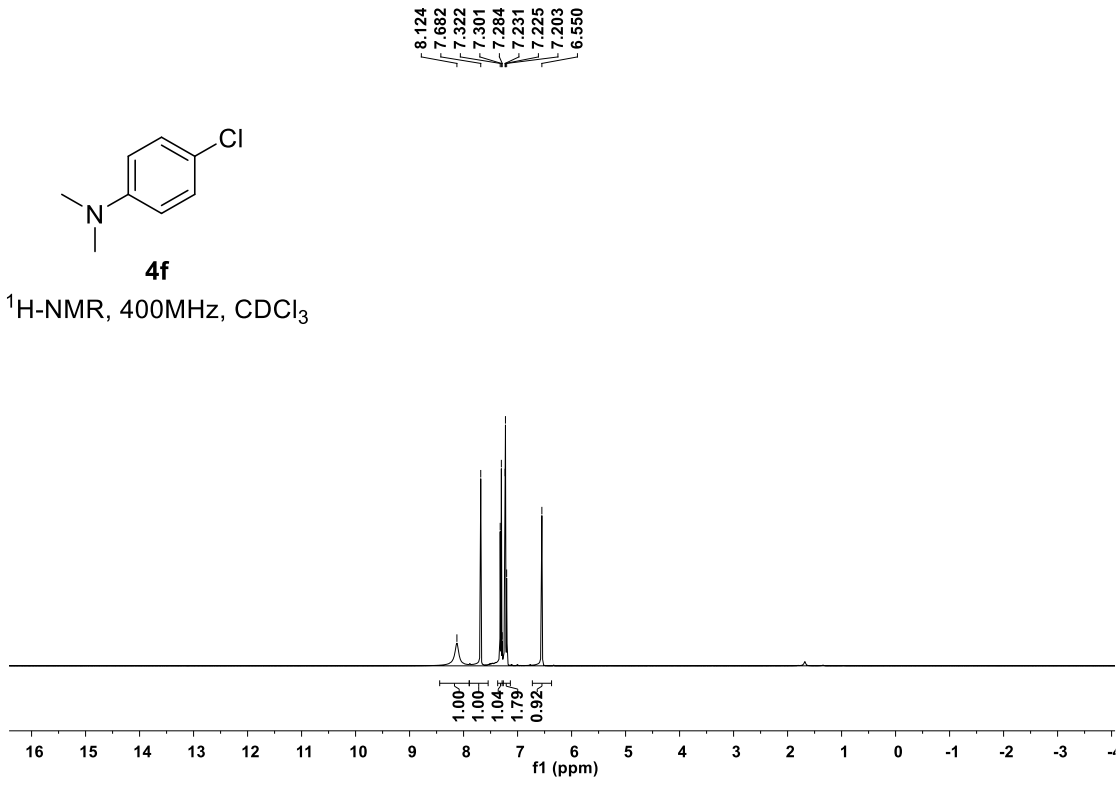






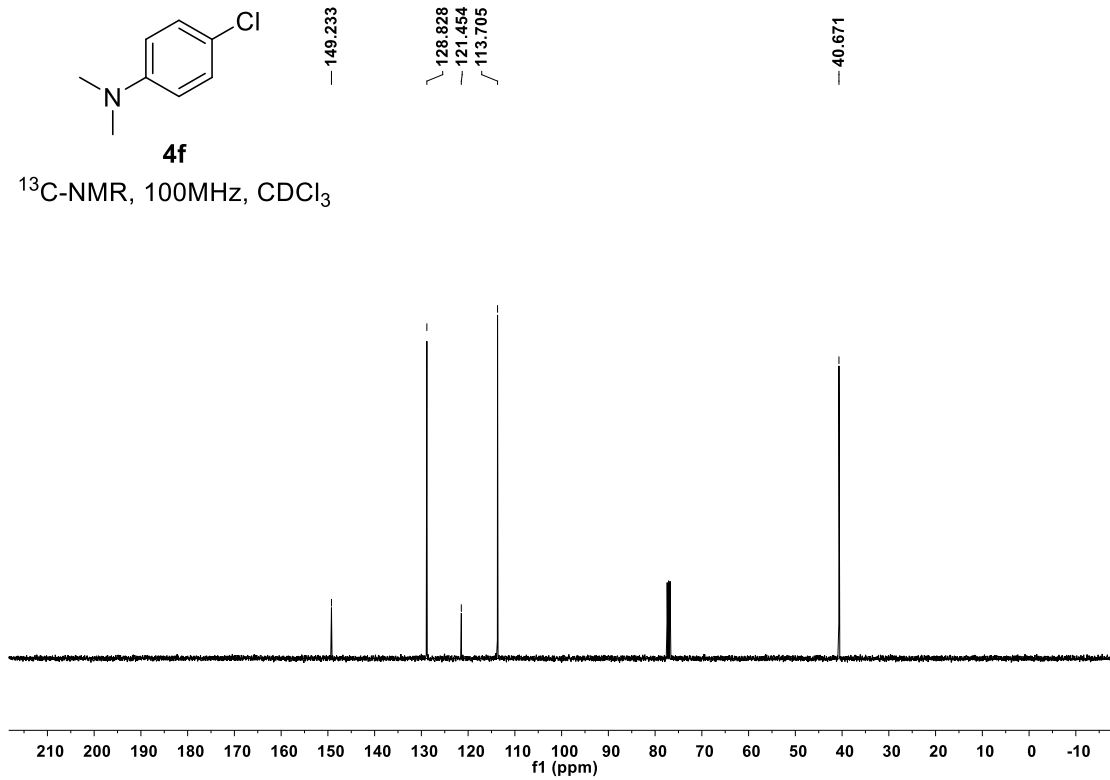
**4f**

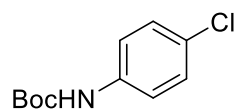
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**4f**

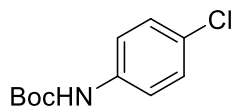
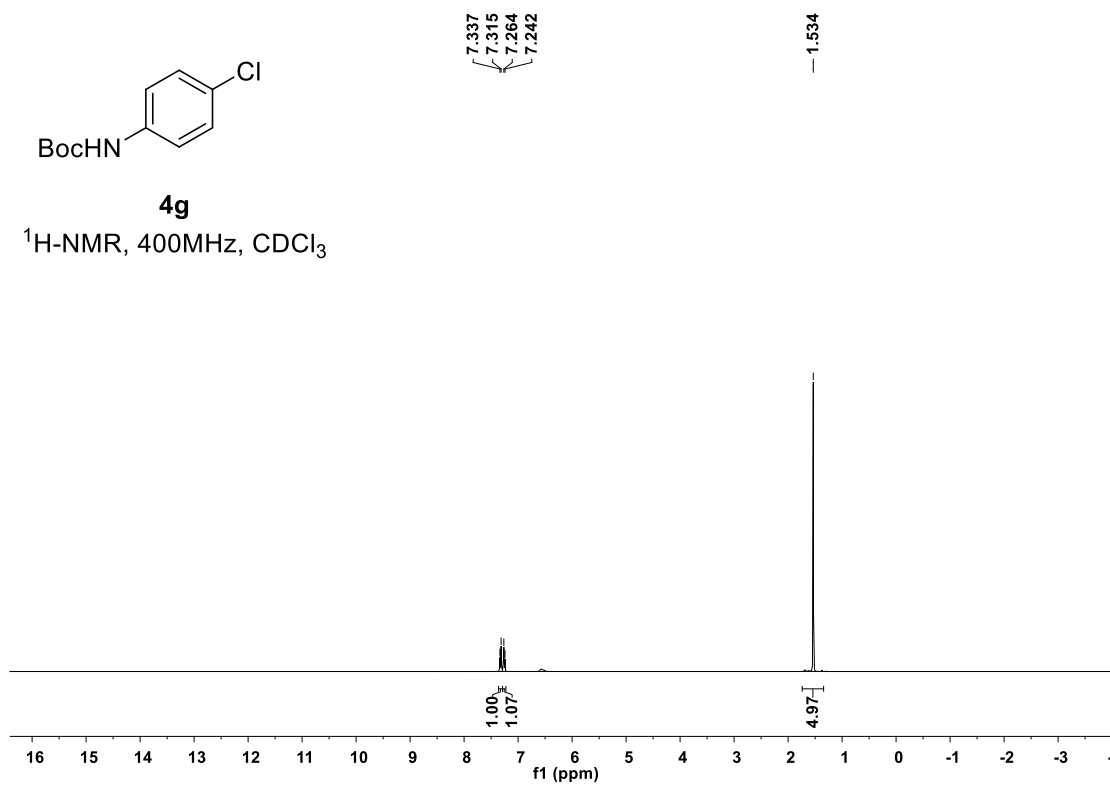
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





