

## Supporting Information

### High-throughput C-H Activation in a Bead-Beater Homogenizer: Fast and Regioselective Access to 2-Arylindoles

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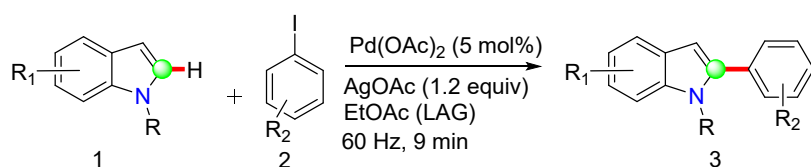
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## Experimental section

### General experimental details

The fine chemicals were obtained from Sigma-Aldrich, TCI India, or BLD pharma and used directly without further purification. Common reagents and solvents of AR grade were obtained from local suppliers. The mechanochemical reactions were carried out in 2 mL homogenizing tubes made of polypropylene with 1 g of 2 mm SS ball in iGene Labserve, an indigenous bead beater homogenizer. The reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel aluminum plates (60F-254) using UV light (254 or 365 nm) to monitor the progress of the reactions. The melting point was measured in the EZ-Melt, Automatic Melting Point Apparatus (Stanford Research System).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance (500 MHz) NMR instrument with  $\text{CDCl}_3$  as the solvent. Tetramethylsilane (TMS) was used as an internal standard for NMR spectroscopy. Chemical shifts are reported in parts per million ( $\delta$ ) units. Coupling constants are reported in hertz (Hz). Standard abbreviations are used for representing the multiplicity of NMR peaks, such as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), and m (multiplet). HRMS spectra were recorded on Agilent Technologies 6545 Q-TOF LC/MS mass spectrometer with ESI as the ion source.

*General procedure for C-2 arylation of indole derivatives in a homogenizer (3):*

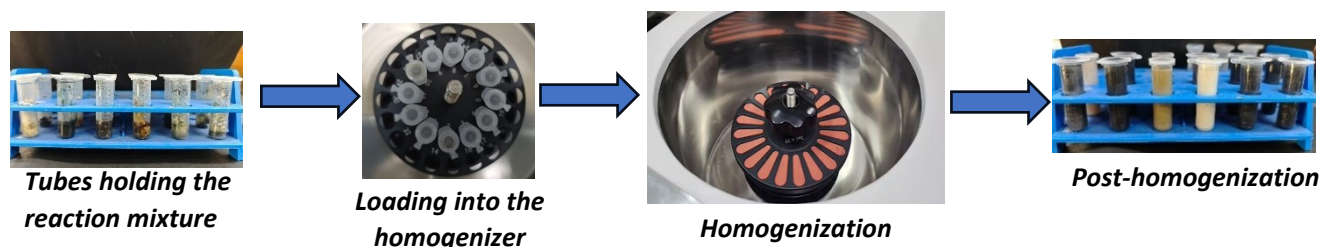


The starting *N*-alkylindoles (**1**) were either procured or prepared using the reported protocol.<sup>1</sup>

In a typical reaction, indole derivative, **1** (0.5 mmol), iodoarene **2** (0.55 mmol),  $\text{Pd}(\text{OAc})_2$  (0.025 mmol, 5 mol%),  $\text{AgOAc}$  (0.6 mmol) were taken in a 2 mL polypropylene Eppendorf tube containing  $\text{EtOAc}$  (0.2 mL) and 1 g SS balls of 2 mm dia. The capped tube was placed in the iGene bead beater homogenizer, closed by a rotor head, and homogenized at a frequency of 60 Hz for  $3 \times 3$  min with a pause of 1 min after each pulse. The progress of the reaction was monitored by TLC. The product was taken out by the addition of a small volume of  $\text{EtOAc}$  (approx 0.5 mL) to the tube, the balls were rinsed with  $\text{EtOAc}$  (0.5 mL) and the combined organic extract was adsorbed in minimum amount of silica gel (230-400 mesh),

subjected to column chromatography and eluted with EtOAc-petroleum ether to afford the corresponding pure compound (**3**).

## 2. Reaction set-up for high throughput C-H activation



**Figure. S1.** A typical reaction set-up for high-throughput C2-H activation of indoles. 12 reactions were set at a time.

## 3. E-factor and Eco-scale score of the model reaction

**Table S1.** E-factor calculation of our model reaction.

| Parameters                                                  | Value<br>s | Remarks                  |
|-------------------------------------------------------------|------------|--------------------------|
| %Yield                                                      | 81         | Calculated for <b>3a</b> |
| Wt. of generated waste (mg)                                 | 378.5      |                          |
| Wt. of end product (mg)                                     | 84         |                          |
| <b>E-factor = Wt. of generated waste/Wt. of end product</b> |            | <b>4.5</b>               |

**Table S2:** Eco-scale score calculation for our model reaction

| Parameters                  | Penalty points | Remarks                        |
|-----------------------------|----------------|--------------------------------|
| %Yield = (100-%Yield)/2     | 9.5            | Calculated for <b>3a</b>       |
| Price of reaction component | 0              | Inexpensive                    |
| Toxic chemical              | 5              |                                |
| Safety                      | 0              | Nontoxic chemicals             |
| Technical setup             | 2              | <b>Bead beater homogenizer</b> |
| Temperature/Time            | 0              | , 9 mins                       |
| Workup and purification     | 10             | Classical chromatography       |

**Sum of penalty points** **26.5**

**Eco-scale score = 73.5**

Notably, for many entries with yields  $\geq 85\%$  (e.g., **3h**), the Eco-score scale would be in the “excellent” category [ $>75$ ].

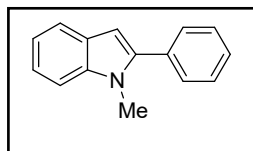
#### 4. Comparative table of ligand free C-2 arylation of indole (Table S3)

**Table S3.** Comparative table of selected ligand free Pd(II)-catalyzed C-2 arylation of indole.

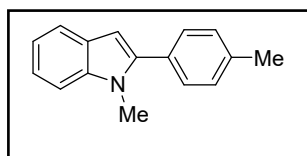
| Sr. No.                                                | Media/Method                         | Solvent                | Substrate Scope    | Temp. (°C) | Time (h) | Yield (%) | E. Factor | Ref. No. |
|--------------------------------------------------------|--------------------------------------|------------------------|--------------------|------------|----------|-----------|-----------|----------|
| Conventional homogeneous catalysis (selected examples) |                                      |                        |                    |            |          |           |           |          |
| 1                                                      | Organic media                        | AcOH                   | R = H, EDG         | rt         | 15-24    | 29-90     | 63.0      | 2        |
| 2                                                      | Organic media                        | DMF                    | R = H, EDG         | rt         | 15       | 58-99     | 13.9      | 3        |
| 3                                                      | Organic media                        | DMA                    | R = H              | 125        | 24-48    | 23-75     | 75.6      | 4        |
| 4                                                      | Organic media                        | DMSO                   | R = H              | 70         | 20       | 39-87     | 48.0      | 5        |
| 5                                                      | Organic media                        | EtOAc/<br>Me-THF       | R = EDG            | rt         | 0.5-16   | 40-92     | 25.2      | 6        |
| 6                                                      | Organic media                        | DCE                    | R = H, EDG,<br>EWG | 80         | 24       | 43-96     | 24.2      | 7        |
| Heterogenous catalysis (selected examples)             |                                      |                        |                    |            |          |           |           |          |
| 7                                                      | Organic phase (MOF)                  | GLV                    | R = H, EDG,<br>EWG | 80         | 5        | 47-92     | 7.4       | 8        |
| 8                                                      | Aqueous (mesoporous silica)          | H <sub>2</sub> O       | R = H, EDG         | 60         | 12       | 29-98     | 63.8      | 9        |
| 9                                                      | Aqueous (organometallic nano-vessel) | H <sub>2</sub> O       | R = H, EDG,<br>EWG | 50         | 12       | 80-93     | 19.8      | 10       |
| Green methods (selected examples)                      |                                      |                        |                    |            |          |           |           |          |
| 10                                                     | Micellar media                       | H <sub>2</sub> O/EtOH  | R = H              | 80         | 24       | 9-87      | 12.9      | 11       |
| 11                                                     | Micellar media                       | H <sub>2</sub> O       | R = H, EDG         | 25         | 1        | 52-90     | 14.4      | 12       |
| 12                                                     | Microwave                            | DMF/CH <sub>3</sub> CN | R = H              | 100        | 4        | 41-83     | 34.7      | 13       |
| 13                                                     | “On-water”                           | H <sub>2</sub> O       | R = H, EDG         | 30         | 16       | 13-99     | 14.0      | 14       |
| 14                                                     | Mechanochemical                      | PEG-400                | R = H, EDG,<br>EWG | ambient    | 1-4      | 75-99     | 3.9       | 1        |

|    |             |       |                    |         |            |       |                 |
|----|-------------|-------|--------------------|---------|------------|-------|-----------------|
| 15 | Homogenizer | EtOAc | R = H, EDG,<br>EWG | ambient | 6-9<br>min | 80-90 | current<br>work |
|----|-------------|-------|--------------------|---------|------------|-------|-----------------|

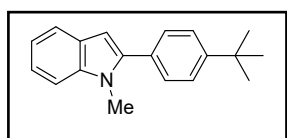
## 5. Spectral characterization



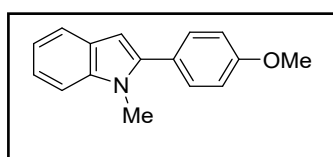
**1-Methyl-2-phenyl-1H-indole (3a):**<sup>1</sup> White solid, 84 mg (81%), m.p. 95-97 °C (lit. m.p. 99-102 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.63 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.39-7.33 (m, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 6.7 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.56 (s, 1H), 3.74 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 141.6, 138.4, 132.9, 129.4, 128.5, 128.0, 127.9, 121.7, 120.5, 119.9, 109.7, 101.7, 31.2; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>N 208.1120; Found 208.1099.



**1-Methyl-2-*p*-tolyl-1H-indole (3b):**<sup>1</sup> White solid, 90 mg (81%), m.p. 95-97 °C (lit. m.p. 96-98 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.62 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.28-7.21 (m, 3H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 3.72 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 141.7, 138.3, 137.8, 129.9, 129.3, 129.2, 128.0, 121.5, 120.4, 119.8, 109.6, 101.3, 31.1, 21.3; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>N 222.1278; Found 222.1270.

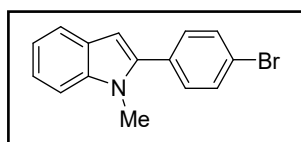


**2-(4-*tert*-Butylphenyl)-1-methyl-1H-indole (3c):**<sup>1</sup> White solid, 116 mg (88%), m.p. 55-58 °C (lit. m.p. 55-60 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.63 (d, *J* = 8.0 Hz, 1H), 7.50-7.44 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.55 (s, 1H), 3.75 (s, 3H), 1.38 (s, 9H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 150.9, 141.7, 138.3, 129.9, 129.1, 128.0, 125.4, 121.5, 120.4, 119.8, 109.6, 101.4, 34.7, 31.2; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>21</sub>N 264.1747; Found 264.1736.

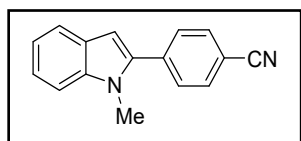


**2-(4-Methoxyphenyl)-1-methyl-1H-indole (3d):**<sup>1</sup> Off-white solid, 89 mg (75%), m.p. 115-117 °C (lit. m.p. 117-120 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.67 (d, *J* = 8.8 Hz, 1H), 7.47

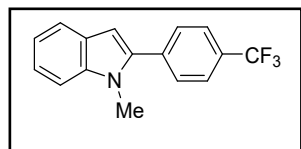
(dt,  $J_1 = 3.0$  Hz,  $J_2 = 11$  Hz, 2H), 7.40 (d,  $J = 8.5$  Hz, 1H), 7.23 (td,  $J_1 = 1.2$  Hz,  $J_2 = 7.2$  Hz, 1H), 7.13 (td,  $J_1 = 0.8$  Hz,  $J_2 = 8.0$  Hz, 1H), 7.27 (dt,  $J_1 = 2.8$  Hz,  $J_2 = 6.8$  Hz, 2H), 6.50 (s, 1H), 3.86 (s, 3H), 3.71 (s, 3H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 159.5, 141.5, 138.2, 130.7, 128.0, 125.3, 121.4, 120.3, 119.8, 114.0, 109.6, 101.0, 55.4, 31.1; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{15}\text{NO}$  238.1226; Found 238.1220.



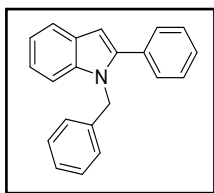
**2-(4-Bromophenyl)-1-methyl-1H-indole (3f):**<sup>1</sup> White solid, 114 mg (80%), m.p. 99-101 °C (lit. m.p. 99-102 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.63 (d,  $J = 7.6$  Hz, 1H), 7.59 (dt,  $J_1 = 2.4$  Hz,  $J_2 = 6.4$  Hz, 2H), 7.38-7.34 (m, 3H), 7.26 (td,  $J_1 = 1.2$  Hz,  $J_2 = 6.8$  Hz, 1H), 7.15 (td,  $J_1 = 1.2$  Hz,  $J_2 = 7.2$  Hz, 1H), 6.56 (d,  $J = 0.8$  Hz, 1H), 3.73 (s, 3H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 140.3, 138.5, 131.7, 130.8, 127.9, 122.2, 122.0, 120.6, 120.1, 109.7, 102.0, 31.2; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{12}\text{BrN}$  286.0226 (for  $^{79}\text{Br}$ ) and 288.0207 (for  $^{81}\text{Br}$ ); Found 286.0233 (for  $^{79}\text{Br}$ ) and 288.0212 (for  $^{81}\text{Br}$ ).



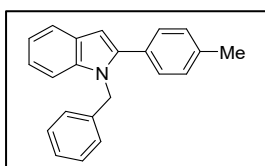
**4-(1-Methyl-1H-indol-2-yl)benzonitrile (3f):**<sup>1</sup> Light brown solid, 99 mg (85%), m.p. 157-158 °C (lit. m.p. 161-162 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.77 (d,  $J_1 = 5$  Hz, 2H), 7.70 (d,  $J_1 = 5$  Hz, 1H), 7.64 (d,  $J_1 = 5$  Hz, 2H), 7.43 (d,  $J_1 = 10$  Hz, 1H), 7.35 (t,  $J_1 = 10$  Hz, 1H), 7.23 (t,  $J_1 = 10$  Hz, 1H), 6.70 (s, 3H), 3.80 (s, 3H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 139.3, 139.1, 137.6, 132.3, 129.5, 127.8, 122.8, 121.0, 120.4, 118.6, 111.2, 109.9, 103.6, 31.5; IR (KBr):  $\tilde{\nu}$  3070, 2939, 2221, 1928, 1602, 1465, 844, 796, 754  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2$  233.1073; Found 233.1062.



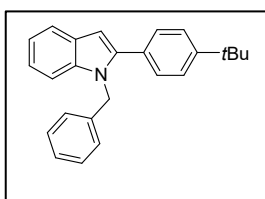
**1-Methyl-2-(4-(trifluoromethyl)phenyl)-1H-indole (3g):**<sup>1</sup> White solid, 113 mg (82%), m.p. 65-67 °C (lit. m.p. 65-68 °C);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.76 (d,  $J = 8.4$  Hz, 2H), 7.68 (t,  $J = 8.8$  Hz, 3H), 7.43 (d,  $J = 8.4$  Hz, 1H), 7.33 (t,  $J = 6.8$  Hz, 1H), 7.21 (t,  $J = 7.2$  Hz, 1H), 6.67 (s, 1H), 3.80 (s, 3H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 139.9, 138.8, 136.4, 129.8 (q,  $^2J_{\text{C-F}} = 32.4$  Hz), 129.4, 128.2, 127.8, 125.5 (q,  $^3J_{\text{C-F}} = 3.8$  Hz), 123.9 (q,  $^1J_{\text{C-F}} = 272.0$  Hz), 122.4, 120.8, 120.2, 109.8, 102.9, 31.3; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}$  276.0995; Found 276.0985.



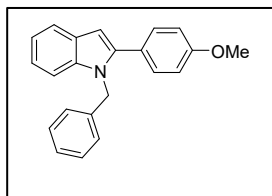
**1-Benzyl-2-phenyl-1H-indole (3h):**<sup>1</sup> Off white solid, 127 mg (90%), m.p. 36-38 °C (lit. m.p. 35-40 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.68-7.65 (m, 1H), 7.43-7.40 (m, 2H), 7.38-7.33 (m, 3H), 7.27-7.21 (m, 3H), 7.17-7.12 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.64 (s, 1H), 5.35 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 141.8, 138.2, 138.0, 132.7, 129.2, 128.8, 128.6, 128.3, 128.0, 127.2, 126.0, 122.0, 120.6, 120.2, 110.6, 102.3, 47.7; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>17</sub>N 284.1434; Found 284.1442.



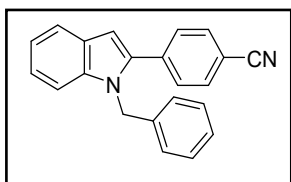
**1-Benzyl-2-*p*-tolyl-1H-indole (3i):**<sup>1</sup> White solid, 134 mg (89%), m.p. 79-82 °C (lit. m.p. 79-92 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.67-7.63 (m, 1H), 7.33-7.31 (m, 2H), 7.28-7.21 (m, 3H), 7.18-7.11 (m, 5H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.62 (s, 1H), 5.35 (s, 2H), 2.37 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 141.9, 138.3, 137.98, 137.94, 129.8, 129.3, 129.1, 128.7, 128.4, 127.1, 126.0, 121.7, 120.4, 120.1, 110.5, 102.0, 47.7, 21.2; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>N 298.1591; Found 298.1602.



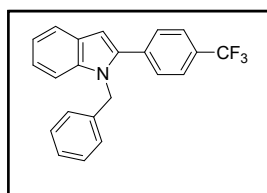
**1-Benzyl-2-(4-*tert*-butylphenyl)-1H-indole (3j):**<sup>1</sup> White solid, 150 mg (88%), m.p. 120-122 °C (lit. m.p. 120-125 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.66-7.64 (m, 1H), 7.40-7.36 (m, 4H), 7.28-7.22 (m, 3H), 7.15-7.11 (m, 3H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.63 (s, 1H), 5.37 (s, 2H), 1.33 (s, 9H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 151.1, 141.9, 138.3, 137.9, 129.7, 128.8, 128.7, 128.4, 127.1, 126.0, 125.5, 121.7, 120.4, 120.1, 110.5, 102.0, 47.8, 34.7, 31.3; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>25</sub>N 340.2040; Found 340.2028.



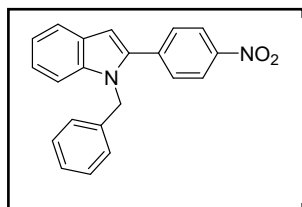
**1-Benzyl-2-(4-methoxyphenyl)-1H-indole (3k):**<sup>1</sup> White solid, 141 mg (90%), m.p. 98-100 °C (lit. m.p. 99-100 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.71-7.69 (m, 1H), 7.41-7.37 (m, 2H), 7.34-7.27 (m, 3H), 7.22-7.16 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.95 (dt, *J*<sub>1</sub> = 3.7 Hz, *J*<sub>2</sub> = 11.5 Hz, 2H), 6.64 (s, 1H), 5.39 (s, 2H), 3.87 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 159.6, 141.7, 138.3, 137.8, 130.5, 128.8, 127.6, 127.2, 126.0, 125.1, 121.7, 120.4, 120.1, 114.0, 110.5, 101.7, 55.4, 47.7; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>NO 314.1539; Found 314.1550.



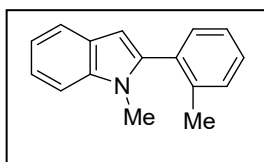
**4-(1-Benzyl-1*H*-indol-2-yl)benzonitrile (3l):**<sup>1</sup> Light brown solid, 101 mg (87%), m.p. 159-161 °C (lit. m.p. 161-162 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.74-7.71 (m, 1H), 7.69-7.66 (m, 2H), 7.57-7.54 (m, 2H), 7.35-7.29 (m, 3H), 7.25-7.19 (m, 3H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.78 (s, 1H), 5.46 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 139.5, 138.8, 137.6, 137.2, 132.3, 129.3, 128.9, 128.0, 127.5, 125.8, 123.0, 121.1, 120.7, 118.7, 111.3, 110.7, 104.2, 47.9; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub> 309.1387; Found 309.1383.



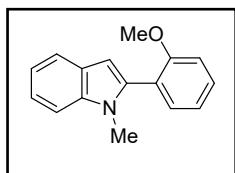
**1-Benzyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (3m):**<sup>1</sup> White solid, 158 mg (90%), m.p. 62-64 °C (lit. m.p. 62-65 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.69 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.29-7.23 (m, 3H), 7.20-7.16 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.72 (s, 1H), 5.36 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 140.1, 138.4, 137.8, 136.2, 129.9 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32.6 Hz), 129.3, 128.9, 128.1, 127.4, 125.8, 125.5 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.7 Hz), 124.1 (q, <sup>1</sup>*J*<sub>C-F</sub> = 270.0 Hz), 122.6, 120.9, 120.5, 110.6, 103.5, 47.8; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>16</sub>F<sub>3</sub>N 352.1308; Found 352.1298.



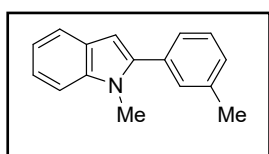
**1-Benzyl-2-(4-nitrophenyl)-1*H*-indole (3n):** White solid, 138 mg (89%), m.p. 155-158 °C (lit. m.p. 155-156 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.25 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.35-7.22 (m, 6H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.83 (s, 1H), 5.42 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 147.1, 139.1, 139.0, 137.5, 129.4, 129.0, 128.0, 127.5, 125.7, 124.1, 123.9, 123.2, 121.1, 120.8, 110.7, 104.7, 48.0; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> 329.1285; Found 309.1292.



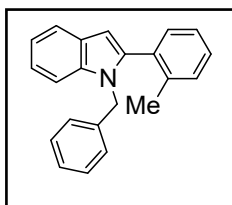
**1-Methyl-2-*o*-tolyl-1*H*-indole (3o):**<sup>1</sup> White solid, 90 mg (81%), m.p. 88-90 °C (lit. m.p. 90-92 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.69 (d, *J* = 7.8 Hz, 1H), 7.41-7.29 (m, 6H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.49 (s, 1H), 3.56 (s, 3H), 2.26 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 140.5, 138.1, 137.3, 132.5, 131.1, 130.1, 128.6, 128.0, 125.5, 121.3, 120.4, 119.6, 109.4, 101.5, 30.3, 20.0; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>N 222.1277; Found 222.1283.



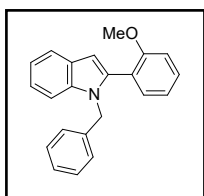
**2-(2-Methoxyphenyl)-1-methyl-1H-indole (3p):**<sup>1</sup> Pale yellow solid, 96 mg (81%), m.p. 74-75 °C (lit. m.p. 75-77 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.64 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.51 (s, 1H), 3.79 (s, 3H), 3.58 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 157.5, 138.6, 137.7, 132.6, 130.1, 128.0, 122.0, 121.3, 120.7, 120.5, 119.4, 110.9, 109.4, 101.7, 55.5, 30.8; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>NO 238.1226; Found 238.1214.



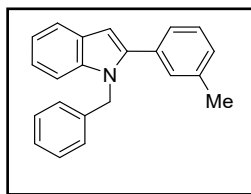
**1-Methyl-2-*m*-tolyl-1H-indole (3q):**<sup>1</sup> White solid, 88 mg (80%), m.p. 35-36 °C (lit. m.p. 35-37 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.68 (d, *J* = 7.9 Hz, 1H), 7.42-7.35 (m, 4H), 7.31-7.26 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 3.80 (s, 3H), 2.49 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 141.7, 138.3, 138.2, 132.8, 130.1, 128.6, 128.3, 128.0, 126.5, 121.6, 120.4, 119.8, 109.6, 101.5, 31.2, 21.5; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>N 222.1277; Found 222.1272.



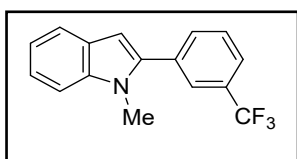
**1-Benzyl-2-*o*-tolyl-1H-indole (3r):**<sup>1</sup> Colourless thick oil, 134 mg (90%), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.75 (d, *J* = 7.8, 1H), 7.38-7.30 (m, 4H), 7.26-7.19 (m, 6H), 6.95 (d, *J* = 7.2, 2H), 6.59 (s, 1H), 5.22 (s, 2H), 2.21 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 140.3, 138.2, 137.9, 136.9, 132.3, 131.1, 130.2, 128.8, 128.5, 128.4, 127.1, 126.4, 125.5, 121.5, 120.5, 119.9, 110.5, 102.5, 47.3, 20.1; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>N 298.1591; Found 298.1599.



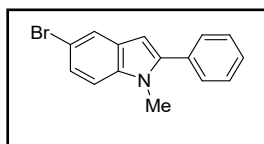
**1-Benzyl-2-(2-methoxyphenyl)-1H-indole (3s):**<sup>1</sup> Colourless thick oil, 140 mg (90%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.70 (d, *J* = 7.2, 1H), 7.44-7.37 (m, 2H), 7.24-7.15 (m, 6H), 7.05-6.97 (m, 4H), 6.62 (s, 1H), 5.23 (s, 2H), 3.65 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 157.5, 138.6, 138.3, 137.2, 132.8, 130.1, 128.43, 128.36, 126.8, 126.4, 121.8, 121.4, 120.7, 120.5, 119.6, 110.7, 110.5, 102.6, 55.1, 47.9; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>NO 314.1539; Found 314.1528.



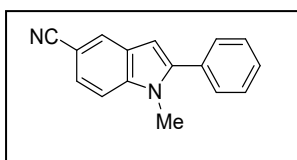
**1-Benzyl-2-*m*-tolyl-1*H*-indole (3t):**<sup>1</sup> White solid, 126 mg (85%), m.p. 75-76 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.75 (d, *J* = 7.2, 1H), 7.38-7.18 (m, 10H), 7.10 (d, *J* = 7.2, 2H), 6.71 (s, 1H), 5.43 (s, 2H), 2.41 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 142.0, 138.4, 138.2, 138.0, 132.6, 130.1, 128.9, 128.8, 128.45, 128.40, 127.1, 126.2, 126.0, 121.8, 120.5, 120.1, 110.5, 102.2, 47.8, 21.4; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>N 298.1591; Found 298.1604.



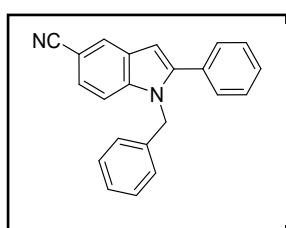
**1-Methyl-2-(3-(trifluoromethyl)phenyl)-1*H*-indole (3u):**<sup>1</sup> Pale yellow solid, 110 mg (80%), m.p. 55-57 °C (lit. m.p. 55-57 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.82 (s, 1H), 7.74-7.68 (m, 3H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 3.79 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 139.8, 138.6, 133.7, 132.5 (q, <sup>4</sup>*J*<sub>C-F</sub> = 1.2 Hz), 131.2 (q, <sup>2</sup>*J*<sub>C-F</sub> = 32 Hz), 129.1, 127.8, 126.0 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.7 Hz), 124.51 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.7 Hz), 124.49 (q, <sup>1</sup>*J*<sub>C-F</sub> = 273.0 Hz), 122.3, 120.7, 120.2, 109.7, 102.6, 31.3; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>12</sub>F<sub>3</sub>N 276.0995; Found 276.0968.



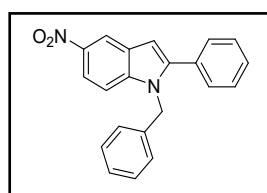
**5-Bromo-1-methyl-2-phenyl-1*H*-indole (3v):**<sup>1</sup> White solid, 102 mg (72%), m.p. 108-110 °C (lit. m.p. 108-110 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.79 (s, 1H), 7.53-7.45 (m, 5H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 8.7 Hz, 1H), 6.54 (s, 1H), 3.75 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 142.7, 137.0, 132.3, 129.6, 129.4, 128.6, 128.2, 124.4, 122.9, 113.1, 111.1, 101.1, 31.3; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>12</sub>BrN 286.0226 (for <sup>79</sup>Br) and 288.0207 (for <sup>81</sup>Br); Found 286.022 (for <sup>79</sup>Br) and 288.0201 (for <sup>81</sup>Br).



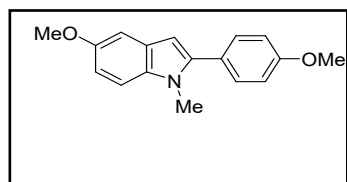
**1-Methyl-2-phenyl-1*H*-indole-5-carbonitrile (3w):**<sup>1</sup> White solid, 102 mg (87%), m.p. 165-166 °C (lit. m.p. 166-170 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.99 (s, 1H), 7.53-7.48 (m, 6H), 7.42 (d, *J* = 8.5 Hz, 1H), 6.64 (s, 1H), 3.79 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 143.9, 139.7, 131.6, 129.4, 128.74, 128.67, 127.7, 125.9, 124.5, 120.8, 110.4, 102.8, 102.3, 31.4; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>, 233.1073; found, 233.1067.



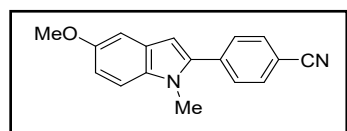
**1-Benzyl-2-phenyl-1H-indole-5-carbonitrile (3x):**<sup>15</sup> White solid, 120 mg (78%), m.p. 86-88 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.03 (s, 1H), 7.45 (bs, 5H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.34-7.29 (m, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.74 (s, 1H), 5.42 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 144.2, 139.3, 137.1, 131.5, 129.3, 129.0, 128.87, 128.82, 128.0, 127.6, 126.0, 125.8, 124.8, 120.7, 111.4, 103.2, 102.9, 47.9; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub> 309.1395; Found 309.1399.



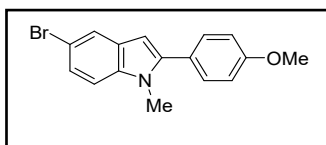
**1-Benzyl-5-nitro-2-phenyl-1H-indole (3y):**<sup>16</sup> Off white solid, 126 mg (77%), m.p. 55-58 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.64 (s, 1H), 8.07 (dd, *J*<sub>1</sub> = 2.4 Hz, *J*<sub>2</sub> = 9.0 Hz, 1H), 7.45 (bs, 5H), 7.36-7.28 (m, 3H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.82 (s, 1H), 5.43 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 145.0, 142.1, 140.6, 136.9, 131.4, 129.2, 129.0, 128.9, 128.8, 127.7, 127.5, 125.8, 117.6, 117.5, 110.4, 104.3, 48.1; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> 329.1285; Found 329.1287.



**5-Methoxy-2-(4-methoxyphenyl)-1-methyl-1H-indole (3z):**<sup>1</sup> Yellowish solid, 114 mg (85%), m.p. 76-78 °C (lit. m.p. 78-80 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.46 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.14 (s, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 6.4 Hz, 1H), 6.47 (s, 1H), 3.91 (s, 6H), 3.73 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 159.4, 154.3, 142.0, 133.6, 130.5, 128.3, 125.4, 114.0, 111.5, 110.2, 102.1, 100.7, 55.9, 55.3, 31.2; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub> 268.1332; Found 268.1324.



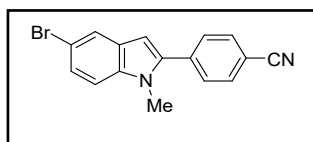
**4-(5-Methoxy-1-methyl-1H-indol-2-yl)benzonitrile (3aa):**<sup>1</sup> Light pink solid, 107 mg (82%), m.p. 120-121 °C (lit. m.p. 118-120 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.76 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.13 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.60 (s, 1H), 3.90 (s, 3H), 3.76 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 154.6, 139.8, 137.3, 134.5, 132.3, 129.4, 128.0, 118.8, 113.2, 111.0, 110.7, 103.1, 102.3, 55.9, 31.6; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O 263.1179; Found 263.1175.



