

## Electronic Supplementary Information

*for*

### 2-Pyridyl Sulfoxide Directed Pd(II)-Catalyzed Regioselective C2-Arylation/Alkenylation of Indoles

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## 1. General Information

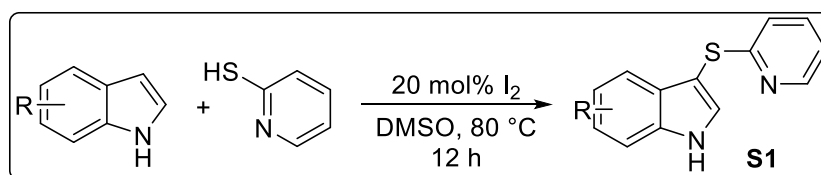
$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at 25 °C on a Bruker Avance III 500 MHz spectrometer operating at 500 MHz for  $^1\text{H}$  NMR, and 125 MHz for  $^{13}\text{C}\{^1\text{H}\}$  NMR experiments. Chemical shifts were calibrated to the residual proton and carbon resonance of the solvent,  $\text{CDCl}_3$  ( $^1\text{H}$   $\delta$  7.26;  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  77.0)/  $\text{DMSO-d}_6$  ( $^1\text{H}$   $\delta$  2.50;  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  39.52). The following abbreviations were used to illuminate the diversities:  $\delta$  = chemical shifts,  $J$  = coupling constant, s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet. Chemical shifts are given in ppm relative to the internal standard of tetramethylsilane (TMS). High-resolution mass spectra (HRMS) were obtained by using a TOF analyzer in ESI mode. X-ray data were taken at 273K with a Bruker APEX-II CCD single crystal diffractometer by using graphite monochromated  $\text{Mo-K}\alpha$  radiation (0.71073 Å). Data integration was done using SAINT.<sup>1a</sup> Intensities for absorption were corrected using SADABS.<sup>1b</sup> Structure solution and refinement were carried out using Bruker SHELX-TL.<sup>1c-d</sup> TLC analysis was performed with pre-coated TLC plates (0.2 mm, Silica gel 60 F-254, Merck). For column chromatography, silica gel (100-200 mesh) was used as an adsorbent. Unless otherwise stated, all reagents and starting materials obtained from commercial suppliers were used without further purification. Indole, 2-mercapto pyridine, iodine, sodium hydride, m-CPBA, aryl halides,  $\text{AgOAc}$ ,  $\text{Ag}_2\text{O}$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{OAc})_2$  and HFIP were purchased from standard commercial sources (Sigma-Aldrich, TCI, Avra, Alfa-Aesar, Ottokemi, and CDH India). DCM, DMSO, PhMe and DMF were vacuum distilled over 4Å molecular sieves and stored under nitrogen. All the reactions were performed in an oven-dried glass pressure tube (capacity 15 mL) procured from Sigma-Aldrich India (catalog No Z181099) under an atmosphere of  $\text{N}_2$ . Reactions were monitored by thin-layer chromatography (TLC). The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

## 2. Experimental Section

### 2.1 General procedure for starting materials

#### 2.1.1 Procedure for the preparation of 3-(pyridin-2-ylthio)-1*H*-indoles: GP-1

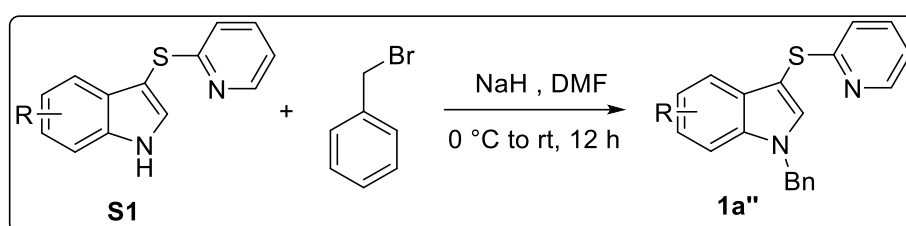
3-(Pyridin-2-ylthio)-1*H*-indoles **S1** was synthesized *via* the reported procedure.<sup>2</sup>



Substituted indoles (4.26 mmol), 2-mercapto pyridine (4.69 mmol), and iodine (20 mol%) were taken in an oven-dried round-bottom flask. Dry DMSO was added to this mixture. The resulting solution was stirred at 80 °C for 12 h. The reaction was then quenched with aqueous sodium thiosulfate and extracted with ethyl acetate (EtOAc). The combined organic layers were washed with H<sub>2</sub>O and brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The crude product was purified by column chromatography.

### 2.1.2 Procedure for the preparation of N-benylation of 3-(pyridin-2-ylthio)-1*H*-indoles: GP-2

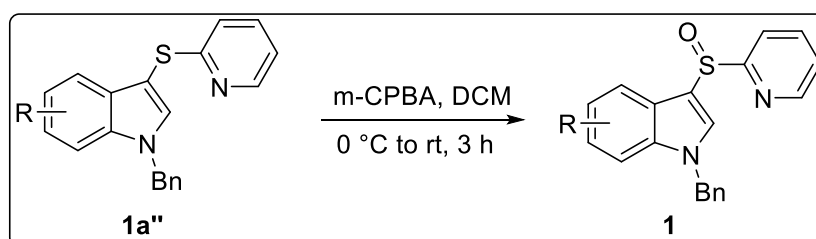
N-Benylation of 3-(pyridin-2-ylthio)-1*H*-indoles **1a''** was synthesized *via* the reported procedure.<sup>3</sup>



To a solution of sodium hydride (22.80 mmol) in DMF at 0 °C was added **S1** (3.80 mmol) solution. The solution was allowed to warm to 0 °C over 30 minutes, and then benzyl bromide (1.2 equiv.) was added dropwise to the reaction mixture. The reaction mixture was allowed to warm at room temperature and stirred at room temperature for 12 hours. The reaction was quenched with an aqueous solution of NH<sub>4</sub>Cl, and the reaction mixture was extracted with EtOAc. The combined organic layers were washed with H<sub>2</sub>O and saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography.

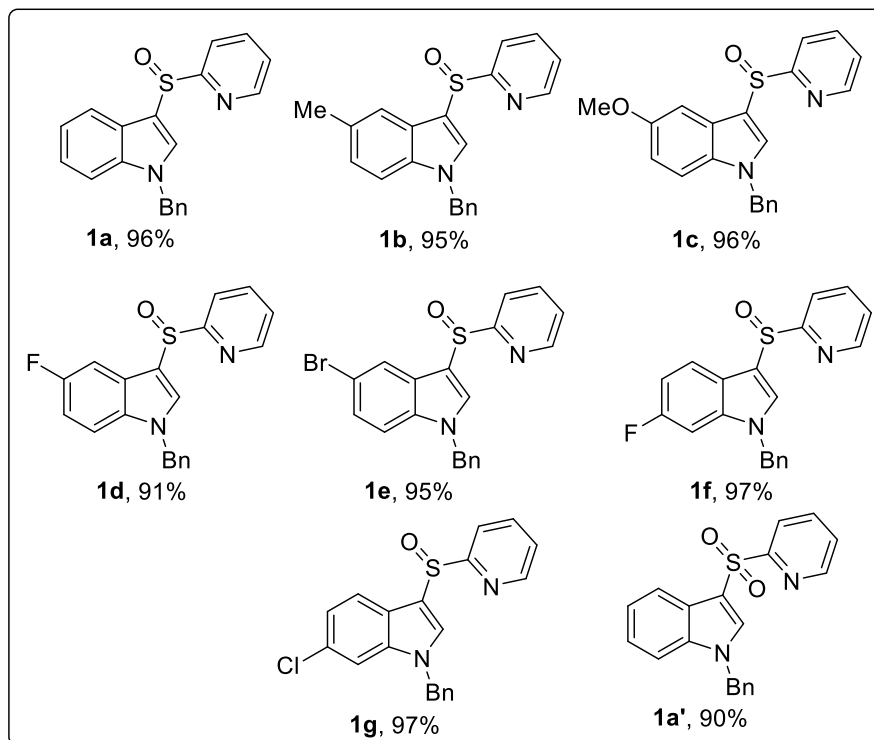
### 2.1.3 Procedure for the oxidation of N-benzylated 3-(pyridin-2-ylthio)-1*H*-indoles: GP-3

Substituted 1-benzyl-3-(pyridin-2-ylsulfinyl)-1*H*-indole **1** was synthesized *via* the reported procedure.<sup>4</sup>



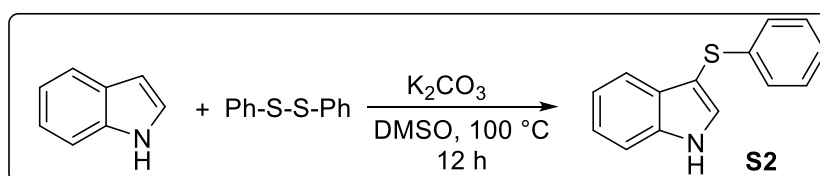
A solution of the **1a''** (3.42 mmol) in DCM (20 mL) at 0 °C was added portion-wise to m-CPBA (3.42 mmol). Further, the resulting solution was stirred at rt for 3 hours, and upon completion of the reaction (monitored by TLC), the mixture was diluted with an aqueous

solution of NaHCO<sub>3</sub> (30 mL) and extracted with dichloromethane (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude product was purified by column chromatography. Same procedure was followed for the preparation of **1a'** (with m-CPBA 3 equiv.). The following compounds were synthesized using the same experimental procedure.



#### 2.1.4 Procedure for the preparation of 3-(phenylthio)-1H-indole: GP-4

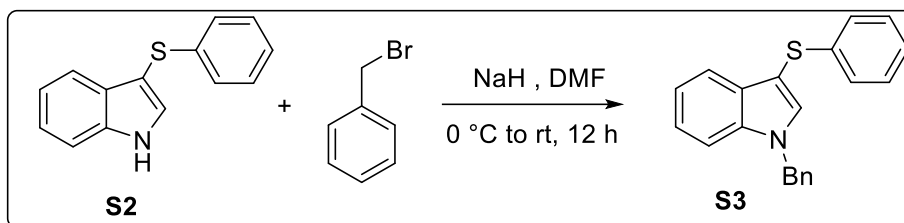
3-(Phenylthio)-1H-indole **S2** was synthesized *via* the reported procedure with modification.<sup>2</sup>



To a solution of indole **1** (1.70 mmol) in DMSO (10 mL) were added diphenyldisulfide (1.70 mmol), K<sub>2</sub>CO<sub>3</sub> (0.85 mmol). The resulting mixture was stirred at 100 °C for 12 h. The mixture was cooled to room temperature, the crude reaction mixture was purified using column chromatography on silica gel to provide the desired product **S2**.

#### 2.1.5 Procedure for the preparation of N-benylation of 3-(phenylthio)-1H-indole: GP-5

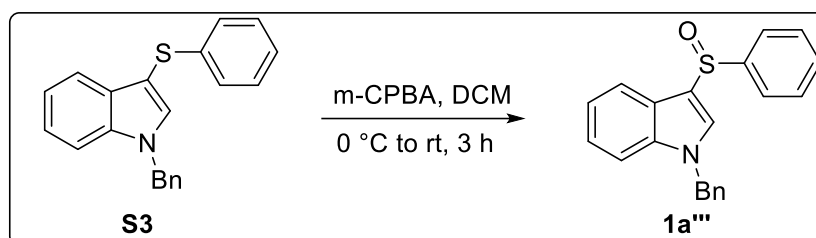
N-Benylation of 3-(phenylthio)-1H-indole **S3** was synthesized *via* the reported procedure.<sup>3</sup>



To a solution of sodium hydride (22.80 mmol) in DMF at 0 °C was added **S2** (0.77 mmol) solution. The solution was allowed to warm to 0 °C over 30 minutes, and then benzyl bromide (1.2 equiv.) was added dropwise to the reaction mixture. The reaction mixture was allowed to warm at room temperature and stirred at room temperature for 12 hours. The reaction was quenched with an aqueous solution of NH<sub>4</sub>Cl, and the reaction mixture was extracted with EtOAc. The combined organic layers were washed with H<sub>2</sub>O and saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography.

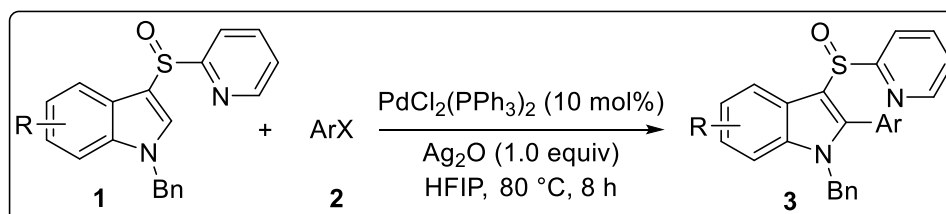
### 2.1.6 Procedure for the oxidation of N-benzylated 3-(phenylthio)-1H-indole: GP-6

Substituted 1-benzyl-3-(phenylsulfinyl)-1H-indole **1a'''** was synthesized *via* the reported procedure.<sup>4</sup>



A solution of the **1a'''** (1.01 mmol) in DCM (10 mL) at 0 °C was added portion-wise to m-CPBA (1.01 mmol). Further, the resulting solution was stirred at rt for 3 hours, and upon completion of the reaction (monitored by TLC), the mixture was diluted with an aqueous solution of NaHCO<sub>3</sub> (30 mL) and extracted with dichloromethane (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude product was purified by column chromatography.

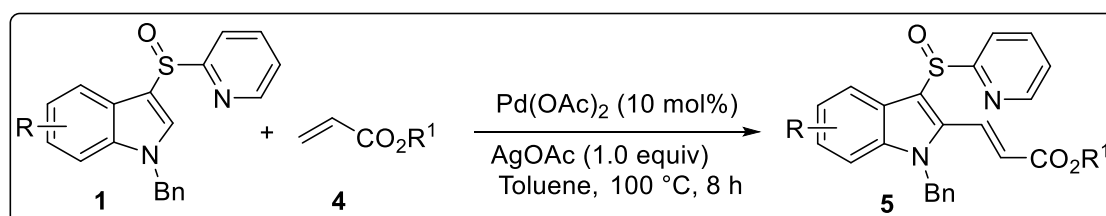
### 2.2 General procedure for the synthesis of C2-arylation of C3-substituted indole compounds : GP-7



A dry screw cap pressure tube (15 mL) equipped with a magnetic stirring bar was charged with 2-pyridyl sulfoxide substituted indoles **1** (0.30 mmol), aryl iodides (0.60 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>

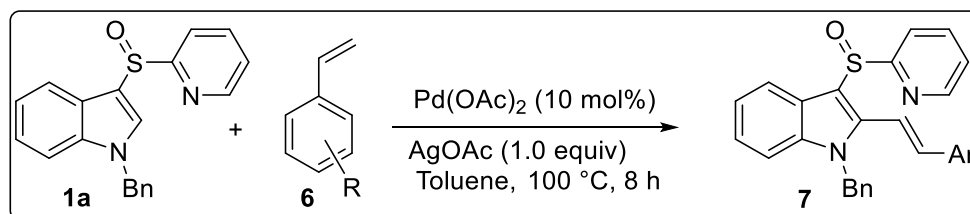
(10 mol%), Ag<sub>2</sub>O (1.0 equiv) in HFIP was stirred at 80 °C in an oil bath for 8 h. Upon completion of the reaction (monitored by TLC), the mixture was passed through a small pad of Celite. After evaporation of the solvent, the crude reaction mixture was purified using column chromatography on silica gel to provide the desired C2-arylated indole compounds **3**.

### 2.3.1 General procedure for the synthesis of C2-olefination of C3-substituted indole compounds : GP-8



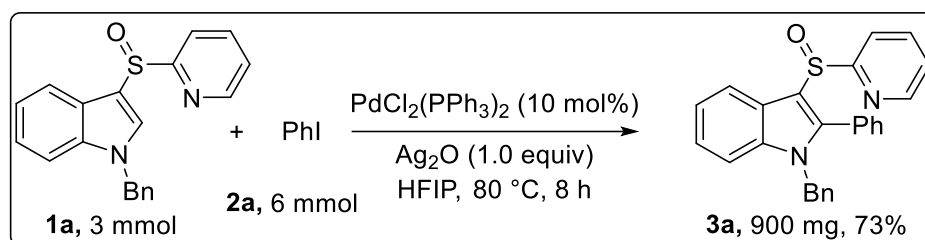
A dry screw cap pressure tube (15 mL) equipped with a magnetic stirring bar was charged with 2-pyridyl sulfoxide directed indoles **1** (0.30 mmol), acrylates (0.60 mmol), Pd(OAc)<sub>2</sub> (10 mol%), AgOAc (1.0 equiv) in toluene was stirred at 100 °C in an oil bath for 8 h. Upon completion of the reaction (monitored by TLC), the mixture was passed through a small pad of Celite. After solvent evaporation, the crude reaction mixture was purified by column chromatography on silica gel to yield the desired C2-olefinated indole compounds **5**.

### 2.3.2 General procedure for the synthesis of C2-olefination of C3-substituted indole compounds : GP-9



A dry screw cap pressure tube (15 mL) equipped with a magnetic stirring bar was charged with 2-pyridyl sulfoxide directed indole **1a** (0.30 mmol), styrenes (0.60 mmol), Pd(OAc)<sub>2</sub> (10 mol%), AgOAc (1.0 equiv) in Toluene was stirred at 100 °C in an oil bath for 8 h. Upon completion of the reaction (monitored by TLC), the mixture was passed through a small pad of Celite. After evaporation of the solvent, the crude reaction mixture was purified using column chromatography on silica gel to provide the desired C2-alkylated indole compounds **7**.

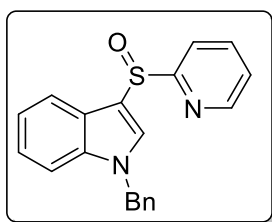
## 2.4 Large-scale synthesis of 3a



A dry screw cap pressure tube (15 mL) equipped with a magnetic stirring bar was charged with 1-benzyl-3-(pyridin-2-ylsulfonyl)-1H-indole (**1a**, 1.0 g, 3.01 mmol), iodobenzene (6.01 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol%), Ag<sub>2</sub>O (1.0 equiv) in DMSO was stirred at 80 °C in an oil bath for 8 h. The mixture was passed through a small pad of Celite with EtOAc. After evaporation of the solvent, the crude reaction mixture was purified using column chromatography on silica gel to provide the desired 1-benzyl-2-phenyl-3-(pyridin-2-ylsulfonyl)-1H-indole **3a** as a pale yellow solid (0.90 g, 2.2 mmol, 73% yield).

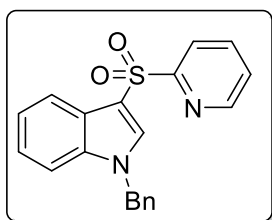
## 2.5 Characterization data for starting materials

### 1-Benzyl-3-(pyridin-2-ylsulfonyl)-1H-indole (**1a**):



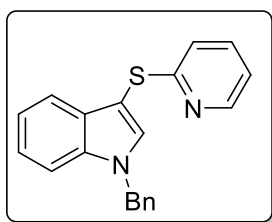
Following the general synthetic procedure GP-3. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 60:40); Yield: 96% (0.87 g), white solid; mp 143-144 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.51 (d, *J* = 3.8 Hz, 1H), 8.37 (s, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.13 (t, *J* = 7.3 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.45 (dd, *J* = 6.7, 5.0 Hz, 1H), 7.31 (dt, *J* = 13.3, 7.0 Hz, 6H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 5.49 (s, 2H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 164.3, 149.8, 138.1, 137.0, 136.6, 134.3, 128.7, 127.7, 127.3, 124.6, 124.1, 123.0, 121.1, 119.7, 119.0, 114.9, 111.6, 49.5 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>OS<sup>+</sup>: 333.1056; found: 333.1051.

### 1-Benzyl-3-(pyridin-2-ylsulfonyl)-1H-indole (**1a'**):



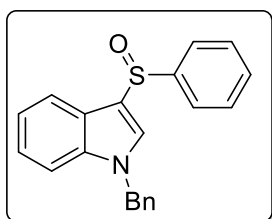
Following the general synthetic procedure GP-3 (with 3 equiv. of mcpba). The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 40:60); Yield: 90% (0.18 g), pale yellow solid; mp 133-134 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.65 (s, 1H), 8.49 (s, 1H), 8.22 (d, *J* = 7.3 Hz, 1H), 8.10 (d, *J* = 6.6 Hz, 1H), 7.83 (d, *J* = 6.9 Hz, 1H), 7.60 (s, 2H), 7.32 (d, *J* = 11.7 Hz, 4H), 7.24 (dd, *J* = 17.4, 8.1 Hz, 3H), 5.55 (s, 2H) ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup>: 349.1005; found: 349.1009.

**1-Benzyl-3-(pyridin-2-ylthio)-1H-indole (1a'')**:



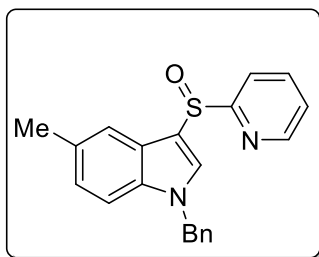
Following the general synthetic procedure GP-2. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 95% (1.60 g), yellow solid; mp 150-151 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.45 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.33 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 (dt, *J* = 6.2, 3.6 Hz, 3H), 6.93 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 5.38 (s, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 162.94, 149.21, 137.28, 136.53, 134.66, 129.78, 128.95, 128.01, 127.01, 122.93, 120.91, 119.80, 119.67, 119.17, 110.37, 100.25, 50.55 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>S<sup>+</sup>: 317.1107; found: 317.1103.

**1-Benzyl-3-(phenylsulfinyl)-1H-indole (1a''')**:



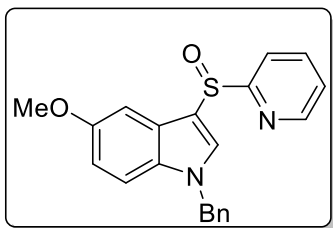
Following the general synthetic procedure GP-6. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 83% (0.28 g), yellow solid; mp 128-129 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 7.3 Hz, 2H), 7.59 (s, 1H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.33 (d, *J* = 7.3 Hz, 2H), 7.29 (dd, *J* = 16.6, 8.3 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.31 (s, 2H) ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>NOS<sup>+</sup>: 332.1104; found: 332.1107.

**1-Benzyl-5-methyl-3-(pyridin-2-ylsulfinyl)-1H-indole (1b)**:



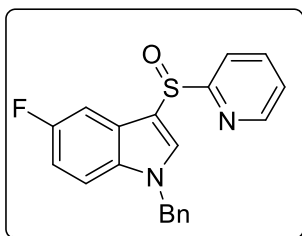
Following the general synthetic procedure GP-3. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 70:30); Yield: 95% (0.35g), off white solid; mp 170-171 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.51 (s, 1H), 8.27 (s, 1H), 8.13 (d, *J* = 3.2 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.31 (s, 2H), 7.24 (d, *J* = 23.9 Hz, 2H), 7.05 (s, 3H), 6.94 (d, *J* = 4.3 Hz, 1H), 5.51 (s, 2H), 2.67 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO) δ 164.4, 150.0, 143.1, 138.1, 137.1, 136.6, 128.9, 127.5, 126.4, 124.5, 123.8, 122.4, 121.1, 120.0, 118.3, 112.0, 110.9, 46.2, 10.89 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>OS<sup>+</sup>: 347.1213; found: 347.1209.

**1-Benzyl-5-methoxy-3-(pyridin-2-ylsulfinyl)-1H-indole (1c)**:



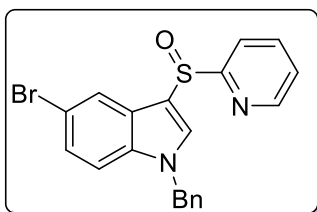
Following the general synthetic procedure GP-3. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 70:30); Yield: 96% (0.6 g), white solid; mp 105-106 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.53 (d,  $J$  = 3.9 Hz, 1H), 8.28 (d,  $J$  = 7.3 Hz, 2H), 8.15 (t,  $J$  = 7.1 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 6.78 (dd,  $J$  = 8.9, 2.1 Hz, 1H), 6.64 (d,  $J$  = 2.0 Hz, 1H), 5.44 (s, 2H), 3.55 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.2, 154.6, 150.0, 138.0, 137.1, 134.7, 131.7, 128.7, 127.8, 127.3, 124.8, 124.6, 119.9, 114.3, 112.8, 112.5, 100.9, 55.2, 49.8 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_2\text{S}^+$ : 363.1162; found: 363.1154.

**1-Benzyl-5-fluoro-3-(pyridin-2-ylsulfinyl)-1H-indole (1d):**



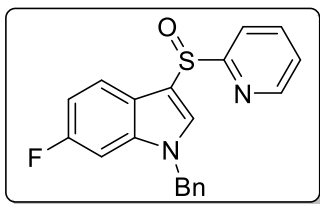
Following the general synthetic procedure GP-3. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 60:40); Yield: 91% (149 mg), off white solid; mp 107-108 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.53 (d,  $J$  = 4.1 Hz, 1H), 8.45 (s, 1H), 8.28 (d,  $J$  = 7.8 Hz, 1H), 8.14 (t,  $J$  = 7.1 Hz, 1H), 7.58 (dd,  $J$  = 9.0, 4.3 Hz, 1H), 7.46 (dd,  $J$  = 7.0, 4.9 Hz, 1H), 7.35 – 7.25 (m, 5H), 7.03 (td,  $J$  = 9.2, 2.2 Hz, 1H), 6.98 (dd,  $J$  = 9.4, 2.0 Hz, 1H), 5.49 (s, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.0, 157.64 (d,  $J_{\text{C-F}}$  = 235.0 Hz), 150.0, 138.3, 136.8, 135.8, 133.4, 128.8, 127.9, 127.4, 124.8, 124.4 (d,  $J_{\text{C-F}}$  = 10.0 Hz), 119.7, 114.9, 114.9, 113.2, 113.1, 111.4 (d,  $J_{\text{C-F}}$  = 25.0 Hz), 104.0 (d,  $J_{\text{C-F}}$  = 23.8 Hz), 49.9 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{FOS}^+$ : 351.0962; found: 351.0961.

**1-Benzyl-5-bromo-3-(pyridin-2-ylsulfinyl)-1H-indole (1e):**



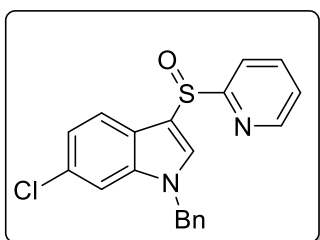
Following the general synthetic procedure GP-3. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 60:40); Yield: 95% (0.65 g), white solid; mp 90-91 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.54 (s, 1H), 8.44 (s, 1H), 8.26 (d,  $J$  = 7.6 Hz, 1H), 8.15 (t,  $J$  = 7.4 Hz, 1H), 7.54 (d,  $J$  = 8.6 Hz, 1H), 7.45 (d,  $J$  = 20.1 Hz, 2H), 7.29 (dd,  $J$  = 21.7, 7.1 Hz, 6H), 5.49 (s, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO)  $\delta$  164.0, 150.0, 138.4, 136.7, 135.5, 135.4, 128.6, 127.9, 127.3, 125.7, 124.9, 121.2, 119.7, 114.5, 113.8, 49.8 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{BrOS}^+$ : 411.0161; found: 411.0154.

**1-Benzyl-6-fluoro-3-(pyridin-2-ylsulfinyl)-1H-indole (1f):**



Following the general synthetic procedure GP-3. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 60:40); Yield: 97% (0.87g), White solid; mp 160-161 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.52 (d,  $J$  = 4.1 Hz, 1H), 8.39 (s, 1H), 8.26 (d,  $J$  = 7.8 Hz, 1H), 8.13 (t,  $J$  = 7.4 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.33 (t,  $J$  = 7.4 Hz, 4H), 7.28 (dd,  $J$  = 8.6, 4.7 Hz, 2H), 6.89 (dd,  $J$  = 13.1, 5.1 Hz, 1H), 5.46 (s, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.1, 159.4 (d,  $J_{\text{C-F}}$  = 236.3 Hz), 150.0, 138.3, 137.1, 137.0, 136.8, 135.0, 128.8, 127.9, 127.5, 124.8, 120.6, 120.4 (d,  $J_{\text{C-F}}$  = 10.0 Hz), 119.7, 115.3, 109.8 (d,  $J_{\text{C-F}}$  = 25.0 Hz), 98.3 (d,  $J_{\text{C-F}}$  = 27.6 Hz), 49.7 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{16}\text{FN}_2\text{OS}^+$ : 351.0962; found: 351.0961.

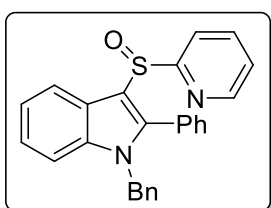
**1-Benzyl-6-chloro-3-(pyridin-2-ylsulfinyl)-1H-indole (1g):**



Following the general synthetic procedure GP-3. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 60:40); Yield: 97% (0.6 g), shiny white solid; mp 118-119 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.52 (d,  $J$  = 4.0 Hz, 1H), 8.41 (s, 1H), 8.25 (d,  $J$  = 7.8 Hz, 1H), 8.13 (t,  $J$  = 7.2 Hz, 1H), 7.72 (s, 1H), 7.46 (dd,  $J$  = 6.9, 4.9 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 (d,  $J$  = 7.3 Hz, 4H), 7.03 (dd,  $J$  = 8.5, 1.0 Hz, 1H), 5.50 (s, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.0, 15.0, 138.4, 137.2, 136.8, 135.2, 128.8, 128.0, 127.9, 127.4, 124.8, 122.8, 121.6, 120.4, 119.7, 115.4, 111.6, 49.6 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{16}\text{ClN}_2\text{OS}^+$ : 367.0666; found: 367.0663.

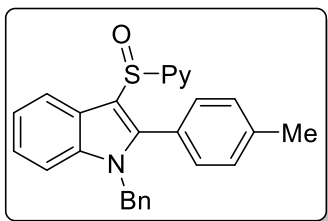
**3.2 Characterization data for products**

**1-Benzyl-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (3a):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 75% (92 mg), pale yellow solid; mp 180-181 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.58 (d,  $J$  = 4.0 Hz, 1H), 8.29 (d,  $J$  = 7.8 Hz, 1H), 8.16 – 8.10 (m, 1H), 7.74 (s, 2H), 7.60 – 7.55 (m, 3H), 7.49 – 7.43 (m, 2H), 7.34 (d,  $J$  = 8.0 Hz, 1H), 7.20 (ddd,  $J$  = 23.9, 15.0, 7.3 Hz, 4H), 7.01 (t,  $J$  = 7.5 Hz, 1H), 6.90 (d,  $J$  = 7.3 Hz, 2H), 5.43 (q,  $J$  = 16.8 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.5, 150.1, 145.7, 138.0, 137.0, 136.6, 131.5, 131.4, 131.0, 129.8, 128.8, 128.7, 128.7, 128.6, 128.3, 127.4, 126.1, 124.4, 123.8, 123.3, 121.5, 120.1, 119.0, 114.3, 112.0, 47.0 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{21}\text{N}_2\text{OS}^+$ : 409.1369; found: 409.1374.

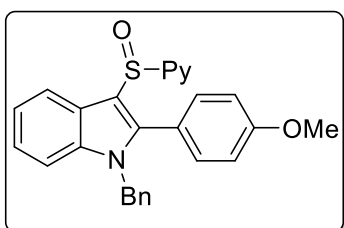
**1-Benzyl-3-(pyridin-2-ylsulfinyl)-2-(p-tolyl)-1H-indole (3b):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 89% (113 mg), yellow solid; mp 137-138 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.57 (d, *J* = 2.6 Hz, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 8.13 (t, *J* = 7.2 Hz, 1H),

7.62 (d, *J* = 6.6 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.20 (d, *J* = 6.8 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 6.9 Hz, 2H), 5.41 (q, *J* = 16.9 Hz, 2H), 2.39 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 164.6, 150.1, 146.0, 139.6, 138.0, 137.1, 136.5, 130.9, 129.2, 128.7, 127.4, 126.0, 125.4, 124.4, 123.8, 123.3, 121.5, 120.2, 119.0, 114.1, 111.9, 47.0, 21.0 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>OS<sup>+</sup>: 423.1526; found: 423.1517.

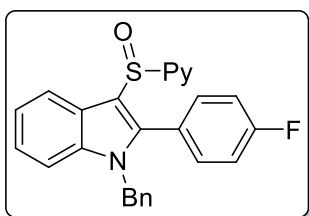
**1-Benzyl-2-(4-methoxyphenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3c):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 91% (120 mg), yellow solid; mp 139-140 °C; <sup>1</sup>H NMR (500 MHz, MeOD) δ 8.50 (d, *J* = 3.2 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 8.06 (t, *J* = 7.5 Hz, 1H),

7.58 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 6.8 Hz, 2H), 5.39 – 5.26 (m, 2H), 3.82 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 164.6, 160.4, 150.0, 145.8, 138.0, 137.1, 136.5, 132.4, 132.0, 131.5, 131.4, 128.8, 128.7, 128.6, 127.3, 126.0, 124.4, 123.8, 123.1, 121.4, 120.3, 120.1, 118.8, 114.1, 111.8, 55.3, 46.9 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup>: 439.1475; found: 439.1480.

**1-Benzyl-2-(4-fluorophenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3d):**

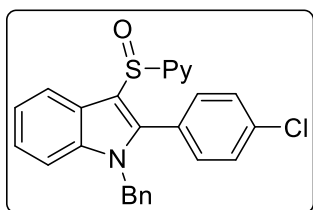


Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 85% (109 mg), white solid; mp 163-164 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.57 (d, *J* = 4.0 Hz, 1H),

8.28 (d, *J* = 7.8 Hz, 1H), 8.13 (t, *J* = 7.6 Hz, 1H), 7.77 (s, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.44 (dd, *J* = 18.2, 9.8 Hz, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.1 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.3 Hz, 2H), 5.47 – 5.37 (m, 2H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 165.1, 163.7 (d, *J*<sub>C-F</sub> = 246.2 Hz), 150.7, 145.2, 138.7, 137.7, 137.3, 134.0 (d, *J*<sub>C-F</sub> = 7.6 Hz), 129.4, 128.1, 126.7, 125.4 (d, *J*<sub>C-F</sub> = 2.5 Hz), 125.2, 124.4, 124.1,

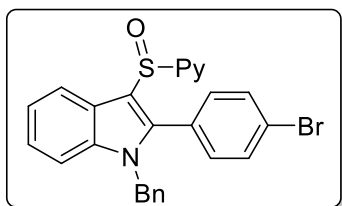
122.3, 120.8, 119.7, 116.4 (d,  $J_{C-F} = 22.0$  Hz), 115.2, 112.6, 47.7 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}FN_2OS^+$ : 427.1275; found: 427.1280.

**1-Benzyl-2-(4-chlorophenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3e):**



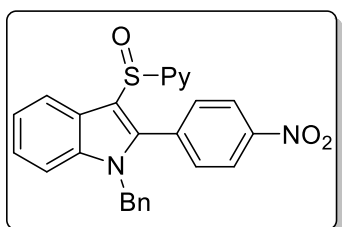
Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 90% (120 mg), light brown solid; mp 101-102 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.52 (d,  $J = 3.4$  Hz, 1H), 8.36 (d,  $J = 7.7$  Hz, 1H), 7.94 (t,  $J = 7.4$  Hz, 1H), 7.64 (dd,  $J = 18.5, 10.3$  Hz, 2H), 7.52 (d,  $J = 7.9$  Hz, 1H), 7.42 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 6.9$  Hz, 4H), 7.20 – 7.12 (m, 2H), 7.05 (t,  $J = 7.1$  Hz, 1H), 6.96 (d,  $J = 6.5$  Hz, 2H), 5.26 (q,  $J = 16.9$  Hz, 2H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  164.8, 149.8, 145.1, 137.3, 137.2, 136.5, 136.1, 132.6, 132.1, 132.0, 131.9, 128.9, 128.7, 128.4, 127.7, 127.1, 125.9, 124.4, 123.9, 123.7, 122.0, 120.6, 119.8, 114.7, 111.2, 48.0 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}ClN_2OS^+$ : 443.0979; found: 443.0976.

**1-Benzyl-2-(4-bromophenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3f):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 92% (135 mg), off white solid; mp 102-103 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.52 (s, 1H), 8.36 (d,  $J = 5.8$  Hz, 1H), 7.94 (s, 1H), 7.55 (d,  $J = 17.1$  Hz, 5H), 7.26 (s, 4H), 7.16 (d,  $J = 11.8$  Hz, 2H), 7.05 (s, 1H), 6.97 (s, 2H), 5.26 (q,  $J = 16.7$  Hz, 2H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  164.8, 149.8, 145.1, 137.3, 137.2, 136.5, 132.8, 132.1, 131.6, 128.9, 128.5, 128.4, 127.6, 127.5, 125.8, 124.4, 124.4, 123.9, 123.7, 122.0, 120.5, 119.8, 114.7, 111.2, 48.08 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}BrN_2OS^+$ : 487.0474; found: 487.0467.

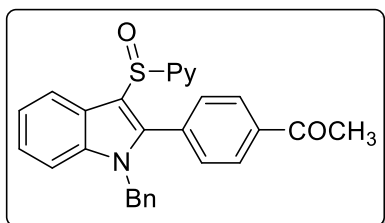
**1-Benzyl-2-(4-nitrophenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3g):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 65% (89 mg), orange solid; mp 125-126 °C;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ )  $\delta$  8.58 (d,  $J = 3.1$  Hz, 1H), 8.40 (d,  $J = 8.1$  Hz, 1H), 8.27 (d,  $J = 7.6$  Hz, 1H), 8.13 (t,  $J = 7.4$  Hz, 1H), 8.02 (d,  $J = 7.9$  Hz, 1H), 7.66 – 7.58 (m, 1H), 7.56 (d,  $J = 7.8$  Hz, 2H), 7.49 – 7.40 (m, 2H), 7.27 – 7.18 (m, 4H), 7.06 (t,  $J = 7.4$  Hz, 1H), 6.86 (d,  $J = 6.9$  Hz, 2H), 5.47 (s, 2H) ppm;  $^{13}C$  NMR (126 MHz,  $DMSO-d_6$ )  $\delta$  164.2, 150.1, 148.2, 142.9, 138.2, 137.0,

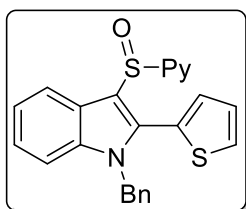
136.8, 134.9, 132.5, 132.1, 131.5, 131.5, 128.8, 128.3, 127.5, 126.1, 124.6, 124.0, 123.7, 123.6, 121.9, 120.1, 119.2, 115.5, 112.2, 47.2 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}N_3O_3S^+$ : 454.1220; found: 454.1225.

**1-(4-(1-Benzyl-3-(pyridin-2-ylsulfinyl)-1H-indol-2-yl)phenyl)ethan-1-one (3h):**



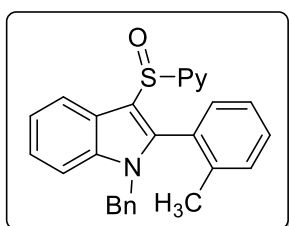
Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 67% (91 mg), pale yellow solid; mp 175-176 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.59 (d,  $J$  = 3.2 Hz, 1H), 8.29 (d,  $J$  = 7.9 Hz, 1H), 8.13 (d,  $J$  = 7.6 Hz, 2H), 7.90 (d,  $J$  = 7.8 Hz, 1H), 7.62 (s, 2H), 7.55 (d,  $J$  = 6.4 Hz, 3H), 7.48 – 7.45 (m, 1H), 7.39 (d,  $J$  = 7.9 Hz, 1H), 7.24 (d,  $J$  = 7.3 Hz, 1H), 7.20 (d,  $J$  = 7.4 Hz, 1H), 7.04 (t,  $J$  = 7.4 Hz, 1H), 6.89 (d,  $J$  = 7.1 Hz, 2H), 5.51 – 5.41 (q, 2H), 2.65 (s, 3H) ppm;  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  197.6, 164.3, 150.1, 144.3, 138.1, 137.4, 136.9, 136.8, 133.1, 132.8, 132.0, 131.5, 131.4, 128.8, 128.7, 128.2, 127.4, 126.0, 124.5, 123.7, 123.6, 121.7, 120.1, 119.1, 114.9, 112.0, 47.1, 26.9 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{28}H_{23}N_2O_2S^+$ : 451.1475; found: 451.1470.

**1-Benzyl-3-(pyridin-2-ylsulfinyl)-2-(thiophen-2-yl)-1H-indole (3i):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 40:60); Yield: 72% (90 mg), pale yellow solid; mp 219-220 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.57 (d,  $J$  = 4.1 Hz, 1H), 8.32 – 8.27 (m, 1H), 8.14 (t,  $J$  = 7.6 Hz, 1H), 7.91 (d,  $J$  = 4.9 Hz, 1H), 7.60 (ddd,  $J$  = 18.8, 14.0, 8.4 Hz, 2H), 7.49 (d,  $J$  = 8.0 Hz, 1H), 7.34 (d,  $J$  = 8.0 Hz, 1H), 7.29 (t,  $J$  = 6.2 Hz, 3H), 7.26 – 7.21 (m, 1H), 7.19 (t,  $J$  = 7.7 Hz, 1H), 7.02 (t,  $J$  = 7.4 Hz, 1H), 6.96 (d,  $J$  = 7.4 Hz, 2H), 5.53 (q,  $J$  = 17.0 Hz, 2H) ppm;  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.4, 150.1, 138.1, 138.1, 137.1, 136.8, 132.4, 130.7, 128.7, 127.8, 127.6, 127.5, 126.1, 124.5, 123.8, 123.6, 121.7, 120.1, 119.0, 115.9, 111.9, 47.2 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{22}H_{20}NO^+$ : 415.0933; found: 415.0929.

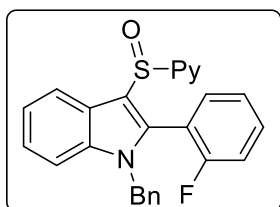
**1-Benzyl-3-(pyridin-2-ylsulfinyl)-2-(o-tolyl)-1H-indole (3j):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 55% (70 mg), brick orange solid; mp 133-134 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.57 (d,  $J$  = 2.6 Hz, 1H), 8.30 (d,  $J$  = 7.5 Hz, 1H), 8.13 (t,  $J$  = 7.2 Hz, 1H), 7.62 (d,  $J$  = 6.6 Hz, 2H), 7.43 (d,  $J$  = 7.9 Hz, 2H), 7.38 (d,  $J$  = 7.4 Hz, 2H), 7.31 (d,  $J$  = 7.7 Hz, 1H), 7.23 (d,  $J$

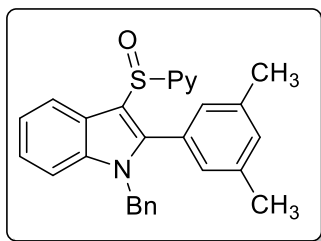
= 7.1 Hz, 2H), 7.20 (d,  $J = 6.8$  Hz, 1H), 7.14 (t,  $J = 7.4$  Hz, 1H), 7.00 (t,  $J = 7.3$  Hz, 1H), 6.90 (d,  $J = 6.9$  Hz, 2H), 5.41 (q,  $J = 16.9$  Hz, 2H), 2.39 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.6, 150.1, 146.0, 139.6, 138.0, 137.1, 136.5, 130.9, 129.2, 128.7, 127.4, 126.0, 125.4, 124.4, 123.8, 123.3, 121.5, 120.2, 119.0, 114.1, 111.9, 47.0, 21.0 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{27}\text{H}_{23}\text{N}_2\text{OS}^+$ : 423.1526; found: 423.1531.

**1-Benzyl-2-(2-fluorophenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3k):**



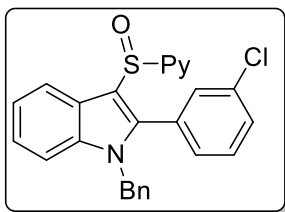
Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 65% (83 mg), yellow solid; mp 160-161 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.57 (d,  $J = 4.0$  Hz, 1H), 8.28 (d,  $J = 7.8$  Hz, 1H), 8.13 (t,  $J = 7.6$  Hz, 1H), 7.77 (s, 2H), 7.49 (d,  $J = 8.3$  Hz, 1H), 7.44 (dd,  $J = 18.2, 9.8$  Hz, 3H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.24 (t,  $J = 7.1$  Hz, 2H), 7.22 – 7.15 (m, 2H), 7.03 (t,  $J = 7.5$  Hz, 1H), 6.88 (d,  $J = 7.3$  Hz, 2H), 5.47 – 5.37 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.4, 163.0 (d,  $J_{\text{C-F}} = 246.3$  Hz), 150.1, 144.5, 138.0, 137.0, 136.6, 133.3 (d,  $J_{\text{C-F}} = 7.5$  Hz), 133.3, 128.7, 127.4, 126.0, 124.8, 124.7, 124.5, 123.7, 123.4, 121.6, 120.1, 119.0, 115.7 (d,  $J_{\text{C-F}} = 22.5$  Hz), 114.5, 111.9, 47.0 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{20}\text{FN}_2\text{OS}^+$ : 427.1275; found: 427.1270.

**1-Benzyl-2-(3,5-dimethylphenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3l):**



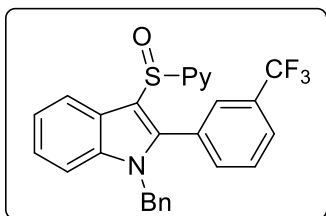
Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 70% (92 mg), yellow solid; mp 152-153 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.57 (d,  $J = 3.4$  Hz, 1H), 8.26 (d,  $J = 7.7$  Hz, 1H), 8.12 (t,  $J = 7.4$  Hz, 1H), 7.64 – 7.52 (m, 1H), 7.46 (t,  $J = 9.3$  Hz, 2H), 7.29 – 7.24 (m, 4H), 7.21 (d,  $J = 10.7$  Hz, 2H), 7.18 – 7.13 (m, 1H), 7.00 (t,  $J = 7.4$  Hz, 1H), 6.91 (d,  $J = 7.1$  Hz, 2H), 5.40 (dd,  $J = 39.5, 16.8$  Hz, 2H), 2.32 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.5, 150.0, 146.1, 137.9, 137.7, 137.2, 136.5, 131.2, 128.6, 128.2, 127.3, 126.1, 124.3, 123.8, 123.2, 121.4, 120.2, 118.9, 114.1, 111.9, 47.1, 20.90 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{28}\text{H}_{25}\text{N}_2\text{OS}^+$ : 437.1682; found: 437.1685.