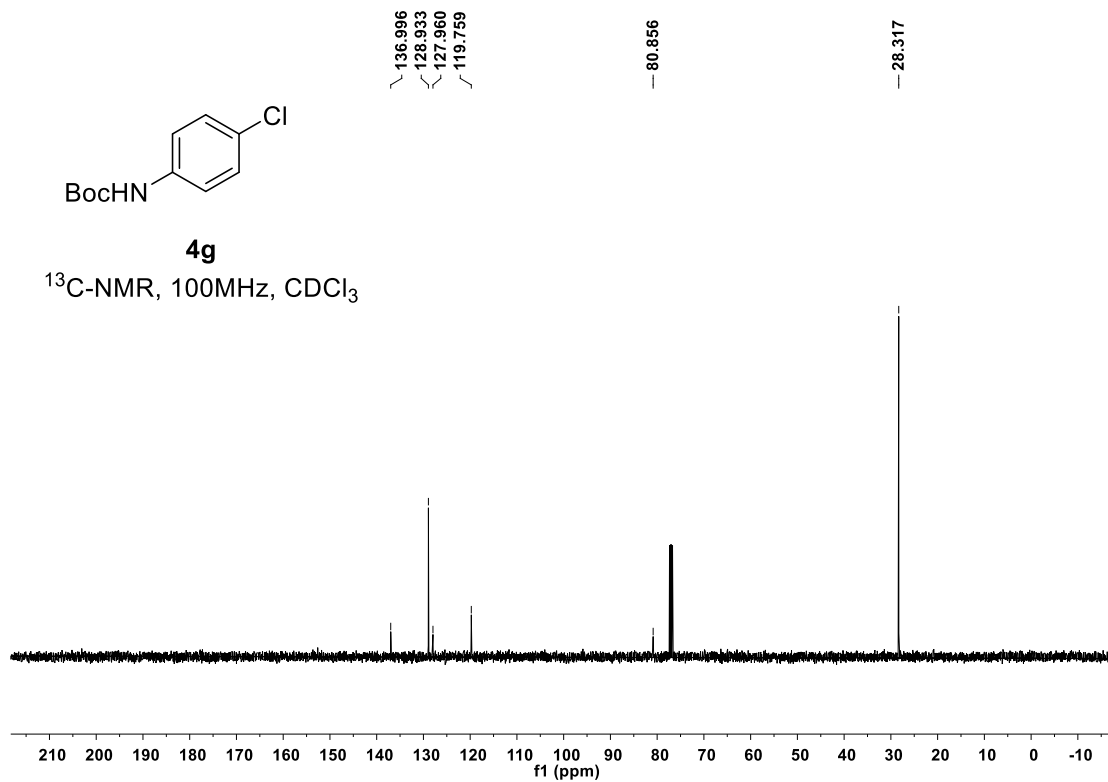
**4g**

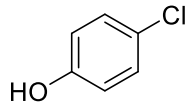
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**4g**

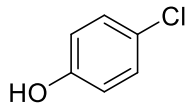
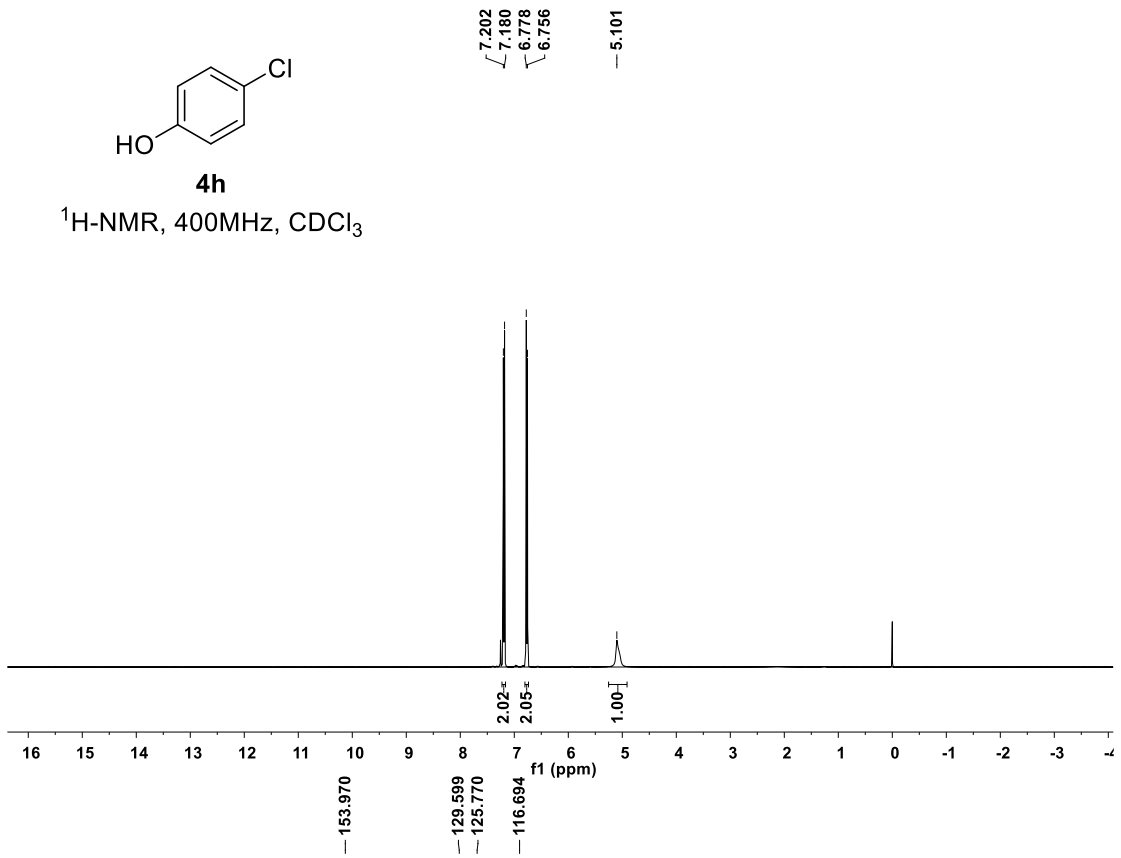
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





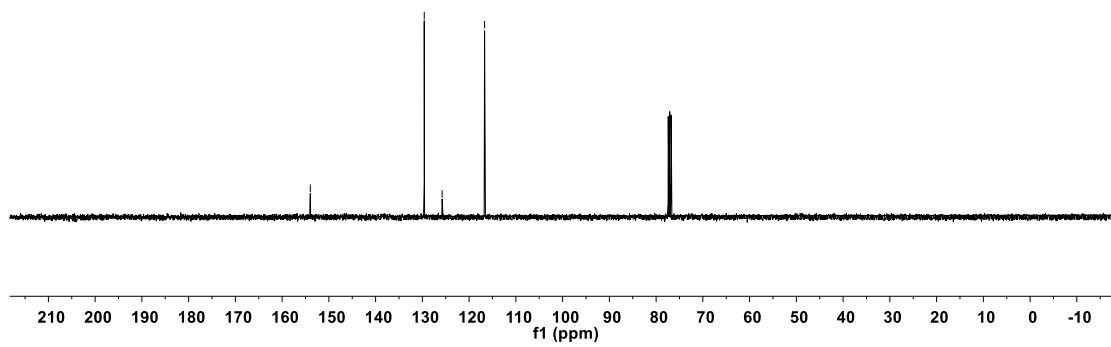
**4h**

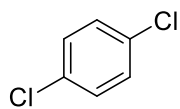
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**4h**