**5-Bromo-2-(4-methoxyphenyl)-1-methyl-1H-indole (3ab):<sup>1</sup>**

Yellow solid, 123 mg (78%), m.p. 98-99 °C (lit. m.p. 98-100 °C);

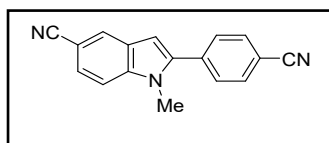
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.75 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.46 (s, 1H), 3.90 (s, 3H), 3.72 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 159.7, 142.6, 136.8, 130.6, 129.6, 124.6, 124.1, 122.6, 114.0, 112.9, 110.9, 100.5, 55.4, 31.2; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>BrNO 316.0332 (for <sup>79</sup>Br) and 318.0312 (for <sup>81</sup>Br); Found 316.0326 (for <sup>79</sup>Br) and 318.0307 (for <sup>81</sup>Br).



**4-(5-Bromo-1-methyl-1H-indol-2-yl)benzonitrile (3ac):<sup>1</sup>**

White solid, 117 mg (75%), m.p. 158-160 °C (lit. m.p. 158-160 °C); <sup>1</sup>H

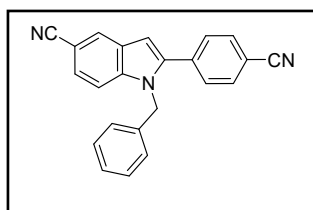
NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.81-7.76 (m, 3H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 1H), 6.60 (s, 1H), 3.76 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 140.4, 137.6, 136.7, 132.4, 129.6, 129.3, 125.5, 123.3, 118.6, 113.5, 111.6, 111.3, 102.8, 31.6; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>11</sub>BrN<sub>2</sub> 311.0179 (for <sup>79</sup>Br) and 313.0158 (for <sup>81</sup>Br); Found 311.0174 (for <sup>79</sup>Br) and 313.0156 (for <sup>81</sup>Br).



**2-(4-Cyanophenyl)-1-methyl-1H-indole-5-carbonitrile (3ad):<sup>1</sup>**

White solid, 92 mg (71%), m.p. 202-204 °C (lit. m.p. 206-211 °C);

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.01 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 6.73 (s, 1H), 3.82 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 141.5, 140.2, 136.1, 132.5, 129.7, 127.4, 126.4, 125.4, 120.5, 118.4, 112.2, 110.7, 103.9, 103.5, 31.7; HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>11</sub>N<sub>3</sub> 258.1026; Found 258.1023.

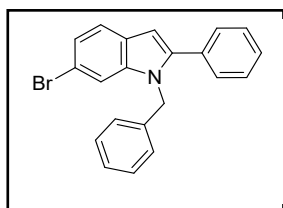


**1-Benzyl-2-(4-cyanophenyl)-1H-indole-5-carbonitrile (3ae):**

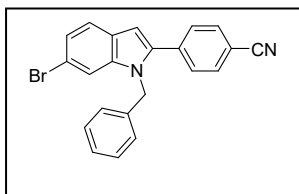
White solid, 127 mg (76%), m.p. 156-159 °C (lit. m.p. 155-156 °C);

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.05 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.44 (dd, *J*<sub>1</sub> = 1.6 Hz, *J*<sub>2</sub> = 8.5 Hz, 1H), 7.33-7.29 (m, 4H), 6.98 (d, *J* = 6.1 Hz, 2H), 6.82 (s, 1H), 5.42 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 141.8, 139.9, 136.5, 136.0, 132.5, 129.6,

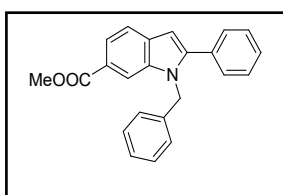
129.2, 127.9, 127.7, 126.5, 125.7, 125.6, 120.3, 118.3, 112.4, 111.5, 104.5, 103.9, 48.1; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{23}H_{15}N_3$  334.1339; Found 334.1345.



**1-Benzyl-6-bromo-2-phenyl-1H-indole (3af):** White solid, 126 mg (70%), m.p. 108-110 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.67 (d,  $J = 8.2$ , 2H), 7.57 (d,  $J = 8.4$ , 1H), 7.52 (d,  $J = 8.2$ , 2H), 7.40 (s, 1H), 7.35-7.27 (m, 4H), 7.00 (d,  $J = 7.4$  Hz, 2H), 6.73 (s, 1H), 5.34 (s, 2H);  $^{13}C$   $\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 142.5, 138.8, 137.6, 132.1, 129.1, 128.9, 128.6, 128.3, 127.4, 127.1, 125.8, 123.4, 121.7, 115.3, 113.4, 102.4, 47.7; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{21}H_{16}BrN$  362.0539 (for  $^{79}Br$ ) and 364.0519 (for  $^{81}Br$ ); Found 362.0559 (for  $^{79}Br$ ) and 364.0512 (for  $^{81}Br$ ).



**4-(1-Benzyl-6-bromo-1H-indol-2-yl)benzonitrile (3ag):** White solid, 140 mg (72%), m.p. 158-160 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 7.68 (d,  $J = 8.0$  Hz, 2H), 7.57 (d,  $J = 8.4$  Hz, 1H), 7.52 (d,  $J = 8.2$  Hz, 2H), 7.40 (s, 1H), 7.35-7.27 (m, 4H), 7.00 (d,  $J = 7.4$  Hz, 2H), 6.73 (s, 1H), 5.34 (s, 2H);  $^{13}C$   $\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 140.1, 139.5, 137.0, 136.6, 132.4, 129.3, 129.1, 127.7, 126.8, 125.6, 124.0, 122.2, 118.5, 116.5, 113.5, 111.7, 104.2, 47.9; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{22}H_{15}BrN_2$  387.0492 (for  $^{79}Br$ ) and 389.0471 (for  $^{81}Br$ ); Found 387.0478 (for  $^{79}Br$ ) and 389.0486 (for  $^{81}Br$ ).



**1-Benzyl-2-phenyl-1H-indole-6-carboxylate (3ah):** White solid, 126 mg (74%), m.p. 95-97 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.01 (s, 1H), 7.87 (d,  $J = 8.2$  Hz, 1H), 7.70 (d,  $J = 8.2$  Hz, 1H), 7.47-7.40 (m, 5H), 7.31-7.24 (m, 3H), 7.00 (d,  $J = 7.6$  Hz, 2H), 6.71 (s, 1H), 5.46 (s, 2H), 3.91 (s, 3H);  $^{13}C$   $\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 168.1, 145.0, 137.7, 137.3, 132.0, 131.9, 129.2, 128.8, 128.6, 127.3, 125.9, 123.4, 121.3, 120.0, 112.7, 102.7, 51.9, 47.7; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{23}H_{19}NO_2$  342.1489; Found 342.1475.

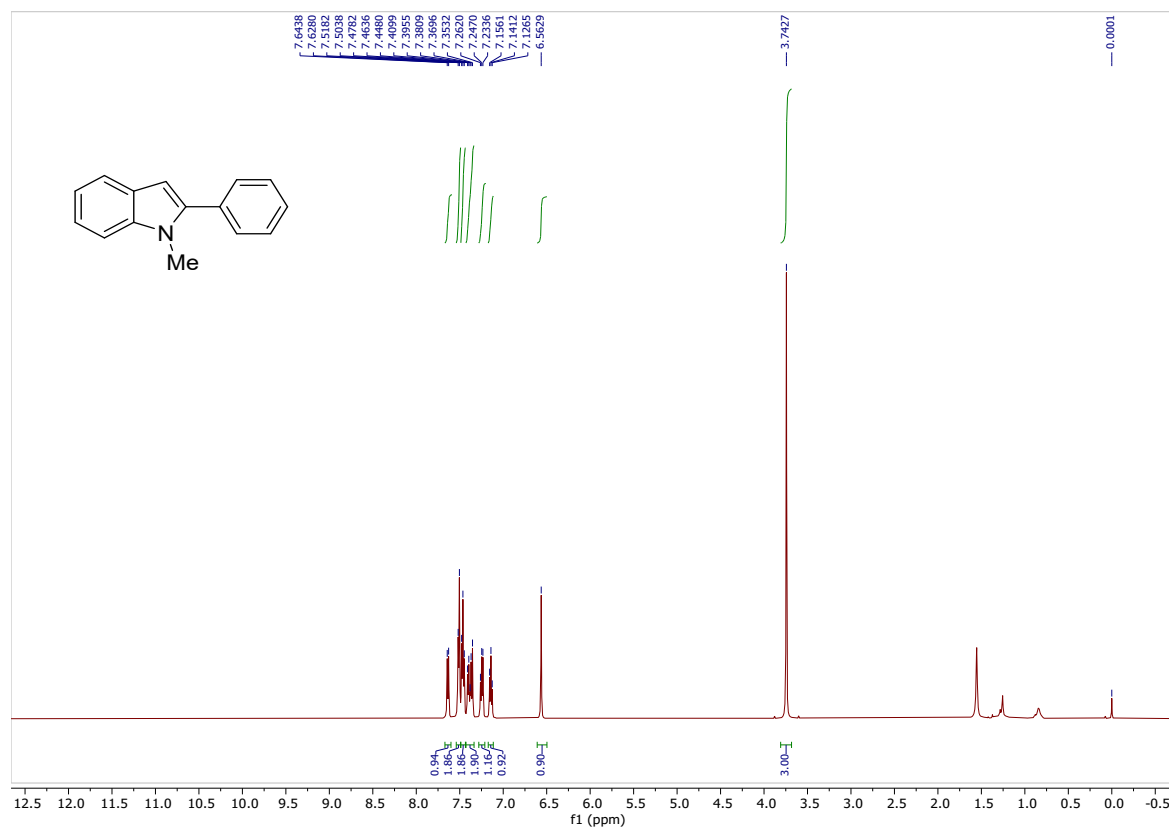
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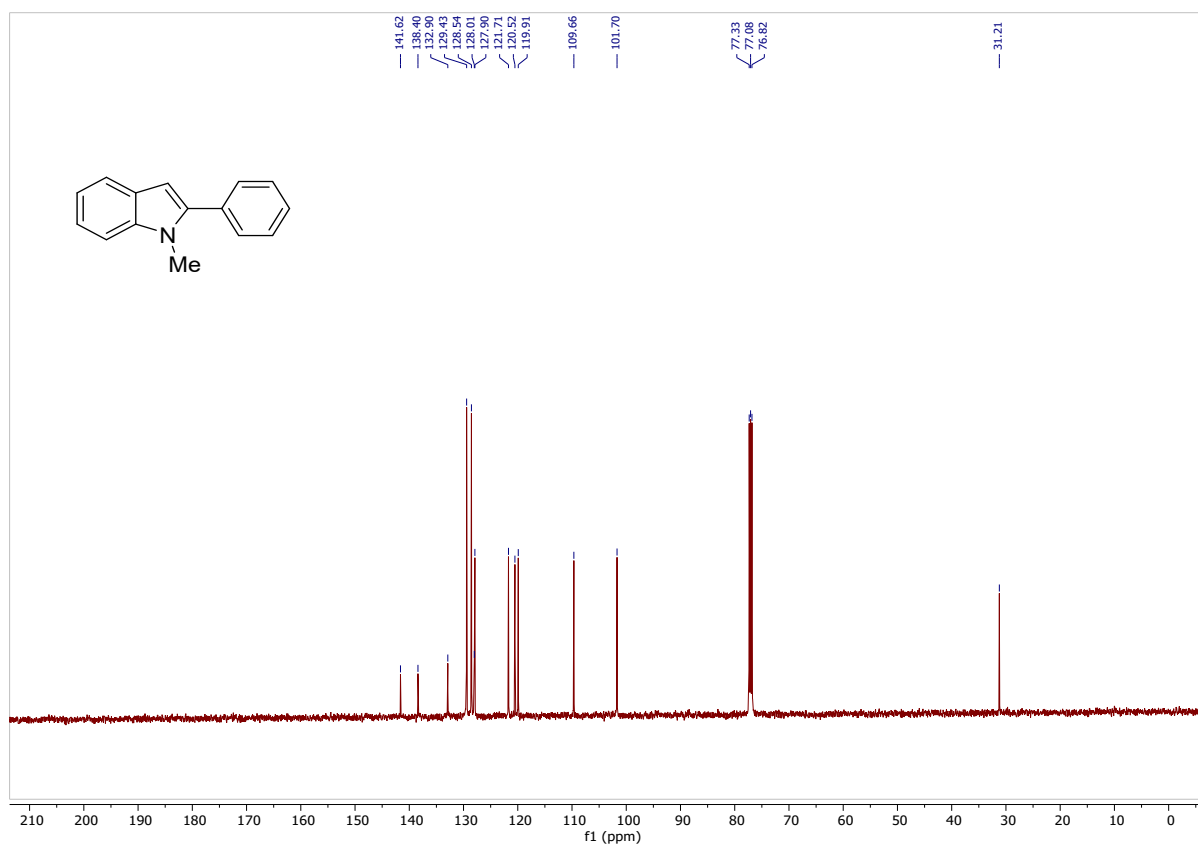
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## 7. Copies of $^1\text{H}$ & $^{13}\text{C}$ NMR of 2-arylindole derivatives

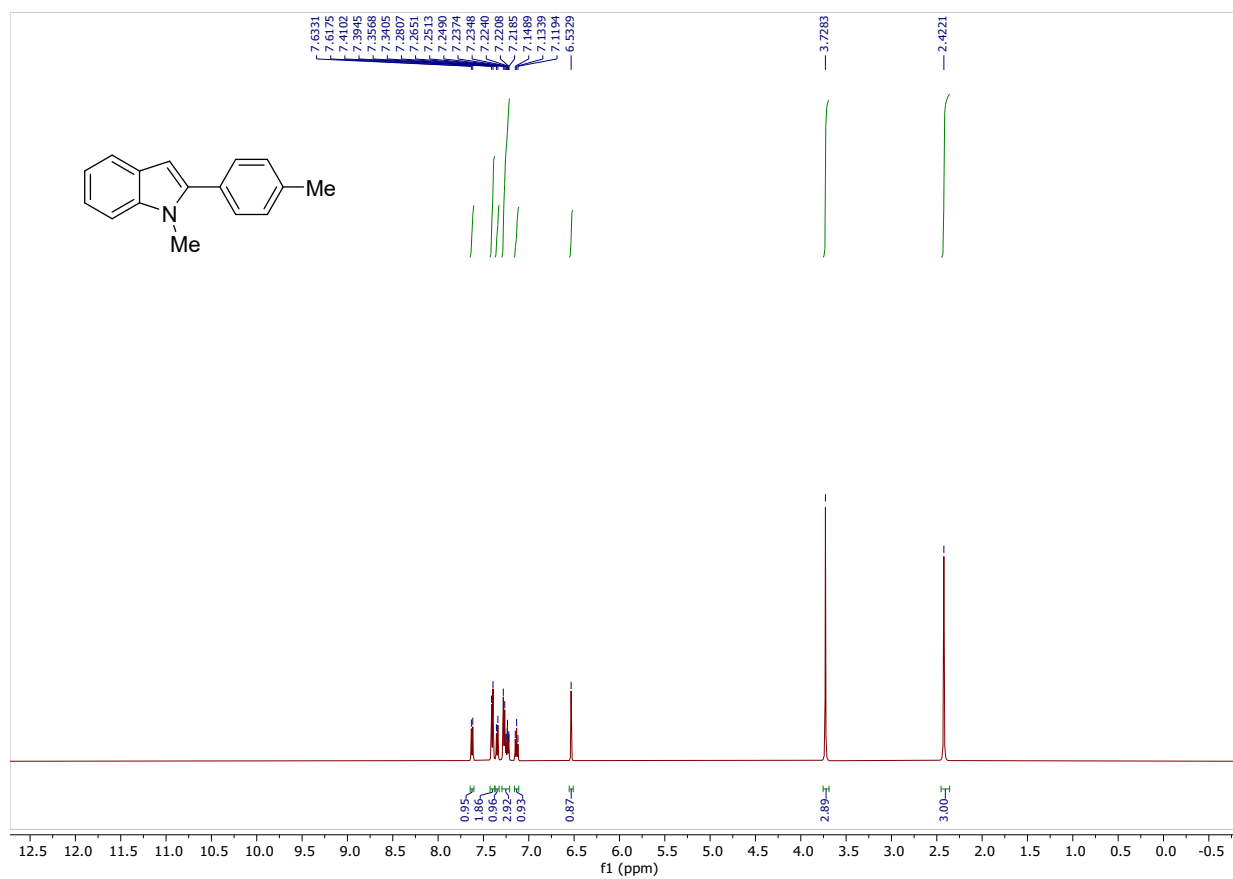
$^1\text{H}$  NMR spectrum of compound **3a**, ( $\text{CDCl}_3$ , 500 MHz).



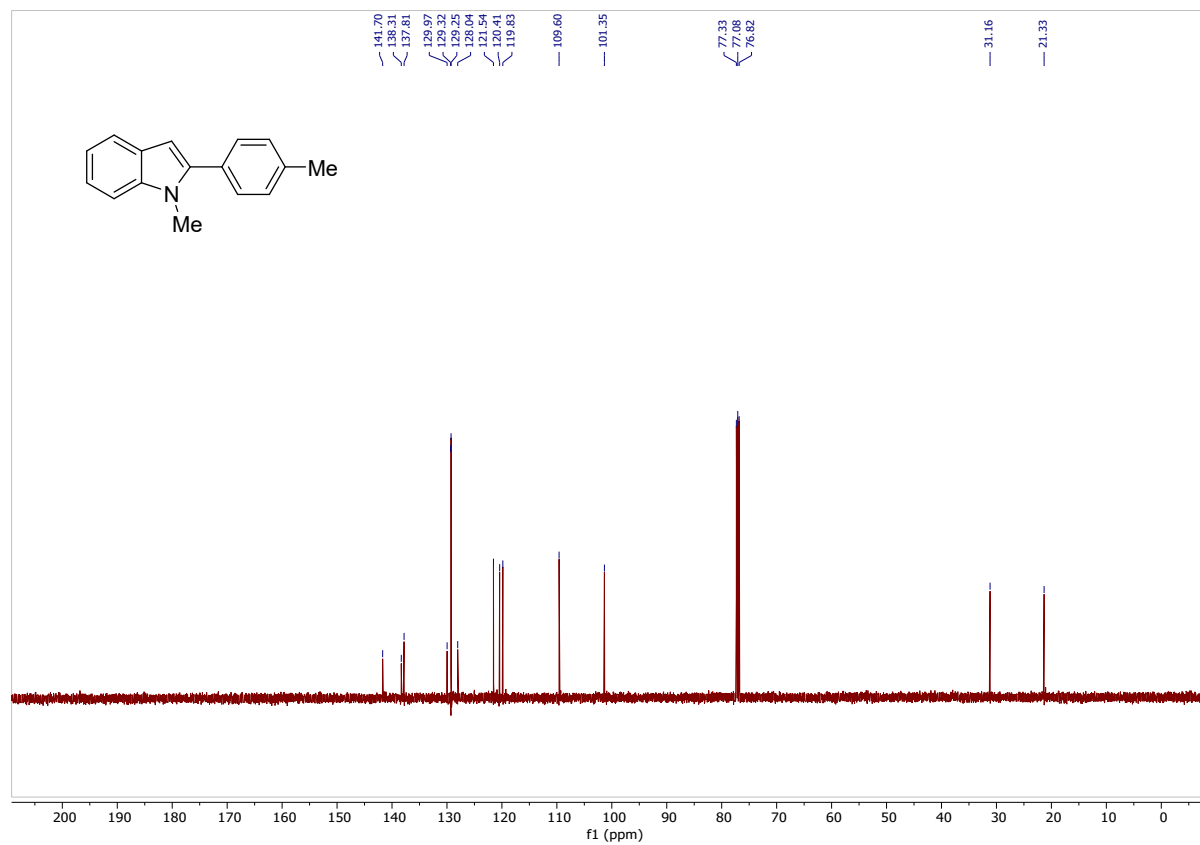
$^{13}\text{C}$  NMR spectrum of compound **3a**, ( $\text{CDCl}_3$ , 125 MHz).



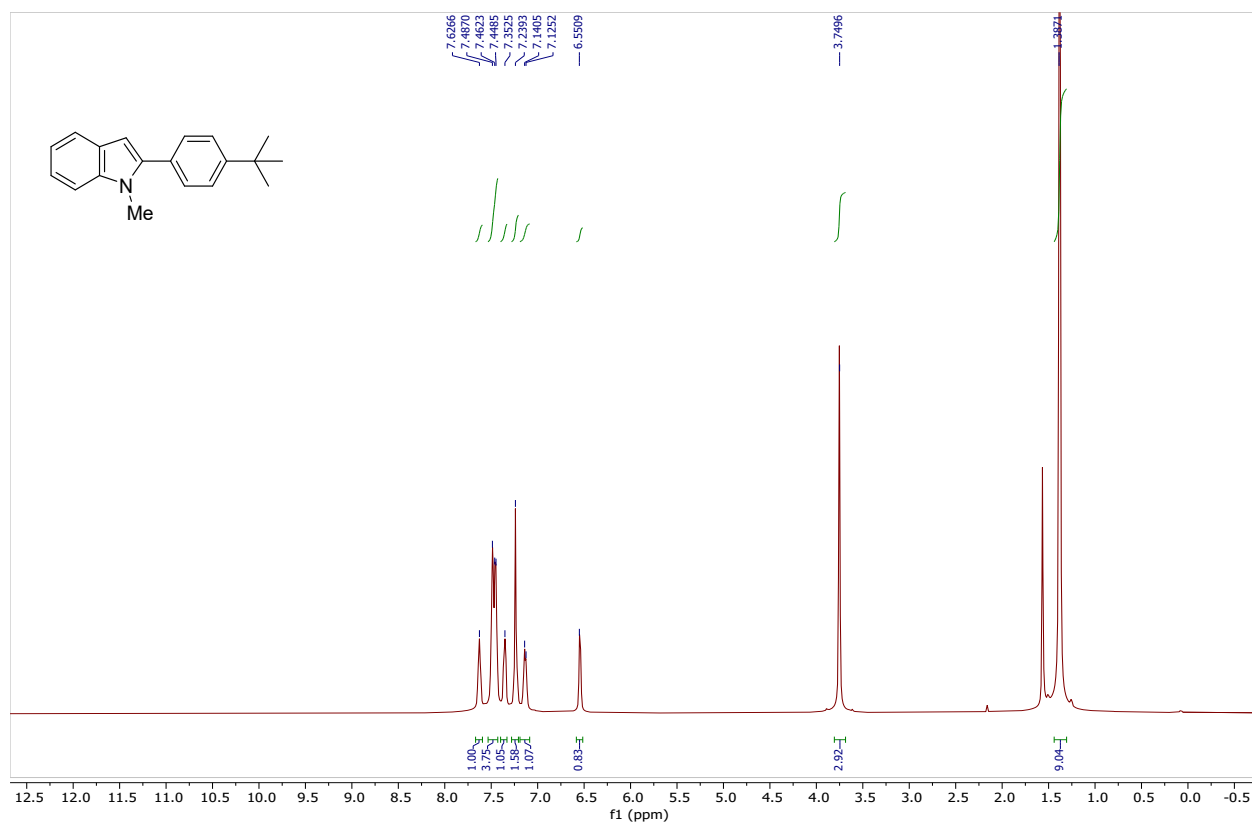
$^1\text{H}$  NMR spectrum of compound **3b**, ( $\text{CDCl}_3$ , 500 MHz).



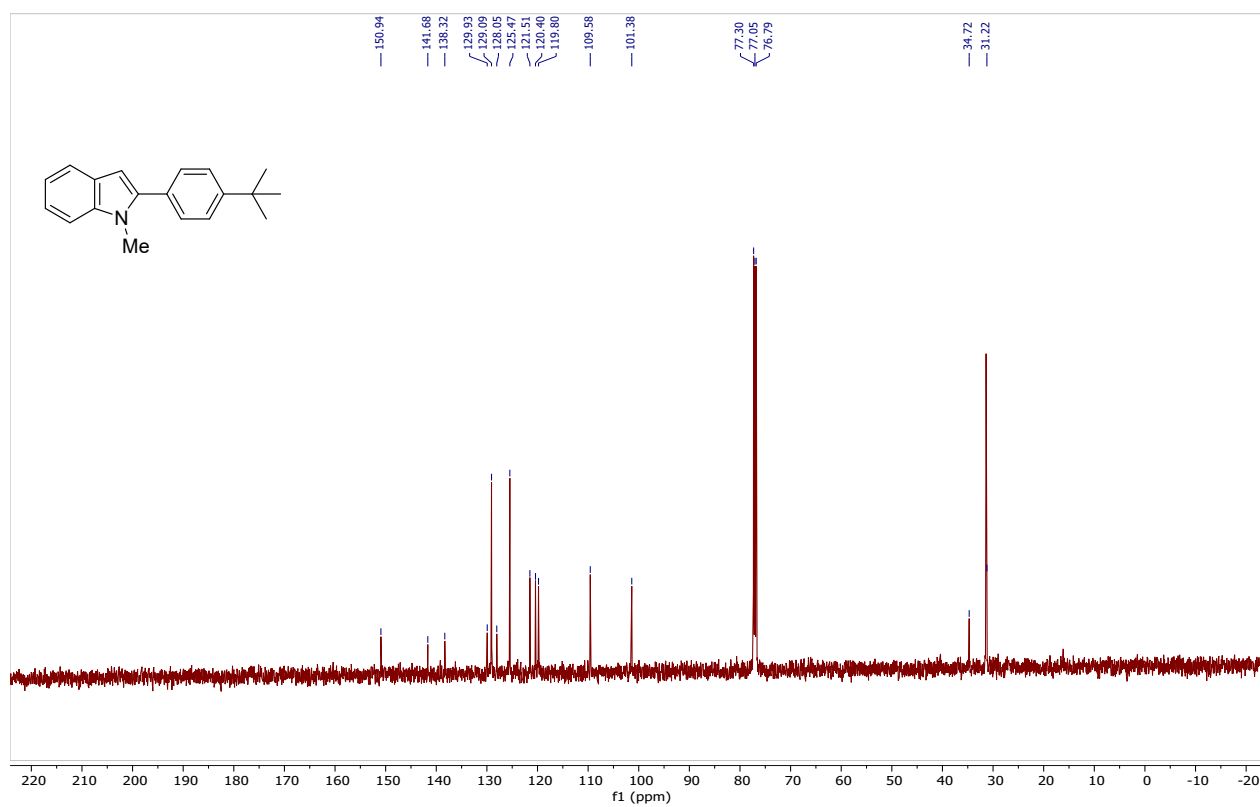
$^{13}\text{C}$  NMR spectrum of compound **3b**, ( $\text{CDCl}_3$ , 125 MHz).



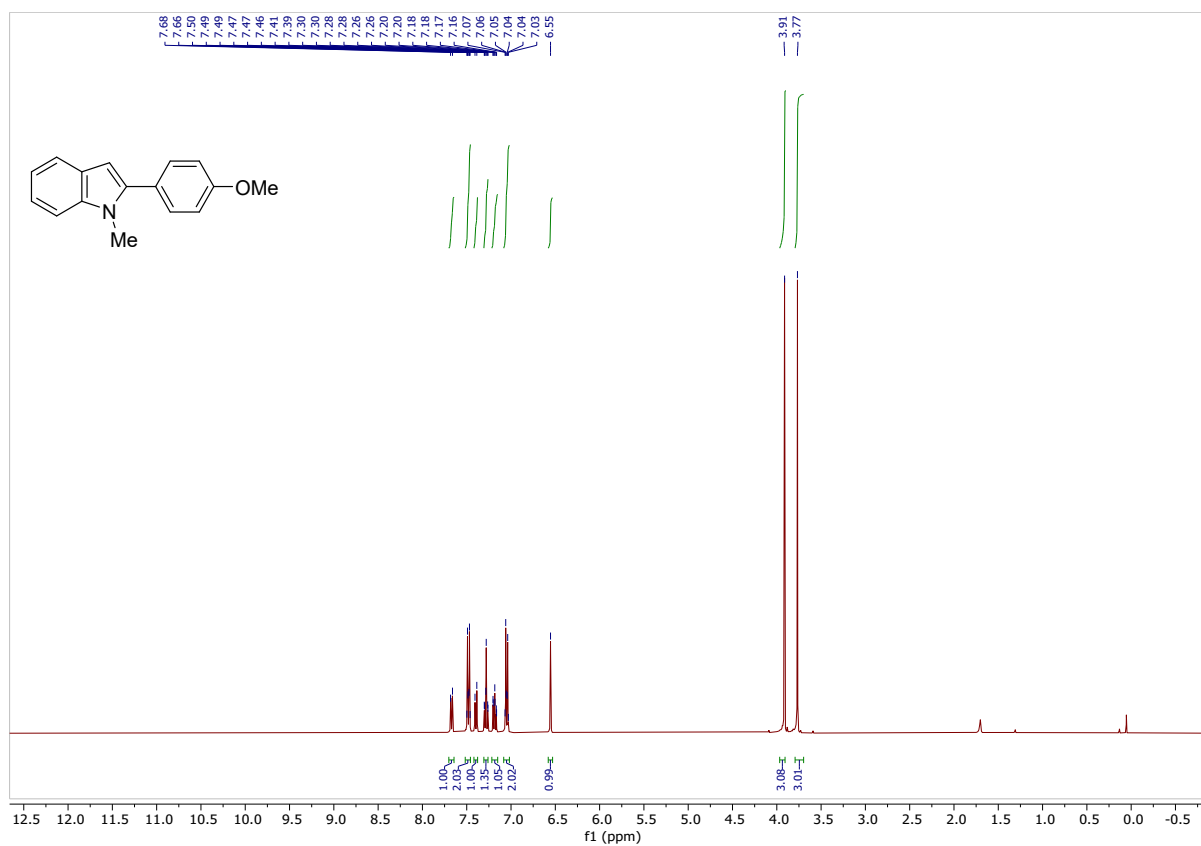
$^1\text{H}$  NMR spectrum of compound **3c**, ( $\text{CDCl}_3$ , 500 MHz).



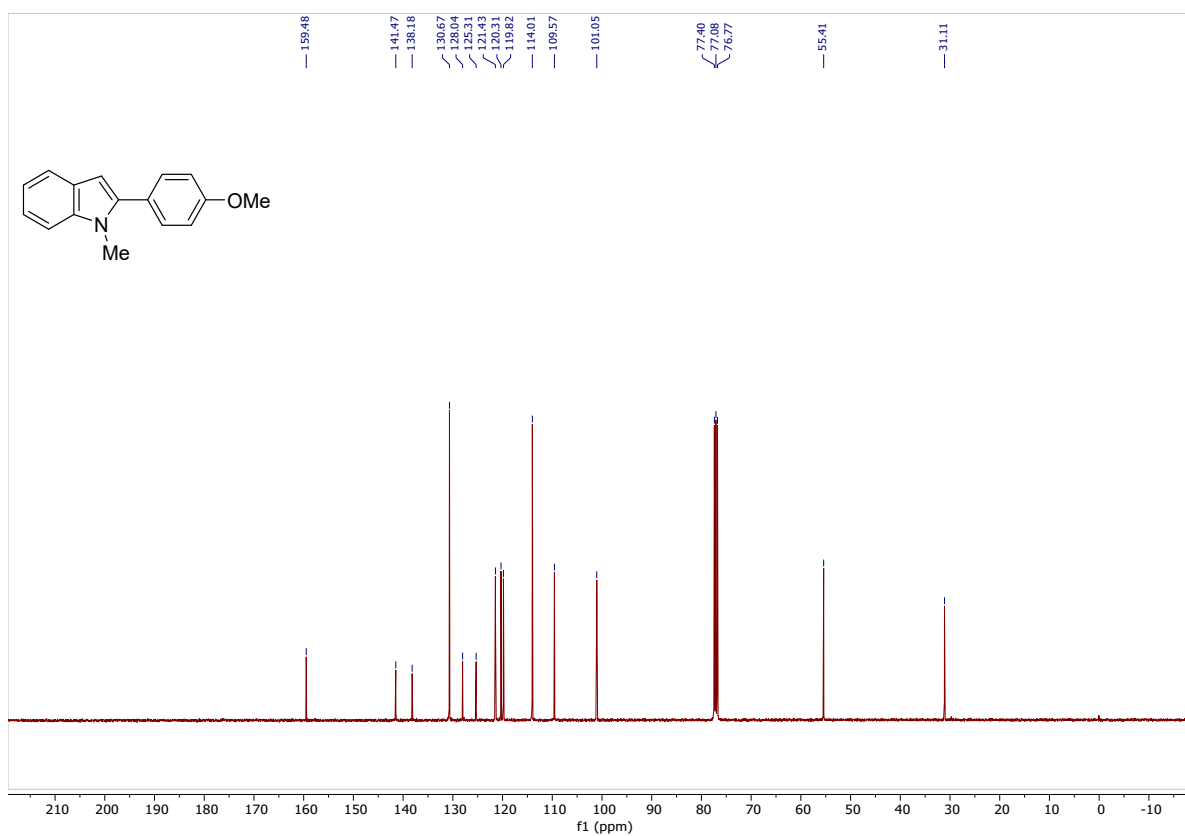
$^{13}\text{C}$  NMR spectrum of compound **3c**, ( $\text{CDCl}_3$ , 125 MHz).