**1-Benzyl-2-(3-chlorophenyl)-3-(pyridin-2-ylsulfinyl)-1H-indole (3m):**



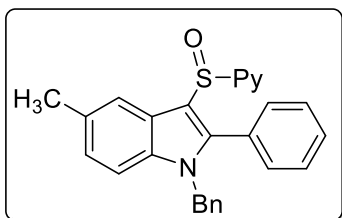
Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 75% (100 mg), pale yellow solid; mp 105-106 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.58 (s, 1H), 8.27 (d,  $J = 7.3$  Hz, 1H), 8.14 (d,  $J = 6.4$  Hz, 1H), 7.77 (s, 1H), 7.63 (dd,  $J = 16.6, 9.0$  Hz, 3H), 7.58 – 7.50 (m, 2H), 7.46 (s, 1H), 7.40 (d,  $J = 7.6$  Hz, 1H), 7.25 (d,  $J = 6.6$  Hz, 2H), 7.21 (d,  $J = 5.6$  Hz, 1H), 7.05 (d,  $J = 7.1$  Hz, 1H), 6.88 (d,  $J = 6.3$  Hz, 2H), 5.43 (q,  $J = 17.1$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.4, 150.1, 143.6, 138.0, 137.0, 136.7, 133.2, 132.0, 131.5, 131.4, 130.7, 130.4, 129.8, 128.8, 128.7, 127.4, 126.0, 124.5, 123.7, 123.6, 121.7, 120.0, 119.1, 114.8, 112.0, 47.2 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{20}\text{N}_2\text{ClOS}^+$ : 443.0979; found: 443.0975.

**1-Benzyl-3-(pyridin-2-ylsulfinyl)-2-(3-(trifluoromethyl)phenyl)-1H-indole (3n):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 71% (102 mg), pale yellow solid; mp 121-122 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.57 (d,  $J = 4.0$  Hz, 1H), 8.25 (d,  $J = 7.8$  Hz, 1H), 8.12 (dd,  $J = 10.9, 4.5$  Hz, 1H), 8.00 (d,  $J = 8.1$  Hz, 2H), 7.93 (d,  $J = 7.7$  Hz, 1H), 7.80 (t,  $J = 7.7$  Hz, 1H), 7.57 (d,  $J = 8.3$  Hz, 1H), 7.50 – 7.42 (m, 2H), 7.26 – 7.20 (m, 4H), 7.08 (t,  $J = 7.5$  Hz, 1H), 6.85 (d,  $J = 7.0$  Hz, 2H), 5.43 (q,  $J = 17.0$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.3, 150.1, 143.4, 138.1, 137.0, 136.8, 134.9, 129.8, 129.4, 128.7, 127.8 (q,  $J_{\text{C-F}} = 32.5$  Hz), 127.5, 126.6 (q,  $J_{\text{C-F}} = 3.8$  Hz), 126.0, 124.6, 124.3 (q,  $J_{\text{C-F}} = 271.3$  Hz), 123.8, 121.8, 120.0, 119.1, 115.0, 112.0, 47.2 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{27}\text{H}_{20}\text{N}_2\text{F}_3\text{OS}^+$ : 477.1243; found: 477.1247.

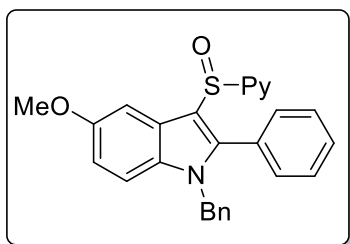
**1-Benzyl-5-methyl-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (3o):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 85% (109 mg), off white solid; mp 260-261 °C;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.58 (d,  $J = 4.1$  Hz, 1H), 8.28 (d,  $J = 7.8$  Hz, 1H), 8.13 (t,  $J = 7.2$  Hz, 1H), 7.72 (s, 2H), 7.57 (d,  $J = 2.7$  Hz, 3H), 7.46 (dd,  $J = 7.0, 4.9$  Hz, 1H), 7.34 (d,  $J = 8.4$  Hz, 1H), 7.27 – 7.18 (m, 3H), 7.13 (s, 1H), 6.99 (d,  $J = 8.4$  Hz, 1H), 6.87 (d,  $J = 7.3$  Hz, 2H), 5.39 (q,  $J = 16.8$  Hz, 2H), 2.22 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.5, 150.1, 145.6, 138.0, 137.1, 135.0, 131.0, 130.5, 129.8, 128.7, 128.6, 127.4, 126.0, 124.9, 124.4, 120.2,

118.6, 113.7, 111.7, 47.1, 21.1 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{27}H_{23}N_2OS^+$ : 423.1526; found: 423.1523.

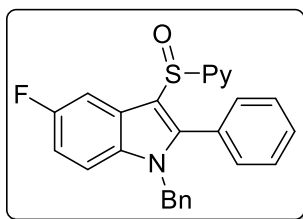
**1-Benzyl-5-methoxy-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (3p):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 75% (100 mg), brown solid; mp 221-222 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.59 (d,  $J$  = 3.7 Hz, 1H), 8.30 (d,  $J$  = 7.7 Hz, 1H), 8.14 (t,  $J$  = 7.4 Hz, 1H),

7.71 (d,  $J$  = 2.6 Hz, 2H), 7.57 (s, 3H), 7.49 – 7.45 (m, 1H), 7.36 (d,  $J$  = 9.0 Hz, 1H), 7.24 (t,  $J$  = 7.1 Hz, 2H), 7.20 (d,  $J$  = 6.9 Hz, 1H), 6.88 (d,  $J$  = 7.2 Hz, 2H), 6.83 – 6.77 (m, 1H), 6.69 (s, 1H), 5.38 (q,  $J$  = 16.8 Hz, 2H), 3.56 (s, 3H) ppm;  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.4, 154.7, 150.2, 146.0, 137.9, 137.1, 132.1, 131.5, 131.5, 131.0, 129.8, 128.8, 128.7, 128.7, 128.6, 128.5, 127.4, 126.1, 124.5, 120.3, 113.6, 112.9, 100.8, 55.2, 47.1 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{27}H_{23}N_2O_2S^+$ : 439.1475; found: 439.1470.

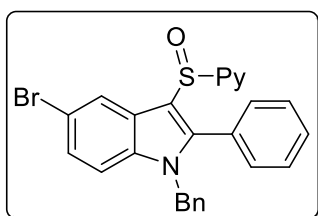
**1-Benzyl-5-fluoro-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (3q):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 96% (126 mg), light brown solid; mp 195-196 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.60 (s, 1H), 8.30 (d,

$J$  = 7.6 Hz, 1H), 8.14 (t,  $J$  = 7.0 Hz, 1H), 7.75 (s, 2H), 7.64 – 7.52 (m, 4H), 7.47 (s, 1H), 7.22 (dd,  $J$  = 15.9, 6.7 Hz, 3H), 7.04 (dd,  $J$  = 21.0, 9.3 Hz, 2H), 6.89 (d,  $J$  = 6.7 Hz, 2H), 5.43 (q,  $J$  = 16.8 Hz, 2H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  164.6, 158.6 (d,  $J_{C-F}$  = 236.2 Hz), 149.9, 148.0, 137.4, 136.4, 133.6, 132.0 (d,  $J_{C-F}$  = 8.7 Hz), 131.2, 129.9, 128.9, 128.4, 127.7, 125.9, 125.0, 123.9, 120.6, 112.2, 112.2, 111.9 (d,  $J_{C-F}$  = 26.2 Hz), 105.1 (d,  $J_{C-F}$  = 25.2 Hz), 48.2 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}N_2FOS^+$ : 427.1275; found: 427.1271.

**1-Benzyl-5-bromo-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (3r):**

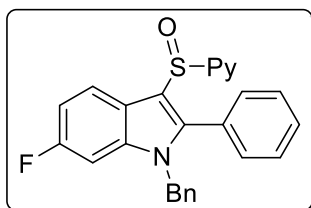


Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 88% (130 mg), brown solid; mp 149-150 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.61 (s, 1H), 8.26

(d,  $J$  = 7.4 Hz, 1H), 8.17 (t,  $J$  = 7.1 Hz, 1H), 7.74 (s, 2H), 7.59 (s, 3H), 7.48 (d,  $J$  = 8.8 Hz, 2H), 7.43 (s, 1H), 7.32 (d,  $J$  = 8.2 Hz, 1H), 7.22 (dd,  $J$  = 13.5, 6.8 Hz, 3H), 6.86 (d,  $J$  = 6.5 Hz, 2H), 5.43 (q,  $J$  = 16.7 Hz, 2H) ppm;  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.2, 150.38, 146.8, 138.3,

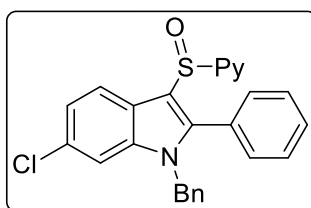
136.7, 135.5, 134.6, 134.6, 131.6, 131.0, 130.5, 130.4, 130.2, 128.7, 127.9, 127.5, 126.0, 125.4, 124.7, 121.0, 120.1, 114.2, 113.9, 47.2 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}BrN_2OS^+$ : 487.0474; found: 487.0469.

**1-Benzyl-6-fluoro-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (3s):**



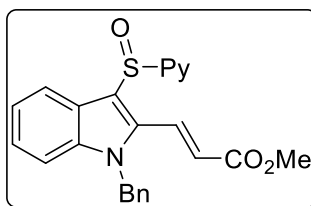
Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 80% (103 mg), off white solid; mp 188-189 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.59 (s, 1H), 8.27 (d,  $J = 7.6$  Hz, 1H), 8.13 (t,  $J = 7.1$  Hz, 1H), 7.72 (s, 2H), 7.58 (s, 3H), 7.47 (s, 1H), 7.42 (d,  $J = 9.3$  Hz, 1H), 7.32 (d,  $J = 7.7$  Hz, 1H), 7.22 (dd,  $J = 13.4, 6.9$  Hz, 3H), 6.89 (dd,  $J = 25.6, 7.3$  Hz, 3H), 5.42 (q,  $J = 17.0$  Hz, 2H) ppm;  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  162.6, 156.6 (d,  $J_{C-F} = 236.3$  Hz), 147.9, 146.0, 135.4, 134.4, 131.6, 130.0 (d,  $J_{C-F} = 10.0$  Hz), 129.9, 129.2, 127.9, 126.9, 126.4, 125.7, 123.9, 121.9, 118.6, 110.2, 110.2, 109.9 (d,  $J_{C-F} = 26.2$  Hz), 103.1 (d,  $J_{C-F} = 25.0$  Hz), 46.2 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}N_2FOS^+$ : 427.1275; found: 427.1273.

**1-Benzyl-6-chloro-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (3t):**



Following the general synthetic procedure GP-7. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 92% (122 mg), White solid; mp 159-160 °C;  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.58 (d,  $J = 3.6$  Hz, 1H), 8.27 (d,  $J = 7.6$  Hz, 1H), 8.13 (t,  $J = 7.4$  Hz, 1H), 7.73 (s, 2H), 7.65 (s, 1H), 7.57 (s, 3H), 7.49 – 7.44 (m, 1H), 7.34 (d,  $J = 8.5$  Hz, 1H), 7.28 – 7.18 (m, 3H), 7.07 (d,  $J = 8.3$  Hz, 1H), 6.86 (d,  $J = 7.1$  Hz, 2H), 5.50 – 5.39 (m, 2H) ppm;  $^{13}C$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  164.2, 150.2, 146.6, 138.2, 137.3, 136.7, 131.0, 130.1, 128.8, 128.7, 128.2, 128.0, 127.5, 126.1, 124.6, 122.5, 122.0, 120.4, 120.1, 114.7, 111.9, 47.1 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{26}H_{20}N_2OCIS^+$ : 443.0979; found: 443.0978.

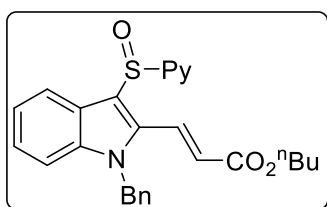
**Methyl (E)-3-(1-benzyl-3-(pyridin-2-ylsulfinyl)-1H-indol-2-yl)acrylate (5a):**



Following the general synthetic procedure GP-8. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 80% (100 mg), orange solid; mp 157-158 °C;  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.55 (d,  $J = 3.8$  Hz, 1H), 8.35 (d,  $J = 7.8$  Hz, 1H), 8.15 (dd,  $J = 7.6, 6.5$  Hz, 1H), 7.94 (d,  $J = 15.9$  Hz, 1H), 7.65 (t,  $J = 8.2$  Hz, 2H), 7.46 (dd,  $J = 6.7, 4.9$  Hz, 1H), 7.31 (t,  $J = 7.2$  Hz, 2H), 7.28 – 7.22 (m, 2H),

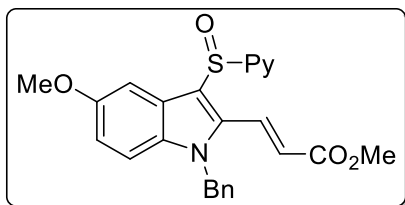
7.09 (t,  $J = 7.6$  Hz, 1H), 7.03 (d,  $J = 7.2$  Hz, 2H), 6.98 (d,  $J = 15.9$  Hz, 1H), 5.68 (q,  $J = 17.2$  Hz, 2H), 3.75 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  165.9, 164.8, 150.6, 138.8, 138.2, 137.9, 137.3, 130.5, 129.3, 128.1, 126.6, 126.6, 125.2, 124.5, 122.4, 120.3, 120.3, 117.3, 112.1, 52.4, 47.4 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+$ : 417.1267; found: 417.1262.

**Butyl (E)-3-(1-benzyl-3-(pyridin-2-ylsulfinyl)-1H-indol-2-yl)acrylate (5b):**



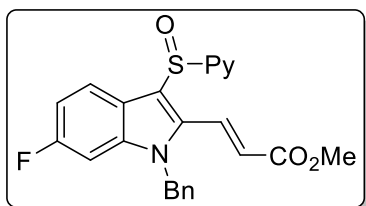
Following the general synthetic procedure GP-8. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 50% (70 mg), yellow solid; mp 128-129 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.54 (d,  $J = 4.0$  Hz, 1H), 8.34 (d,  $J = 7.8$  Hz, 1H), 8.14 (t,  $J = 7.2$  Hz, 1H), 7.90 (d,  $J = 15.9$  Hz, 1H), 7.68 – 7.62 (m, 2H), 7.45 (dd,  $J = 6.9, 5.0$  Hz, 1H), 7.31 (t,  $J = 7.2$  Hz, 2H), 7.28 – 7.22 (m, 2H), 7.09 (t,  $J = 7.6$  Hz, 1H), 7.04 (d,  $J = 7.3$  Hz, 2H), 6.94 (d,  $J = 15.9$  Hz, 1H), 5.68 (q,  $J = 17.1$  Hz, 2H), 4.16 (t,  $J = 6.2$  Hz, 2H), 1.65 – 1.56 (m, 2H), 1.34 (dd,  $J = 14.9, 7.4$  Hz, 2H), 0.89 (t,  $J = 7.3$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  165.5, 164.7, 150.6, 138.7, 138.2, 137.9, 137.4, 130.4, 129.3, 128.1, 126.8, 126.7, 125.2, 124.6, 122.4, 120.4, 120.2, 117.2, 112.1, 64.8, 47.4, 30.6, 19.1, 14.0 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}_3\text{S}^+$ : 459.1737; found: 459.1743.

**Methyl (E)-3-(1-benzyl-5-methoxy-3-(pyridin-2-ylsulfinyl)-1H-indol-2-yl)acrylate (5c):**



Following the general synthetic procedure GP-8. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 30:70); Yield: 88% (119 mg), yellow solid; mp 151-152 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.56 (d,  $J = 4.0$  Hz, 1H), 8.35 (d,  $J = 7.8$  Hz, 1H), 8.17 (dd,  $J = 10.9, 4.5$  Hz, 1H), 7.90 (d,  $J = 15.9$  Hz, 1H), 7.56 (d,  $J = 9.1$  Hz, 1H), 7.47 (dd,  $J = 7.1, 5.1$  Hz, 1H), 7.31 (t,  $J = 7.2$  Hz, 2H), 7.28 – 7.22 (m, 1H), 7.00 (d,  $J = 7.4$  Hz, 3H), 6.95 – 6.88 (m, 2H), 5.65 (q,  $J = 17.2$  Hz, 2H), 3.74 (s, 3H), 3.64 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  166.0, 164.6, 155.4, 150.6, 138.6, 138.2, 137.4, 133.1, 130.5, 129.3, 128.0, 126.6, 125.9, 125.3, 125.2, 120.5, 116.5, 115.5, 113.2, 101.2, 55.8, 52.4, 47.5 ppm; HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_4\text{S}^+$ : 447.1373; found: 447.1369.

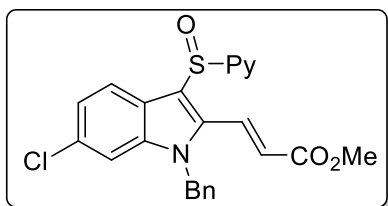
**Methyl (E)-3-(1-benzyl-6-fluoro-3-(pyridin-2-ylsulfinyl)-1H-indol-2-yl)acrylate (5d):**



Following the general synthetic procedure GP-8. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 25:75); Yield: 76% (100 mg), light yellow solid; mp 161-162 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)

δ 8.56 (d, *J* = 4.0 Hz, 1H), 8.33 (d, *J* = 7.9 Hz, 1H), 8.16 (td, *J* = 7.8, 1.5 Hz, 1H), 7.90 (d, *J* = 15.8 Hz, 1H), 7.67 (dd, *J* = 8.8, 5.4 Hz, 1H), 7.62 (dd, *J* = 10.1, 1.9 Hz, 1H), 7.47 (dd, *J* = 6.8, 4.8 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.97 (d, *J* = 15.8 Hz, 2H), 5.66 (q, *J* = 17.1 Hz, 2H), 3.74 (s, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.0, 164.7, 160.9 (d, *J*<sub>C-F</sub> = 240.5 Hz), 150.7, 139.0, 138.6, 138.4, 137.1, 130.3, 129.4, 128.2, 126.7, 126.5, 125.4, 121.8 (d, *J*<sub>C-F</sub> = 10.0 Hz), 121.1, 120.3, 117.6, 111.39 (d, *J*<sub>C-F</sub> = 24.9 Hz), 98.71 (d, *J*<sub>C-F</sub> = 27.0 Hz), 52.5, 47.6 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>20</sub>FN<sub>2</sub>O<sub>3</sub>S<sup>+</sup>: 435.1173; found: 435.1170.

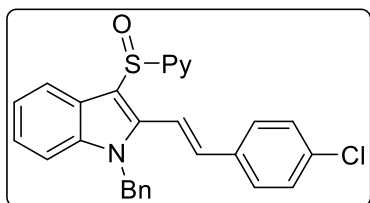
**Methyl (E)-3-(1-benzyl-6-chloro-3-(pyridin-2-ylsulfinyl)-1H-indol-2-yl)acrylate (5e):**



Following the general synthetic procedure GP-9. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 78% (106 mg), light yellow solid; mp 160-161 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)

δ 8.56 (d, *J* = 4.0 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.16 (dd, *J* = 10.9, 4.5 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.47 (dd, *J* = 6.8, 4.8 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.13 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.04 – 6.97 (m, 3H), 5.70 (q, *J* = 17.2 Hz, 2H), 3.74 (s, 3H) ppm; <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 165.8, 164.7, 150.6, 139.2, 138.9, 138.4, 137.1, 130.2, 130.1, 129.4, 128.1, 127.1, 126.6, 125.3, 123.1, 122.9, 121.6, 120.3, 117.6, 112.0, 52.5, 47.5 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>3</sub>S<sup>+</sup>: 451.0878; found: 451.0873.

**(E)-1-Benzyl-2-(4-chlorostyryl)-3-(pyridin-2-ylsulfinyl)-1H-indole (7a):**

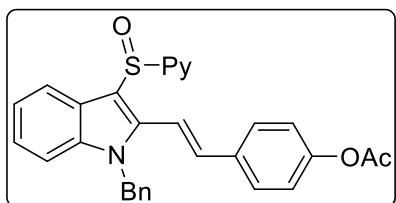


Following the general synthetic procedure GP-9. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 82% (116 mg), orange solid; mp 83-84 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 8.57 (s,

1H), 8.36 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.65 (s, 1H), 7.53 (d, *J* = 4.0 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 6.8 Hz, 3H), 7.19 (dd, *J* = 17.1, 7.3 Hz, 3H), 7.12 (d, *J* = 6.6 Hz, 2H), 7.03 (d, *J* = 7.1 Hz, 1H), 5.75 – 5.61 (m, 2H) ppm; <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 165.3, 150.5, 142.7, 138.5, 138.2, 137.7, 137.2, 135.3, 133.9,

129.4, 129.4, 129.2, 127.9, 127.9, 127.0, 125.0, 124.9, 123.9, 121.8, 120.5, 119.7, 116.0, 113.8, 111.8, 47.1 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{28}H_{22}ClN_2OS^+$ : 469.1136; found: 469.1136.

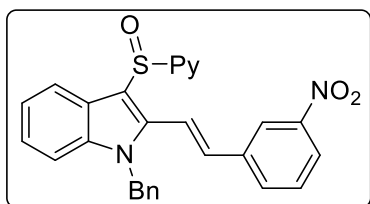
**(E)-4-(2-(1-Benzyl-3-(pyridin-2-ylsulfinyl)-1H-indol-2-yl)vinyl)phenyl acetate (7b):**



Following the general synthetic procedure GP-9. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 75% (110 mg), brick orange solid; mp 105-106 °C;  $^1H$  NMR

(500 MHz, DMSO- $d_6$ )  $\delta$  8.59 (s, 1H), 8.35 (d,  $J = 7.2$  Hz, 1H), 8.13 (s, 1H), 7.71 (d,  $J = 13.8$  Hz, 3H), 7.59 (s, 1H), 7.55 (d,  $J = 8.4$  Hz, 1H), 7.51 – 7.44 (m, 2H), 7.29 (s, 3H), 7.20 (d,  $J = 8.1$  Hz, 3H), 7.14 (s, 2H), 7.04 – 6.99 (m, 1H), 5.68 (q,  $J = 16.8$  Hz, 2H), 2.28 (s, 3H) ppm;  $^{13}C$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  169.6, 165.3, 151.4, 150.5, 143.1, 138.8, 138.6, 137.8, 137.2, 134.1, 129.2, 128.9, 128.0, 127.1, 125.0, 125.0, 123.8, 122.9, 121.8, 120.6, 119.7, 115.3, 111.8, 47.2, 21.4 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{30}H_{25}N_2O_3S^+$ : 493.1580; found: 493.1572.

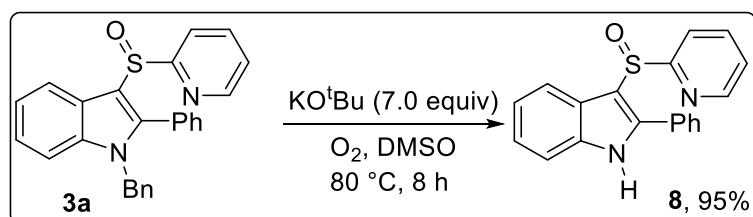
**(E)-1-Benzyl-2-(3-nitrostyryl)-3-(pyridin-2-ylsulfinyl)-1H-indole (7c):**



Following the general synthetic procedure GP-9. The reaction mixture was purified by silica gel column chromatography (EtOAc: petroleum ether, 20:80); Yield: 68% (100 mg), brick orange solid; mp 97-98 °C;  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$

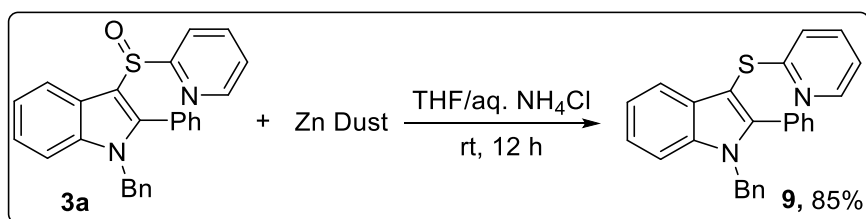
8.57 (d,  $J = 21.1$  Hz, 2H), 8.34 (s, 1H), 8.16 (d,  $J = 20.8$  Hz, 3H), 7.85 (dd,  $J = 31.7, 16.1$  Hz, 2H), 7.72 (s, 1H), 7.59 – 7.49 (m, 2H), 7.47 (s, 1H), 7.29 (s, 2H), 7.26 – 7.17 (m, 2H), 7.13 (s, 2H), 7.03 (s, 1H), 5.74 (s, 2H) ppm;  $^{13}C$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  165.3, 150.5, 148.9, 142.2, 138.6, 138.1, 137.8, 137.2, 137.0, 134.1, 130.9, 129.2, 127.9, 127.0, 125.0, 124.0, 123.7, 121.9, 120.5, 119.8, 118.3, 114.3, 111.9, 47.2 ppm; HRMS (ESI-TOF):  $m/z$   $[M+H]^+$  calcd for  $C_{28}H_{22}N_3O_3S^+$ : 480.1376; found: 480.1367.

**4. Post-functionalization of compound 3a**

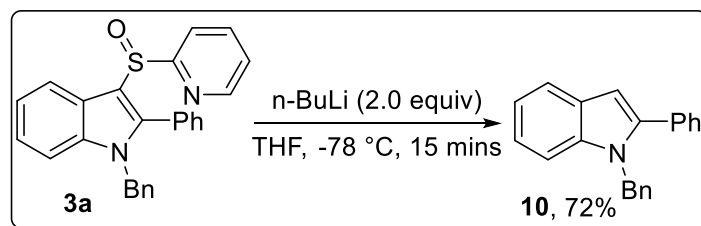


A dry screw cap pressure tube (15 mL) equipped with a magnetic stirring bar was charged with 1-benzyl-2-phenyl-3-(pyridin-2-ylsulfinyl)-1H-indole (**3a**, 50 mg, 0.122 mmol), KO<sup>t</sup>Bu (7.0

equiv.), in DMSO in the presence of O<sub>2</sub>, and was stirred at 80 °C in an oil bath for 8 h. Upon completion of the reaction (monitored by TLC), the mixture was diluted with water (30 mL) and extracted with EtOAc (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude product was purified by column chromatography ( hexane-EtOAc, 60:40 ) to provide 2-phenyl-3-(pyridin-2-ylsulfinyl)-1*H*-indole (**8**) as an off white solid ( 37 mg, 0.116 mmol, 95% yield), mp 190-191 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.30 (s, 1H), 8.55 (d, *J* = 3.9 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 8.15 (td, *J* = 7.7, 1.4 Hz, 1H), 7.99 (d, *J* = 7.1 Hz, 2H), 7.60 (dt, *J* = 23.5, 7.1 Hz, 3H), 7.47 (dd, *J* = 9.8, 6.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H) ppm; <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 165.23, 150.48, 144.12, 138.52, 136.62, 130.39, 130.09, 129.24, 125.17, 124.90, 123.53, 121.34, 120.61, 119.54, 112.85, 112.34 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>OS<sup>+</sup>: 319.0900; found: 319.0898.



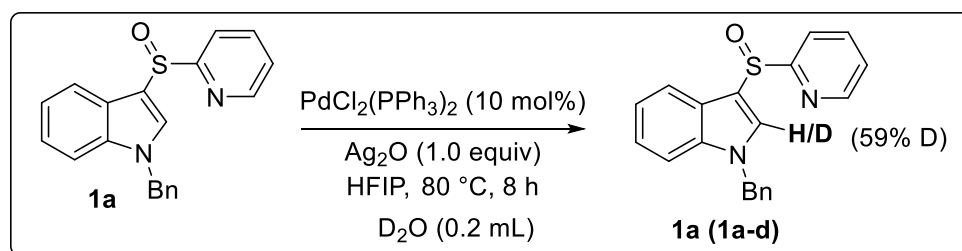
A dry round bottom flask (25 mL) equipped with a magnetic stirring bar was charged with 1-benzyl-2-phenyl-3-(pyridin-2-ylsulfinyl)-1*H*-indole (**3a**, 50 mg, 0.122 mmol), zinc dust (5, 593 mg, 9.065 mmol), in THF/aq. NH<sub>4</sub>Cl (1:1) (5.0 mL) was stirred at room temperature for 12 h. The mixture was passed through a small pad of Celite with EtOAc, and the mixture was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane-EtOAc, 80:20) to provide 1-benzyl-2-phenyl-3-(pyridin-2-ylthio)-1*H*-indole (**9**) as white solid (29 mg, 0.067 mmol, 85% yield), mp 173-174 °C; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.34 (d, *J* = 3.9 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 5H), 7.25 (dd, *J* = 13.7, 6.6 Hz, 3H), 7.20 (d, *J* = 7.0 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.06 – 7.03 (m, 1H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 5.47 (s, 2H) ppm; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 161.6, 149.3, 146.12 137.9, 137.1, 136.8, 130.2, 129.9, 129.1, 129.0, 128.6, 128.4, 127.2, 126.0, 123.0, 121.2, 119.6, 118.9, 118.7, 111.6, 98.1, 47.5 ppm; HRMS (ESI-TOF): *m/z* [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>21</sub>N<sub>2</sub>S<sup>+</sup>: 393.1420; found: 393.1417.



To a solution of 1-benzyl-2-phenyl-3-(pyridin-2-ylsulfinyl)-1*H*-indole (**3a**, 50 mg, 0.122 mmol) in THF at -78 °C was added *n*-BuLi (0.244 mmol) solution. The solution was allowed to warm to -78 °C over 15 minutes. The reaction was quenched with water, and the reaction mixture was extracted with EtOAc. The combined organic layers were washed with H<sub>2</sub>O and saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane-EtOAc, 99:01) to provide 1-benzyl-2-phenyl-1*H*-indole (**10**) as yellow liquid (25 mg, 0.088 mmol, 72% yield), mp 173-174 °C Analytical data were in good accordance with those reported in the literature.<sup>5</sup>

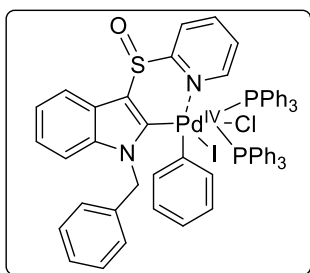
## 5. Mechanistic Investigation

### 5.1 Deuterium scrambling experiment:



A dry screw cap pressure tube (15 mL) equipped with a magnetic stirring bar was charged with 2-pyridyl sulfoxide substituted indoles **1a** (0.15 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol%), Ag<sub>2</sub>O (1.0 equiv) and excess of D<sub>2</sub>O (0.2 mL) in HFIP was stirred at 80 °C for 8 h. The resulting reaction mixture was cooled to room temperature and passed through a small pad of Celite in EtOAc. After evaporation of the solvent, the deuterium incorporation was determined using crude reaction mixture. <sup>1</sup>H NMR analysis shows 59% deuterium incorporation at C2-H of the **1a/1a-d** (see spectra).

### 5.2 LC-HRMS data of palladacycle intermediate C:



HRMS (ESI-TOF) calcd for  $C_{62}H_{54}ClIN_3OP_2PdS^+ [M+NH_4]^+$  1218.1225, found 1218.1207.

Compound Spectra

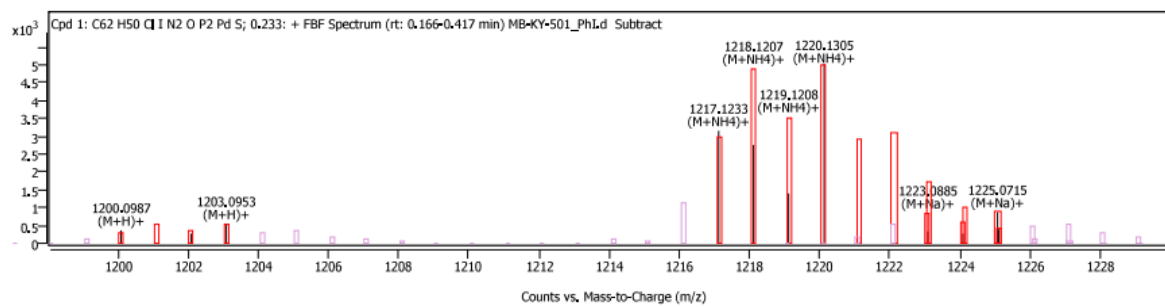
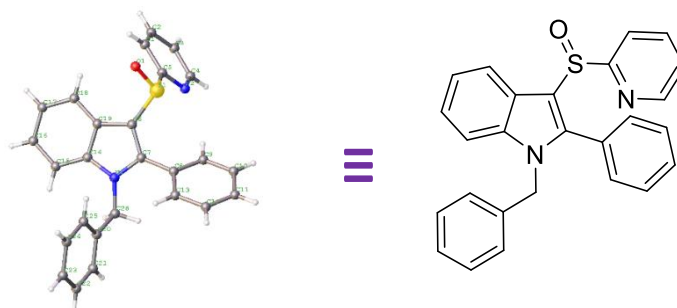


Figure S1: HRMS spectrum of palladacycle intermediate C.

## 6. Single Crystal X-ray Structures

### 6.1 Single Crystal X-ray Structure of 3a:

**Crystallization:** Crystal of compound **3a** (15 mg) was grown in a 2 mL of acetonitrile solvent by slow evaporation method for 5 days.



**Figure S2:** X-ray crystallography of **3a** (the ellipsoid contour probability level is 50%).

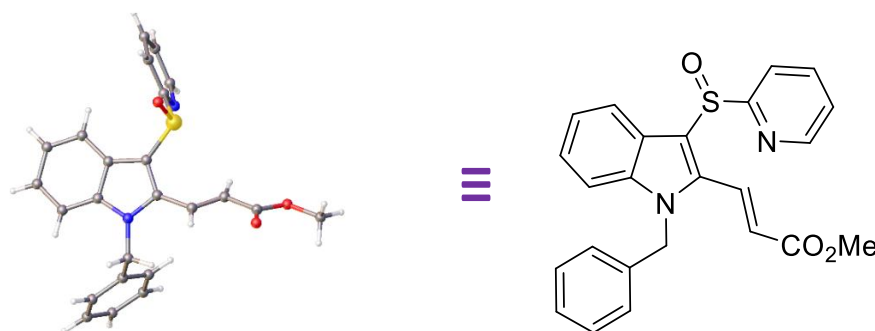
**Table S2:** Crystal data and structure refinement for **3a**.

<b>CCDC Number</b>	2506848
<b>Identification code</b>	<b>3a</b>
<b>Empirical formula</b>	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> OS
<b>Formula weight</b>	408.50
<b>Temperature</b>	298(2) K
<b>Wavelength</b>	1.54178 Å
<b>Crystal system, space group</b>	Triclinic, P-1
<b>Unit cell dimensions</b>	a = 10.0779(5) Å      α = 101.235(2)° b = 10.3450(5) Å      β = 112.2530(10)° c = 11.3372(6) Å      γ = 97.941(2)°
<b>Volume</b>	1043.32(9) Å <sup>3</sup>
<b>Z, Calculated density</b>	2, 1.300 Mg/m <sup>3</sup>
<b>Absorption coefficient</b>	1.528 mm <sup>-1</sup>
<b>F(000)</b>	428
<b>Crystal size</b>	0.276 x 0.126 x 0.075 mm <sup>3</sup>
<b>Theta range for data collection</b>	4.376 to 66.488°
<b>Limiting indices</b>	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
<b>Reflections collected / Independent reflections</b>	27678 / 3622 [R(int) = 0.0613]

Completeness to theta = 66.488°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7426 and 0.6409
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3622 / 0 / 271
Goodness-of-fit on F <sup>2</sup>	1.086
Final R indices [I>2σ(I)]	R <sub>1</sub> = 0.0708, wR <sub>2</sub> = 0.2028
R indices (all data)	R <sub>1</sub> = 0.0731, wR <sub>2</sub> = 0.2064
Extinction coefficient	n/a
Largest diff. peak and hole	0.301 and -0.406 e.Å <sup>-3</sup>

## 6.2 Single Crystal X-ray Structure of 5a:

**Crystallization:** Crystal of compound **5a** (15 mg) was grown in a 2 mL of acetonitrile solvent by slow evaporation method for 7 days.



**Figure S3:** X-ray crystallography of **5a** (the ellipsoid contour probability level is 50%).

**Table S3:** Crystal data and structure refinement for **5a**.

CCDC Number	2506375
Identification code	<b>5a</b>
Empirical formula	C <sub>24</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> S
Formula weight	416.48
Temperature	100 (10) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.4219(5) Å      α = 96.178(3)°
	b = 10.5863(5) Å      β = 116.703(4)°

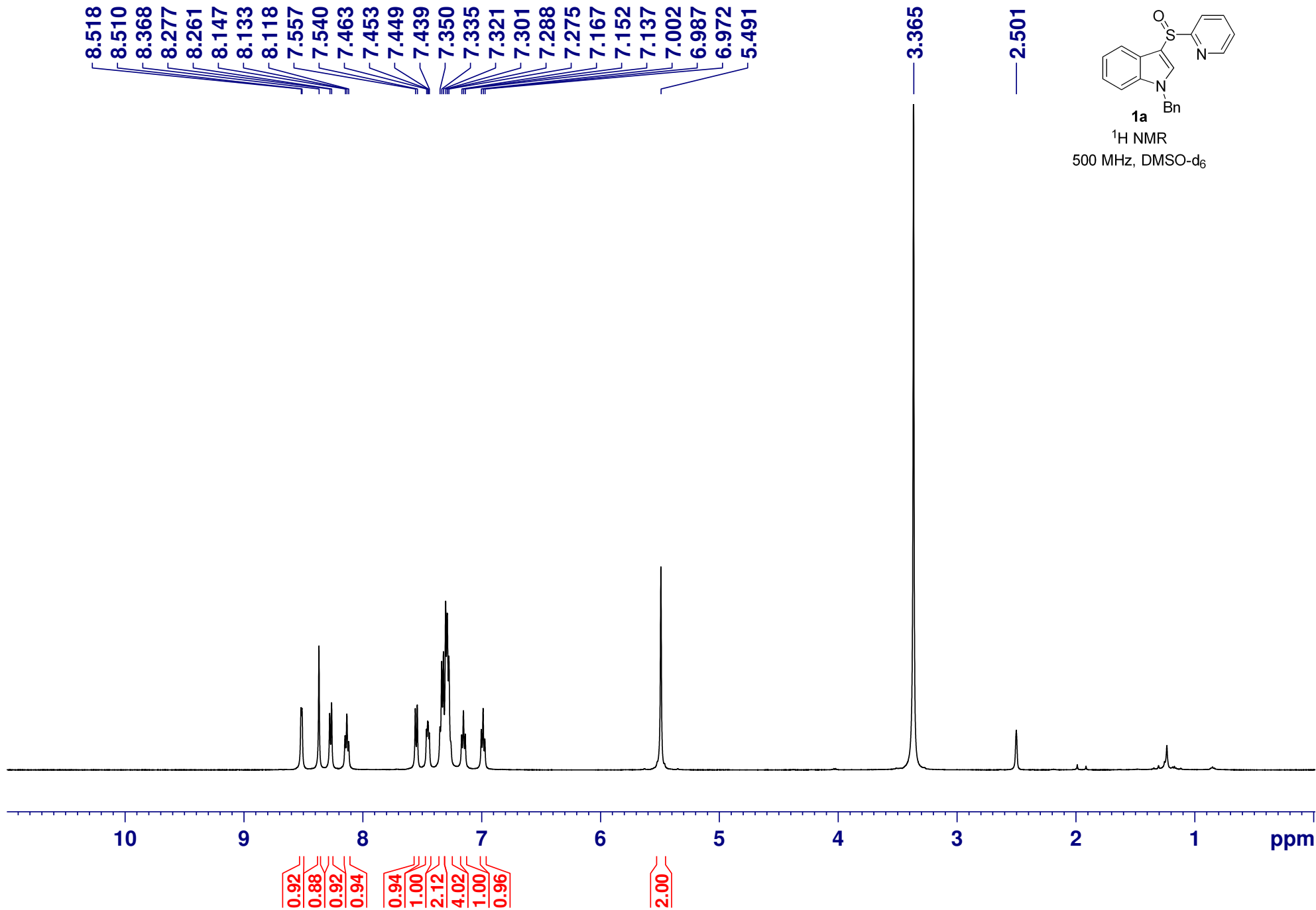
	$c = 11.5849(5) \text{ \AA}$ $\gamma = 111.389(4)^\circ$
<b>Volume</b>	1004.97(11) $\text{\AA}^3$
<b>Z, Calculated density</b>	14, 1.376 $\text{Mg/m}^3$
<b>F(000)</b>	438.5
<b>Crystal size</b>	0.16 x 0.13 x 0.09 $\text{mm}^3$
<b>Theta range for data collection</b>	4.16 to 52.72°
<b>Limiting indices</b>	-13<=h<=13, -11<=k<=13, -14<=l<=14
<b>Reflections collected / Independent reflections</b>	12692 / 4119 [R(int) = 0.0357]
<b>Completeness to theta = 26.360°</b>	100 %
<b>Max. and min. transmission</b>	1.0000 and 0.9480
<b>Data / restraints / parameters</b>	4119 / 0 / 53
<b>Goodness-of-fit on F<sup>2</sup></b>	0.978
<b>Final R indices [I&gt;2σ(I)]</b>	R <sub>1</sub> = 0.0369, wR <sub>2</sub> = 0.0929
<b>R indices (all data)</b>	R <sub>1</sub> = 0.0449, wR <sub>2</sub> = 0.1020
<b>Extinction coefficient</b>	n/a
<b>Largest diff. peak and hole</b>	0.49 and -0.39 $\text{e.\AA}^{-3}$

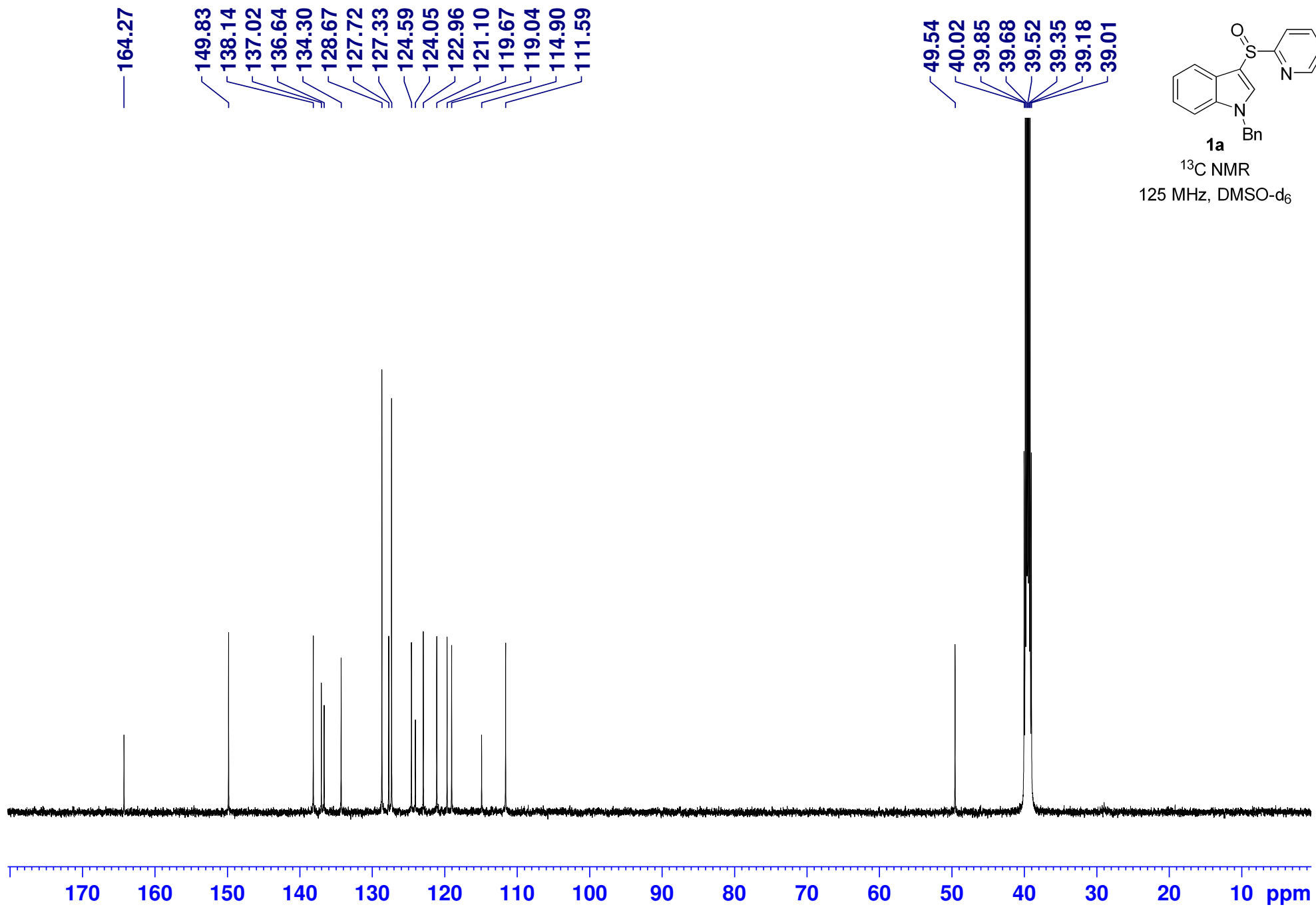
## 7. References

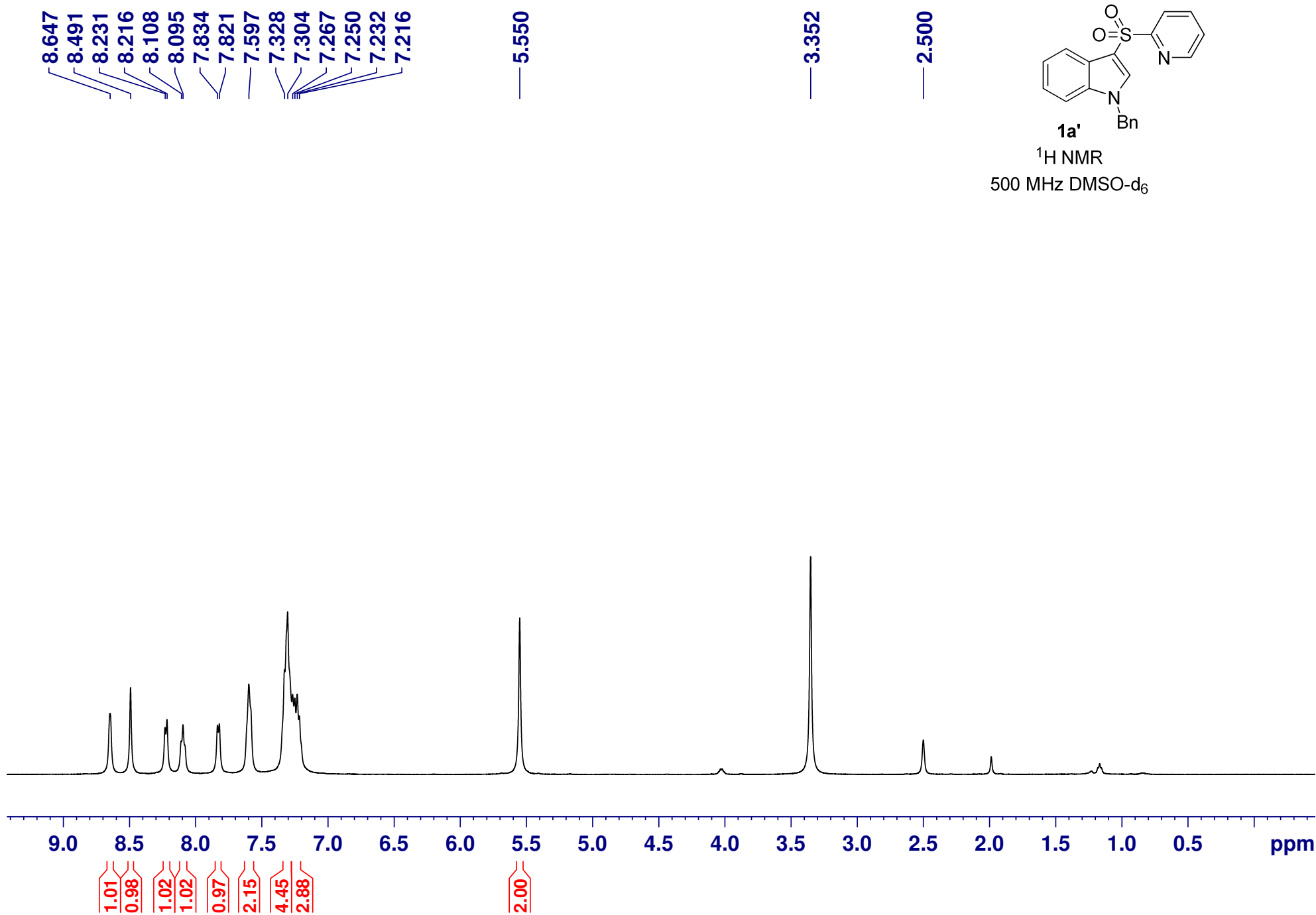
1. (a) *SAINT-Plus, version 6.45*, Bruker AXS Inc., Madison, WI, 2003. (b) G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Gottingen, Germany, 1997. (c) *SMART (version 5.625), SHELX-TL (version 6.12)*, Bruker AXS Inc., Madison, WI, 2000. (d) G. M. Sheldrick, *SHELXS-97*, University of Gottingen, Germany, 1997.