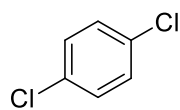
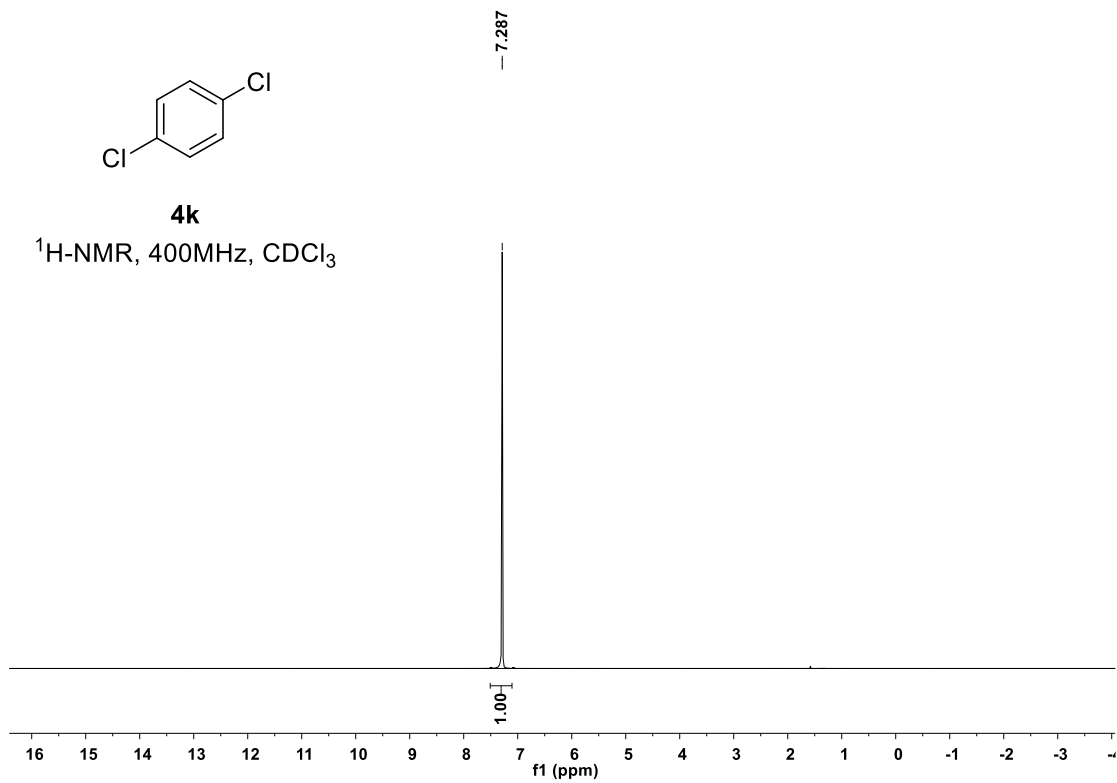
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





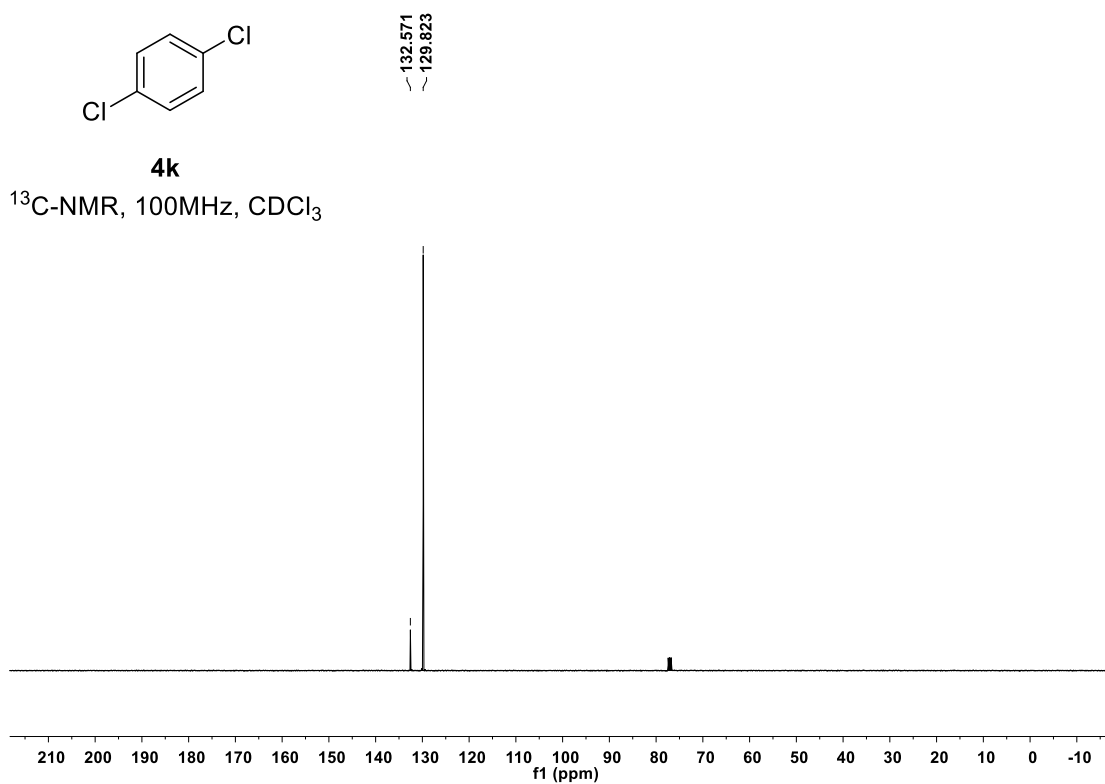
**4k**

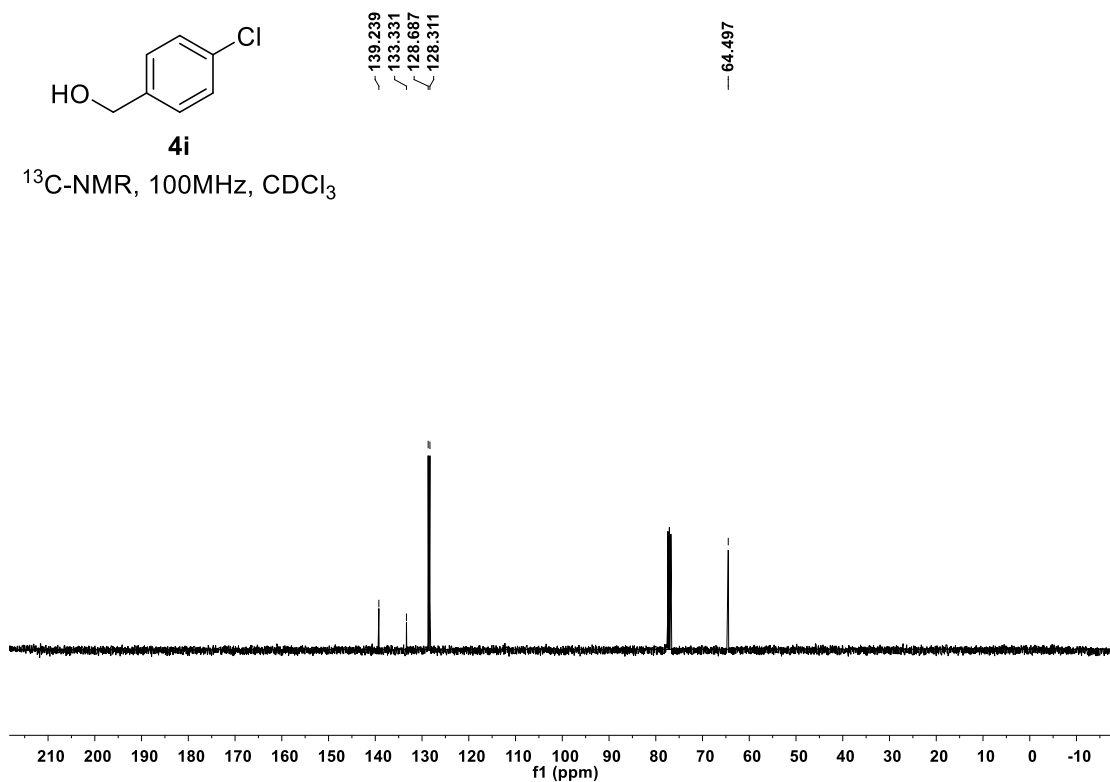
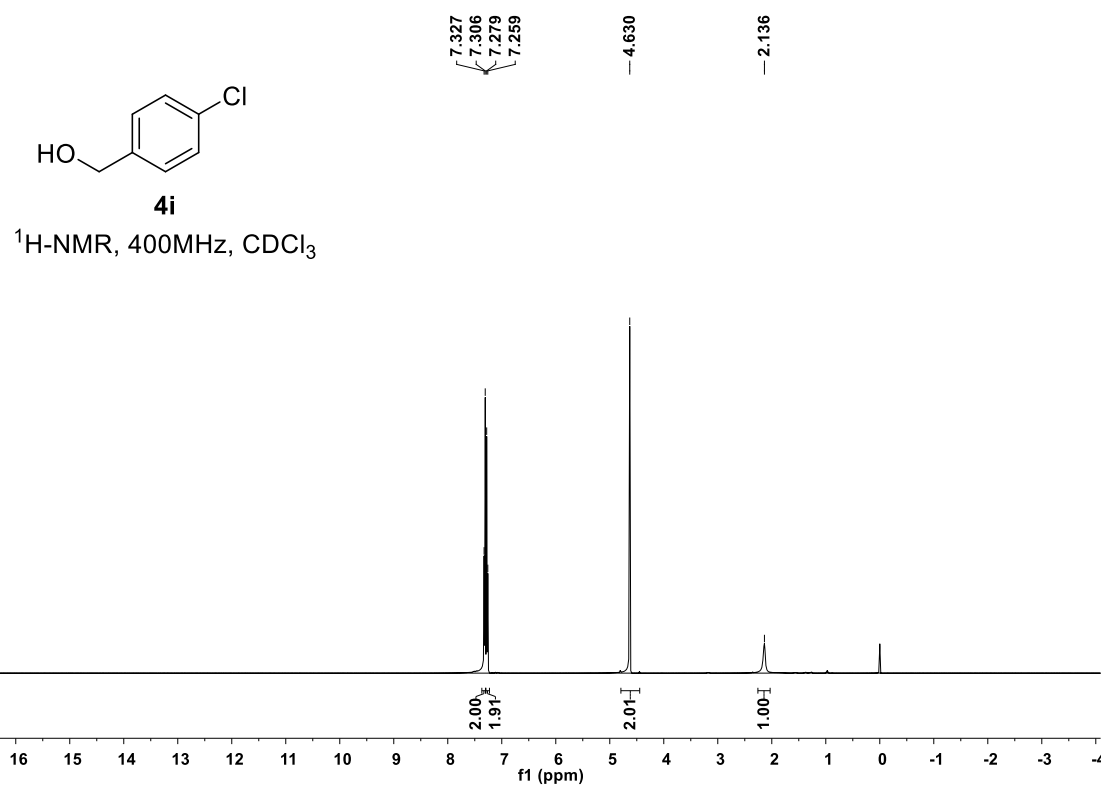
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>