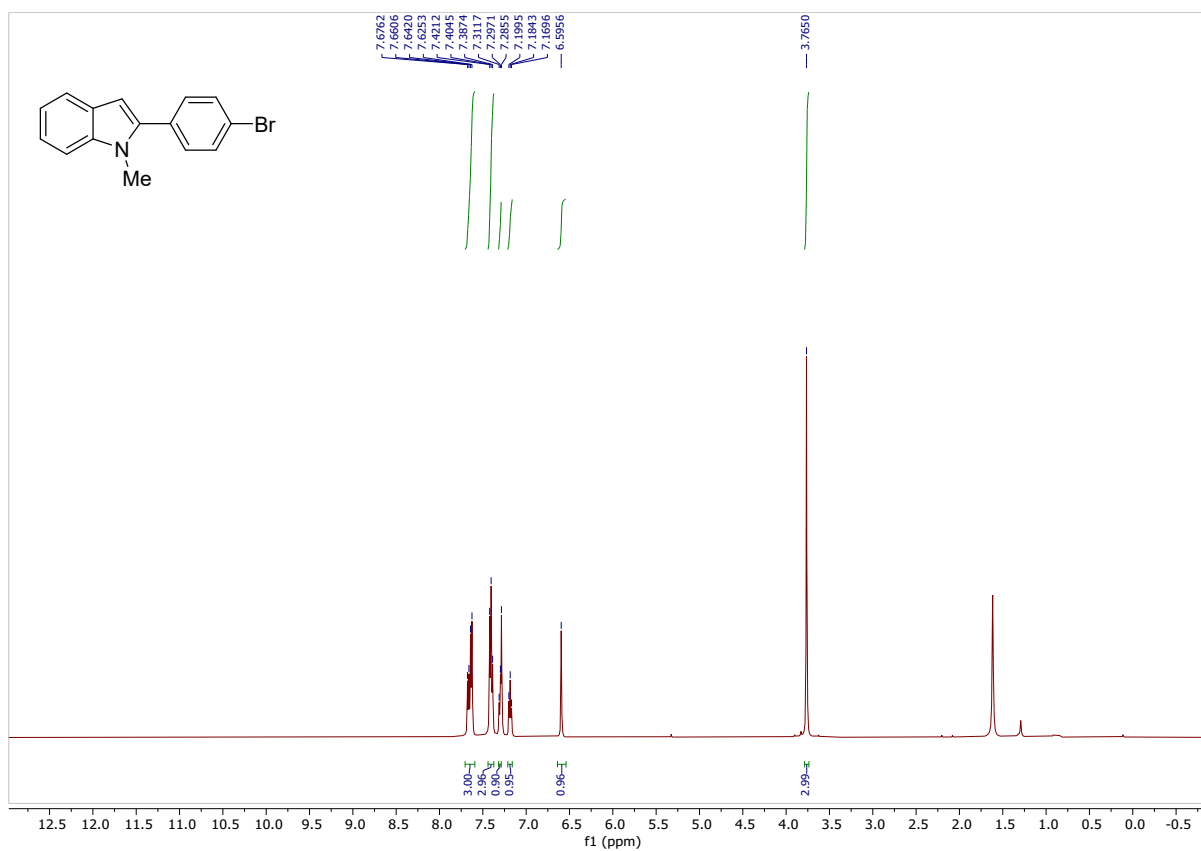
$^1\text{H}$  NMR spectrum of compound **3d**, ( $\text{CDCl}_3$ , 500 MHz).



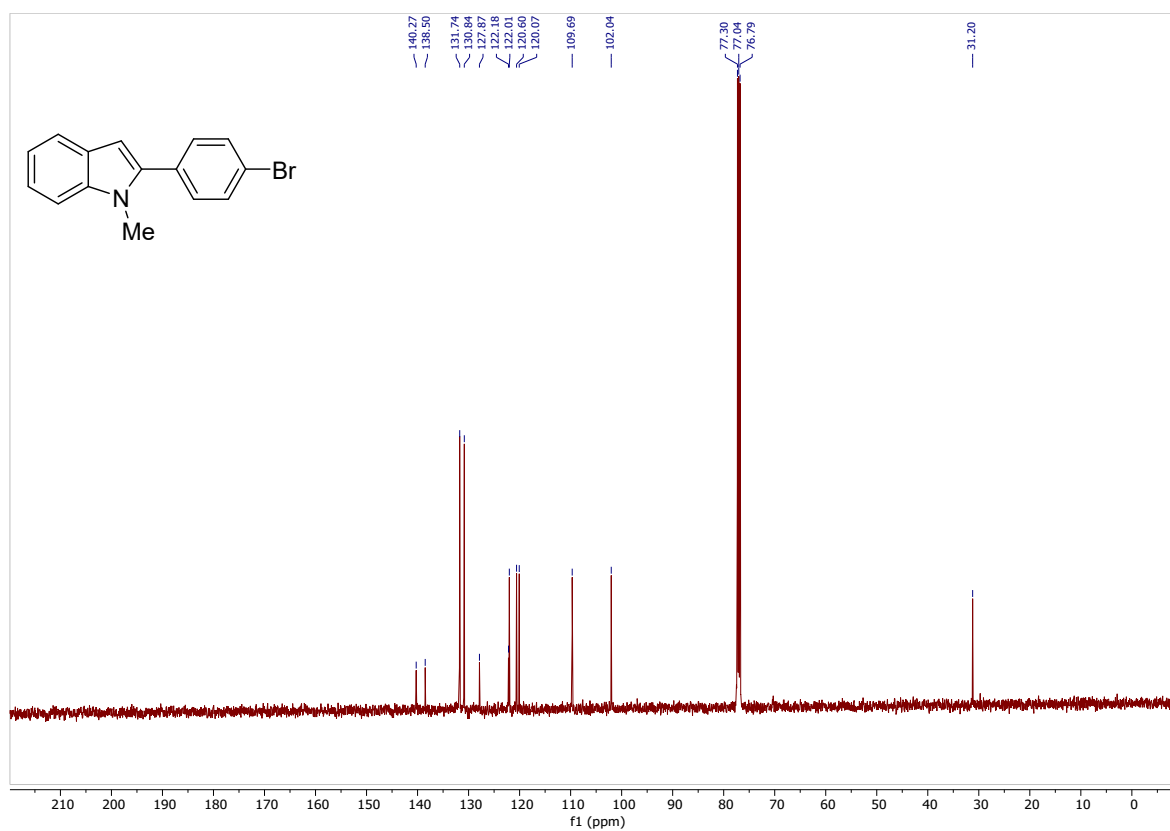
$^{13}\text{C}$  NMR spectrum of compound **3d**, ( $\text{CDCl}_3$ , 125 MHz).



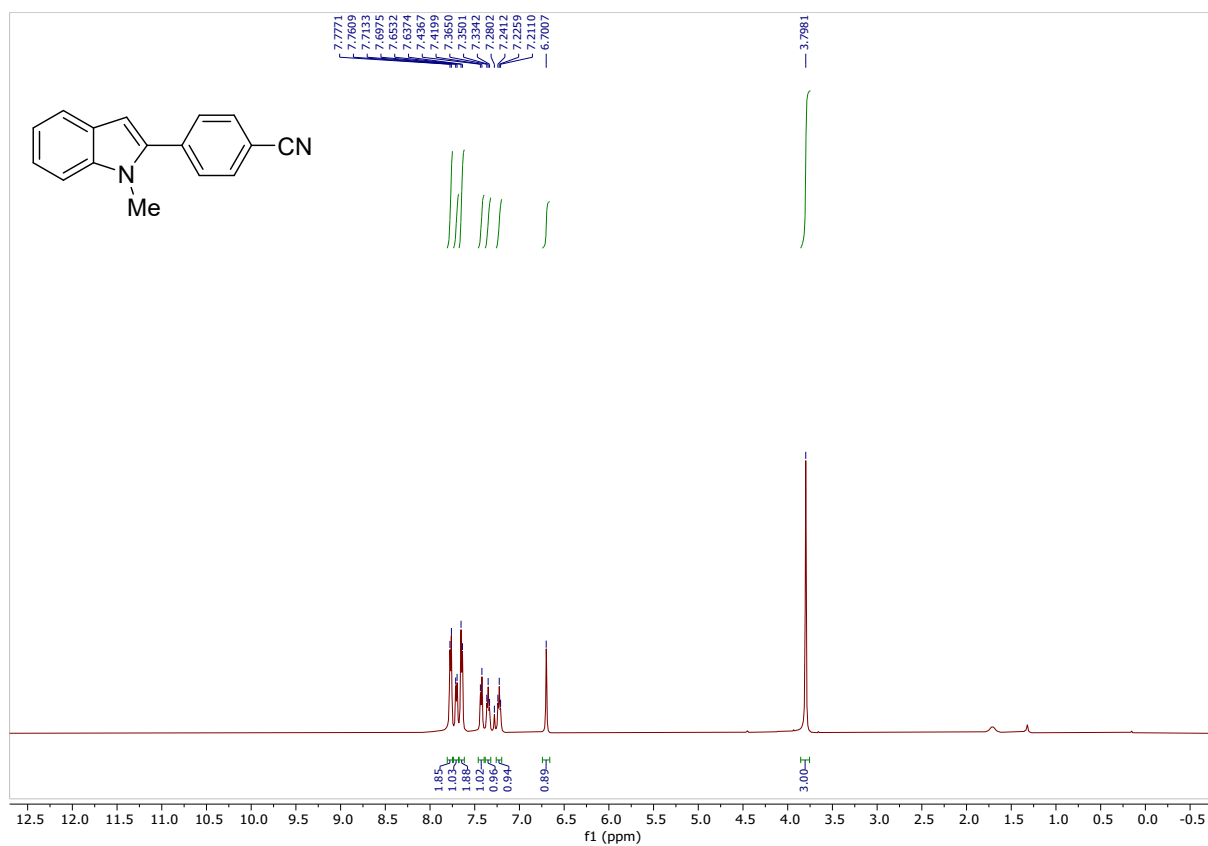
$^1\text{H}$  NMR spectrum of compound **3e**, ( $\text{CDCl}_3$ , 500 MHz).



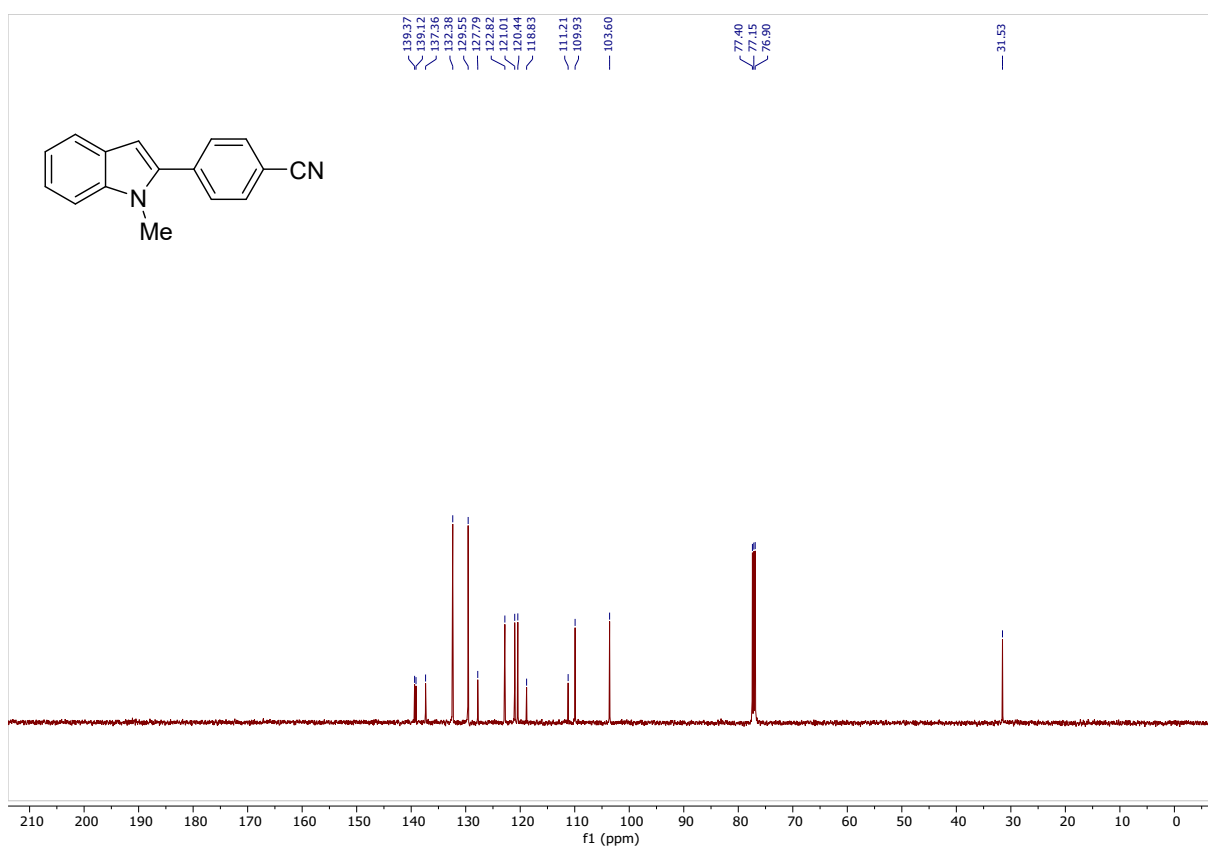
$^{13}\text{C}$  NMR spectrum of compound **3e**, ( $\text{CDCl}_3$ , 125 MHz).



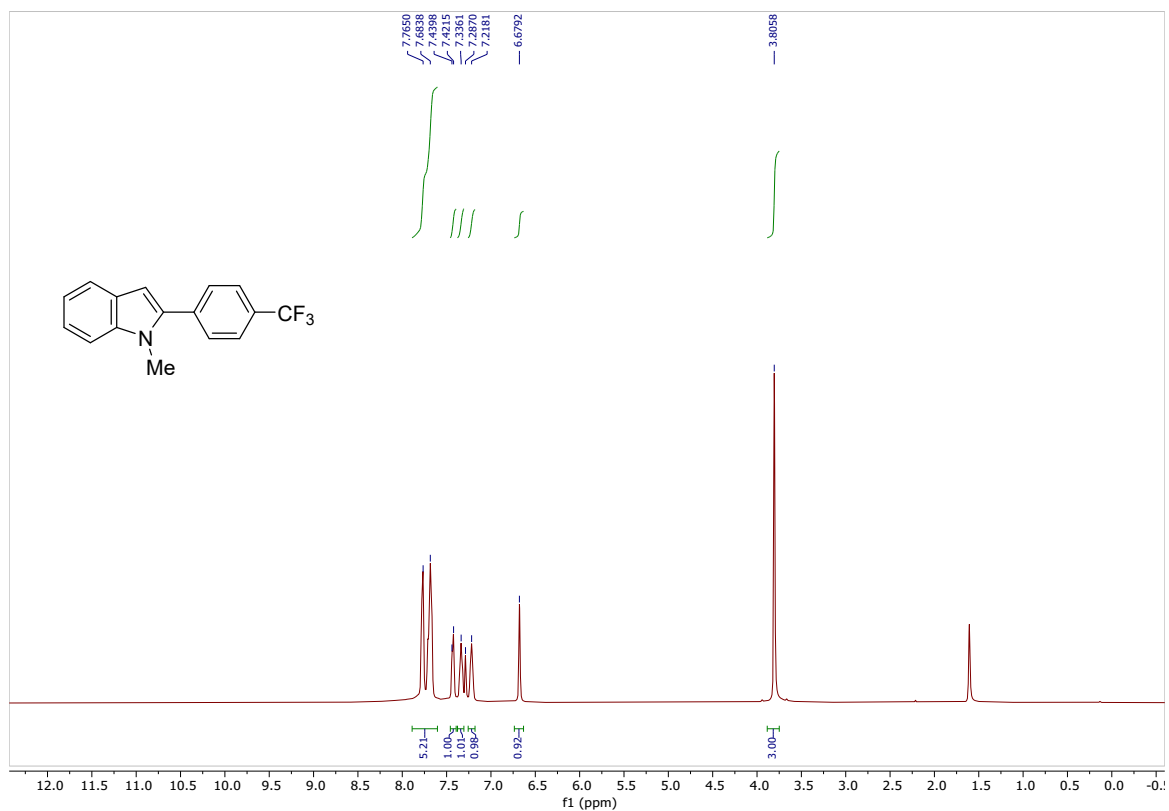
$^1\text{H}$  NMR spectrum of compound **3f**, ( $\text{CDCl}_3$ , 500 MHz).



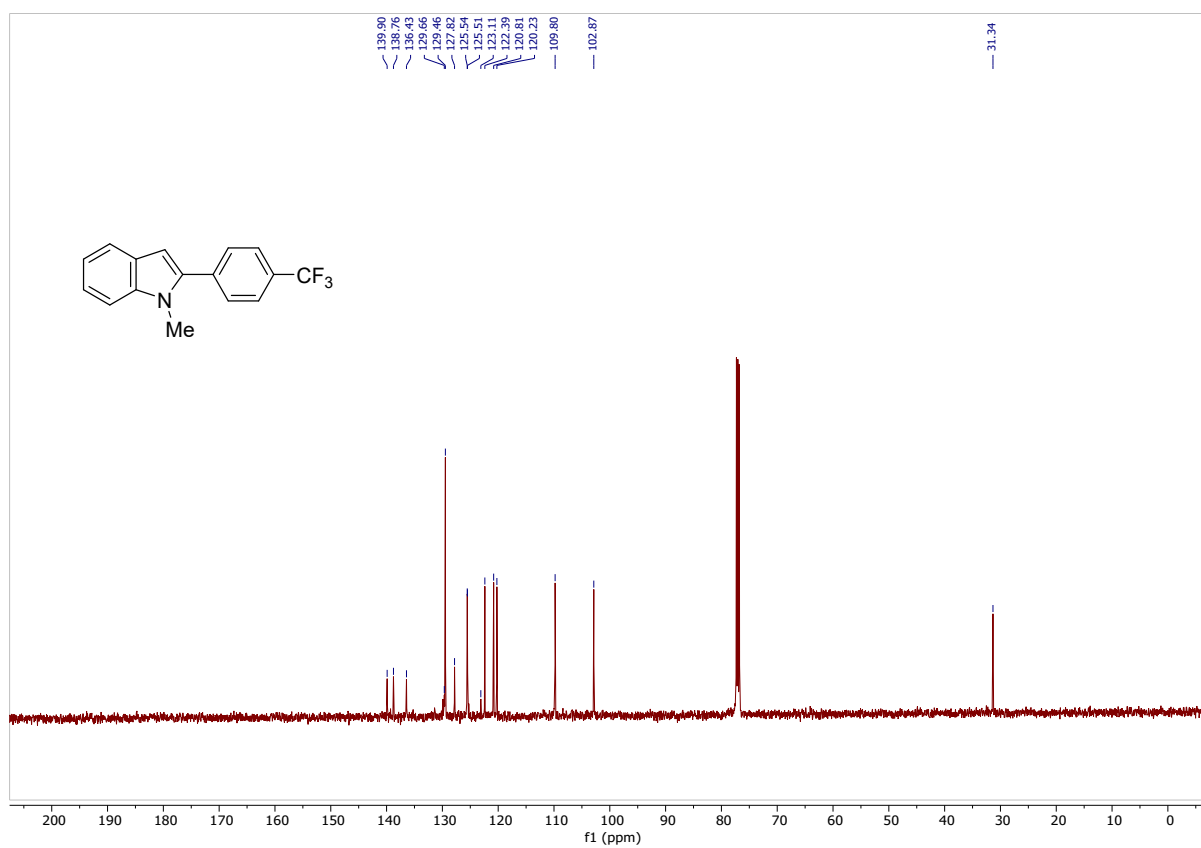
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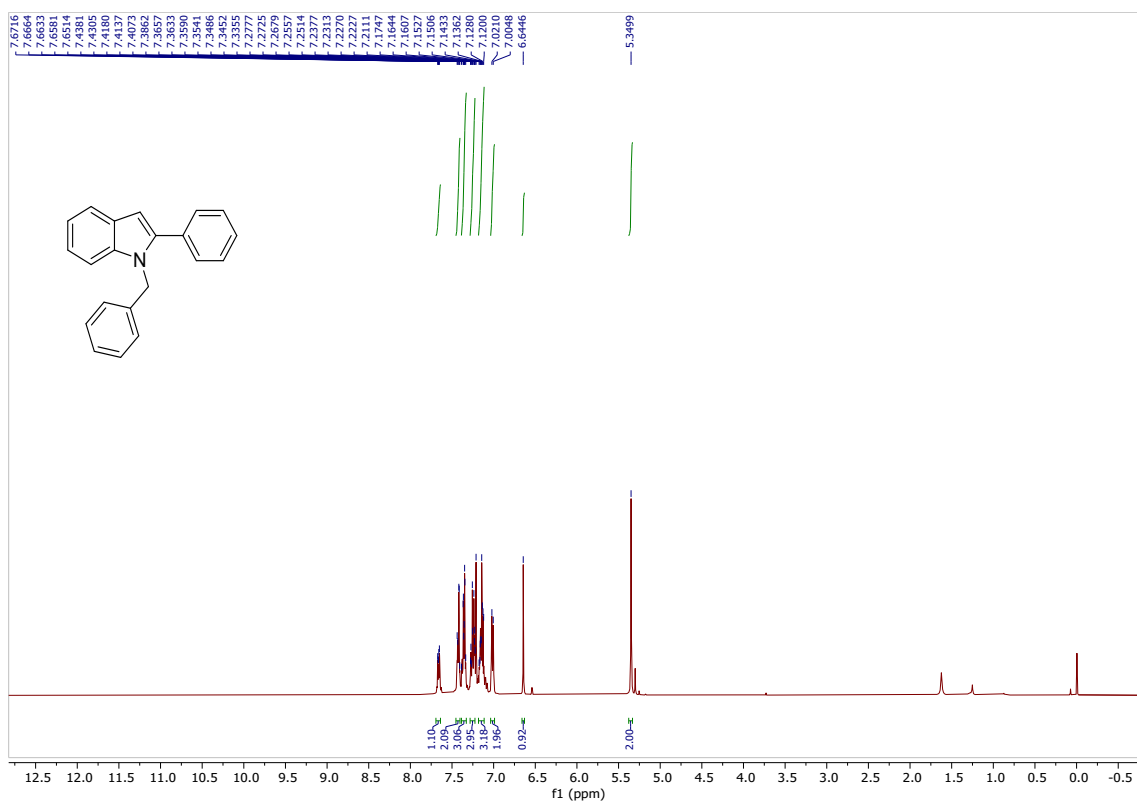
<sup>1</sup>H NMR spectrum of compound **3g**, (CDCl<sub>3</sub>, 500 MHz).



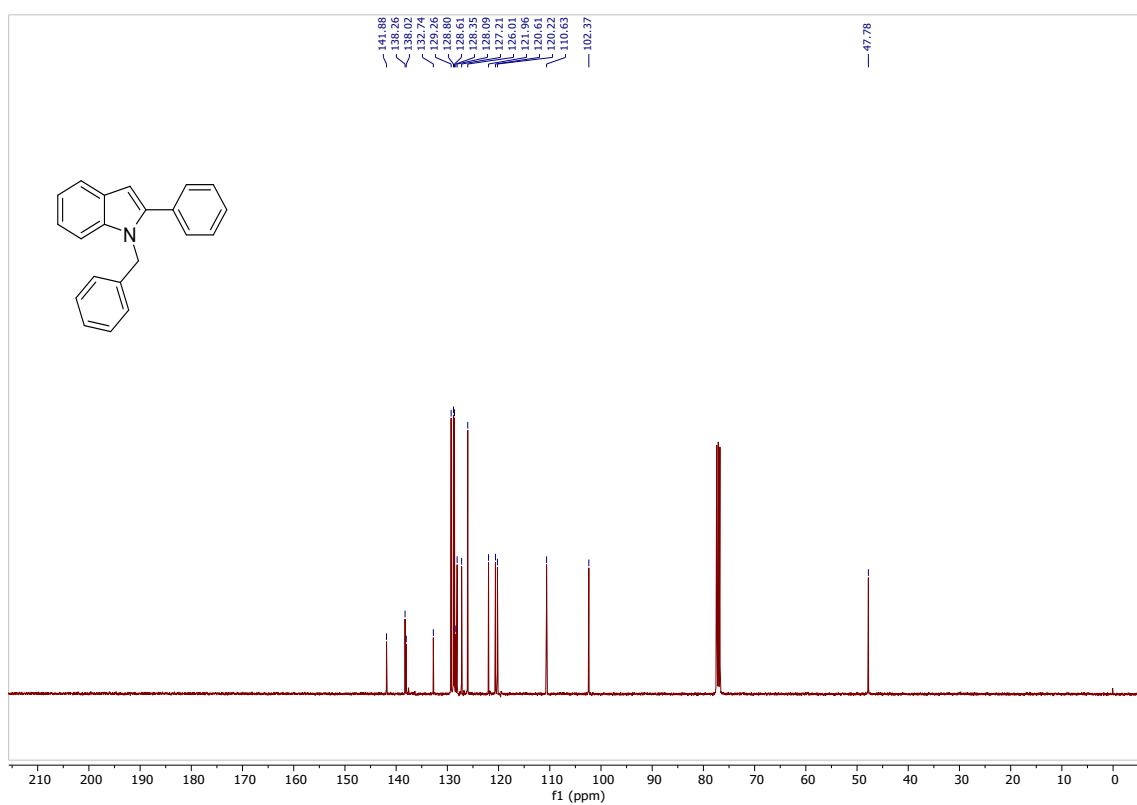
<sup>13</sup>C NMR spectrum of compound **3g**, (CDCl<sub>3</sub>, 125 MHz).



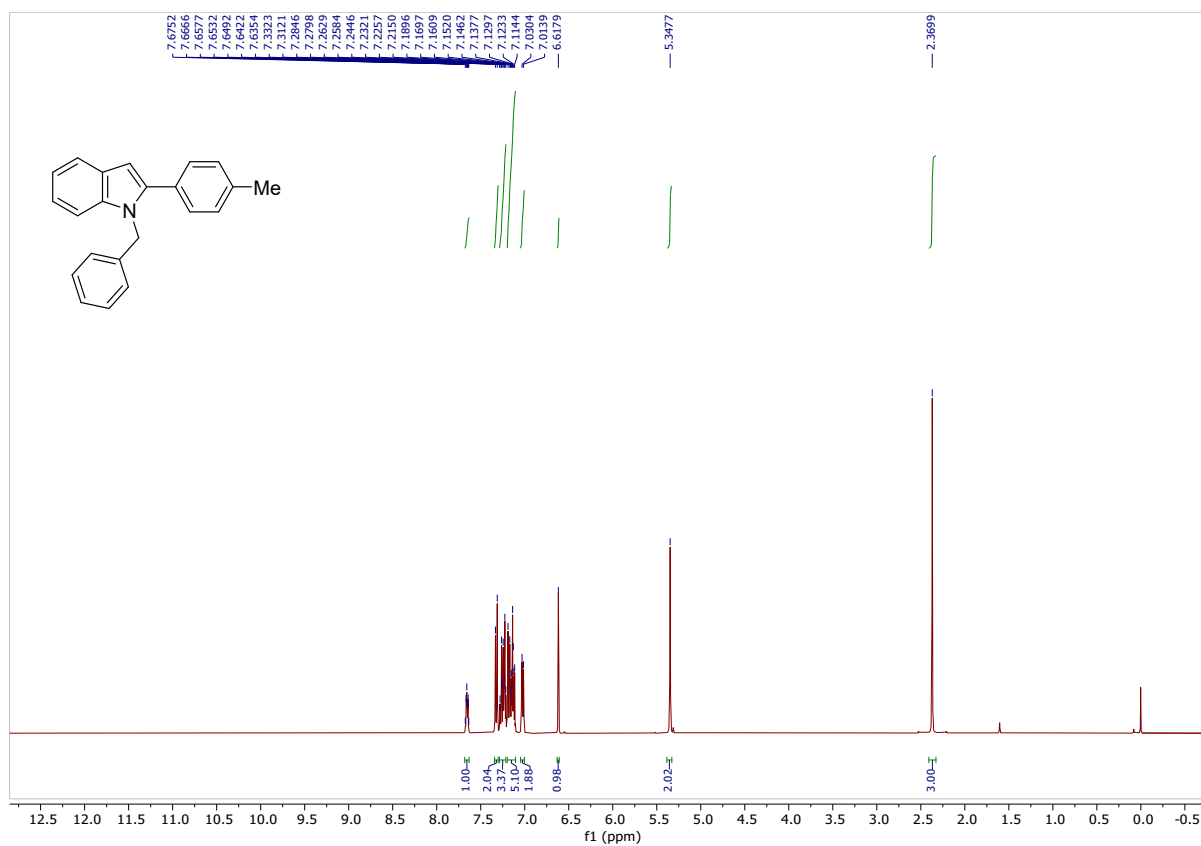
<sup>1</sup>H NMR spectrum of compound **3h**, (CDCl<sub>3</sub>, 500 MHz).