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5. B. S. Lane, D. Sames, Direct C-H Bond Arylation: Selective Palladium-Catalyzed C2-Arylation of *N*-Substituted Indoles, *Org. Lett.* 2004, **6**, 2897-2900.

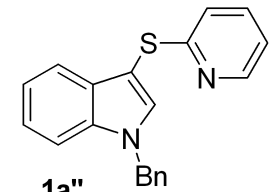
## 8. NMR Spectra



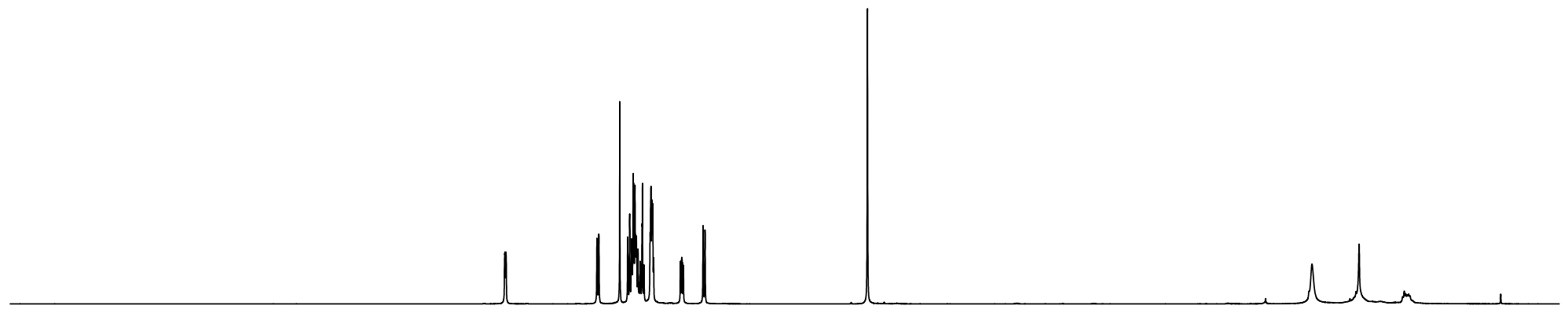




8.412  
8.410  
8.409  
8.403  
8.401  
7.640  
7.625  
7.450  
7.383  
7.366  
7.350  
7.346  
7.337  
7.334  
7.322  
7.319  
7.315  
7.311  
7.297  
7.279  
7.277  
7.262  
7.260  
7.248  
7.246  
7.195  
7.188  
7.181  
7.180  
7.175  
7.167  
6.943  
6.941  
6.933  
6.931  
6.928  
6.926  
6.918  
6.917  
6.753  
6.736  
5.378

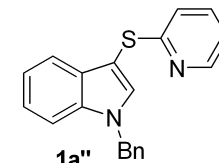
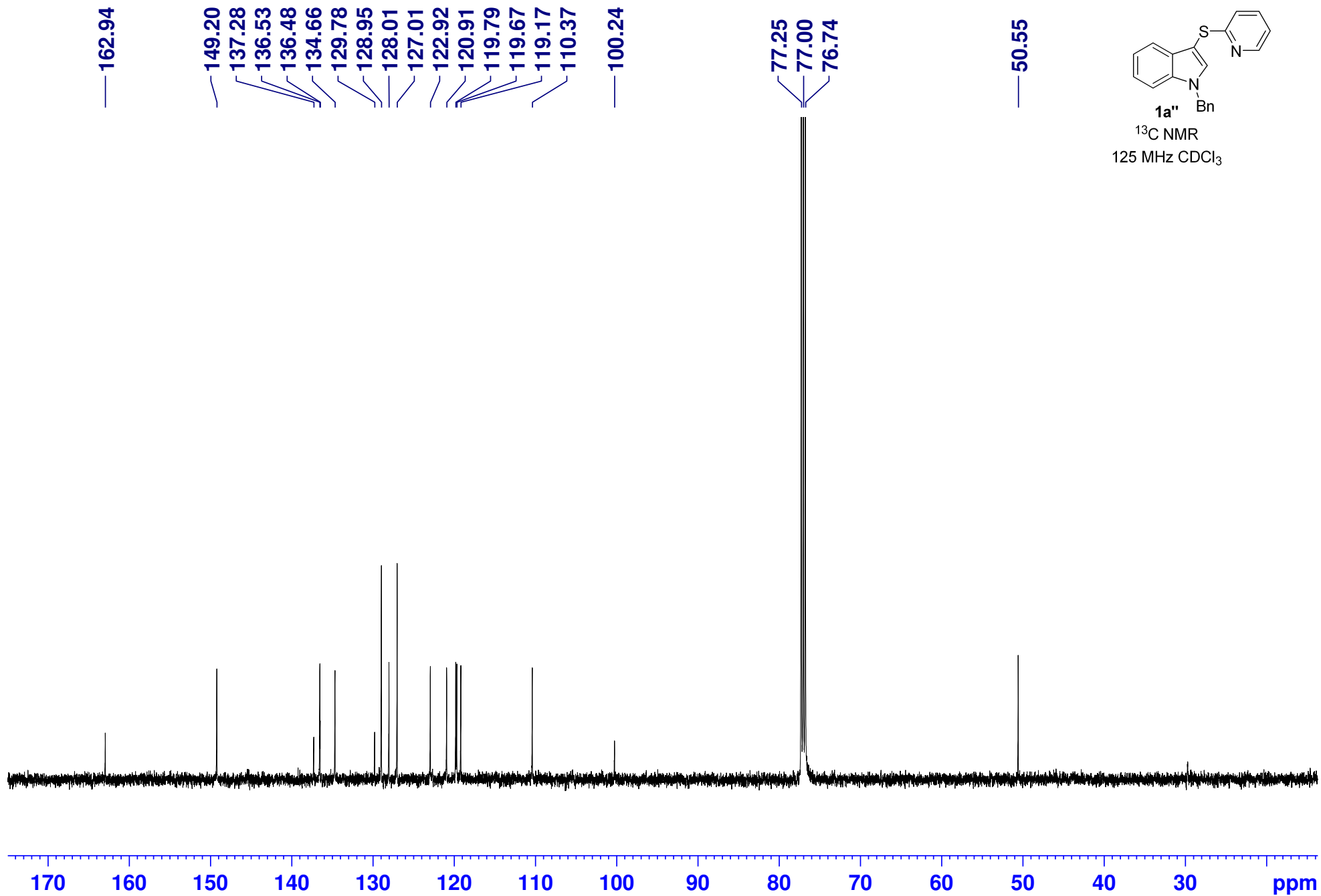


<sup>1</sup>H NMR  
500 MHz CDCl<sub>3</sub>



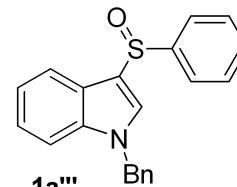
12 11 10 9 8 7 6 5 4 3 2 1 ppm

0.97  
0.99  
0.99  
1.02  
2.04  
2.40  
1.08  
3.00  
1.01  
0.95  
2.05

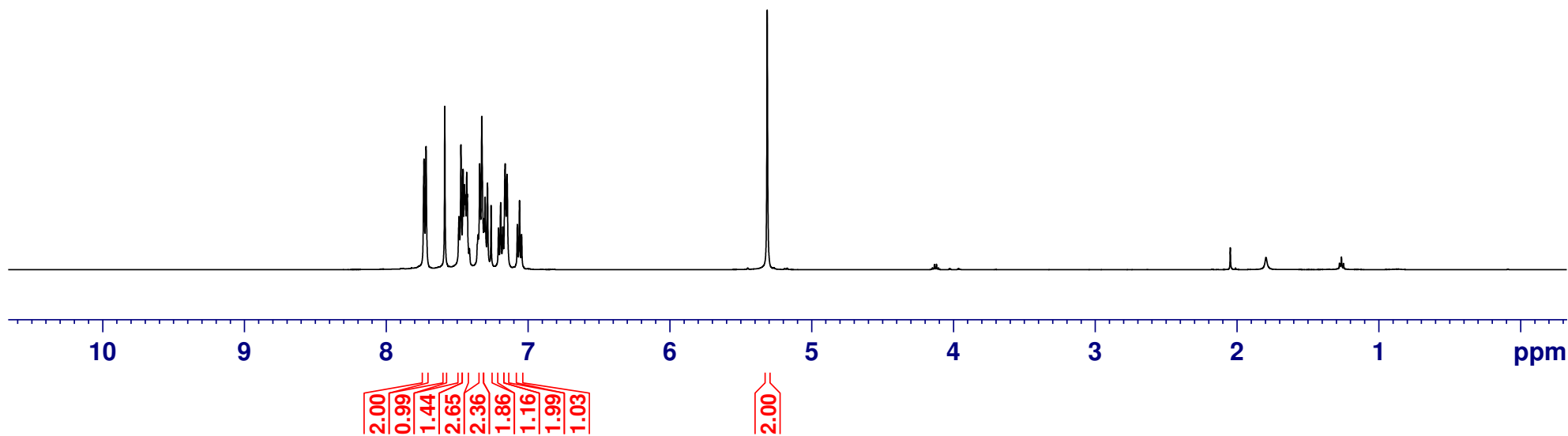


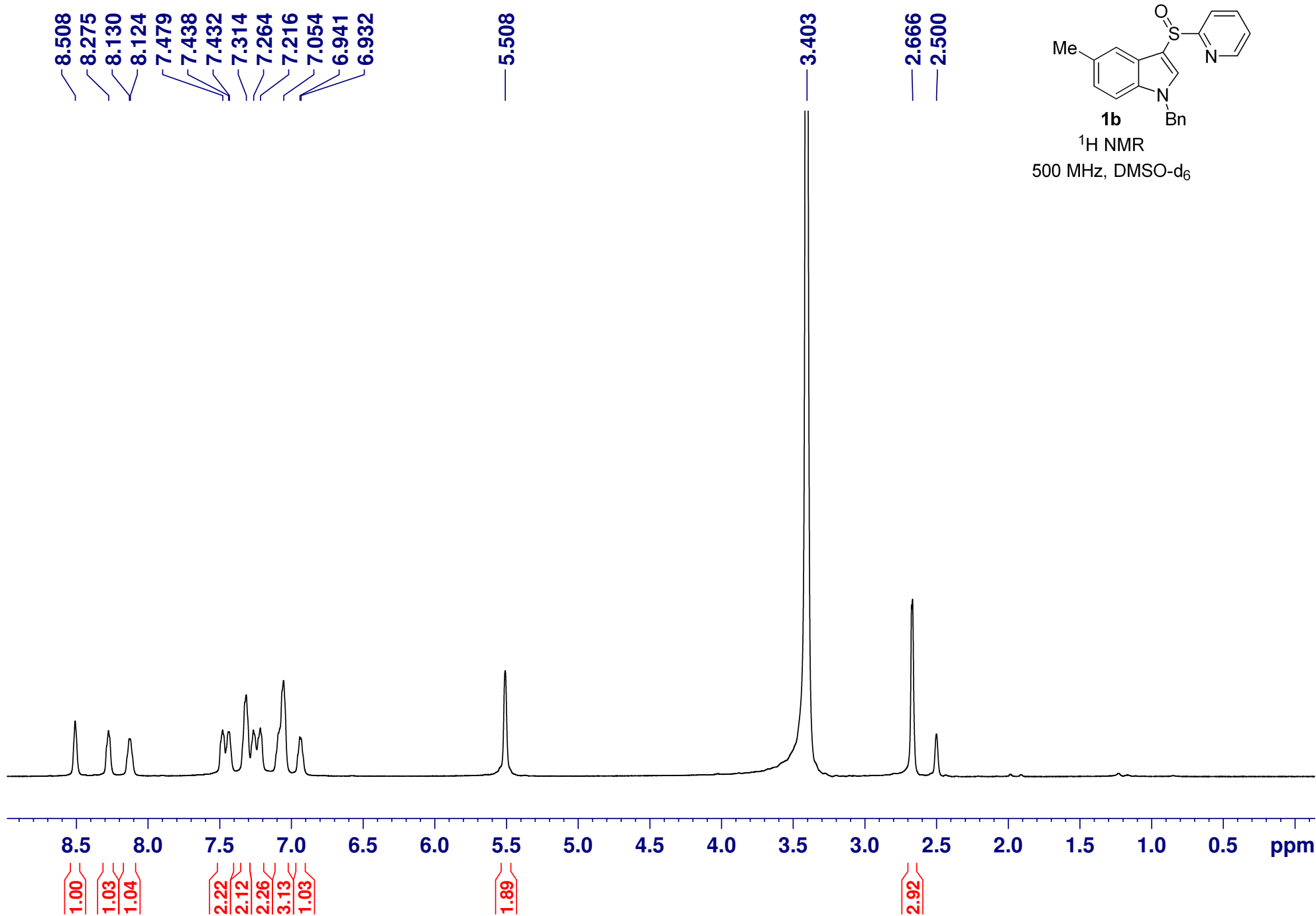
**13C NMR**  
125 MHz CDCl<sub>3</sub>

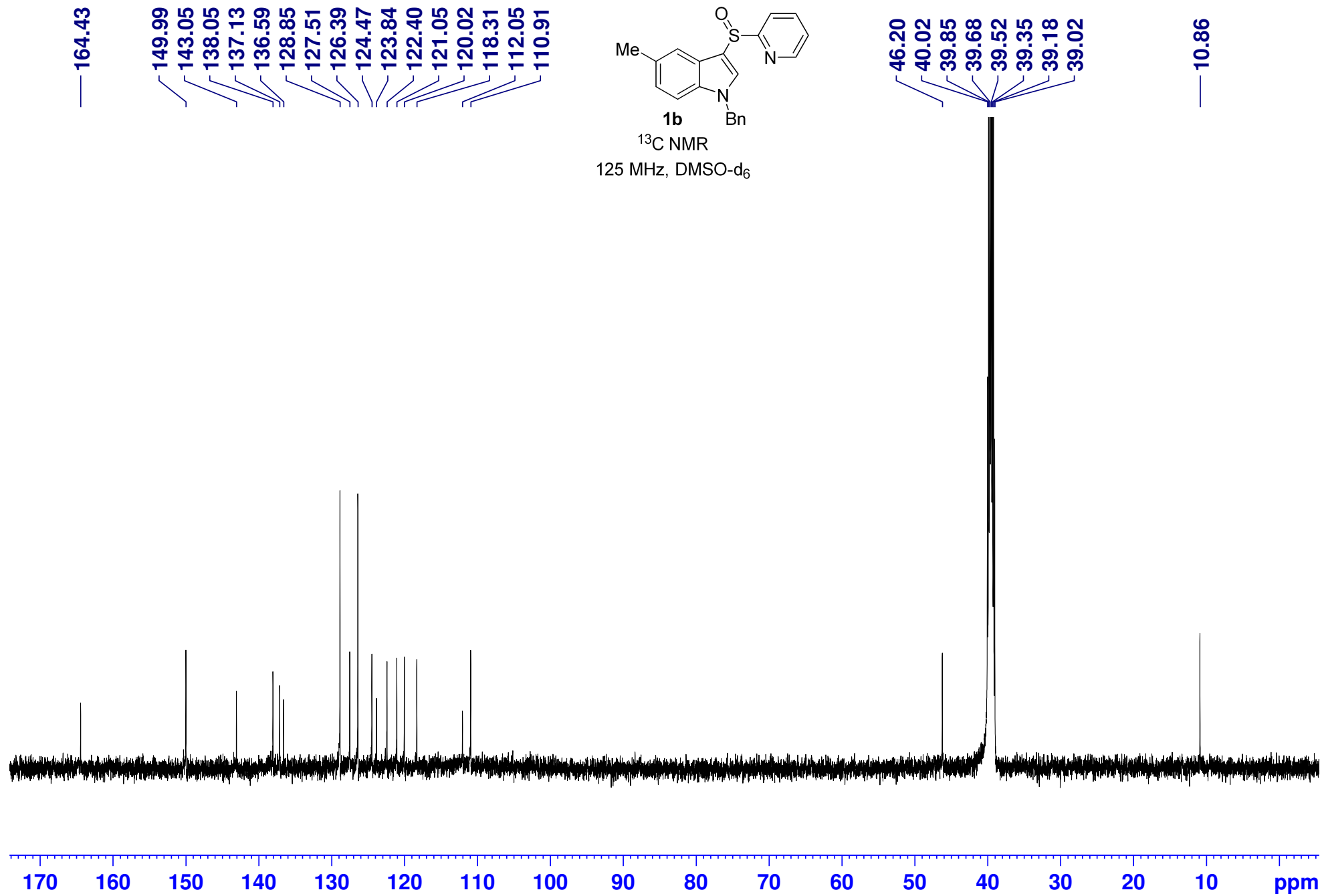
7.733  
7.718  
7.587  
7.486  
7.473  
7.457  
7.448  
7.441  
7.432  
7.427  
7.412  
7.357  
7.353  
7.340  
7.326  
7.310  
7.302  
7.285  
7.260  
7.207  
7.193  
7.177  
7.160  
7.147  
7.075  
7.060  
7.044  
5.312

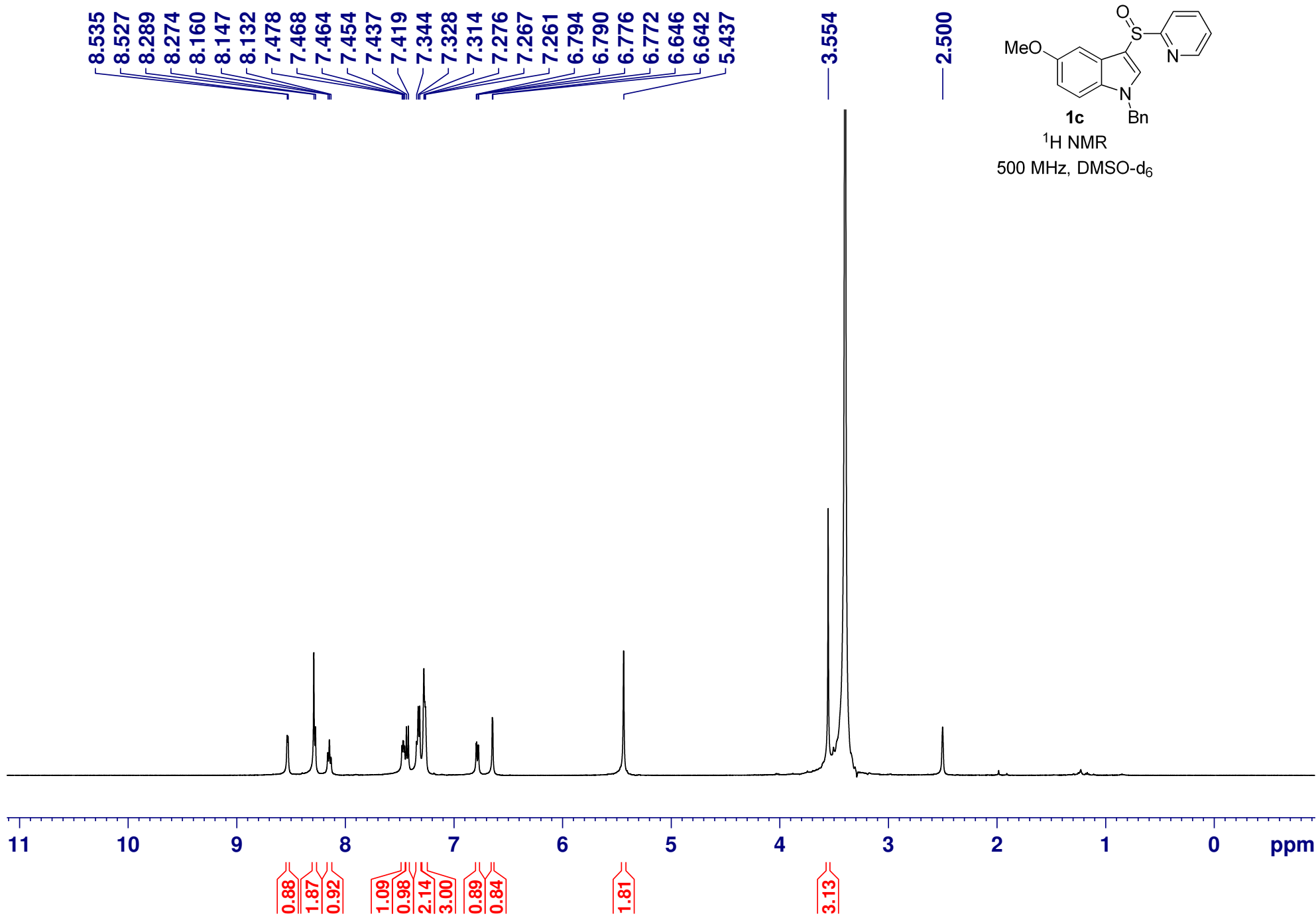


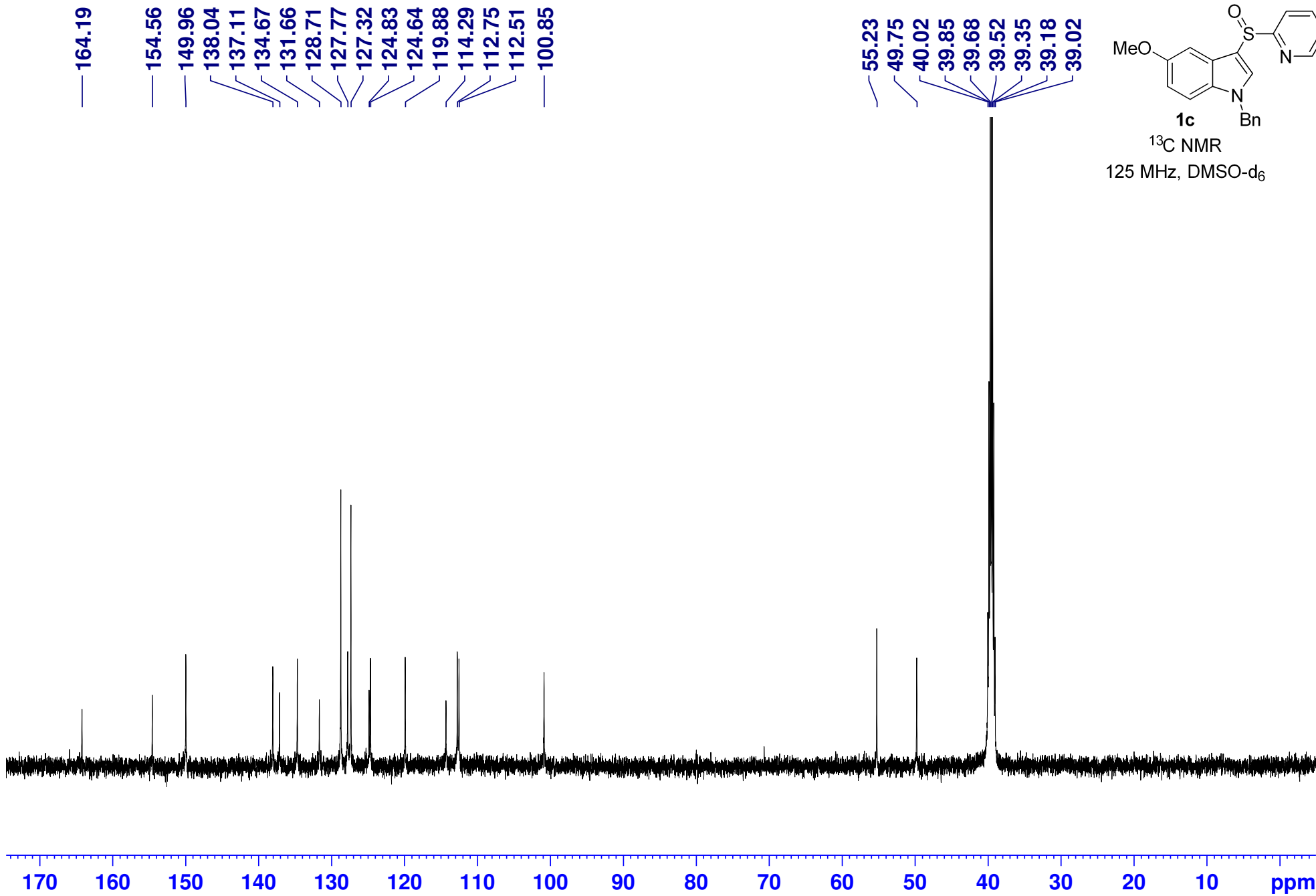
<sup>1</sup>H NMR  
500 MHz CDCl<sub>3</sub>

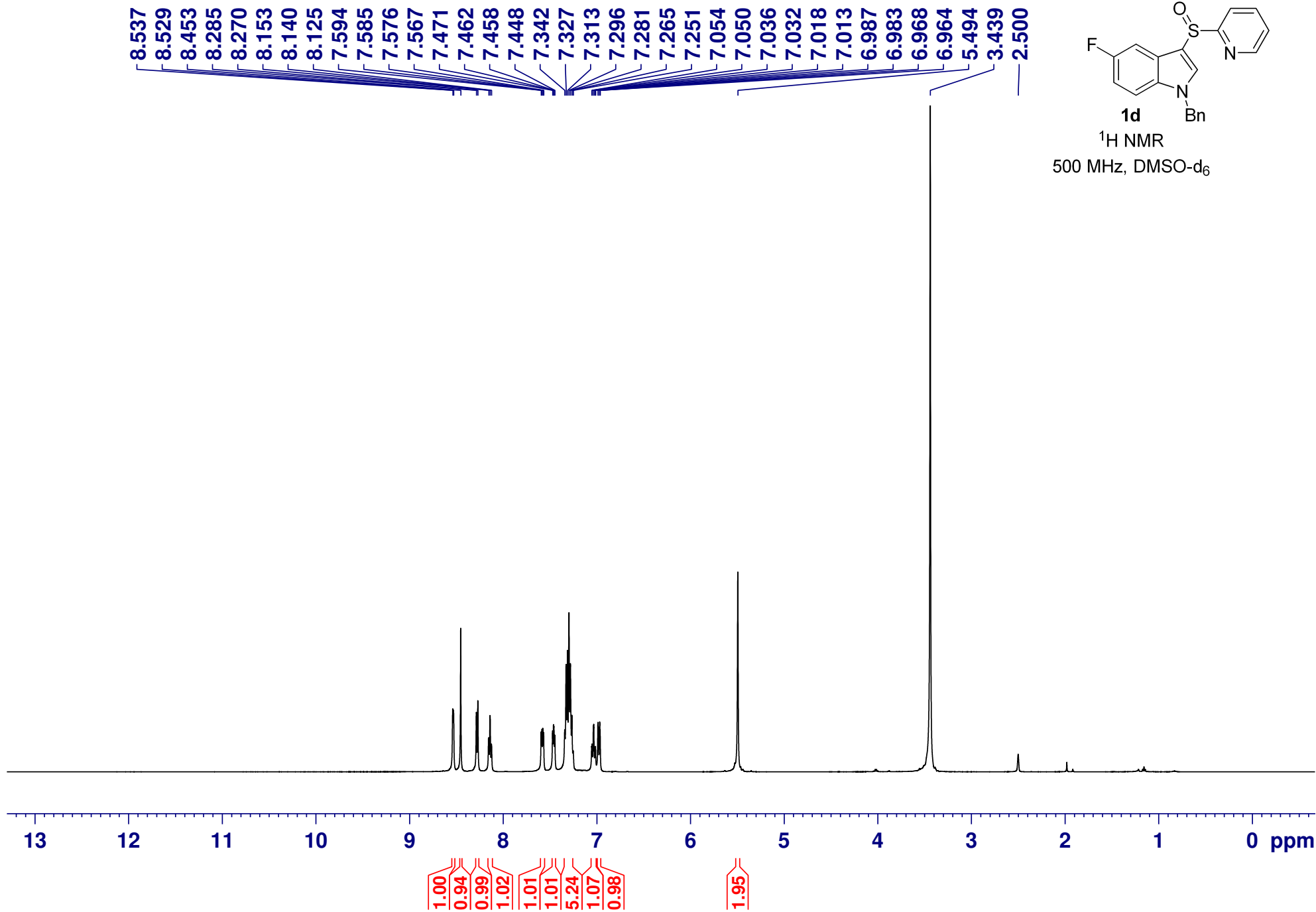


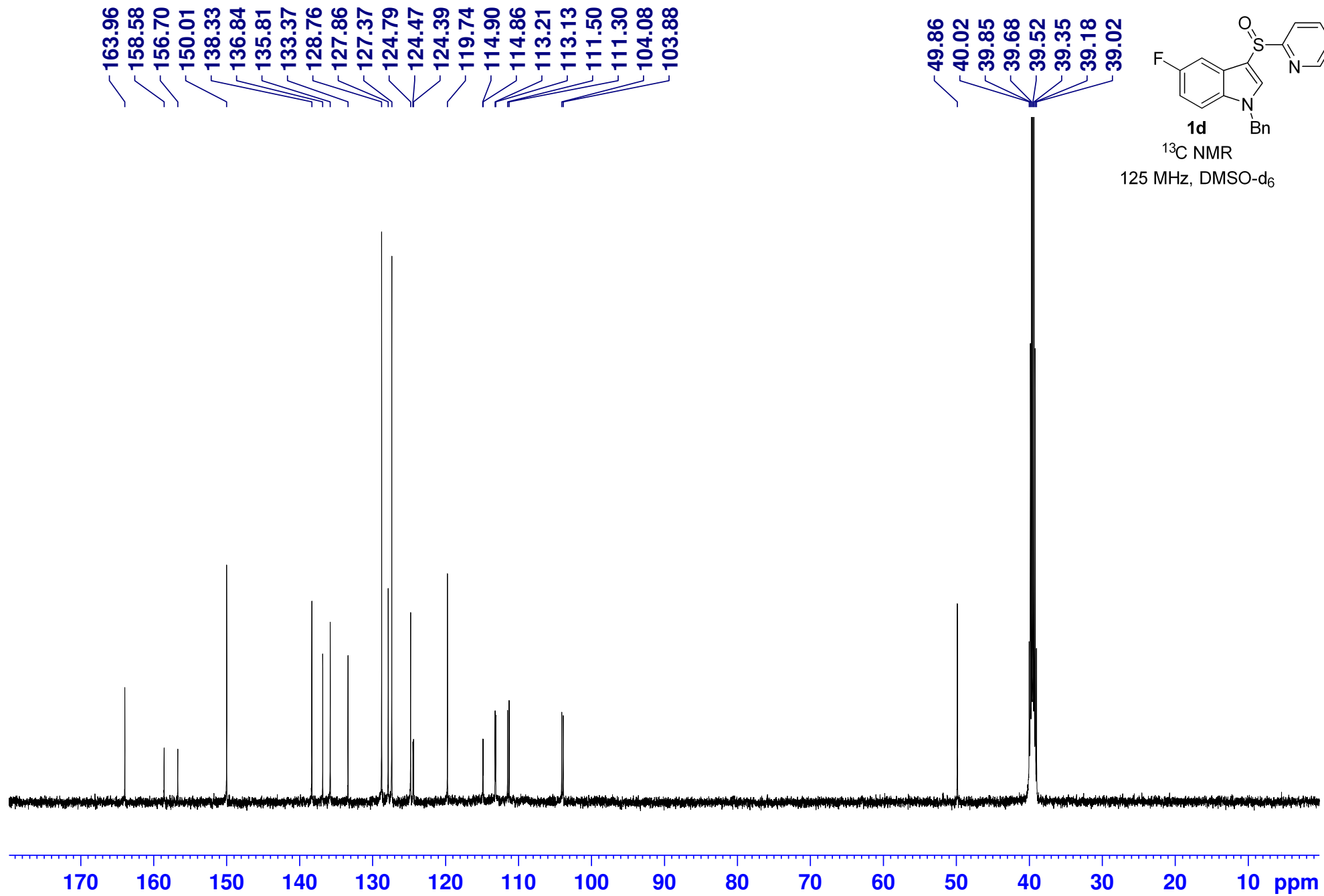










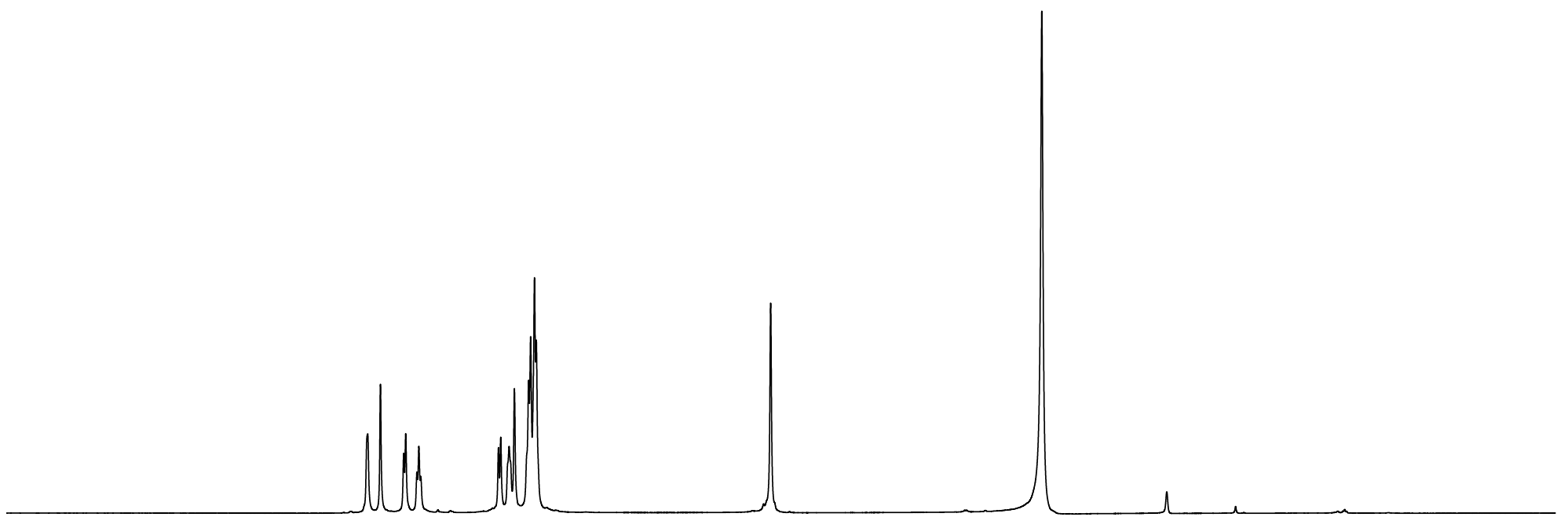
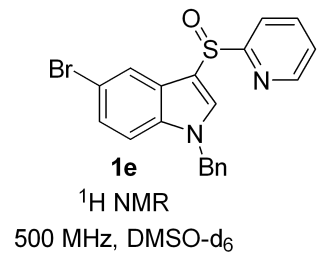


8.535  
8.439  
8.263  
8.248  
8.164  
8.149  
8.134  
7.548  
7.530  
7.467  
7.427  
7.319  
7.305  
7.276  
7.262

5.492

3.444

2.500

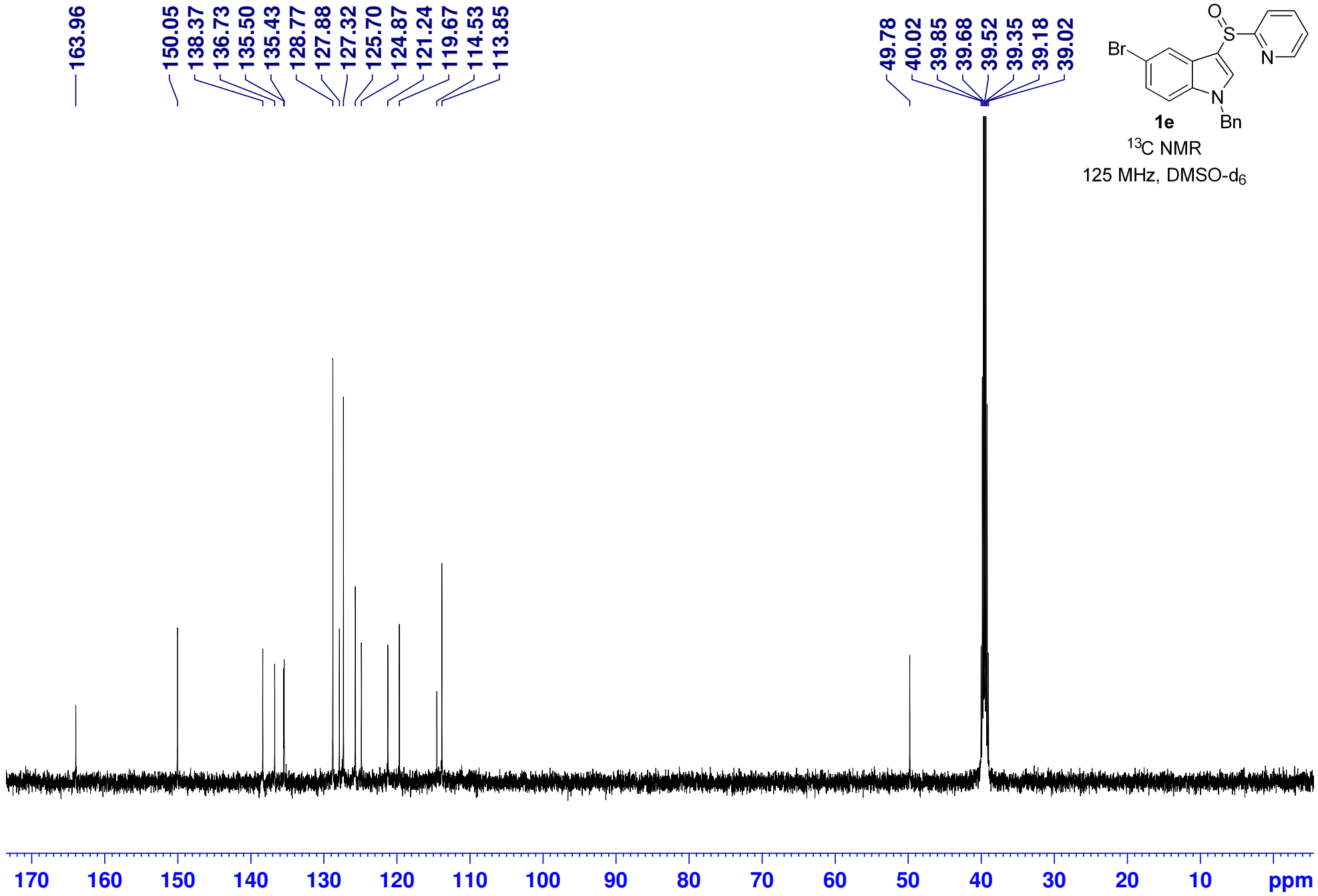


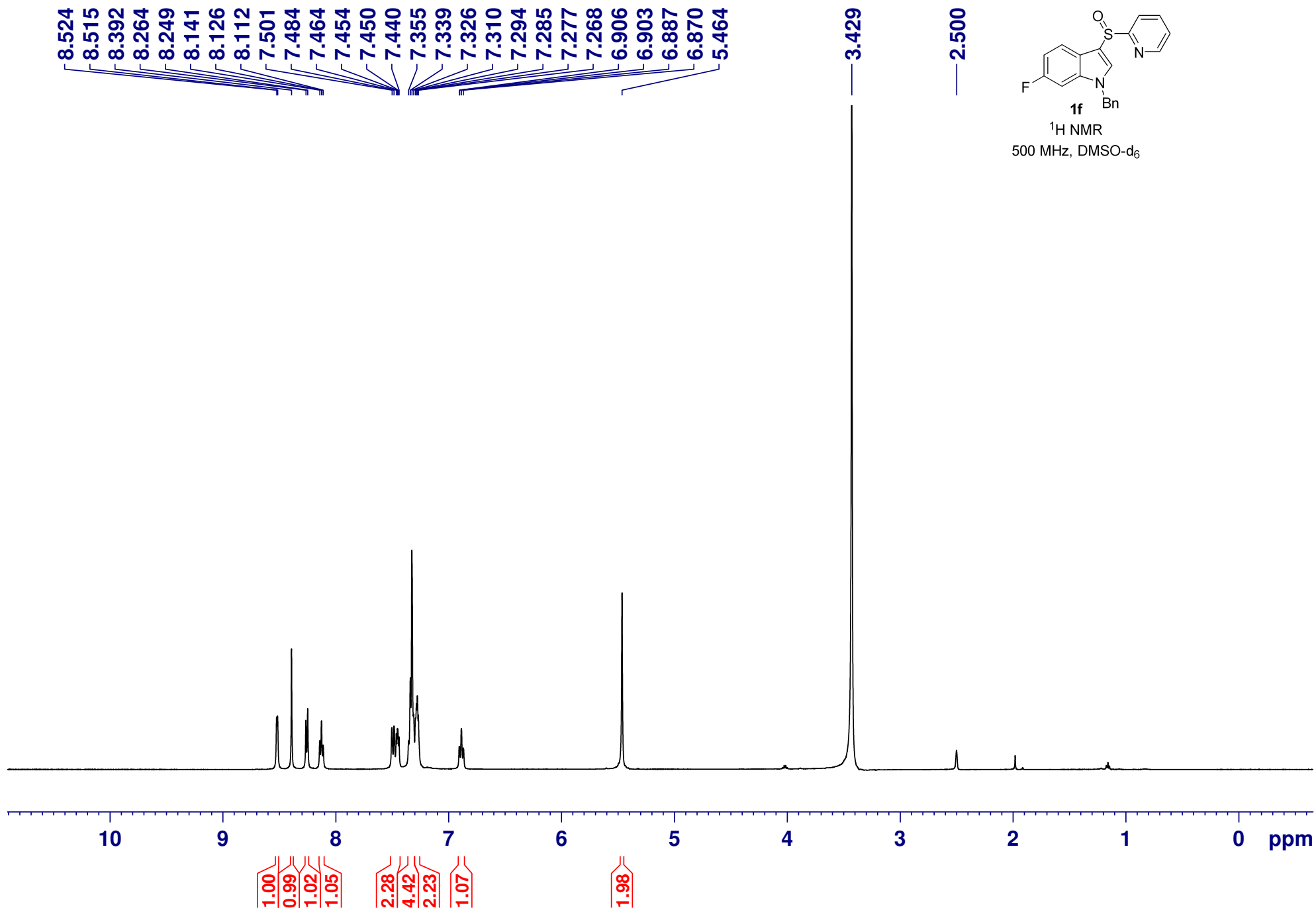
11 10 9 8 7 6 5 4 3 2 1 ppm

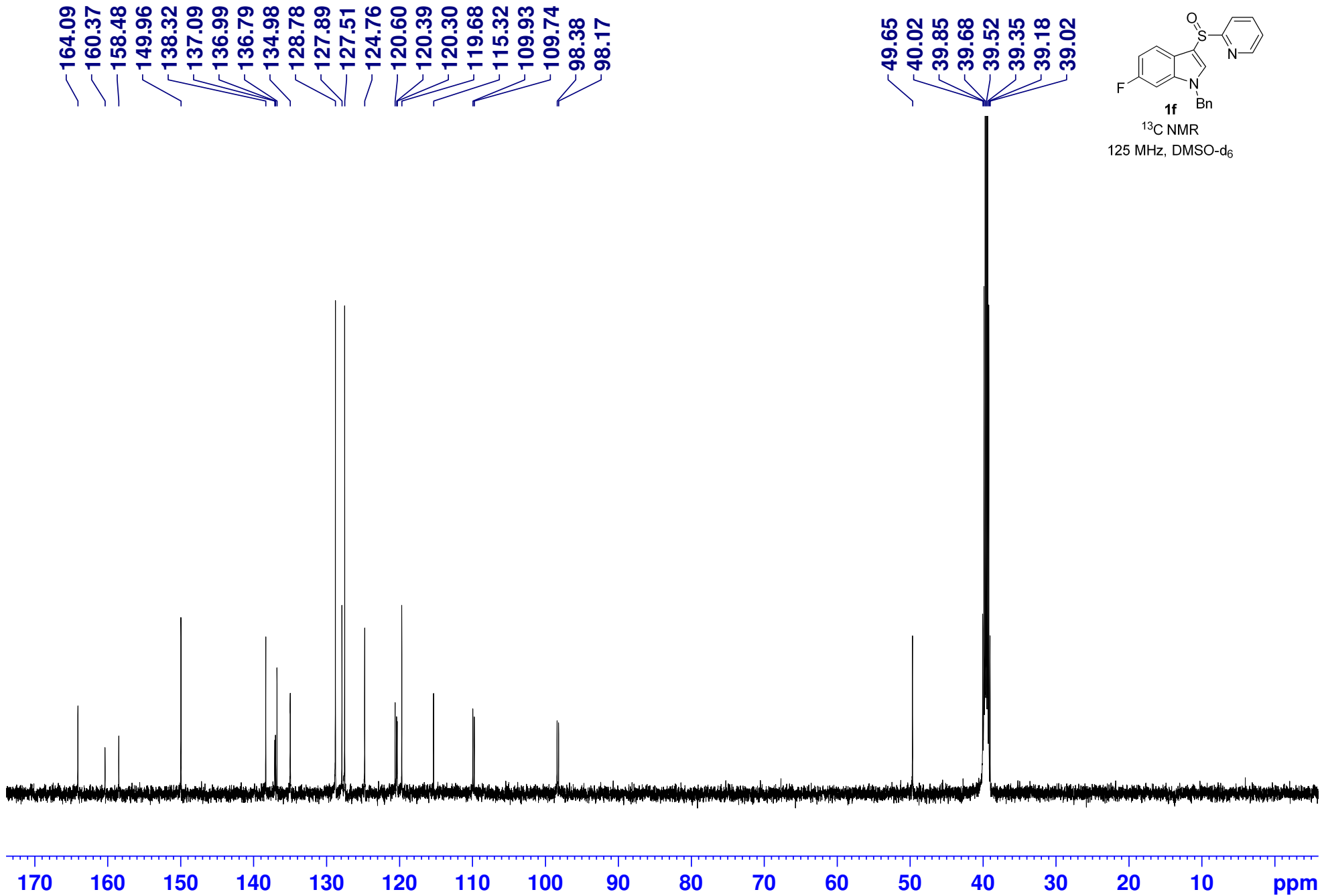
0.92  
0.91  
0.98  
0.96

0.98  
2.05  
6.05

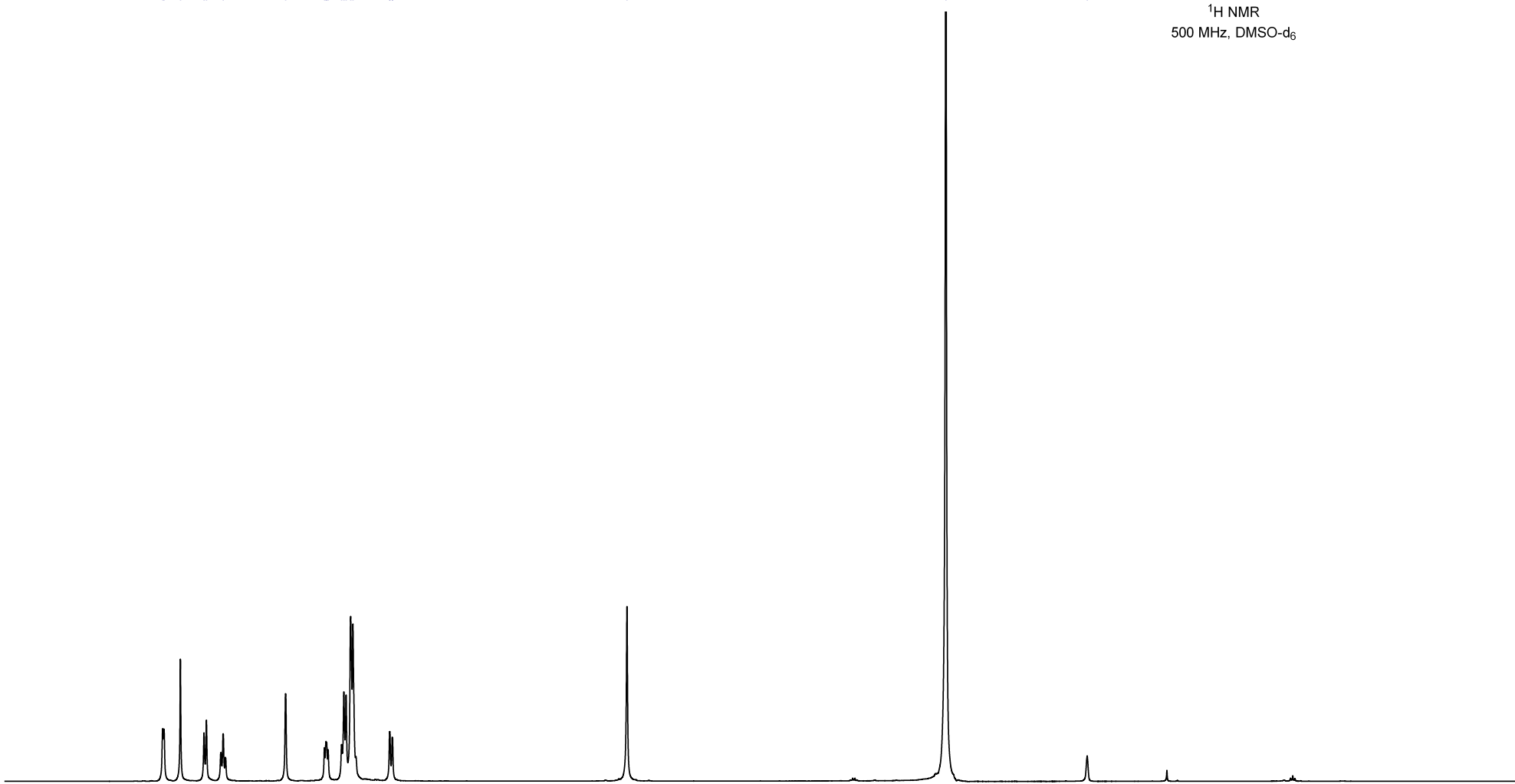
1.90







8.522  
8.514  
8.407  
8.253  
8.238  
8.129  
7.722  
7.469  
7.459  
7.455  
7.445  
7.357  
7.342  
7.328  
7.298  
7.283  
7.044  
7.042  
7.027  
7.025  
— 5.498