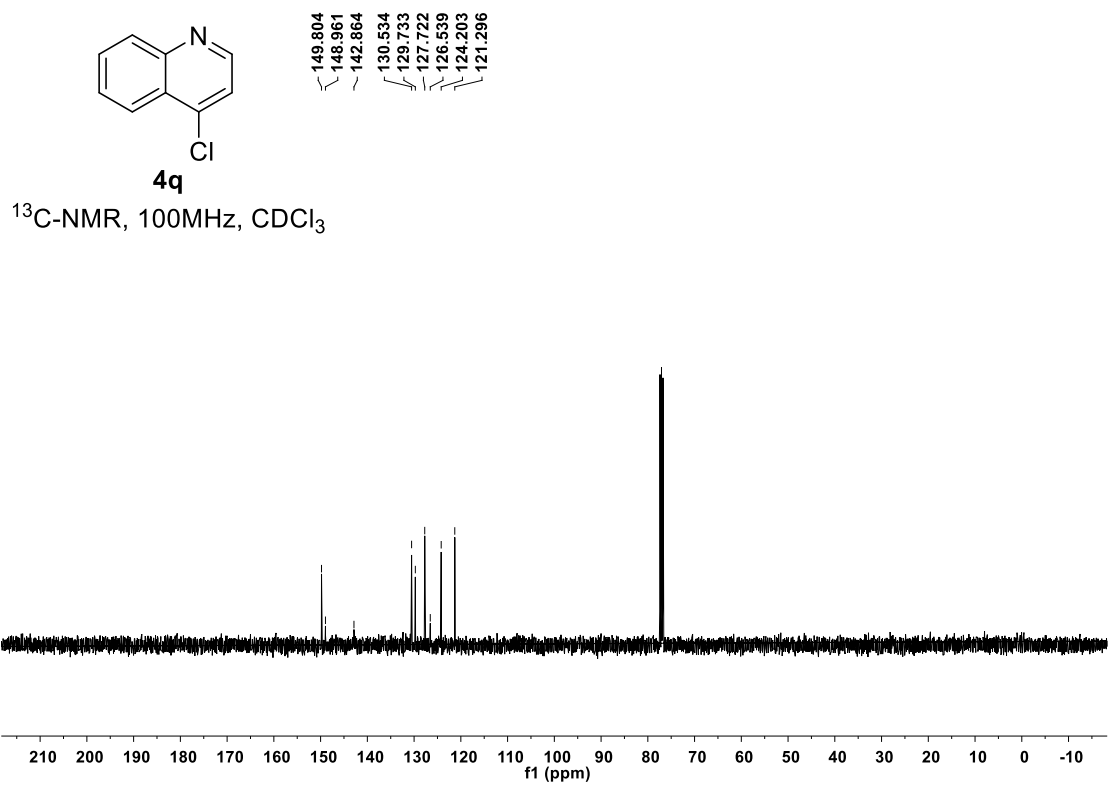
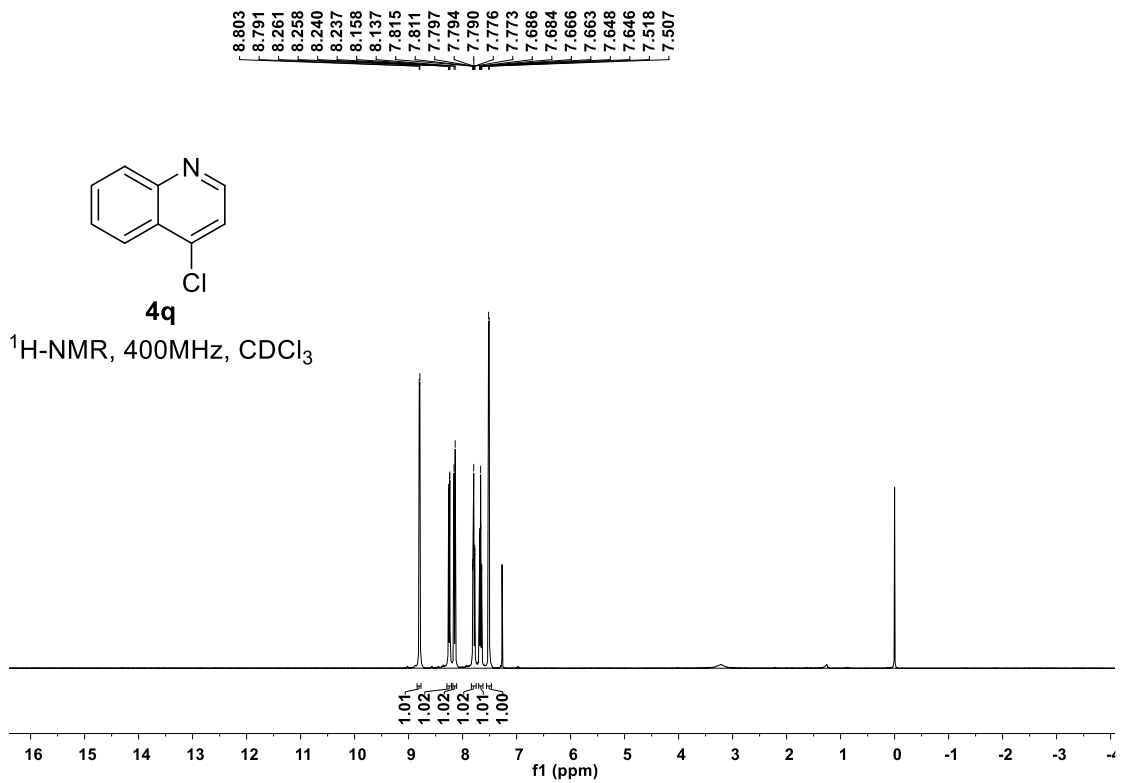


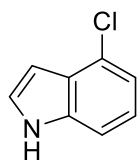
**4k**

<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>



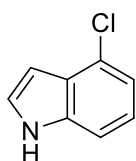
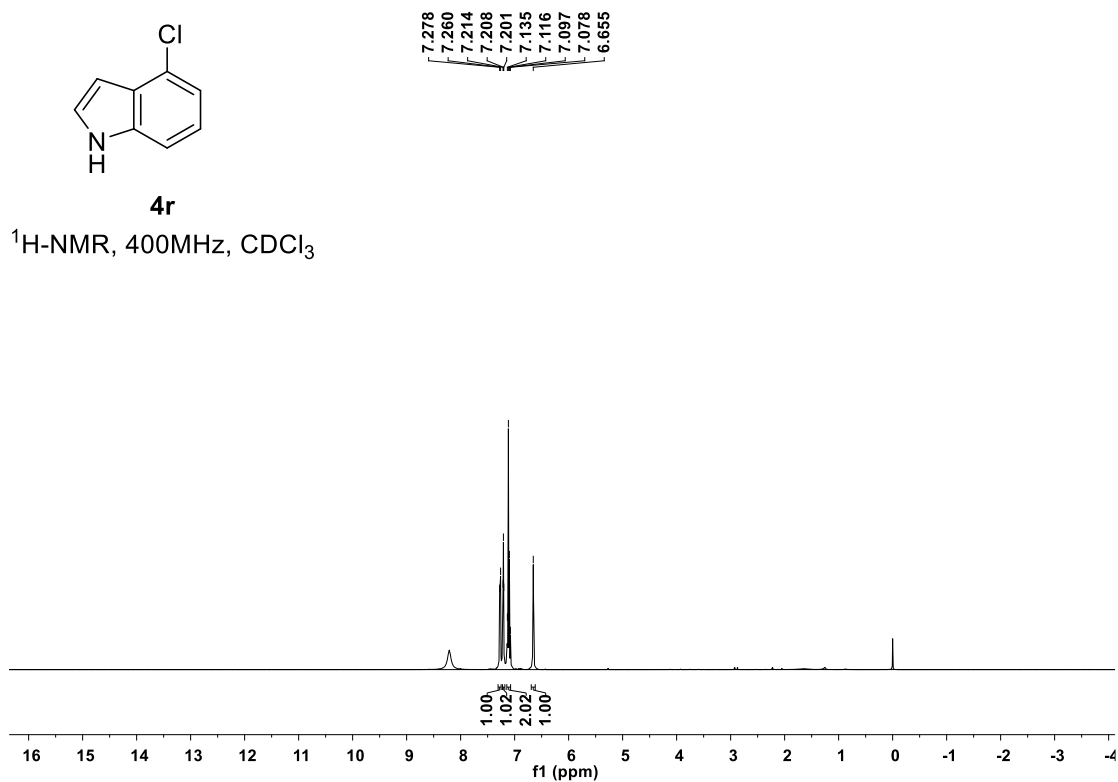