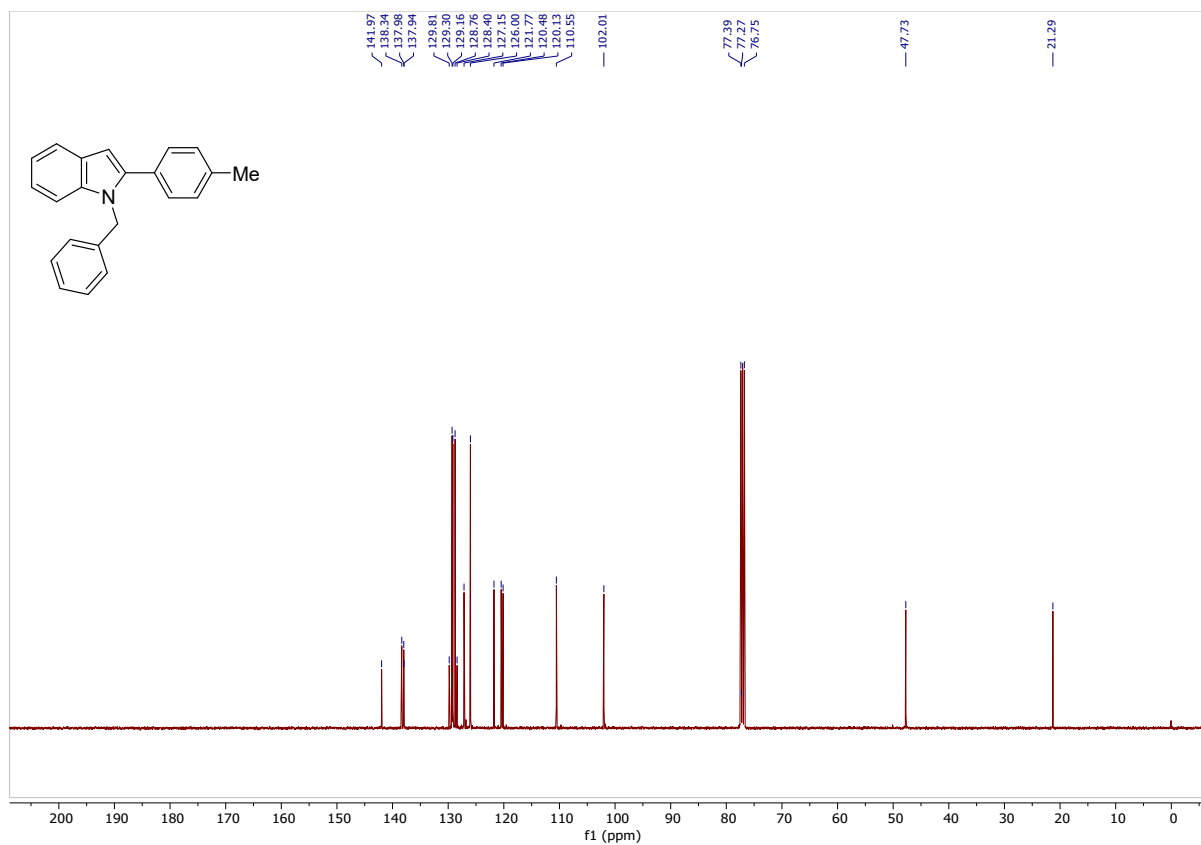
<sup>13</sup>C NMR spectrum of compound **3h**, (CDCl<sub>3</sub>, 125 MHz).



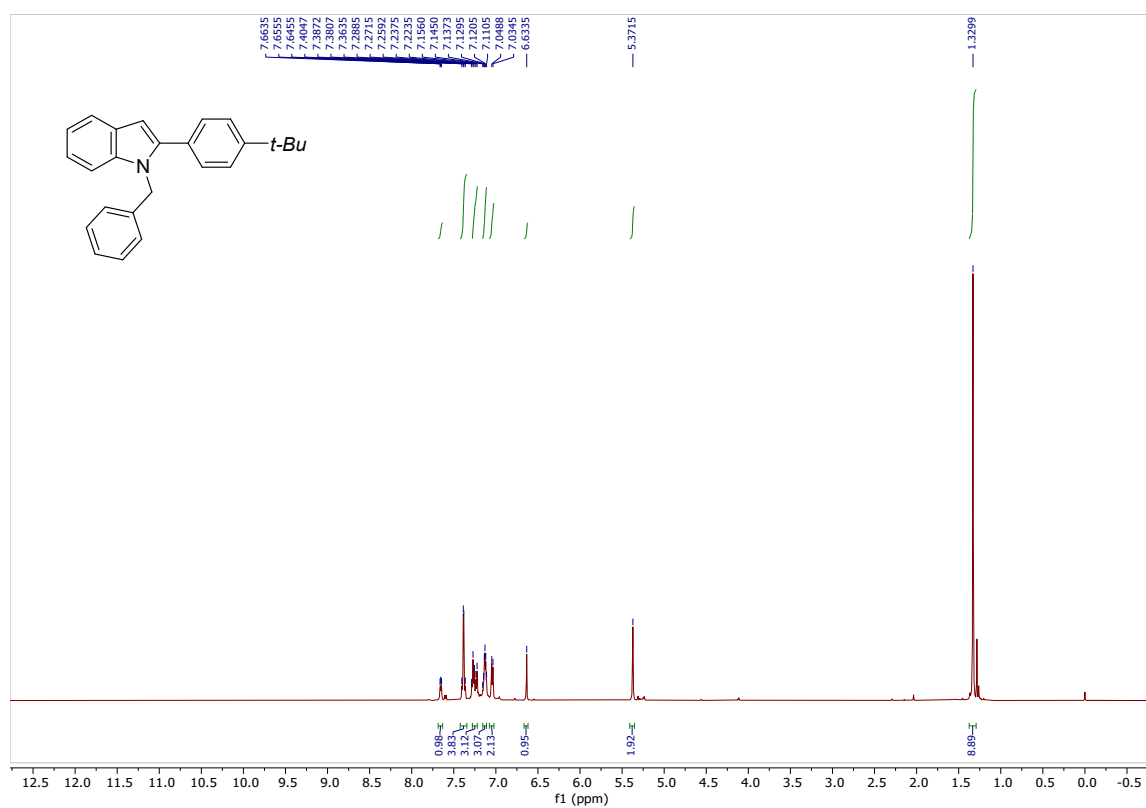
$^1\text{H}$  NMR spectrum of compound **3i**, ( $\text{CDCl}_3$ , 500 MHz).



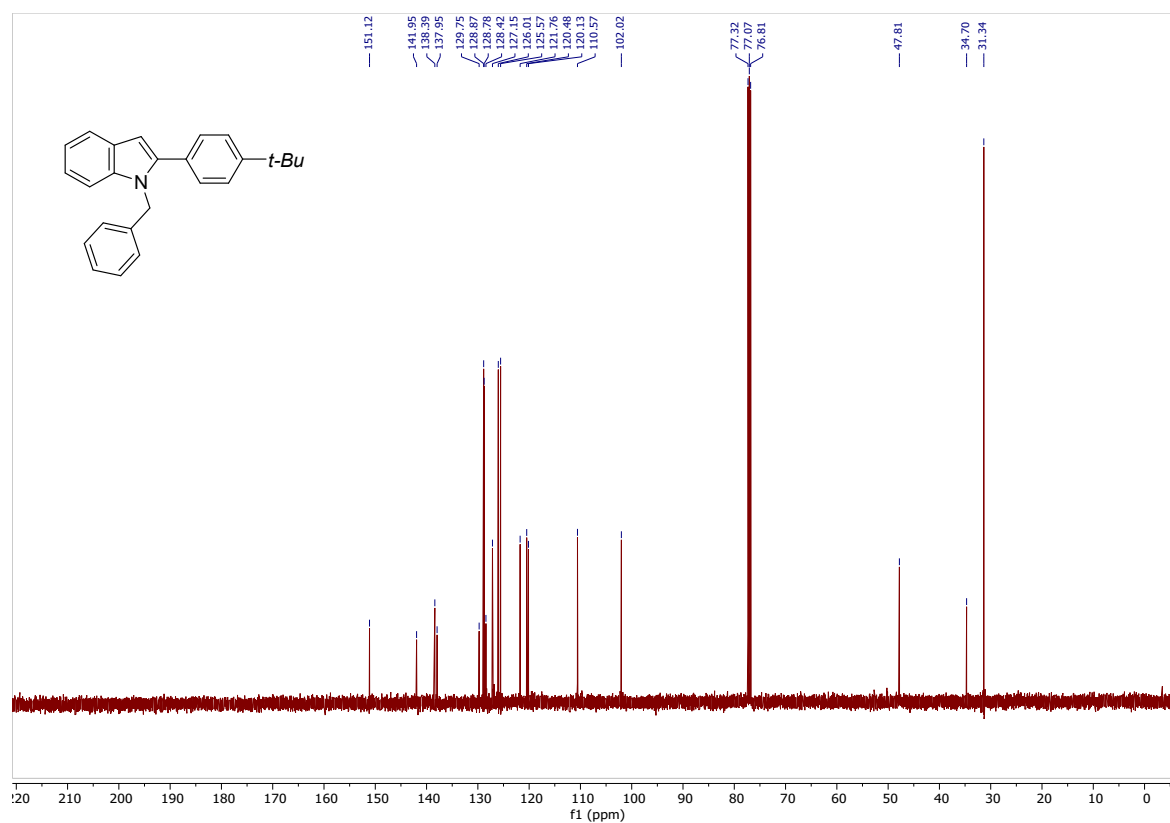
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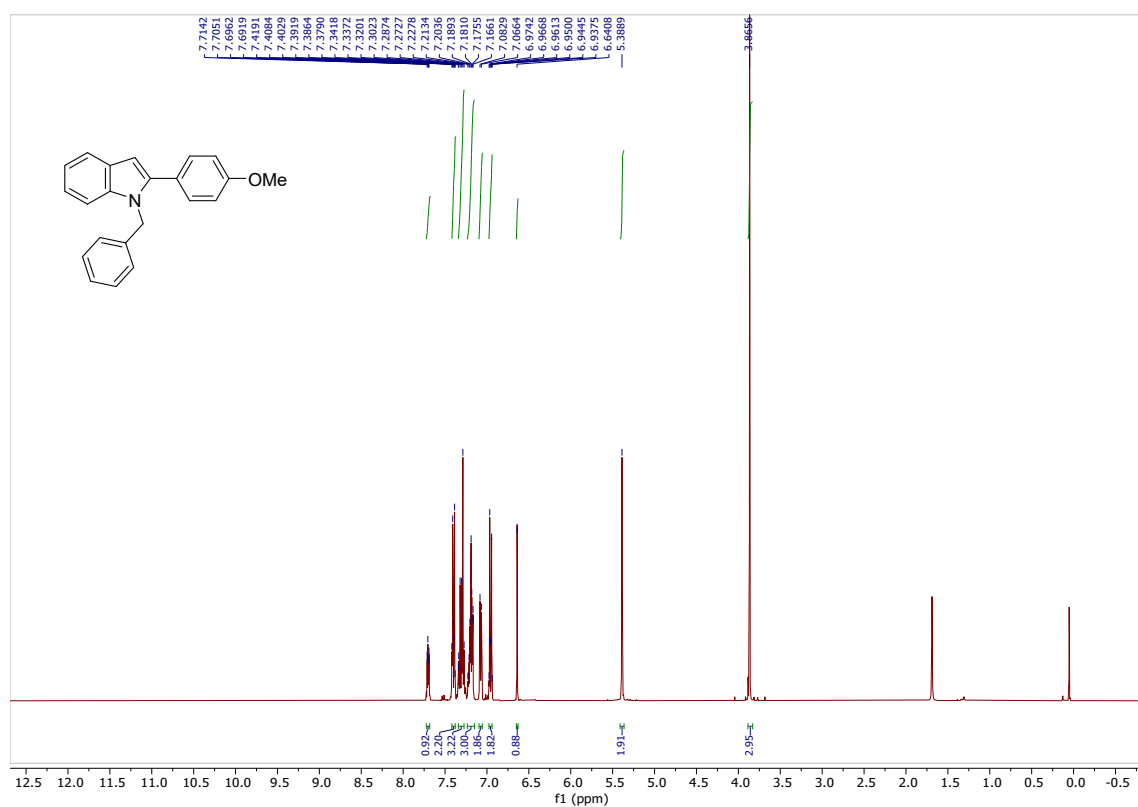
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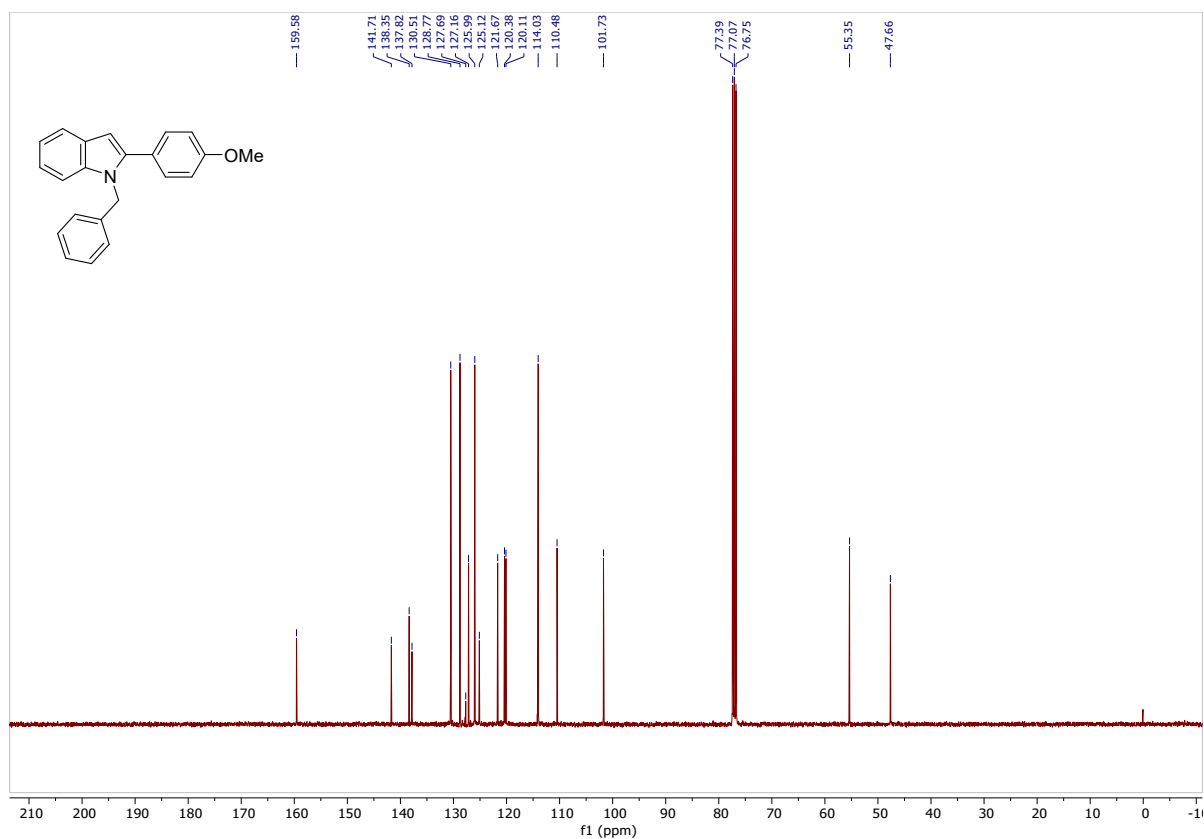
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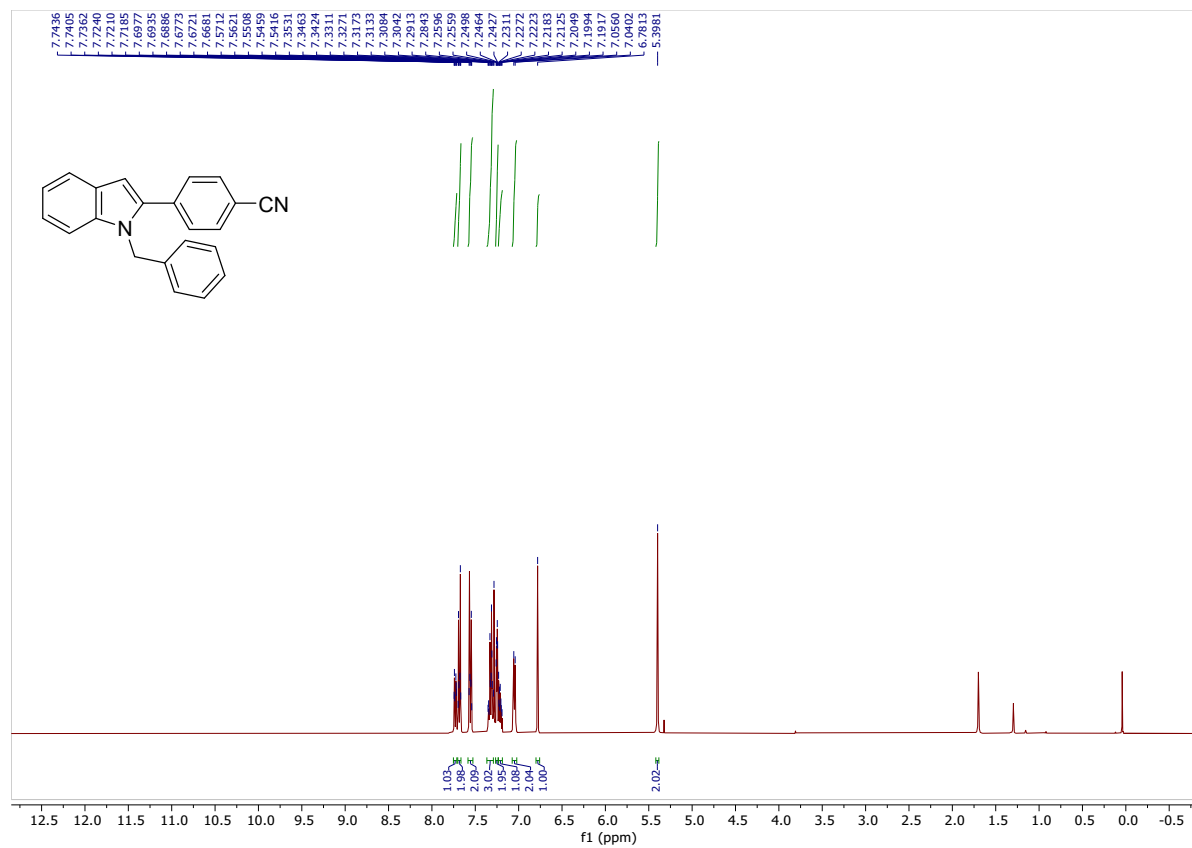
<sup>1</sup>H NMR spectrum of compound **3k**, (CDCl<sub>3</sub>, 500 MHz).



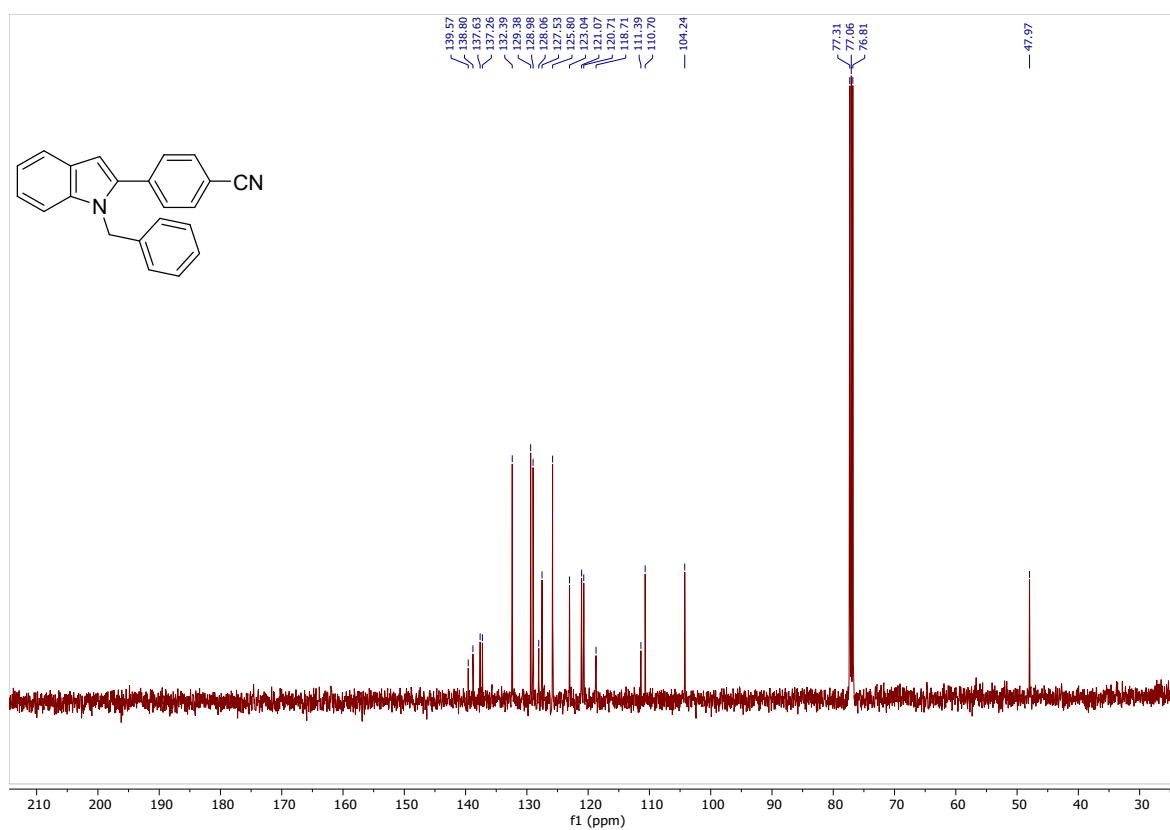
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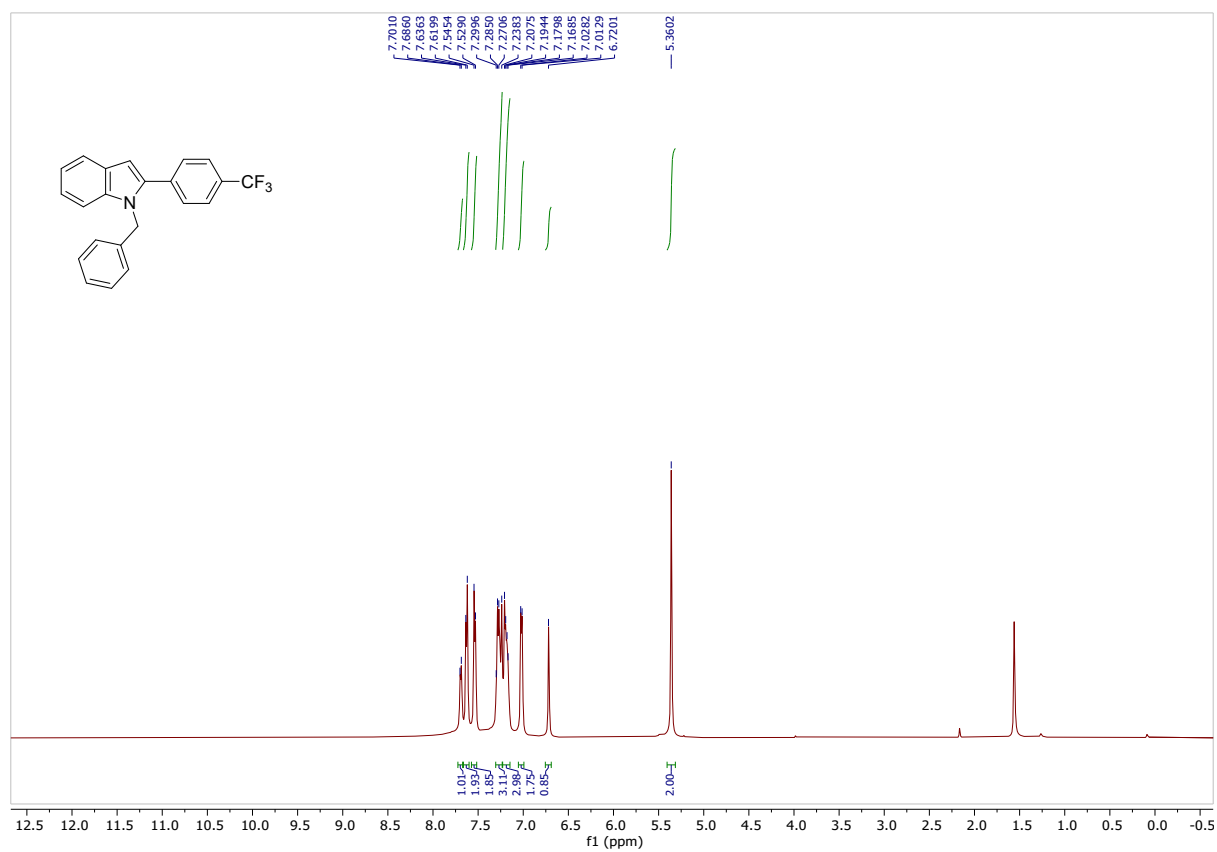
$^1\text{H}$  NMR spectrum of compound **3l**, ( $\text{CDCl}_3$ , 500 MHz).



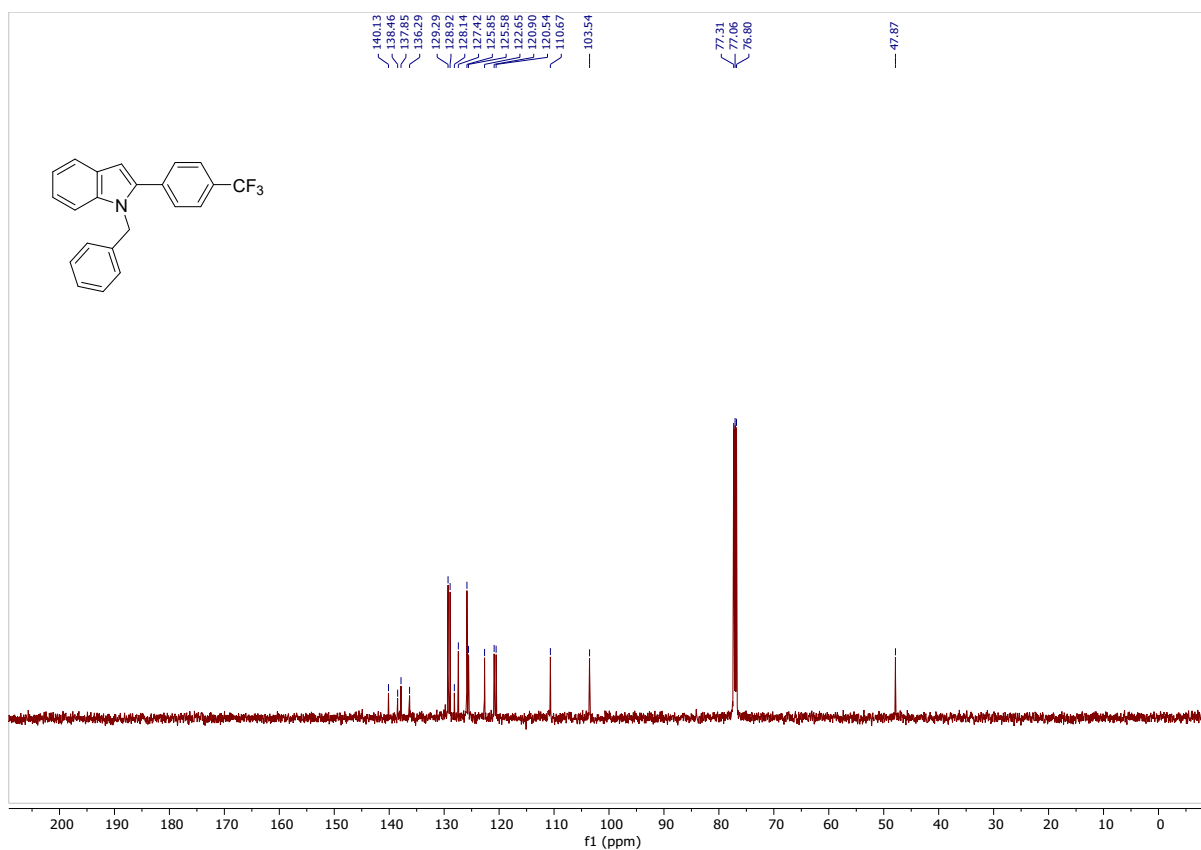
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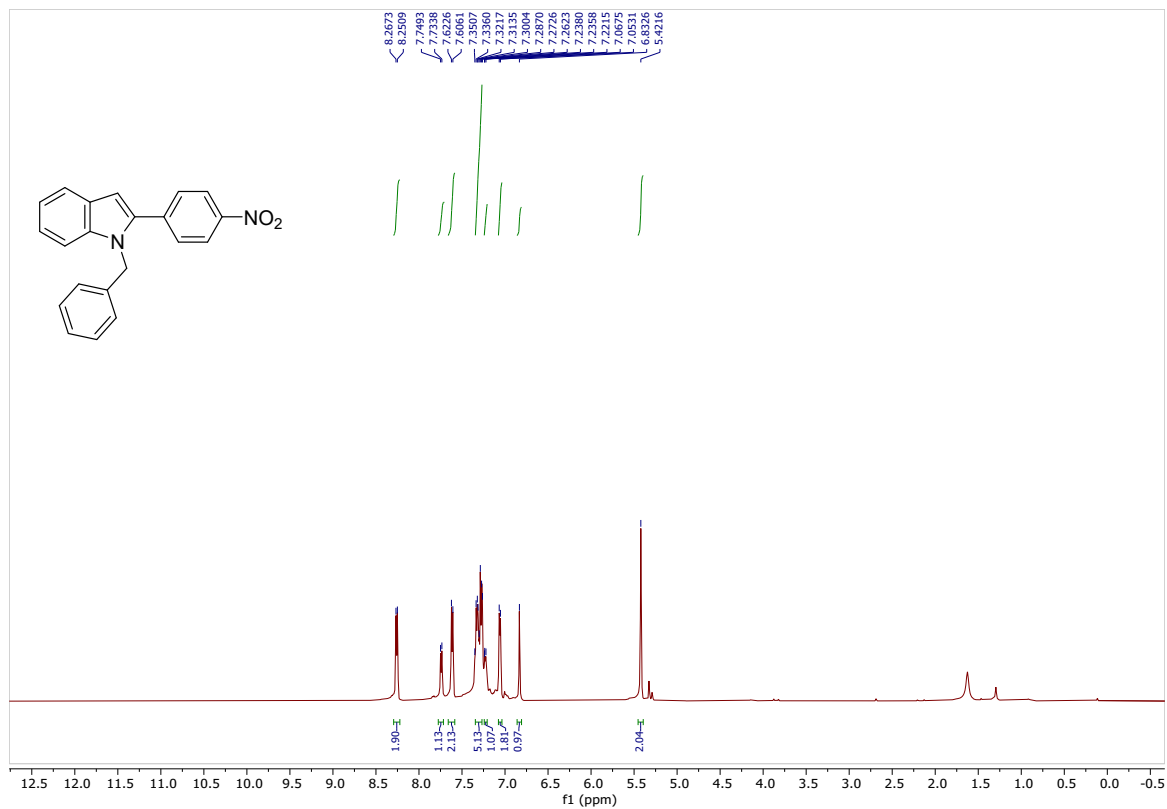
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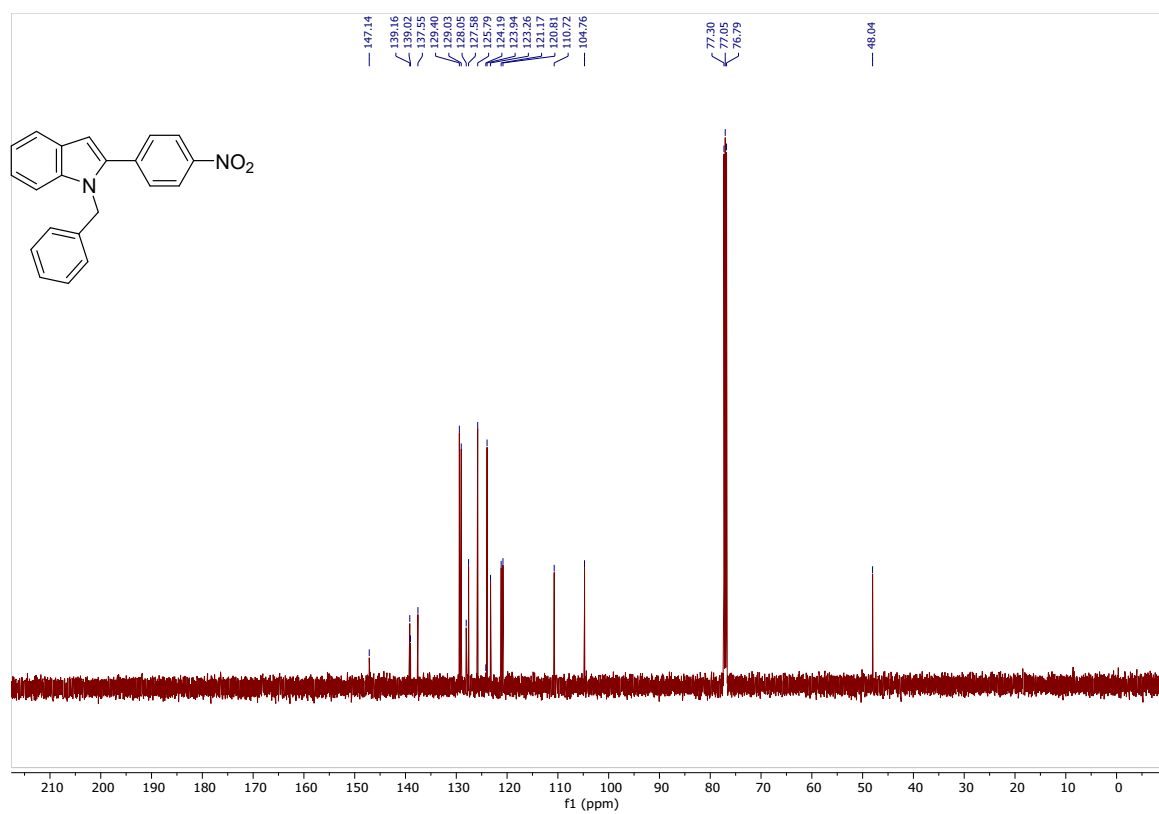
$^{13}\text{C}$  NMR spectrum of compound **3m**, ( $\text{CDCl}_3$ , 125 MHz).