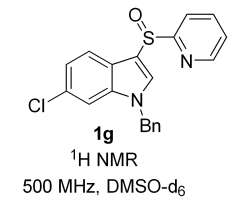


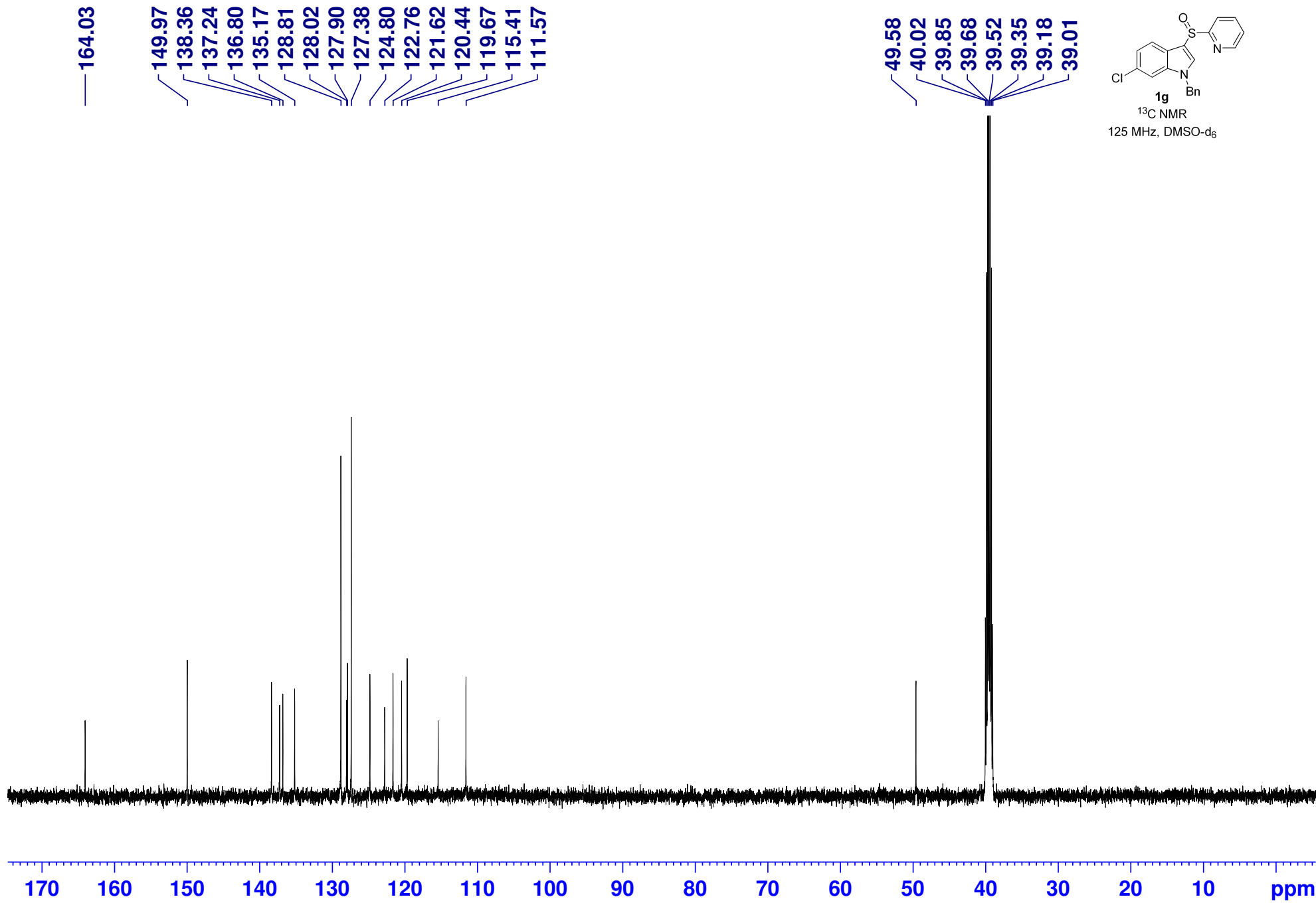
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

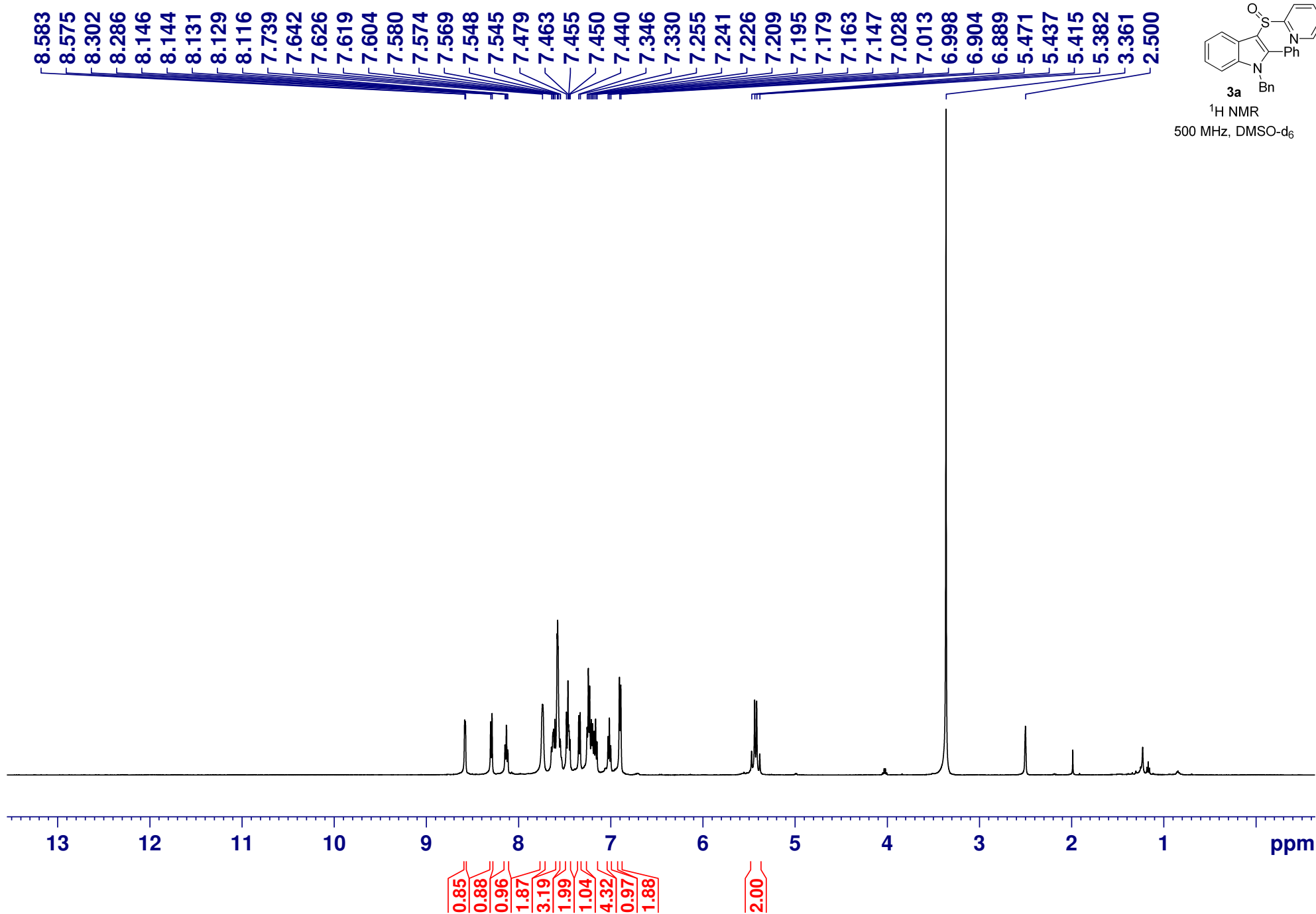
1.00  
0.95  
1.01  
1.07  
1.04  
1.07  
2.27  
4.40  
1.06

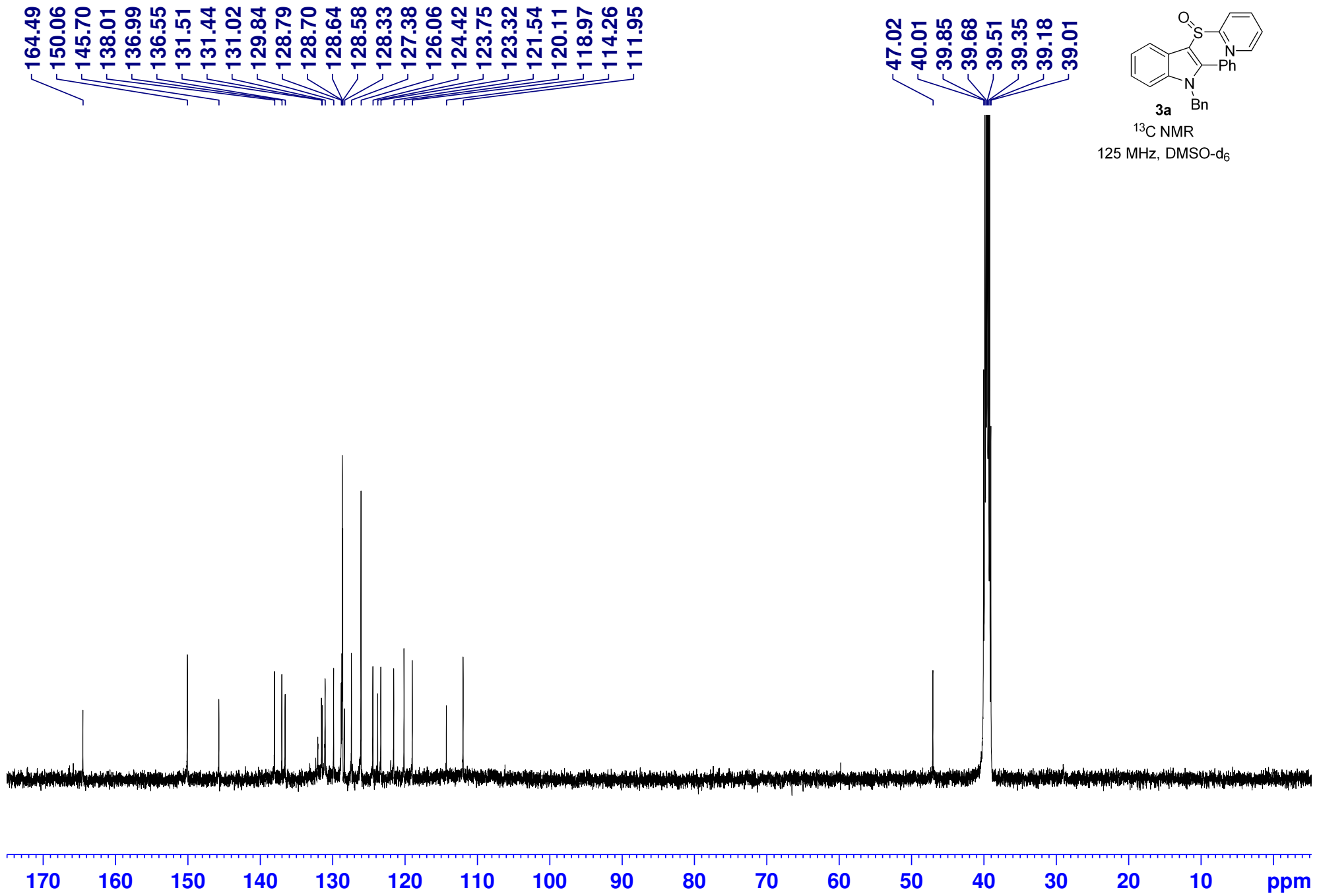
2.04

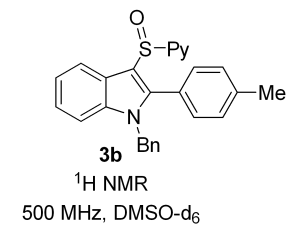
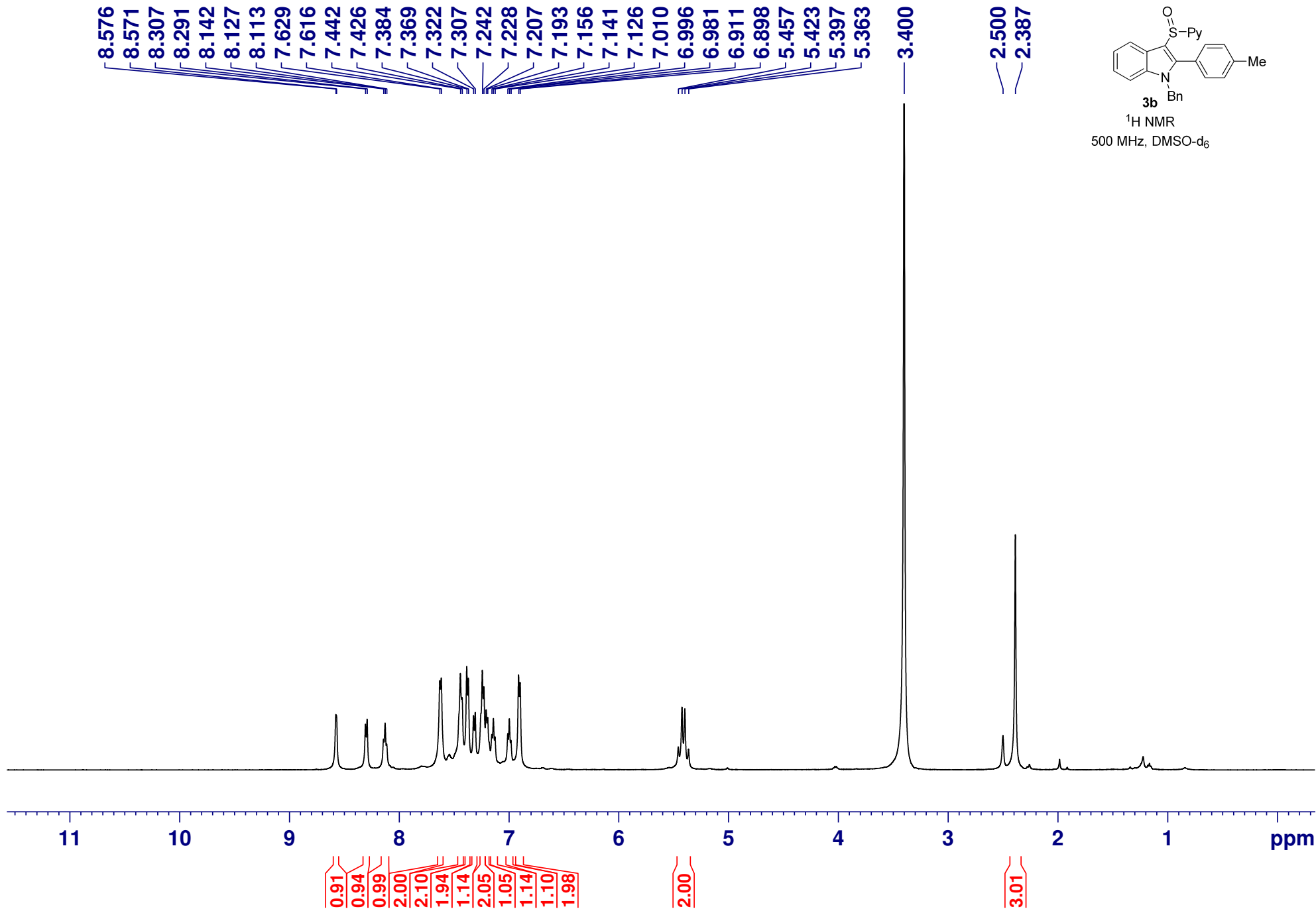
3.421  
— 2.500

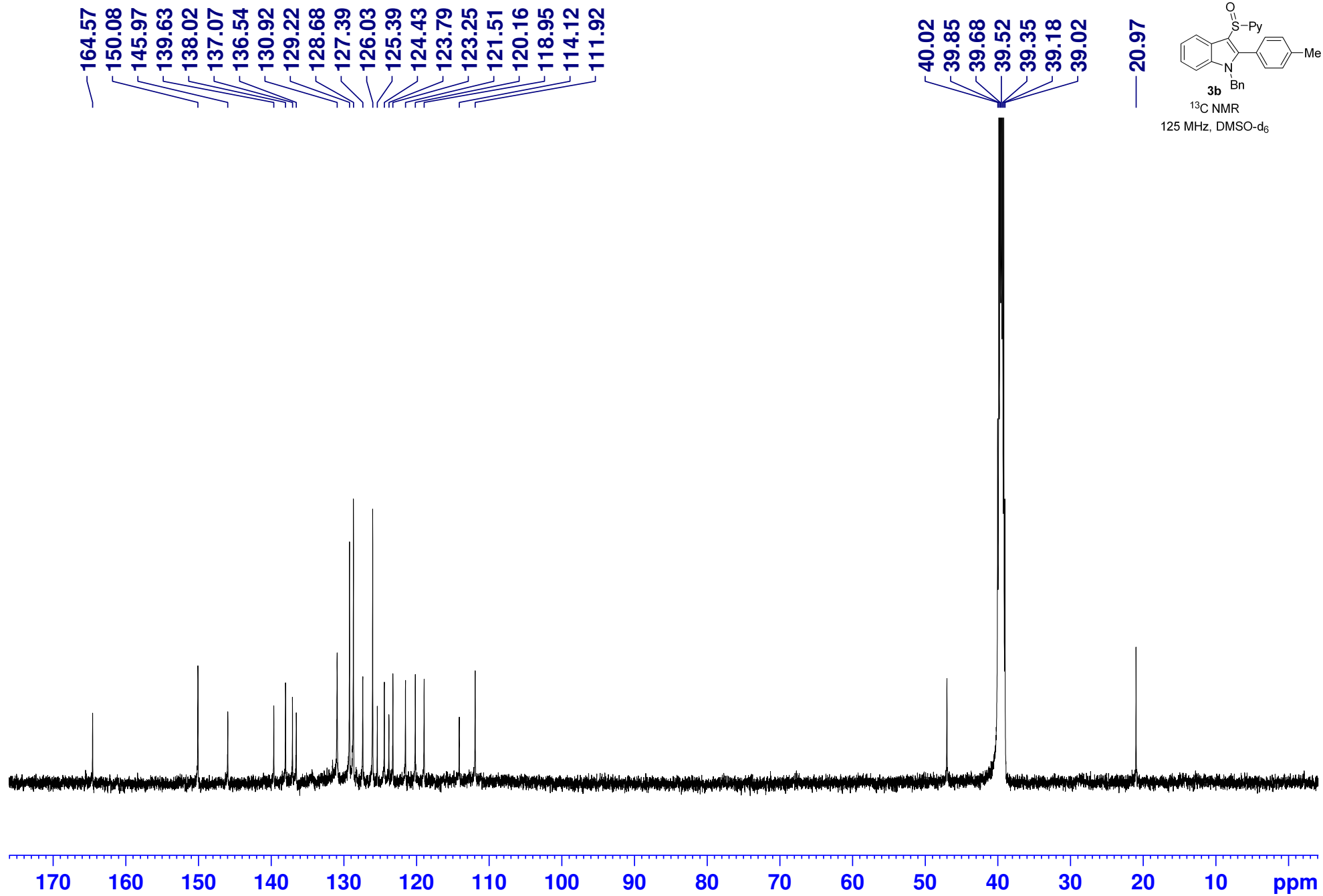


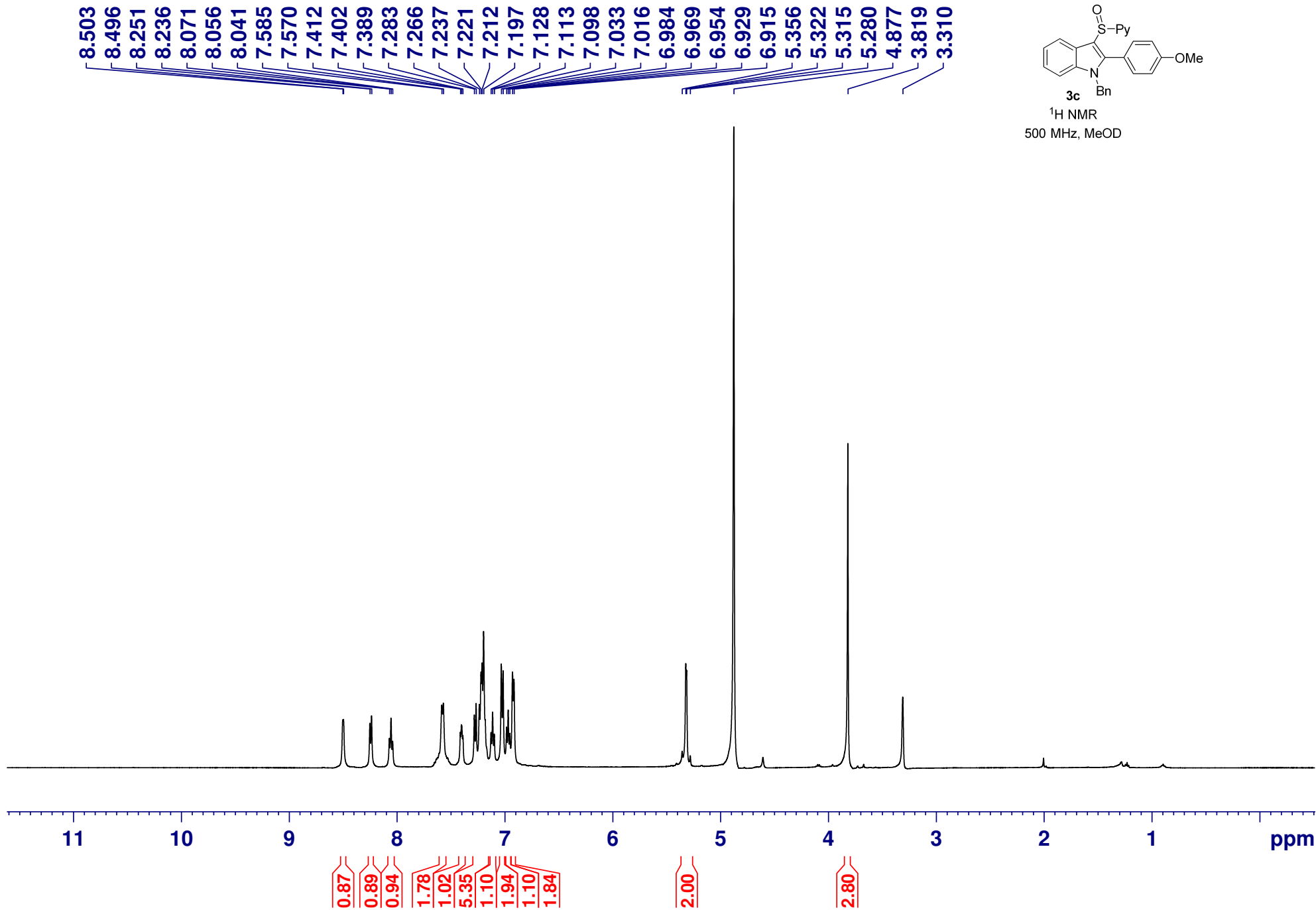






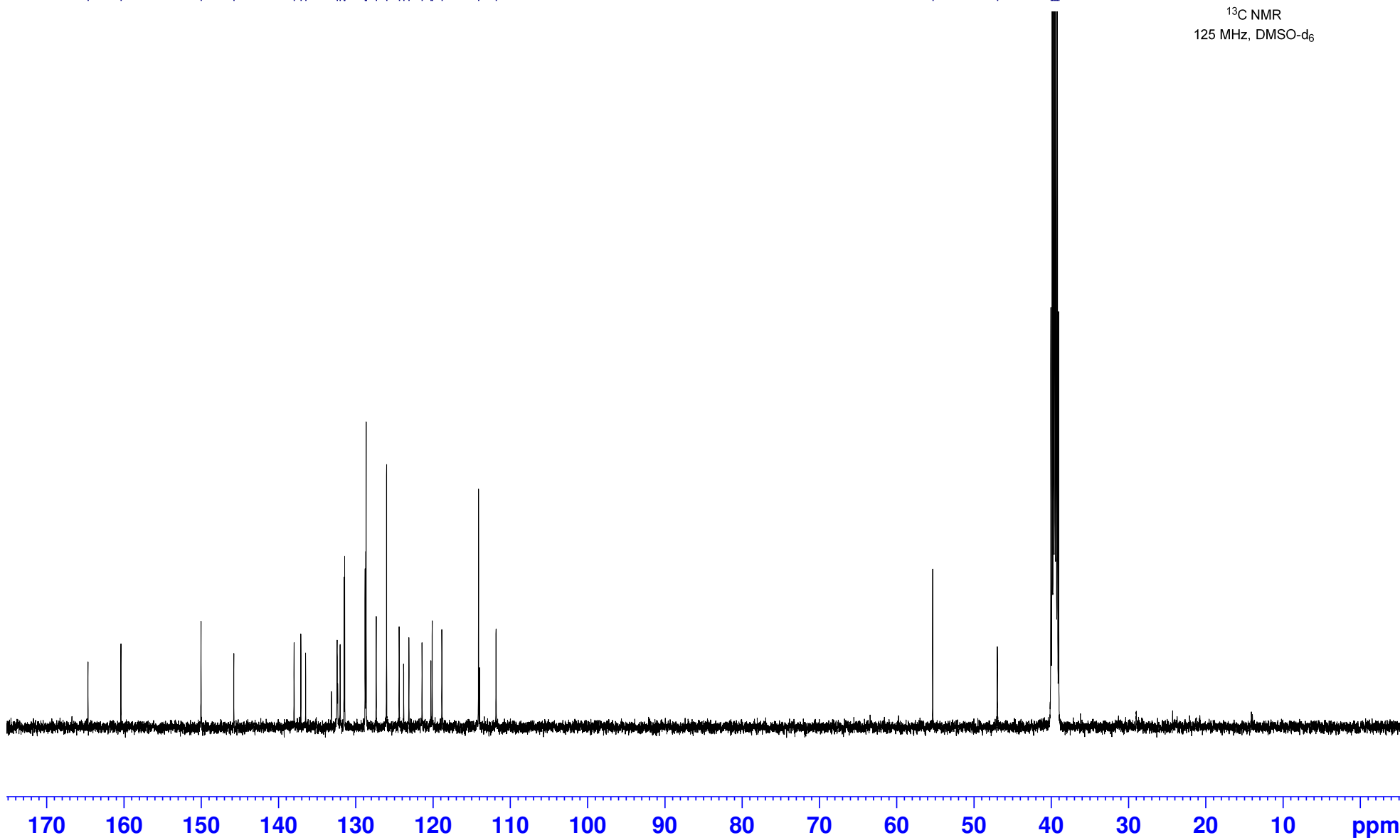
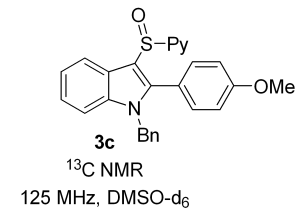


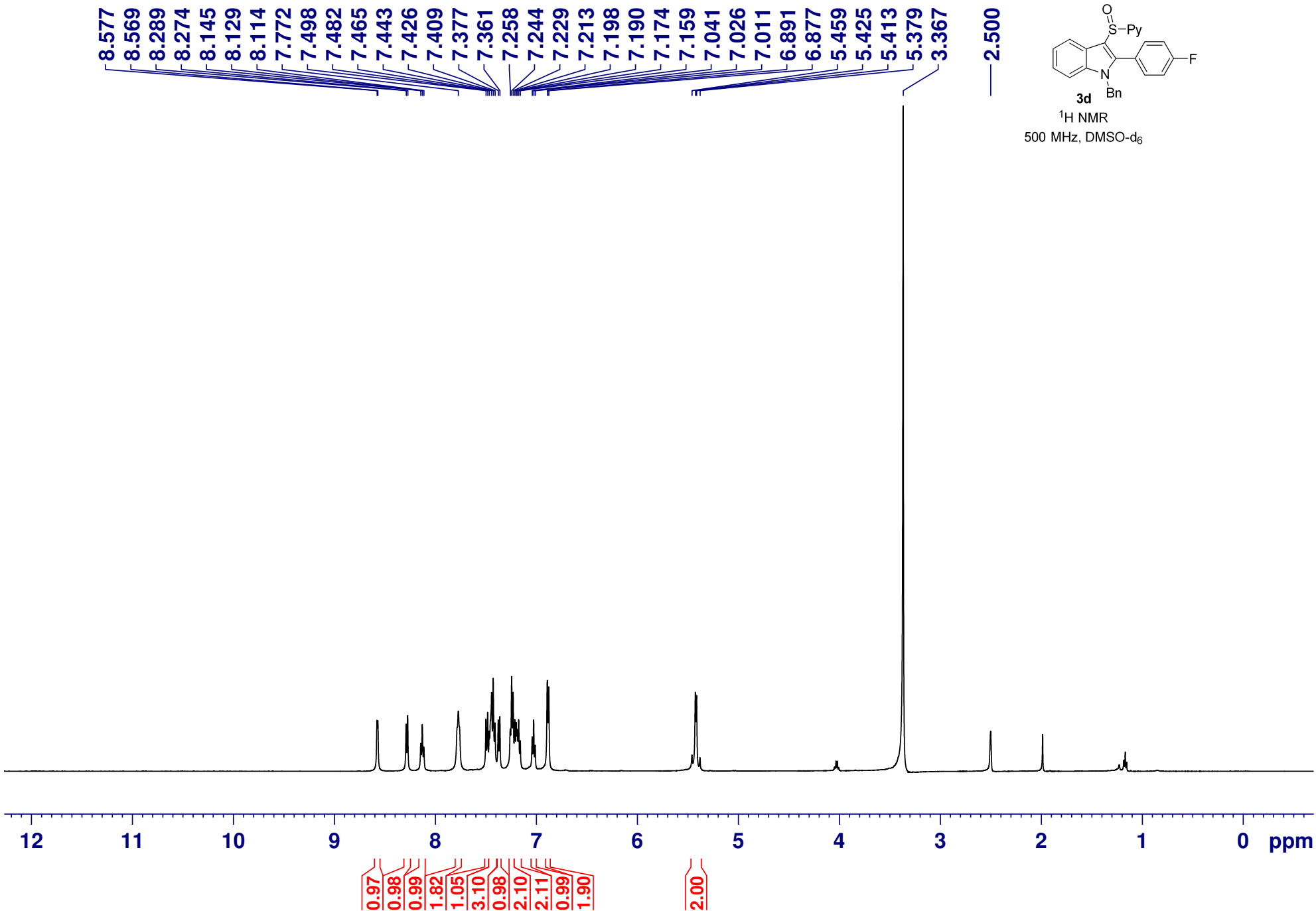




164.64  
160.38  
150.01  
145.77  
137.97  
137.09  
136.47  
132.39  
132.01  
131.50  
131.42  
128.77  
128.68  
128.64  
127.33  
125.99  
124.36  
123.79  
123.10  
121.40  
120.26  
120.09  
118.83  
114.09  
111.83

55.30  
46.94  
40.01  
39.85  
39.68  
39.51  
39.35  
39.18  
39.01

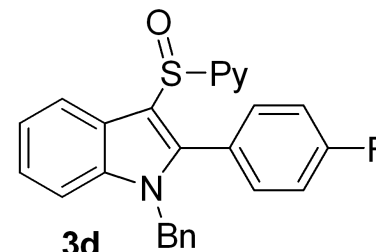




165.12  
164.65  
162.68

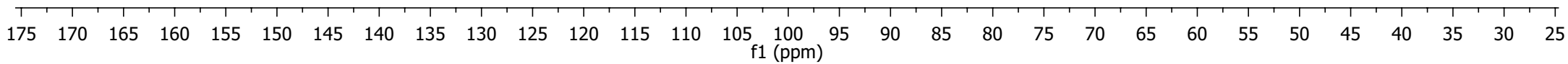
150.75

145.17  
138.74  
137.66  
137.26  
134.05  
133.99  
129.36  
128.10  
126.74  
125.46  
125.44  
125.16  
124.40  
124.11  
122.29  
120.76  
119.66  
116.50  
116.32  
115.20  
112.63

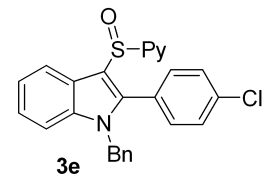


<sup>13</sup>C NMR  
125 MHz, DMSO-d<sub>6</sub>

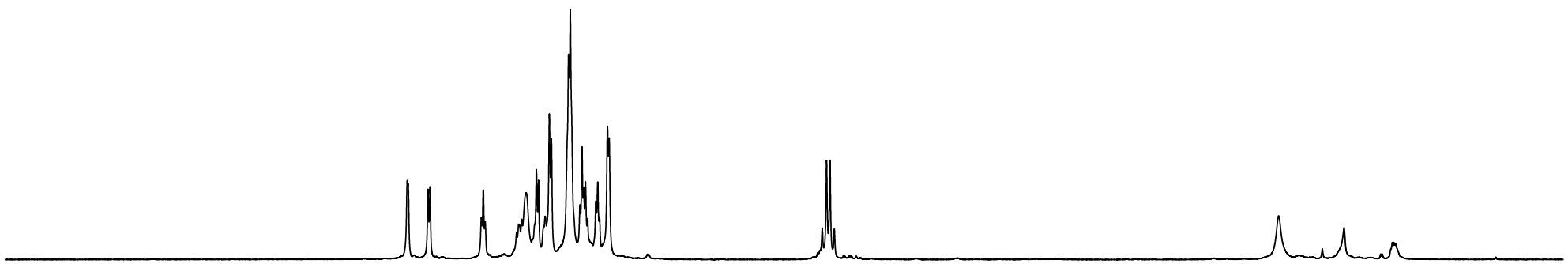
47.70



8.526  
8.520  
8.365  
8.350  
7.951  
7.936  
7.921  
7.677  
7.661  
7.654  
7.637  
7.603  
7.523  
7.507  
7.455  
7.422  
7.406  
7.273  
7.259  
7.184  
7.169  
7.155  
7.142  
7.126  
7.061  
7.047  
7.033  
6.970  
6.957  
5.302  
5.269  
5.242  
5.208

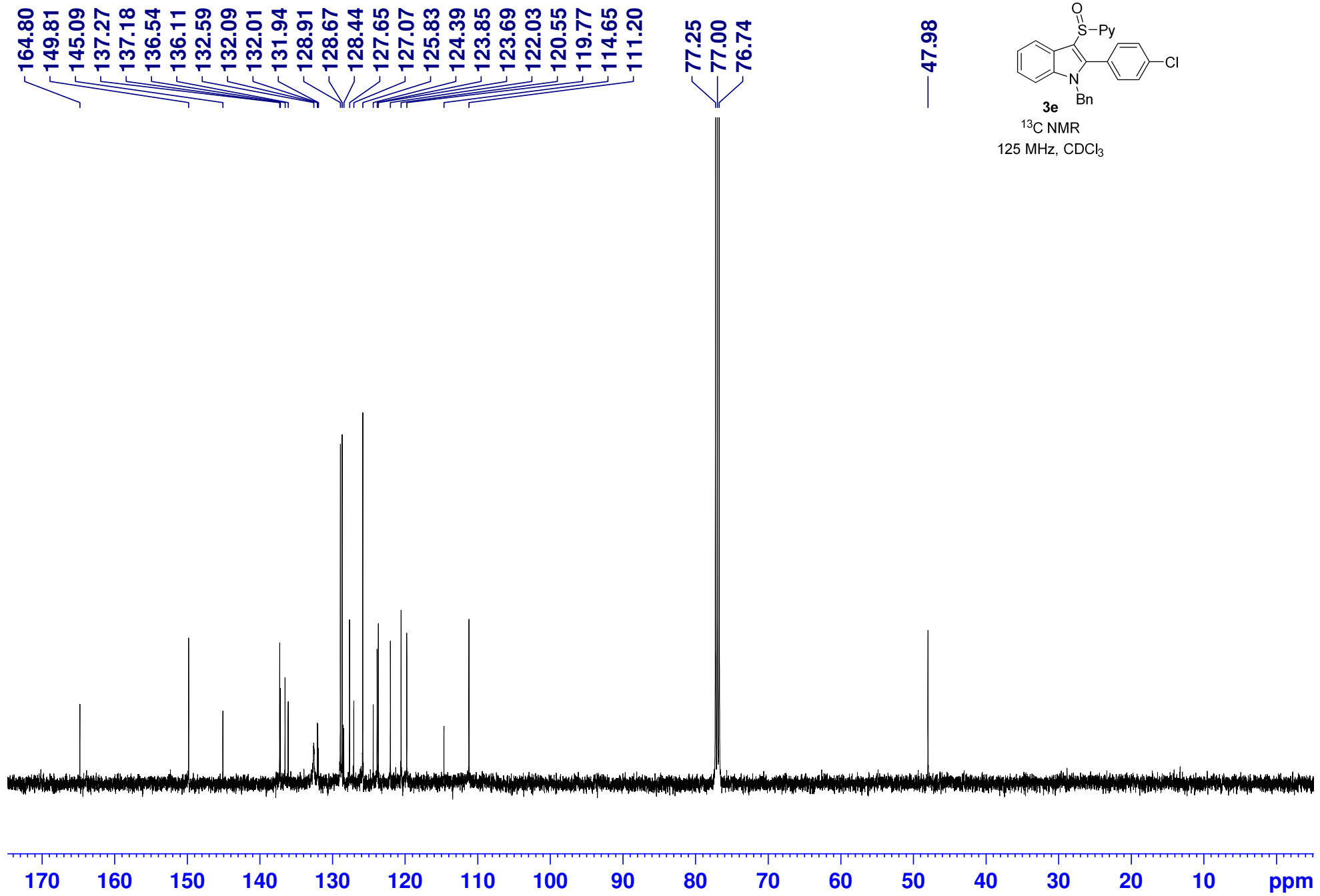


<sup>1</sup>H NMR  
500 MHz, CDCl<sub>3</sub>



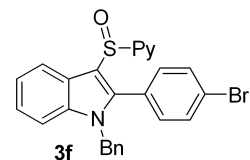
11 10 9 8 7 6 5 4 3 2 1 ppm

0.86  
0.88  
0.99  
2.37  
1.20  
2.24  
4.17  
2.23  
1.09  
2.00  
1.96

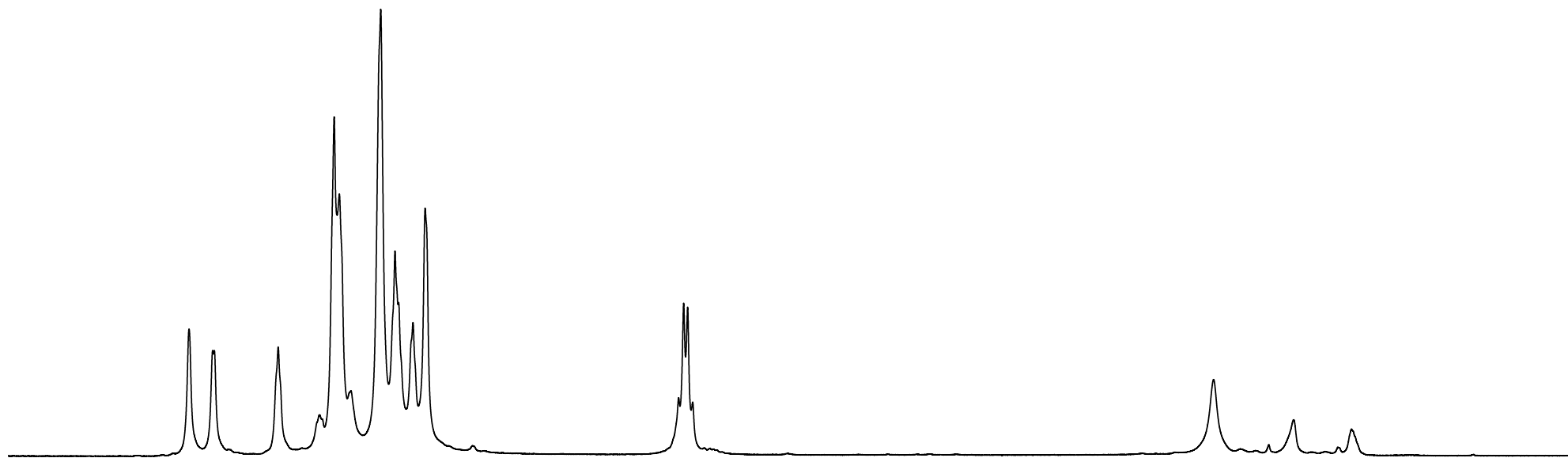


8.523  
8.367  
8.356  
7.936  
7.664  
7.568  
7.534  
7.457  
7.262  
7.168  
7.144  
7.049  
6.970