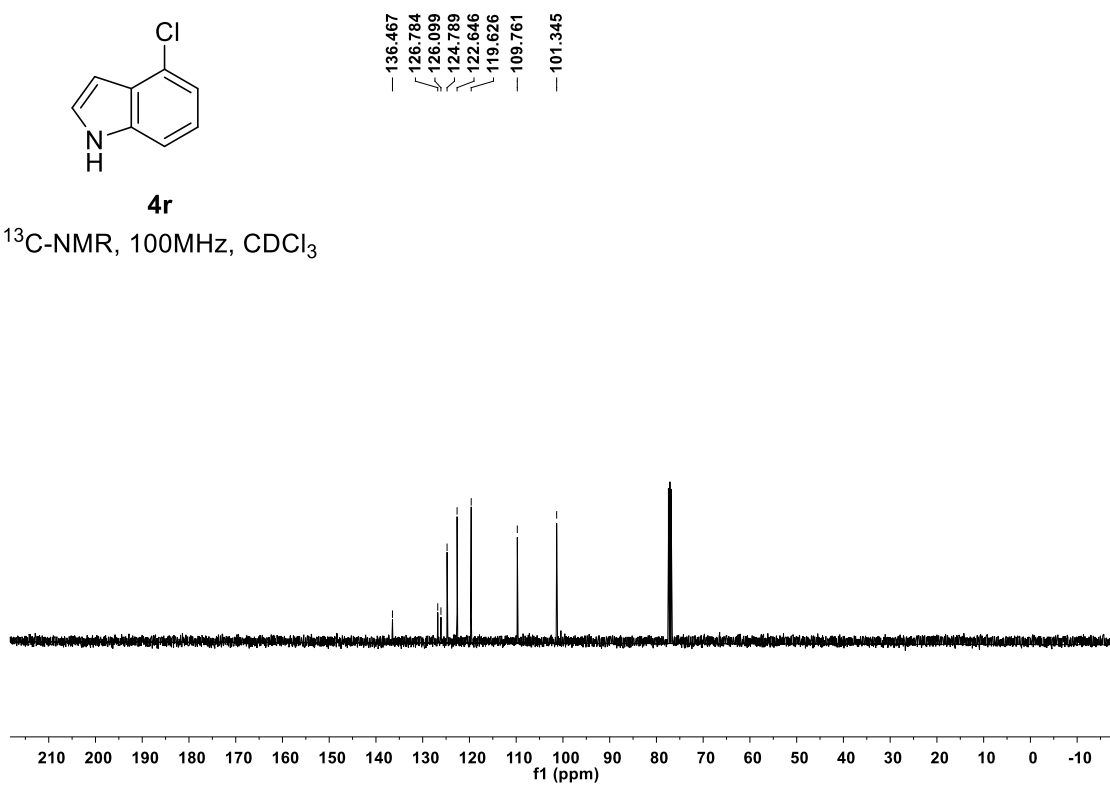
**4r**

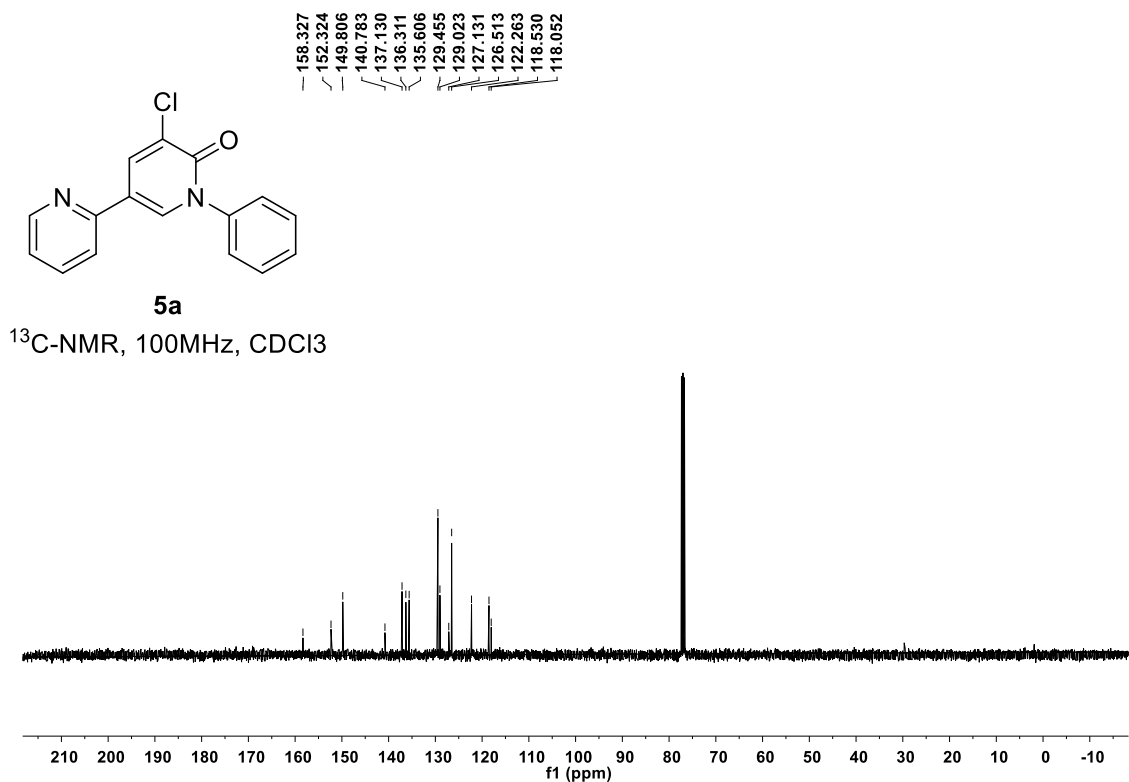
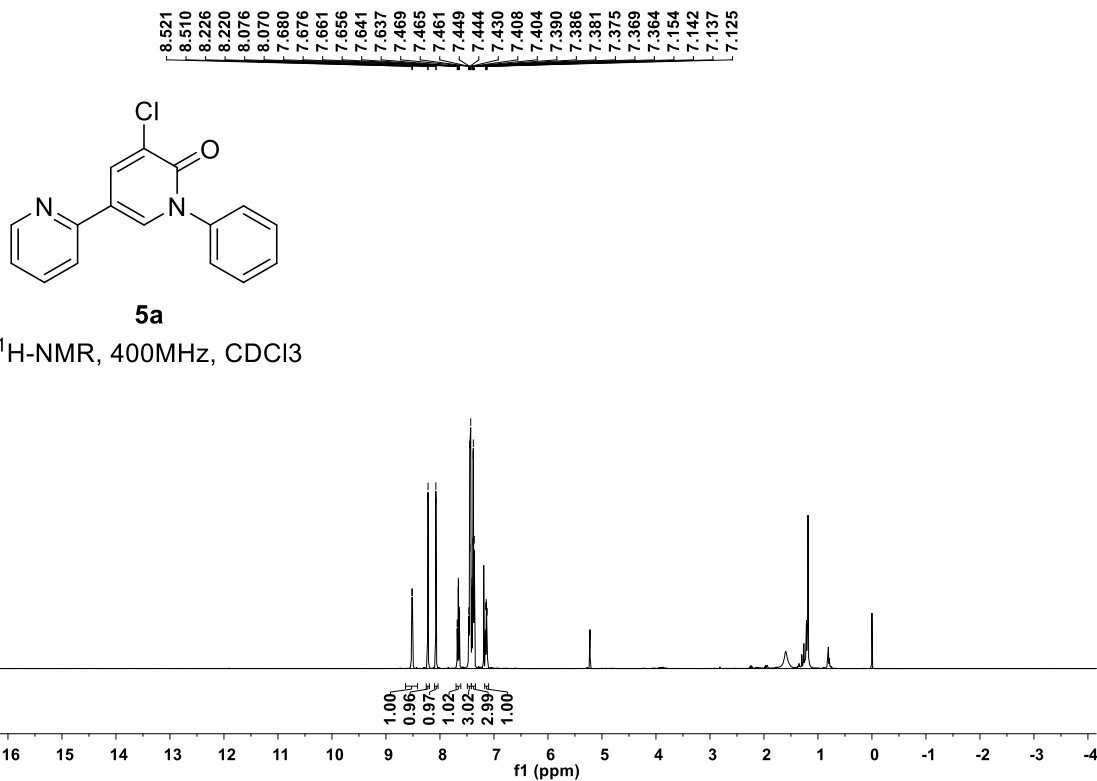
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