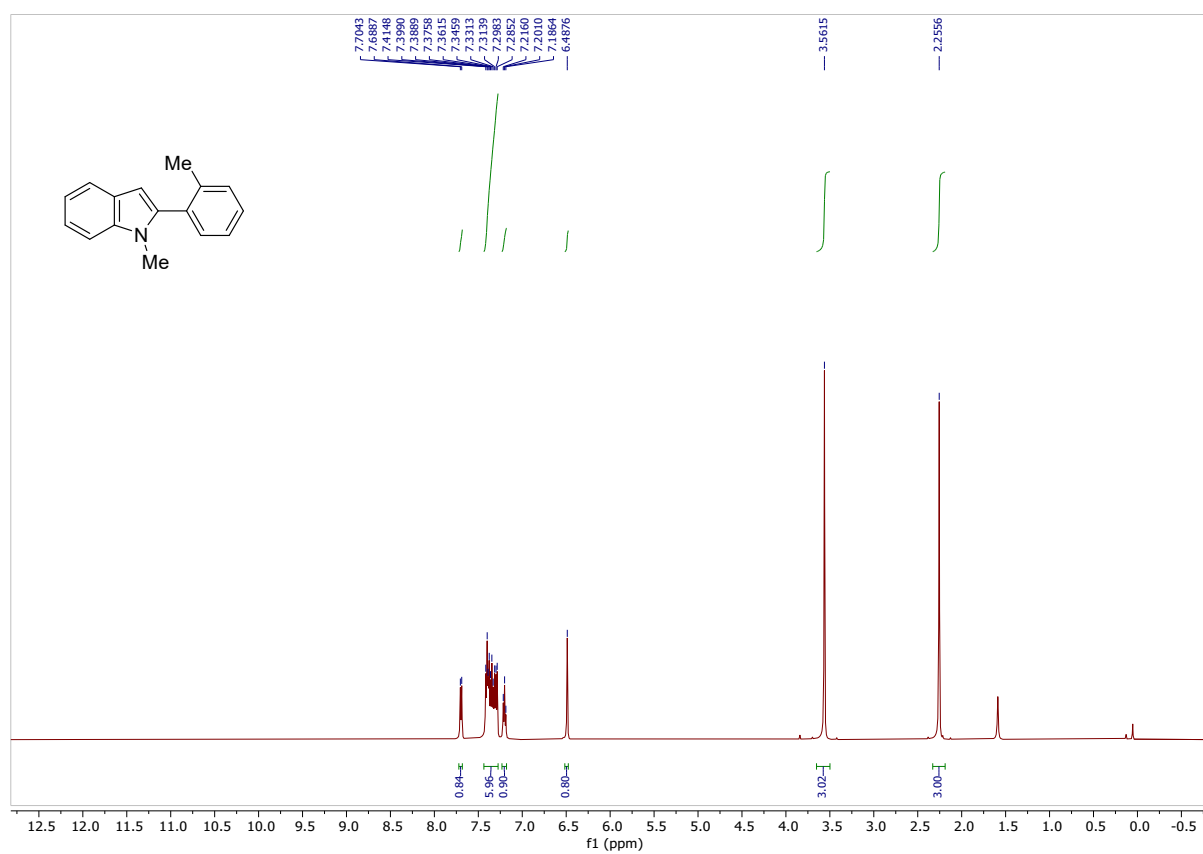
$^1\text{H}$  NMR spectrum of compound **3n**, ( $\text{CDCl}_3$ , 500 MHz).



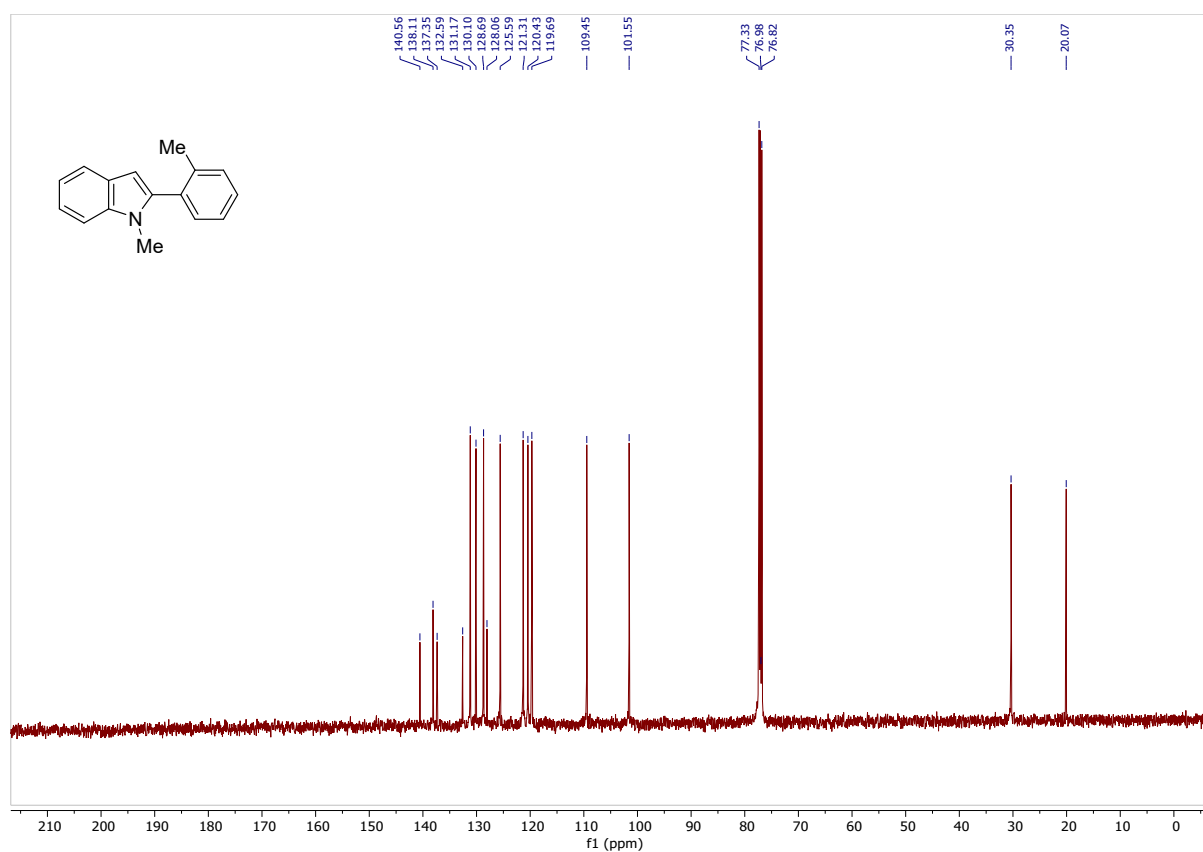
$^{13}\text{C}$  NMR spectrum of compound **3n**, ( $\text{CDCl}_3$ , 125 MHz).



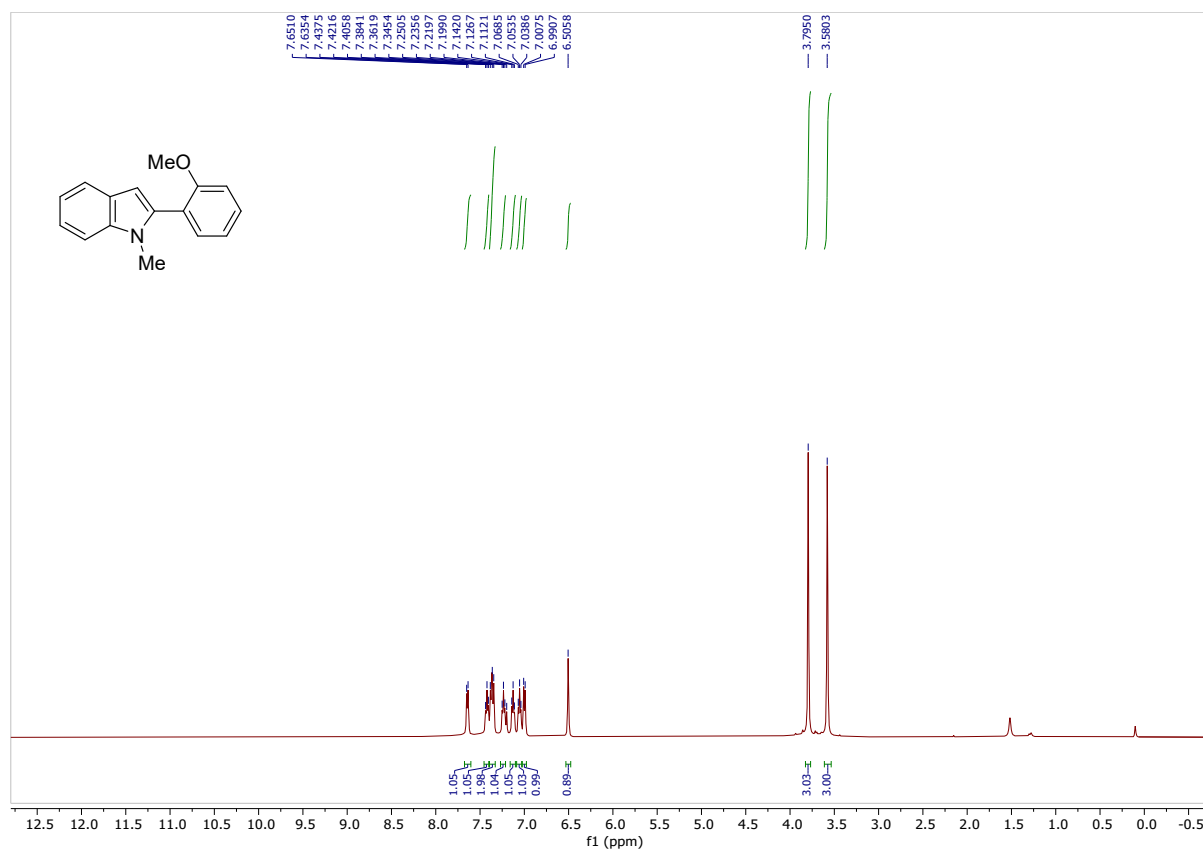
<sup>1</sup>H NMR spectrum of compound **30**, (CDCl<sub>3</sub>, 500 MHz).



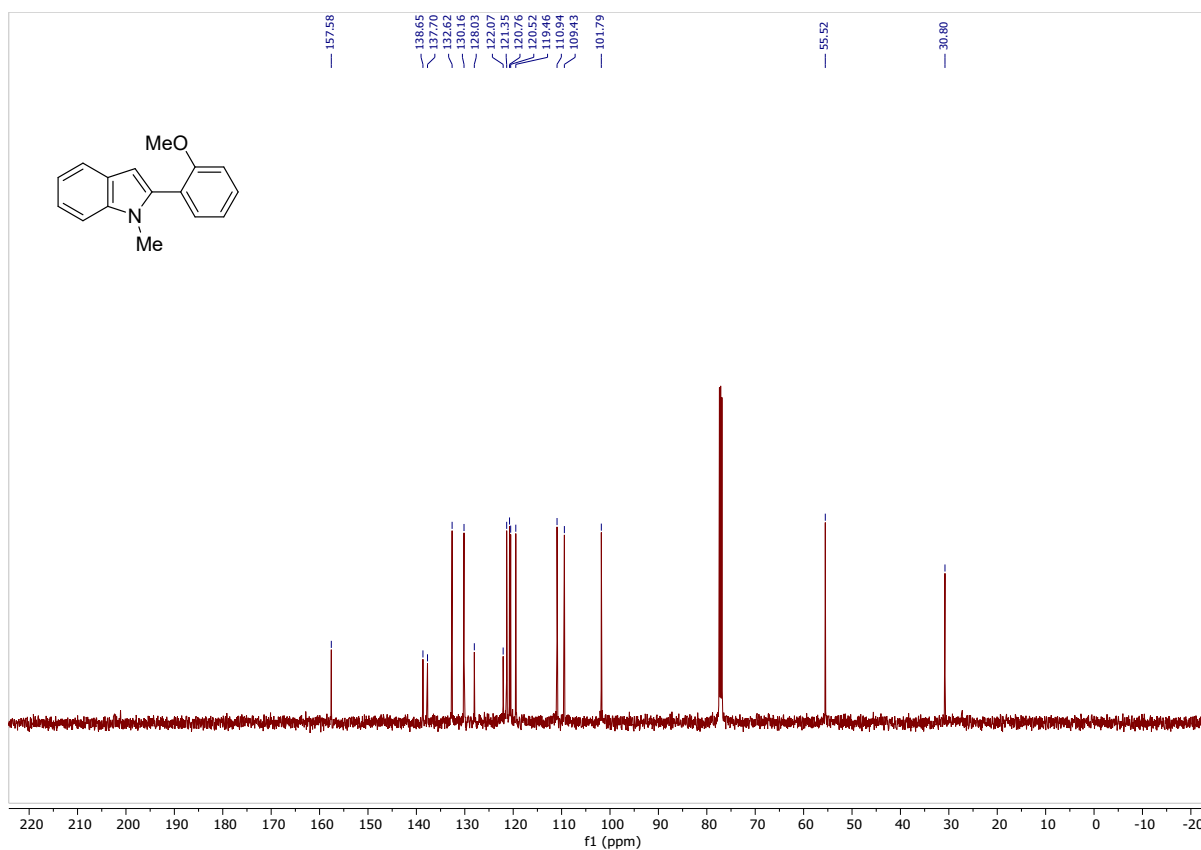
$^{13}\text{C}$  NMR spectrum of compound **3o**, ( $\text{CDCl}_3$ , 125 MHz).



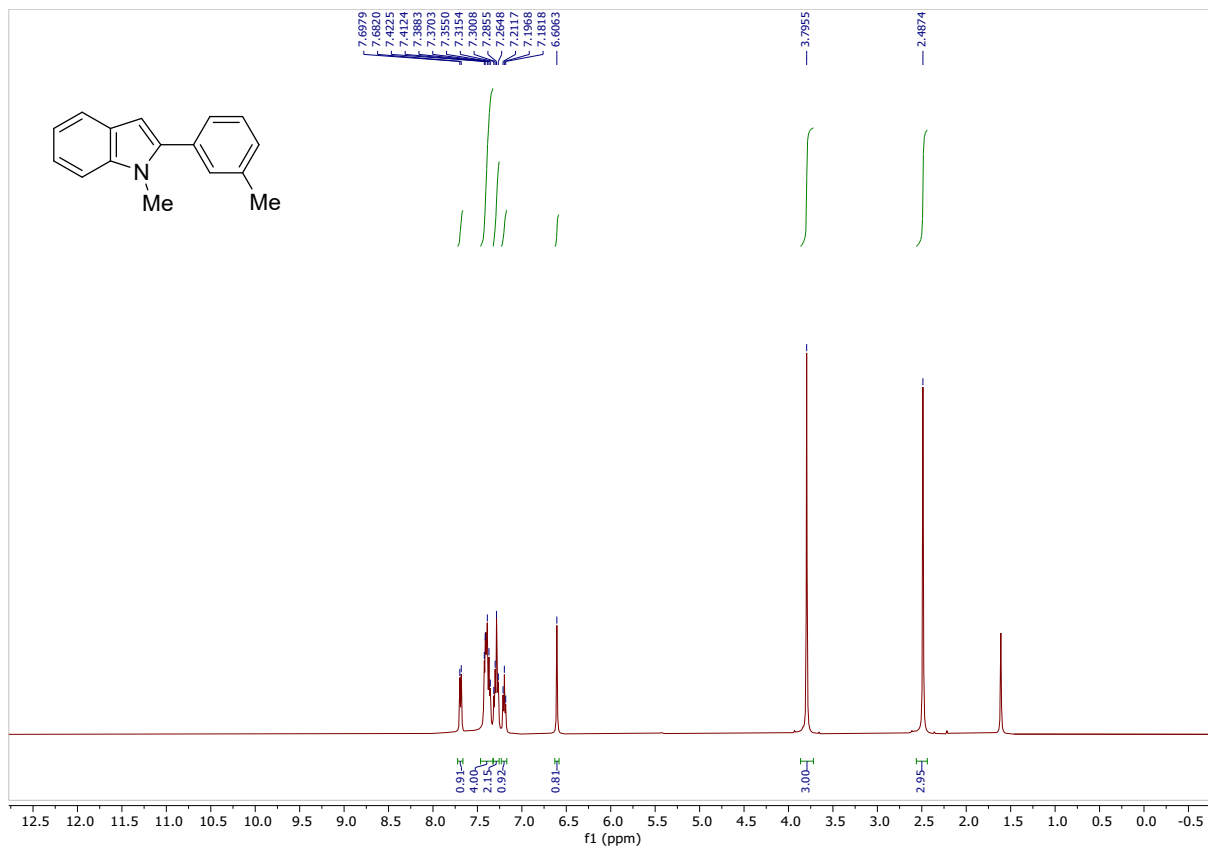
$^1\text{H}$  NMR spectrum of compound **3p**, ( $\text{CDCl}_3$ , 500 MHz).



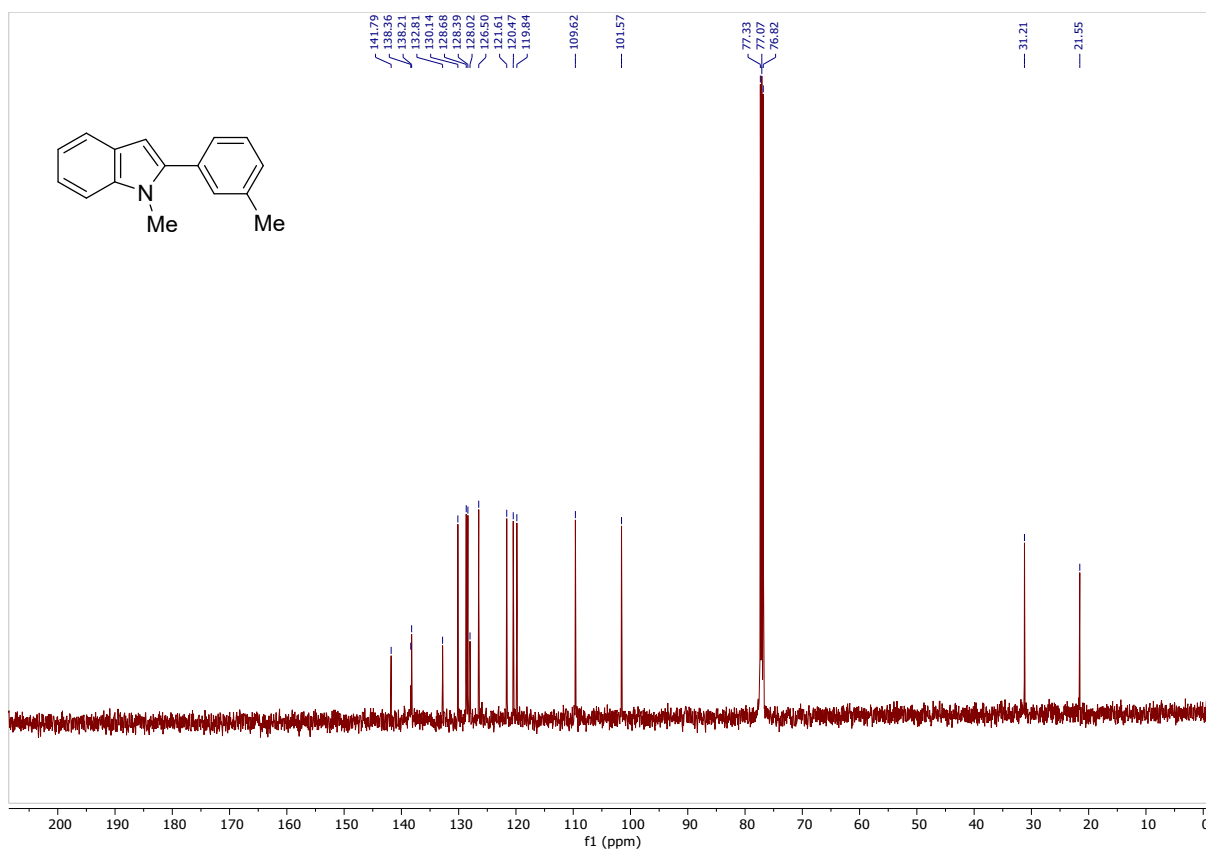
$^{13}\text{C}$  NMR spectrum of compound **3p**, ( $\text{CDCl}_3$ , 125 MHz).



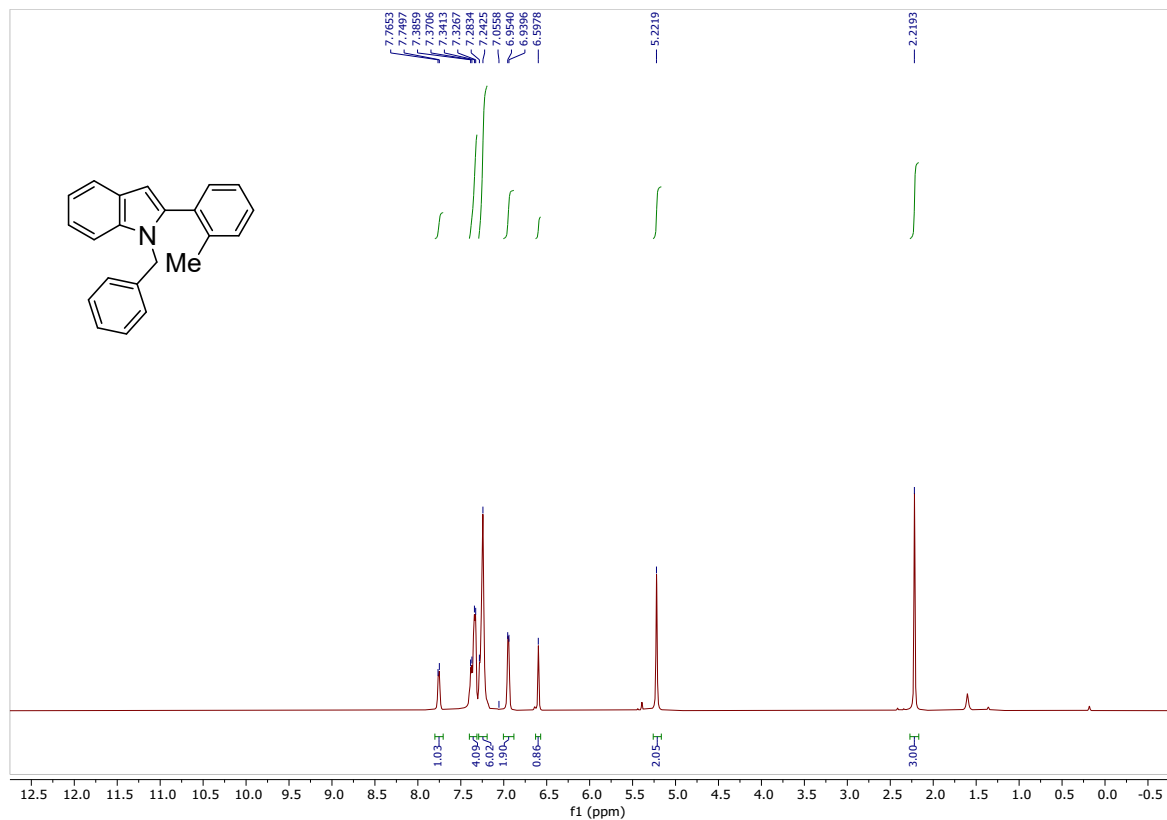
$^1\text{H}$  NMR spectrum of compound **3q**, ( $\text{CDCl}_3$ , 500 MHz).



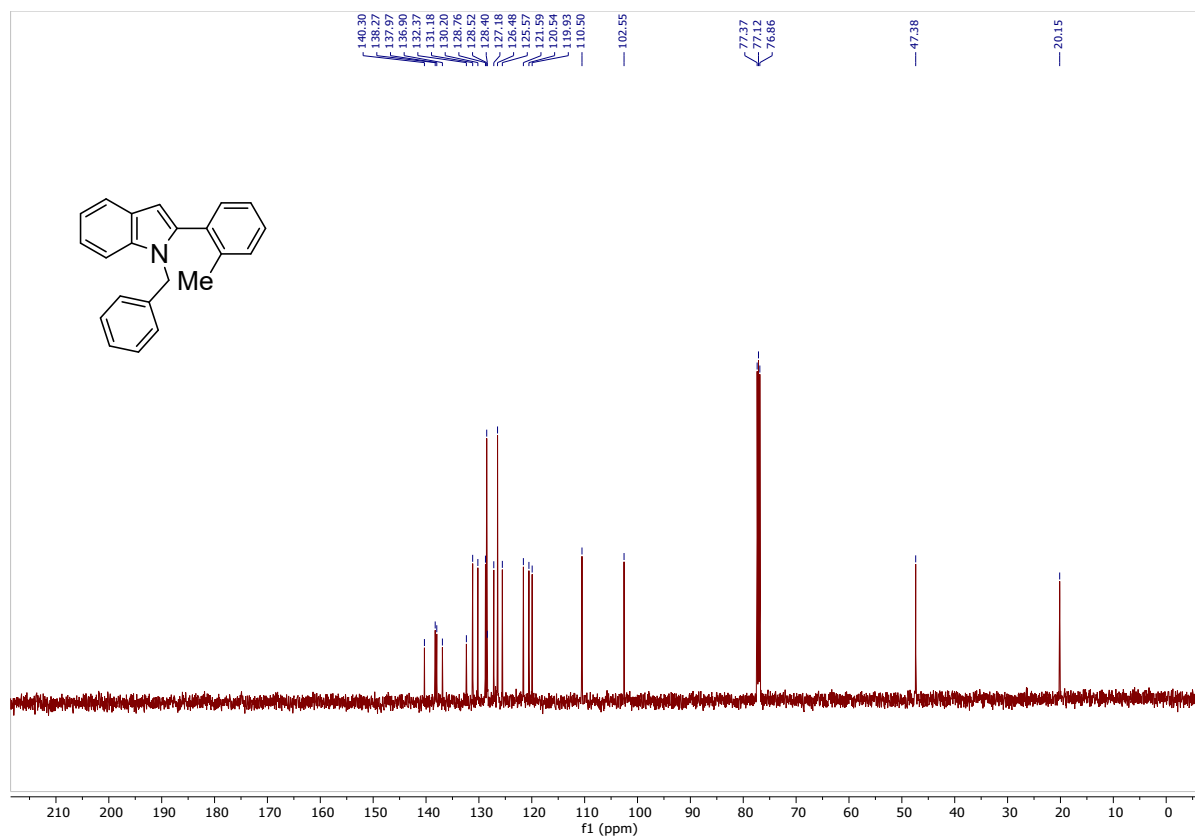
$^{13}\text{C}$  NMR spectrum of compound **3q**, ( $\text{CDCl}_3$ , 125 MHz).



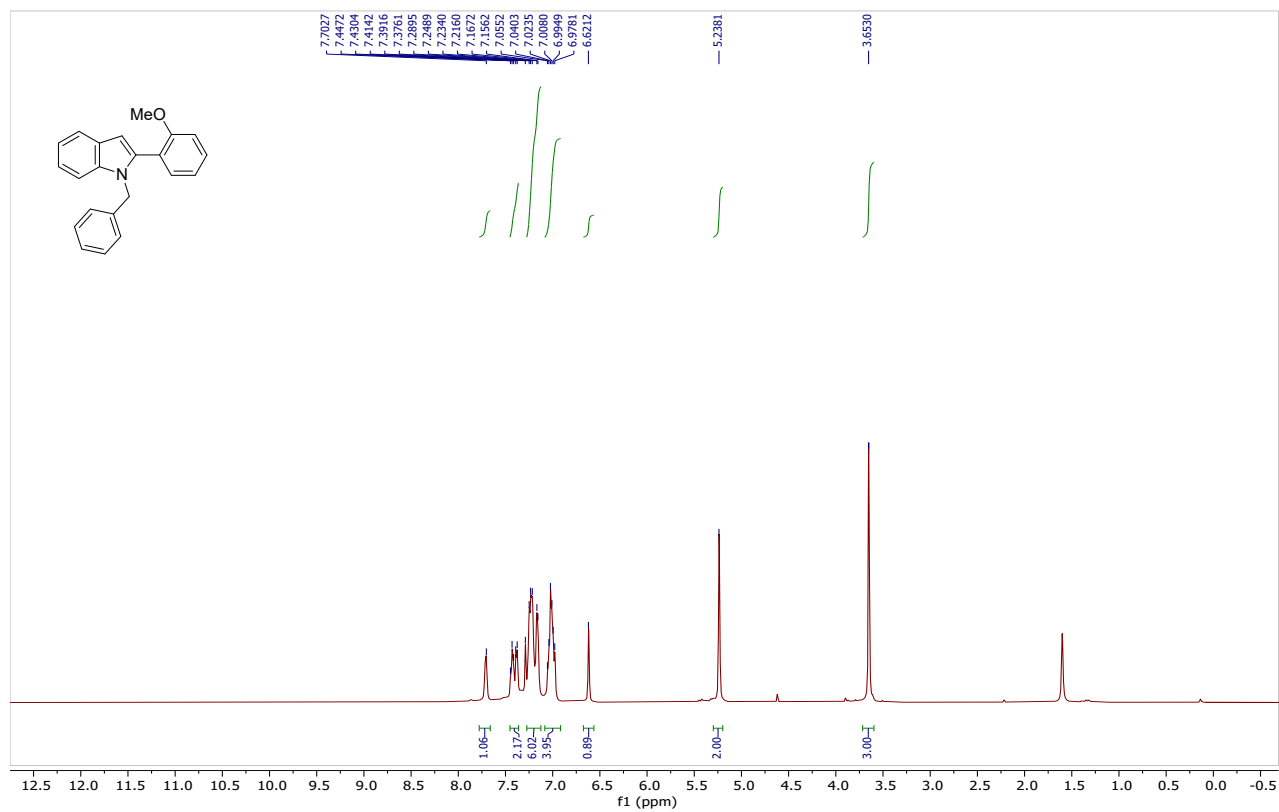
$^1\text{H}$  NMR spectrum of compound **3r**, ( $\text{CDCl}_3$ , 500 MHz).