5.302  
5.269  
5.243  
5.210



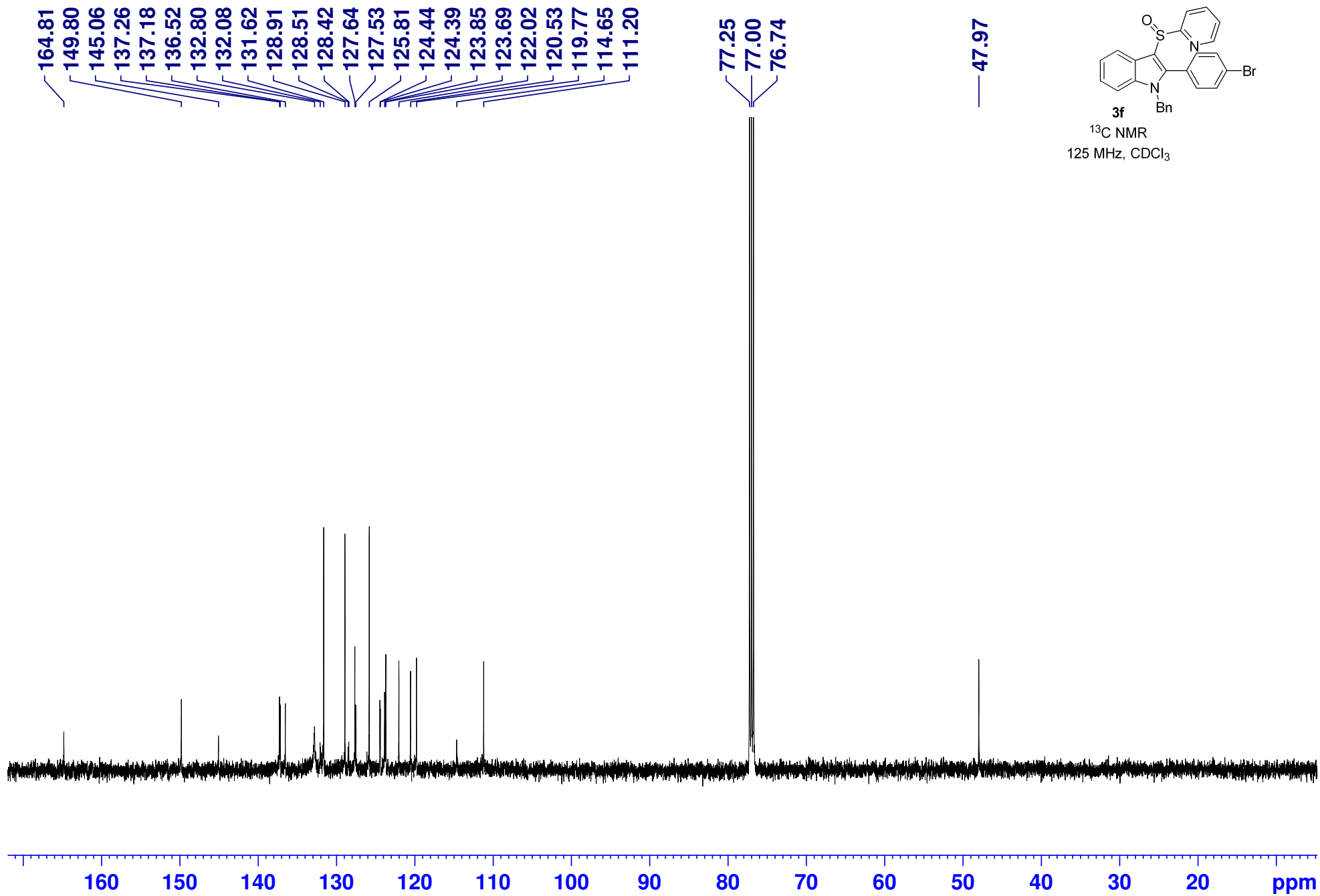
<sup>1</sup>H NMR  
500 MHz, CDCl<sub>3</sub>

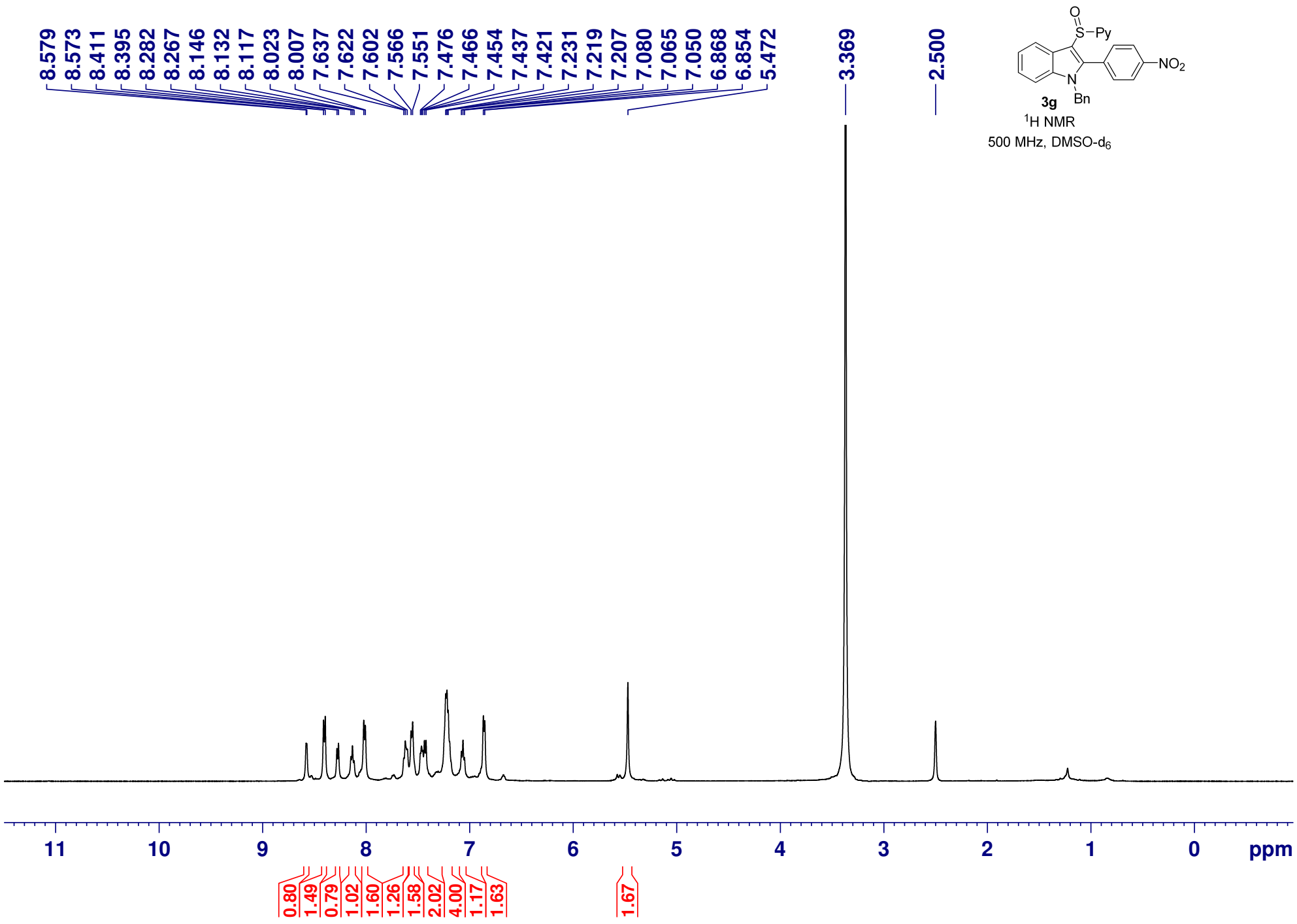


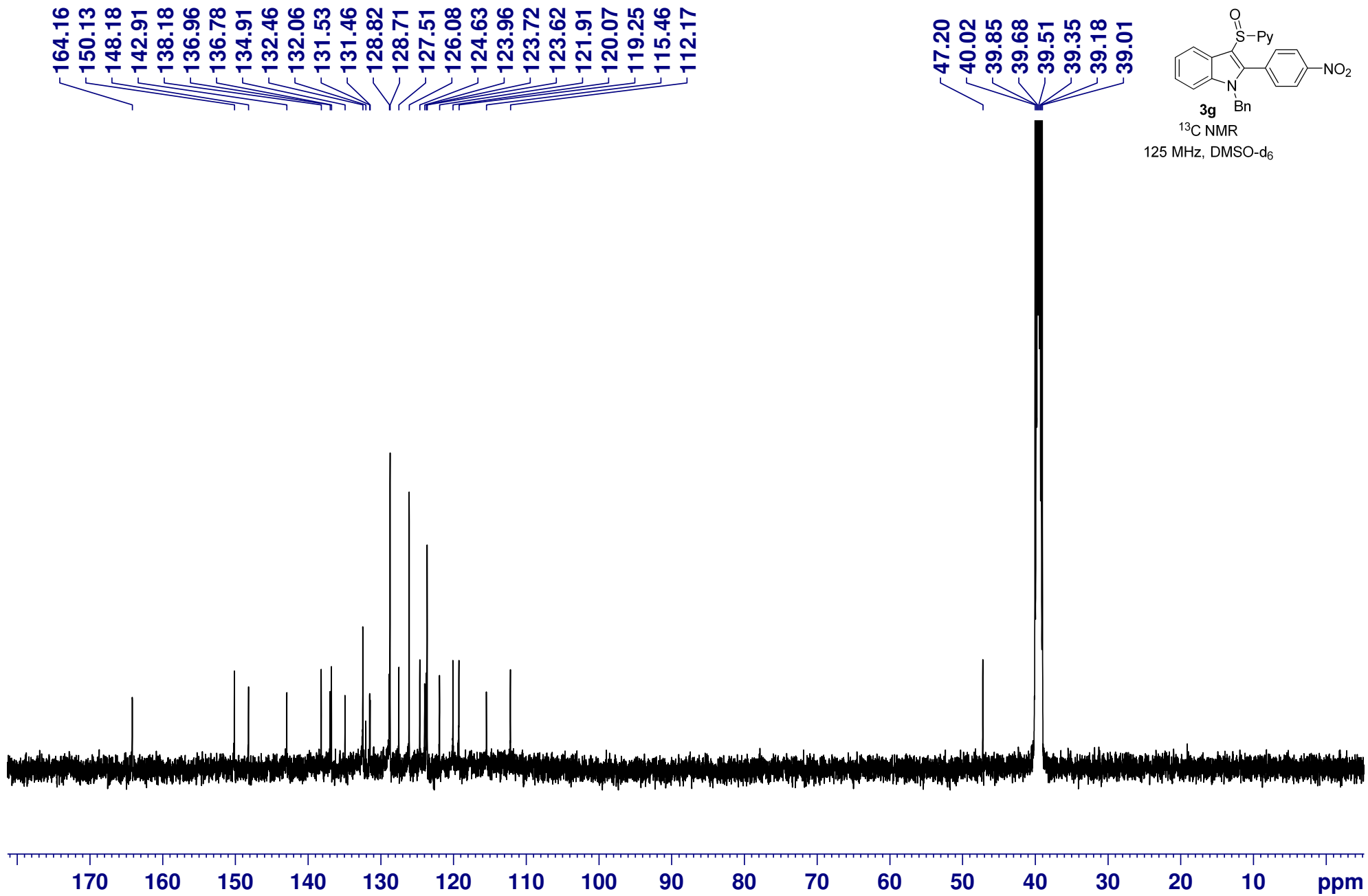
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

0.97  
0.92  
0.97  
4.79  
4.54  
2.36  
1.17  
2.07

2.00



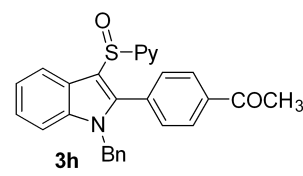




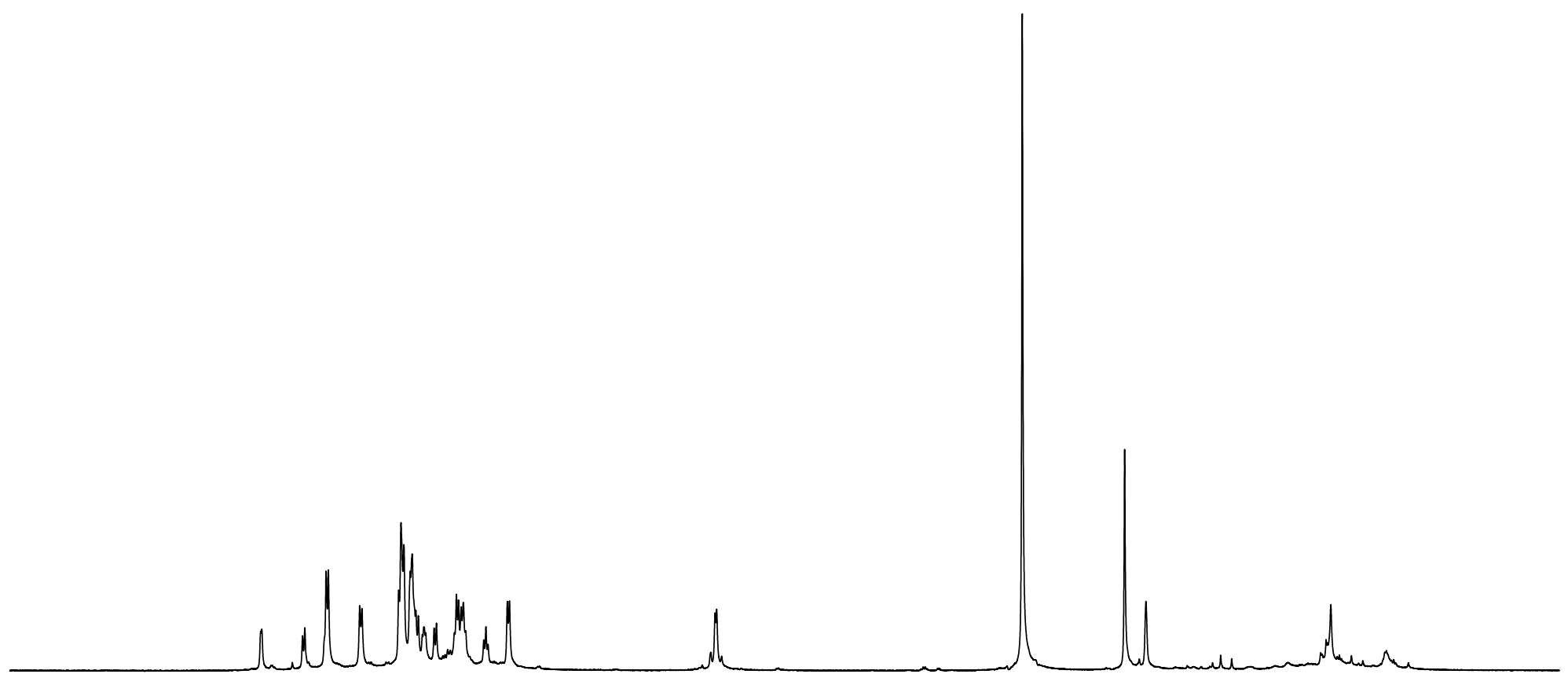
8.580  
8.299  
8.283  
8.137  
8.121  
7.906  
7.890  
7.622  
7.601  
7.558  
7.545  
7.475  
7.463  
7.451  
7.394  
7.378  
7.241  
7.226  
7.208  
7.193  
7.053  
7.038  
7.023  
6.890  
6.876  
5.491  
5.462  
5.451  
5.416

3.349

2.645  
2.498



<sup>1</sup>H NMR  
500 MHz, DMSO-d<sub>6</sub>

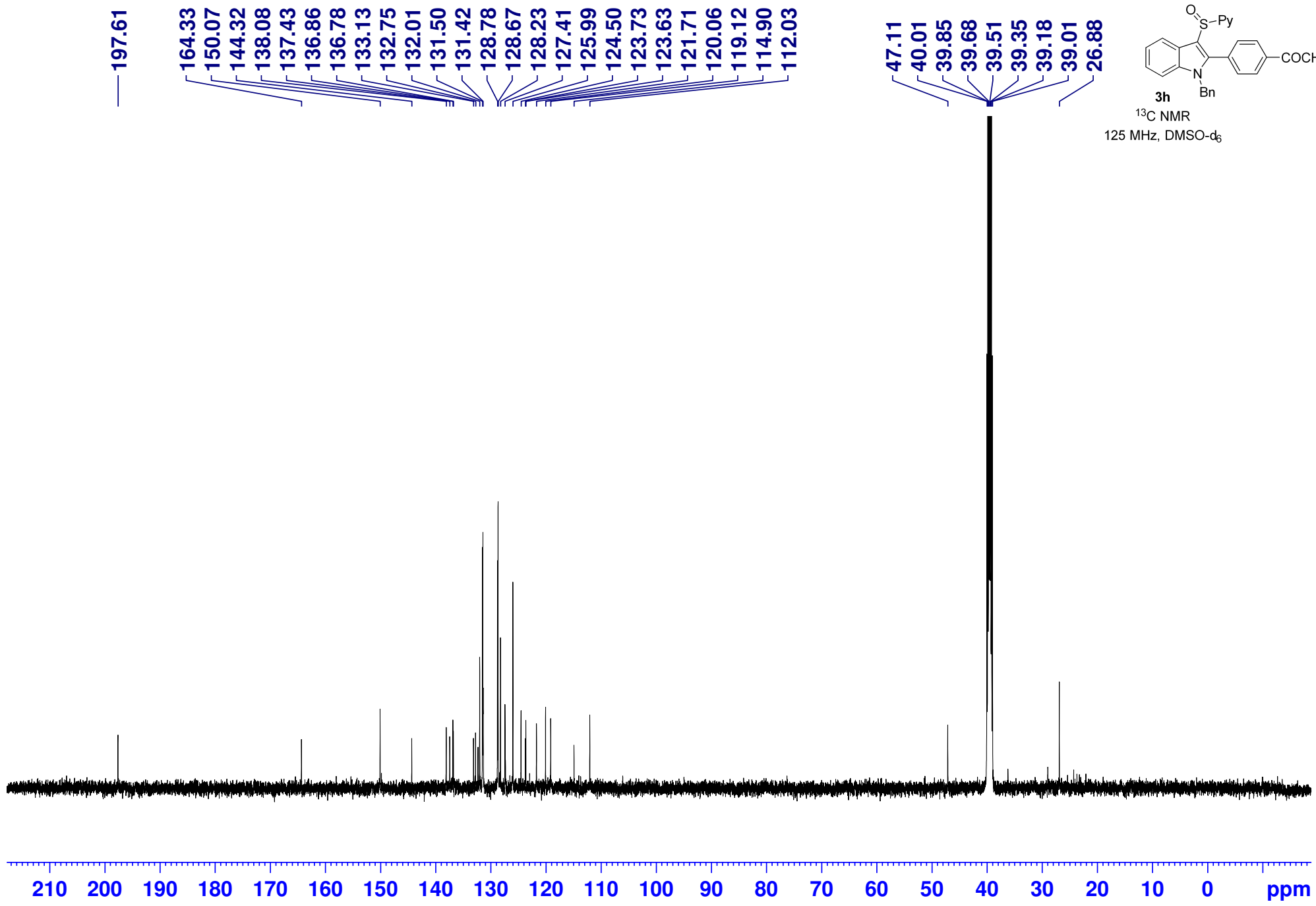


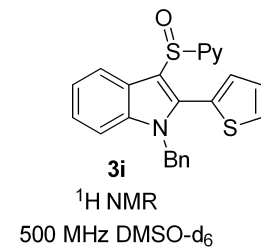
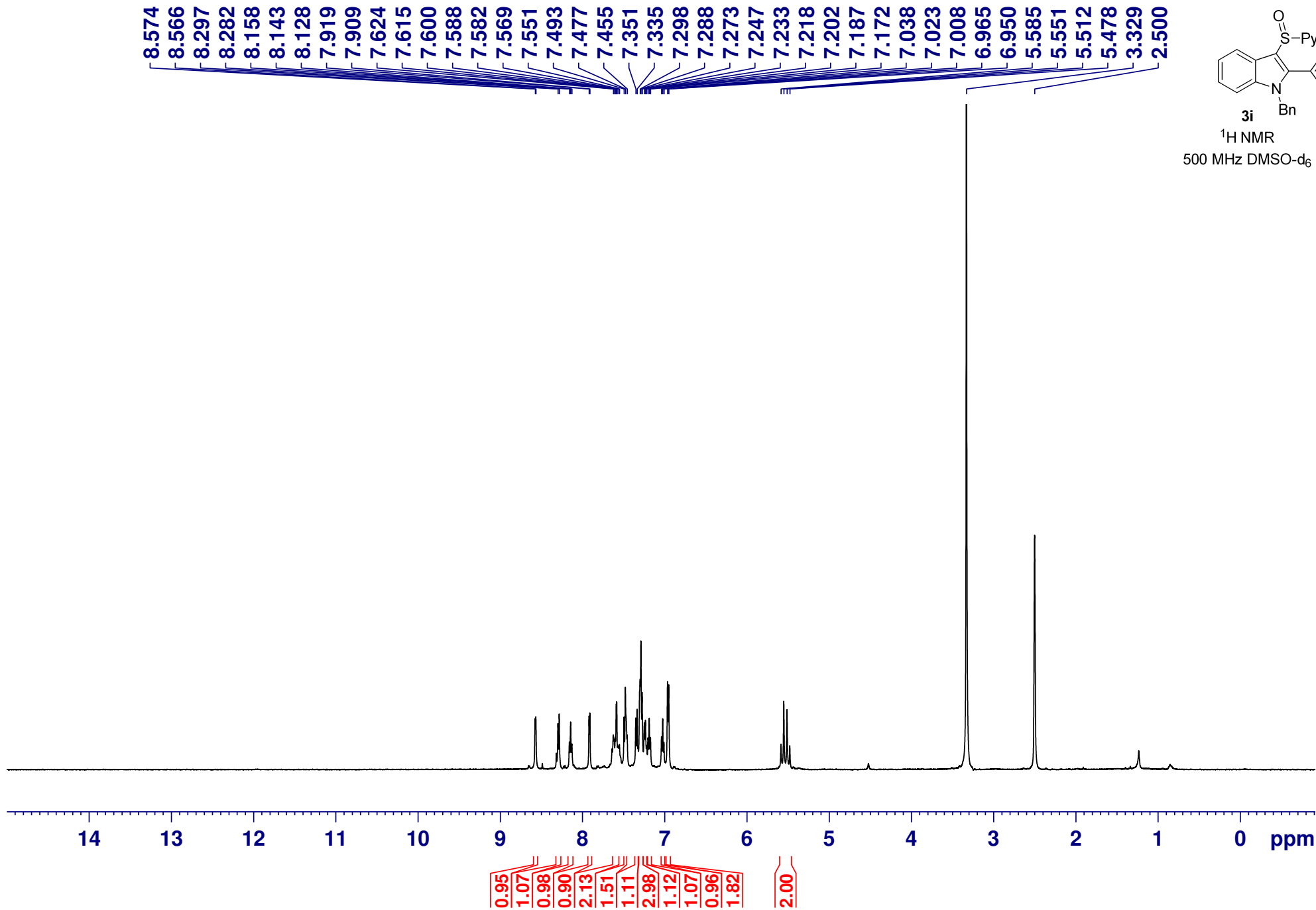
10 9 8 7 6 5 4 3 2 1 ppm

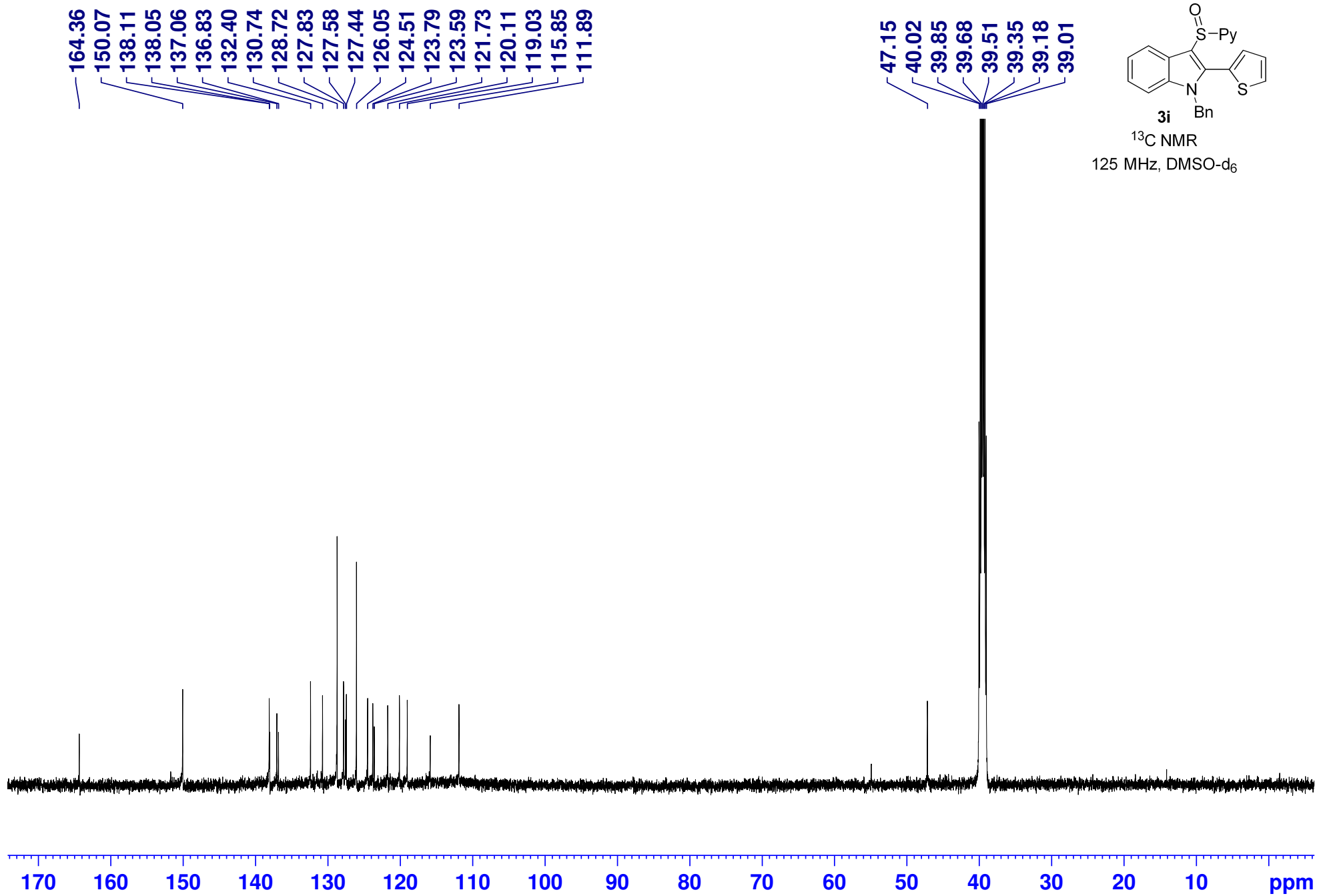
0.92  
0.96  
1.85  
1.45  
2.28  
3.02  
1.14  
1.01  
1.22  
1.37  
1.22  
1.85

