

# Highly Diastereo- and Enantioselective CuH-Catalyzed Synthesis of 2,3-Disubstituted Indolines

Erhad Ascic, Stephen L. Buchwald\*

*Department of Chemistry, Massachusetts Institute of Technology,  
Cambridge, Massachusetts 02139, USA*

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## I. General Information

### A) General Reagent Information:

Anhydrous MTBE and anhydrous *t*-BuOH were purchased from Sigma-Aldrich in a Sure-Seal® bottle and used as received. Anhydrous *t*-BuOD was purchased from Cambridge Isotope Laboratories and used as received. Diethoxymethylsilane (DEMS) was purchased from TCI America (stored at 4 °C) and used as received. Reaction solvents THF and toluene were dried by passing through a column packed with neutral alumina under a positive pressure of argon prior to use. Copper(II) acetate and (+)-1,2-Bis((2*S*,5*S*)-2,5-diphenylphospholano)ethane ((*S,S*)-Ph-BPE) were purchased from Sigma-Aldrich and stored in a nitrogen-filled glovebox. All other commercial reagents were purchased from Sigma-Aldrich, Strem, or Combi-Blocks and used as received. All of the compounds were purified by flash column chromatography using Silicycle SiliaFlash P69 (230-400 mesh) silica gel. Purification of imine substrates were performed on deactivated silica gel. The deactivated silica gel was prepared by washing the silica gel with hexanes/triethylamine (20:1 v/v) prior to purification. Molecular sieves 4Å, powder <50 μm, were purchased from Acros Organics and activated (with Bunsen burner heating under vacuum) prior to use.

### B) General Analytical Information:

Reactions were monitored by TLC, GC, and/or NMR analysis. Final products and all new intermediate compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectroscopy, melting point (when applicable), and elemental analysis or high-resolution mass spectrometry. <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker 400 MHz spectrometer. The spectra were calibrated according to residual solvent peaks (CDCl<sub>3</sub>: δ 7.26 ppm, DMSO-*d*<sub>6</sub>: δ 2.50 ppm for <sup>1</sup>H NMR and CDCl<sub>3</sub>: δ 77.16 ppm, DMSO-*d*<sub>6</sub>: 39.5 for <sup>13</sup>C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, and m = multiplet. IR spectra were obtained on a Thermo Scientific iD5 ATR Nicolet iS5 FT-IR spectrometer. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA. ESI-MS spectra were recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). Melting points (M.p.) were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic (GC) analyses were performed on an Agilent 7890A instrument (FID detector) using a J&W DB-1 column (10m, 0.1 mm I.D.). Thin-layer chromatography (TLC) was performed on 0.25 mm E. Merck silica gel plates (60F-254), and visualized by UV and/or KMnO<sub>4</sub> staining solutions. High-pressure liquid chromatography (HPLC) was performed on Agilent 1200 Series chromatographs using a chiral column (25 cm) as noted for each compound. Optical rotations were measured on a Jasco P-1010 polarimeter with [α]<sub>D</sub> values reported in degrees; concentration (c) is in g/100 mL. The yields reported for the CuH-catalyzed synthesis of 2,3-disubstituted indolines are of isolated compounds on a 1 mmol scale, and represent an average of two experiments.

Large-sized tubes was used for all 1 mmol reactions:

Gray septa: Thermo Scientific SPTA SPTA PTFE/SIL F/18-400 10 (Cat. No. 03394B)

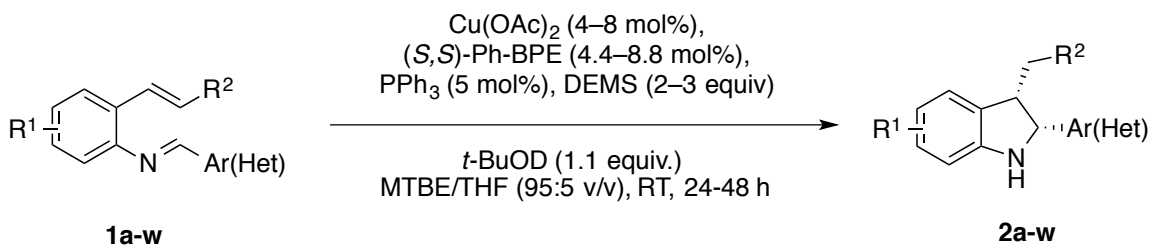


Large tubes (tall): Fisher 20 x 150 mm tubes (Cat. No. 1495937C)



## II. Experimental Procedures and Characterization Data.

### A) CuH-Catalyzed Synthesis of 2,3-Disubstituted Indolines.

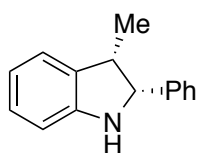


### General Procedure A for the CuH-Catalyzed Synthesis of 2,3-Disubstituted Indolines **2a-w**.

In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube (Fisher 20 x 150 mm, Cat. # 1495937C) equipped with a magnetic stir bar was charged with  $Cu(OAc)_2$  (4–8 mol%), (*S,S*)-Ph-BPE (4.4–8.8 mol%) and triphenylphosphine (5 mol%, when used as an additive). The tube was sealed with a Thermo Scientific PTFE screw cap (Cat # 03394B) equipped with a septum, removed from the glovebox, and purged with argon. Anhydrous THF (0.5 mL) was added *via* syringe and the reaction mixture was stirred for 15 min, until a blue homogeneous solution was obtained. Diethoxymethylsilane (DEMS, 2.0–3.0 equiv) was added *via* syringe and stirring was continued for 10 min at room temperature. The resulting red solution (the solution was yellow in the absence of  $PPh_3$ ) was diluted with anhydrous MTBE (9.5 mL) and stirring was continued for another 10 min. Into a separate flame-dried screw-cap reaction tube (Fisher 20 x 150 mm, Cat. # 1495937C) equipped with a magnetic stir bar was added 2-alkenylimine **1a-w** (1 mmol). This tube was sealed with a Thermo Scientific PTFE screw cap (Cat # 03394B) equipped with a septum, and evacuated and backfilled with argon (this process was repeated a total of three times). The catalyst solution was then transferred *via* syringe to the reaction tube containing the substrates. Anhydrous *t*-BuOD (1.1 equiv) was added *via* syringe and the screw cap was sealed with parafilm. The reaction mixture was stirred at room temperature for 24–48 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with saturated aqueous  $Na_2CO_3$  solution, extracted with EtOAc and the combined organic layers were concentrated *in vacuo*. The resulting crude product was purified by flash column chromatography on silica gel to obtain indolines **2a-w**.

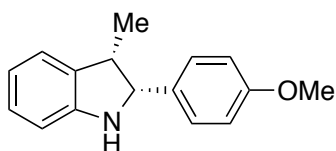


### (2*R*,3*S*)-3-Methyl-2-phenylindoline (Table 2, 2a).



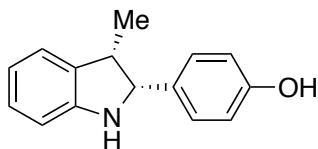
Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-1-phenyl-*N*-(2-vinylphenyl)methanimine **1a** (207 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1 v/v) to obtain the title compound as colorless liquid. 1<sup>st</sup> Run: 188 mg, 90% yield. 2<sup>nd</sup> Run: 192 mg, 92% yield. IR (thin film) 3367, 3027, 2924, 1606, 1482, 1464 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36–7.25 (m, 5H), 7.13–7.06 (m, 2H), 6.78 (td, *J* = 7.4, 1.0 Hz, 1H), 6.72 (d, *J* = 7.2 Hz, 1H), 5.00 (d, *J* = 8.8 Hz, 1H), 4.08 (bs, 1H), 3.63–3.53 (m, 1H), 0.83 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CHCl<sub>3</sub>)  $\delta$  150.6, 140.9, 133.9, 128.3, 127.6, 127.4, 127.3, 124.1, 119.0, 108.8, 67.4, 41.3, 15.9; HRMS (ESI) calculated for C<sub>15</sub>H<sub>16</sub>N [M+H]<sup>+</sup> *m/z* 210.1283, found 210.1264; Anal. Calcd. for C<sub>15</sub>H<sub>15</sub>N: C, 86.08; H 7.22. Found: C, 85.83; H, 7.24; [ $\alpha$ ]<sub>D</sub><sup>24</sup> = +155.3 (c 0.5, CH<sub>2</sub>Cl<sub>2</sub>); HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 90% ee: t<sub>R</sub> (major) = 6.7 min, t<sub>R</sub> (minor) = 6.0 min.

### (2*R*,3*S*)-2-(4-Methoxyphenyl)-3-methylindoline (Table 2, 2b).



Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-1-(4-methoxyphenyl)-*N*-(2-vinylphenyl)methanimine **1b** (237 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (9:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> Run: 196 mg, 82% yield. 2<sup>nd</sup> run: 206 mg, 86% yield. IR (thin film) 3362, 2962, 2927, 2834, 1608, 1510 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27–7.21 (m, 2H), 7.12–7.05 (m, 2H), 6.90–6.84 (m, 2H), 6.77 (td, *J* = 7.4, 1.0 Hz, 1H), 6.73–6.68 (m, 1H), 4.95 (d, *J* = 8.7 Hz, 1H), 4.05 (bs, 1H), 3.81 (s, 3H), 3.58–3.49 (m, 1H), 0.83 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.9, 150.6, 133.9, 133.0, 128.3, 127.5, 124.1, 118.9, 113.7, 108.8, 66.9, 55.3, 41.3, 15.8; HRMS (ESI) calculated for C<sub>16</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> *m/z* 240.1383, found 240.1385; Anal. Calcd. for C<sub>16</sub>H<sub>17</sub>NO: C, 80.30; H 7.16. Found: C, 80.08; H, 7.17; [ $\alpha$ ]<sub>D</sub><sup>24</sup> = +123.5 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 91% ee: t<sub>R</sub> (major) = 9.6 min, t<sub>R</sub> (minor) = 8.3 min.

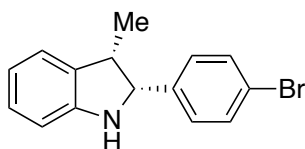
### 4-((2*R*,3*S*)-3-Methylindolin-2-yl)phenol (Table 2, 2c).



Prepared following **general procedure A** (except using a modified work-up), with Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%),

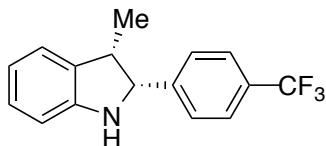
triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (403  $\mu$ L, 3.0 mmol), (*E*)-4-(((2-vinylphenyl)imino)methyl)phenol **1c** (223 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature. The reaction mixture was quenched dropwise with a saturated solution of  $\text{NH}_4\text{F}$  in methanol (15 mL) and then stirred at room temperature for 30 min. The resulting mixture was filtered over celite and washed with  $\text{CH}_2\text{Cl}_2$ . The combined filtrates were concentrated under reduced pressure and the crude product was purified *via* silica gel chromatography, eluting with hexanes/EtOAc (6:1 v/v) to obtain the title compound as yellow solid. 1<sup>st</sup> run: 148 mg, 66% yield. Second run gave 142 mg (64%). IR (thin film) 3365, 3305, 2962, 1609, 1461, 1449  $\text{cm}^{-1}$ ; M.p. 136–137  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  9.23 (s, 1H), 7.08 (d,  $J$  = 8.5 Hz, 2H), 7.01–6.90 (m, 2H), 6.70 (d,  $J$  = 8.5 Hz, 2H), 6.59–6.52 (m, 2H), 5.90 (d,  $J$  = 2.1 Hz, 1H), 4.79 (dd,  $J$  = 8.7, 2.0 Hz, 1H), 3.36 (q,  $J$  = 7.5 Hz, 1H), 0.66 (d,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 151.4, 133.3, 131.1, 128.0, 127.1, 123.5, 117.0, 114.6, 107.8, 65.7, 40.4, 15.8; HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{16}\text{NO}$  [ $\text{M}+\text{H}$ ] $^+$   $m/z$  226.1226, found 226.1218;  $[\alpha]_{\text{D}}^{24}$  = +110.4 ( $c$  = 1.0, MeOH). HPLC analysis (IA, 10% IPA/hexane, 0.8 mL/min, 230 nm) indicated 91% ee:  $t_{\text{R}}$  (major) = 19.5 min,  $t_{\text{R}}$  (minor) = 17.5 min.

**(2*R*,3*S*)-2-(4-Bromophenyl)-3-methylindoline (Table 2, 2d).**



Prepared following **general procedure A**, (*except without*  $\text{PPh}_3$ ) using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-1-(4-bromophenyl)-*N*-(2-vinylphenyl)methanimine **1d** (285 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/ $\text{CH}_2\text{Cl}_2$  (2:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> run: 259 mg, 90% yield. 2<sup>nd</sup> run: 263 mg, 92% yield. IR (thin film) 3365, 2962, 2922, 1607, 1481, 1462, 1448  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J$  = 8.4 Hz, 2H), 7.22 (d,  $J$  = 8.3 Hz, 2H), 7.14–7.05 (m, 2H), 6.78 (td,  $J$  = 7.4, 1.0 Hz, 1H), 6.71 (d,  $J$  = 7.5 Hz, 1H), 4.96 (d,  $J$  = 8.7 Hz, 1H), 4.05 (br s, 1H), 3.55 (p,  $J$  = 7.4 Hz, 1H), 0.80 (d,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2, 139.9, 133.7, 131.4, 129.0, 127.7, 124.2, 121.0, 119.0, 109.0, 66.7, 41.2, 16.1; HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{15}\text{BrN}$  [ $\text{M}+\text{H}$ ] $^+$   $m/z$  288.0382, found 288.0377; Anal. Calcd. for  $\text{C}_{15}\text{H}_{14}\text{BrN}$ : C, 62.52; H 4.90. Found: C, 62.75; H, 4.96.  $[\alpha]_{\text{D}}^{24}$  = +104.3 ( $c$  = 1.0,  $\text{CH}_2\text{Cl}_2$ ). HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 87% ee:  $t_{\text{R}}$  (major) = 7.8 min,  $t_{\text{R}}$  (minor) = 8.6 min.

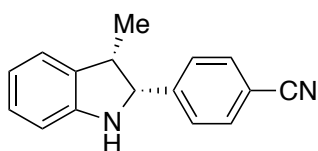
**(2*R*,3*S*)-3-Methyl-2-(4-(trifluoromethyl)phenyl)indoline (Table 2, 2e).**



Prepared following **general procedure A**, (*except without*  $\text{PPh}_3$ ) using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-1-(4-

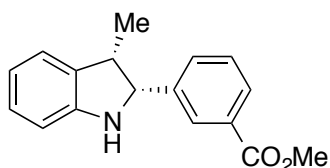
(trifluoromethyl)phenyl)-*N*-(2-vinylphenyl)methanimine **1e** (275 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1 v/v) to obtain the title product as colorless solid. 1<sup>st</sup> run: 260 mg, 94% yield. 2<sup>nd</sup> run: 151 mg, 91% yield. IR (thin film) 3349, 2967, 1606 cm<sup>-1</sup>; M.p. 61–64 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.15–7.07 (m, 2H), 6.80 (td, *J* = 7.4, 1.0 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.06 (d, *J* = 8.7 Hz, 1H), 4.10 (bs, 1H), 3.60 (p, *J* = 7.4 Hz, 1H), 0.8 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.2, 145.1, 133.6, 129.6 (q, *J*<sub>CF</sub> = 32.4 Hz), 127.9, 127.6, 125.3 (q, *J*<sub>CF</sub> = 3.9 Hz), 124.4 (q, *J*<sub>CF</sub> = 272.2 Hz), 124.2, 119.4, 109.1, 66.9, 41.3, 16.2; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.4; HRMS (ESI) calculated for C<sub>16</sub>H<sub>15</sub>F<sub>3</sub>N [M+H]<sup>+</sup> *m/z* 278.1151, found 278.1145; Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>N: C, 69.31; H 5.09. Found: C, 69.20; H, 5.19. [α]<sub>D</sub><sup>24</sup> = +123.1 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 83% ee: t<sub>R</sub> (major) = 6.8 min, t<sub>R</sub> (minor) = 6.2 min.

#### 4-((2*R*,3*S*)-3-Methylindolin-2-yl)benzonitrile (Table 2, 2f).



Prepared following **general procedure A**, (*except without PPh<sub>3</sub>*) using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol), (*E*)-4-(((2-vinylphenyl)imino)methyl)benzonitrile **1f** (285 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (10:1 v/v) to obtain the title product as pink solid. 1<sup>st</sup> run: 210 mg, 89% yield. 2<sup>nd</sup> run: 206 mg, 87% yield. IR (thin film) 3361, 2966, 2227, 1606, 1483, 1465, 1450 cm<sup>-1</sup>; M.p. 82–85 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.14–7.06 (m, 2H), 6.80 (td, *J* = 7.4, 1.0 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.05 (d, *J* = 9.1 Hz, 1H), 4.12 (br s, 1H), 3.60 (p, *J* = 7.4 Hz, 1H), 0.77 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.9, 146.6, 133.3, 132.2, 128.0, 127.9, 124.2, 119.5, 118.9, 111.1, 109.2, 66.8, 41.3, 16.2; HRMS (ESI) calculated for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup> *m/z* 235.1230, found 235.1224; [α]<sub>D</sub><sup>24</sup> = +124.9 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 84% ee: t<sub>R</sub> (major) = 17.6 min, t<sub>R</sub> (minor) = 19.6 min.

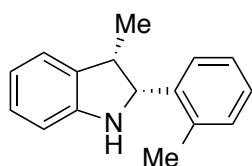
#### Methyl 3-((2*R*,3*S*)-3-methylindolin-2-yl)benzoate (Table 2, 2g).



Prepared following **general procedure A**, (*except without PPh<sub>3</sub>*) using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol), methyl (*E*)-3-(((2-vinylphenyl)imino)methyl)benzoate **1g** (265 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (20:1 to 10:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> run: 249 mg, 93% yield. 2<sup>nd</sup> run: 240 mg, 90% yield. IR

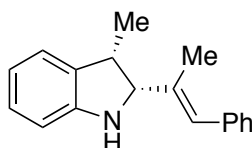
(thin film) 3359, 2962, 1716, 1607, 1482  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05–8.03 (m, 1H), 7.95 (dt,  $J = 7.7, 1.5$  Hz, 1H), 7.57 (d,  $J = 7.7$  Hz, 1H), 7.40 (t,  $J = 7.7$  Hz, 1H), 7.12–7.07 (m, 2H), 6.78 (td,  $J = 7.4, 1.0$  Hz, 1H), 6.73 (d,  $J = 8.1$  Hz, 1H), 5.08 (d,  $J = 8.7$  Hz, 1H), 4.11 (br s, 1H), 3.92 (s, 3H), 3.57 (p,  $J = 7.4$  Hz, 1H), 0.77 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 150.2, 141.3, 133.8, 131.7, 130.2, 128.6, 128.5, 128.4, 127.7, 124.2, 119.2, 109.1, 66.9, 52.2, 41.3, 16.4; HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{18}\text{NO}_2$   $[\text{M}+\text{H}]^+$   $m/z$  268.1332, found 268.1348;  $[\alpha]_{\text{D}}^{24} = +141.3$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ). HPLC analysis (IA, 5 % IPA/hexane, 0.8 mL/min, 230 nm) indicated 74% ee:  $t_{\text{R}}$  (major) = 15.2 min,  $t_{\text{R}}$  (minor) = 20.8 min.