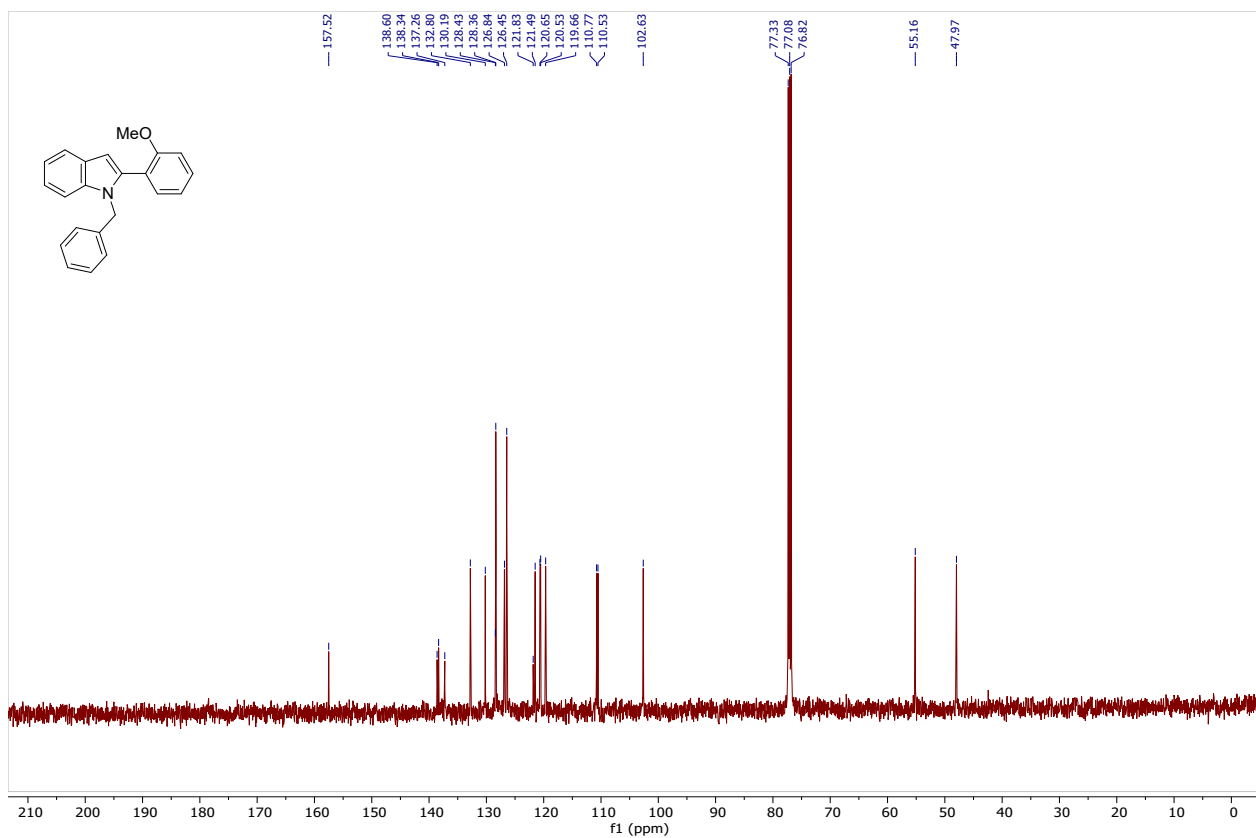
$^{13}\text{C}$  NMR spectrum of compound **3r**, ( $\text{CDCl}_3$ , 125 MHz).



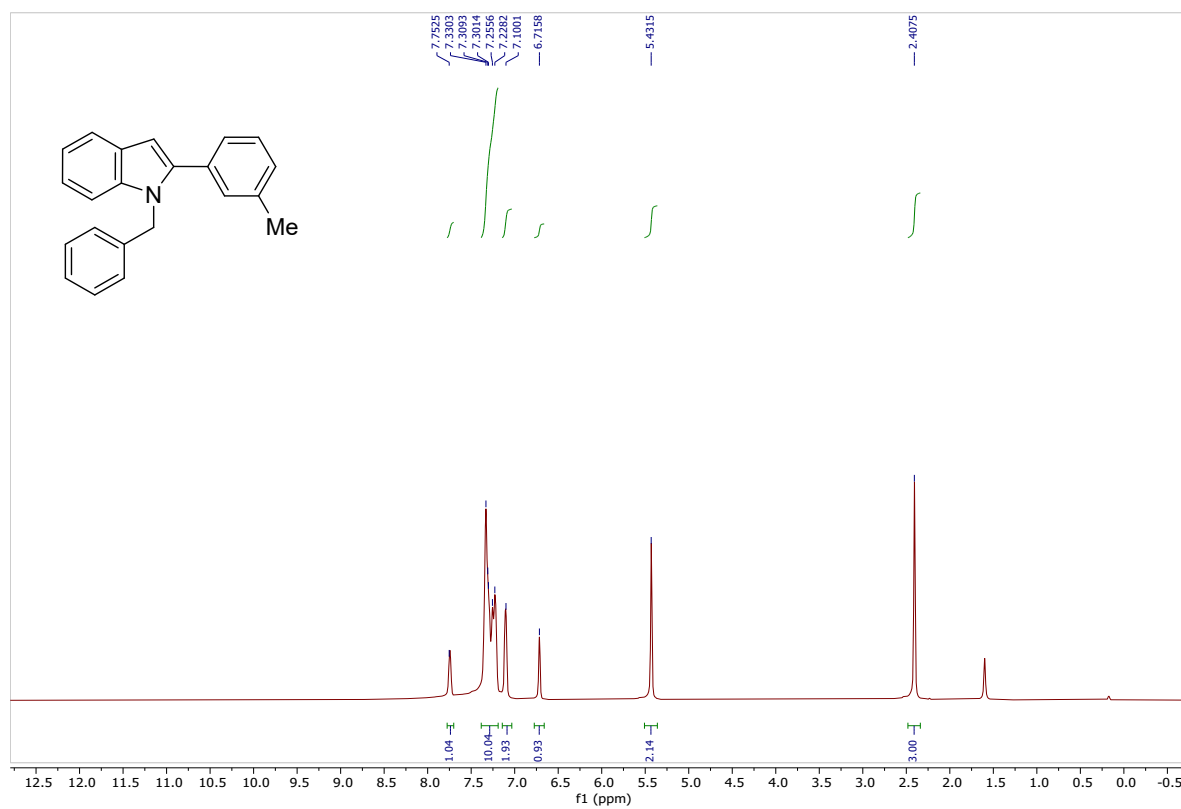
<sup>1</sup>H NMR spectrum of compound **3s**, (CDCl<sub>3</sub>, 500 MHz).



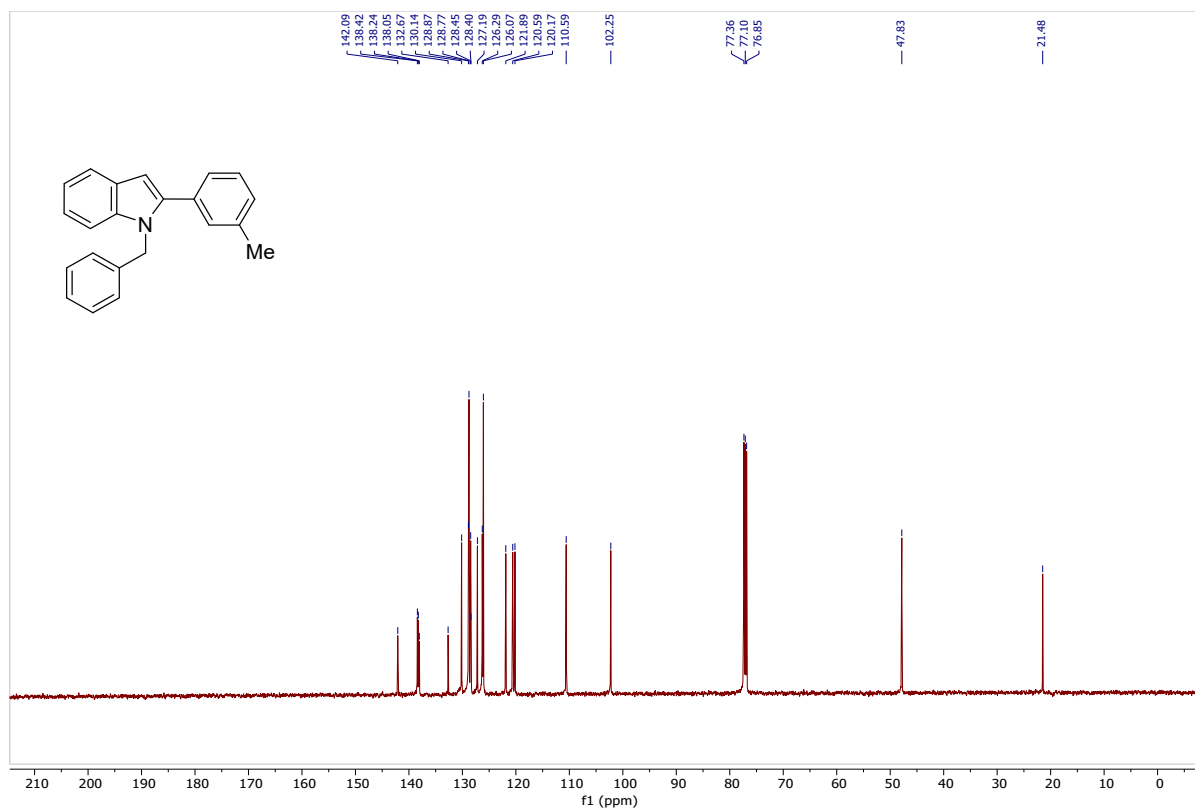
<sup>13</sup>C NMR spectrum of compound **3s**, (CDCl<sub>3</sub>, 125 MHz).



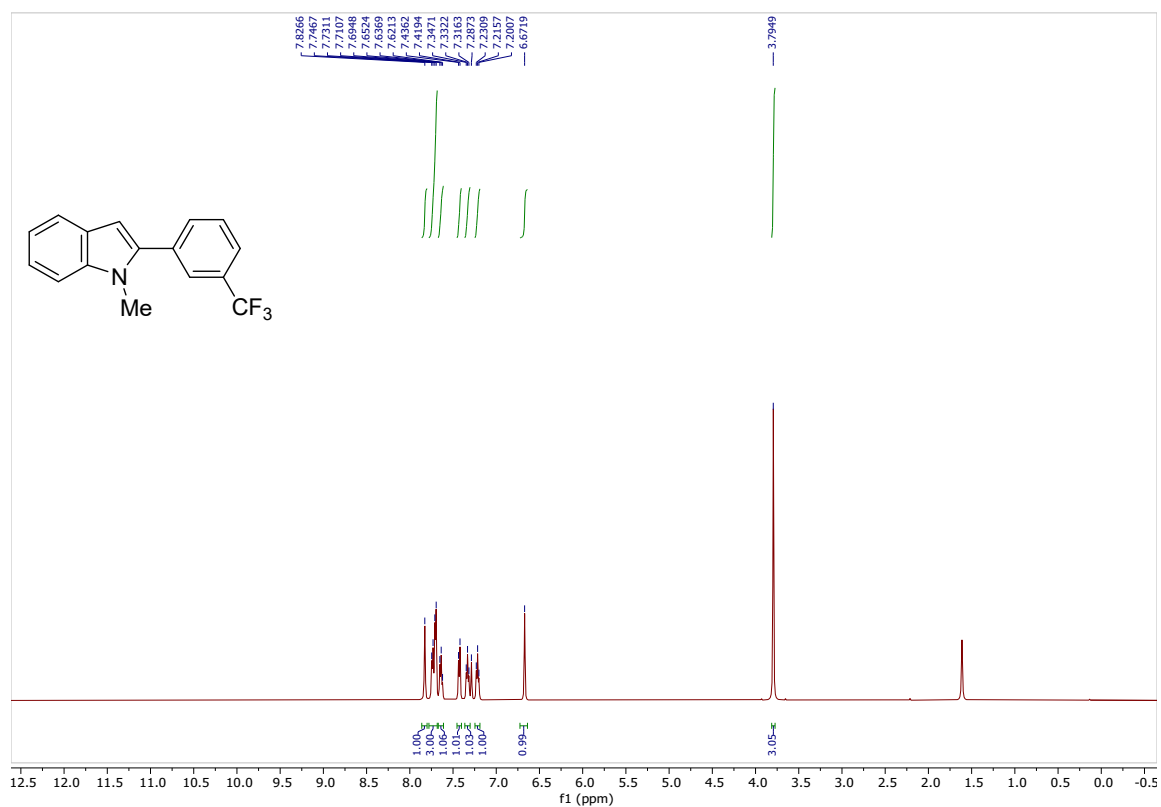
<sup>1</sup>H NMR spectrum of compound **3t**, (CDCl<sub>3</sub>, 500 MHz)



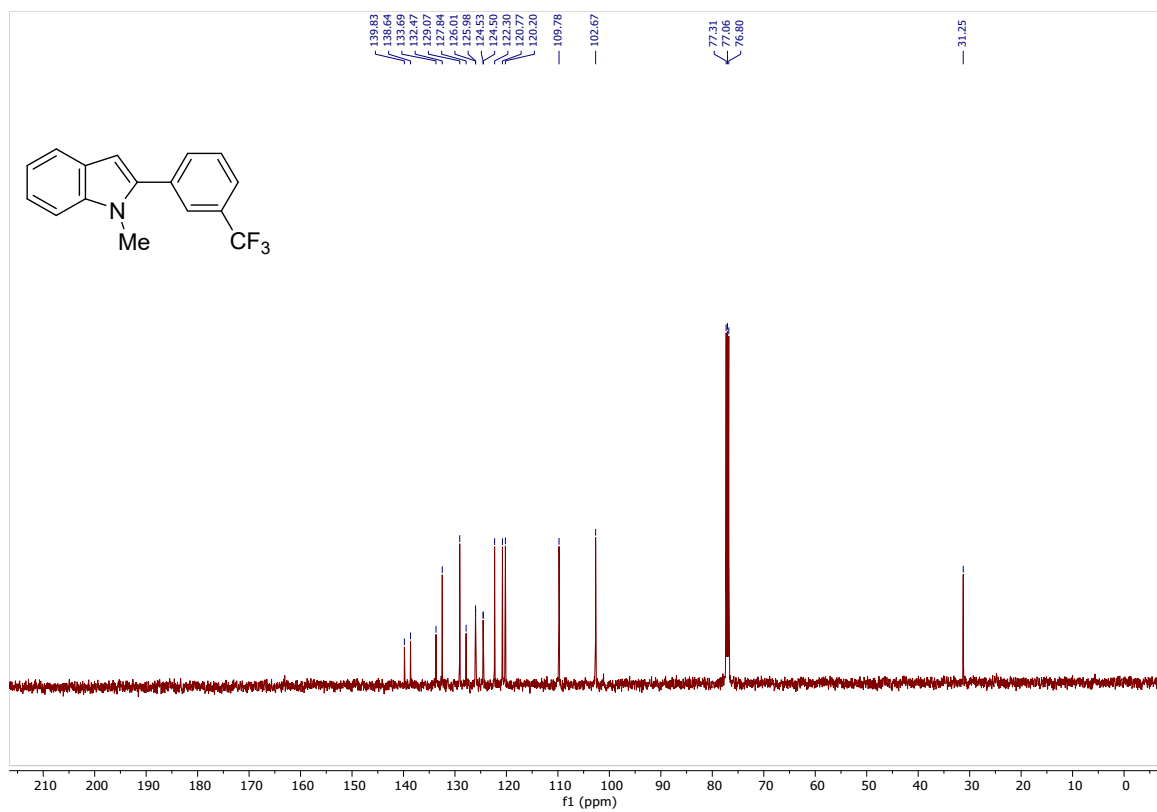
<sup>13</sup>C NMR spectrum of compound **3t**, (CDCl<sub>3</sub>, 125 MHz).



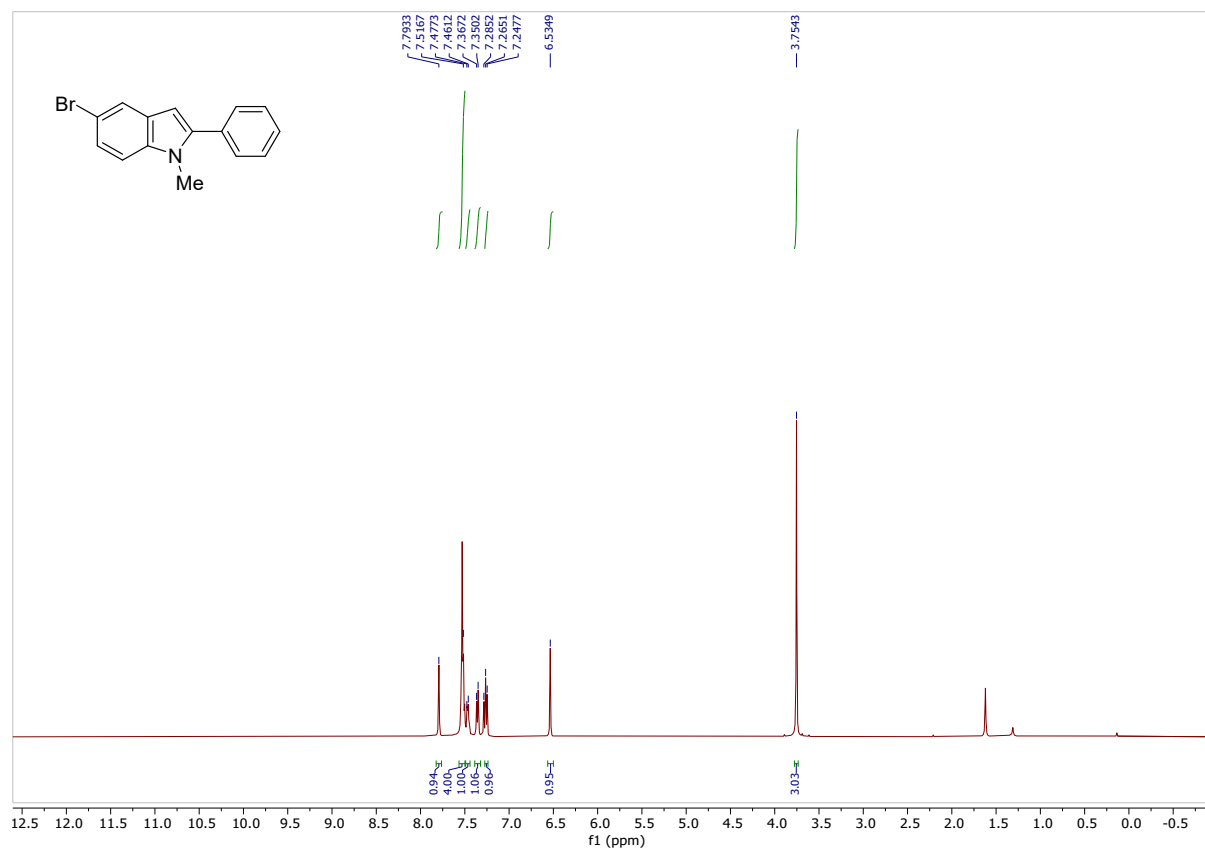
<sup>1</sup>H NMR spectrum of compound **3u**, (CDCl<sub>3</sub>, 500 MHz)



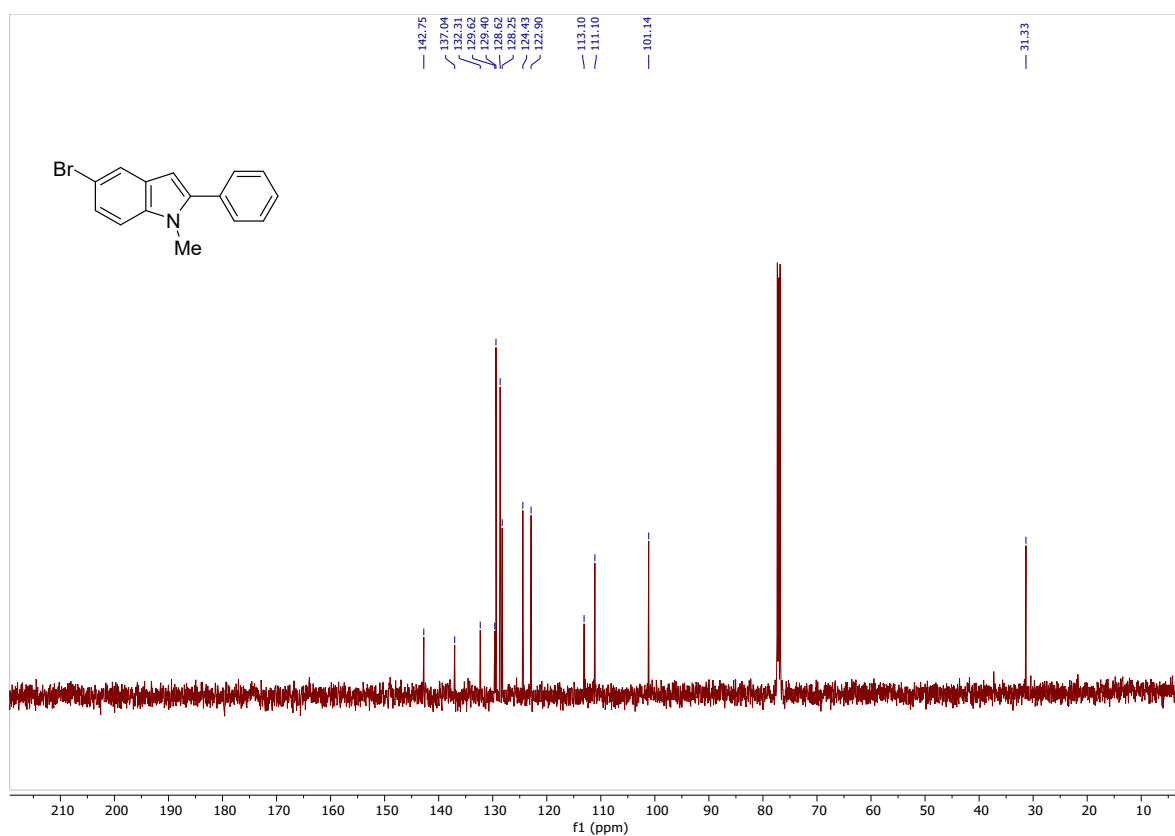
<sup>13</sup>C NMR spectrum of compound **3u**, (CDCl<sub>3</sub>, 125 MHz).



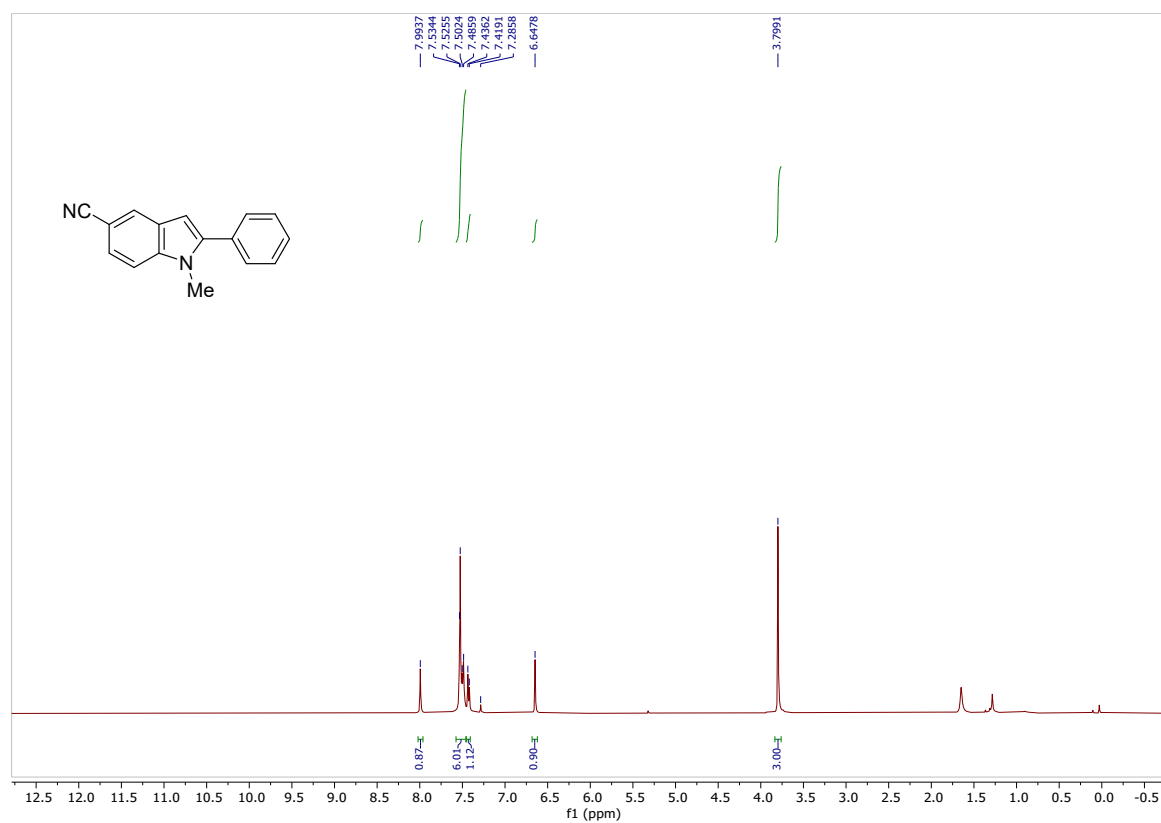
<sup>1</sup>H NMR spectrum of compound **3v**, (CDCl<sub>3</sub>, 500 MHz)



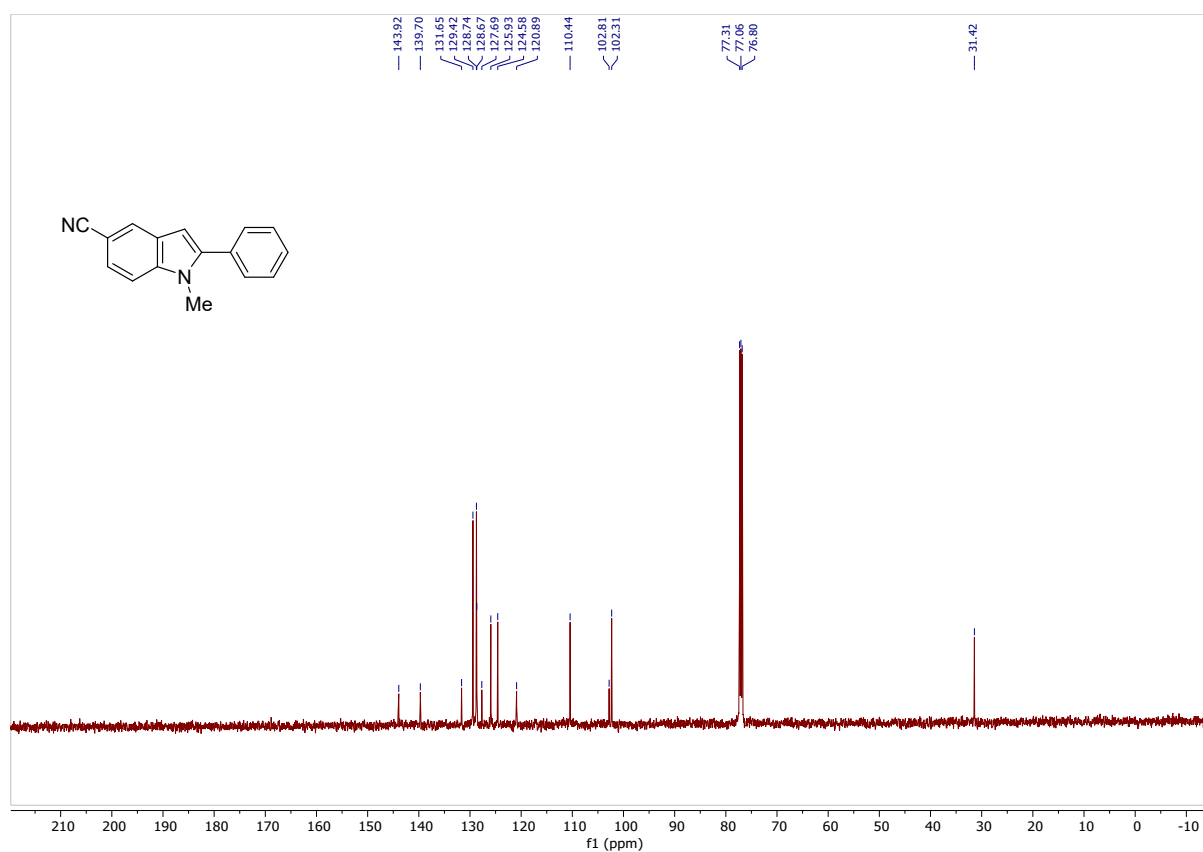
$^{13}\text{C}$  NMR spectrum of compound **3v**, ( $\text{CDCl}_3$ , 125 MHz).



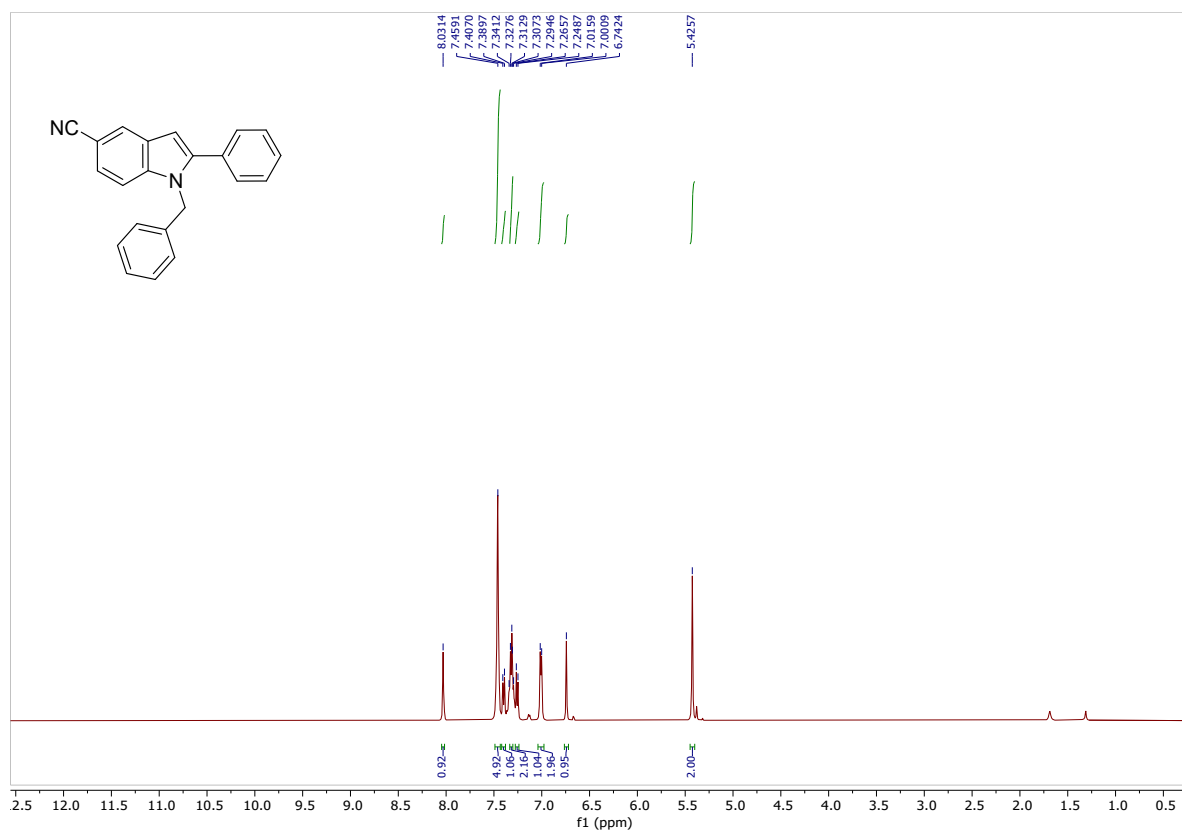
$^1\text{H}$  NMR spectrum of compound **3w**, ( $\text{CDCl}_3$ , 500 MHz).