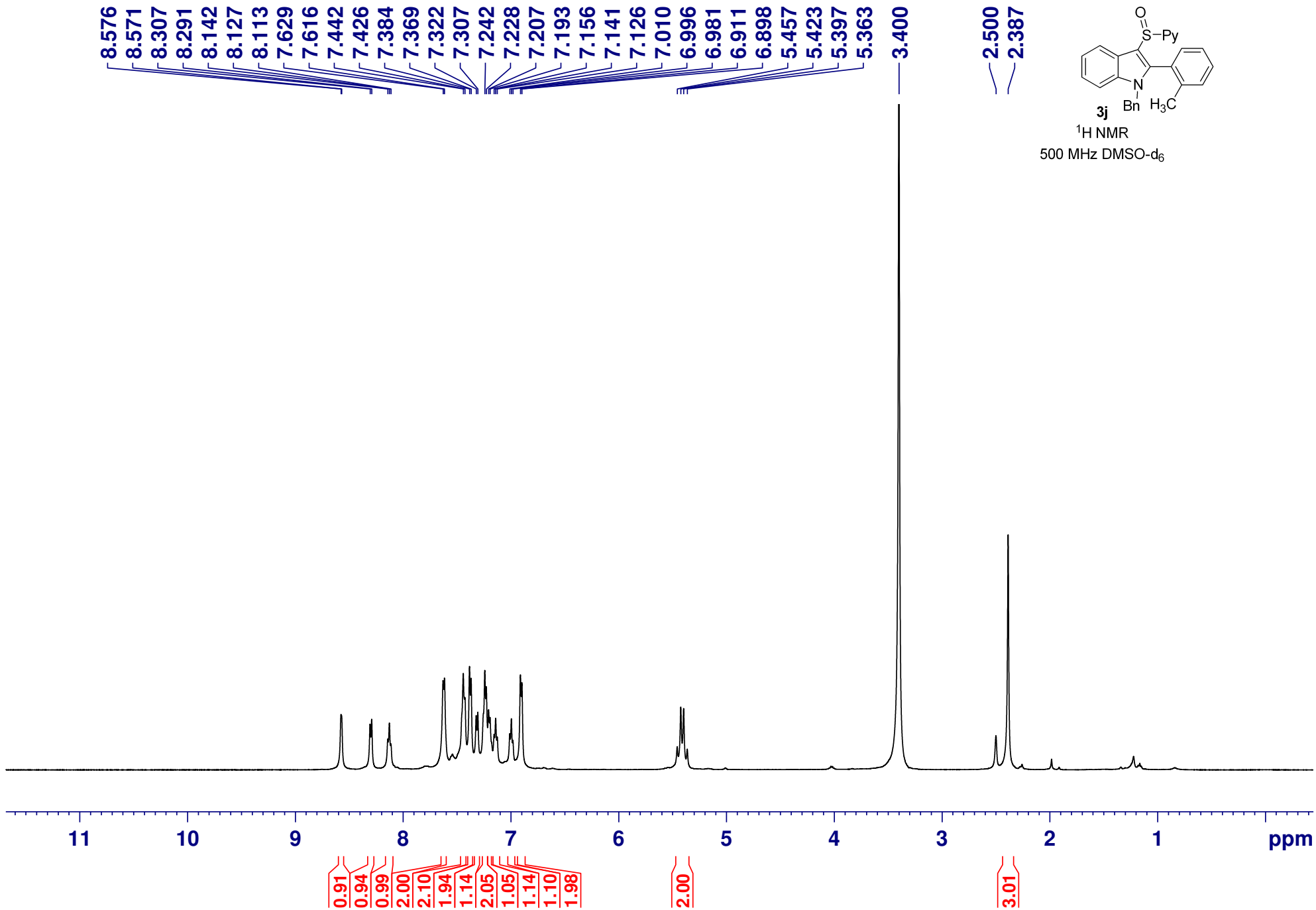
2.09

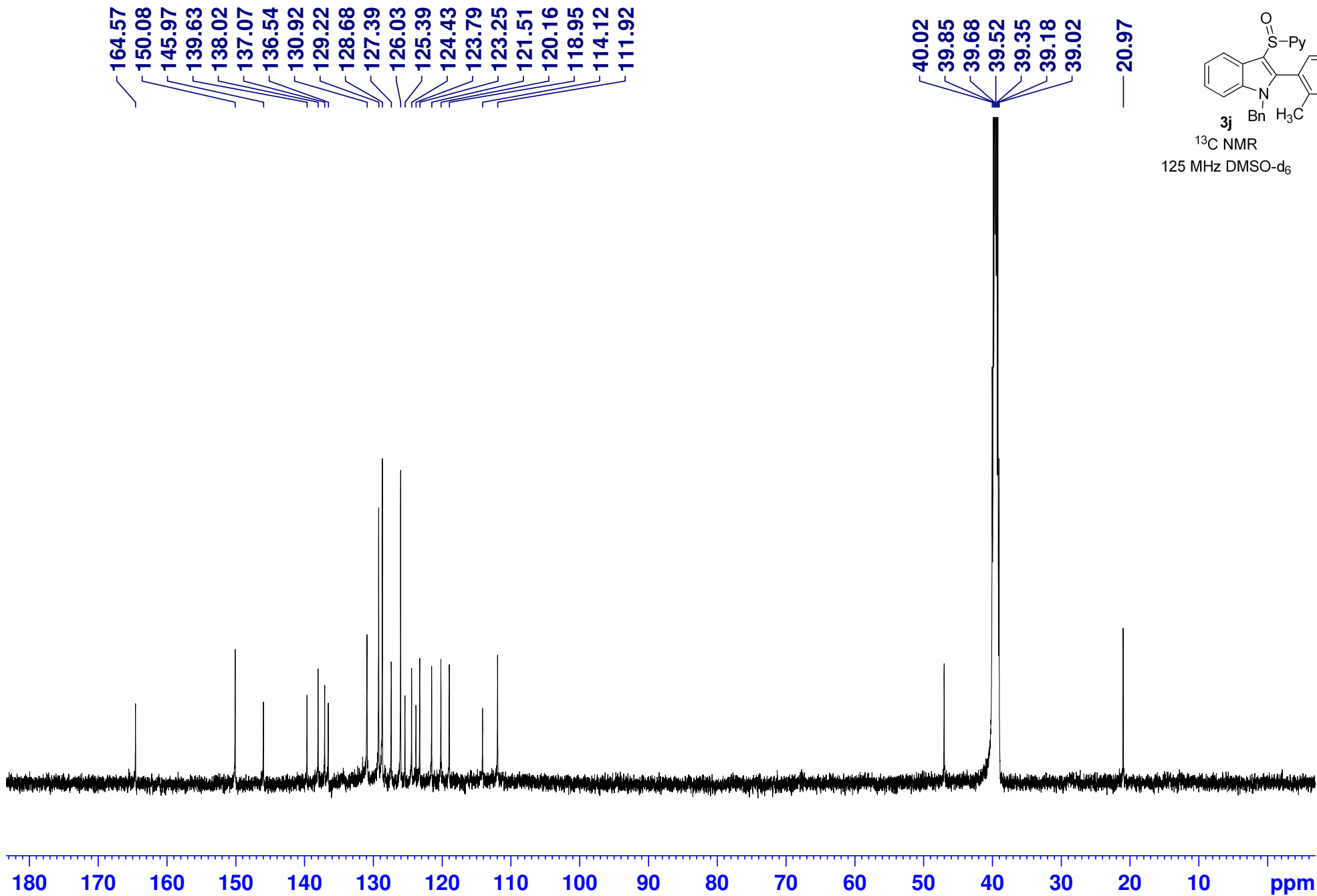
2.82

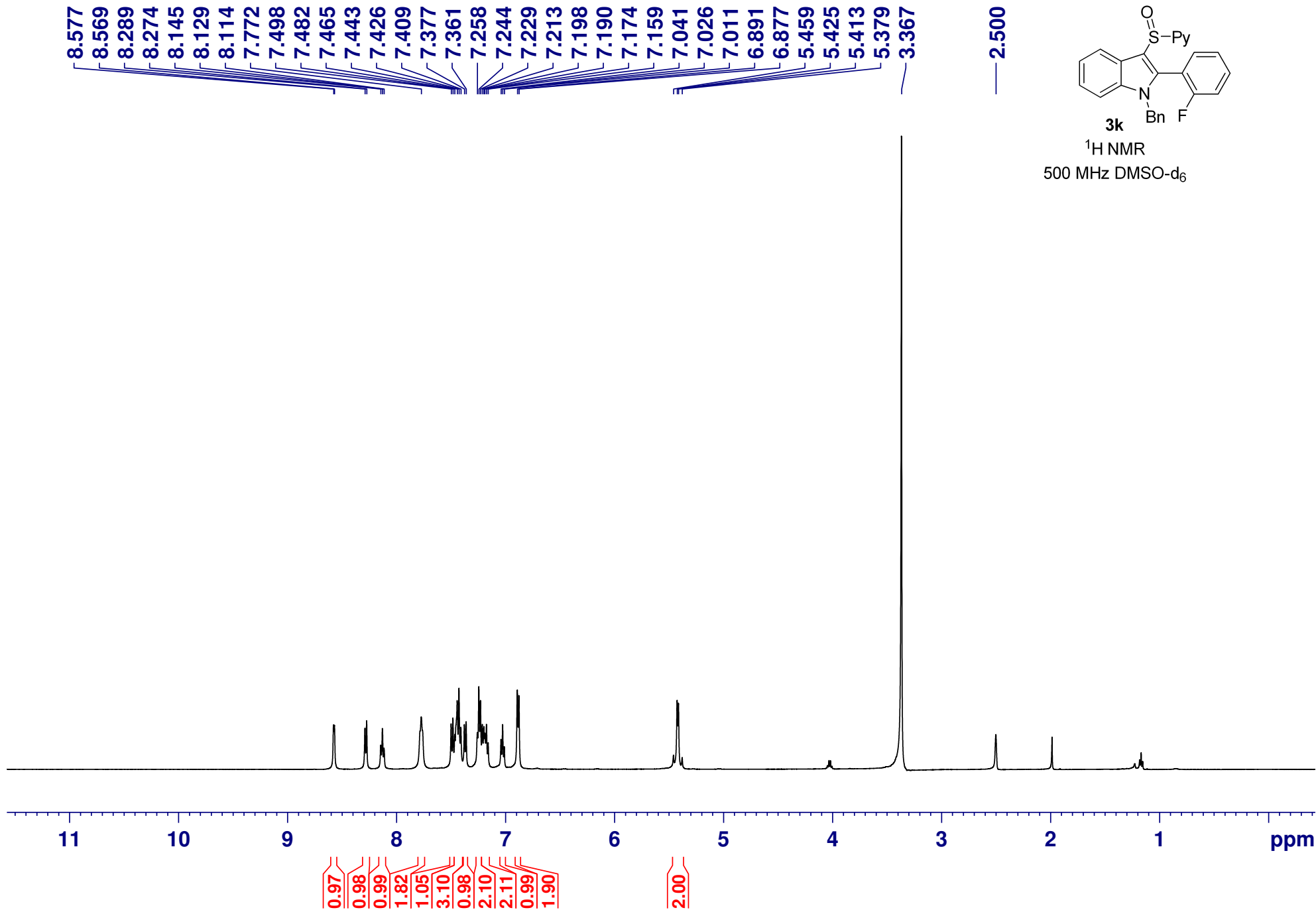












164.42  
163.95  
161.98

150.05

144.47  
138.04

136.96  
136.56

133.35  
133.29

128.66  
127.40

126.04  
124.76

124.74  
124.46

123.70  
123.41

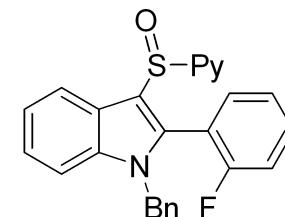
121.59  
120.06

118.96  
115.80

115.62  
114.50

111.93

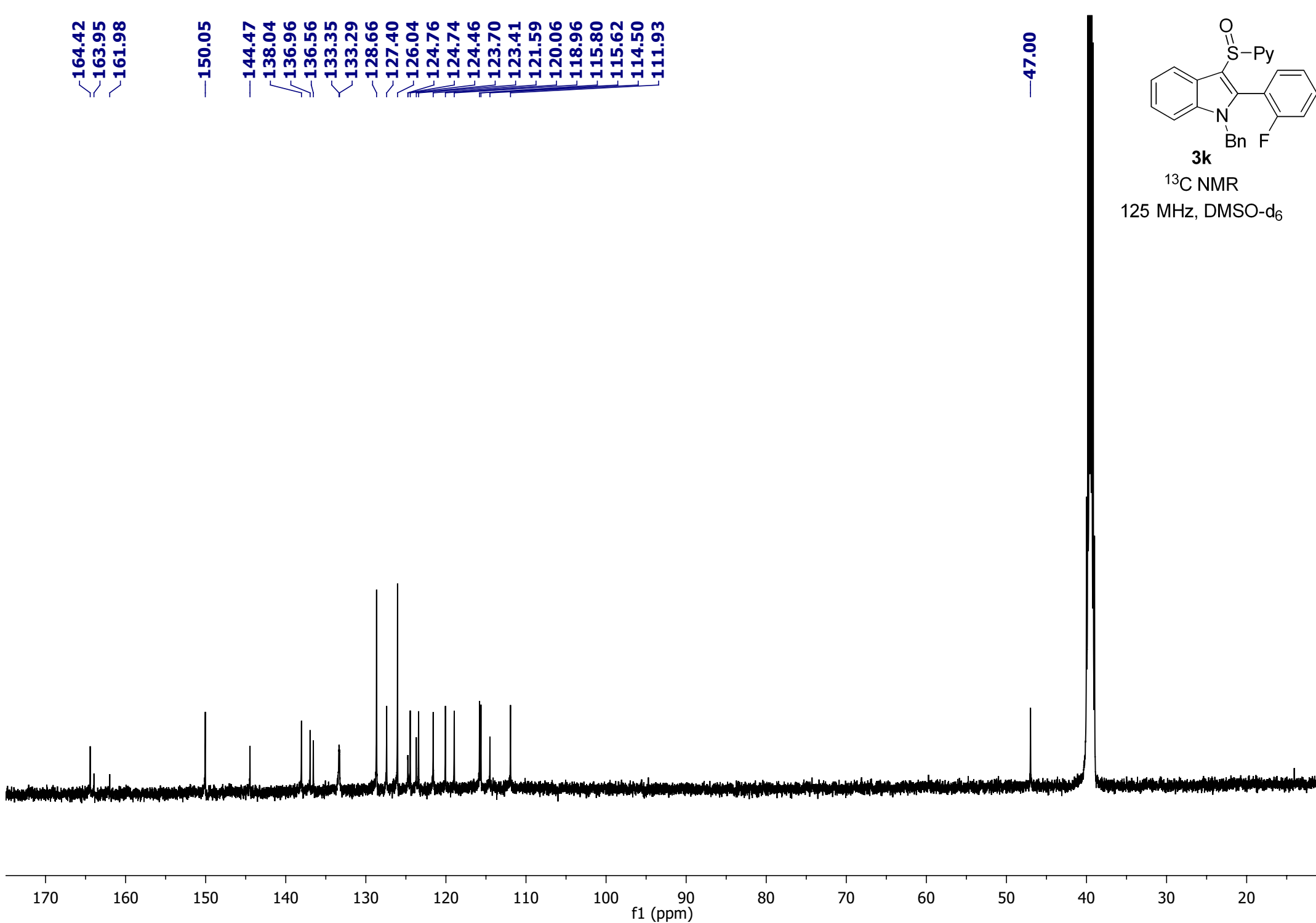
47.00

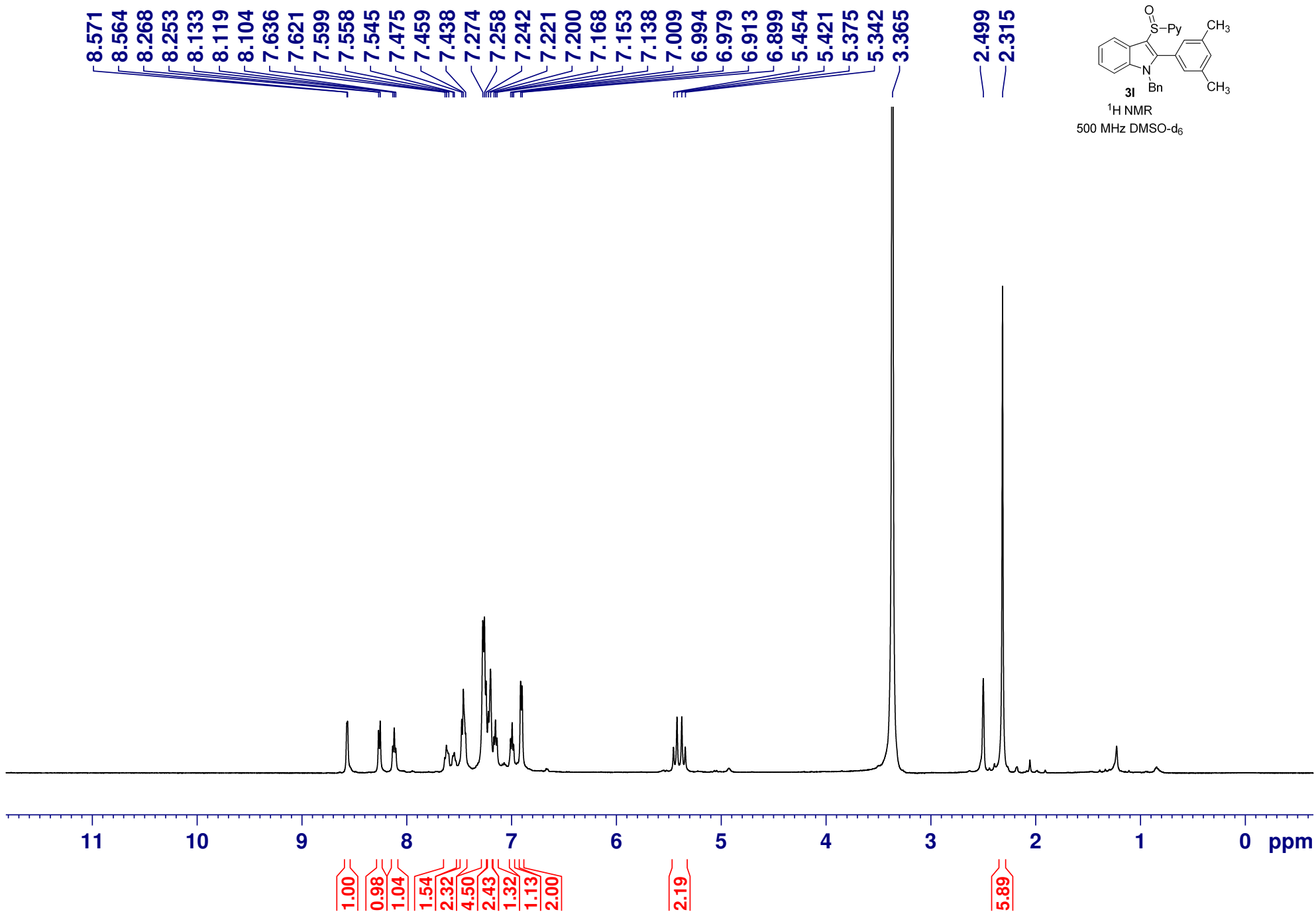


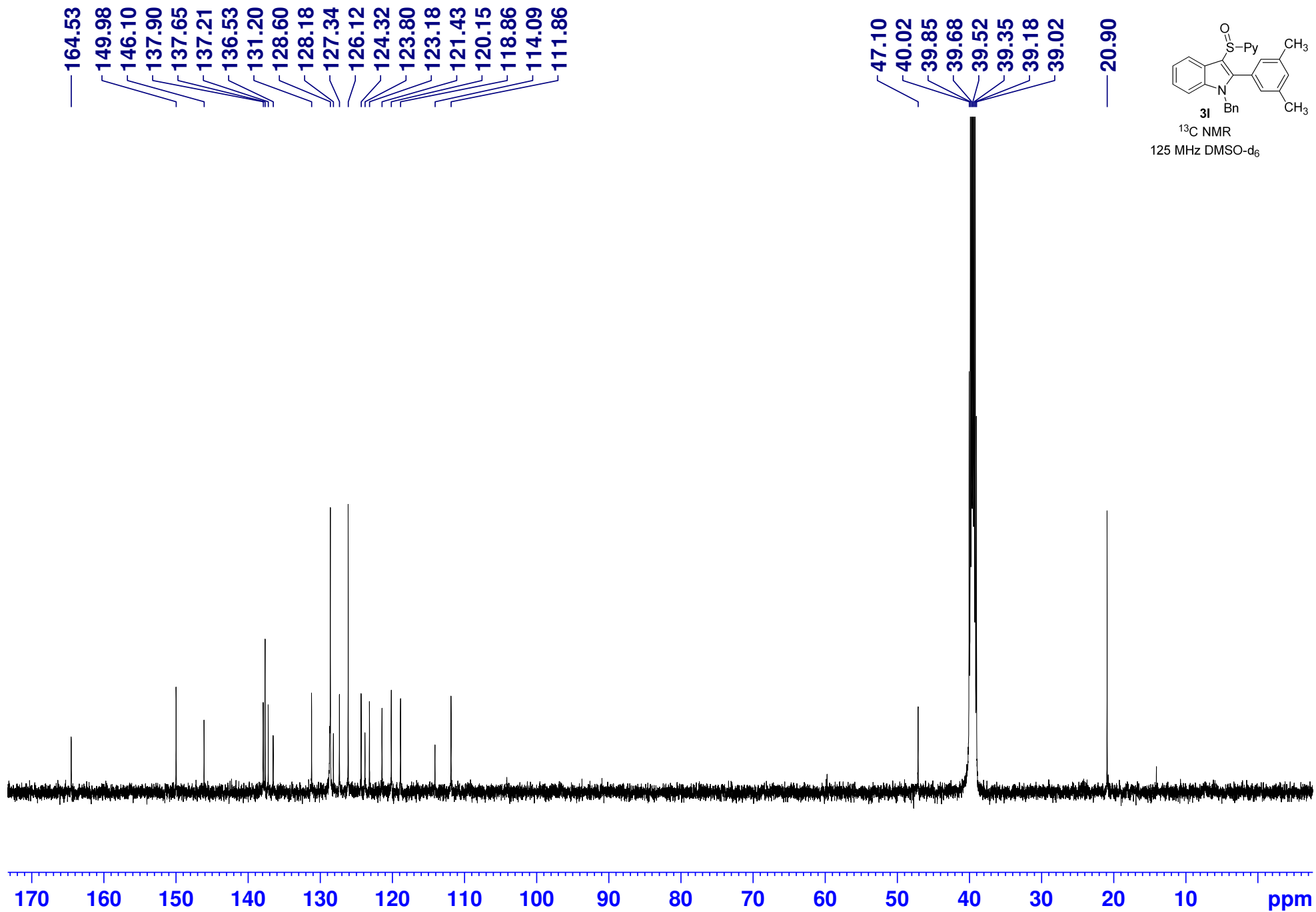
**3k**

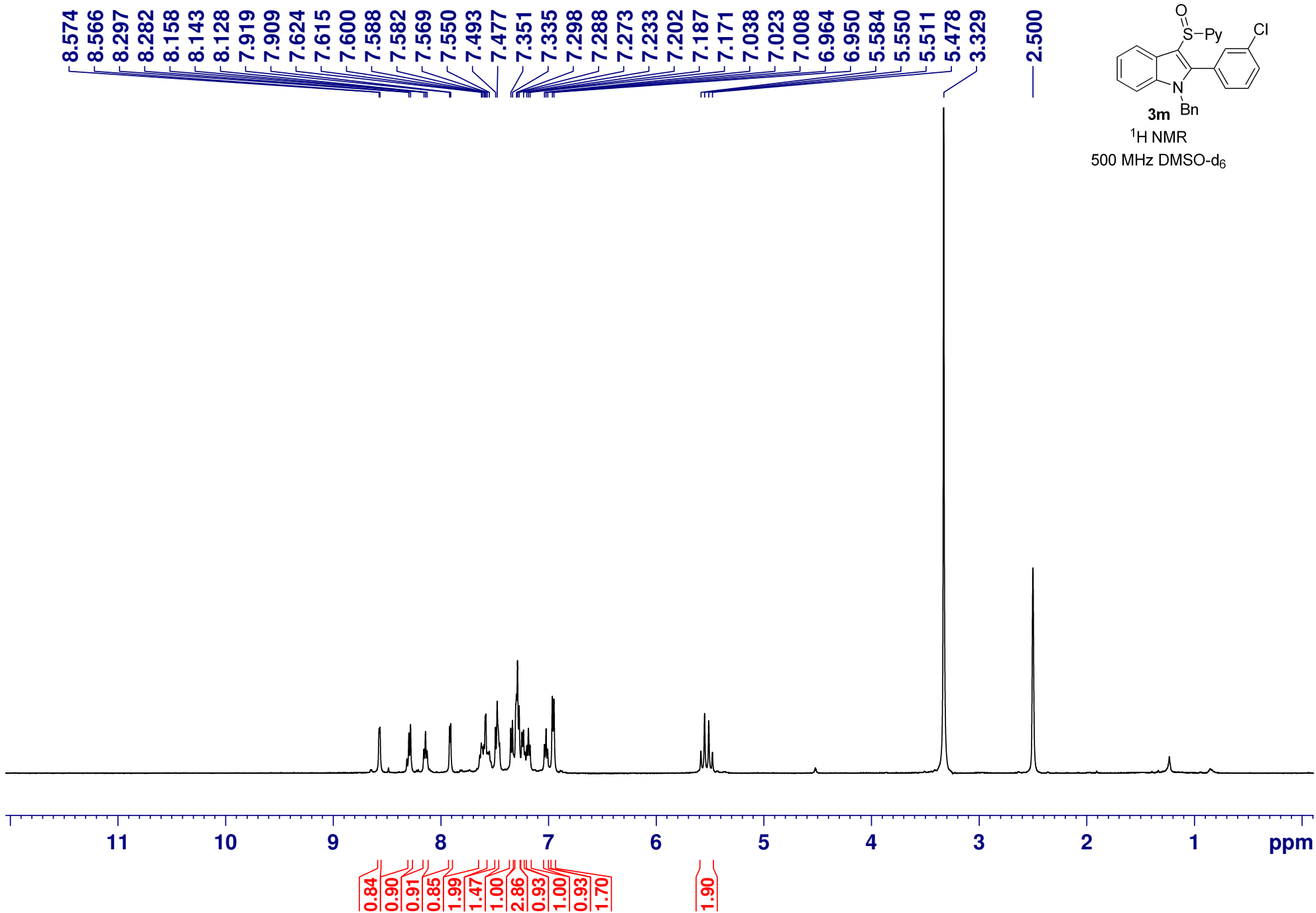
<sup>13</sup>C NMR

125 MHz, DMSO-d<sub>6</sub>



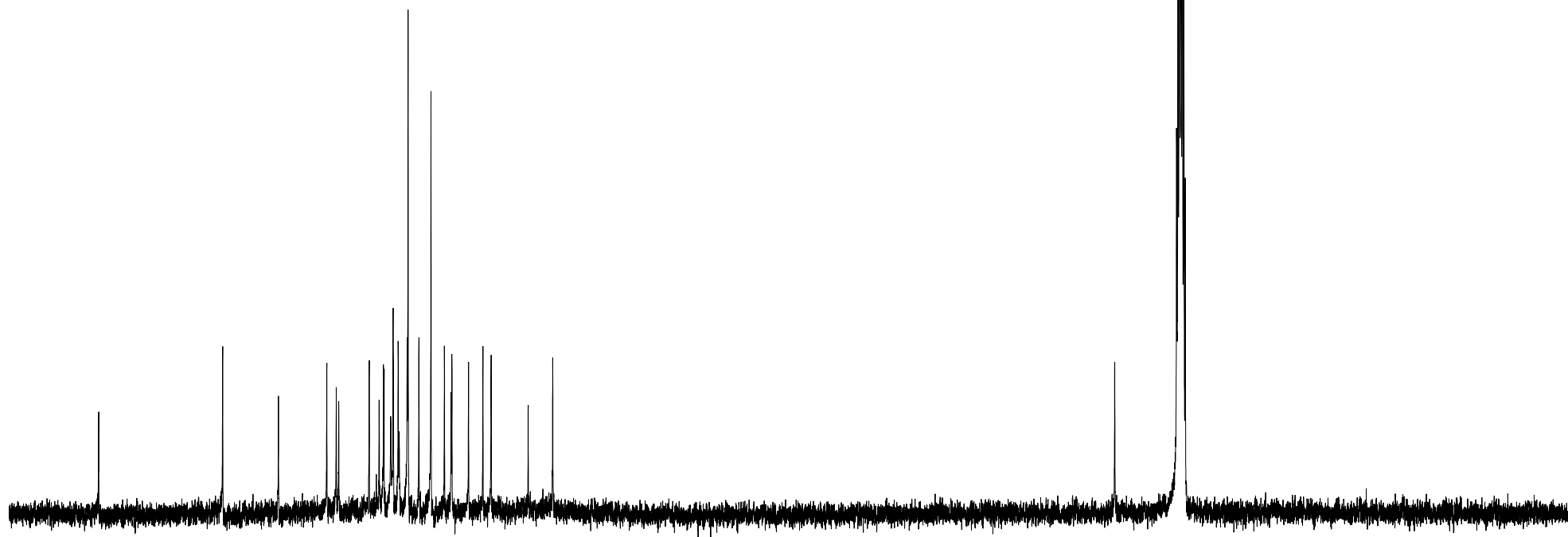
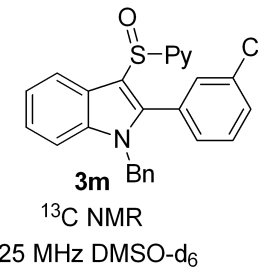




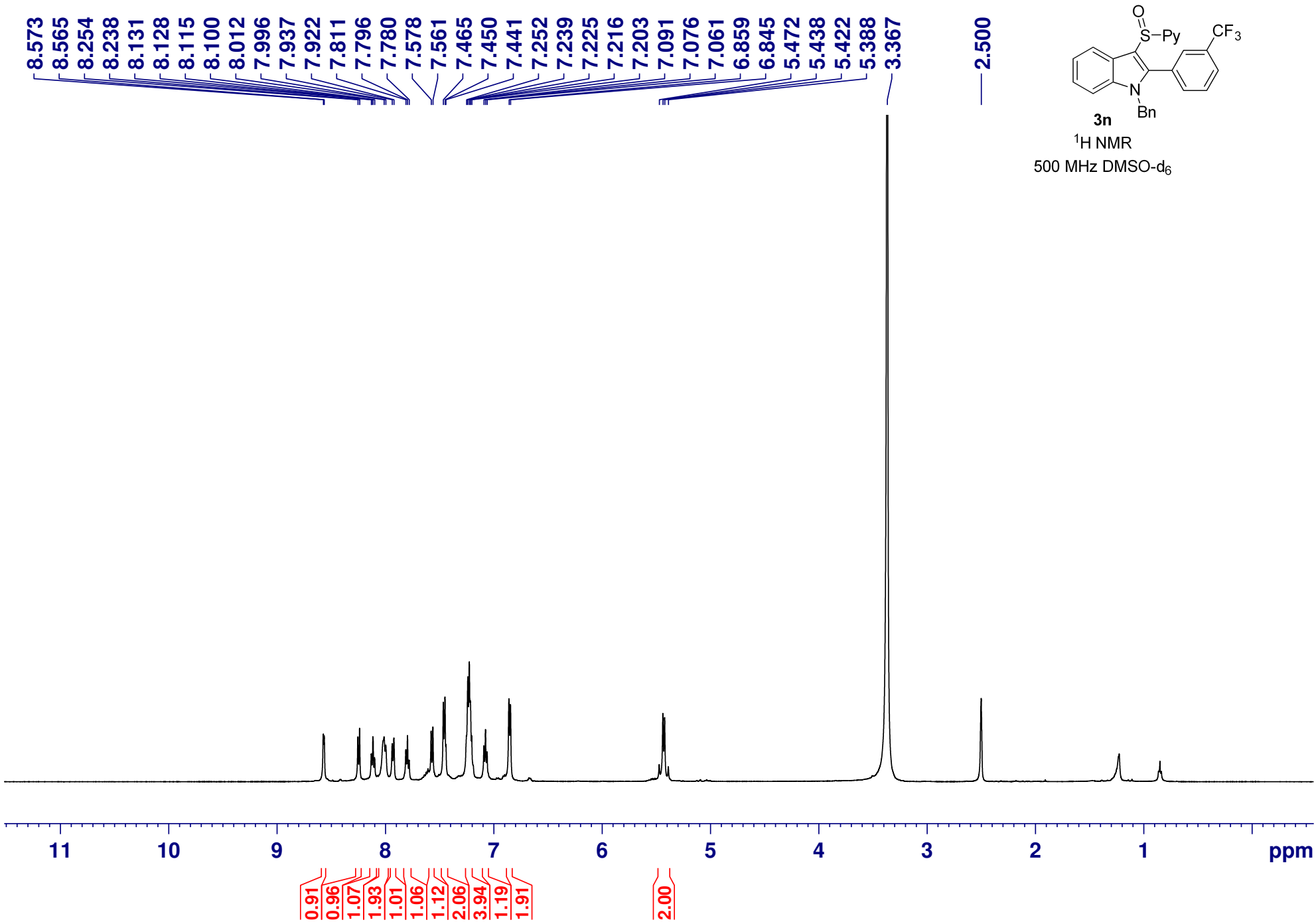


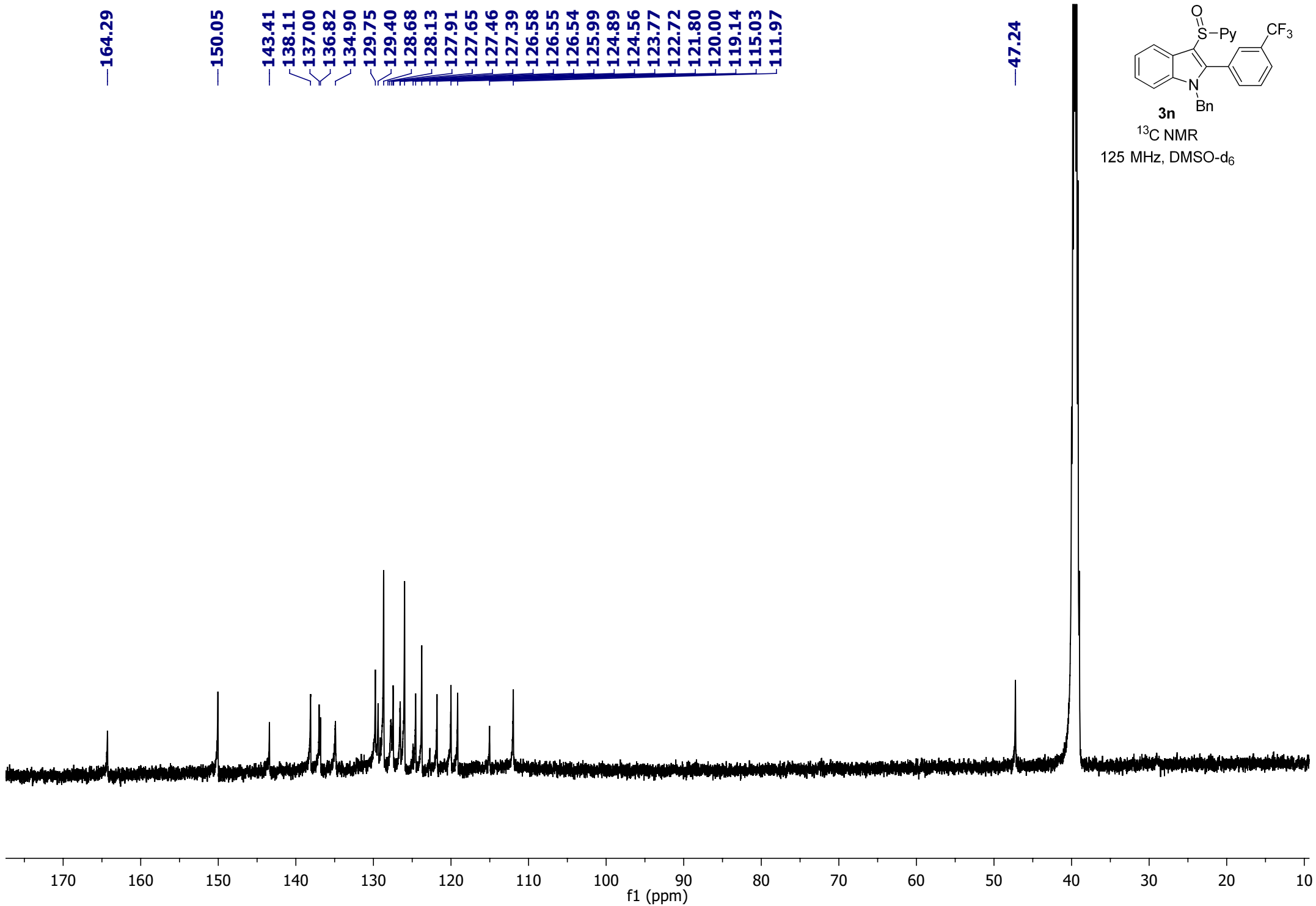
164.35  
150.05  
143.61  
138.04  
136.95  
136.66  
133.14  
132.00  
131.50  
131.43  
130.67  
130.39  
129.80  
128.77  
128.66  
127.41  
126.02  
124.47  
123.70  
123.61  
121.68  
120.03  
119.08  
114.81  
111.97

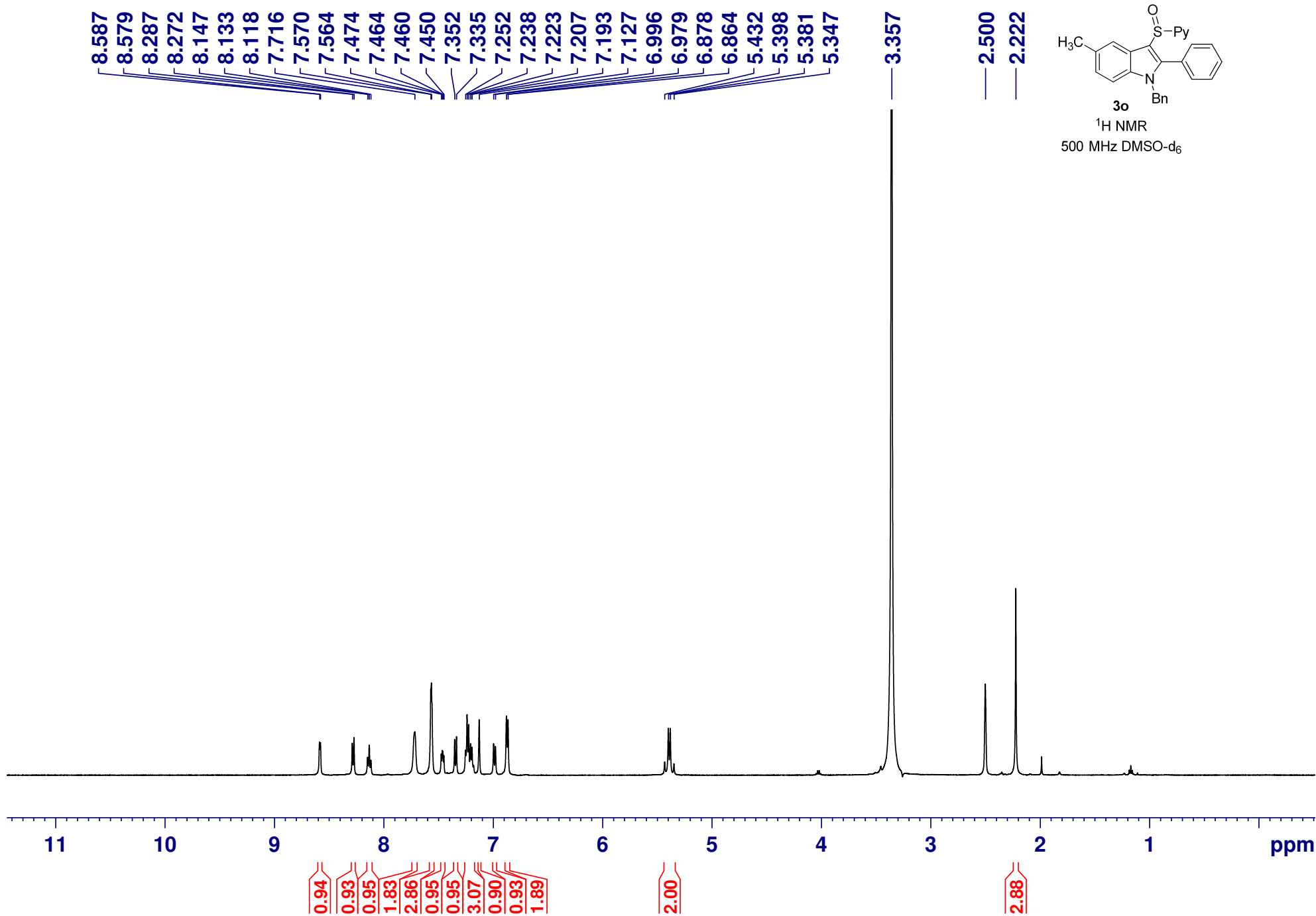
47.15  
40.01  
39.85  
39.68  
39.51  
39.35  
39.18  
39.01

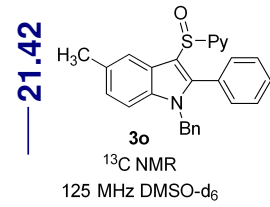
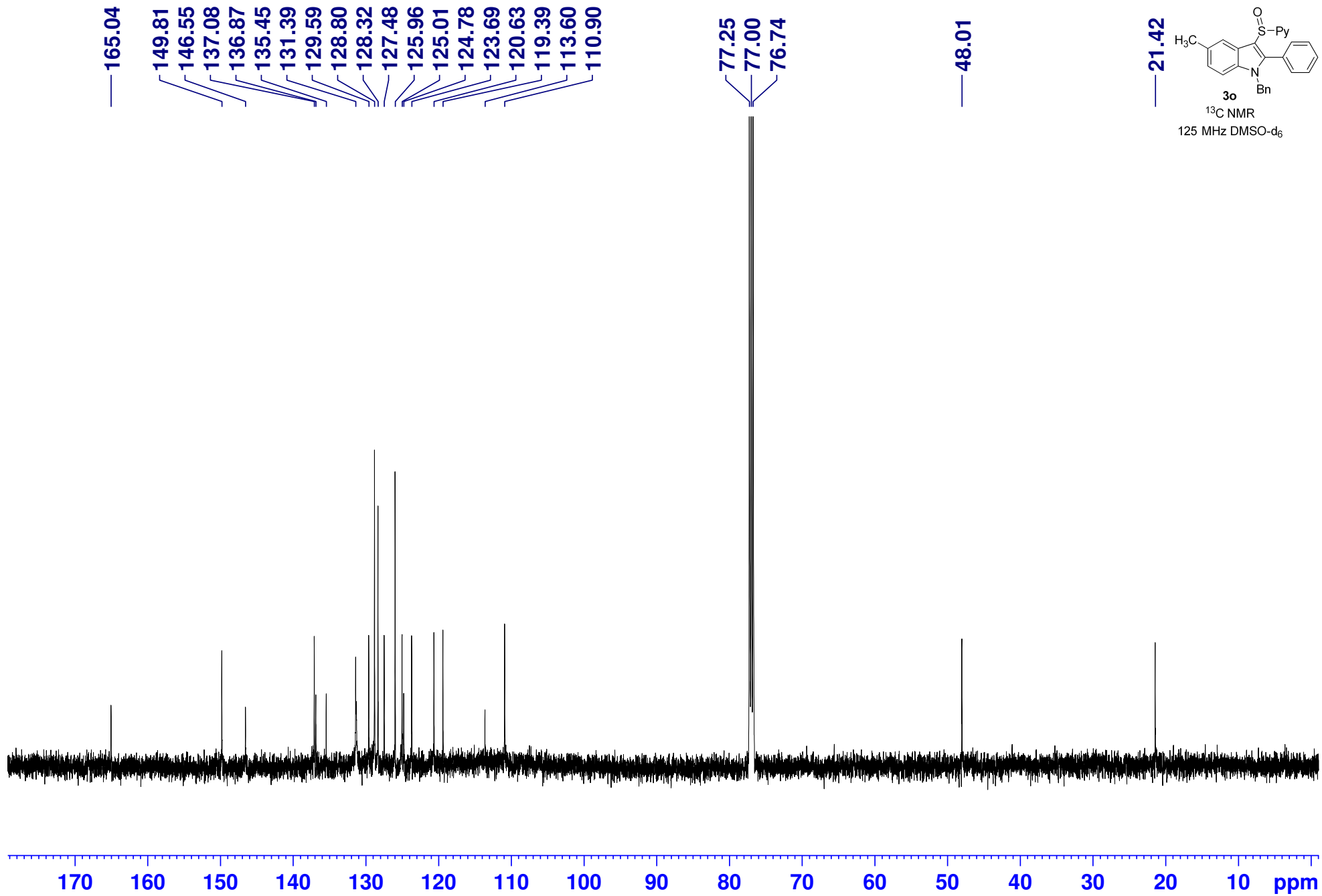


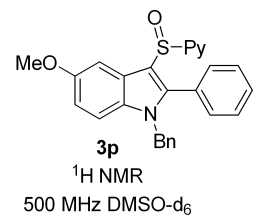
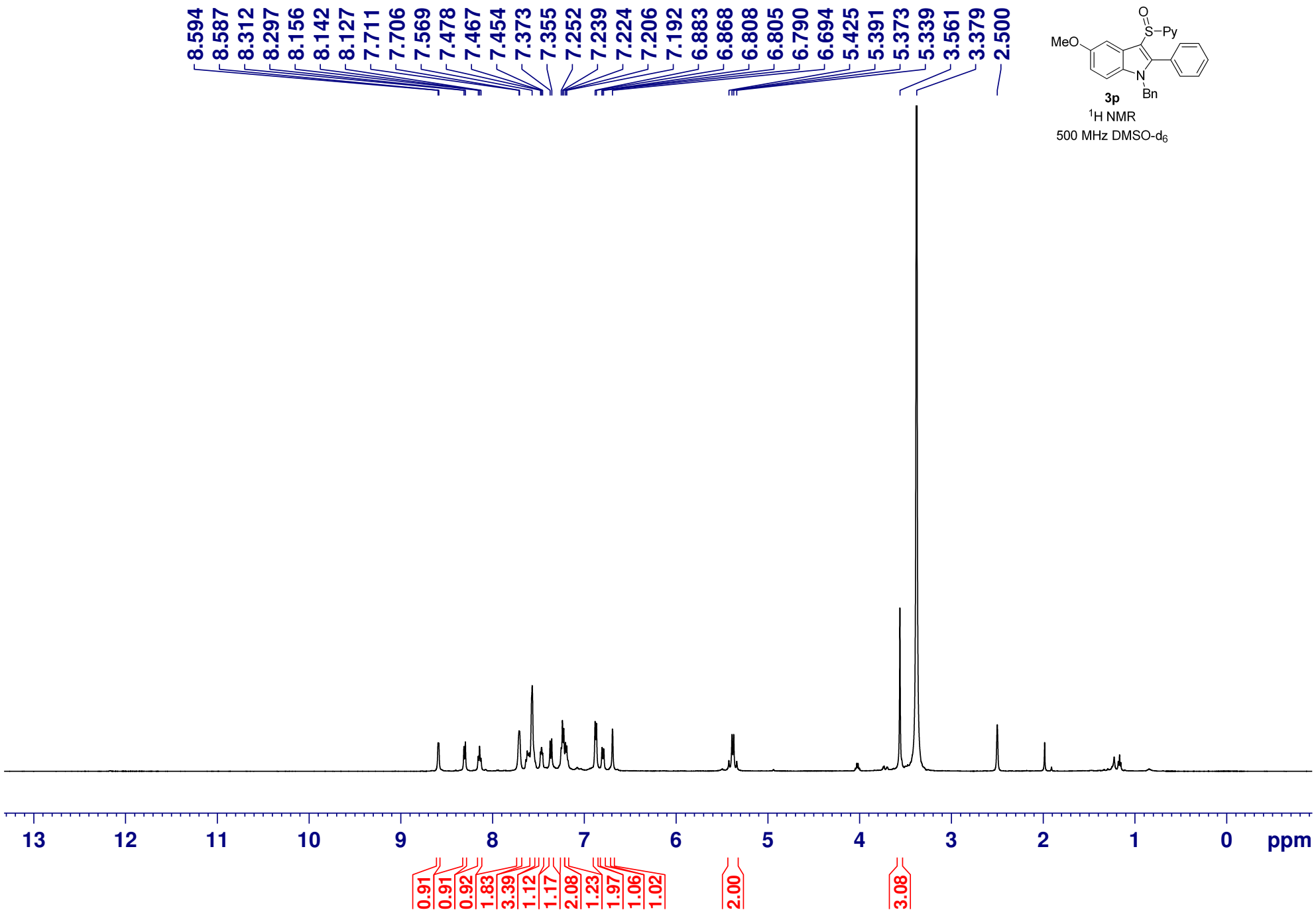
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

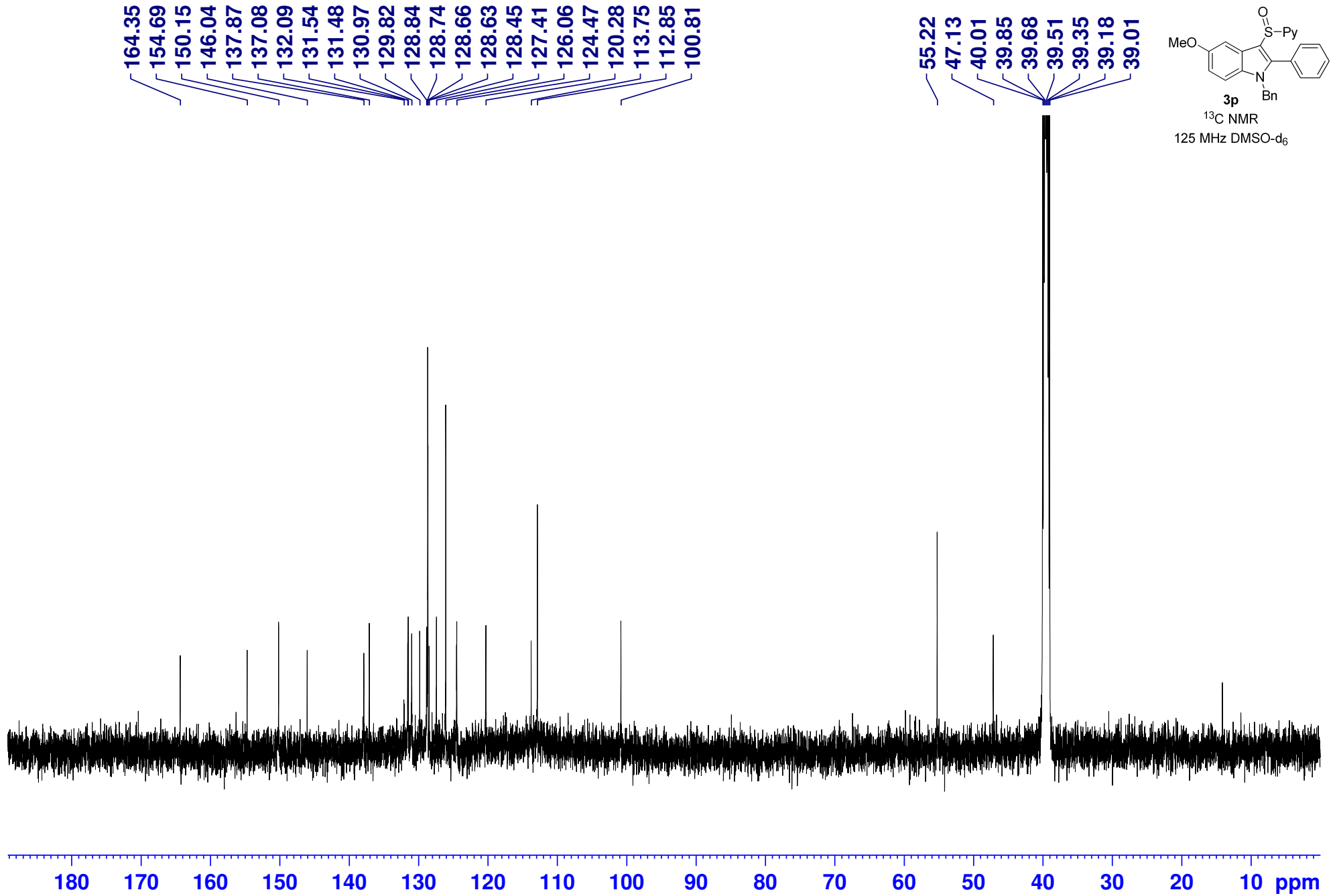


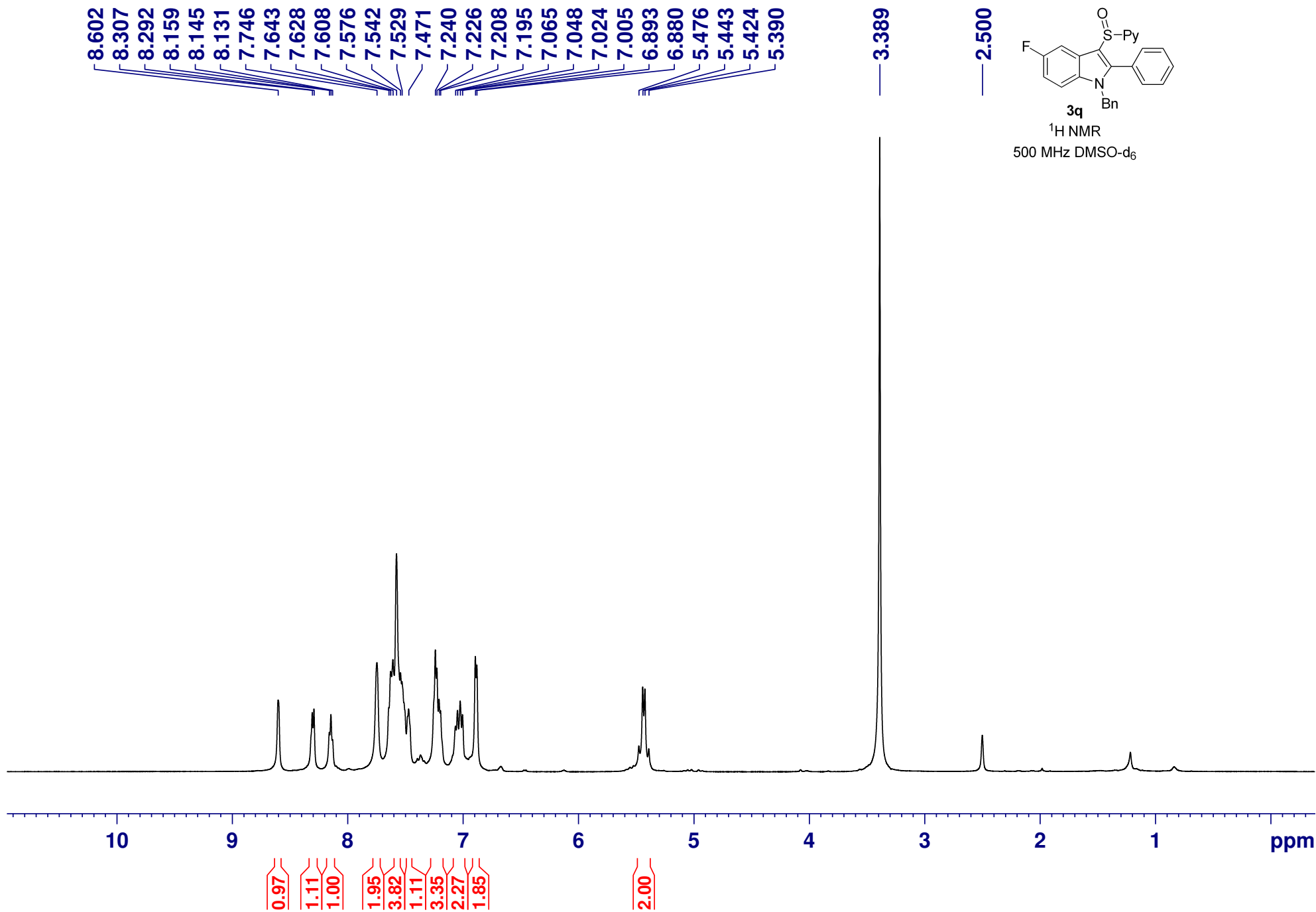












164.62

159.55

157.66

149.89

147.97

137.37

136.40

133.56

132.09

132.02

131.91

129.88

128.90

128.45

127.67

125.89

123.93

120.93

120.53

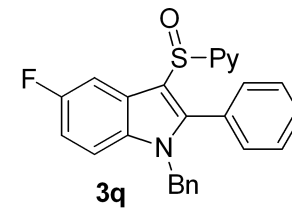
112.16

111.98

111.77

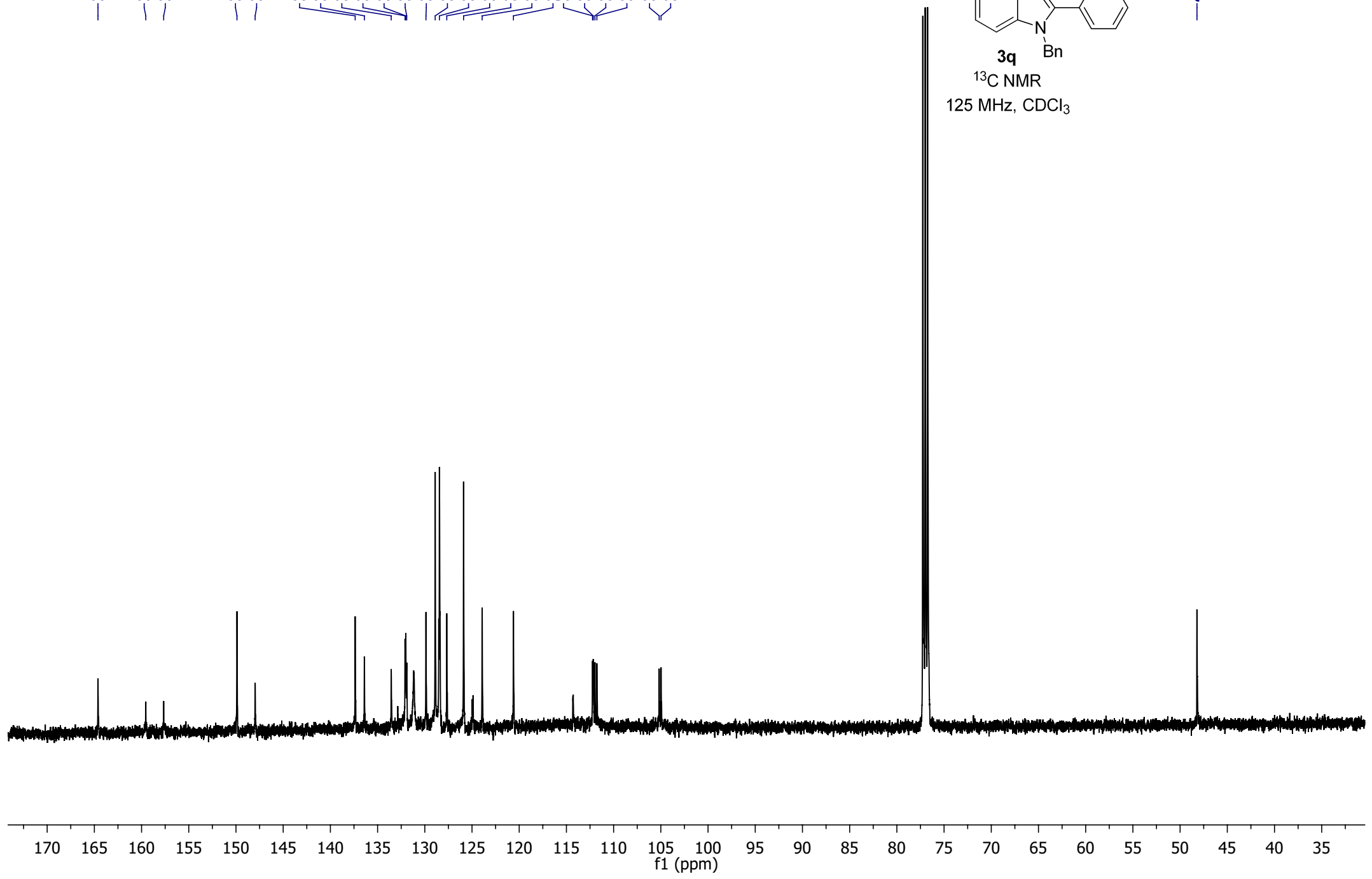
105.18

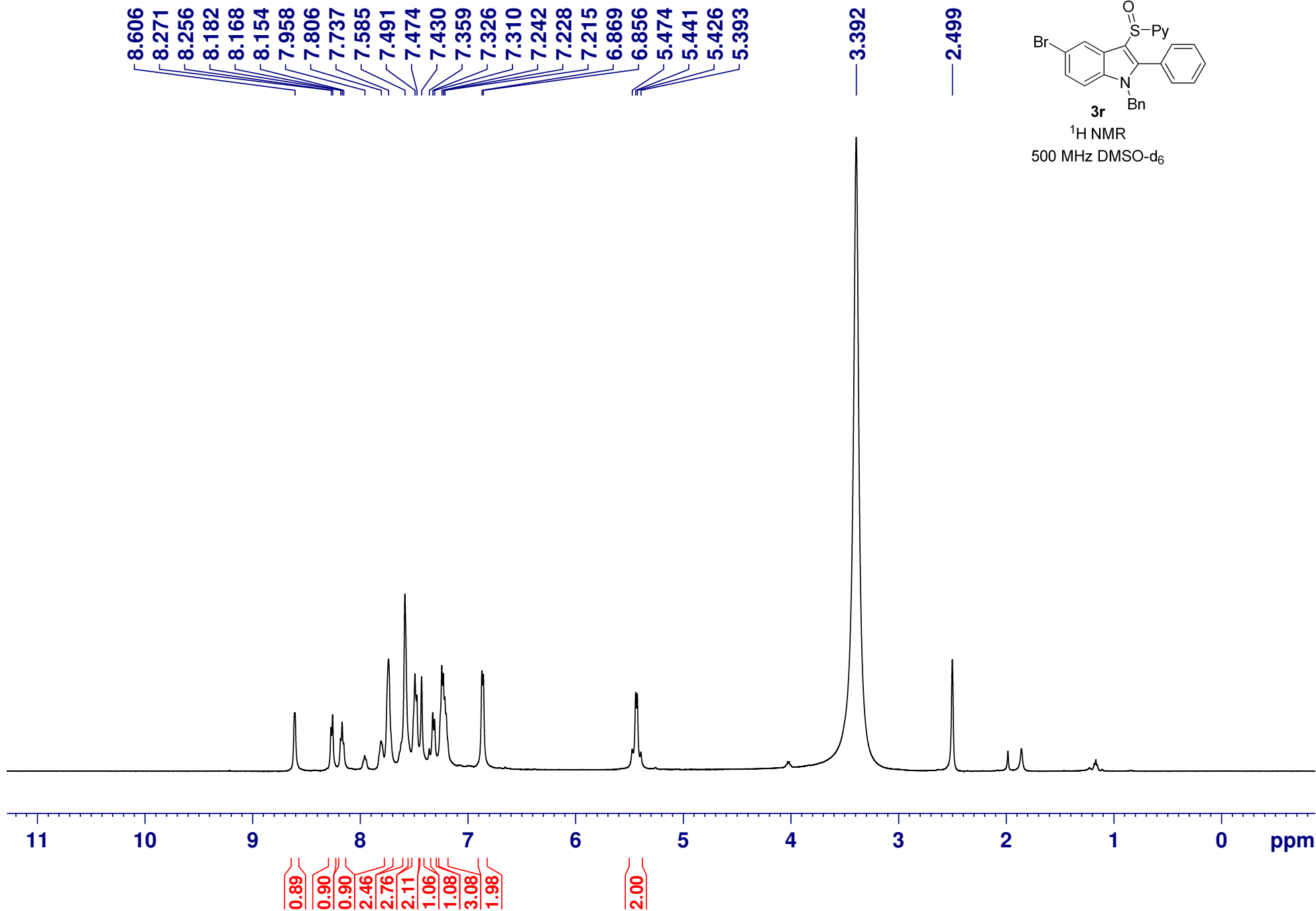
104.98



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

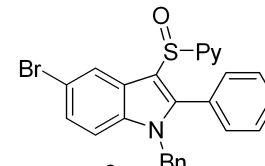
48.21



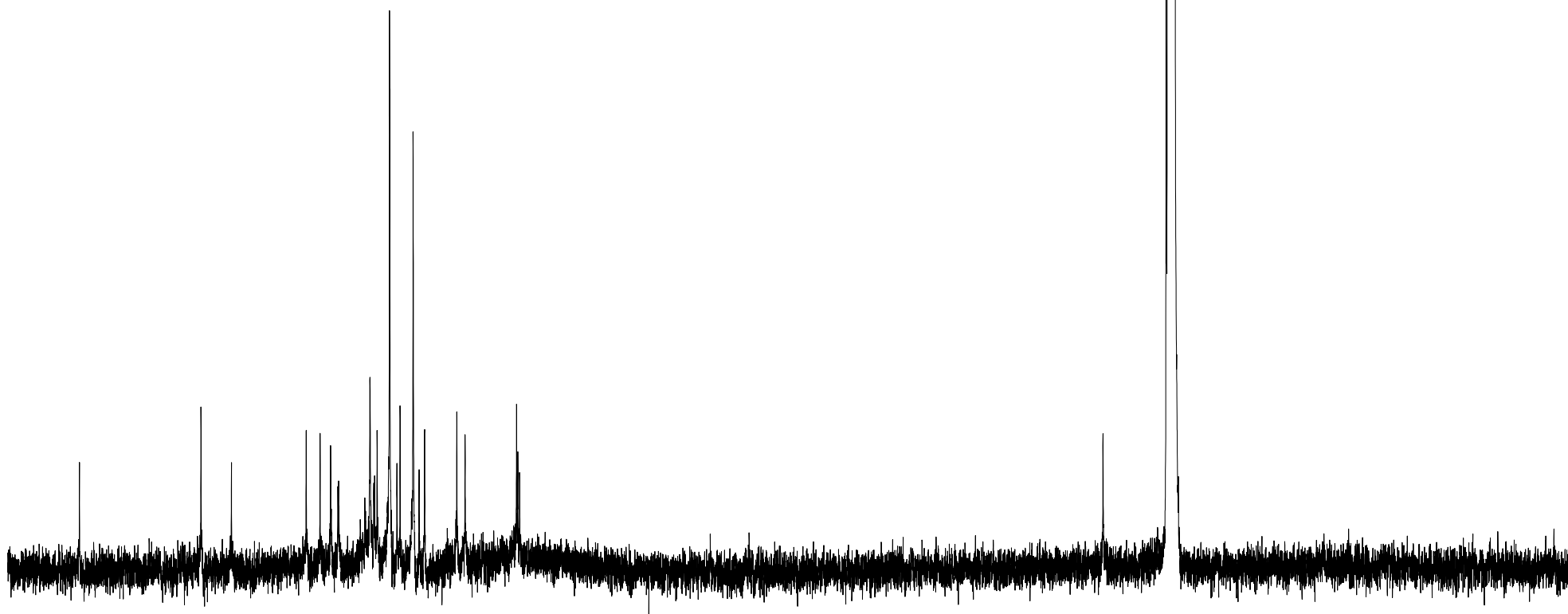


164.16  
150.27  
146.79  
138.25  
136.67  
135.46  
134.63  
134.55  
131.55  
130.97  
130.53  
130.44  
130.15  
128.73  
127.89  
127.53  
126.04  
125.35  
124.72  
121.04  
120.10  
114.22  
114.07  
113.87