### (2R,3S)-3-Methyl-2-(*o*-tolyl)indoline (Table 2, 2h).



Prepared following **general procedure A**, using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu\text{L}$ , 1.1 mmol), DEMS (320  $\mu\text{L}$ , 2.0 mmol), (*E*)-1-*o*-tolyl-*N*-(2-vinylphenyl)methanimine **1h** (221 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/ $\text{CH}_2\text{Cl}_2$  (2:1 v/v) to obtain the title product as colorless solid. 1<sup>st</sup> run: 204 mg, 92% yield. 2<sup>nd</sup> run: 207 mg, 93% yield. IR (thin film) 3346, 2969, 2923, 1602, 1484, 1462, 1449, 1400  $\text{cm}^{-1}$ ; M.p. 97–100  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75–7.65 (m, 1H), 7.25–7.18 (m, 3H), 7.15–7.07 (m, 2H), 6.85–6.71 (m, 2H), 5.25 (d,  $J = 8.6$  Hz, 1H), 3.97 (br s, 1H), 3.64 (p,  $J = 7.4$  Hz, 1H), 2.37 (s, 3H), 0.75 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2, 138.8, 135.2, 134.0, 130.1, 127.6, 127.0, 127.0, 125.9, 124.4, 118.9, 109.0, 63.9, 39.2, 19.3, 16.8; HRMS (ESI) calculated for  $\text{C}_{16}\text{H}_{18}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  224.1434, found 224.1438; Anal. Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}$ : C, 86.05; H 7.67. Found: C, 85.81; H, 7.59.  $[\alpha]_{\text{D}}^{24} = +248.7$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ). HPLC analysis (IA, 2 % IPA/hexane, 0.8 mL/min, 230 nm) indicated 84% ee:  $t_{\text{R}}$  (major) = 8.4 min,  $t_{\text{R}}$  (minor) = 9.2 min.

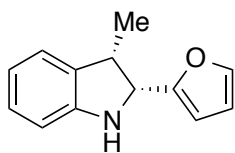
### (2R,3S)-3-Methyl-2-((*E*)-1-phenylprop-1-en-2-yl)indoline (Table 2, 2i).



Prepared following **general procedure A**, using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu\text{L}$ , 1.1 mmol), DEMS (320  $\mu\text{L}$ , 2.0 mmol), (1*E*,2*E*)-2-methyl-3-phenyl-*N*-(2-vinylphenyl)prop-2-en-1-imine **1i** (247 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel, eluting with hexanes/ $\text{EtOAc}$  (40:1 v/v) to obtain the title product (in 11:1 *cis:trans* diastereomeric ratio) as green oil. 1<sup>st</sup> run: in 192 mg, 77% yield. 2<sup>nd</sup> run: 214 mg, 86% yield. IR (thin film) 3370, 3023, 2962, 2921, 1608, 1482, 1464  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.32 (m, 4H), 7.29–7.25 (m, 1H), 7.16–7.07 (2H), 6.84–6.76 (m, 2H), 6.72 (d,  $J = 7.8$  Hz, 1H), 4.51 (d,  $J = 8.3$  Hz, 1H), 3.89 (bs, 1H), 3.52 (p,  $J = 7.2$  Hz, 1H), 1.92 (d,  $J = 1.3$  Hz, 3H), 1.11 (d,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$

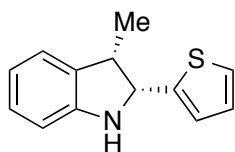
150.1, 138.1, 136.7, 134.4, 129.0, 128.2, 127.6, 126.3, 125.8, 124.0, 118.8, 109.0, 70.1, 39.4, 16.8, 15.6; HRMS (ESI) calculated for C<sub>18</sub>H<sub>20</sub>N [M+H]<sup>+</sup> *m/z* 250.1590, found 250.1608; [α]<sub>D</sub><sup>24</sup> = +117.8 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 1% IPA/hexane, 0.8 mL/min, 230 nm) indicated 89% ee: t<sub>R</sub> (major) = 8.3 min, t<sub>R</sub> (minor) = 7.5 min.

### (2*R*,3*S*)-2-(Furan-2-yl)-3-methylindoline (Table 2, 2j).



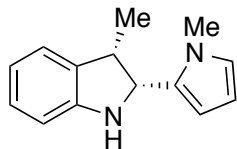
Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol), (*E*)-1-(furan-2-yl)-*N*-(2-vinylphenyl)methanimine **1j** (197 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (40:1 to 10:1 v/v) to obtain the title product as slightly yellow oil. 1<sup>st</sup> run: 167 mg, 84% yield. 2<sup>nd</sup> run: 181 mg, 91% yield. IR (thin film) 3365, 2964, 2926, 2869, 1607, 1503, 1463 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.11–7.05 (m, 2H), 6.79 (td, *J* = 7.4, 1.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.32 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.22 (d, *J* = 3.3 Hz, 1H), 4.98 (d, *J* = 8.7 Hz, 1H), 4.03 (bs, 1H), 3.67–3.57 (m, 1H), 1.00 (d, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CHCl<sub>3</sub>) δ 155.2, 150.0, 141.8, 133.3, 127.6, 123.9, 119.2, 110.1, 109.2, 106.9, 61.5, 41.0, 15.1; HRMS (ESI) calculated for C<sub>13</sub>H<sub>14</sub>NO [M+H]<sup>+</sup> *m/z* 200.1070, found 200.1057; Anal. Calcd. for C<sub>13</sub>H<sub>13</sub>NO: C, 78.36; H 6.58. Found: C, 78.49; H, 6.56. [α]<sub>D</sub><sup>24</sup> = +24.1 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 5 % IPA/hexane, 0.8 mL/min, 230 nm) indicated 92% ee: t<sub>R</sub> (major) = 7.0 min, t<sub>R</sub> (minor) = 6.4 min.

### (2*R*,3*S*)-3-Methyl-2-(thiophen-2-yl)indoline (Table 2, 2k).



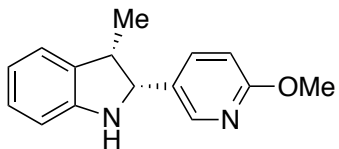
Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol), (*E*)-1-(thiophen-2-yl)-*N*-(2-vinylphenyl)methanimine **1k** (213 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (40:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> run: 196 mg, 91% yield. 2<sup>nd</sup> run: 178 mg, 83% yield. IR (thin film) 3357, 2962, 2922, 2866, 1608, 1481, 1464 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.14–7.07 (m, 2H), 7.01–6.93 (m, 2H), 6.81 (td, *J* = 7.4, 1.0 Hz, 1H), 6.72 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.21 (d, *J* = 8.4 Hz, 1H), 4.20 (bs, 1H), 3.61–3.51 (m, 1H), 1.00 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.7, 144.7, 133.4, 127.6, 126.7, 124.7, 124.1, 123.9, 119.5, 109.4, 63.8, 41.6, 15.1; HRMS (ESI) calculated for C<sub>13</sub>H<sub>14</sub>NS [M+H]<sup>+</sup> *m/z* 216.0841, found 216.0839; Anal. Calcd. for C<sub>13</sub>H<sub>13</sub>NS: C, 72.52; H 6.09. Found: C, 72.55; H, 6.07. [α]<sub>D</sub><sup>24</sup> = +37.3 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 94% ee: t<sub>R</sub> (major) = 7.2 min, t<sub>R</sub> (minor) = 6.4 min.

### (2*R*,3*S*)-3-Methyl-2-(1-methyl-1*H*-pyrrol-2-yl)indoline (Table 2, 2l).



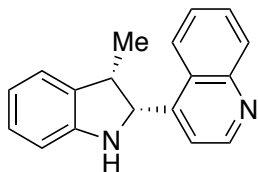
Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol), (*E*)-1-(1-methyl-1*H*-pyrrol-2-yl)-*N*-(2-vinylphenyl)methanimine **1l** (210 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (10:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> run: 155 mg, 73% yield. 2<sup>nd</sup> run: 166 mg, 78% yield. IR (thin film) 3357, 2960, 2920, 1607, 1463, 1447, 1416 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.12–7.06 (m, 2H), 6.78 (td, *J* = 7.4, 1.0 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.61 (t, *J* = 2.3 Hz, 1H), 6.15–6.12 (m, 1H), 6.13–6.07 (m, 1H), 5.06 (d, *J* = 8.4 Hz, 1H), 4.02 (bs, 1H), 3.61 (s, 3H), 3.55 (p, *J* = 7.3 Hz, 1H), 0.91 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.0, 133.6, 132.4, 127.6, 124.2, 122.2, 118.9, 109.0, 107.4, 106.9, 60.5, 40.6, 34.0, 15.8; HRMS (ESI) calculated for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup> *m/z* 213.1386, found 213.1385; [α]<sub>D</sub><sup>24</sup> = +164.3 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 90% ee: t<sub>R</sub> (major) = 10.9 min, t<sub>R</sub> (minor) = 8.5 min.

### (2*R*,3*S*)-2-(6-Methoxypyridin-3-yl)-3-methylindoline (Table 2, 2m).



Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol), (*E*)-1-(6-methoxypyridin-3-yl)-*N*-(2-vinylphenyl)methanimine **1m** (238 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel, eluting with hexanes/EtOAc (8:1 v/v) to obtain the title product as colorless solid. 1<sup>st</sup> run: 199 mg, 83% yield. 2<sup>nd</sup> run: 206 mg, 86% yield. IR (thin film) 3358, 2964, 1605, 1573, 1481, 1450 cm<sup>-1</sup>; M.p. 78–80 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 2.5 Hz, 1H), 7.52 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.11–7.04 (m, 2H), 6.77 (td, *J* = 7.4, 1.0 Hz, 1H), 6.71–6.66 (m, 2H), 4.92 (d, *J* = 8.6 Hz, 1H), 4.04 (br s, 1H), 3.93 (s, 3H), 3.54 (p, *J* = 7.4 Hz, 1H), 0.86 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.9, 150.3, 145.6, 137.9, 133.5, 129.0, 127.7, 124.1, 119.2, 110.5, 109.0, 64.7, 53.5, 41.2, 15.9; HRMS (ESI) calculated for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> *m/z* 241.1335, found 241.1339; [α]<sub>D</sub><sup>24</sup> = +132.4 (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IA, 10% IPA/hexane, 0.8 mL/min, 230 nm) indicated 95% ee: t<sub>R</sub> (major) = 15.6 min, t<sub>R</sub> (minor) = 10.2 min.

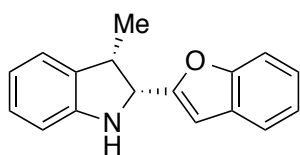
### 4-((2*R*,3*S*)-3-Methylindolin-2-yl)quinoline (Table 2, 2n).



Prepared following **general procedure A**, (*except without PPh<sub>3</sub>*) using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), *t*-BuOD (104 μL, 1.1

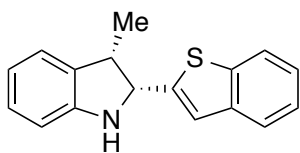
mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-1-(quinolin-4-yl)-*N*-(2-vinylphenyl)methanimine **1n** (258 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel, eluting with hexanes/EtOAc (3:1 to 1:1 v/v) to obtain the title product as pale yellow solid. 1<sup>st</sup> run: 167 mg, 64% yield. 2<sup>nd</sup> run: 188 mg, 72% yield. IR (thin film) 3253, 2969, 1610, 1590, 1506  $\text{cm}^{-1}$ ; M.p 176–180  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (d,  $J$  = 4.5 Hz, 1H), 8.17 (d,  $J$  = 8.4 Hz, 1H), 7.96 (d,  $J$  = 8.36 Hz, 1H), 7.81 (d,  $J$  = 4.5 Hz, 1H), 7.78–7.70 (m, 1H), 7.63–7.55 (m, 1H), 7.18–7.10 (m, 2H), 6.86–6.77 (m, 2H), 5.74 (d,  $J$  = 8.7 Hz, 1H), 4.11 (bs, 1H), 3.86 (p,  $J$  = 7.4 Hz, 1H), 0.62 (d,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 149.5, 148.1, 146.3, 133.7, 130.5, 129.2, 127.9, 126.8, 126.7, 124.4, 122.6, 119.5, 119.4, 109.6, 62.9, 40.7, 16.8; HRMS (ESI) calculated for  $\text{C}_{18}\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$   $m/z$  261.1386, found 261.1375;  $[\alpha]_{\text{D}}^{24} = +387.2$  ( $c$  = 1.0,  $\text{CH}_2\text{Cl}_2$ ). HPLC analysis (IC, 20% IPA/hexane, 0.8 mL/min, 280 nm) indicated 89% ee:  $t_{\text{R}}$  (major) = 9.6 min,  $t_{\text{R}}$  (minor) = 11.6 min.

### (2*R*,3*S*)-2-(Benzofuran-2-yl)-3-methylindoline (Table 2, 2o).



Prepared following **general procedure A**, using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-1-(benzofuran-2-yl)-*N*-(2-vinylphenyl)methanimine **1o** (247 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (40:1 v/v) to obtain the title product as slightly yellow oil that solidified at 4  $^{\circ}\text{C}$ . 1<sup>st</sup> run: 184 mg, 74% yield. 2<sup>nd</sup> run: 184 mg, 74% yield. IR (thin film) 3366, 2964, 2924, 1608  $\text{cm}^{-1}$ ; M.p. 49–55  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57–7.53 (m, 1H), 7.48 (d,  $J$  = 8.2 Hz, 1H), 7.32–7.21 (m, 2H), 7.18–7.11 (m, 2H), 6.84 (td,  $J$  = 7.4, 1.0 Hz, 1H), 6.78 (dd,  $J$  = 8.2, 1.0 Hz, 1H), 6.68 (s, 1H), 5.14 (d,  $J$  = 8.8 Hz, 1H), 4.16 (bs, 1H), 3.76 (p,  $J$  = 7.79 Hz, 1H), 1.07 (d,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 155.0, 149.8, 133.3, 128.3, 127.7, 124.1, 123.8, 122.8, 120.8, 119.5, 111.2, 109.4, 103.8, 61.7, 40.9, 15.6; HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{16}\text{NO}$   $[\text{M}+\text{H}]^+$   $m/z$  250.1226, found 250.1223; Anal. Calcd. for  $\text{C}_{17}\text{H}_{15}\text{NO}$ : C, 81.90; H 6.06. Found: C, 81.67; H, 6.21;  $[\alpha]_{\text{D}}^{24} = +69.0$  ( $c$  = 1.0,  $\text{CH}_2\text{Cl}_2$ ). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 90% ee:  $t_{\text{R}}$  (major) = 8.2 min,  $t_{\text{R}}$  (minor) = 7.1 min.

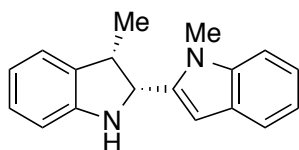
### (2*R*,3*S*)-2-(Benzo[*b*]thiophen-2-yl)-3-methylindoline (Table 2, 2p).



Prepared following **general procedure A**, using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-1-(benzo[*b*]thiophen-2-yl)-*N*-(2-vinylphenyl)methanimine **1p** (263 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then

purified *via* silica gel, eluting with hexanes/EtOAc (40:1 v/v) to obtain the title product as slightly yellow oil. 1<sup>st</sup> run: 200 mg, 76% yield. 2<sup>nd</sup> run: 200 mg, 76% yield. IR (thin film) 3362, 3049, 2962, 2923, 1607, 1480 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79–7.71 (m, 2H), 7.39–7.27 (m, 2H), 7.23 (s, 1H), 7.20–7.12 (m, 2H), 6.87 (td, *J* = 7.4, 1.0 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.27 (dd, *J* = 8.4, 0.8 Hz, 1H), 4.30 (bs, 1H), 3.66 (p, *J* = 7.35 Hz, 1H), 1.10 (d, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.6, 145.6, 139.5, 139.3, 133.2, 127.8, 124.3, 124.2, 124.1, 123.2, 122.4, 121.5, 119.7, 109.5, 64.4, 41.6, 14.9; HRMS (ESI) calculated for C<sub>17</sub>H<sub>16</sub>NS [M+H]<sup>+</sup> *m/z* 266.0998, found 266.0989; Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>NS: C, 76.94; H 5.70. Found: C, 76.34; H, 5.58; [α]<sub>D</sub><sup>24</sup> = -8.65 (*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 92% ee: *t*<sub>R</sub> (major) = 9.0 min, *t*<sub>R</sub> (minor) = 7.9 min.

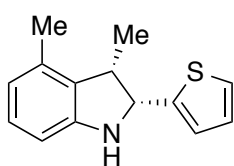
### 1-Methyl-2-((2*R*,3*S*)-3-methylindolin-2-yl)-1*H*-indole (Table 2, 2q).



Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol),

(*E*)-1-(1-methyl-1*H*-indol-2-yl)-*N*-(2-vinylphenyl)methanimine **1q** (260 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (20:1 to 10:1 v/v) to obtain the title product as colorless solid. 1<sup>st</sup> run: 240 mg, 92% yield. 2<sup>nd</sup> run: 241 mg, 92% yield. IR (thin film) 3365, 3049, 2962, 1608 cm<sup>-1</sup>; M.p. 96–100 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.34 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.25–7.20 (m, 1H), 7.16–7.09 (m, 3H), 6.81 (td, *J* = 7.4, 1.0 Hz, 1H), 6.78–6.75 (m, 1H), 6.57 (s, 1H), 5.25 (d, *J* = 8.7 Hz, 1H), 4.14 (bs, 1H), 3.75 (s, 3H), 3.68 (p, *J* = 7.7 Hz, 1H), 0.90 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.8, 140.1, 137.8, 133.5, 127.8, 127.7, 124.3, 121.2, 120.4, 119.6, 119.2, 109.2, 108.9, 100.5, 60.6, 40.6, 30.0, 16.2; HRMS (ESI) calculated for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub> [M+H]<sup>+</sup> *m/z* 263.1543, found 263.1542; Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>: C, 82.41; H 6.92. Found: C, 82.13; H, 7.08. [α]<sub>D</sub><sup>24</sup> = +184.6 (*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 280 nm) indicated 88% ee: *t*<sub>R</sub> (major) = 13.4 min, *t*<sub>R</sub> (minor) = 10.7 min.

### (2*R*,3*S*)-3,4-Dimethyl-2-(thiophen-2-yl)indoline (Table 2, 2r).

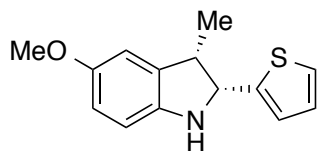


Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104 μL, 1.1 mmol), DEMS (320 μL, 2.0 mmol), (*E*)-*N*-(3-methyl-2-vinylphenyl)-1-(thiophen-2-yl)methanimine **1r** (227 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel, eluting with hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1 v/v) to obtain the title product as colorless solid. 1<sup>st</sup> run: 76 mg, 33% yield. 2<sup>nd</sup> run: 72 mg, 32% yield. IR (thin film) 3337, 3047, 2964, 2925, 1598, 1463, 1450, 1366 cm<sup>-1</sup>; M.p. 110–112 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (dd,



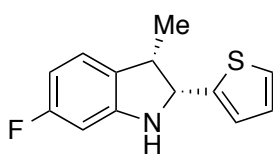
$J = 4.9, 1.3$  Hz, 1H), 7.13–7.07 (m, 2H), 7.04 (t,  $J = 7.7$  Hz, 1H), 6.65 (d,  $J = 7.6$  Hz, 1H), 6.61 (d,  $J = 7.6$  Hz, 1H), 5.31 (d,  $J = 8.0$  Hz, 1H), 4.23 (br s, 1H), 3.45 (p,  $J = 7.3$  Hz, 1H), 2.32 (s, 3H), 0.92 (d,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 144.4, 134.1, 133.1, 127.6, 126.9, 124.4, 123.8, 121.1, 107.2, 63.6, 40.9, 18.1, 14.2; HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{16}\text{NS}$   $[\text{M}+\text{H}]^+$   $m/z$  230.0998, found 230.0979;  $[\alpha]_{\text{D}}^{24} = +205.6$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ). HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 95% ee:  $t_{\text{R}}$  (major) = 8.1 min,  $t_{\text{R}}$  (minor) = 7.6 min.