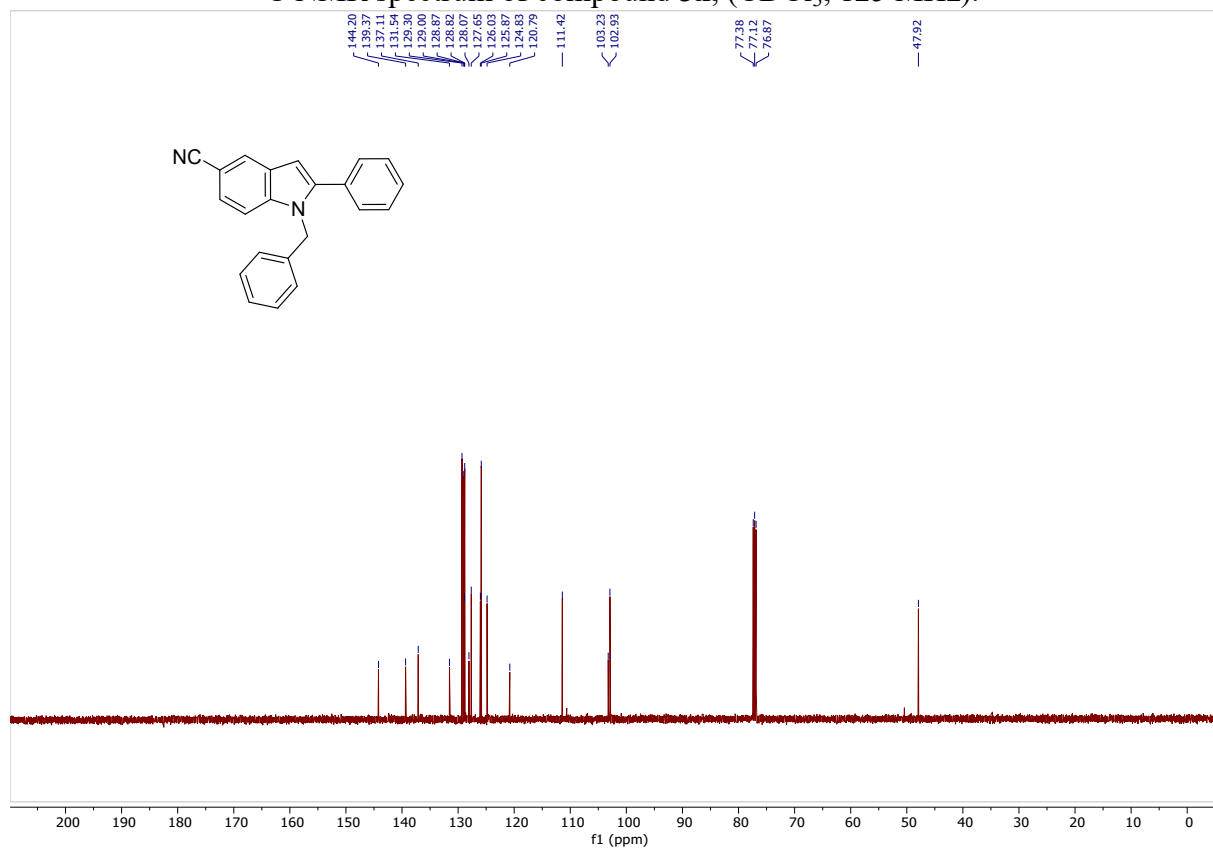
$^{13}\text{C}$  NMR spectrum of compound **3w**, ( $\text{CDCl}_3$ , 125 MHz).



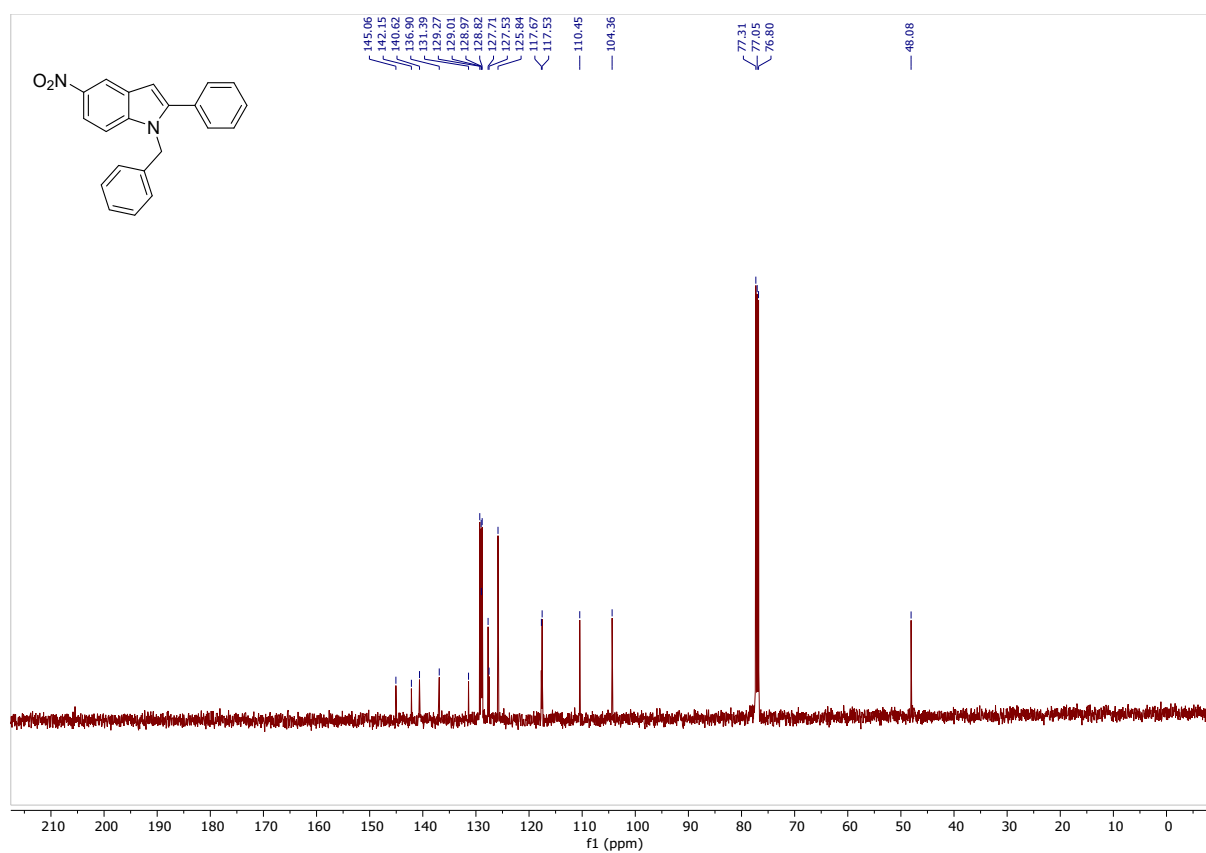
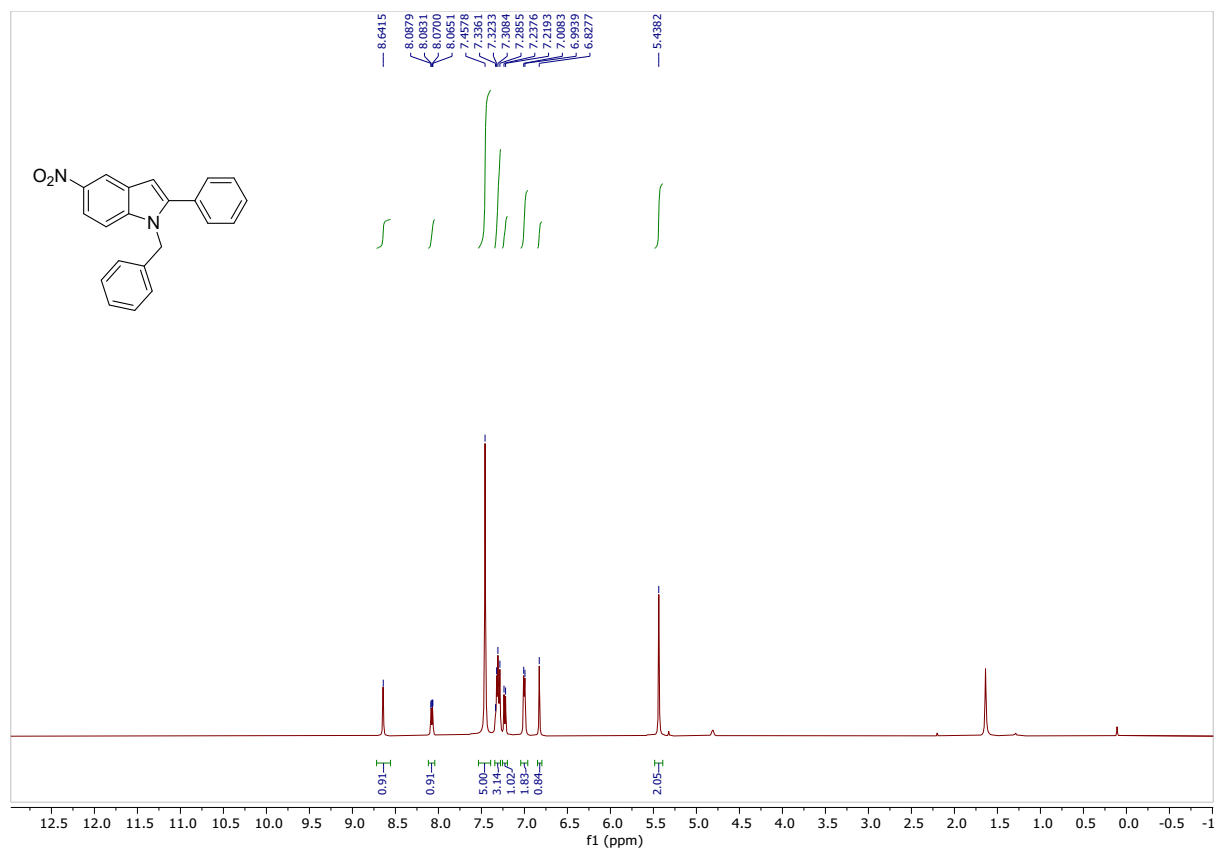
$^1\text{H}$  NMR spectrum of compound **3x**, ( $\text{CDCl}_3$ , 500 MHz).

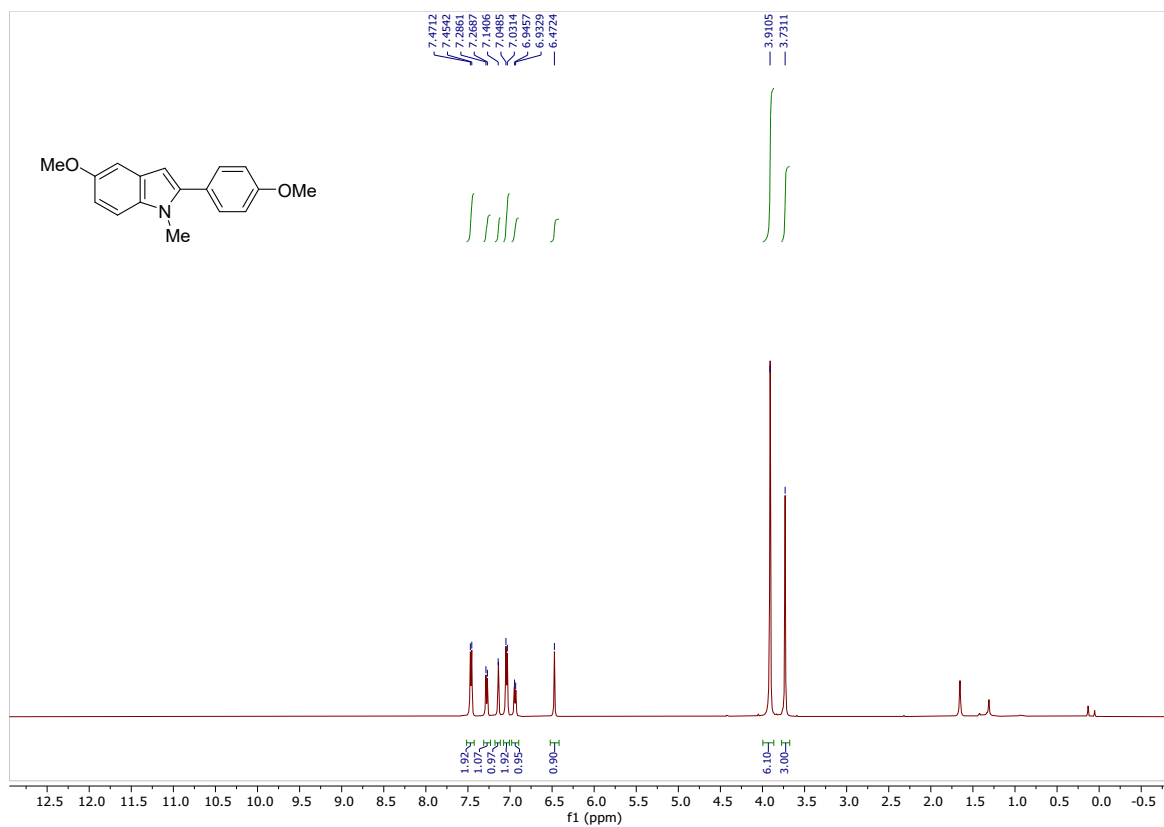


$^{13}\text{C}$  NMR spectrum of compound **3x**, ( $\text{CDCl}_3$ , 125 MHz).

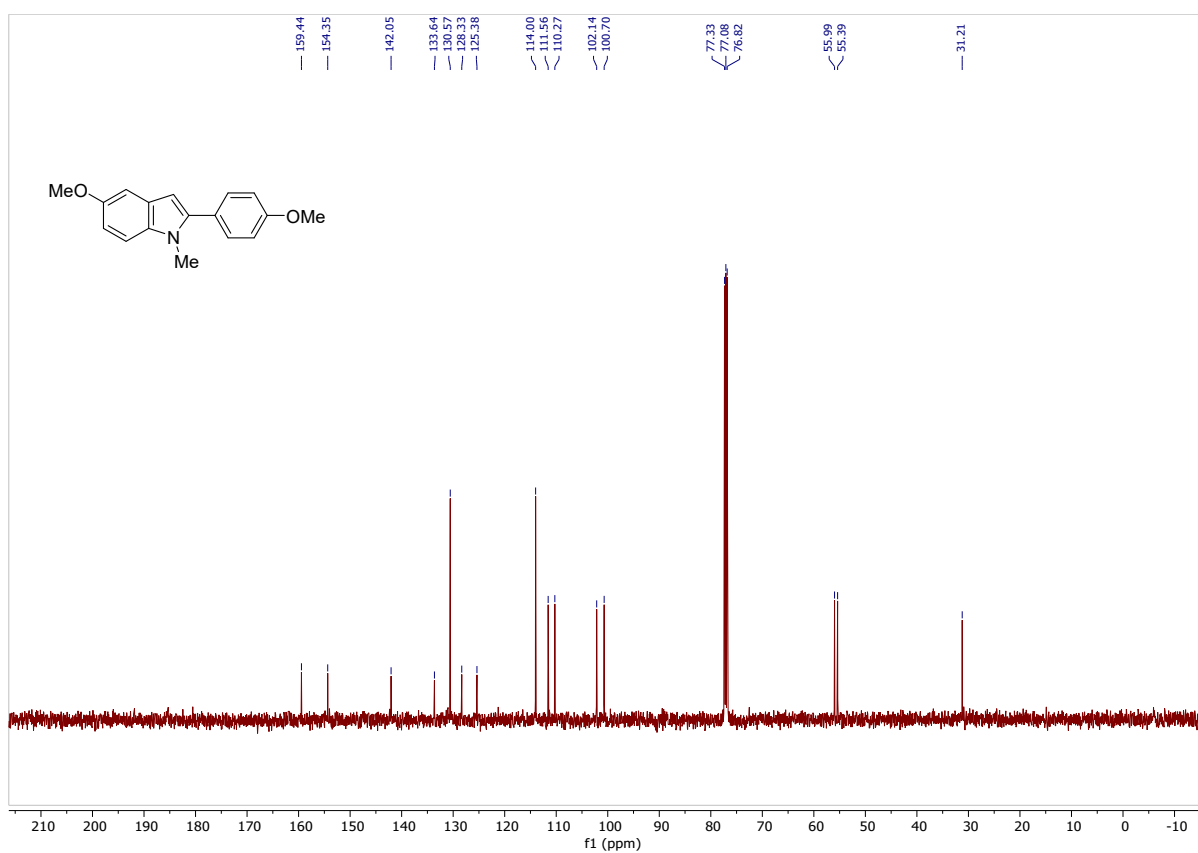


$^1\text{H}$  NMR spectrum of compound **3y**, ( $\text{CDCl}_3$ , 500 MHz).

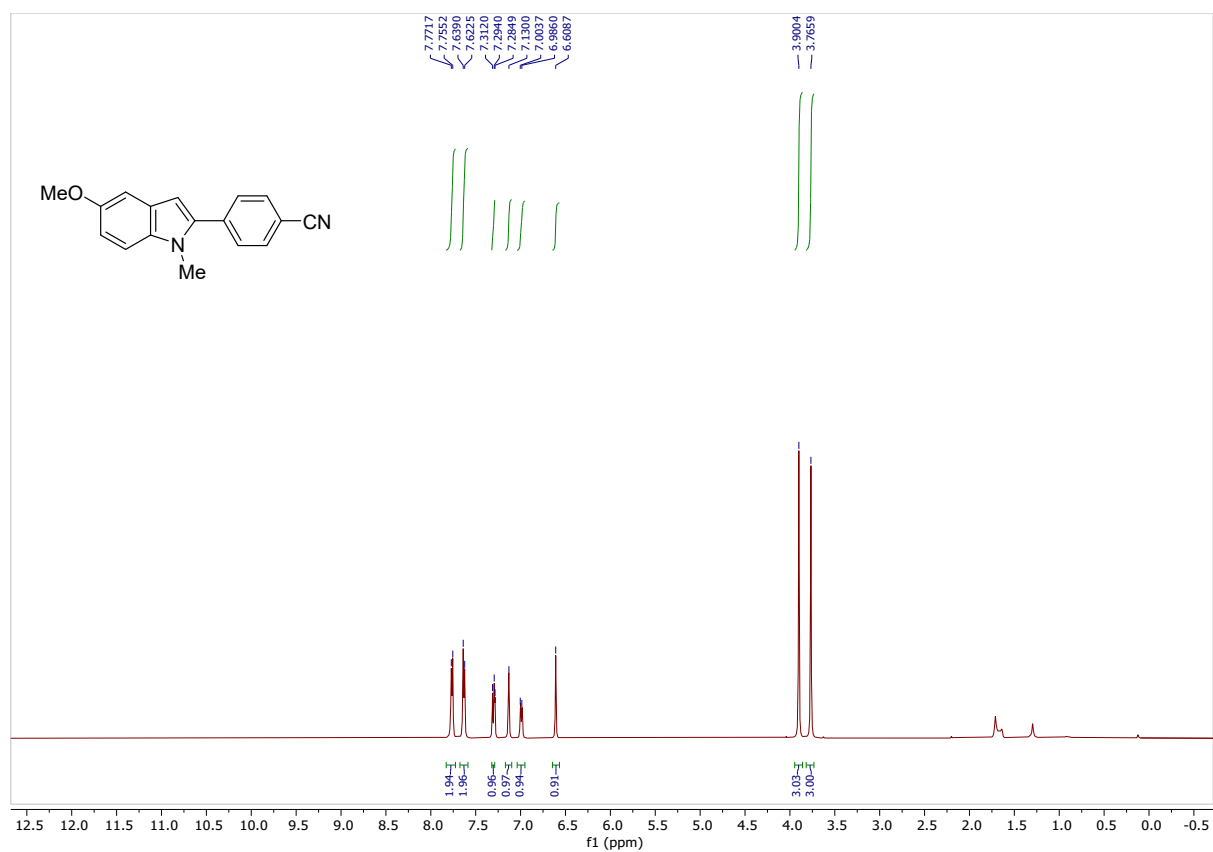




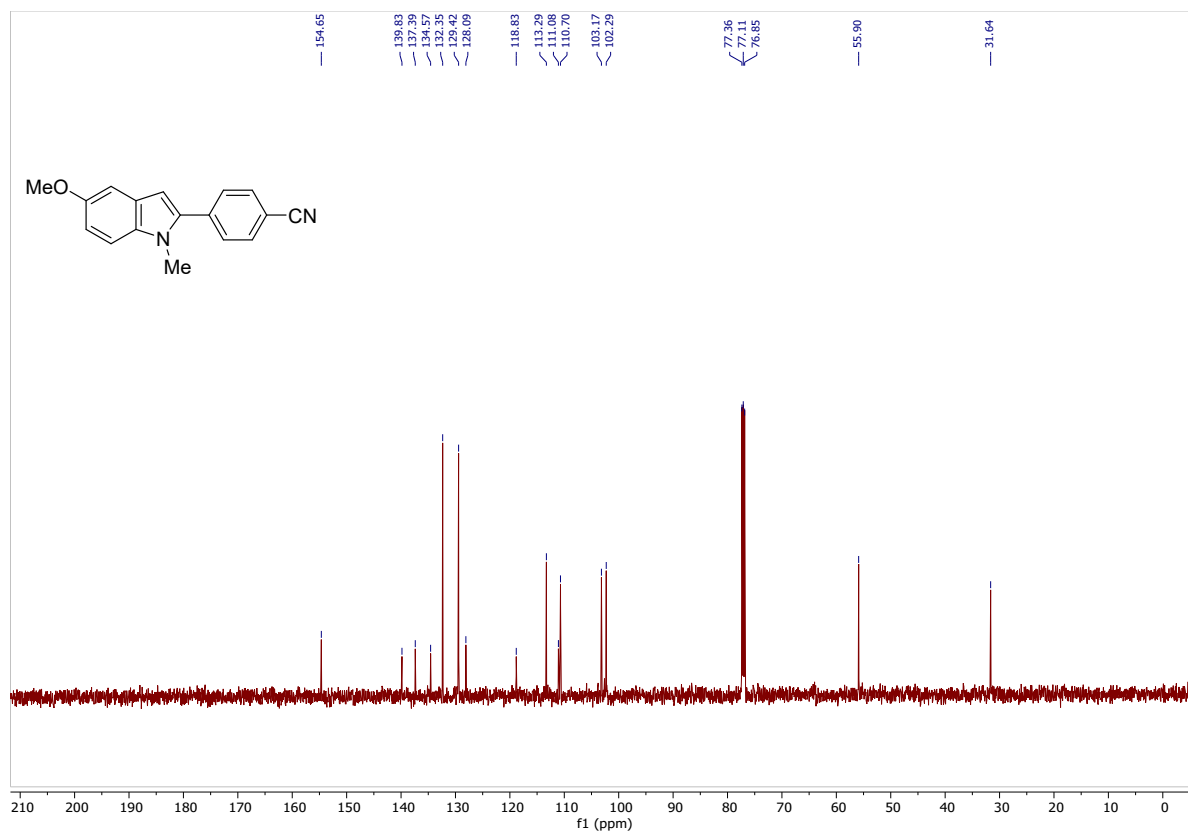
$^{13}\text{C}$  NMR spectrum of compound **3z**, (CDCl<sub>3</sub>, 125 MHz).



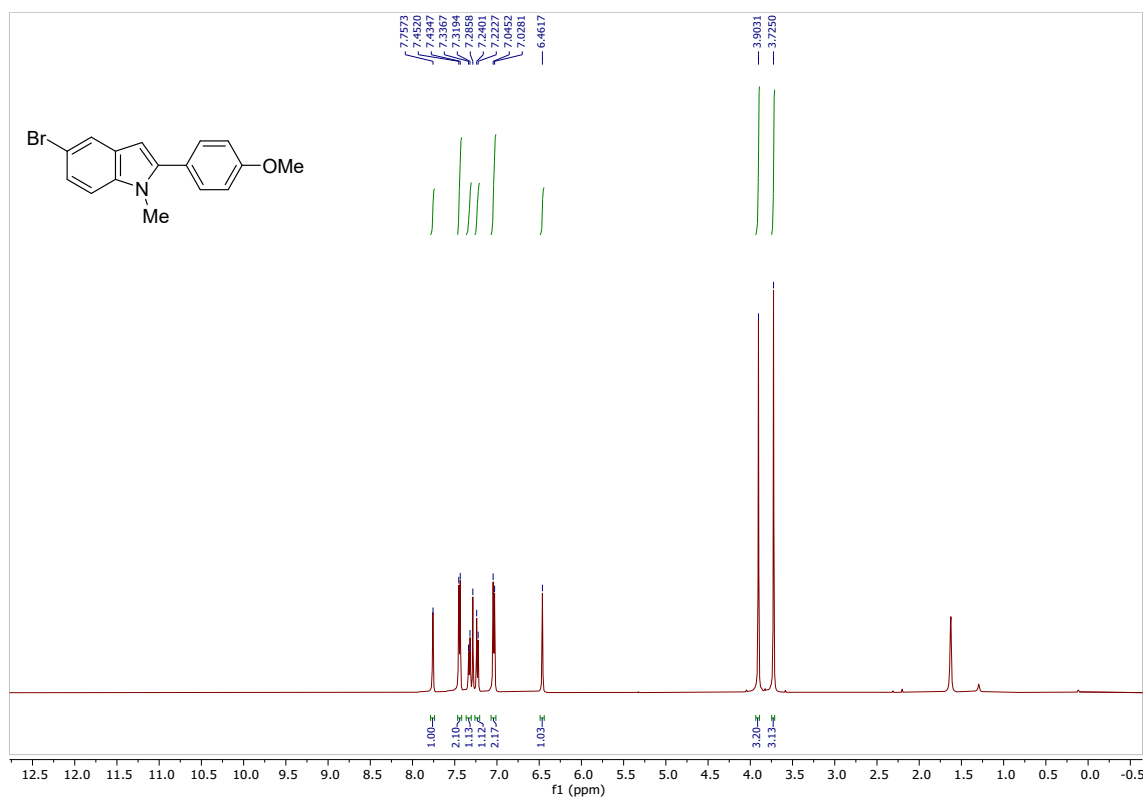
$^1\text{H}$  NMR spectrum of compound **3aa**, (CDCl<sub>3</sub>, 500 MHz).



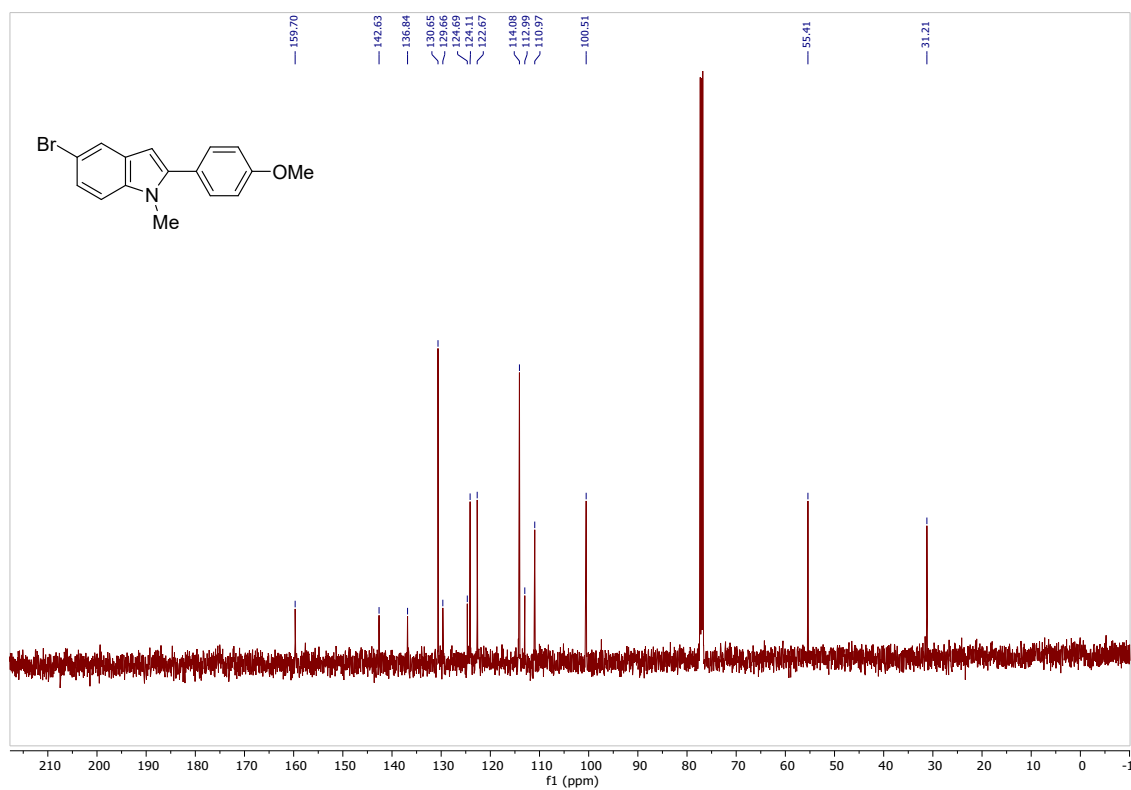
<sup>13</sup>C NMR spectrum of compound **3aa**, (CDCl<sub>3</sub>, 125 MHz).



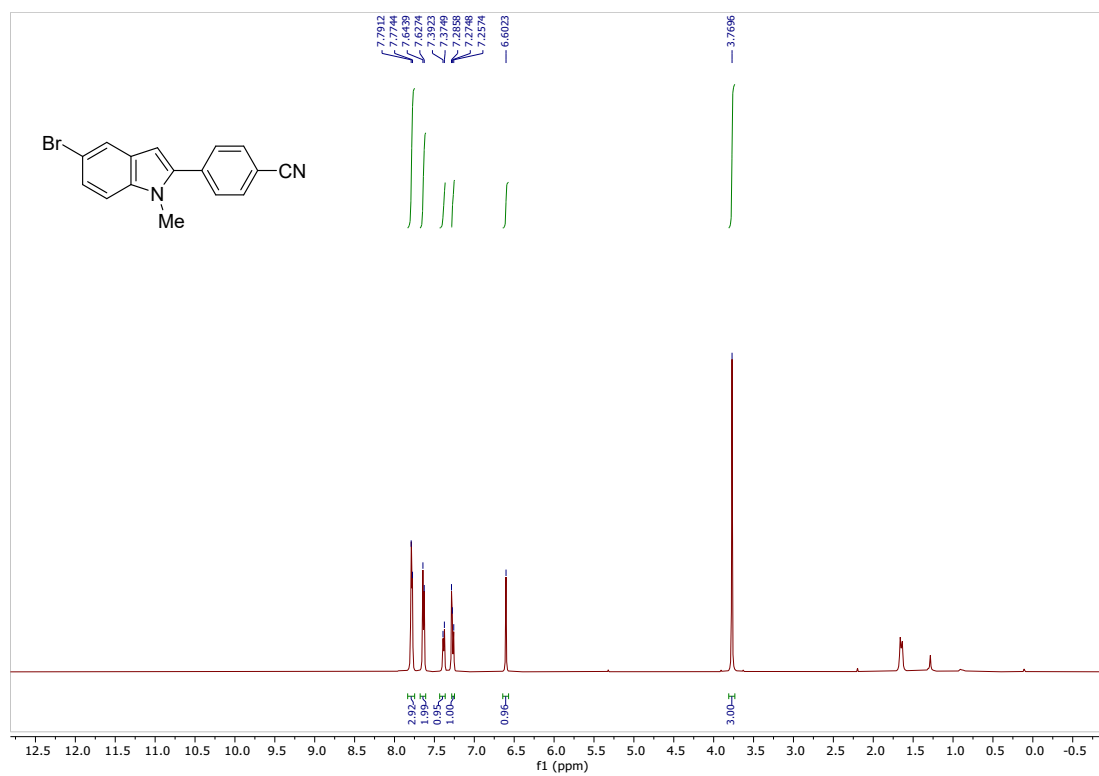
$^1\text{H}$  NMR spectrum of compound **3ab**, ( $\text{CDCl}_3$ , 500 MHz).