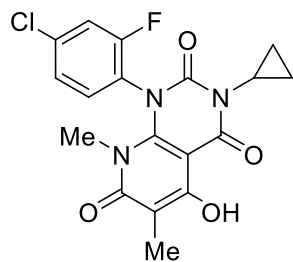
**4r**

<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>



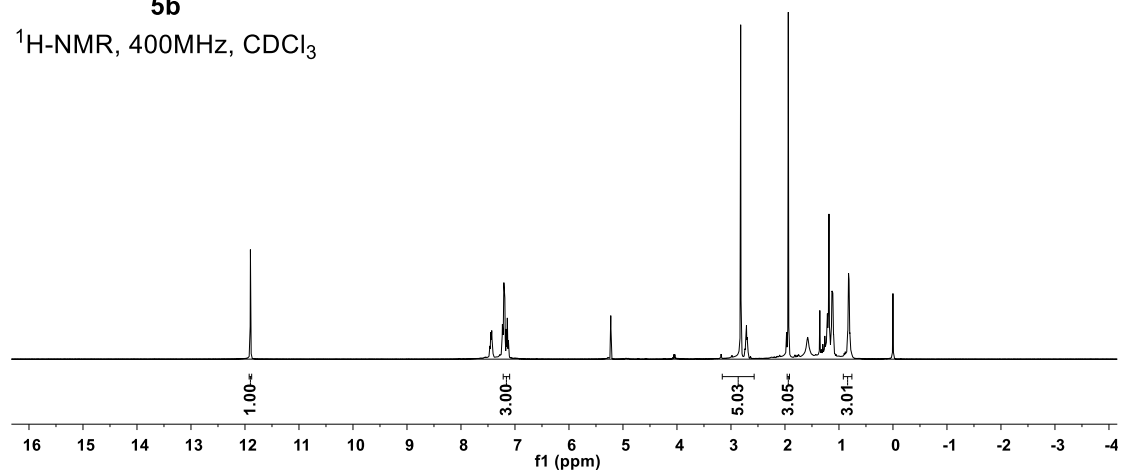




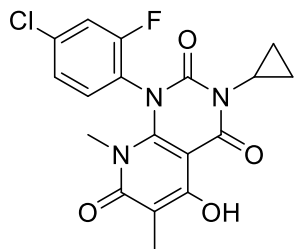


**5b**

<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>

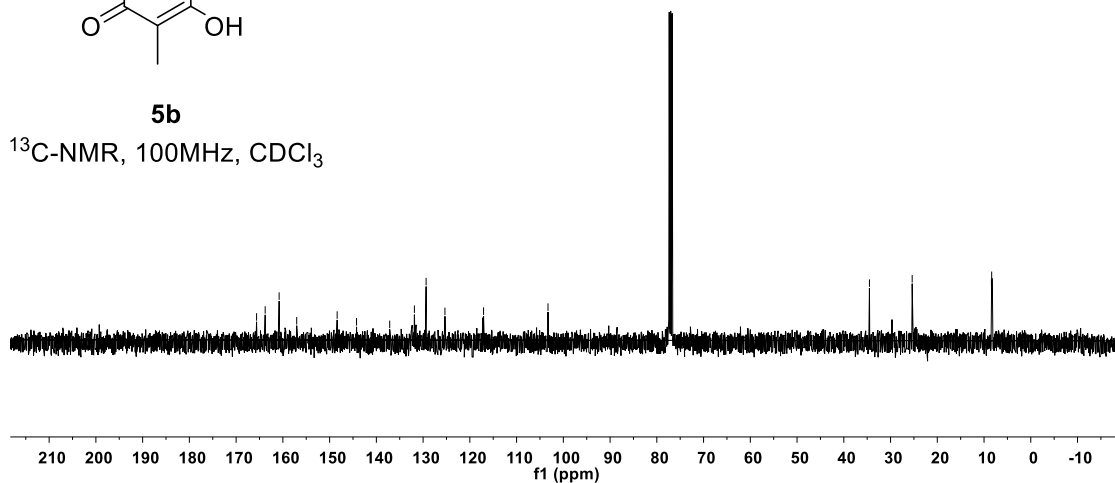


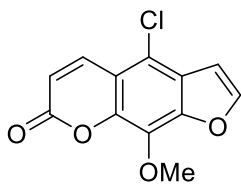
165.623  
 163.785  
 160.796  
 157.040  
 148.387  
 144.238  
 137.145  
 131.861  
 129.356  
 125.328  
 117.291  
 117.065  
 103.277  
 34.511  
 25.372  
 8.419  
 8.364  
 8.212



**5b**

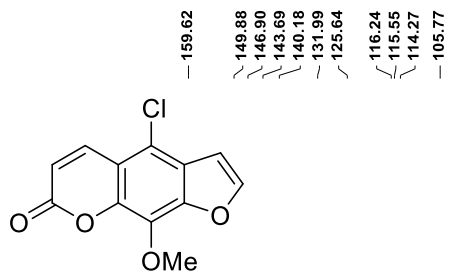
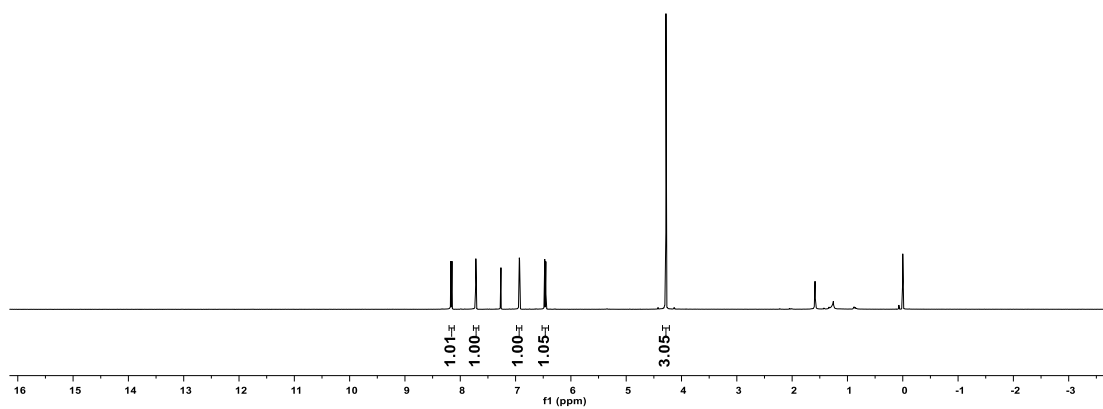
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