### (2R,3S)-5-Methoxy-3-methyl-2-(thiophen-2-yl)indoline (Table 2, 2s).



Prepared following **general procedure A**, using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu\text{L}$ , 1.1 mmol), DEMS (320  $\mu\text{L}$ , 2.0 mmol), (*E*)-*N*-(4-methoxy-2-vinylphenyl)-1-(thiophen-2-yl)methanimine **1s** (243 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel by chromatography, eluting with hexanes/EtOAc (20:1 to 10:1 v/v) to obtain the title product as colorless solid. 1<sup>st</sup> run: 200 mg, 82% yield. 2<sup>nd</sup> run: 195 mg, 80% yield. IR (thin film) 3350, 2961, 2925, 2829, 1598, 1486, 1432, 1178, 907  $\text{cm}^{-1}$ ; M.p. 47–52  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (dd,  $J = 4.9, 1.4$  Hz, 1H), 6.98–6.93 (m, 2H), 6.72–6.70 (m, 1H), 6.68–6.62 (m, 2H), 5.18 (d,  $J = 8.2$  Hz, 1H), 4.01 (bs, 1H), 3.77 (s, 3H), 3.52 (p,  $J = 7.7$  Hz, 1H), 0.98 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 144.8, 143.5, 135.1, 126.5, 124.7, 123.9, 112.3, 111.2, 109.9, 64.3, 56.0, 42.1, 14.9; HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{16}\text{NOS}$   $[\text{M}+\text{H}]^+$   $m/z$  246.0947, found 246.0937; Anal. Calcd. for  $\text{C}_{14}\text{H}_{15}\text{NOS}$ : C, 68.54; H, 6.16. Found: C, 68.59; H, 6.25;  $[\alpha]_{\text{D}}^{24} = +7.6$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ). HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_{\text{R}}$  (major) = 12.8 min,  $t_{\text{R}}$  (minor) = 11.8 min.

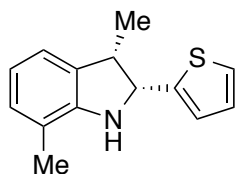
### (2R,3S)-6-Fluoro-3-methyl-2-(thiophen-2-yl)indoline (Table 2, 2t).



Prepared following **general procedure A**, (*except without*  $\text{PPh}_3$ ) using  $\text{Cu}(\text{OAc})_2$  (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), *t*-BuOD (104  $\mu\text{L}$ , 1.1 mmol), DEMS (320  $\mu\text{L}$ , 2.0 mmol), (*E*)-*N*-(5-fluoro-2-vinylphenyl)-1-(thiophen-2-yl)methanimine **1t** (231 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/ $\text{CH}_2\text{Cl}_2$  (2:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> run: 192 mg, 82% yield. 2<sup>nd</sup> run: 198 mg, 85% yield. IR (thin film) 3367, 2965, 2929, 2865, 1615, 1492, 1447, 1367, 1306, 1136  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (dd,  $J = 5.0, 1.2$  Hz, 1H), 7.00–6.93 (m, 3H), 6.46 (ddd,  $J = 9.6, 8.0, 2.3$  Hz, 1H), 6.40 (dd,  $J = 9.7, 2.3$  Hz, 1H), 5.23 (dd,  $J = 8.5, 1.9$  Hz, 1H), 4.25 (br s, 1H), 3.56–3.46 (m, 1H), 0.97 (d,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3 (d,  $J = 242$  Hz), 151.2 (d,  $J = 11.7$  Hz), 144.2, 128.7 (d,  $J = 2.3$  Hz), 126.7, 124.9, 124.6 (d,  $J = 10.4$  Hz), 124.2, 105.3 (d,  $J = 22.7$  Hz), 97.2 (d,  $J = 26.4$  Hz), 64.4, 40.9, 15.1;  $^{19}\text{F}$  NMR (376 MHz,

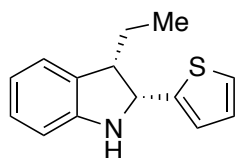
CDCl<sub>3</sub>)  $\delta$  -115.6; HRMS (ESI) calculated for C<sub>13</sub>H<sub>13</sub>FNS [M+H]<sup>+</sup>  $m/z$  234.0747, found 234.0759; Anal. Calcd. for C<sub>13</sub>H<sub>12</sub>FNS : C, 66.93; H 5.18. Found: C, 66.84; H, 5.18;  $[\alpha]_D^{24} = +31.2$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IA, 2% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_R$  (major) = 13.7 min,  $t_R$  (minor) = 26.0 min.

### (2*R*,3*S*)-3,7-Dimethyl-2-(thiophen-2-yl)indoline (Table 2, 2u).



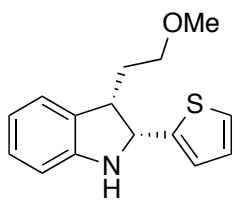
Prepared following **general procedure A**, using Cu(OAc)<sub>2</sub> (7.3 mg, 0.04 mmol, 4 mol%), (*S,S*)-Ph-BPE (22.3 mg, 0.044 mmol, 4.4 mol%), triphenylphosphine (13.1 mg, 0.05 mmol, 5 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-*N*-(2-methyl-6-vinylphenyl)-1-(thiophen-2-yl)methanimine **1u** (227 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (9.5 mL). The reaction mixture was stirred for 24 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1 v/v) to obtain the title product as yellow oil. 1<sup>st</sup> run: 195 mg, 85% yield. 2<sup>nd</sup> run: 200 mg, 87% yield. IR (thin film) 3354, 3048, 2962, 2923, 2853, 1600, 1481, 1464, 1449 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.16 (dd,  $J = 4.5, 1.8$  Hz, 1H), 7.00–6.92 (m, 4H), 6.76 (t,  $J = 7.4$  Hz, 1H), 5.23 (d,  $J = 8.4$  Hz, 1H), 4.08 (bs, 1H), 3.58 (p,  $J = 7.4$  Hz, 1H), 2.20 (s, 3H), 1.00 (d,  $J = 7.2$  Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.3, 144.9, 132.7, 128.6, 126.6, 124.7, 123.9, 121.6, 119.6, 118.7, 63.8, 41.9, 16.8, 15.1; HRMS (ESI) calculated for C<sub>14</sub>H<sub>16</sub>NS [M+H]<sup>+</sup>  $m/z$  230.0998, found 230.0992; Anal. Calcd. for C<sub>14</sub>H<sub>15</sub>NS : C, 73.32; H 6.59. Found: C, 73.39; H, 6.71;  $[\alpha]_D^{24} = +78$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IA, 2% IPA/hexane, 0.8 mL/min, 230 nm) indicated 97% ee:  $t_R$  (major) = 6.9 min,  $t_R$  (minor) = 9.0 min.

### (2*R*,3*S*)-3-ethyl-2-(Thiophen-2-yl)indoline (Table 2, 2v).



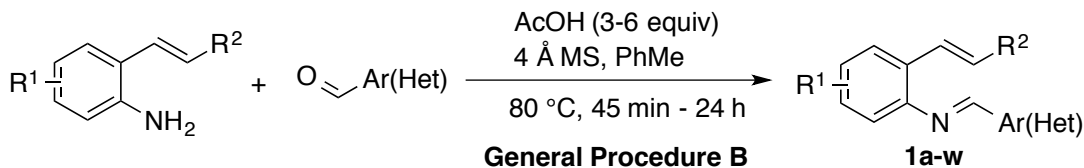
Prepared following **general procedure A**, (*except without PPh<sub>3</sub>*) using Cu(OAc)<sub>2</sub> (14.5 mg, 0.08 mmol, 8 mol%), (*S,S*)-Ph-BPE (44.5 mg, 0.088 mmol, 8.8 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-*N*-(2-((*E*)-prop-1-en-1-yl)phenyl)-1-(thiophen-2-yl)methanimine **1v** (227 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (1.5 mL). The reaction mixture was stirred for 48 h at room temperature and then purified *via* silica gel by eluting with hexanes/EtOAc (40:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> run: 177 mg, 77% yield. 2<sup>nd</sup> run: 159 mg, 69% yield. IR (thin film) 3356, 2959, 2928, 2871, 1606, 1480, 1460, 1369, 1234 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18–7.07 (m, 3H), 7.00–6.95 (m, 2H), 6.81 (td,  $J = 7.4, 1.0$  Hz, 1H), 6.72 (d,  $J = 7.7$  Hz, 1H), 5.25 (d,  $J = 8.0$  Hz, 1H), 4.18 (br s, 1H), 3.28 (q,  $J = 7.7$  Hz, 1H), 1.65–1.51 (m, 1H), 1.35–1.23 (m, 1H), 0.91 (t,  $J = 7.5$  Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.1, 144.2, 132.3, 127.7, 126.4, 125.0, 124.8, 124.0, 119.2, 109.7, 63.9, 48.9, 22.3, 12.3; HRMS (ESI) calculated for C<sub>14</sub>H<sub>16</sub>NS [M+H]<sup>+</sup>  $m/z$  230.0998, found 230.0991; Anal. Calcd. for C<sub>14</sub>H<sub>15</sub>NS : C, 73.32; H 6.59. Found: C, 73.46; H, 6.69;  $[\alpha]_D^{24} = +7.6$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>). HPLC analysis (IC, 2% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_R$  (major) = 8.6 min,  $t_R$  (minor) = 6.7 min.

**(2*R*,3*S*)-3-(2-Methoxyethyl)-2-(thiophen-2-yl)indoline (Table 2, 2w).**



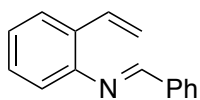
Prepared following **general procedure A**, (*except without*  $PPh_3$ ) using  $Cu(OAc)_2$  (14.5 mg, 0.08 mmol, 8 mol%), (*S,S*)-Ph-BPE (44.5 mg, 0.08 mmol, 8.8 mol%), *t*-BuOD (104  $\mu$ L, 1.1 mmol), DEMS (320  $\mu$ L, 2.0 mmol), (*E*)-*N*-(2-((*E*)-3-methoxyprop-1-en-1-yl)phenyl)-1-(thiophen-2-yl)methanimine **1w** (257 mg, 1.0 mmol), dry THF (0.5 mL) and MTBE (1.5 mL). The reaction mixture was stirred for 48 h at room temperature and then purified *via* silica gel chromatography, eluting with hexanes/EtOAc (20:1 to 10:1 v/v) to obtain the title product as colorless oil. 1<sup>st</sup> run: 220 mg, 85% yield. 2<sup>nd</sup> run: 233 mg, 90% yield. IR (thin film) 3354, 2920, 2869, 1606, 1481, 1462, 1385, 1370  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.16 (dd,  $J = 4.9, 1.3$  Hz, 1H), 7.14–7.08 (m, 2H), 7.01–6.95 (m, 2H), 6.80 (td,  $J = 7.4, 1.0$  Hz, 1H), 6.72 (d,  $J = 7.7$  Hz, 1H), 5.27 (d,  $J = 8.3$  Hz, 1H), 4.20 (br s, 1H), 3.53 (q,  $J = 7.8$  Hz, 1H), 3.43–3.25 (m, 5H), 1.72 (ddt,  $J = 14.2, 8.4, 5.9$  Hz, 1H), 1.64–1.51 (m, 1H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  150.0, 144.0, 131.9, 127.8, 126.7, 125.1, 124.9, 124.1, 119.3, 109.7, 70.4, 63.8, 58.6, 43.5, 29.1; HRMS (ESI) calculated for  $C_{15}H_{18}NOS$  [ $M+H$ ]<sup>+</sup>  $m/z$  260.1104, found 260.1096; Anal. Calcd. for  $C_{15}H_{17}NOS$  : C, 69.46; H 6.61. Found: C, 69.25; H, 6.45;  $[\alpha]_D^{24} = +25.5$  ( $c = 1.0, CH_2Cl_2$ ). HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_R$  (major) = 10.4 min,  $t_R$  (minor) = 12.5 min.

## B) Preparation of 2-Alkenylimine Substrates.



**General Procedure B:** To a solution of 2-alkenylaniline (1 equiv), in toluene (0.2 M) was added an aromatic aldehyde (1 equiv), followed by the addition of glacial acetic acid (3-6 equiv). The reaction mixture was stirred over activated 4 Å molecular sieves (500 mg/mmol of substrate) for 45 min to 24 h at 80 °C and then cooled to room temperature. The reaction mixture was filtered through celite, rinsed with EtOAc (3 x 10 mL) and the filtrate was concentrated *in vacuo*. The imine, **1a-w** was purified *via* flash column chromatography on deactivated silica gel as indicated for each substrate.

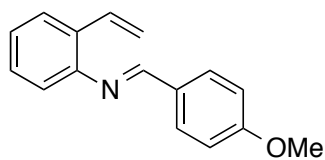
### (*E*)-1-Phenyl-*N*-(2-vinylphenyl)methanimine (**1a**).



Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), benzaldehyde (446 mg, 4.20 mmol), activated molecular sieves 4 Å (2.1 g), glacial acetic acid (721 μL, 12.6 mmol) and toluene (21 mL). The reaction mixture was stirred for 18 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 782 mg (90% yield) as orange oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42 (s, 1H), 8.01–7.94 (m, 2H), 7.64 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.57–7.49 (m, 3H), 7.33 (td, *J* = 7.5, 1.6 Hz, 1H), 7.31–7.21 (m, 2H), 7.00 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.80 (dd, *J* = 17.7, 1.4 Hz, 1H), 5.34 (dd, *J* = 11.1, 1.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.2, 149.9, 136.4, 133.4, 131.5, 131.3, 129.0, 128.9, 128.8, 125.9, 125.8, 118.5, 114.9. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were in accordance with literature data.

1

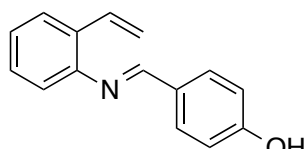
### (*E*)-1-(4-Methoxyphenyl)-*N*-(2-vinylphenyl)methanimine (**1b**).



Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), 4-methoxybenzaldehyde (511 μL, 4.20 mmol), activated molecular sieves 4 Å (2.1 g), glacial acetic acid (721 μL, 12.6 mmol) and toluene (21 mL). The reaction mixture was stirred for 12 h at 80 °C before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 766 mg (77% yield) as yellow oil. IR (thin film) 1621, 1601, 1589, 1574,

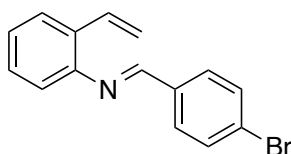
1564  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (s, 1H), 7.91 (d,  $J = 8.4$  Hz, 2H), 7.61 (d,  $J = 7.8$  Hz, 1H), 7.34–7.17 (m, 3H), 7.02 (d,  $J = 8.4$  Hz, 2H), 6.97 (d,  $J = 7.8$  Hz, 1H), 5.78 (d,  $J = 17.7$  Hz, 1H), 5.31 (d,  $J = 11.1$  Hz, 1H), 3.91 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 159.5, 150.3, 133.5, 131.2, 130.6, 129.5, 128.7, 125.7, 125.5, 118.7, 114.7, 114.3, 55.5; Anal. Calcd. for  $\text{C}_{16}\text{H}_{15}\text{NO}$ : C, 80.98; H 6.37. Found: C, 80.75; H, 6.41.

#### (E)-4-(((2-Vinylphenyl)imino)methyl)phenol (1c).



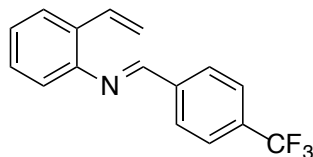
To a solution of 2-vinylaniline (400 mg, 3.36 mmol), in anhydrous THF (7 mL) was added 4-hydroxybenzaldehyde (390 mg, 3.19 mmol), followed by addition of pyrrolidine (276  $\mu\text{L}$ , 3.36 mmol). The reaction mixture was stirred over activated molecular sieves 4 $\text{\AA}$  (3.36 g) for 45 min at 80  $^\circ\text{C}$ , before it was cooled to room temperature, then filtered through celite and washed with EtOAc (3 x 10 mL). The filtrate was concentrated *in vacuo* and the resulting imine was purified by flash column chromatography on deactivated silica gel by eluting with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (20:1 v/v). The title product was dried on high vacuum (70  $^\circ\text{C}$ , 0.1 Torr, 24 h) to obtain a 65% yield (483 mg) as yellow solid. M.p. 154–156  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.15 (br s, 1H), 8.36 (s, 1H), 7.80 (d,  $J = 8.6$  Hz, 2H), 7.61 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.30 (td,  $J = 7.6, 1.5$  Hz, 1H), 7.21–7.12 (m, 2H), 7.03 (dd,  $J = 7.9, 1.3$  Hz, 1H), 6.91 (d,  $J = 8.6$  Hz, 2H), 5.79 (dd,  $J = 17.9, 1.6$  Hz, 1H), 5.26 (dd,  $J = 11.2, 1.5$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  160.7, 159.8, 149.6, 133.0, 130.7, 130.4, 128.8, 127.5, 125.3, 125.3, 118.6, 115.6, 114.7; HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$   $m/z$  224.1070, found 224.1065.

#### (E)-1-(4-Bromophenyl)-N-(2-vinylphenyl)methanimine (1d).



Prepared following **general procedure B**, using 2-vinylaniline (600 mg, 5.00 mmol), 4-bromobenzaldehyde (923 mg, 5.00 mmol), activated molecular sieves 4 $\text{\AA}$  (2.5 g), glacial acetic acid (1.7 mL, 30 mmol) and toluene (25 mL). The reaction mixture was stirred for 20 h at 80  $^\circ\text{C}$ , before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes) to obtain the title product in 1.29 g (91% yield) as orange oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (s, 1H), 7.82 (d,  $J = 8.4$  Hz, 2H), 7.67–7.60 (m, 3H), 7.36–7.16 (m, 3H), 6.98 (dd,  $J = 7.7, 1.4$  Hz, 1H), 5.77 (dd,  $J = 17.7, 1.4$  Hz, 1H), 5.33 (dd,  $J = 11.1, 1.4$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 149.5, 135.3, 133.3, 132.1, 131.5, 130.3, 128.8, 126.2, 126.0, 125.8, 118.3, 115.0; HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{13}\text{BrN}$   $[\text{M}+\text{H}]^+$   $m/z$  286.0226, found 286.0239.

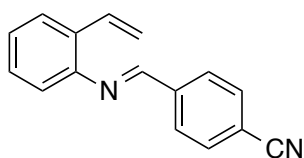
#### (E)-1-(4-(Trifluoromethyl)phenyl)-N-(2-vinylphenyl)methanimine (1e).



Prepared following **general procedure B**, using 2-vinylaniline (400 mg, 3.36 mmol), 4-trifluoromethylbenzaldehyde (459  $\mu\text{L}$ , 3.36 mmol),

activated molecular sieves 4Å (1.68 g), glacial acetic acid (577 µL, 10.1 mmol) and toluene (17 mL). The reaction mixture was stirred for 16 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 927 mg (99% yield) as yellow oil. IR (thin film) 1624, 1580, 1476, 1446, 1413, 1321, 1309 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.52 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.70 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 (td, *J* = 7.5, 1.6 Hz, 1H), 7.37–7.27 (m, 2H), 7.06 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.85 (dd, *J* = 17.7, 1.3 Hz, 1H), 5.40 (dd, *J* = 11.1, 1.3 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.5, 149.2, 139.45, 133.2, 132.9 (q, *J*<sub>CF</sub> = 32.5 Hz), 131.7, 129.1, 128.9, 126.6, 125.9, 125.8 (q, *J*<sub>CF</sub> = 3.8 Hz), 123.9 (q, *J*<sub>CF</sub> = 271.5 Hz), 118.3, 115.3; Anal. Calcd. for C<sub>16</sub>H<sub>12</sub>F<sub>3</sub>N : C, 69.81; H 4.39. Found: C, 69.82; H, 4.54.