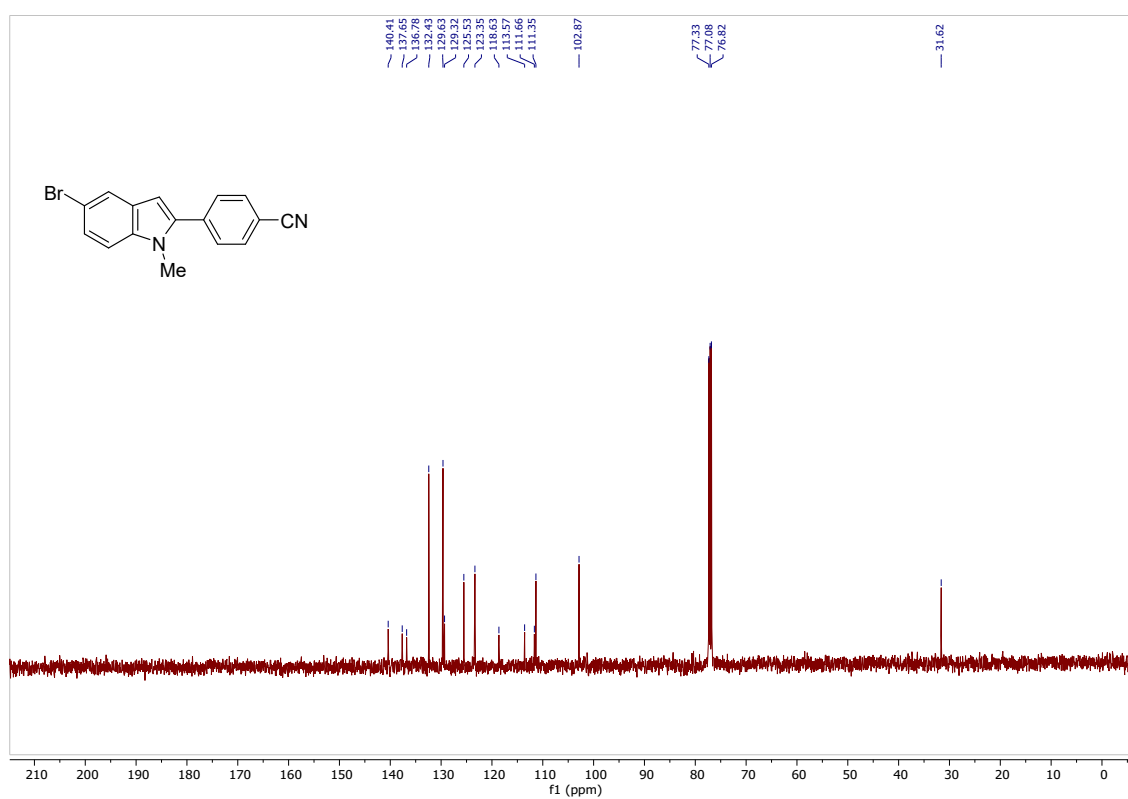
$^{13}\text{C}$  NMR spectrum of compound **3ab**, ( $\text{CDCl}_3$ , 125 MHz).



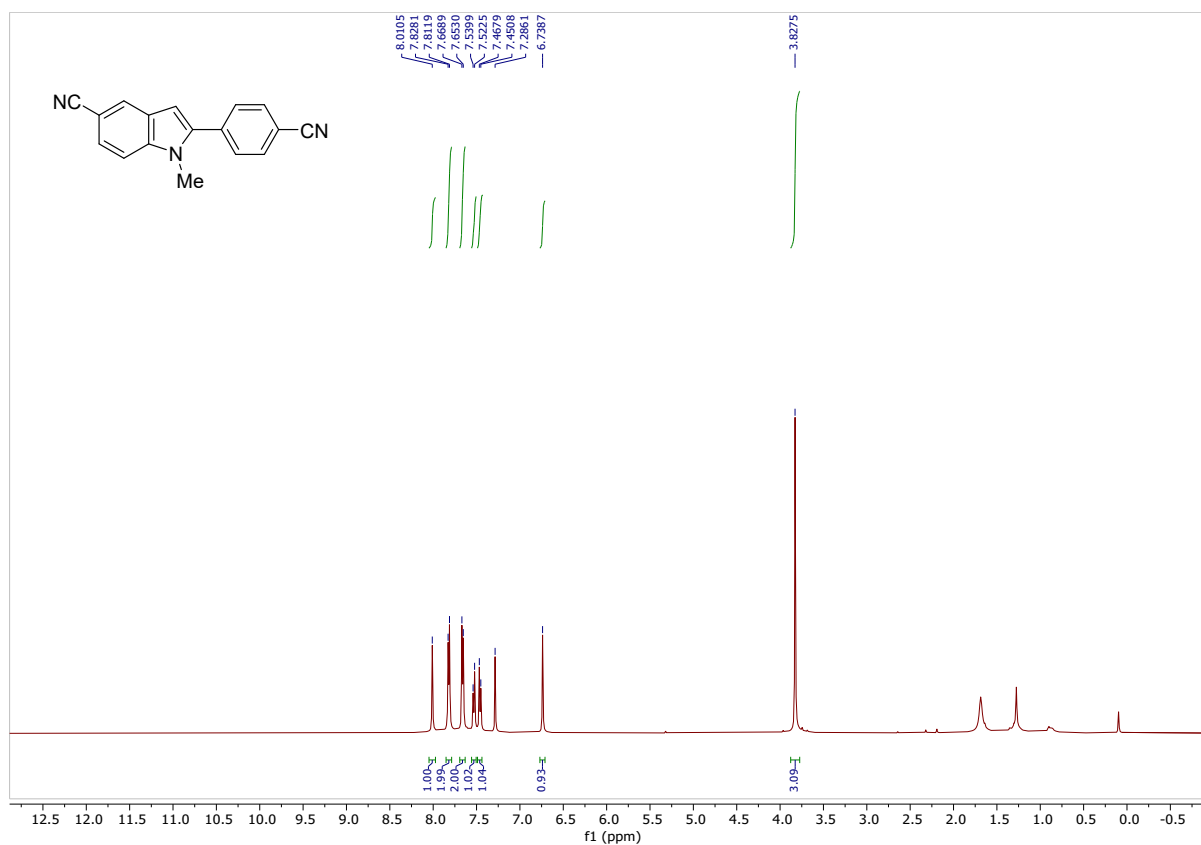
$^1\text{H}$  NMR spectrum of compound **3ac**, ( $\text{CDCl}_3$ , 500 MHz).



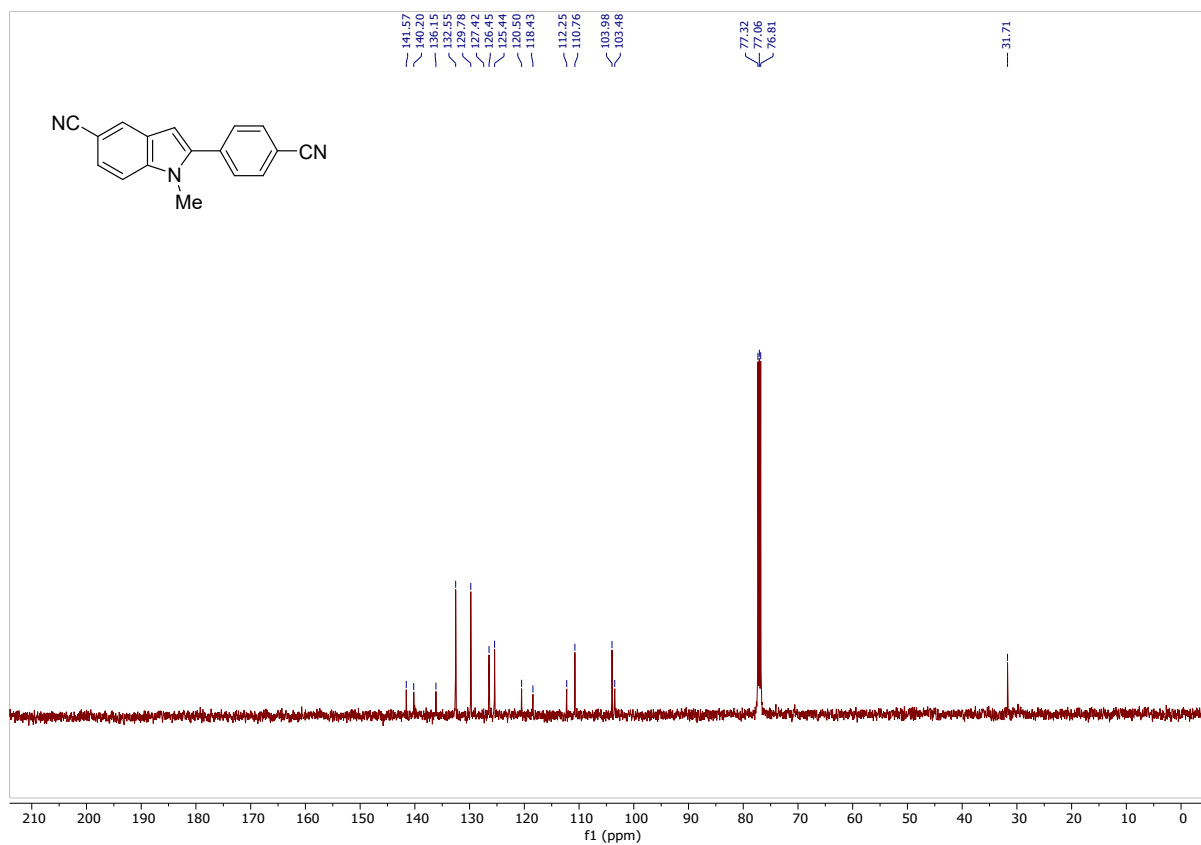
$^{13}\text{C}$  NMR spectrum of compound **3ac**, ( $\text{CDCl}_3$ , 125 MHz).



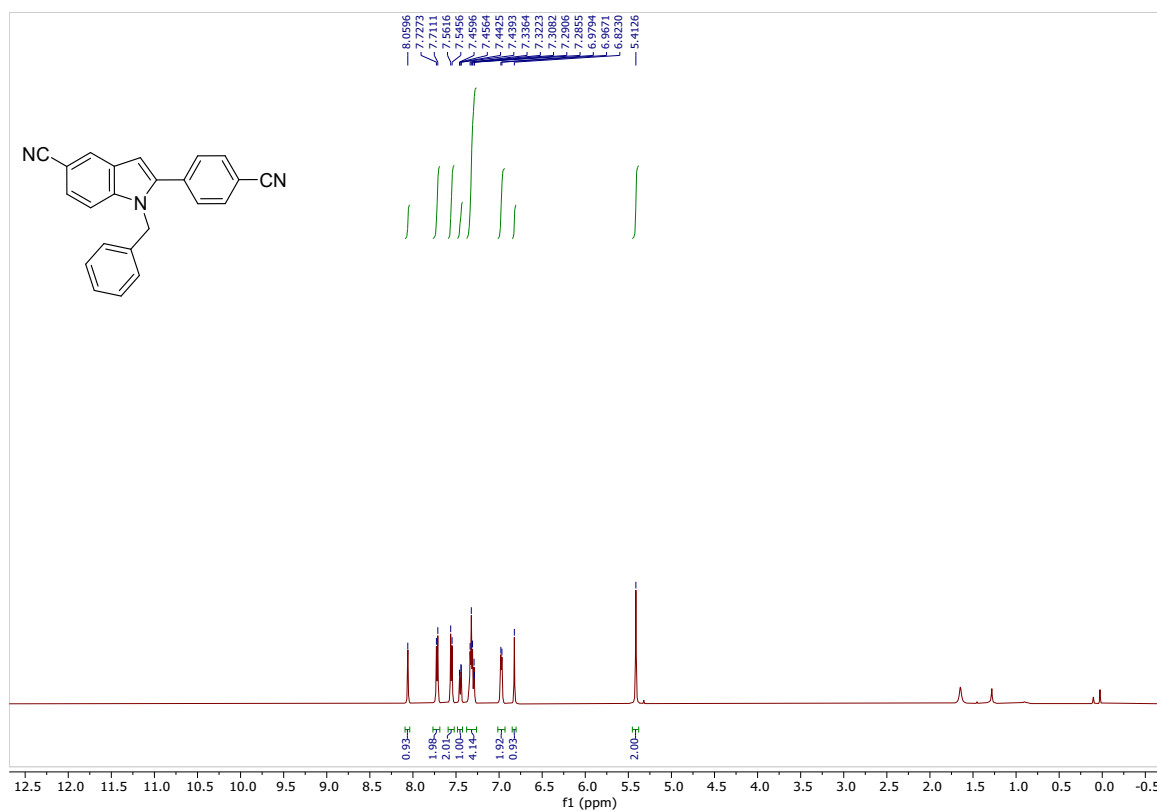
$^1\text{H}$  NMR spectrum of compound **3ad**, ( $\text{CDCl}_3$ , 500 MHz).



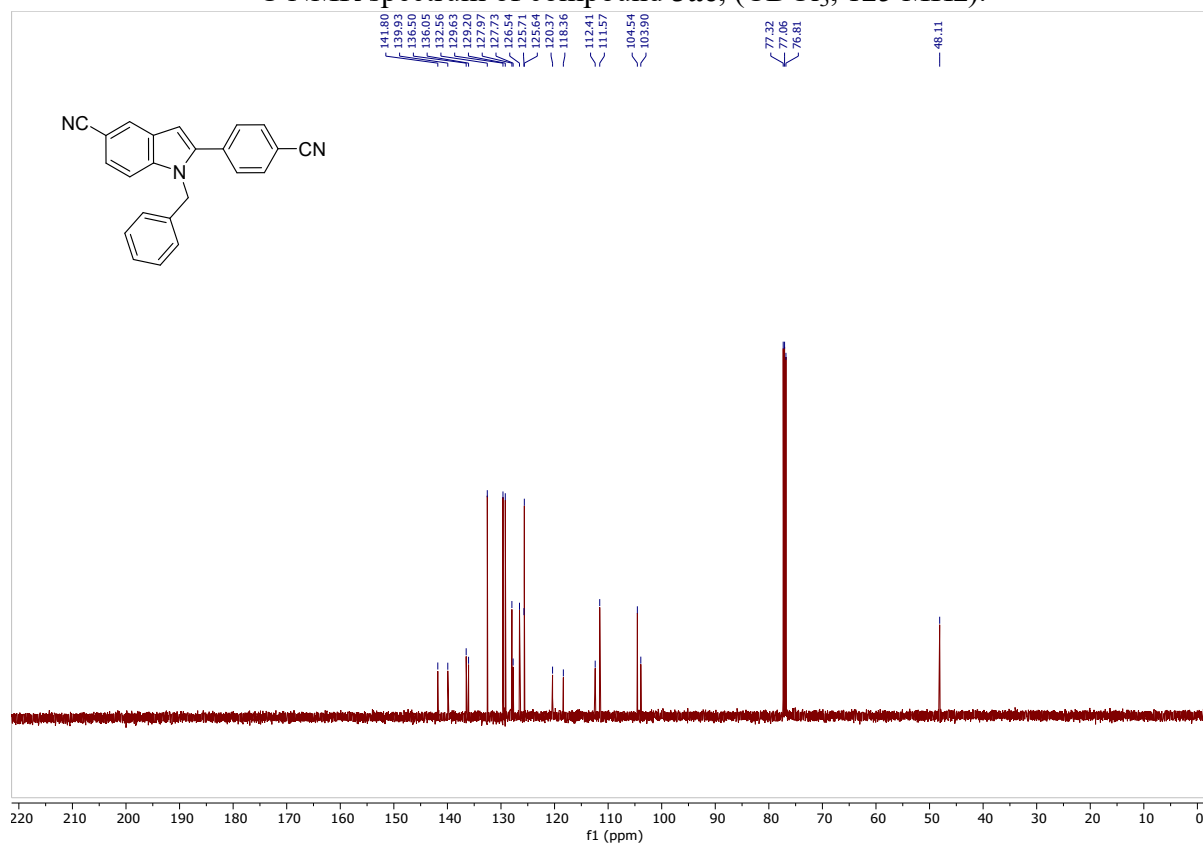
$^{13}\text{C}$  NMR spectrum of compound **3ad**, ( $\text{CDCl}_3$ , 125 MHz).



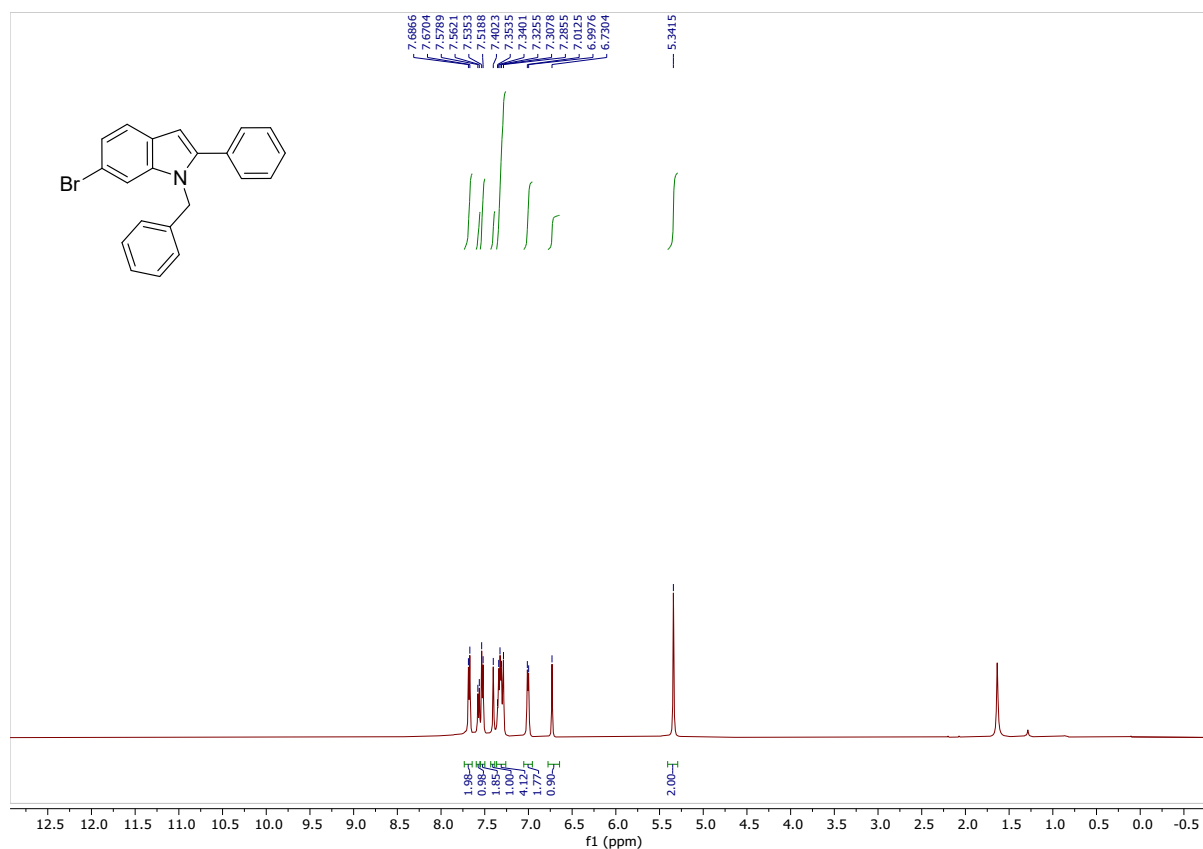
$^1\text{H}$  NMR spectrum of compound **3ae**, ( $\text{CDCl}_3$ , 500 MHz).



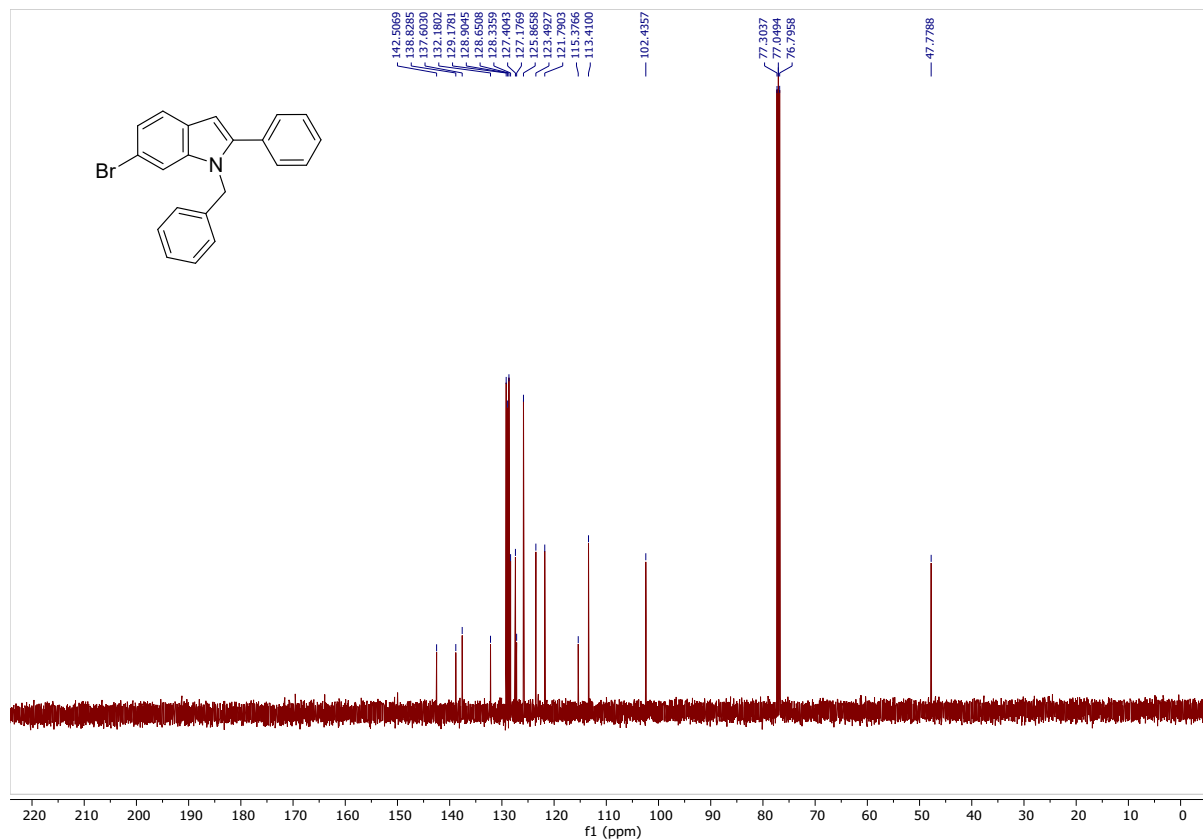
$^{13}\text{C}$  NMR spectrum of compound **3ae**, ( $\text{CDCl}_3$ , 125 MHz).



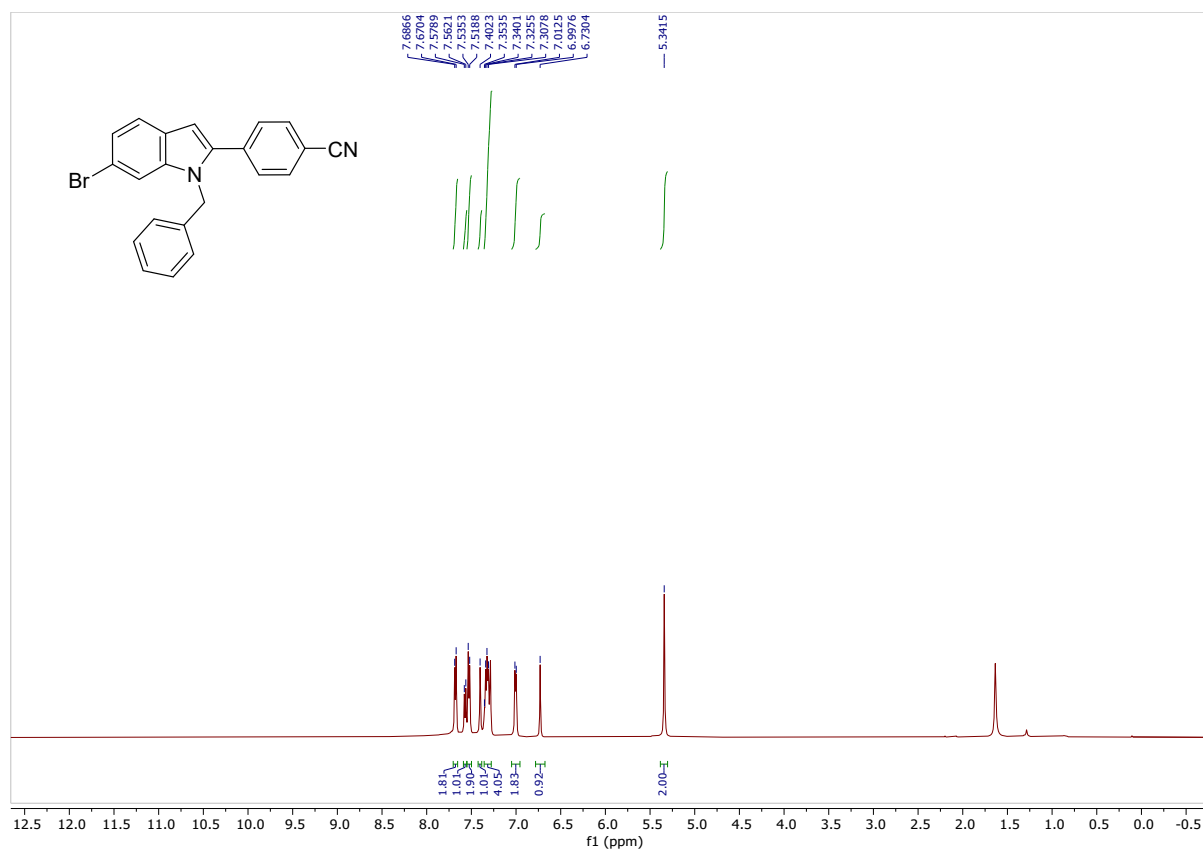
<sup>1</sup>H NMR spectrum of compound **3af**, (CDCl<sub>3</sub>, 500 MHz).



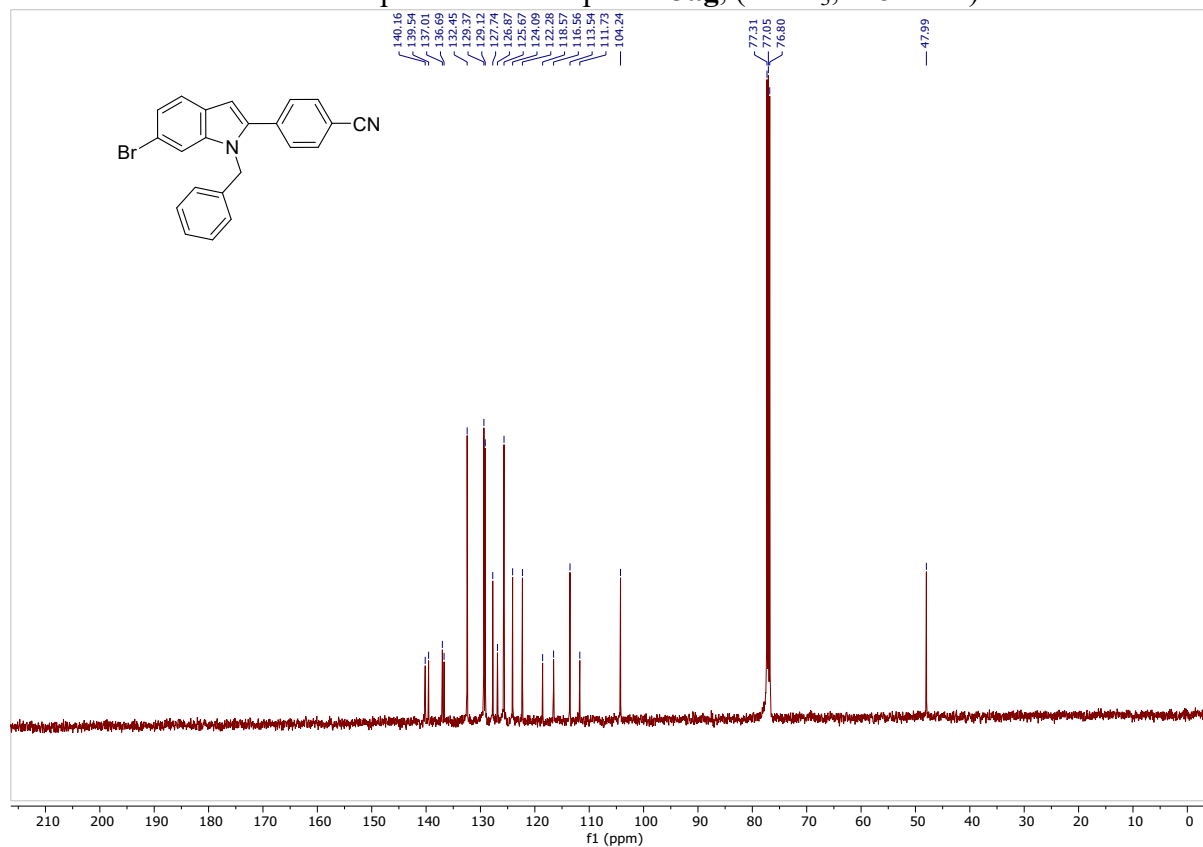
<sup>13</sup>C NMR spectrum of compound **3af**, (CDCl<sub>3</sub>, 125 MHz).



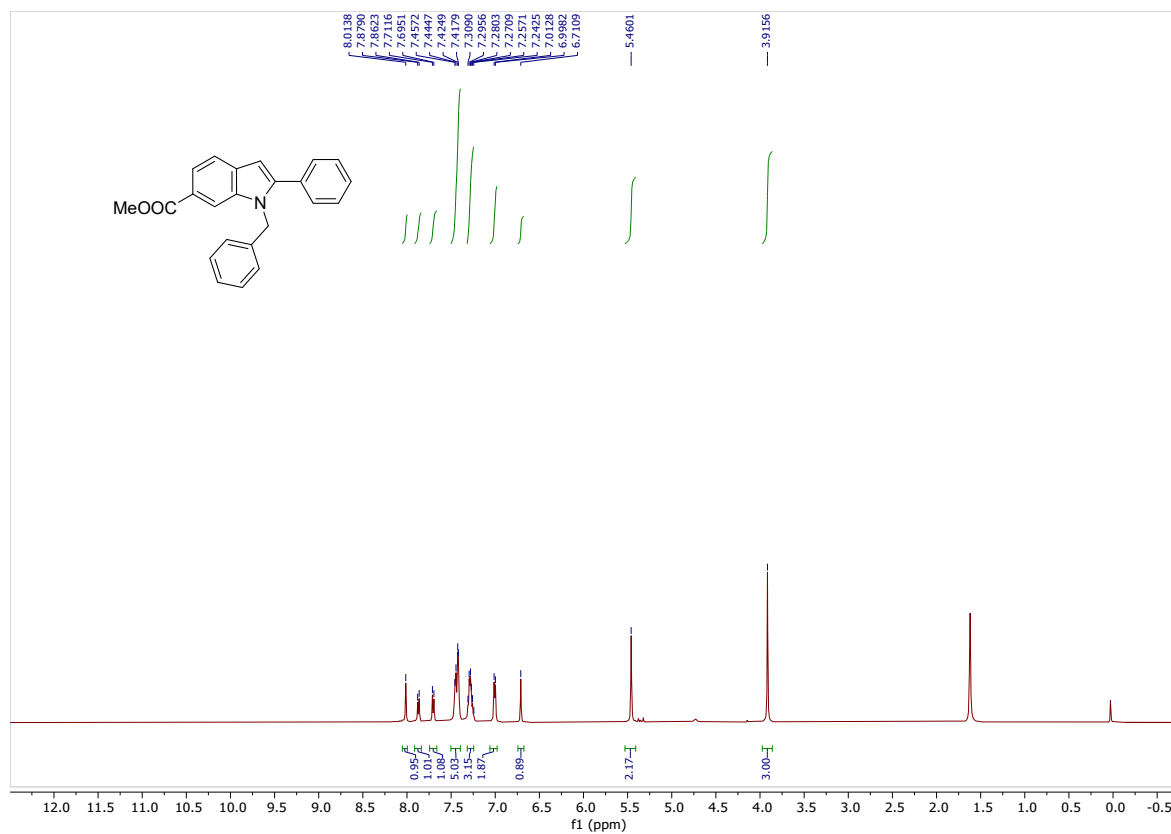
<sup>1</sup>H NMR spectrum of compound **3ag**, (CDCl<sub>3</sub>, 500 MHz).



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



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



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