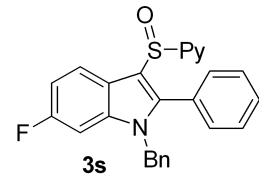
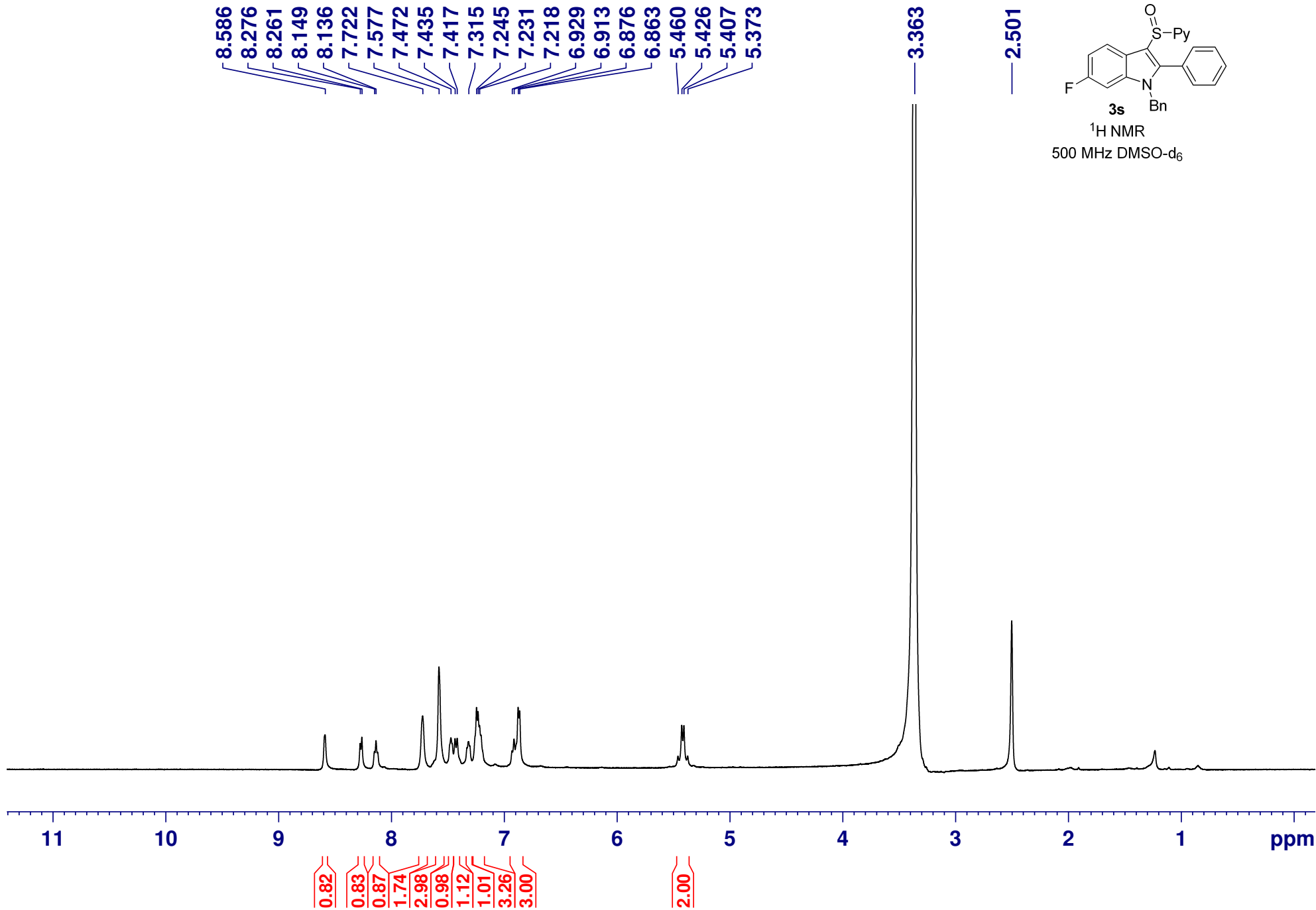
47.22  
40.02  
39.85  
39.68  
39.52  
39.35  
39.18  
39.02



<sup>13</sup>C NMR  
125 MHz DMSO-d<sub>6</sub>



160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



<sup>1</sup>H NMR  
500 MHz DMSO-d<sub>6</sub>

—162.62

—157.55

—155.66

—147.89

—145.97

—135.37

—134.40

—131.56

—130.09

—130.02

—129.91

—129.18

—127.88

—126.90

—126.45

—125.67

—123.89

—121.93

—118.61

—110.23

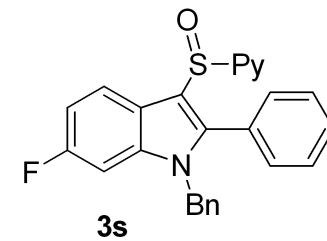
—110.16

—109.98

—109.77

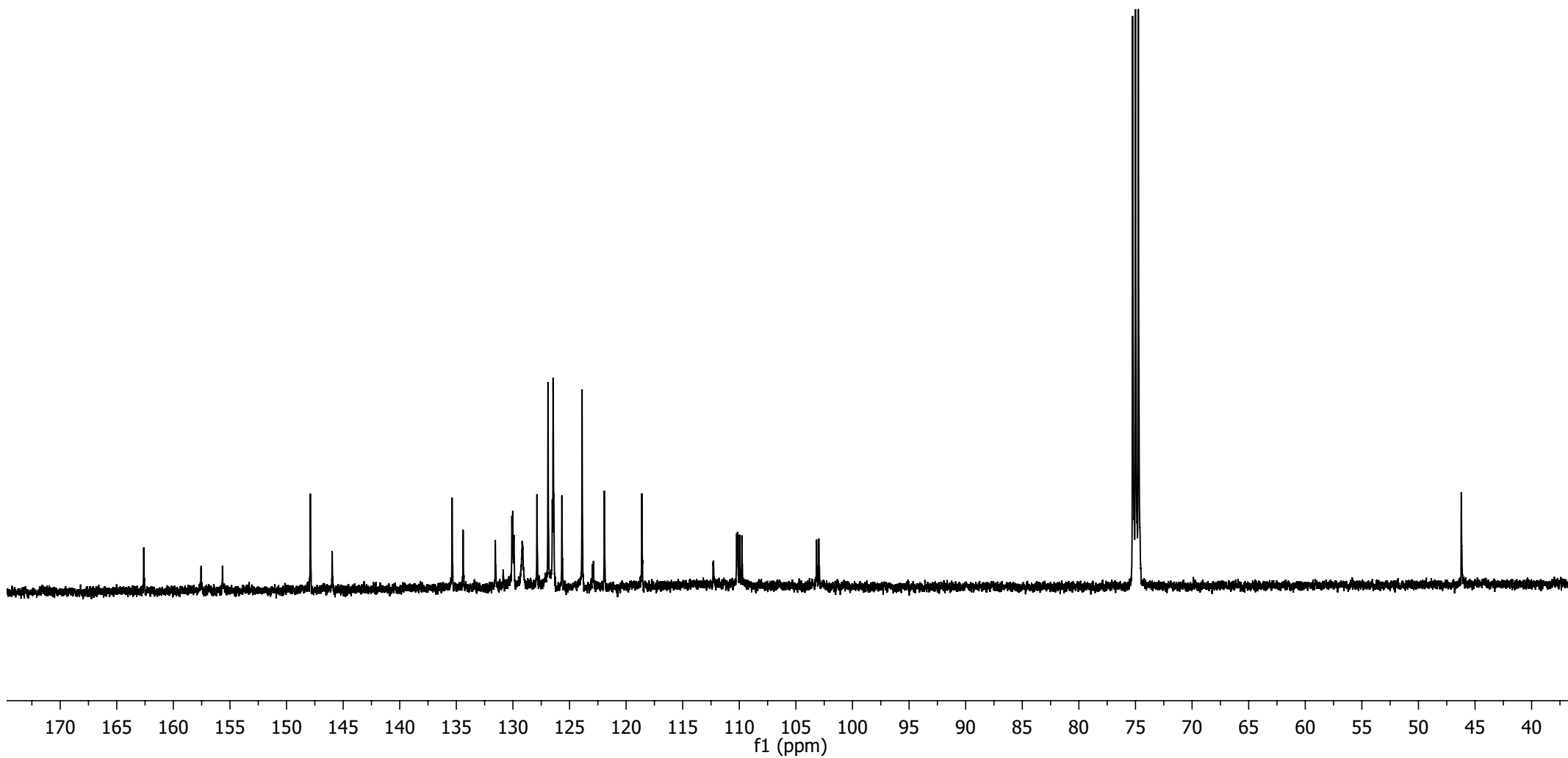
—103.18

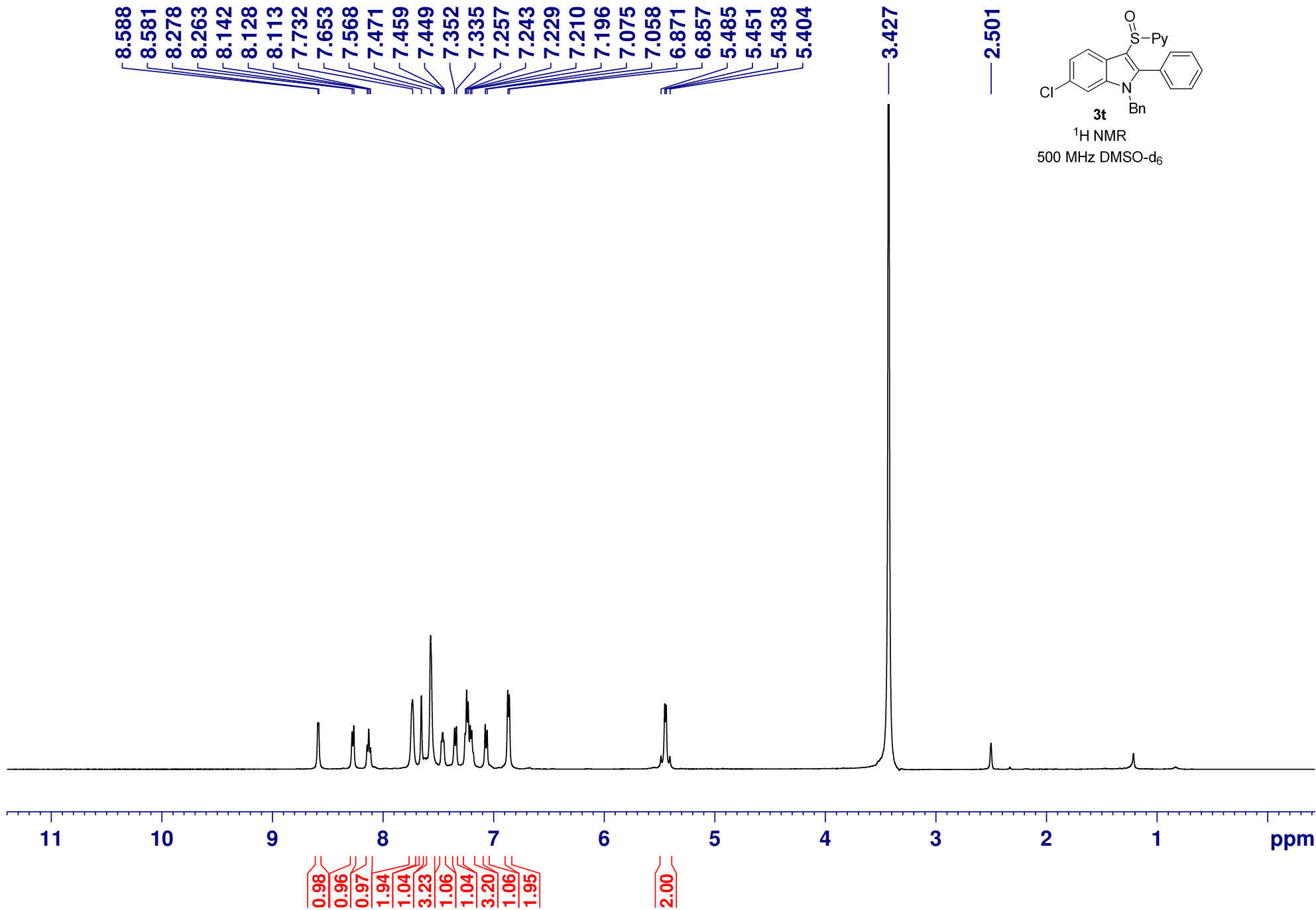
—102.98

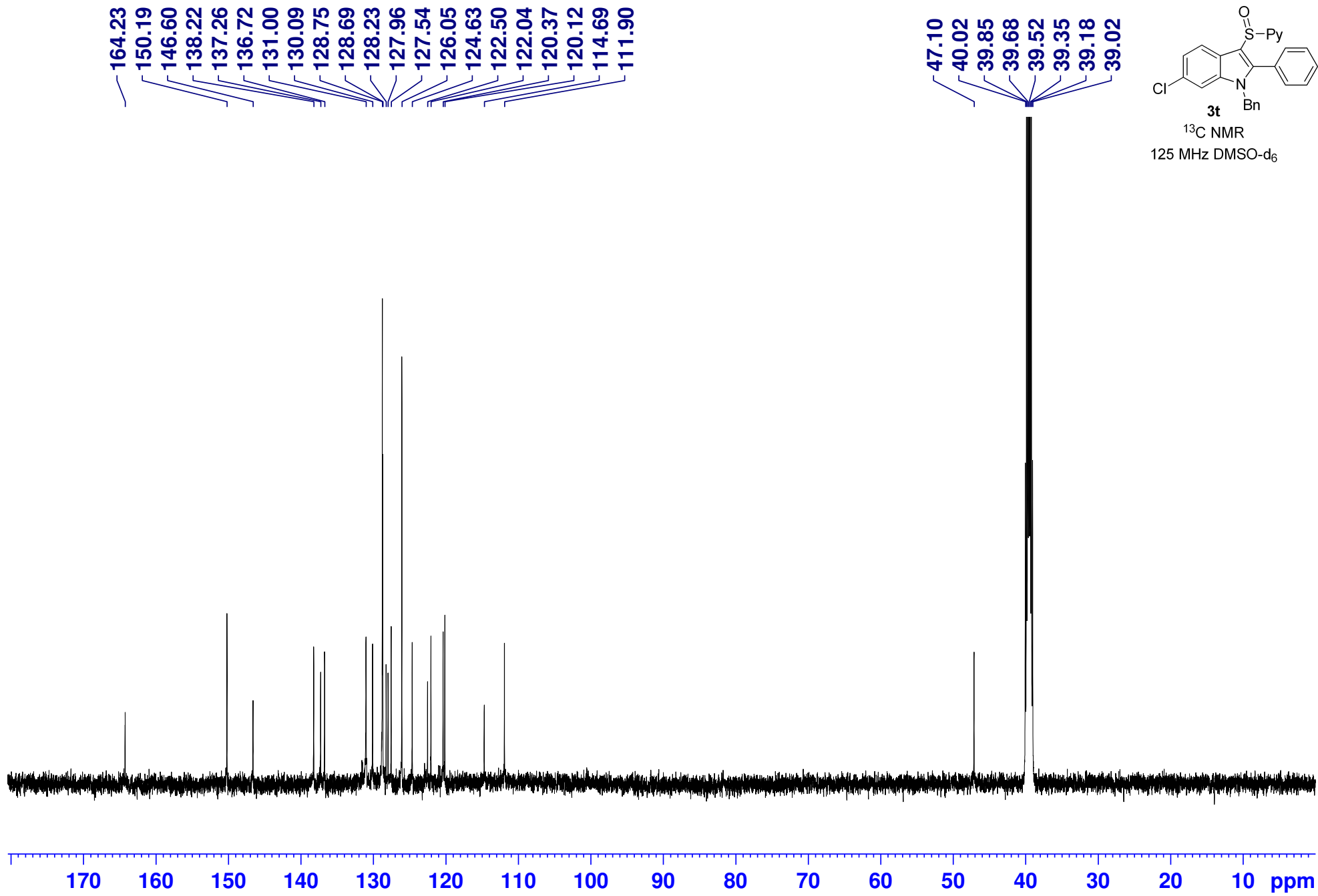


<sup>13</sup>C NMR  
125 MHz, CDCl<sub>3</sub>

—46.21

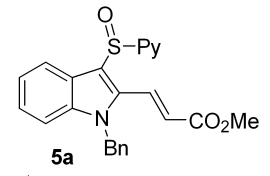




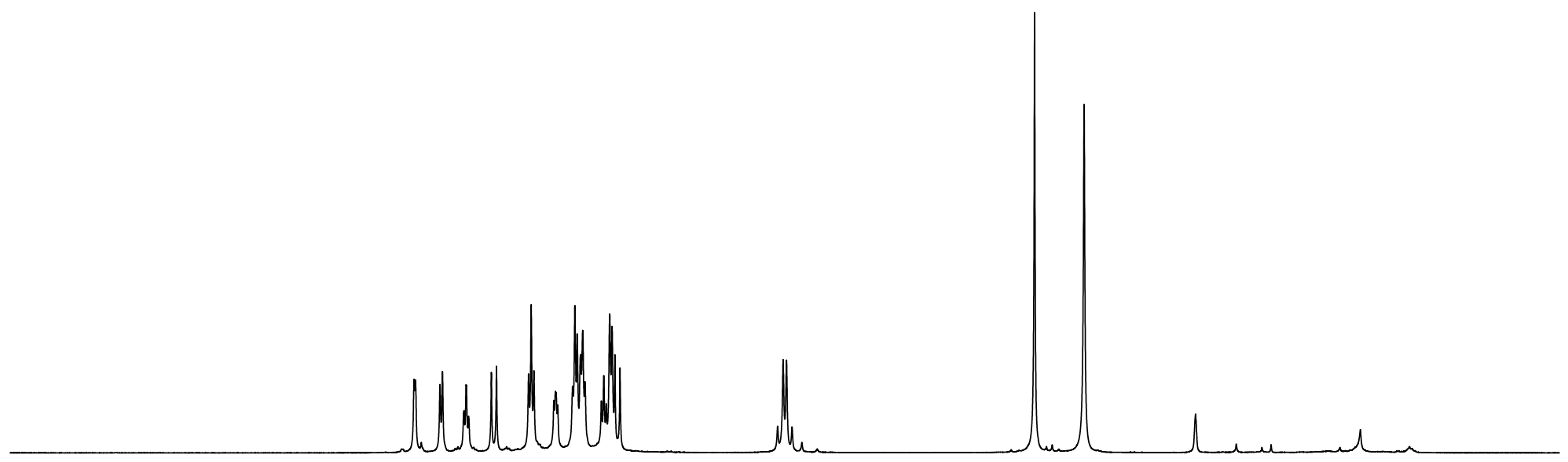


8.555  
8.546  
8.355  
8.336  
8.169  
8.153  
8.150  
8.134  
7.957  
7.917  
7.668  
7.648  
7.627  
7.472  
7.460  
7.456  
7.443  
7.328  
7.310  
7.291  
7.265  
7.248  
7.231  
7.105  
7.086  
7.067  
7.040  
7.022  
7.000  
6.960  
5.739  
5.696  
5.670  
5.627  
3.747  
3.364

2.500



<sup>1</sup>H NMR  
400 MHz, DMSO-d<sub>6</sub>

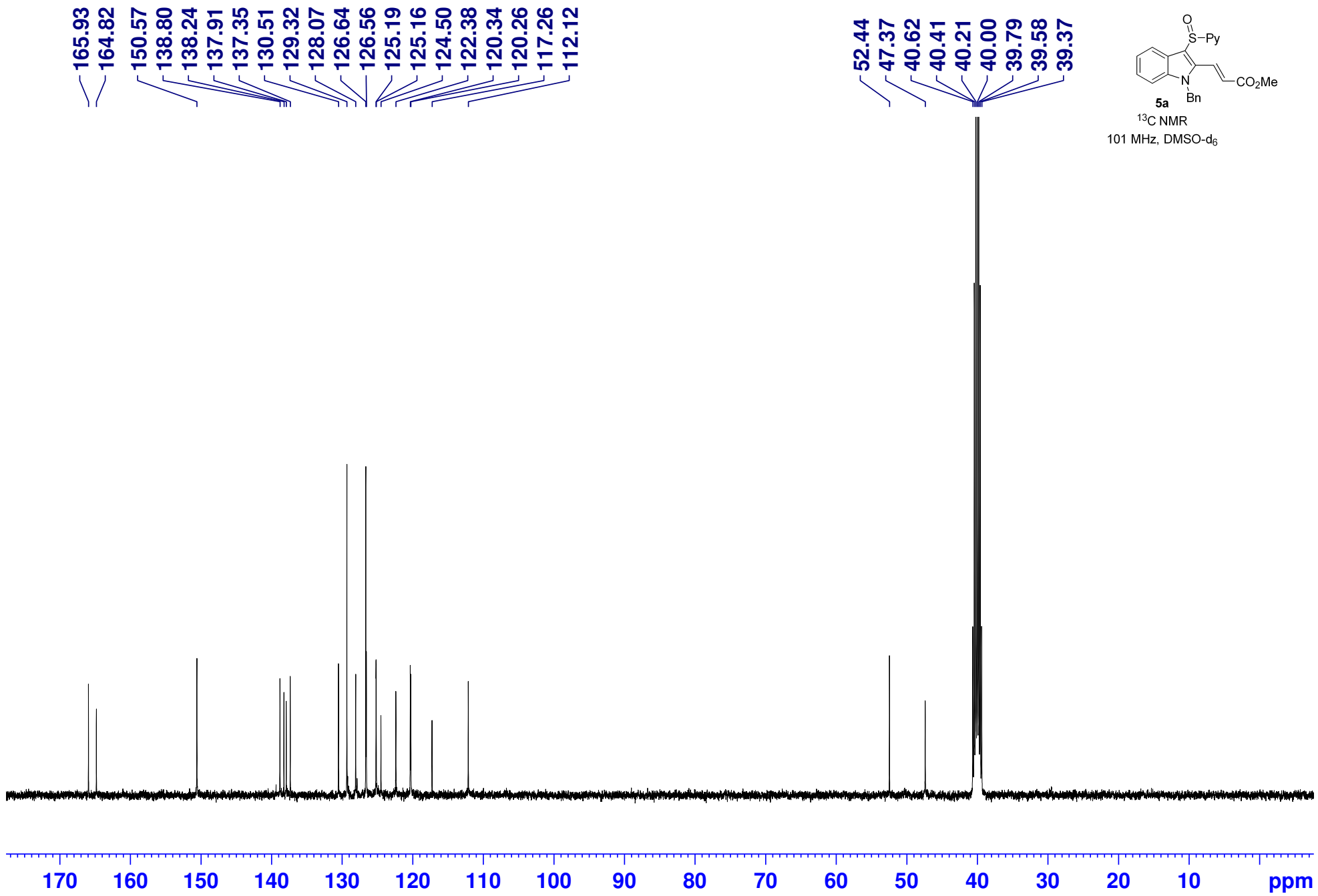


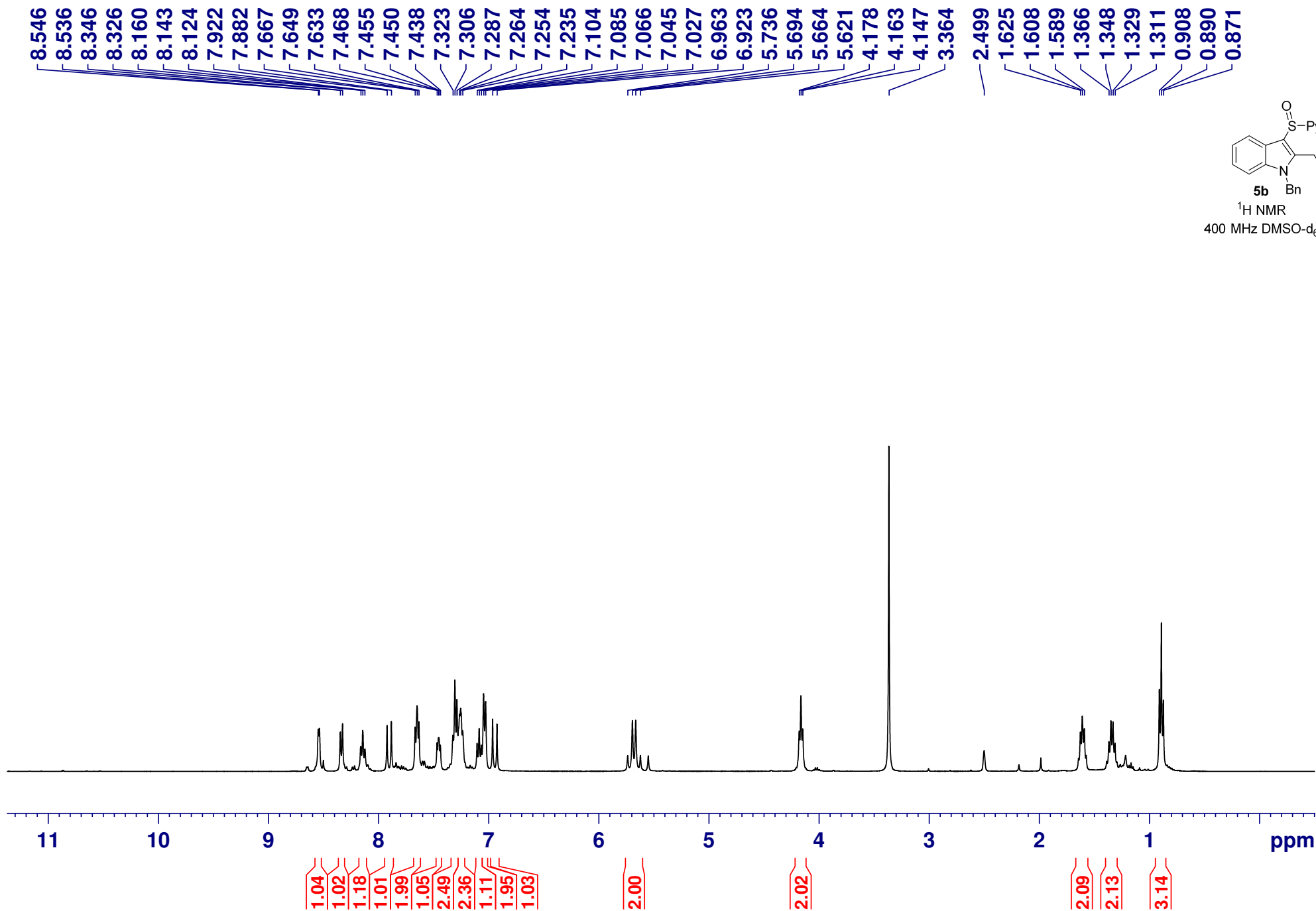
11 10 9 8 7 6 5 4 3 2 1 ppm

1.01  
1.07  
1.12  
1.07  
2.15  
1.22  
2.02  
2.26  
1.20  
1.95  
1.15

2.00

3.12

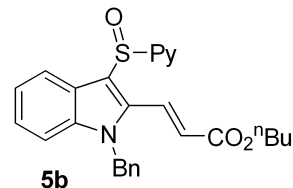




165.52  
164.74

150.57

138.75  
138.23  
137.92  
137.37  
130.40  
129.30  
128.08  
126.78  
126.68  
125.17  
125.15  
124.57  
122.38  
120.40  
120.21  
117.21  
112.10



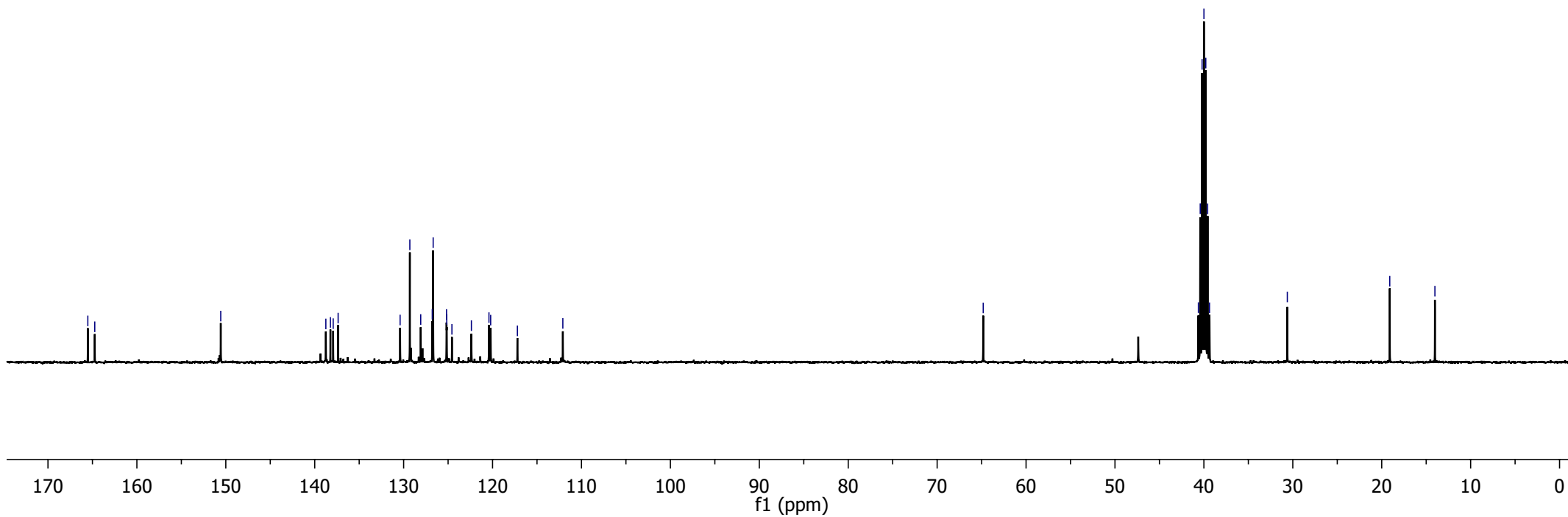
<sup>13</sup>C NMR  
101 MHz, DMSO-d<sub>6</sub>

64.82

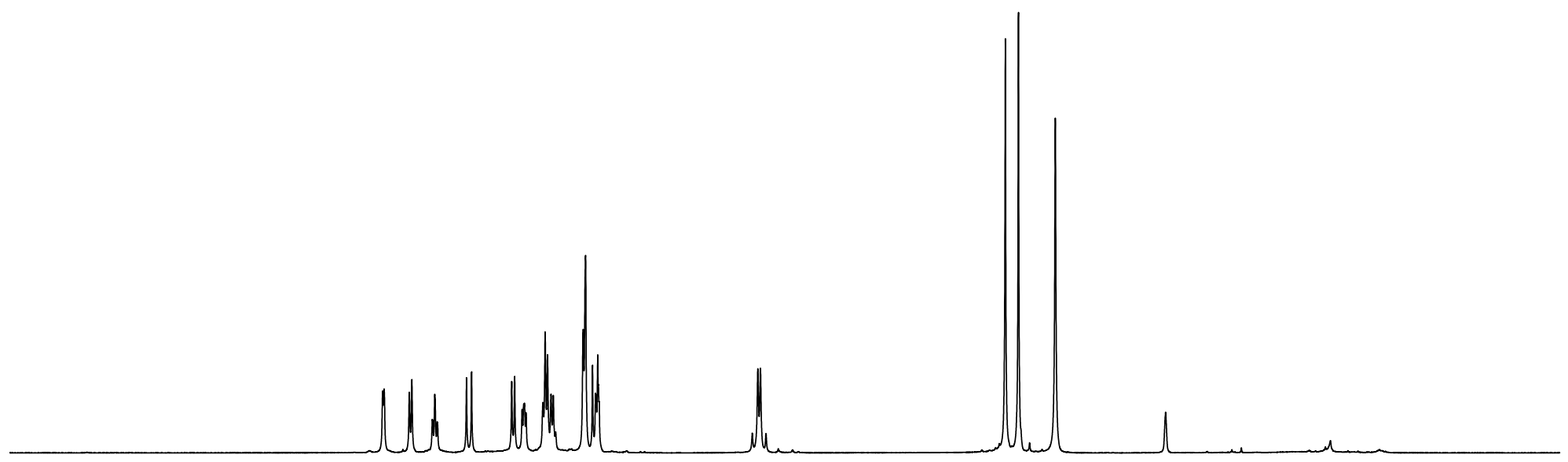
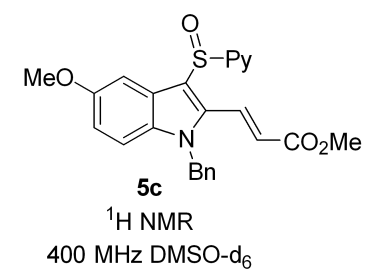
40.62  
40.41  
40.20  
39.99  
39.79  
39.58  
39.37  
30.62

19.10

14.02



8.566  
8.556  
8.360  
8.341  
8.183  
8.179  
8.163  
8.144  
7.917  
7.878  
7.567  
7.544  
7.487  
7.473  
7.468  
7.456  
7.325  
7.308  
7.289  
7.262  
7.244  
7.226  
7.013  
6.994  
6.940  
6.917  
6.911  
6.901  
6.895  
6.889  
5.703  
5.660  
5.639  
5.596  
3.742  
3.640  
3.354  
2.500

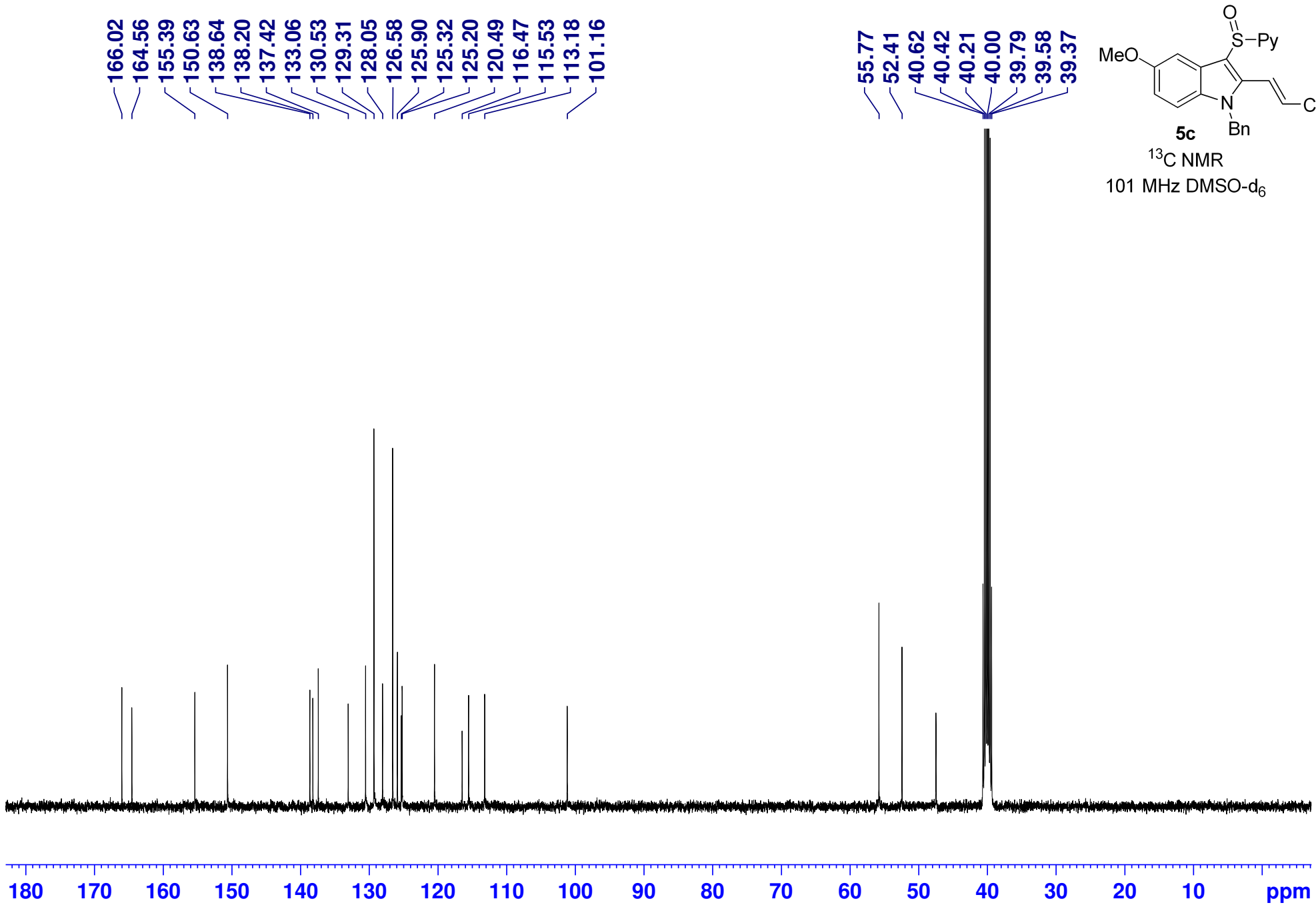


11 10 9 8 7 6 5 4 3 2 1 ppm

0.97  
1.02  
1.01  
1.01  
1.00  
1.07  
1.94  
1.15  
3.04  
1.96

2.00

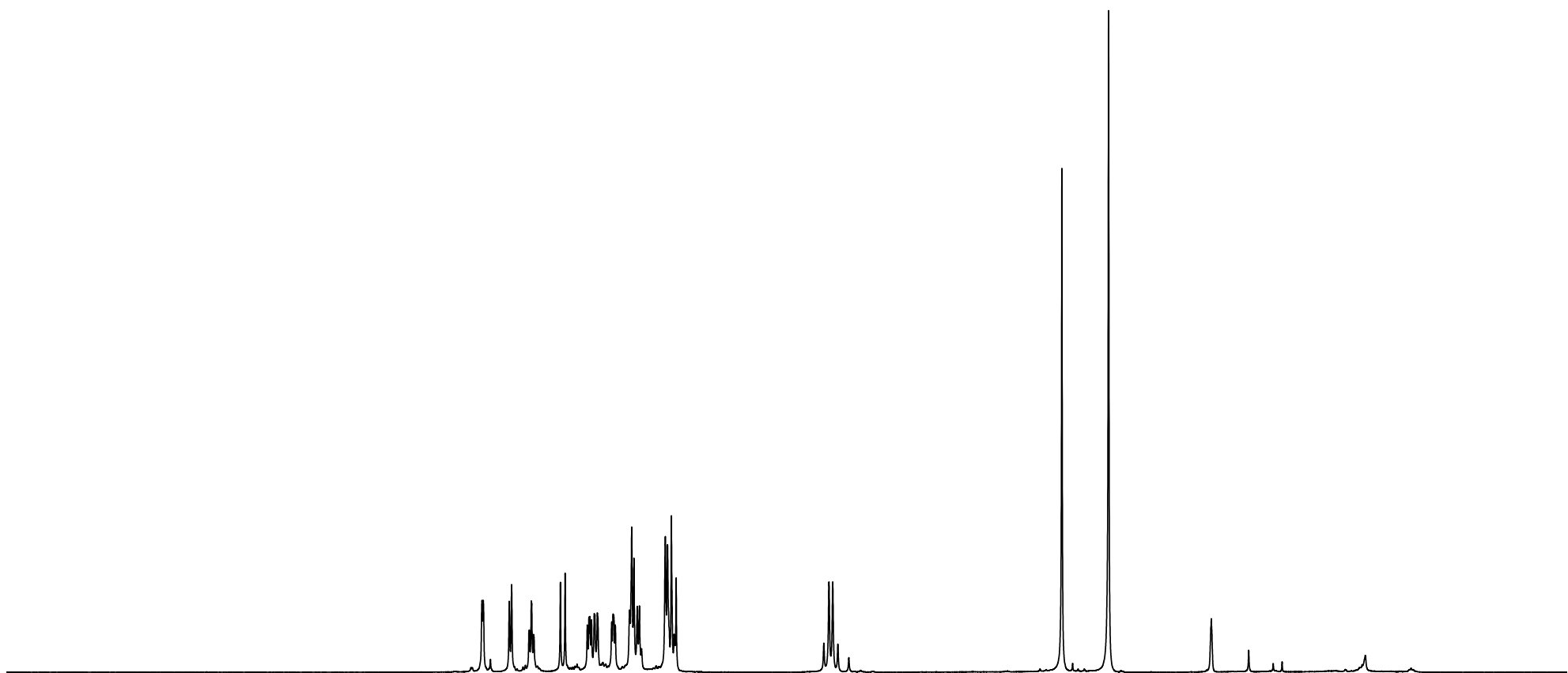
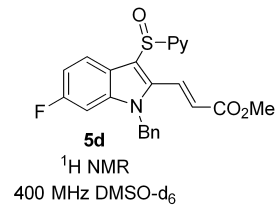
3.07  
3.19



166.02  
164.56  
155.39  
150.63  
138.64  
138.20  
137.42  
133.06  
130.53  
129.31  
128.05  
126.58  
125.90  
125.32  
125.20  
120.49  
116.47  
115.53  
113.18  
101.16

55.77  
52.41  
40.62  
40.42  
40.21  
40.00  
39.79  
39.58  
39.37

8.573  
8.563  
8.347  
8.327  
8.183  
8.180  
8.164  
8.161  
8.145  
8.141  
7.922  
7.882  
7.698  
7.685  
7.676  
7.663  
7.640  
7.635  
7.614  
7.610  
7.495  
7.483  
7.478  
7.466  
7.346  
7.329  
7.310  
7.282  
7.264  
7.049  
7.030  
6.998  
6.976  
6.970  
6.959  
5.730  
5.687  
5.656  
5.613  
3.750  
3.361  
2.507