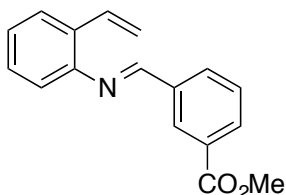
#### (*E*)-4-(((2-Vinylphenyl)imino)methyl)benzonitrile (**1f**).



Prepared following **general procedure B**, using 2-vinylaniline (600 mg, 5.00 mmol), 4-formylbenzonitrile (660 mg, 5.00 mmol), activated molecular sieves 4Å (2.5 g), glacial acetic acid (1.7 mL, 30 mmol) and toluene (25 mL). The reaction mixture was stirred for 16 h at 80 °C, before

allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 1.0 g (86% yield) as yellow solid. IR (thin film) 2227, 1622, 1475, 1409, 1364, 1200, 1169 cm<sup>-1</sup>; M.p. 94–96 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.64 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.36–7.18 (m, 3H), 7.00 (dd, *J* = 7.6, 1.5 Hz, 1H), 5.78 (dd, *J* = 17.7, 1.3 Hz, 1H), 5.34 (dd, *J* = 11.1, 1.3 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.7, 148.8, 140.0, 133.0, 132.6, 131.8, 129.2, 128.8, 126.9, 125.9, 118.5, 118.0, 115.4, 114.5; Anal. Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub> : C, 82.73; H 5.21. Found: C, 82.47; H, 5.40.

#### Methyl (*E*)-3-(((2-vinylphenyl)imino)methyl)benzoate (**1g**).

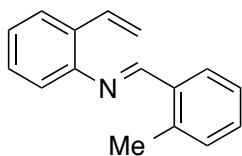


Prepared following **general procedure B**, using 2-vinylaniline (300 mg, 2.52 mmol), methyl 3-formylbenzoate (414 mg, 2.52 mmol), activated molecular sieves 4Å (1.3 g), glacial acetic acid (870 µL, 15.1 mmol) and toluene (13 mL). The reaction mixture was stirred for 17 h at 80 °C, before

allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 617 mg (93% yield) as yellow oil. NMR (400 MHz, CDCl<sub>3</sub>) δ 8.56 (t, *J* = 1.7 Hz, 1H), 8.45 (s, 1H), 8.22–8.16 (m, 2H), 7.66–7.56 (m, 2H), 7.32 (td, *J* = 7.5, 1.6 Hz, 1H), 7.29–7.20 (m, 2H), 6.99 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.78 (dd, *J* = 17.8, 1.4 Hz, 1H), 5.33 (dd, *J* = 11.1, 1.4 Hz, 1H), 3.99 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.6, 159.0, 149.5, 136.7,

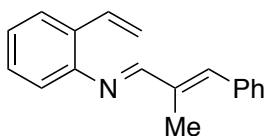
133.3, 132.6, 132.3, 131.5, 130.9, 130.3, 129.0, 128.8, 126.3, 125.8, 118.4, 115.0, 52.4; HRMS (ESI) calculated for C<sub>17</sub>H<sub>16</sub>NO<sub>2</sub> [M+H]<sup>+</sup> *m/z* 266.1176, found 266.1192.

### (*E*)-1-*o*-Tolyl-*N*-(2-vinylphenyl)methanimine (**1h**).



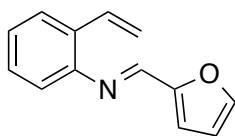
Prepared following **general procedure B**, using 2-vinylaniline (600 mg, 5.00 mmol), 2-methylbenzaldehyde (600 mg, 5.00 mmol), activated molecular sieves 4Å (2.3 g), glacial acetic acid (1.7 mL, 30 mmol) and toluene (25 mL). The reaction mixture was stirred for 23 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes) to obtain the title product in 827 mg (75% yield) as yellow oil. IR (thin film) 3060, 3019, 1619, 1598, 1588 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (s, 1H), 8.19 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.48–7.27 (m, 6H), 7.02 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.84 (dd, *J* = 17.7, 1.4 Hz, 1H), 5.37 (dd, *J* = 11.1, 1.4 Hz, 1H), 2.70 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.1, 150.6, 138.8, 134.2, 133.5, 131.3, 131.2, 131.1, 128.8, 128.4, 126.4, 125.8, 125.7, 118.7, 114.8, 19.7; Anal. Calcd. for C<sub>16</sub>H<sub>15</sub>N : C, 86.84; H 6.83. Found: C, 86.55; H, 6.82.

### (*1E,2E*)-2-Methyl-3-phenyl-*N*-(2-vinylphenyl)prop-2-en-1-imine (**1i**).



Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), (*E*)-2-methyl-3-phenylacrylaldehyde (527 μL, 3.78 mmol), activated molecular sieves 4Å (2.1 g), glacial acetic acid (1.4 mL, 25 mmol) and toluene (21 mL). The reaction mixture was stirred for 23 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes) to obtain the title product (as 8:1 *E:Z* imine) in 630 mg (61% yield) as yellow oil. IR (thin film) 1604, 1585, 1019, 906 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.62 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.54–7.49 (m, 2H), 7.48–7.42 (m, 2H), 7.34–7.17 (m, 4H), 7.02 (s, 1H), 6.94 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.79 (dd, *J* = 17.7, 1.4 Hz, 1H), 5.32 (dd, *J* = 11.1, 1.4 Hz, 1H), 2.36 (d, *J* = 1.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.1, 150.1, 141.6, 137.8, 136.6, 133.4, 131.1, 129.6, 128.7, 128.5, 128.4, 128.2, 125.6, 118.6, 114.5, 13.2; Anal. Calcd. for C<sub>18</sub>H<sub>17</sub>N : C, 87.41; H 6.93. Found: C, 87.57; H, 6.95.

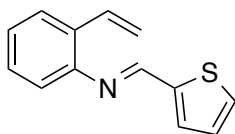
### (*E*)-1-(Furan-2-yl)-*N*-(2-vinylphenyl)methanimine (**1j**).



Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), furan-2-carbaldehyde (347 μL 4.20 mmol), activated molecular sieves 4Å (2.1 g), glacial acetic acid (721 μL, 12.6 mmol) and toluene (21 mL). The reaction mixture was stirred for 23 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column

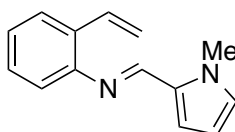
chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 703 mg (85% yield) as dark red oil. IR (thin film) 1620, 1589, 1469, 1445, 1016, 996 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (s, 1H), 7.65 (d, *J* = 1.7 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.35–7.18 (m, 3H), 7.00 (d, *J* = 3.4 Hz, 1H), 6.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.58 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.77 (dd, *J* = 17.7, 1.4 Hz, 1H), 5.32 (dd, *J* = 11.1, 1.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.4, 149.7, 148.2, 145.7, 133.3, 131.4, 128.7, 126.0, 125.7, 118.5, 115.9, 114.9, 112.2; Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>NO : C, 79.17; H 5.62. Found: C, 79.04; H, 5.78.

### (*E*)-1-(Thiophen-2-yl)-*N*-(2-vinylphenyl)methanimine (1k).



Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), thiophene-2-carbaldehyde (393 μL 4.20 mmol), activated molecular sieves 4Å (2.1 g), glacial acetic acid (721 μL, 12.6 mmol) and toluene (21 mL). The reaction mixture was stirred for 21 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/EtOAc/Et<sub>3</sub>N (9:1:0.5 v/v)) to obtain the title product in 757 mg (99% yield) as yellow oil. IR (thin film) 1610, 1586, 1425, 1201 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (s, 1H), 7.63 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.55 (dt, *J* = 5.0, 1.1 Hz, 1H), 7.51 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.38–7.20 (m, 3H), 7.17 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.81 (dd, *J* = 17.7, 1.4 Hz, 1H), 5.35 (dd, *J* = 11.1, 1.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.9, 149.2, 143.2, 133.4, 132.0, 131.5, 130.5, 128.7, 127.8, 126.0, 125.8, 118.5, 115.0; Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>NS : C, 73.20; H 5.20. Found: C, 73.18; H, 5.30.

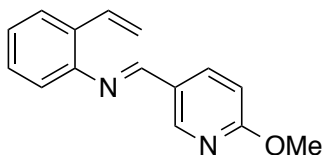
### (*E*)-1-(1-Methyl-1*H*-pyrrol-2-yl)-*N*-(2-vinylphenyl)methanimine (1l).



Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), 1-methyl-1*H*-pyrrole-2-carbaldehyde (451 μL 4.20 mmol), activated molecular sieves 4Å (2.1 g), glacial acetic acid (1.44 mL, 25 mmol) and toluene (21 mL). The reaction mixture was stirred for 24 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 550 mg (63% yield) as orange oil. IR (thin film) 1610, 1587, 1420, 1201, 1052 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (s, 1H), 7.63 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.38–7.18 (m, 3H), 6.98 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.88–6.84 (m, 1H), 6.72 (dd, *J* = 3.9, 1.8 Hz, 1H), 6.26 (dd, *J* = 3.9, 2.5 Hz, 1H), 5.79 (dd, *J* = 17.8, 1.4 Hz, 1H), 5.31 (dd, *J* = 11.1, 1.4 Hz, 1H), 4.14 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.9, 150.7, 133.7, 131.4, 130.6, 129.3, 128.9, 125.5, 125.1, 119.1, 118.3, 114.2, 108.8, 37.2; Anal. Calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub> : C, 79.97; H 6.71. Found: C, 80.11; H, 6.76.

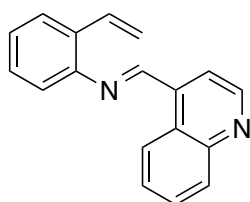


**(E)-1-(6-Methoxypyridin-3-yl)-N-(2-vinylphenyl)methanimine (1m).**



Prepared following **general procedure B**, using 2-vinylaniline (300 mg, 2.52 mmol), 6-methoxynicotinaldehyde (345 mg, 2.52 mmol), activated molecular sieves 4Å (1.3 g), glacial acetic acid (870 µL, 15.1 mmol) and toluene (13 mL). The reaction mixture was stirred for 24 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 511 mg (85% yield) as orange oil. IR (thin film) 3013, 2946, 2849, 1621, 1602, 1563, 1411 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.52 (d, *J* = 1.8 Hz, 1H), 8.36 (s, 1H), 8.31 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.36–7.17 (m, 3H), 6.98 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 5.77 (dd, *J* = 17.7, 1.4 Hz, 1H), 5.31 (dd, *J* = 11.1, 1.4 Hz, 1H), 4.04 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.1, 156.8, 149.9, 149.7, 137.2, 133.3, 131.4, 128.8, 126.3, 126.0, 125.8, 118.4, 114.8, 111.8, 54.0; HRMS (ESI) calculated for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> *m/z* 239.1179, found 239.1167.

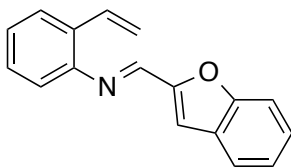
**(E)-1-(Quinolin-4-yl)-N-(2-vinylphenyl)methanimine (1n).**



Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), quinoline-4-carbaldehyde (660 mg, 4.20 mmol), activated molecular sieves 4Å (2.1 g), glacial acetic acid (960 µL, 16.8 mmol) and toluene (21 mL). The reaction mixture was stirred for 19 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/EtOAc/Et<sub>3</sub>N (10:5:1 v/v)) to obtain the title product in 932 mg (86% yield) as yellow solid. IR (thin film) 1620, 1578, 1562, 1606 cm<sup>-1</sup>; M.p. 85-87 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.11 (d, *J* = 4.4 Hz, 1H), 9.06 (s, 1H), 8.95 (dd, *J* = 8.5, 0.7 Hz, 1H), 8.25 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.97 (d, *J* = 4.4 Hz, 1H), 7.86–7.80 (m, 1H), 7.75–7.65 (m, 2H), 7.42–7.27 (m, 3H), 7.09 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.83 (dd, *J* = 17.7, 1.2 Hz, 1H), 5.37 (dd, *J* = 11.1, 1.3 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.7, 150.4, 149.5, 149.2, 138.5, 133.1, 131.8, 130.4, 129.6, 128.9, 127.9, 127.0, 125.9, 125.8, 124.1, 121.6, 118.2, 115.5; Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub> : C, 83.69; H 5.46. Found: C, 83.39; H, 5.66.

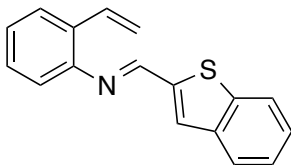
**(E)-1-(Benzofuran-2-yl)-N-(2-vinylphenyl)methanimine (1o).**

Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), benzofuran-2-carbaldehyde (613 mg, 4.20 mmol), activated molecular sieves 4Å (2.1 g), glacial acetic acid (1.44 mL, 25.0 mmol) and toluene (21 mL). The reaction mixture was stirred for 21 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 956 mg (92% yield) as orange oil. IR (thin film) 1619,



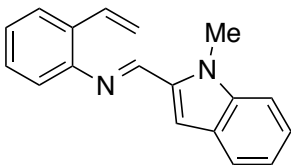
1588, 1559, 1474, 1448  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (s, 1H), 7.72–7.68 (m, 1H), 7.67–7.63 (m, 2H), 7.48–7.42 (m, 1H), 7.37–7.23 (m, 5H), 7.02 (dd,  $J = 7.7, 1.4$  Hz, 1H), 5.81 (dd,  $J = 17.7, 1.3$  Hz, 1H), 5.36 (dd,  $J = 11.1, 1.3$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 153.3, 149.5, 148.9, 133.2, 131.6, 128.7, 127.8, 127.1, 126.5, 125.8, 123.6, 122.3, 118.4, 115.2, 112.7, 112.2; HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$   $m/z$  248.1070, found 248.1056.

### (E)-1-(benzo[b]thiophen-2-yl)-N-(2-vinylphenyl)methanimine (1p).



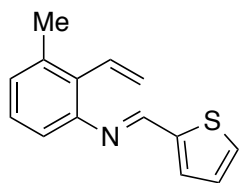
Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), benzo[b]thiophene-2-carbaldehyde (681 mg, 4.20 mmol), activated molecular sieves  $4\text{\AA}$  (2.1 g), glacial acetic acid (1.44 mL, 25 mmol) and toluene (21 mL). The reaction mixture was stirred for 22 h at  $80\text{ }^\circ\text{C}$ , before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/EtOAc/ $\text{Et}_3\text{N}$  (10:1:0.5 v/v)) to obtain the title product in 1.05 g (95% yield) as orange oil. IR (thin film) 3056, 1608, 1585, 1563, 1524, 1475  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (s, 1H), 7.93–7.89 (m, 1H), 7.88–7.84 (m, 1H), 7.71 (s, 1H), 7.64 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.49–7.38 (m, 2H), 7.36–7.23 (m, 3H), 7.05 (dd,  $J = 7.9, 1.4$  Hz, 1H), 5.83 (dd,  $J = 17.7, 1.3$  Hz, 1H), 5.37 (dd,  $J = 11.1, 1.3$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 148.8, 143.4, 141.3, 139.4, 133.3, 131.8, 129.4, 128.7, 126.6, 126.4, 125.9, 124.9, 124.8, 122.9, 118.4, 115.2; HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{14}\text{NS}$   $[\text{M}+\text{H}]^+$   $m/z$  264.0841, found 264.0839.

### (E)-1-(1-Methyl-1H-indol-2-yl)-N-(2-vinylphenyl)methanimine (1q).



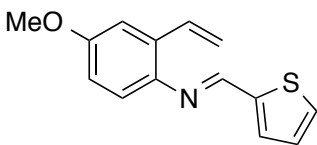
Prepared following **general procedure B**, using 2-vinylaniline (500 mg, 4.20 mmol), 1-methyl-1H-indole-2-carbaldehyde (667 mg, 4.20 mmol), activated molecular sieves  $4\text{\AA}$  (2.1 g), glacial acetic acid (1.44 mL, 25 mmol) and toluene (21 mL). The reaction mixture was stirred for 15 h at  $80\text{ }^\circ\text{C}$ , before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/ $\text{Et}_3\text{N}$  (20:1 v/v)) to obtain the title product in 907 mg (83%) as yellow solid. IR (thin film) 3057, 2941, 2863, 1668, 1618  $\text{cm}^{-1}$ ; M.p.  $91\text{--}96\text{ }^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (s, 1H), 7.72 (dt,  $J = 8.0, 1.0$  Hz, 1H), 7.66 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.48–7.42 (m, 1H), 7.42–7.37 (m, 1H), 7.37–7.33 (m, 1H), 7.32–7.24 (m, 2H), 7.20 (ddd,  $J = 8.0, 6.8, 1.1$  Hz, 1H), 7.07–7.02 (m, 2H), 5.82 (dd,  $J = 17.7, 1.4$  Hz, 1H), 5.35 (dd,  $J = 11.1, 1.3$  Hz, 1H), 4.32 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 150.0, 140.5, 135.6, 133.5, 131.6, 128.9, 127.1, 125.9, 125.6, 124.8, 122.0, 120.3, 118.1, 114.7, 112.2, 109.9, 32.3; HRMS (ESI) calculated for  $\text{C}_{18}\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$   $m/z$  261.1386, found 261.1386.

**(E)-N-(3-Methyl-2-vinylphenyl)-1-(thiophen-2-yl)methanimine (1r).**



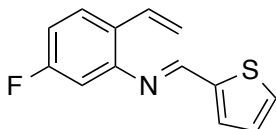
Prepared following **general procedure B**, using 3-methyl-2-vinylaniline (400 mg, 3.00 mmol), thiophene-2-carbaldehyde (337 mg, 3.00 mmol), activated molecular sieves 4Å (1.5 g), glacial acetic acid (1.0 mL, 18 mmol) and toluene (15 mL). The reaction mixture was stirred for 19 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes) to obtain the title product in 550 mg (81% yield) as orange oil. IR (thin film) 3055, 2946, 1609, 1564, 1456, 1425 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.49 (s, 1H), 7.51 (dt, *J* = 5.0, 1.1 Hz, 1H), 7.47 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.20–7.12 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 17.8, 11.8 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.58 (dd, *J* = 11.8, 1.9 Hz, 1H), 5.47 (dd, *J* = 17.8, 1.9 Hz, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.6, 150.3, 143.3, 137.0, 132.3, 131.6, 130.6, 130.4, 128.0, 127.8, 127.6, 121.1, 116.6, 21.0; HRMS (ESI) calculated for C<sub>14</sub>H<sub>14</sub>NS [M+H]<sup>+</sup> *m/z* 228.0841, found 228.0818.

**(E)-N-(4-Methoxy-2-vinylphenyl)-1-(thiophen-2-yl)methanimine (1s).**



Prepared following **general procedure B**, using 4-methoxy-2-vinylaniline (300 mg, 2.00 mmol), thiophene-2-carbaldehyde (225 mg, 2.00 mmol), activated molecular sieves 4Å (1.0 g), glacial acetic acid (690 μL, 12.0 mmol) and toluene (10 mL). The reaction mixture was stirred for 19 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 456 mg (94% yield) as red oil. IR (thin film) 3082, 2936, 2831, 1606, 1564, 1463 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.49 (d, *J* = 0.9 Hz, 1H), 7.48 (dt, *J* = 5.0, 1.1 Hz, 1H), 7.45 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.29 (dd, *J* = 17.8, 11.1 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.5 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.8 Hz, 1H), 5.75 (dd, *J* = 17.7, 1.3 Hz, 1H), 5.32 (dd, *J* = 11.1, 1.3 Hz, 1H), 3.85 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.2, 151.3, 143.6, 142.6, 133.4, 133.1, 131.5, 130.0, 127.7, 119.1, 115.0, 114.6, 110.4, 55.6; Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>NOS : C, 69.11; H 5.39. Found: C, 69.21; H, 5.33.