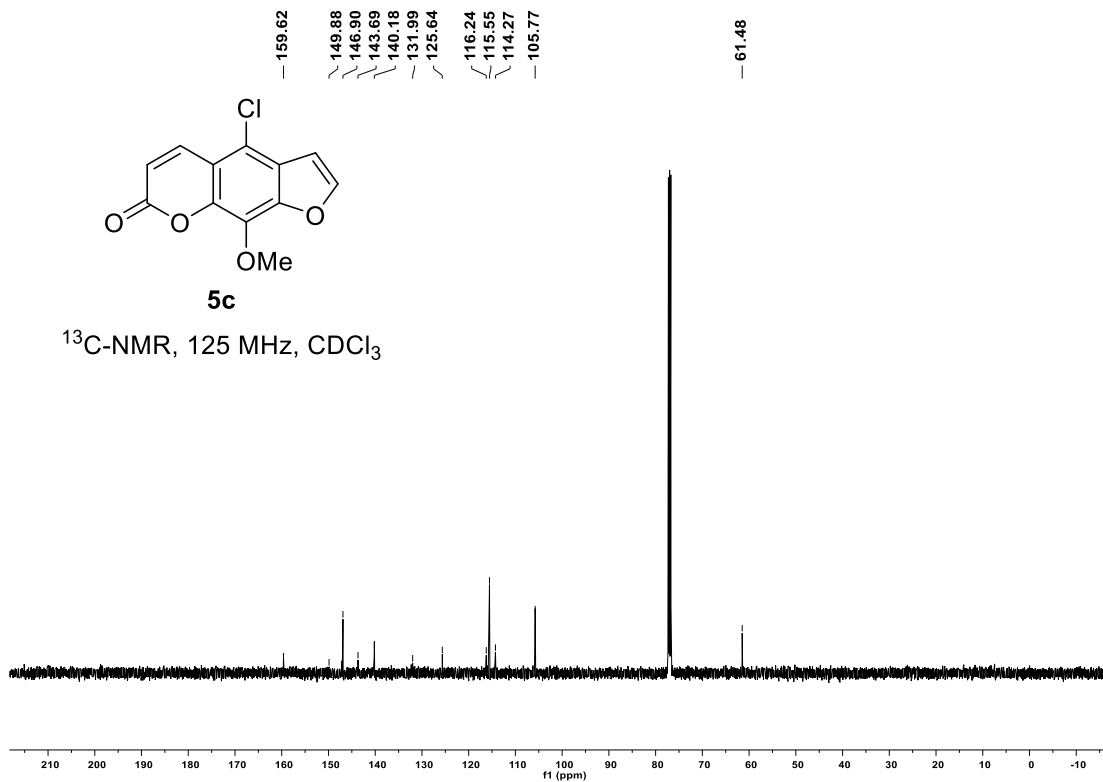
**5c**

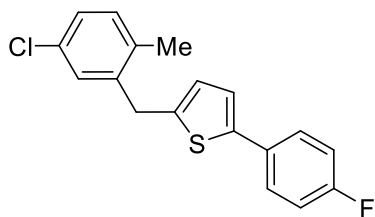
$^1\text{H-NMR}$ , 500 MHz,  $\text{CDCl}_3$



**5c**

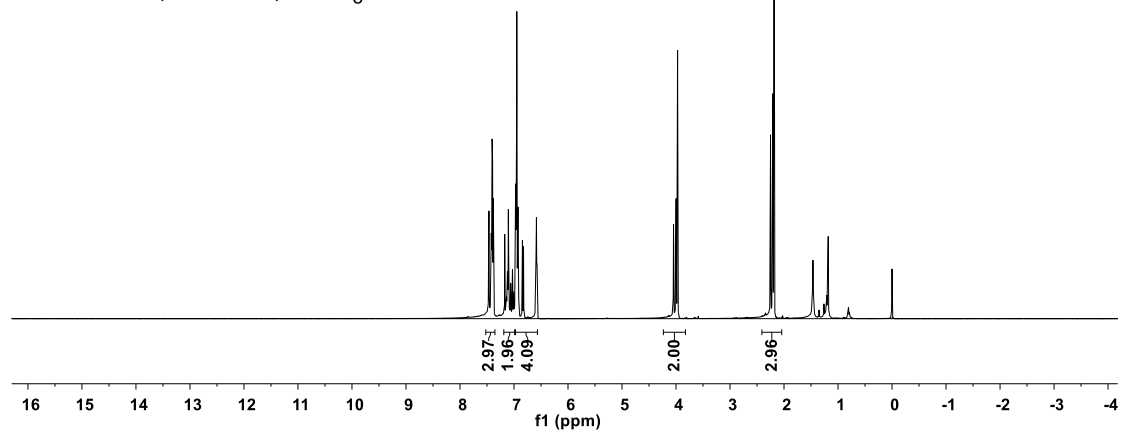
$^{13}\text{C-NMR}$ , 125 MHz,  $\text{CDCl}_3$





**5d**

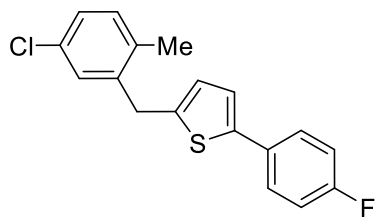
$^1\text{H-NMR}$ , 400MHz,  $\text{CDCl}_3$



140.613  
138.126  
136.077  
135.989  
132.380  
131.685  
127.226  
127.149  
126.204  
122.742  
115.858  
115.642

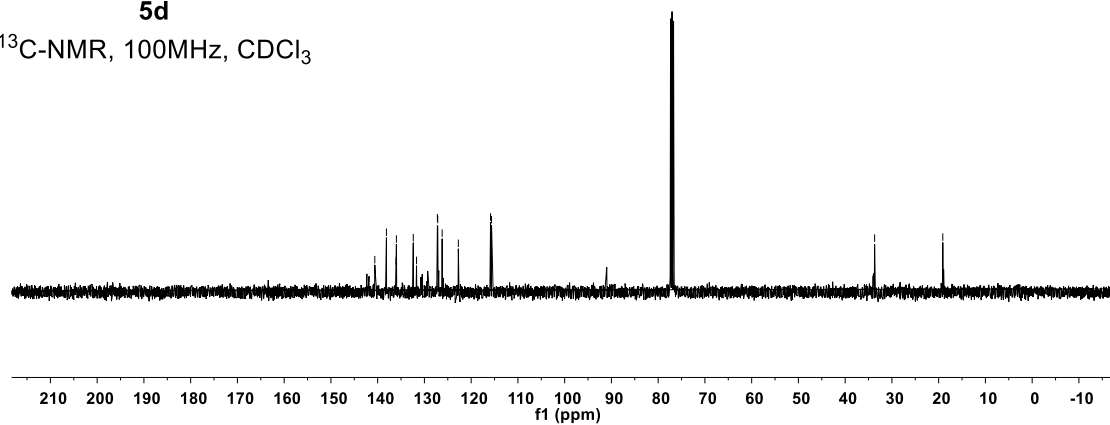
33.701

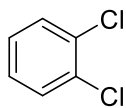
19.115



**5d**

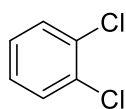
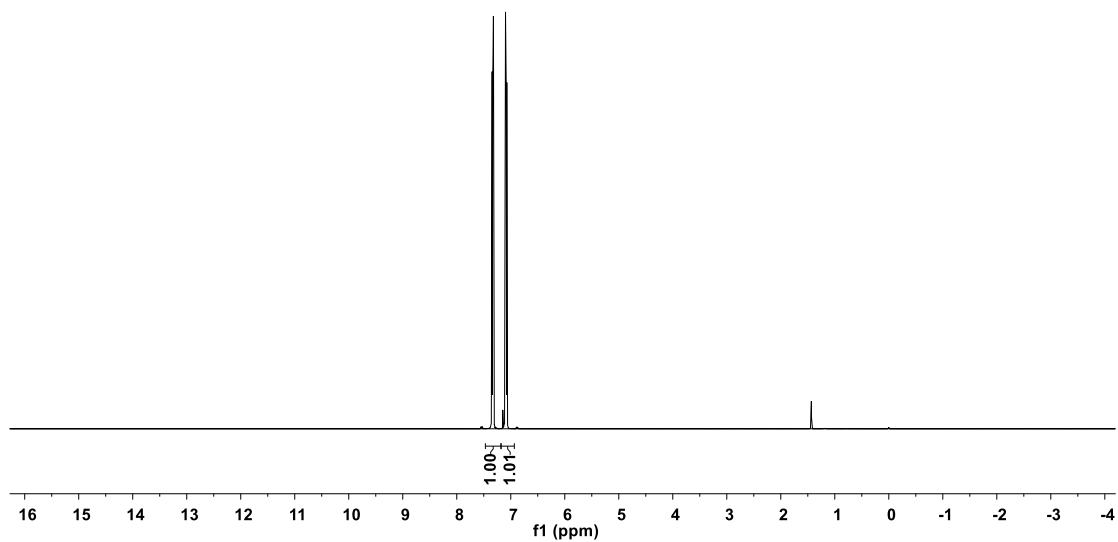
$^{13}\text{C-NMR}$ , 100MHz,  $\text{CDCl}_3$