12

11

10

9

8

7

6

5

4

3

2

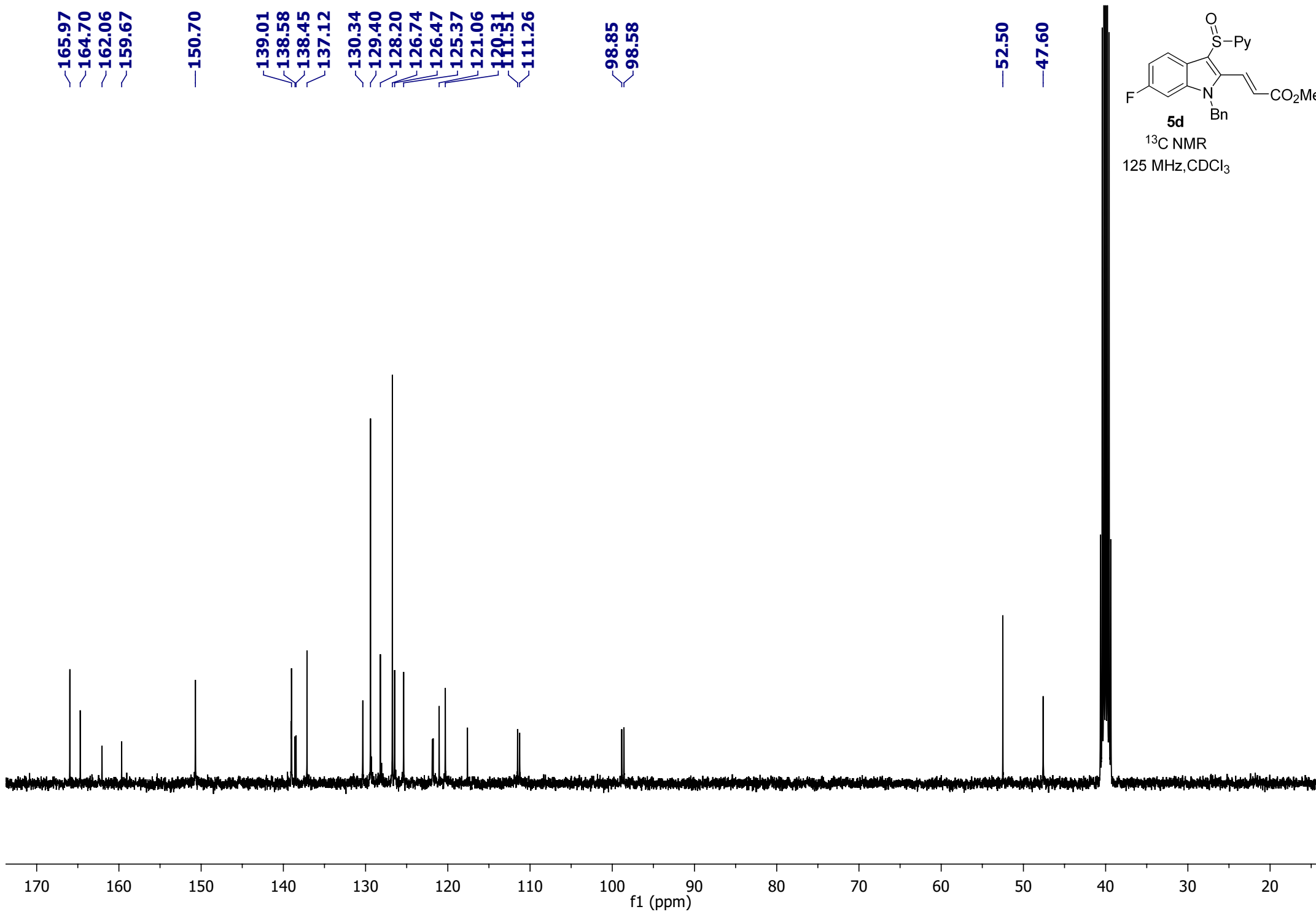
1

ppm

1.03  
1.07  
1.21  
1.08  
1.13  
1.13  
1.18  
2.33  
1.12  
2.25  
1.76

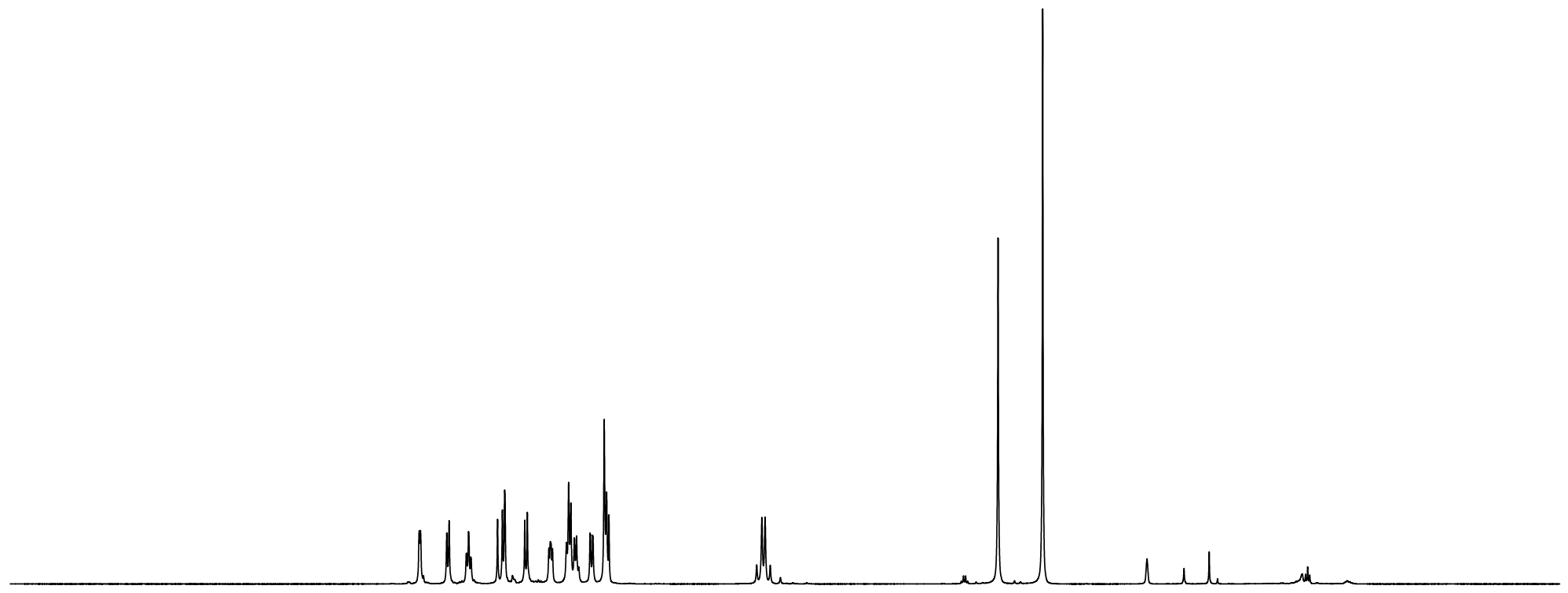
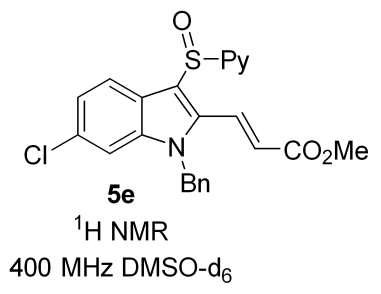
2.00

2.71



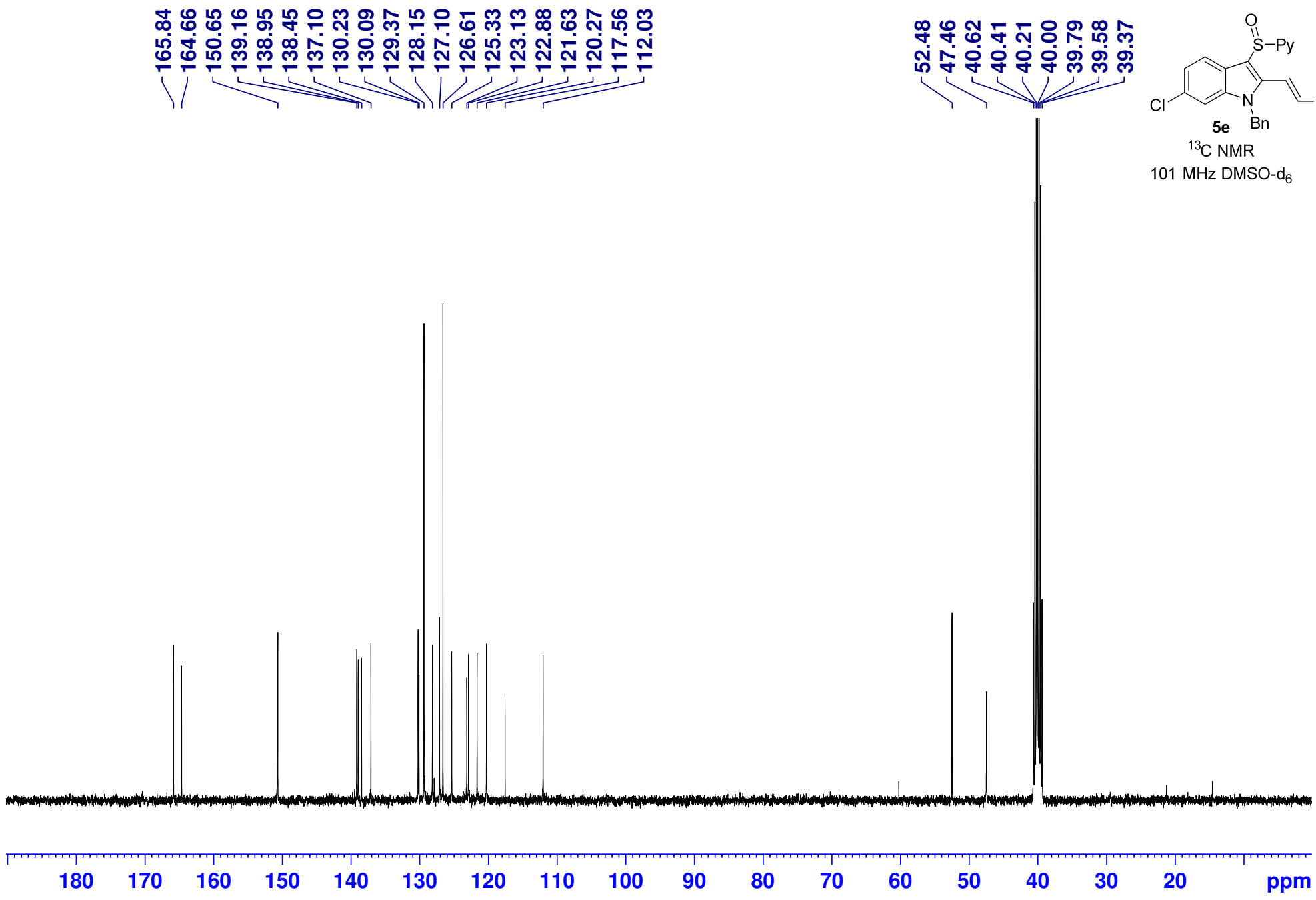
8.563  
8.553  
8.334  
8.314  
8.172  
8.169  
8.153  
8.133  
7.910  
7.871  
7.851  
7.684  
7.662  
7.483  
7.471  
7.466  
7.454  
7.336  
7.319  
7.300  
7.270  
7.252  
7.140  
7.137  
7.119  
7.115  
7.022  
7.002  
6.983  
5.708  
5.682  
3.741  
3.369

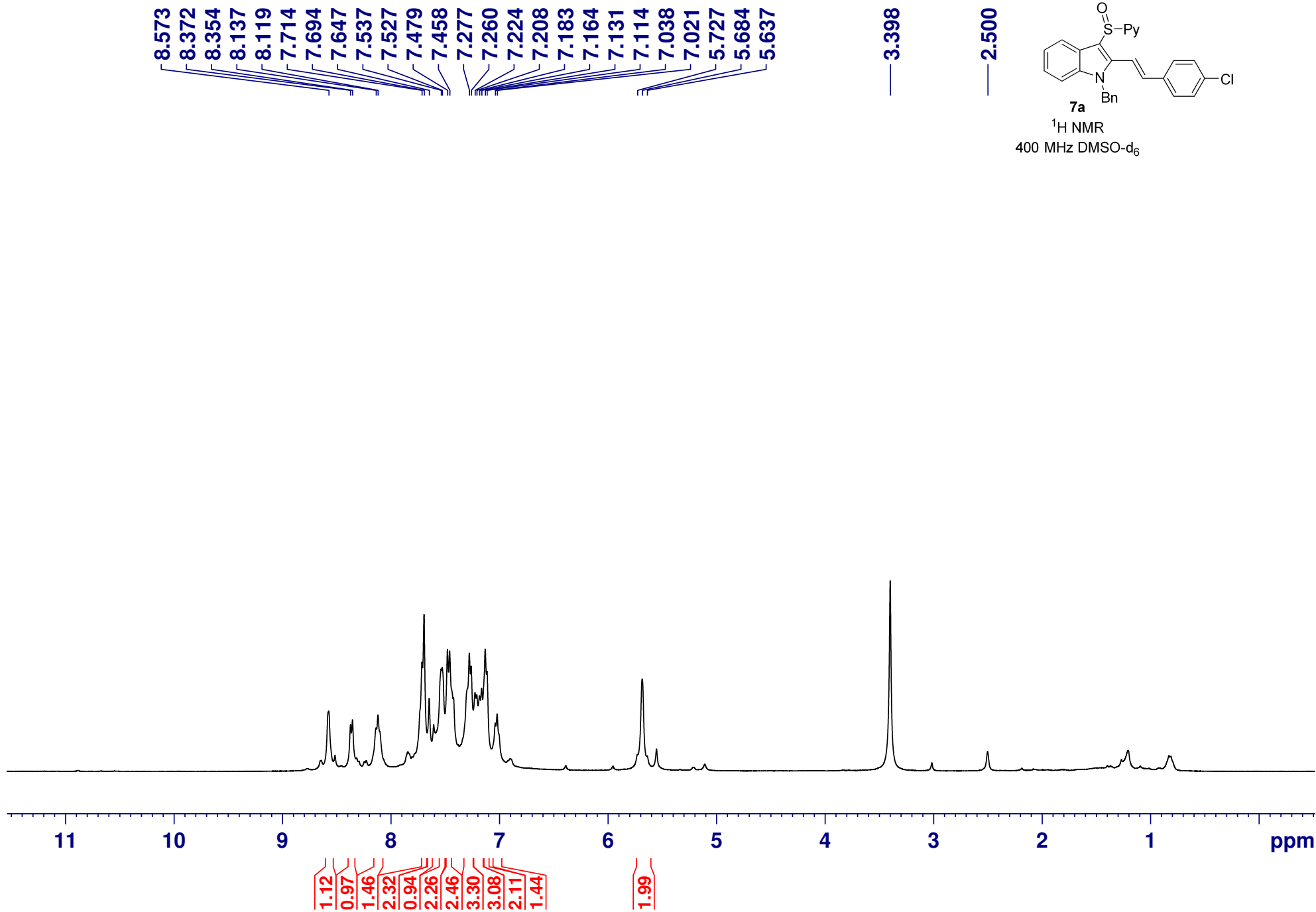
2.500

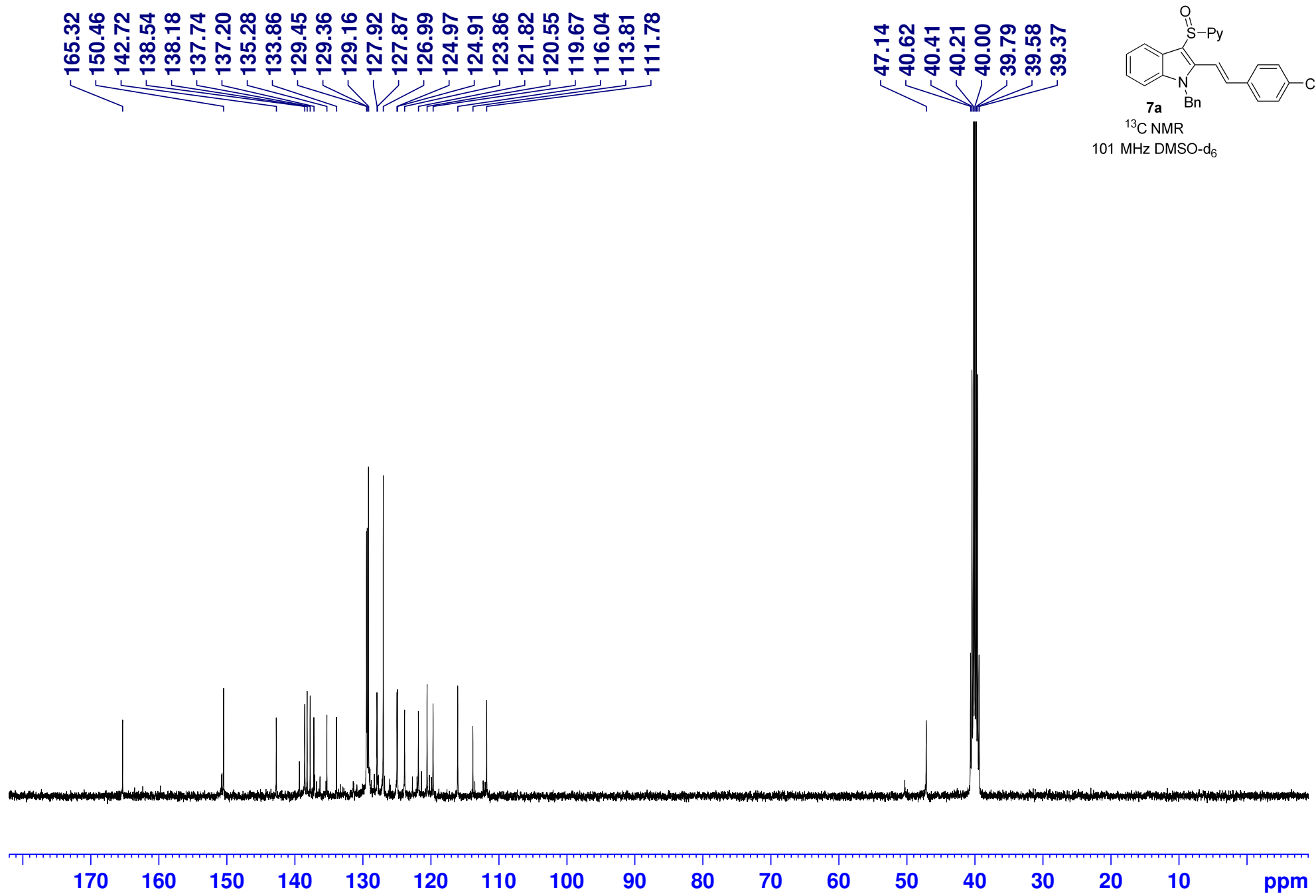


11 10 9 8 7 6 5 4 3 2 1 0 ppm

1.04  
1.04  
1.14  
2.10  
1.10  
1.16  
2.12  
1.15  
1.08  
3.01  
2.00  
2.97



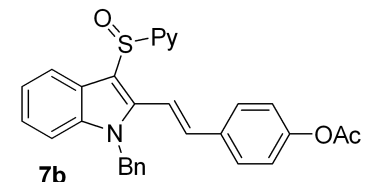




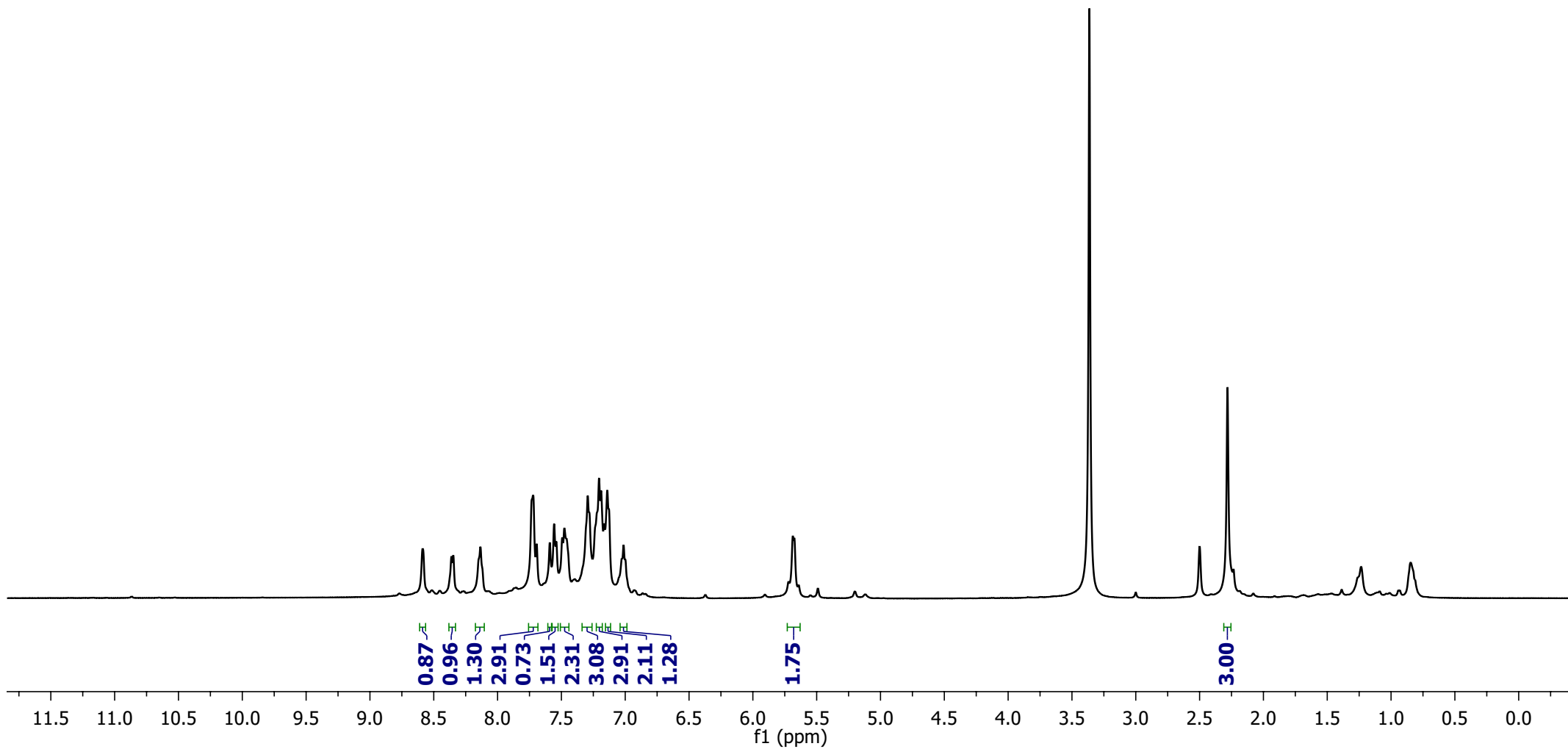
8.59  
8.36  
8.35  
8.13  
7.72  
7.56  
7.49  
7.48  
7.46  
7.29  
7.20  
7.19  
7.17  
7.14  
5.72  
5.69  
5.68  
5.64

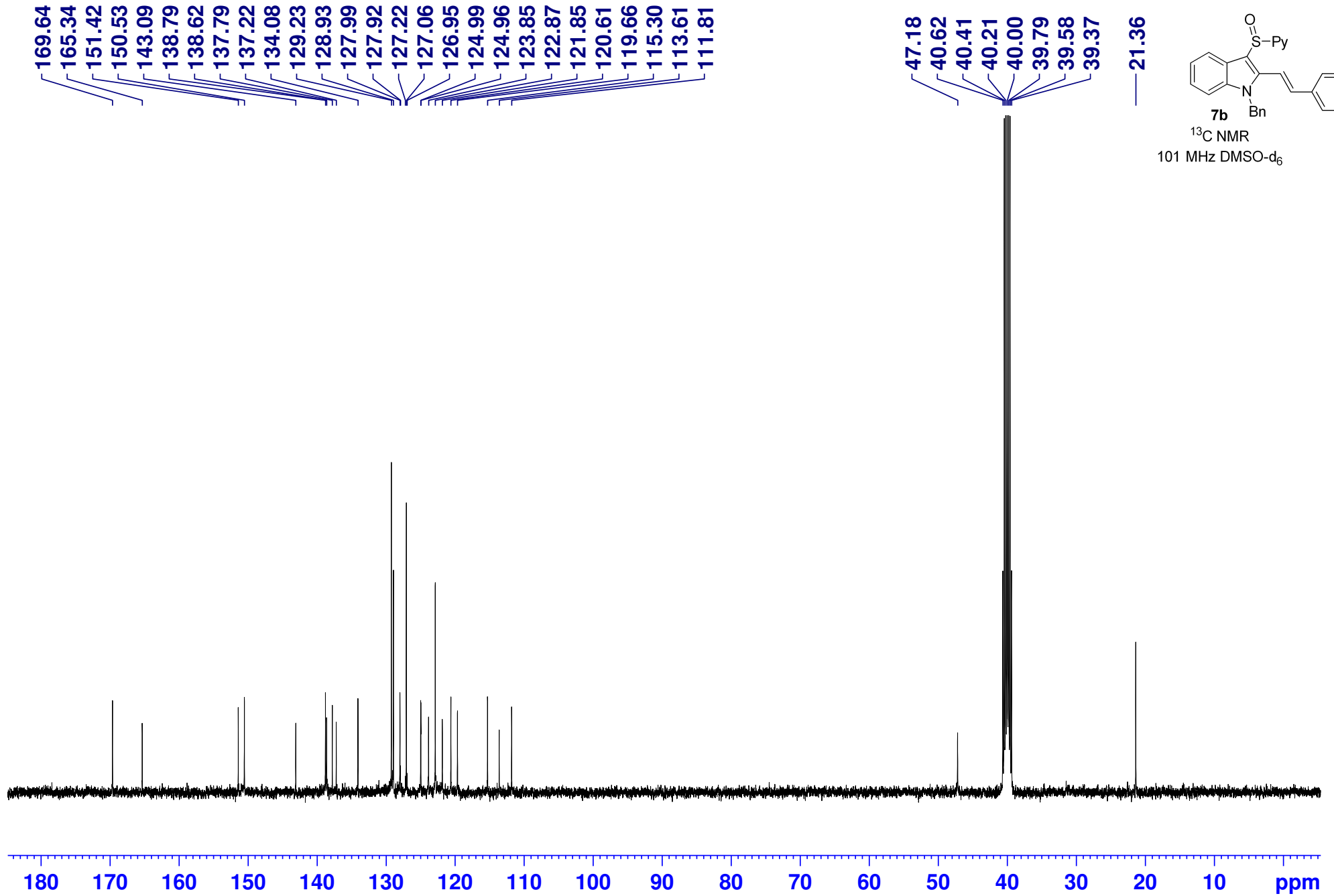
3.36

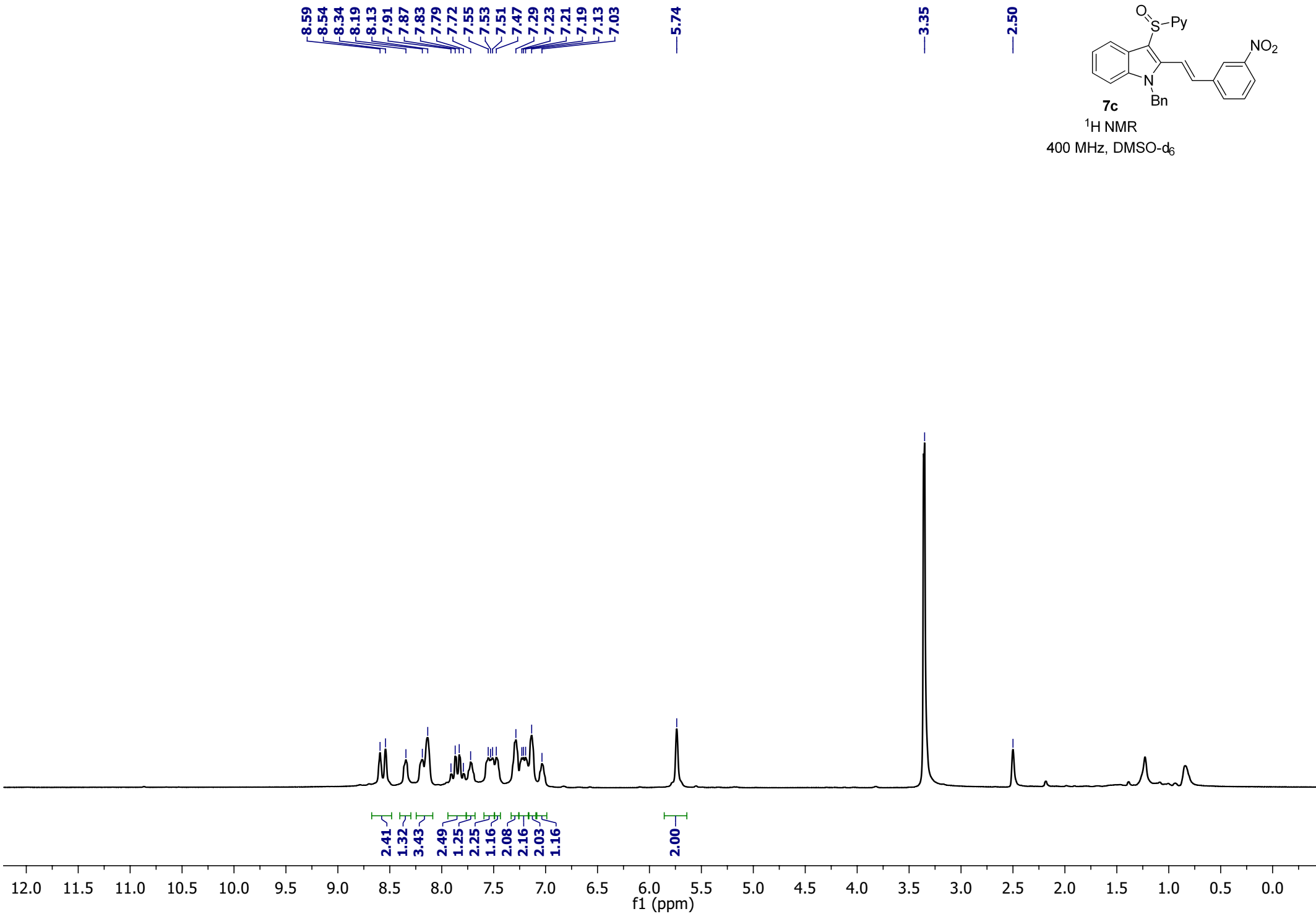
2.50  
2.28

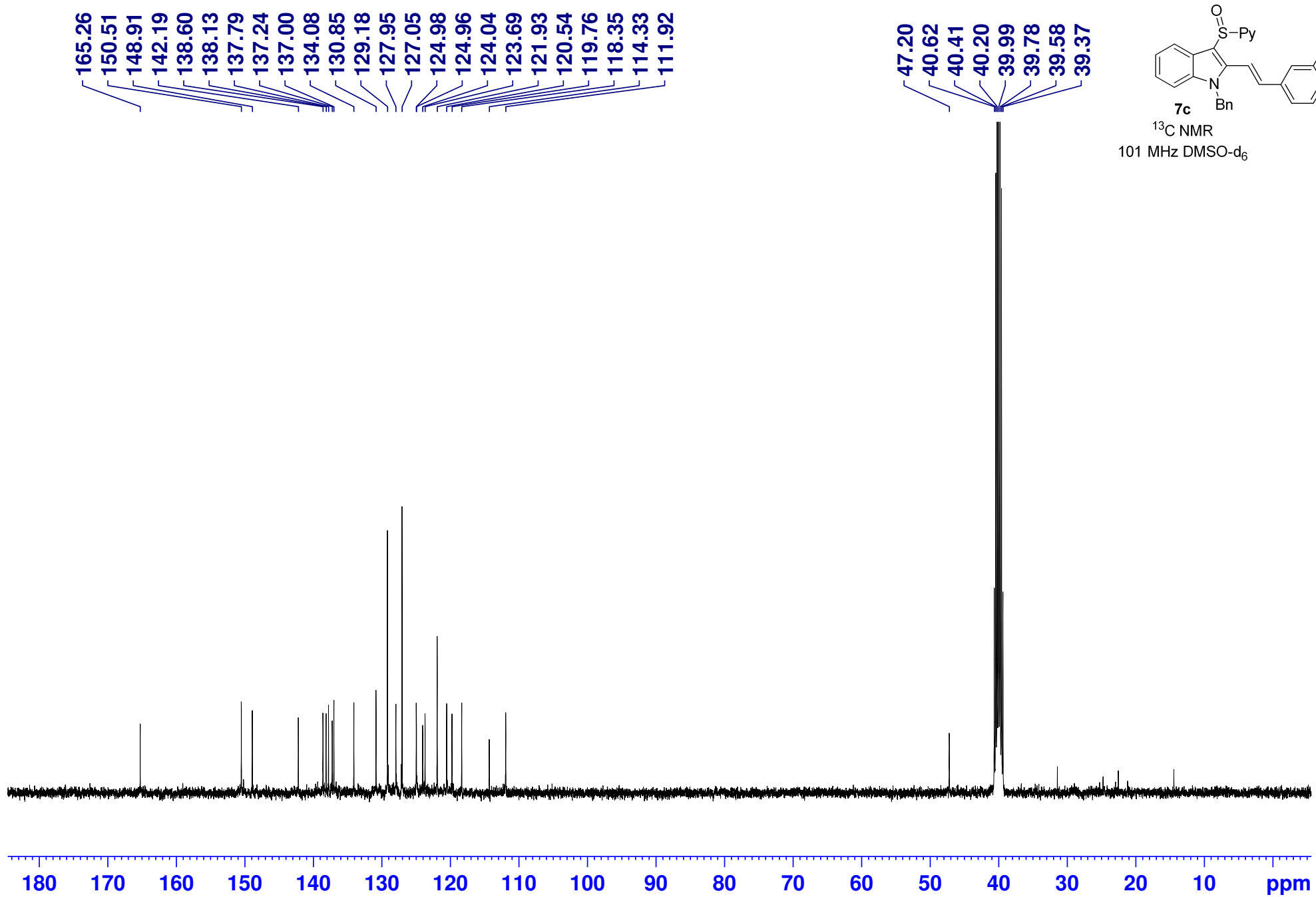


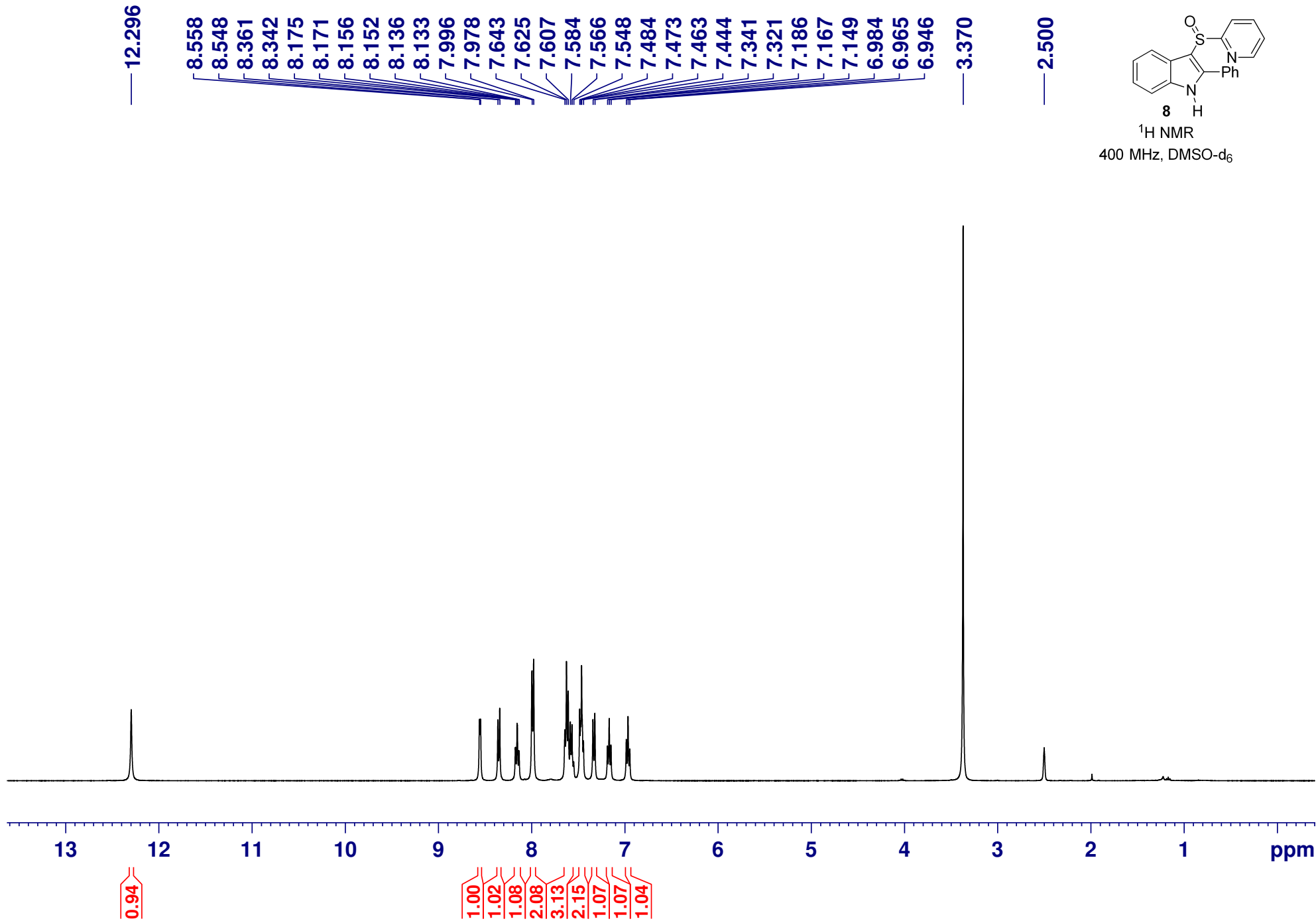
<sup>1</sup>H NMR  
500 MHz, DMSO-d<sub>6</sub>

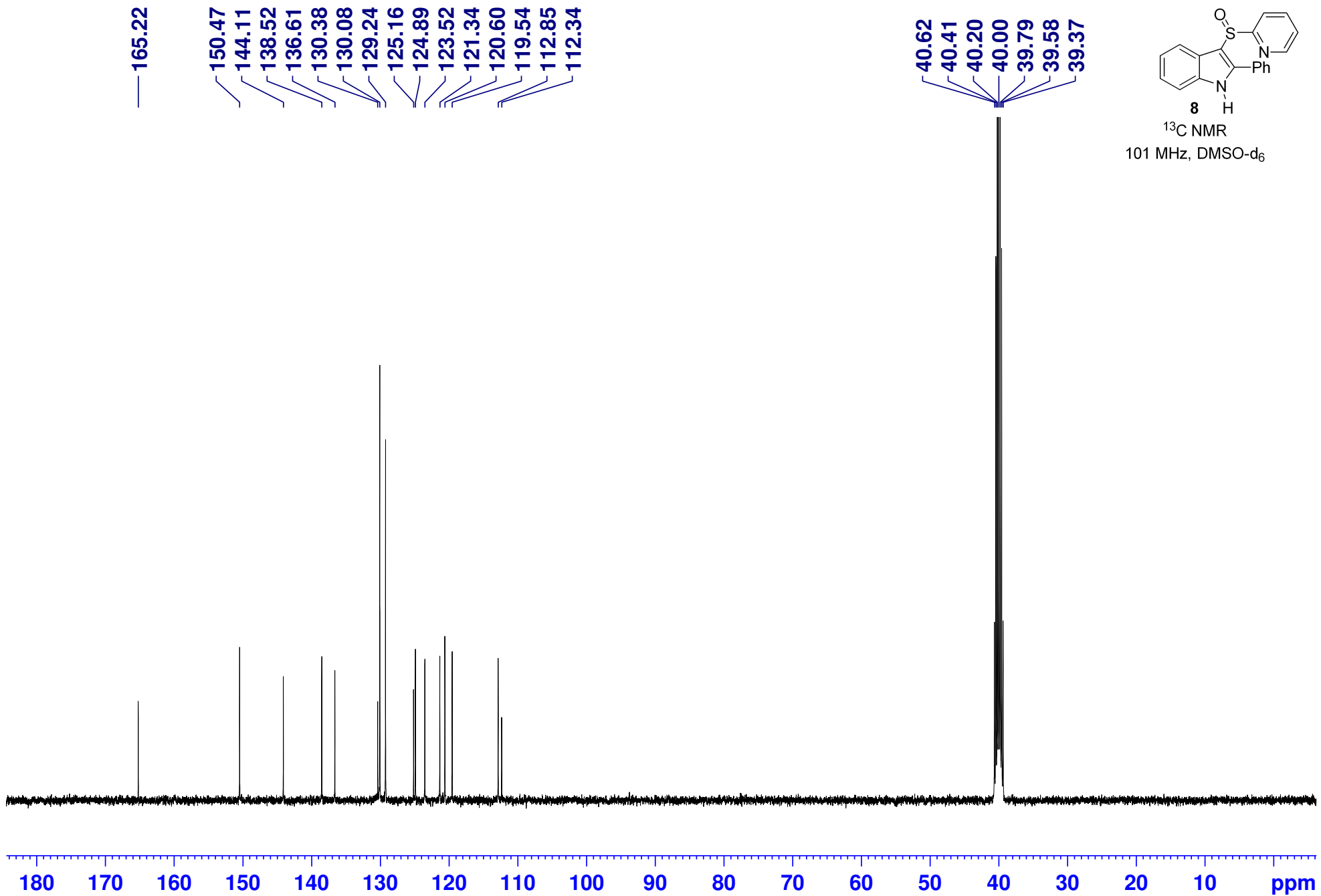




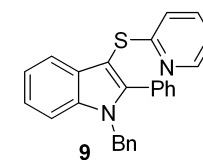




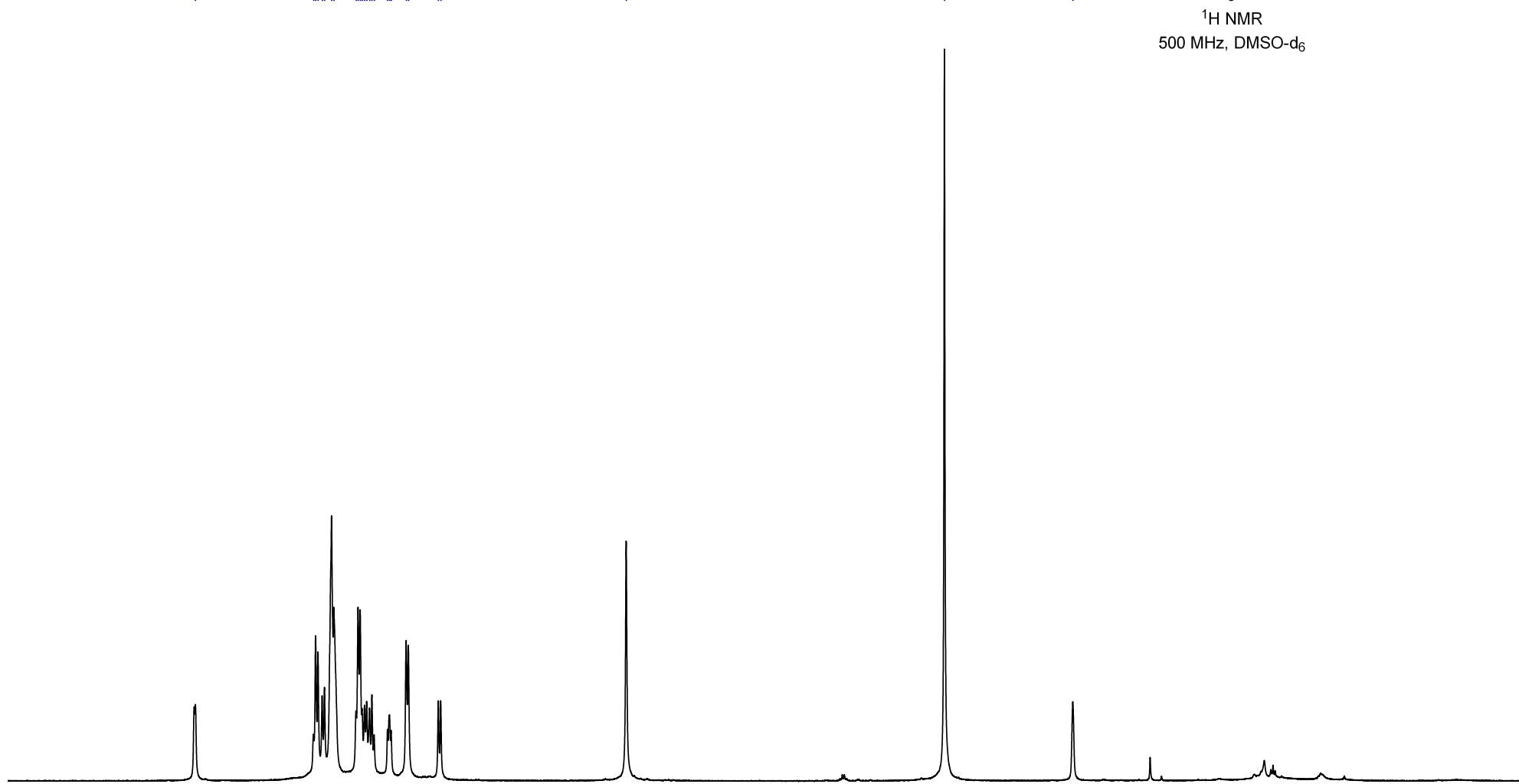




8.333  
7.548  
7.534  
7.518  
7.491  
7.475  
7.428  
7.413  
7.266  
7.252  
7.238  
7.225  
7.209  
7.195  
7.175  
7.160  
7.145  
7.056  
7.043  
7.032  
6.932  
6.917  
6.718  
6.702  
5.469

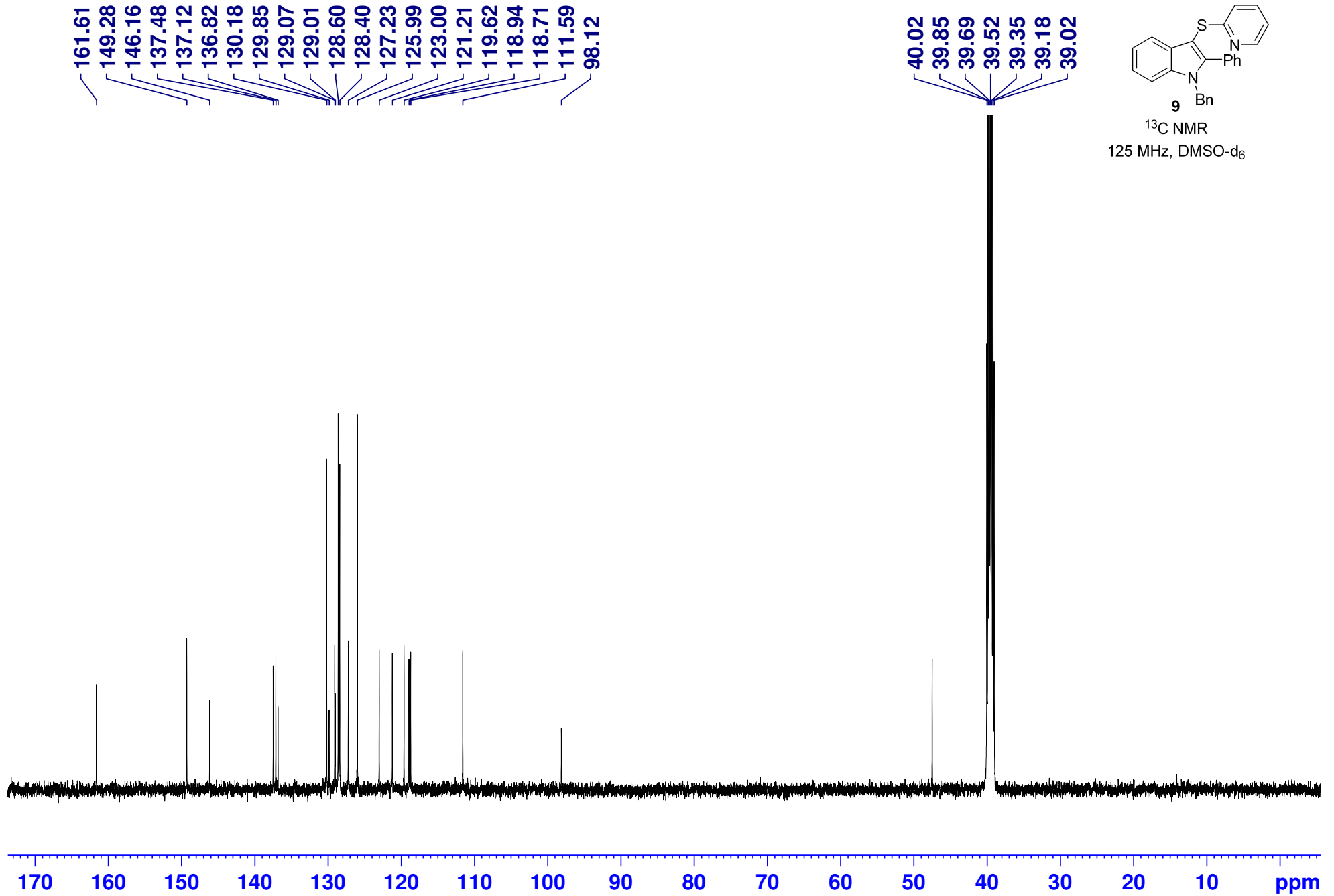


<sup>1</sup>H NMR  
500 MHz, DMSO-d<sub>6</sub>



9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.03  
2.32  
1.34  
5.32  
3.16  
1.16  
1.41  
1.13  
2.14  
1.05  
2.00



MB-KY-521