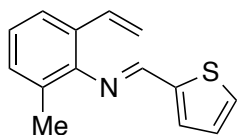
**(E)-N-(5-Fluoro-2-vinylphenyl)-1-(thiophen-2-yl)methanimine (1t).**



Prepared following **general procedure B**, using 5-fluoro-2-vinylaniline (500 mg, 3.65 mmol), thiophene-2-carbaldehyde (408 mg, 3.65 mmol), activated molecular sieves 4Å (1.8 g), glacial acetic acid (1.25 mL, 21.9 mmol) and toluene (18 mL). The reaction mixture was stirred for 21 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes) to obtain the title product in 682 mg (81% yield) as orange oil. IR (thin film) 1613, 1591, 1575, 1488, 1406, 1250, 1215, 1147 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz,

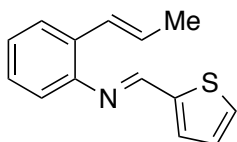
CDCl<sub>3</sub>)  $\delta$  8.46 (s, 1H), 7.56–7.49 (m, 3H), 7.17–7.07 (m, 2H), 6.90 (td,  $J$  = 8.3, 2.5 Hz, 1H), 6.71 (dd,  $J$  = 9.7, 2.6 Hz, 1H), 5.68 (dd,  $J$  = 17.9, 1.1 Hz, 1H), 5.27 (d,  $J$  = 11.3 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.9 (d,  $J$  = 247 Hz), 153.7, 150.5 (d,  $J$  = 7.64 Hz), 142.7, 132.7, 132.4, 131.2, 128.0, 127.9 (d,  $J$  = 3.4 Hz), 127.3 (d,  $J$  = 9.2 Hz), 114.6 (d,  $J$  = 2.0 Hz), 112.8 (d,  $J$  = 21.7 Hz), 105.5 (d,  $J$  = 22.4 Hz); HRMS (ESI) calculated for C<sub>13</sub>H<sub>11</sub>FNS [M+H]<sup>+</sup>  $m/z$  232.0591, found 232.0579.

**(E)-N-(2-Methyl-6-vinylphenyl)-1-(thiophen-2-yl)methanimine (1u).**



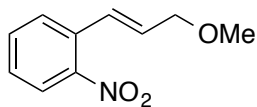
Prepared following **general procedure B**, using 2-methyl-6-vinylaniline (600 mg, 4.50 mmol), thiophene-2-carbaldehyde (505 mg, 4.50 mmol), activated molecular sieves 4Å (2.3 g), glacial acetic acid (1.55 mL, 27.0 mmol) and toluene (23 mL). The reaction mixture was stirred for 20 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product in 761 mg (80% yield) as orange oil. IR (thin film) 1620, 1586, 1457, 1424, 1404, 1181, 1092, 1043, 992, 907, 839 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 (d,  $J$  = 1.0 Hz, 1H), 7.55 (dt,  $J$  = 5.0, 1.1 Hz, 1H), 7.46 (dd,  $J$  = 3.7, 1.2 Hz, 1H), 7.42 (d,  $J$  = 7.9 Hz, 1H), 7.18–7.12 (m, 2H), 7.04 (t,  $J$  = 7.6 Hz, 1H), 6.75 (dd,  $J$  = 17.5, 11.1 Hz, 1H), 5.67 (dd,  $J$  = 17.5, 1.4 Hz, 1H), 5.19 (dd,  $J$  = 11.0, 1.4 Hz, 1H), 2.20 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.6, 149.3, 142.6, 133.9, 132.2, 130.5, 129.9, 128.8, 128.2, 127.8, 124.2, 123.8, 114.6, 18.4; HRMS (ESI) calculated for C<sub>14</sub>H<sub>14</sub>NS [M+H]<sup>+</sup>  $m/z$  228.0841, found 228.0833.

**(E)-N-(2-((E)-Prop-1-en-1-yl)phenyl)-1-(thiophen-2-yl)methanimine (1v).**



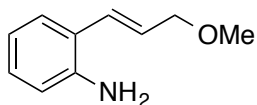
Prepared following **general procedure B**, using (*E*)-2-(prop-1-en-1-yl)aniline (900 mg, 6.77 mmol), thiophene-2-carbaldehyde (758 mg, 6.77 mmol), activated molecular sieves 4Å (3.3 g), glacial acetic acid (2.33 mL, 41.0 mmol) and toluene (34 mL). The reaction mixture was stirred for 23 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/Et<sub>3</sub>N (20:1 v/v)) to obtain the title product (as 17:1 *trans:cis* imine) in 1.39 g (91% yield) as red oil. IR (thin film) 3031, 2908, 2871, 1610, 1587, 1564, 1424, 1203, 963 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.48 (s, 1H), 7.54–7.47 (m, 3H), 7.25–7.12 (m, 3H), 6.94 (dd,  $J$  = 7.7, 1.5 Hz, 1H), 6.85 (dd,  $J$  = 15.9, 1.8 Hz, 1H), 6.26 (dq,  $J$  = 15.9, 6.6 Hz, 1H), 1.91 (dd,  $J$  = 6.6, 1.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.6, 148.7, 143.3, 131.9, 131.8, 130.4, 127.8, 127.6, 127.4, 127.2, 126.0, 125.8, 118.5, 19.1; Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>NS : C, 73.97; H 5.76. Found: C, 73.68; H, 5.71.

### **(E)-1-(3-Methoxyprop-1-en-1-yl)-2-nitrobenzene.**



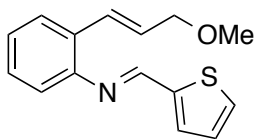
To a solution of (*E*)-3-(2-nitrophenyl)prop-2-en-1-ol<sup>2</sup> (2.0 g, 11 mmol) in anhydrous THF (40 mL) was added NaH (804 mg, 33.5 mmol). The reaction mixture was stirred at room temperature for 1 h, before addition of iodomethane (2.43 mL, 39.1 mmol). The mixture was stirred at room temperature for 21 h, then quenched with water (50 mL) and filtered over celite. The filtrate was washed with CH<sub>2</sub>Cl<sub>2</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40 mL). The combined organic layers were concentrated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (eluting with hexanes/EtOAc (8:1 v/v)) to obtain the title compound as a red oil (763 mg, 35% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.60 (d, *J* = 7.8, 1.7 Hz, 1H), 7.55 (td, *J* = 7.2, 1.2 Hz, 1H), 7.39 (ddd, *J* = 8.5, 7.2, 1.7 Hz, 1H), 7.08 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.8, 5.7 Hz, 1H), 4.13 (dd, *J* = 5.7, 1.6 Hz, 2H), 3.41 (s, 3H); <sup>13</sup>C NMR (101 MHz, CHCl<sub>3</sub>) δ <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.9, 133.1, 132.6, 131.6, 128.8, 128.2, 127.4, 124.6, 72.7, 58.3; HRMS (ESI) calculated for C<sub>10</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> [M+NH<sub>4</sub>]<sup>+</sup> *m/z* 211.1077, found 211.1083.

### **(E)-2-(3-Methoxyprop-1-en-1-yl)aniline.**



A mixture of (*E*)-1-(3-methoxyprop-1-en-1-yl)-2-nitrobenzene (600 mg, 3.10 mmol), and FeSO<sub>4</sub>·7H<sub>2</sub>O (6.90 g, 24.9 mmol), methanol (31 mL), conc. aqueous ammonium hydroxide (28 mL), and water (9.0 mL) was stirred at 80 °C for 4 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (60 mL) and water (60 mL), followed by extraction with EtOAc (3 x 30 mL). The combined EtOAc solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluting with hexanes/EtOAc (4:1 v/v)) to obtain the title compound as red oil in 370 mg (74% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.11 (td, *J* = 7.6, 1.5 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 6.73 – 6.67 (m, 2H), 6.20 (dt, *J* = 15.7, 5.9 Hz, 1H), 4.13 (dd, *J* = 5.9, 1.5 Hz, 2H), 3.77 (br s, 2H), 3.43 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.8, 128.7, 128.1, 127.7, 127.6, 123.1, 119.0, 116.1, 73.4, 58.1; HRMS (ESI) calculated for C<sub>10</sub>H<sub>14</sub>NO [M+H]<sup>+</sup> *m/z* 164.1070, found 164.1076.

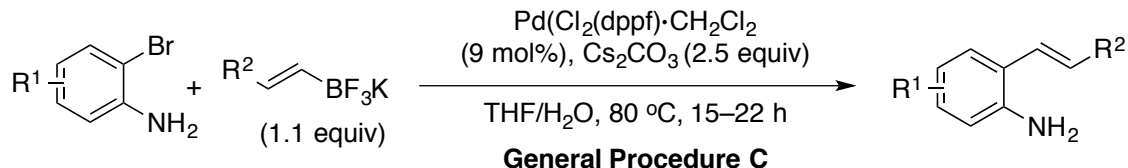
### **(E)-N-(2-((E)-3-Methoxyprop-1-en-1-yl)phenyl)-1-(thiophen-2-yl)methanimine (1w).**



Prepared following **general procedure B**, using (*E*)-2-(3-methoxyprop-1-en-1-yl)aniline (210 mg, 1.29 mmol), thiophene-2-carbaldehyde (144 mg, 1.29 mmol), activated molecular sieves 4 Å (650 mg), glacial acetic acid (440 μL, 7.74 mmol) and toluene (7.0 mL). The reaction mixture was stirred for 18 h at 80 °C, before allowing to cool to room temperature. After workup, the reaction mixture was purified *via* flash column chromatography with deactivated silica gel (eluting with hexanes/EtOAc/Et<sub>3</sub>N (10:1:0.5 v/v)) to obtain the title

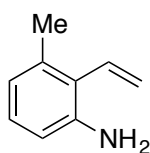
product in 301 mg (91% yield) as orange oil. IR (thin film) 2879, 2921, 2871, 2817, 1611, 1588, 1447, 1425, 1185  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 0.9$  Hz, 1H), 7.55 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.52 (dt,  $J = 5.0, 1.1$  Hz, 1H), 7.48 (dd,  $J = 3.7, 1.2$  Hz, 1H), 7.26 (td,  $J = 7.4, 1.6$  Hz, 1H), 7.19 (td,  $J = 7.6, 1.4$  Hz, 1H), 7.14 (dd,  $J = 5.0, 3.6$  Hz, 1H), 7.07 (d,  $J = 16.0$  Hz, 1H), 6.96 (dd,  $J = 7.8, 1.4$  Hz, 1H), 6.30 (dt,  $J = 16.1, 6.3$  Hz, 1H), 4.11 (dd,  $J = 6.3, 1.4$  Hz, 2H), 3.38 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9, 149.3, 143.2, 132.1, 130.7, 130.5, 129.3, 128.6, 127.8, 127.3, 126.4, 126.1, 118.6, 73.7, 57.9; HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{16}\text{NOS}$   $[\text{M}+\text{H}]^+$   $m/z$  258.0947, found 258.0947.

### C) Preparation of 2-Alkenylaniline Substrates.<sup>3</sup>



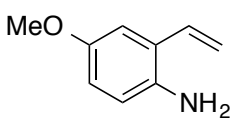
**General Procedure C:** To a suspension of potassium vinyltrifluoroborate (1.1 equiv), Cs<sub>2</sub>CO<sub>3</sub> (2.5 equiv), PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (9 mol%), and 2-bromoaniline (1.0 equiv) in THF, was added water (10:1 v/v). The reaction mixture was stirred at reflux (80 °C) for 15-22 h. After allowing the reaction mixture to cool to room temperature, water (60 mL) was added, followed by extraction with ether (3 x 60 mL). The combined ethereal solutions were concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel.

#### 3-Methyl-2-vinylaniline.



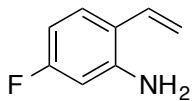
Prepared following **general procedure C**, using potassium vinyltrifluoroborate (1.58 g, 11.8 mmol), Cs<sub>2</sub>CO<sub>3</sub> (8.80 g, 26.9 mmol), PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (790 mg, 0.97 mmol), 2-bromo-3-methylaniline (2.0 g, 10.8 mmol), THF (150 mL) and water (15 mL). The reaction mixture was stirred for 20 h at 80 °C, before allowing to cool to room temperature. After workup, the crude reaction mixture was purified *via* flash column chromatography with silica gel (eluting with hexanes/EtOAc (40:1 to 20:1 v/v)) to obtain the title product in 470 mg (33% yield) as red oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.98 (t, *J* = 7.7 Hz, 1H), 6.70–6.57 (m, 3H), 5.62 (dd, *J* = 11.5, 2.1 Hz, 1H), 5.50 (dd, *J* = 18.1, 2.1 Hz, 1H), 3.86 (br s, 2H), 2.26 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.9, 136.9, 133.4, 127.7, 123.8, 120.2, 119.8, 113.3, 20.6; HRMS (ESI) calculated for C<sub>9</sub>H<sub>12</sub>N [M+H]<sup>+</sup> *m/z* 134.0964, found 134.0961.

#### 4-Methoxy-2-vinylaniline.



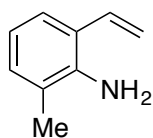
Prepared following **general procedure C**, using 2-bromo-4-methoxyaniline (1.0 g, 4.9 mmol), potassium vinyltrifluoroborate (729 mg, 5.44 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.49 g, 12.4 mmol), PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (364 mg, 0.45 mmol), THF (70 mL) and water (7.5 mL). The reaction mixture was stirred for 18 h at 80 °C, before allowing to cool to room temperature. After workup, the crude reaction mixture was purified *via* flash column chromatography with silica gel (eluting with hexanes/EtOAc (9:1 v/v)) to obtain the title product in 408 mg (55% yield) as orange oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.88 (d, *J* = 2.9 Hz, 1H), 6.78 (dd, *J* = 17.4, 11.1 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 5.64 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.33 (dd, *J* = 11.0, 1.4 Hz, 1H), 3.77 (s, 3H), 3.50 (bs, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.1, 137.5, 132.7, 125.3, 117.6, 115.8, 115.0, 112.1, 55.8. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were in accordance with literature data.<sup>4</sup>

### 5-Fluoro-2-vinylaniline.



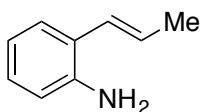
Prepared following **general procedure C**, using 2-bromo-5-fluoroaniline (2.0 g, 9.9 mmol), potassium vinyltrifluoroborate (1.46 g, 10.9 mmol), Cs<sub>2</sub>CO<sub>3</sub> (8.1 g, 25 mmol), PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (727 mg, 0.89 mmol), THF (150 mL) and water (15 mL). The reaction mixture was stirred for 22 h at 80 °C, before allowing to cool to room temperature. After workup, the crude reaction mixture was purified *via* flash column chromatography with silica gel (eluting with hexanes/EtOAc (10:1 v/v)) to obtain the title product in 579 mg (39% yield) as brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (dd, *J* = 8.5, 6.5 Hz, 1H), 6.68 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.46 (td, *J* = 8.5, 2.5 Hz, 1H), 6.38 (dd, *J* = 10.5, 2.5 Hz, 1H), 5.57 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.30 (dd, *J* = 11.1, 1.4 Hz, 1H), 3.85 (br s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.4 (d, *J* = 244 Hz), 145.3 (d, *J* = 10.6 Hz), 131.9, 128.9 (d, *J* = 9.9 Hz), 120.2 (d, *J* = 2.67 Hz), 115.6 (d, *J* = 1.39 Hz), 105.7 (d, *J* = 21.7 Hz), 102.5 (d, *J* = 24.8 Hz); HRMS (ESI) calculated for C<sub>8</sub>H<sub>9</sub>FN [M+H]<sup>+</sup> *m/z* 138.0714, found 138.0711.

### 6-Methyl-2-vinylaniline.



Prepared following **general procedure C**, using 2-bromo-6-methylaniline (1.9 g, 10 mmol), potassium vinyltrifluoroborate (1.5 g, 11 mmol), Cs<sub>2</sub>CO<sub>3</sub> (8.3 g, 25 mmol), PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (750 mg, 0.92 mmol), THF (150 mL) and water (15 mL). The reaction mixture was stirred for 22 h at 80 °C, before allowing to cool to room temperature. After workup, the crude reaction mixture was purified *via* flash column chromatography with silica gel (eluting with hexanes/EtOAc (9:1 v/v)) to obtain the title product in 722 mg (53% yield) as red oil. IR (thin film) 3471, 3392, 3081, 30034, 3005, 2974, 2915, 2854, 1627, 1615, 1477 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.82 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 5.64 (dd, *J* = 17.4, 1.6 Hz, 1H), 5.34 (dd, *J* = 11.0, 1.6 Hz, 1H), 3.75 (bs, 2H), 2.20 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.9, 133.2, 130.0, 125.4, 123.9, 122.6, 118.3, 116.1, 17.7; HRMS (ESI) calculated for C<sub>9</sub>H<sub>12</sub>N [M+H]<sup>+</sup> *m/z* 134.0964, found 134.0961.