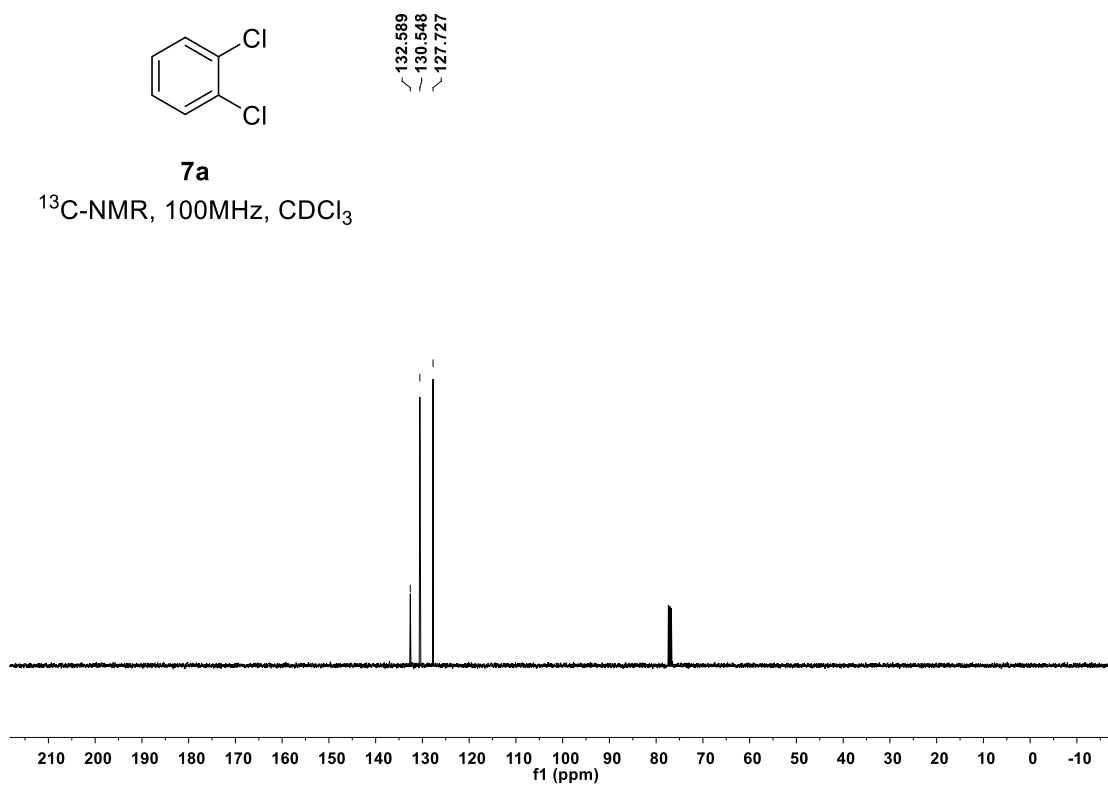
**7a**

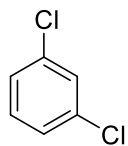
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**7a**

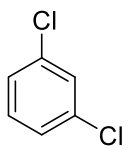
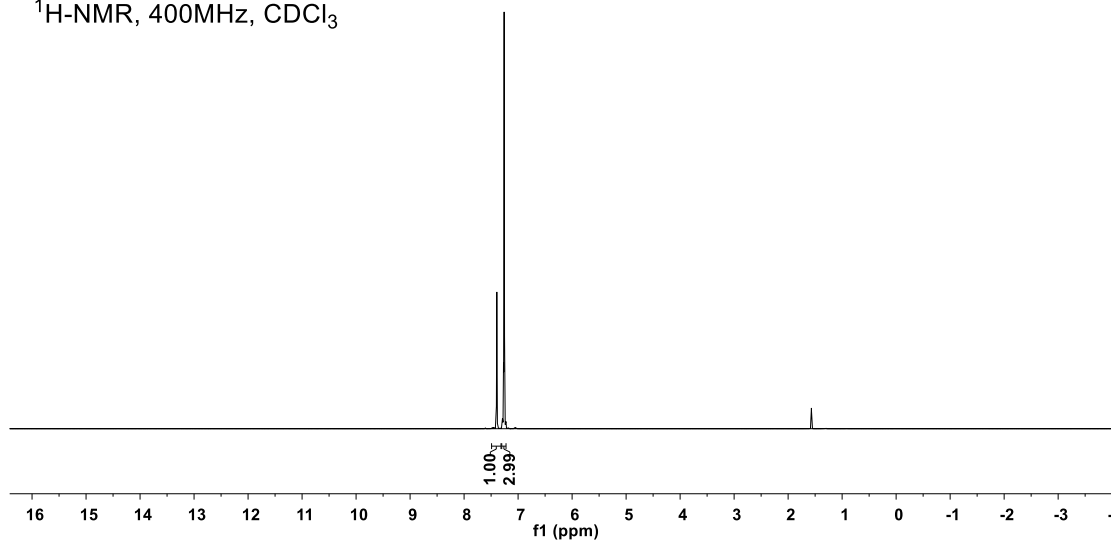
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





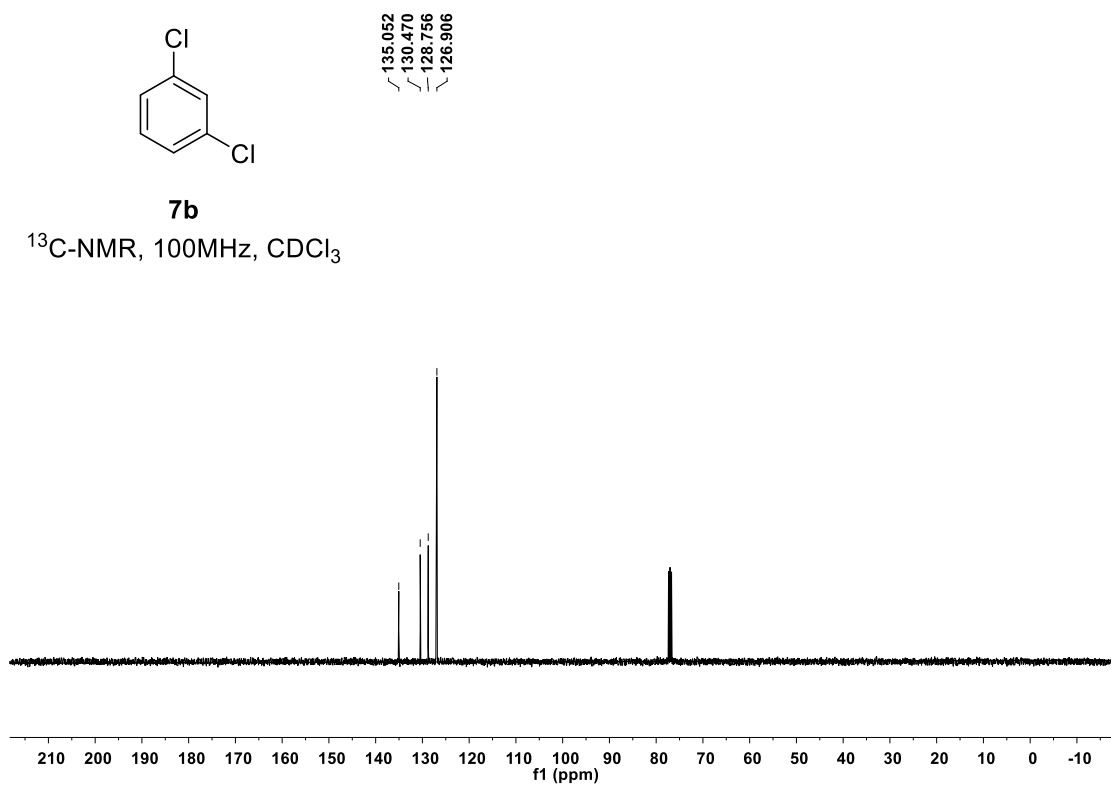
**7b**

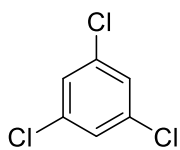
<sup>1</sup>H-NMR, 400MHz, CDCl<sub>3</sub>



**7b**

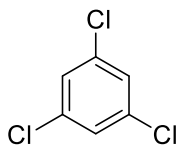
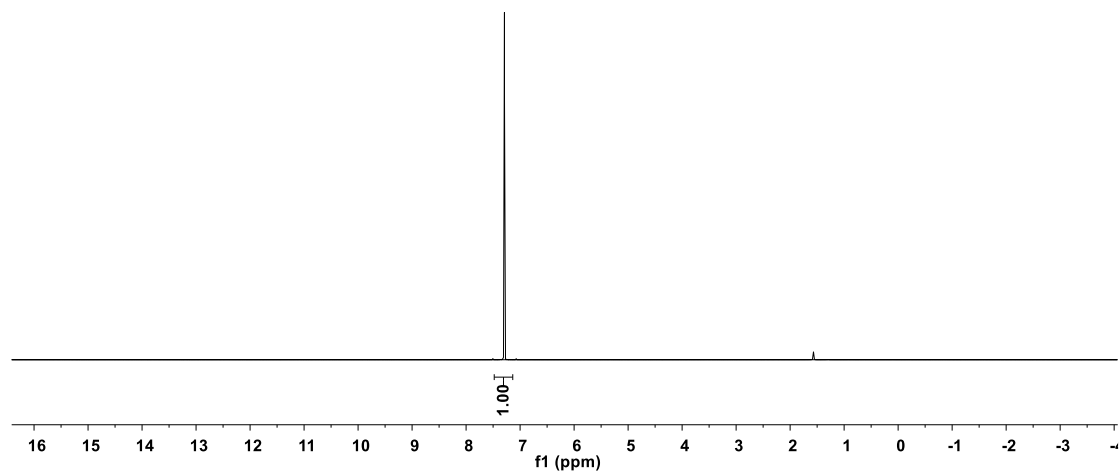
<sup>13</sup>C-NMR, 100MHz, CDCl<sub>3</sub>





**7d**

$^1\text{H-NMR}$ , 400MHz,  $\text{CDCl}_3$



**7d**

$^{13}\text{C-NMR}$ , 100MHz,  $\text{CDCl}_3$