### (*E*)-2-(Prop-1-en-1-yl)aniline.



Prepared following **general procedure C**, using 2-bromoaniline (2.0 g, 12 mmol), potassium *trans*-1-propenyltrifluoroborate (1.5 mg, 13 mmol), Cs<sub>2</sub>CO<sub>3</sub> (9.5 g, 29 mmol), PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (853 mg, 1.00 mmol), THF (168 mL) and water (18 mL). The reaction mixture was stirred for 15 h at 80 °C, before allowing to cool to room temperature. After workup, the crude reaction mixture was purified *via* flash column chromatography with silica gel (eluting with hexanes/EtOAc (4:1 v/v)) to obtain the title product in 1.24 g (80%) as dark red oil. Traces amounts of (*Z*)-2-(prop-1-en-1-yl)aniline could be detected by <sup>1</sup>H NMR. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.06 (td, *J* = 7.6, 1.6 Hz, 1H), 6.76 (td, *J* = 7.2, 0.7 Hz, 1H), 6.68 (dd, *J* =



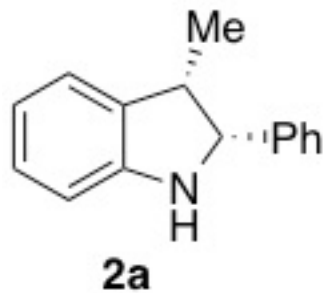
7.9, 1.2 Hz, 1H), 6.44 (dd,  $J = 15.6, 1.8$  Hz, 1H), 6.11 (dq,  $J = 15.6, 6.6$  Hz, 1H), 3.71 (br s, 2H), 1.92 (dd,  $J = 6.6, 1.7$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 127.9, 127.8, 127.4, 126.7, 124.5, 119.0, 115.9, 19.0. The  $^1\text{H}$  NMR spectra were in accordance with literature data.<sup>5</sup>

## References

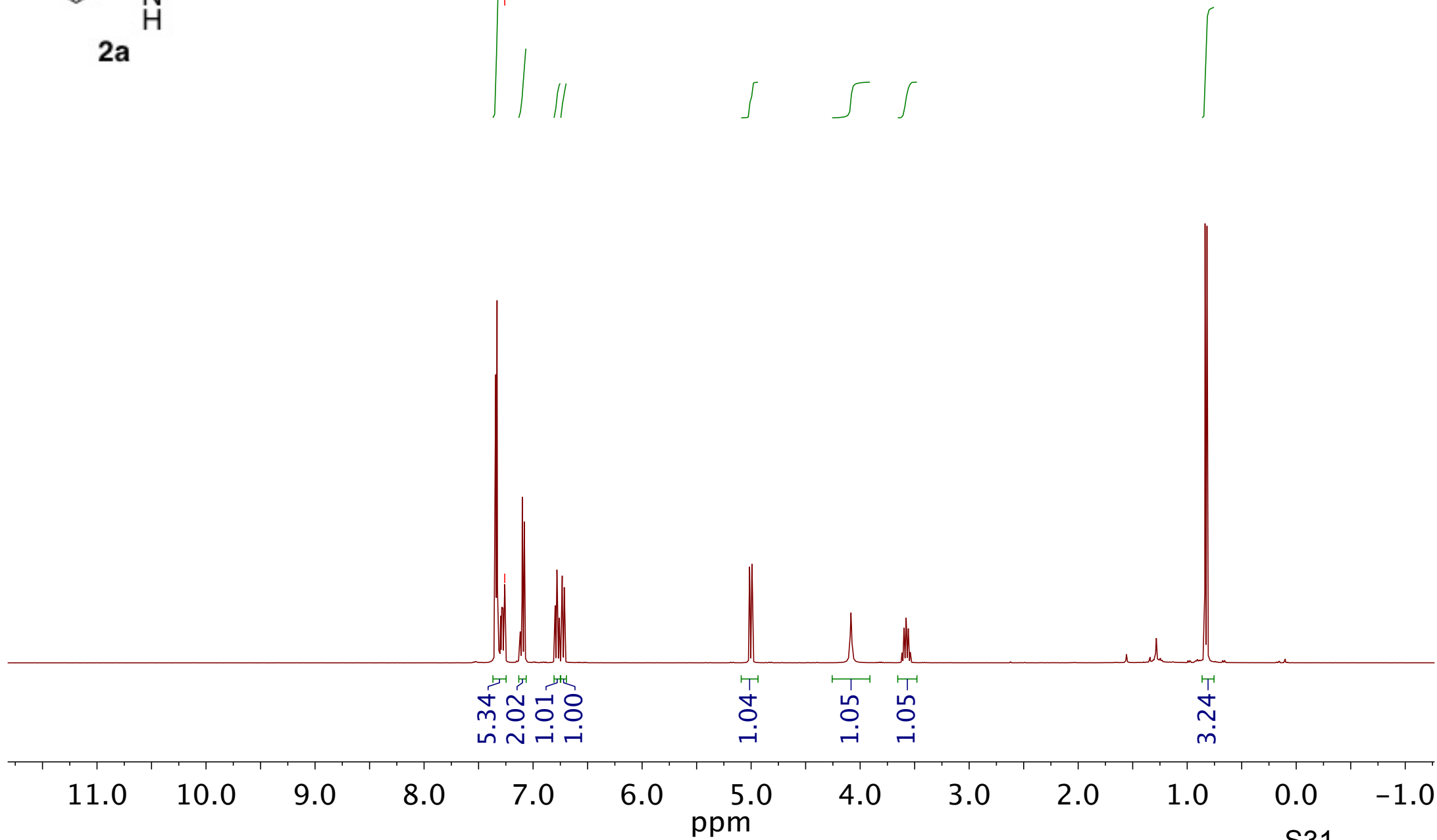
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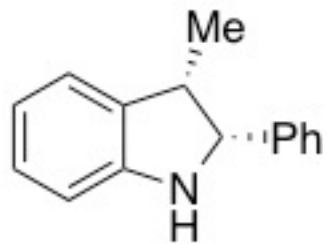
- (1) Slugovc, C.; Burtscher, D.; Stelzer, F.; Mereiter, K. *Organometallics*, **2005**, *24*, 2255.
- (2) Prepared following a known procedure, see: Chiou, W.-H.; Kao, C.-L.; Tsai, J.-C.; Chang, Y.-M. *Chem. Commun.* **2013**, *49*, 8232.
- (3) 2-Vinylaniline derivatives were synthesized following a modified procedure, see: Li, B.; Park, Y.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 1125.
- (4) Soderberg, B. C. G.; Shriver, J. A.; Cooper, S. H.; Shrout, T. L.; Helton, S. E.; Austin, L. R.; Odens, H. H.; Hearn, B. R.; Jones, P. C.; Kouadio, T. N.; Ngi, T. H.; Baswell, R.; Caprara, J. H.; Meritt, M. D.; Mai, T. T. *Tetrahedron*, **2003**, *59*, 8775.
- (5) Padwa, A.; Nahm, S. *J. Org. Chem.* **1981**, *7*, 1402.

### III. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

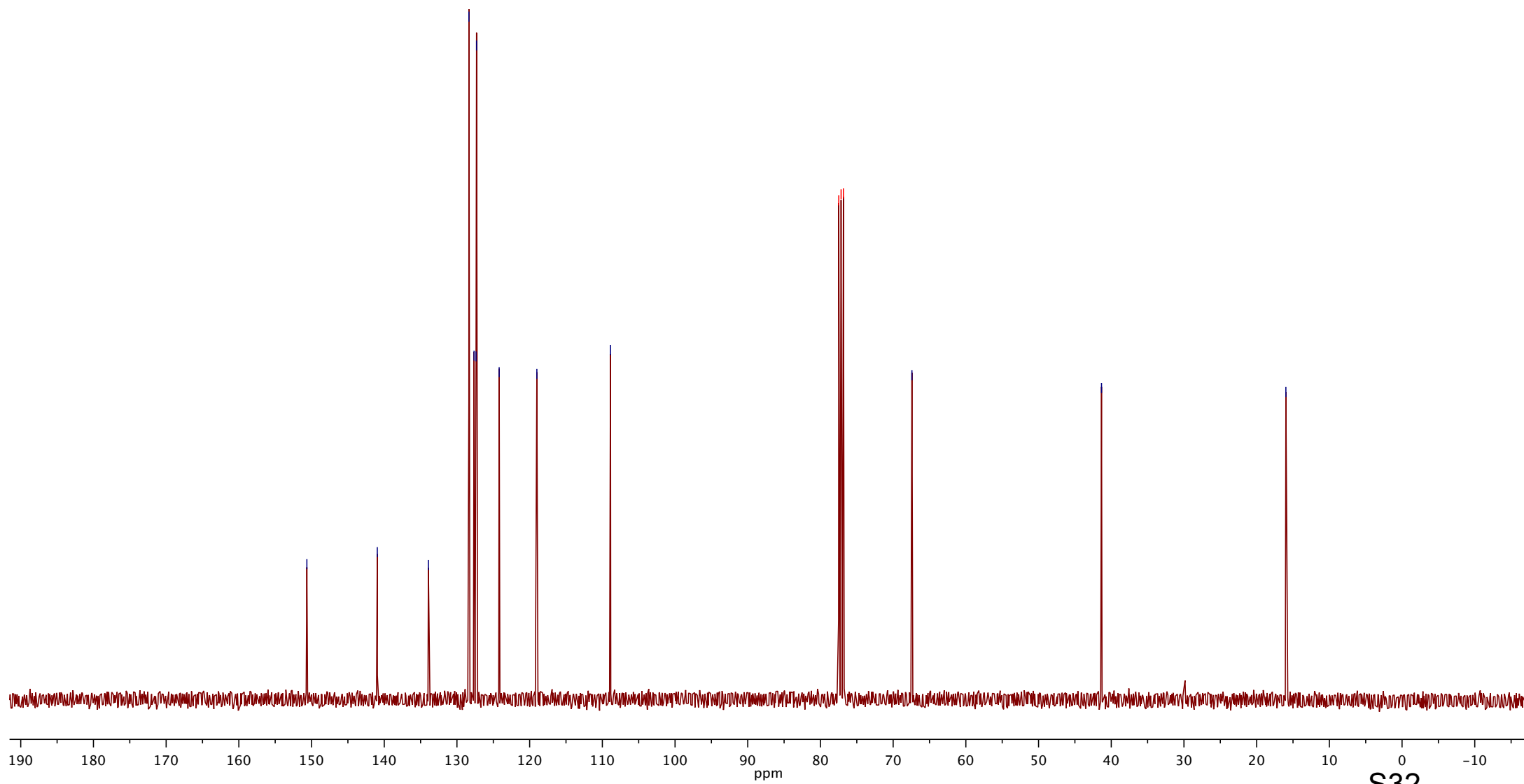
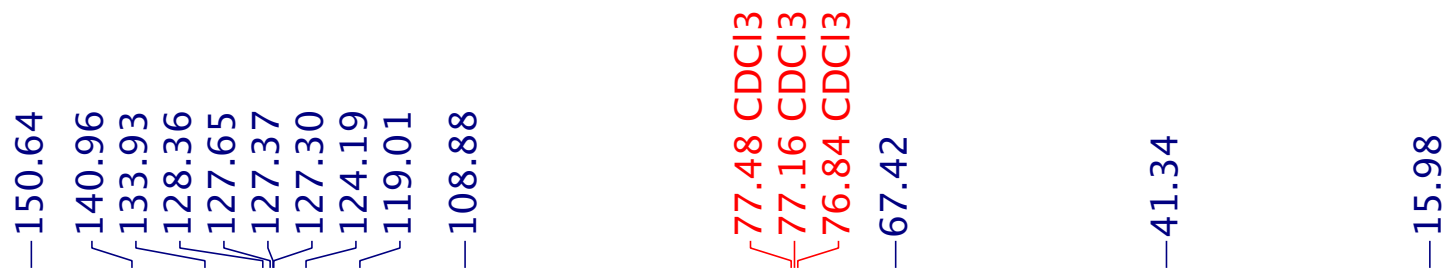


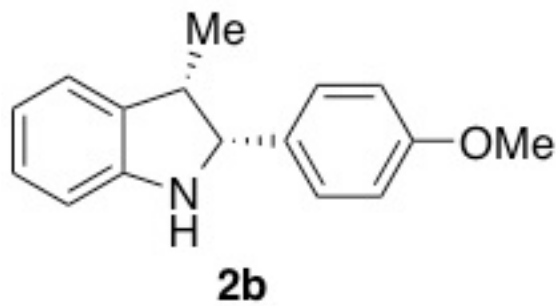
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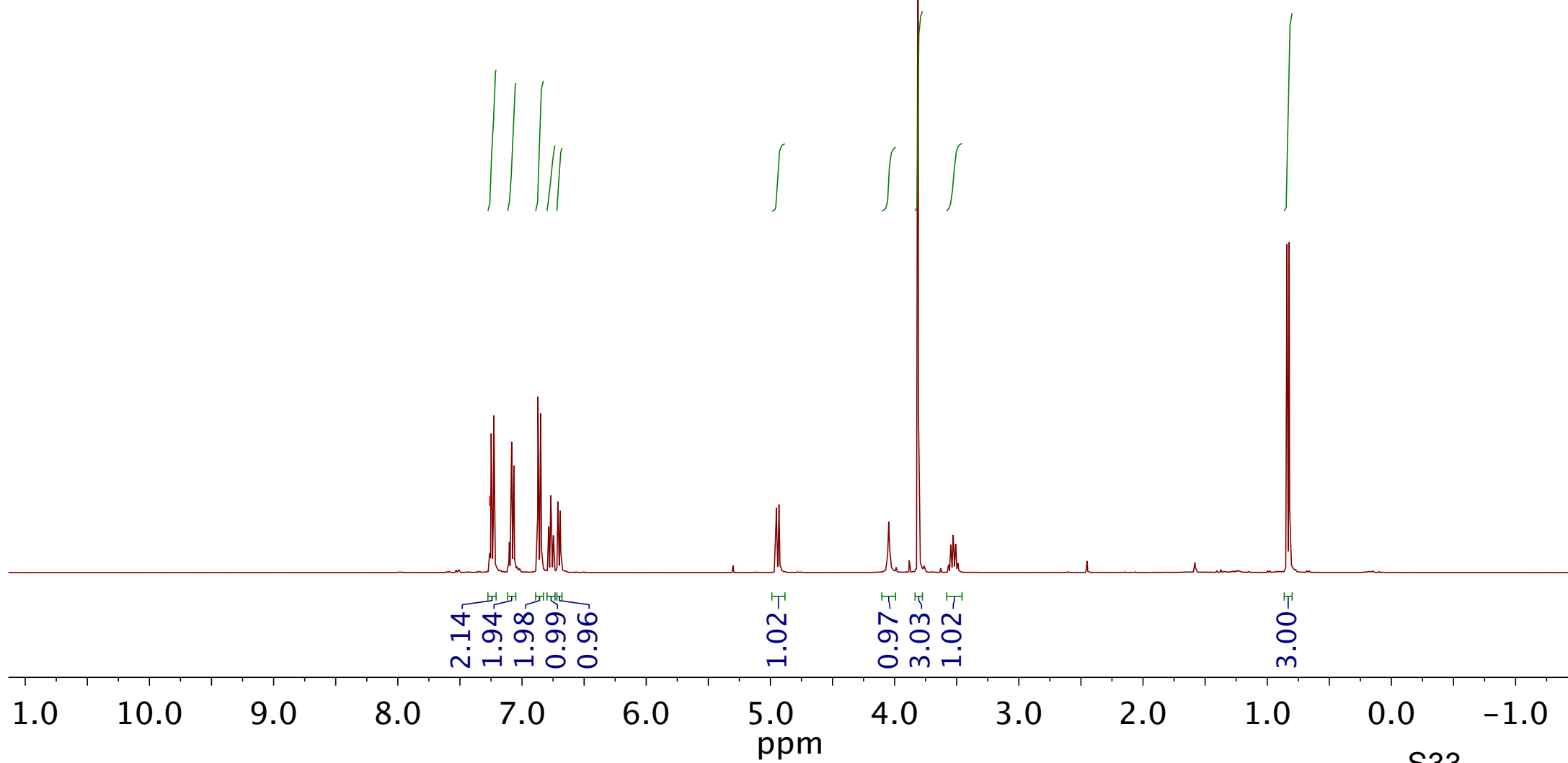


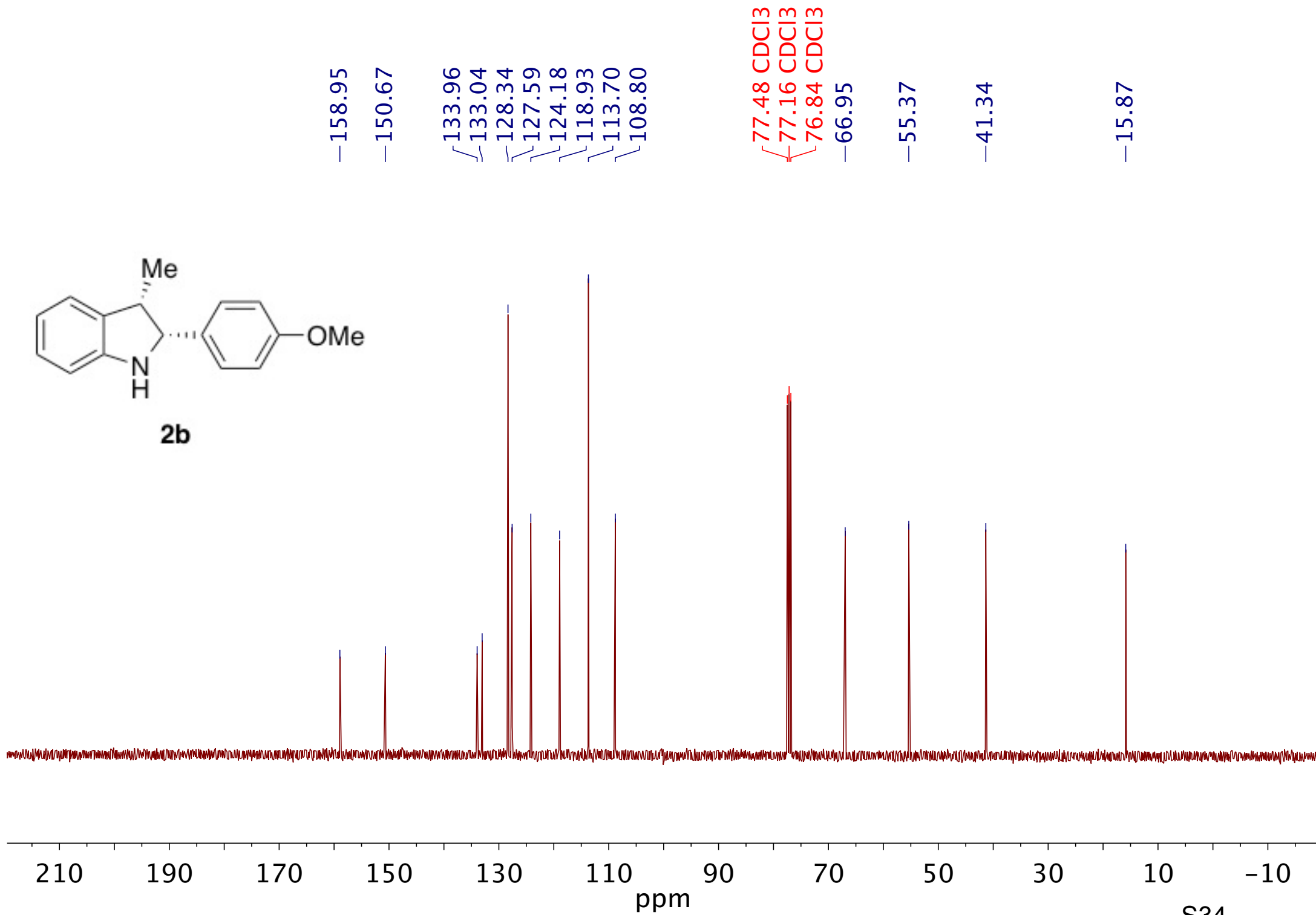
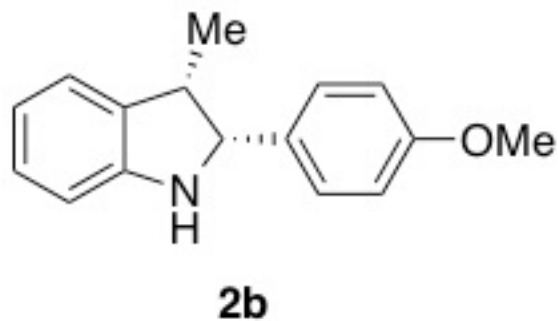
2a

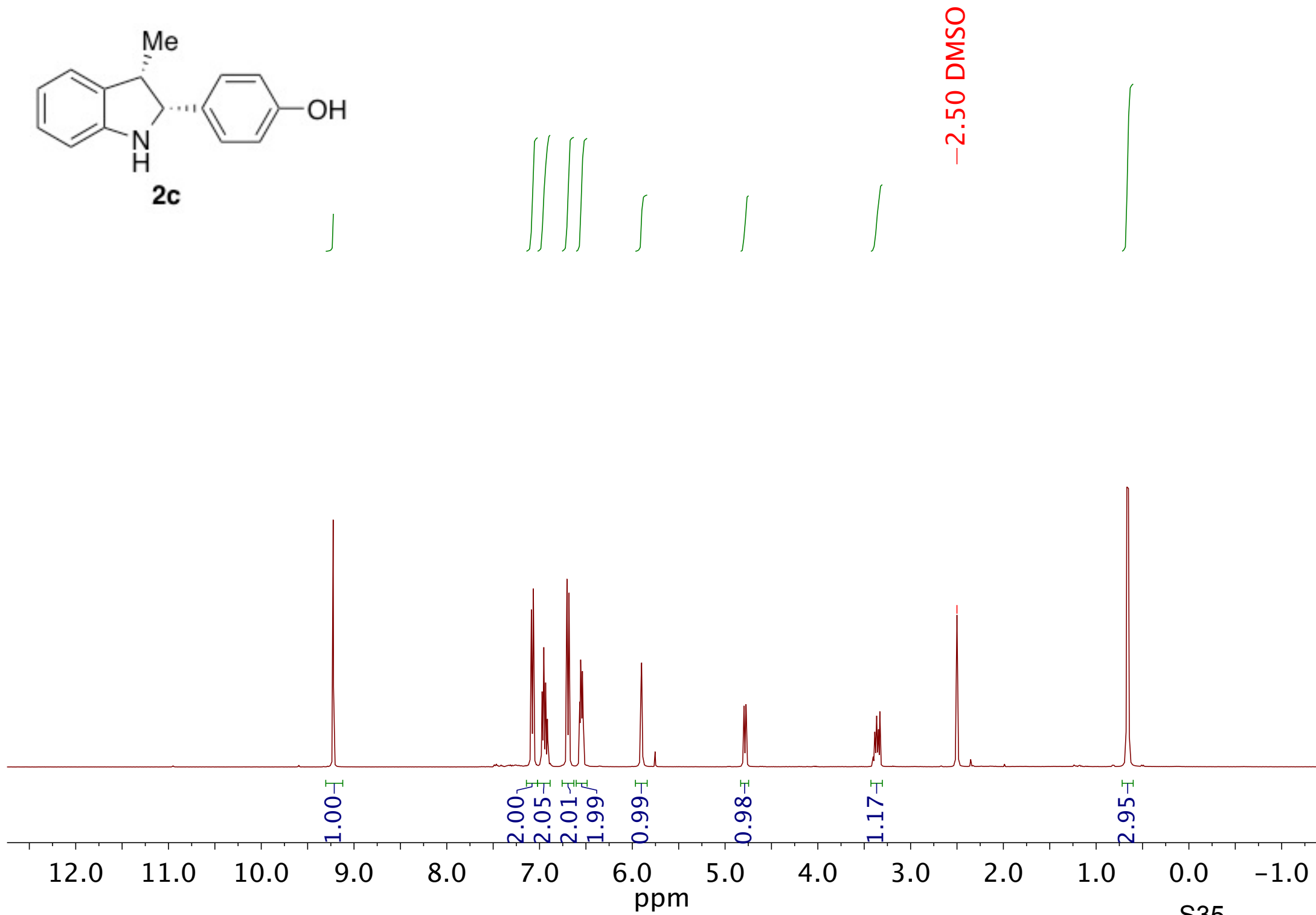
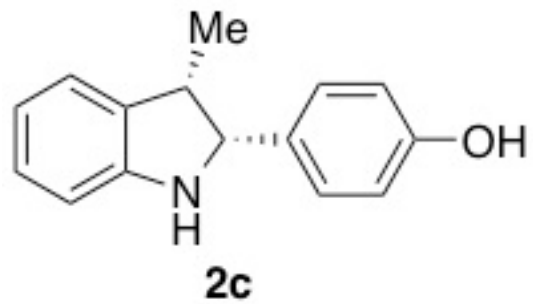


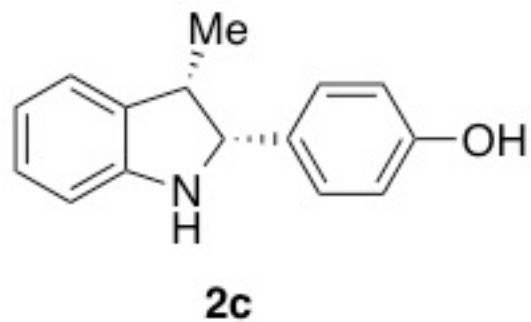


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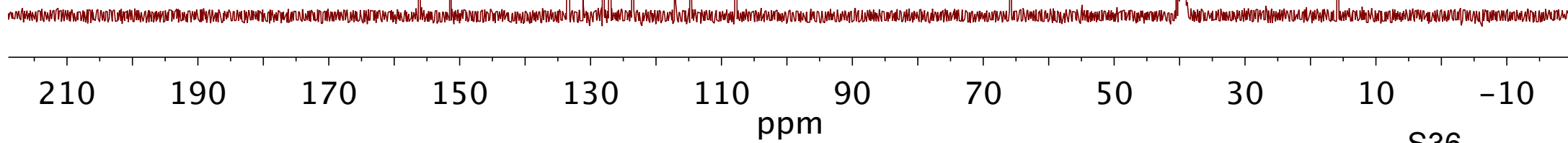


—156.18  
—151.48

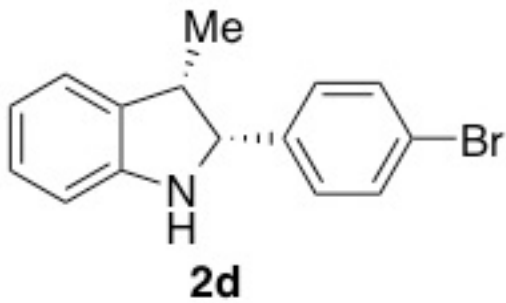
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131.12  
128.04  
127.10  
123.58  
117.04  
114.67  
107.80

—65.75

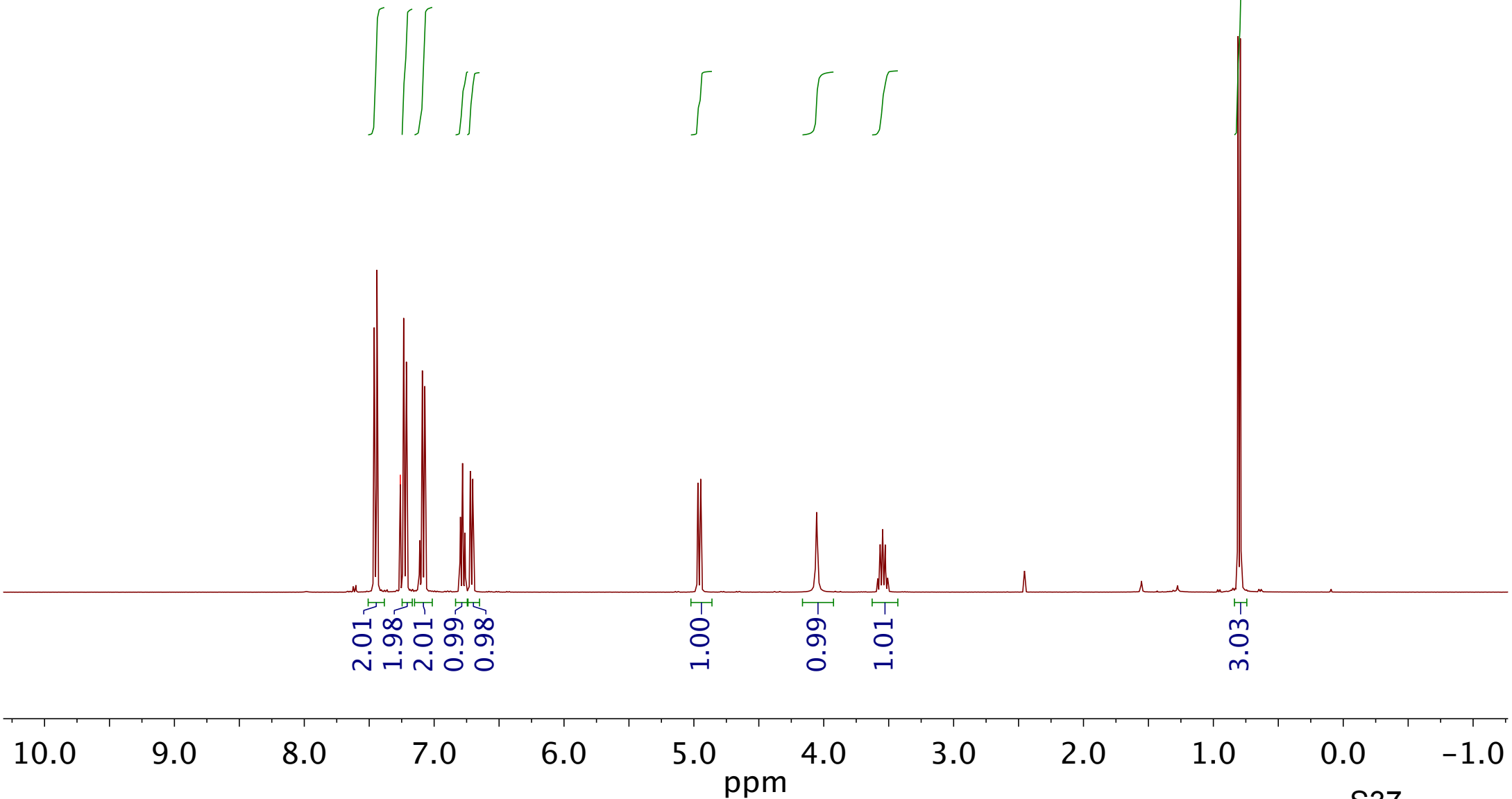
40.46  
40.15 DMSO  
39.94 DMSO  
39.73 DMSO  
39.52 DMSO  
39.31 DMSO  
39.10 DMSO  
38.89 DMSO  
—15.82







-7.26 CDCl<sub>3</sub>



-150.29

-139.98

133.70

131.46

129.04

127.76

124.25

121.09

119.24

-109.02

77.48 CDCl<sub>3</sub>

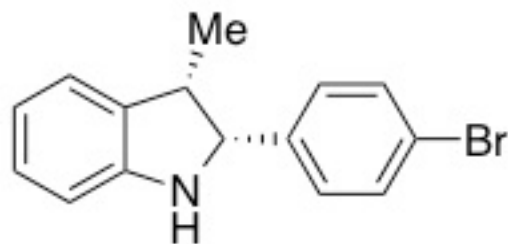
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76.84 CDCl<sub>3</sub>

-66.77

-41.25

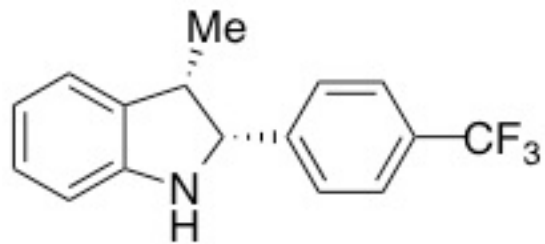
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2d

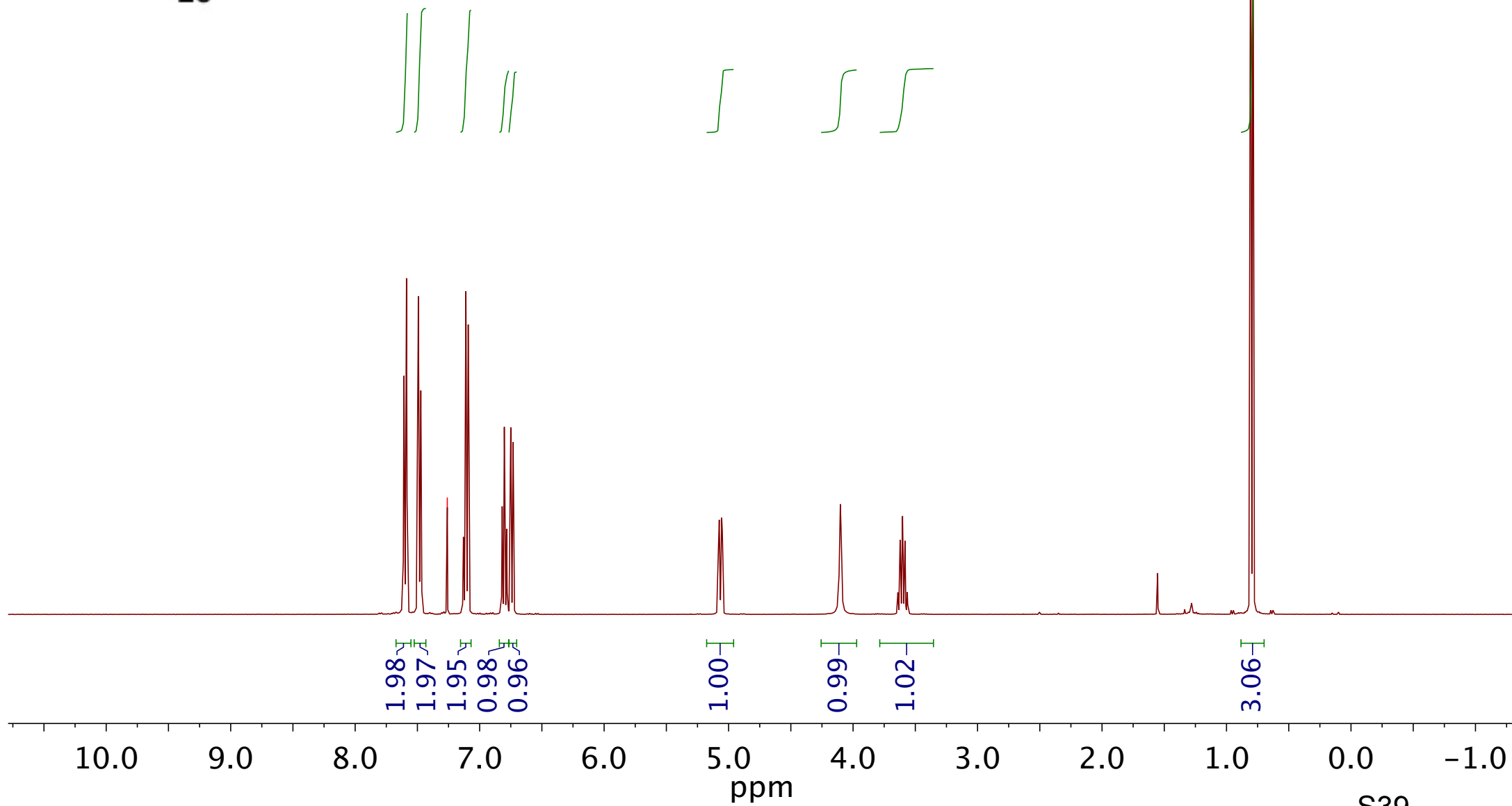
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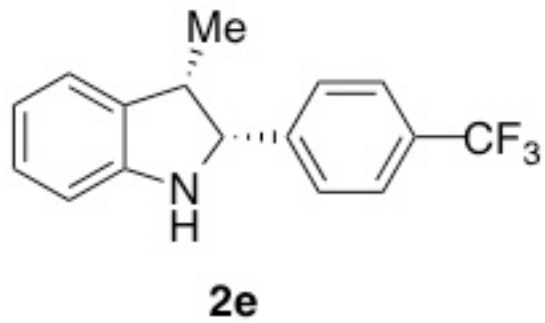
S38



2e

-7.26 CDCl<sub>3</sub>



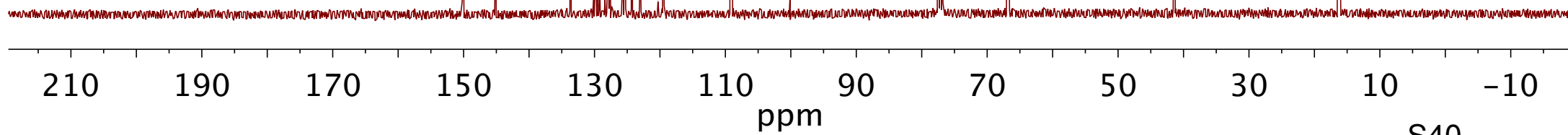


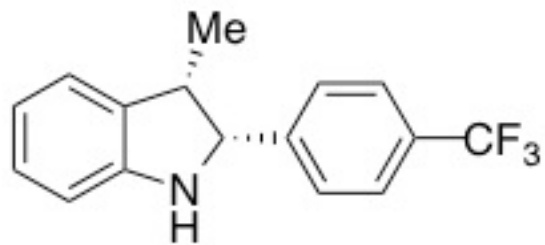
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—145.11  
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127.65  
125.35  
124.28  
119.41  
109.16

77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>  
—66.91

—41.39

—16.23





2e

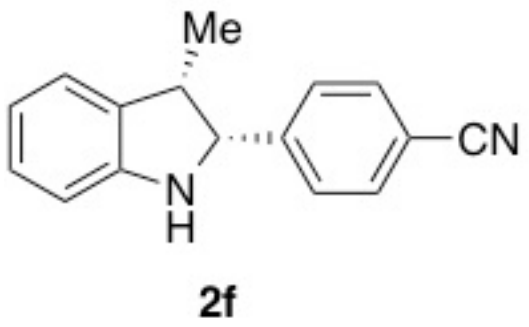
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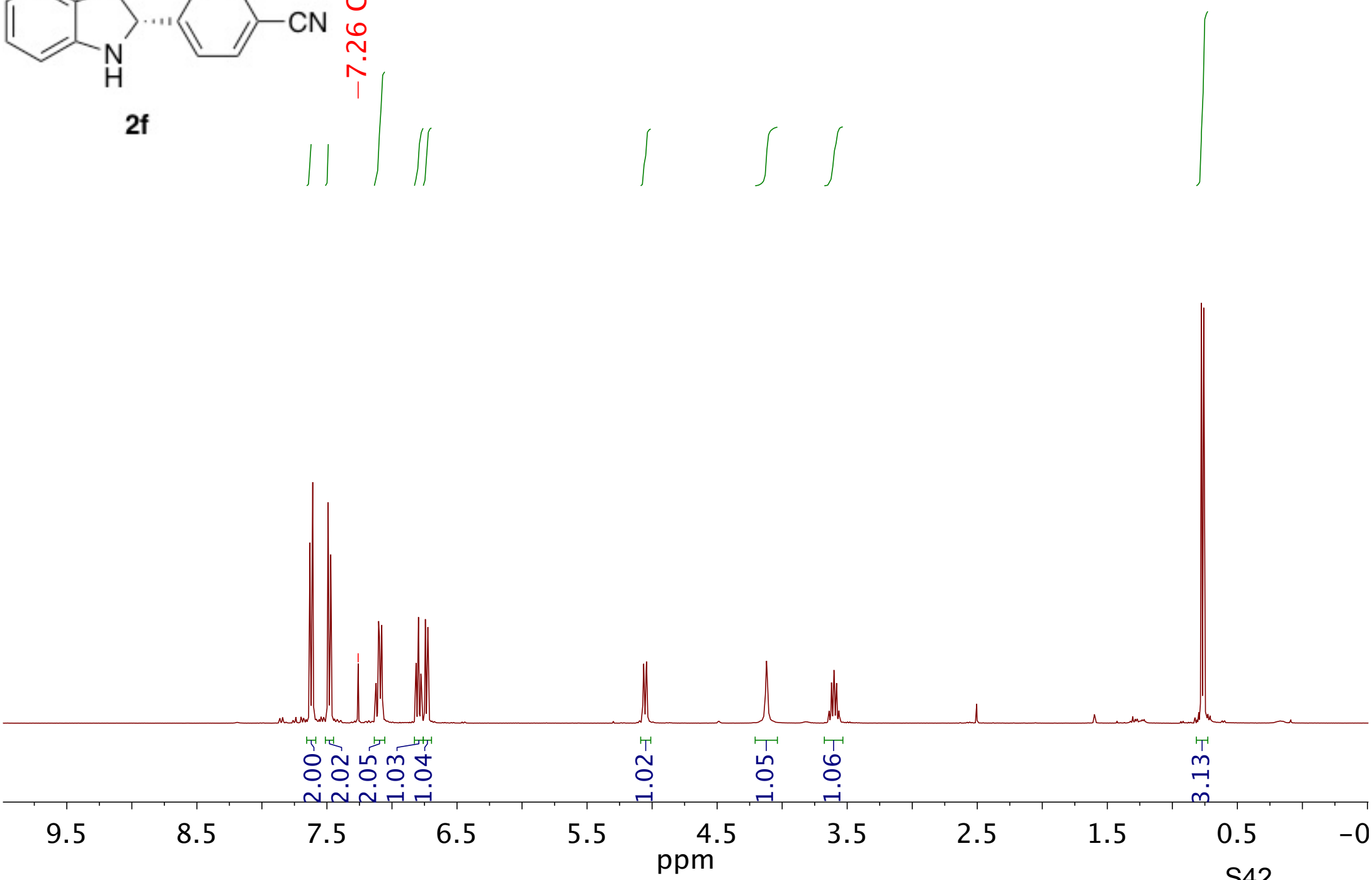
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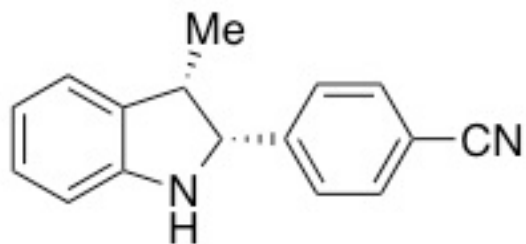
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S41

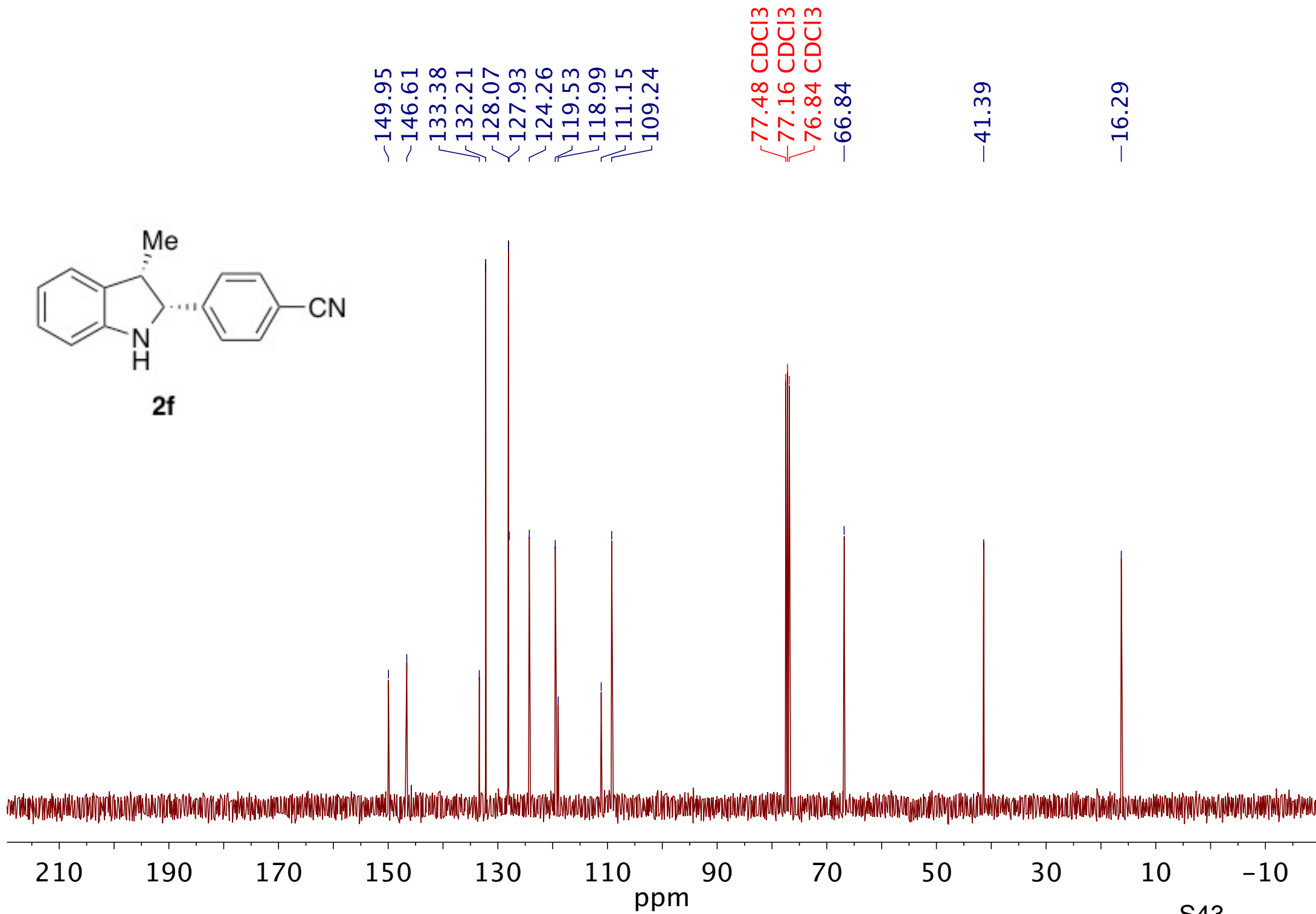


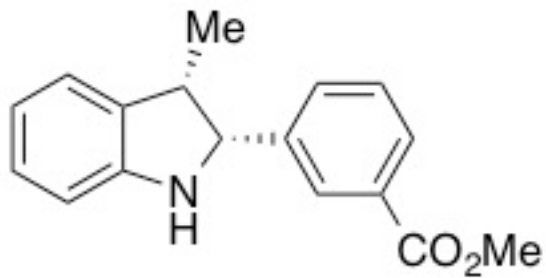
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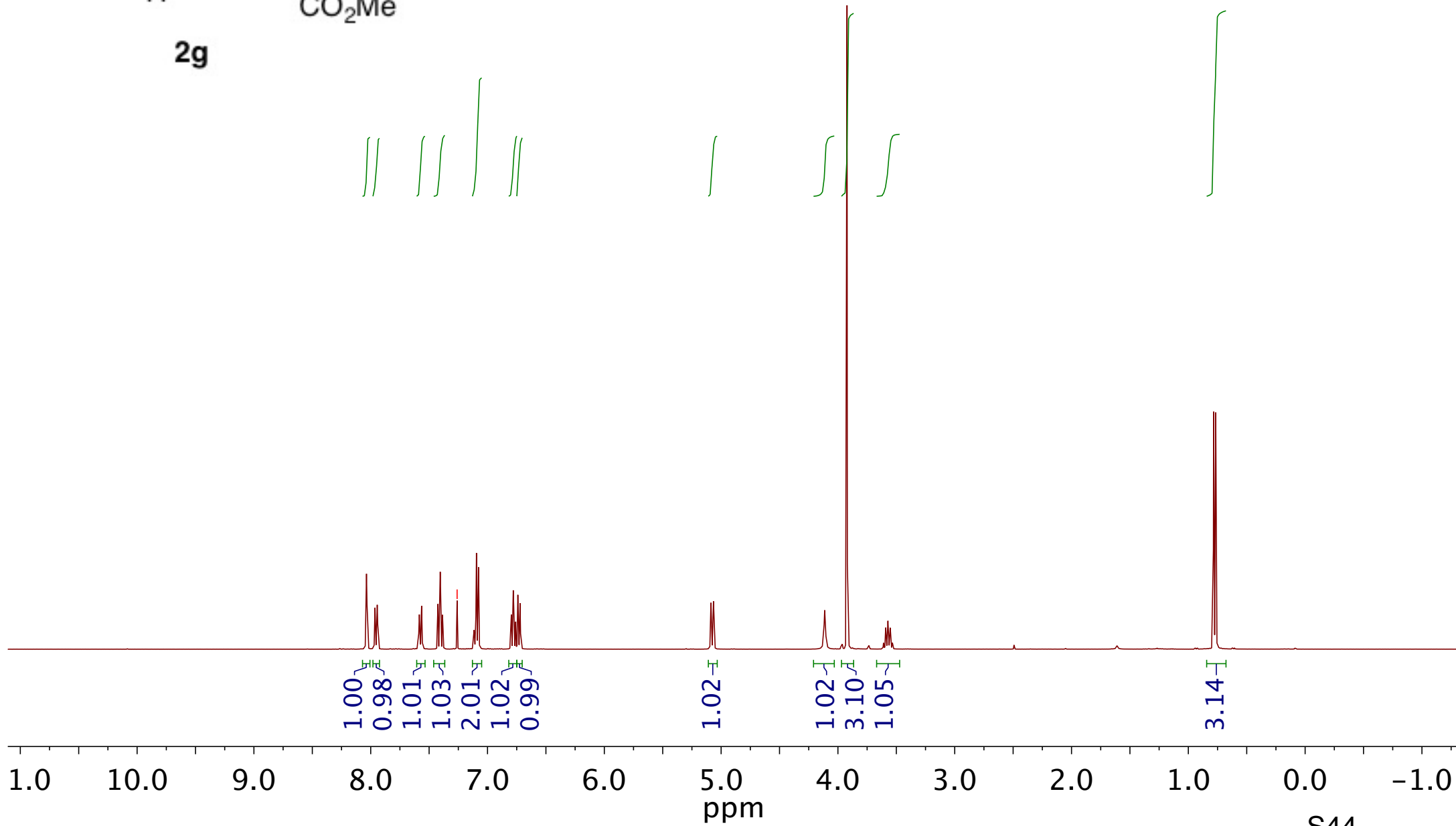
2f



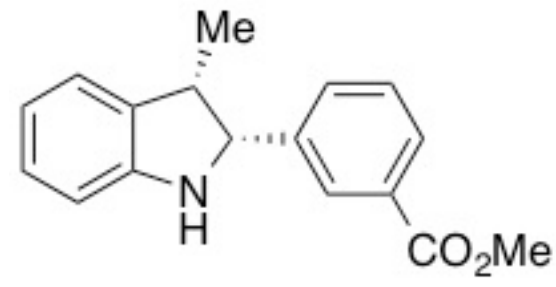
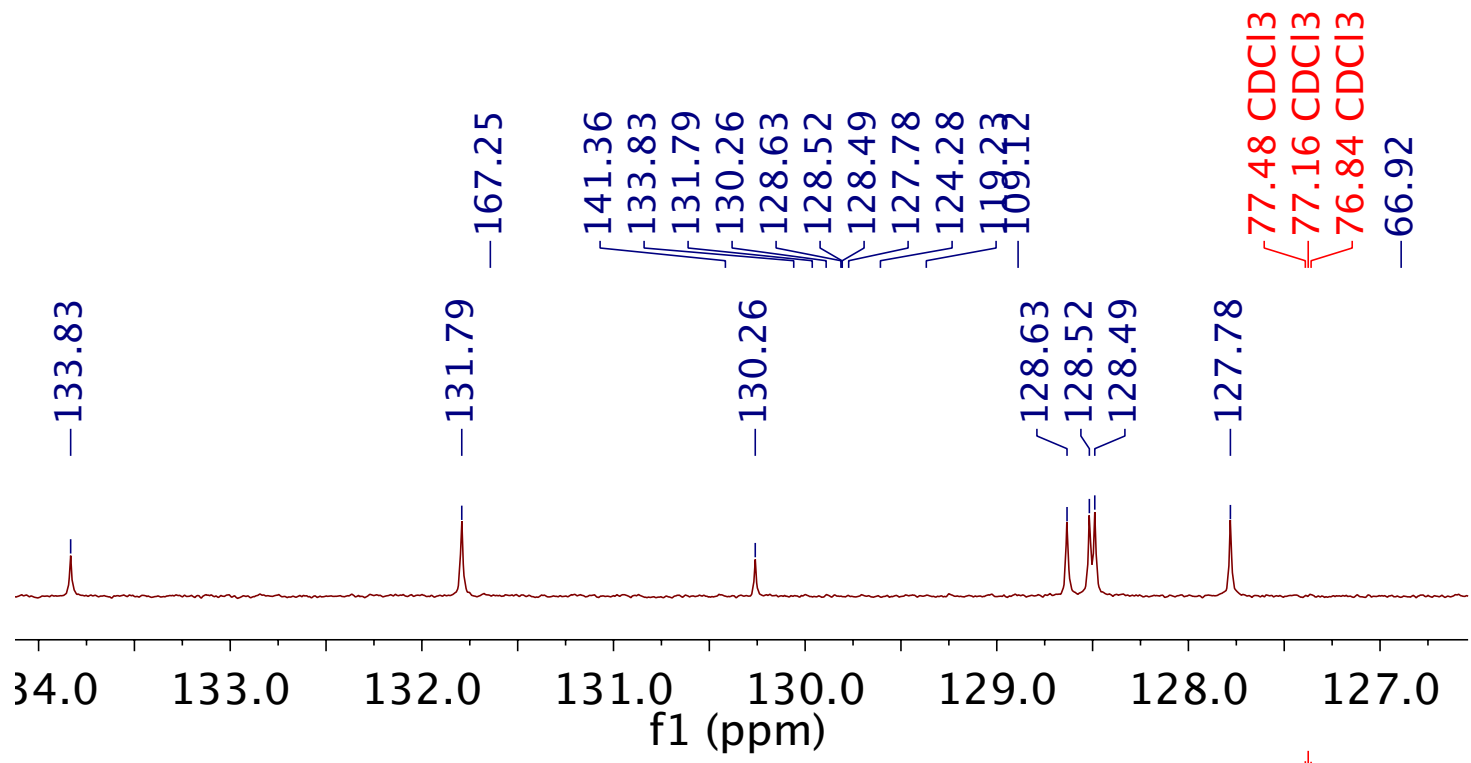


2g

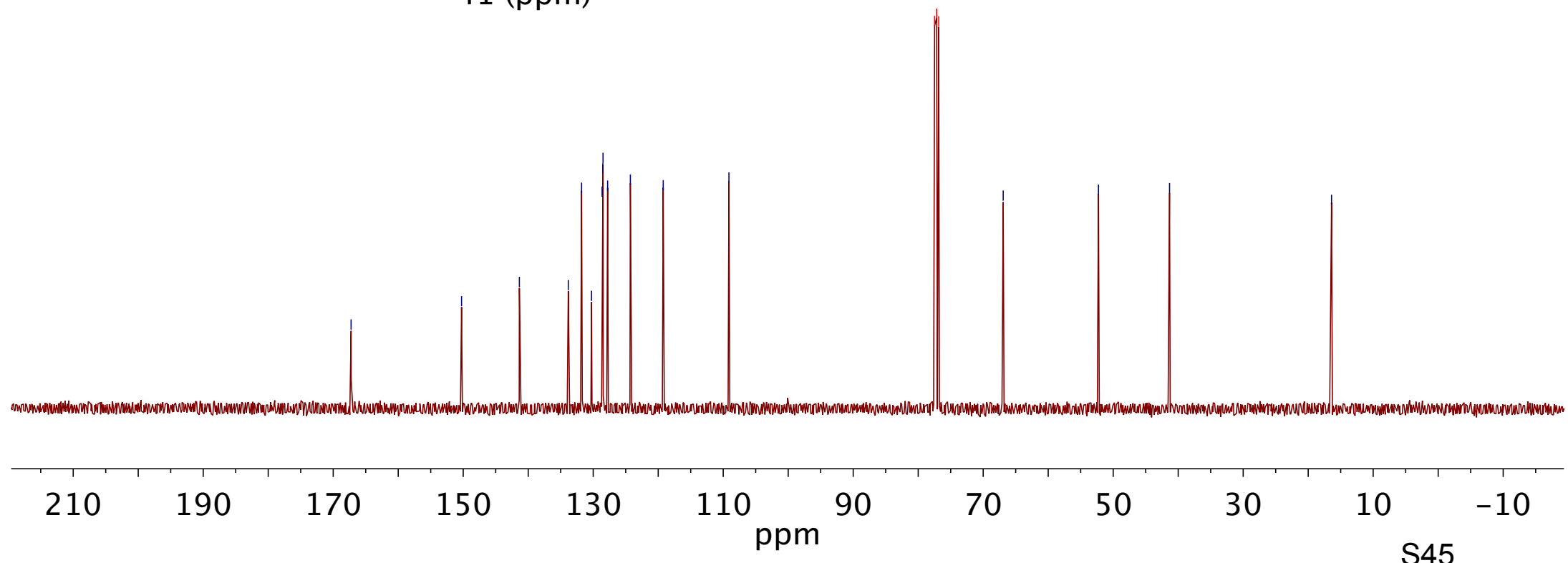
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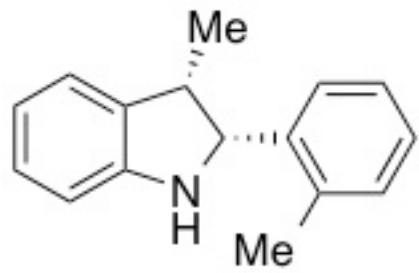






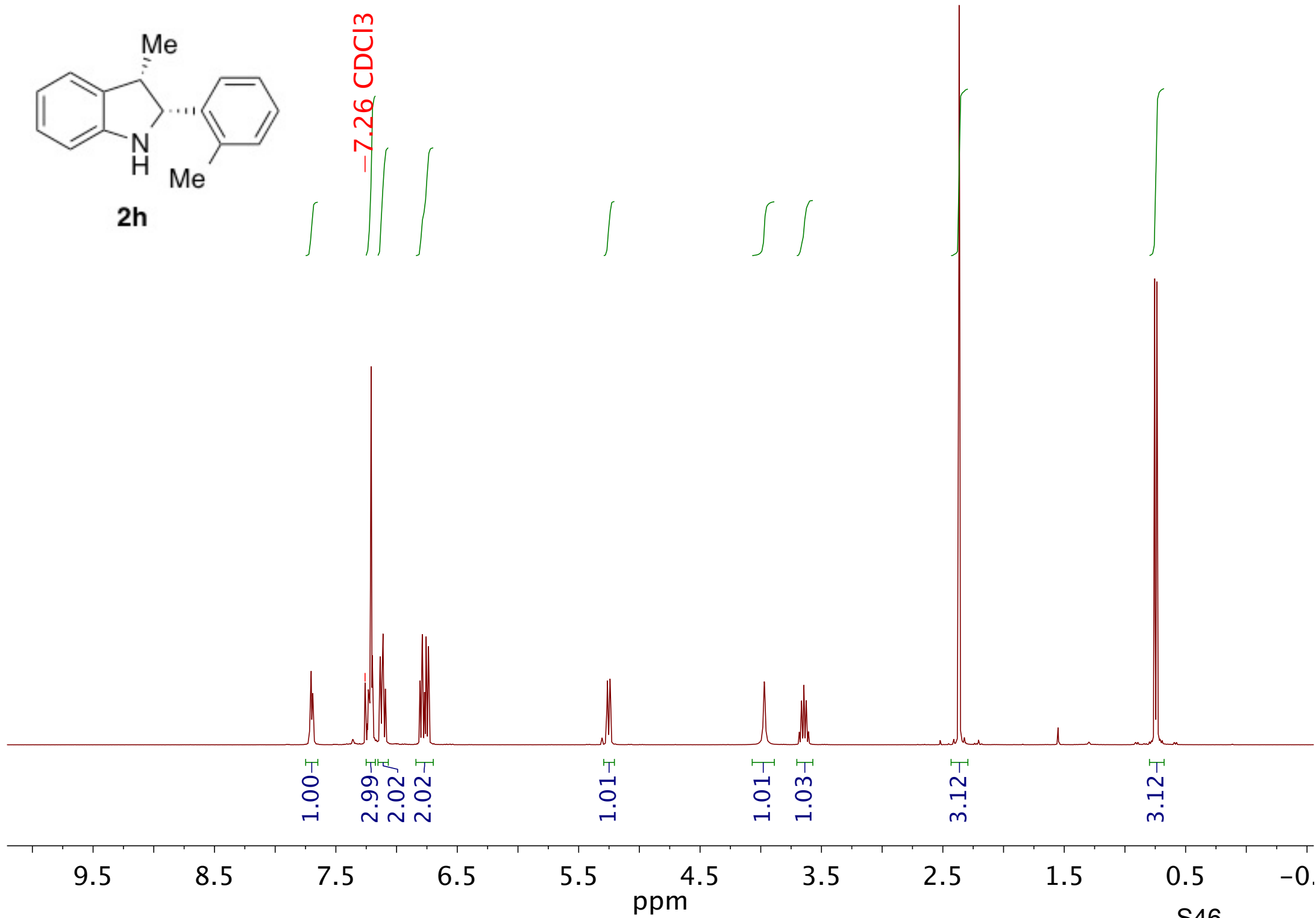
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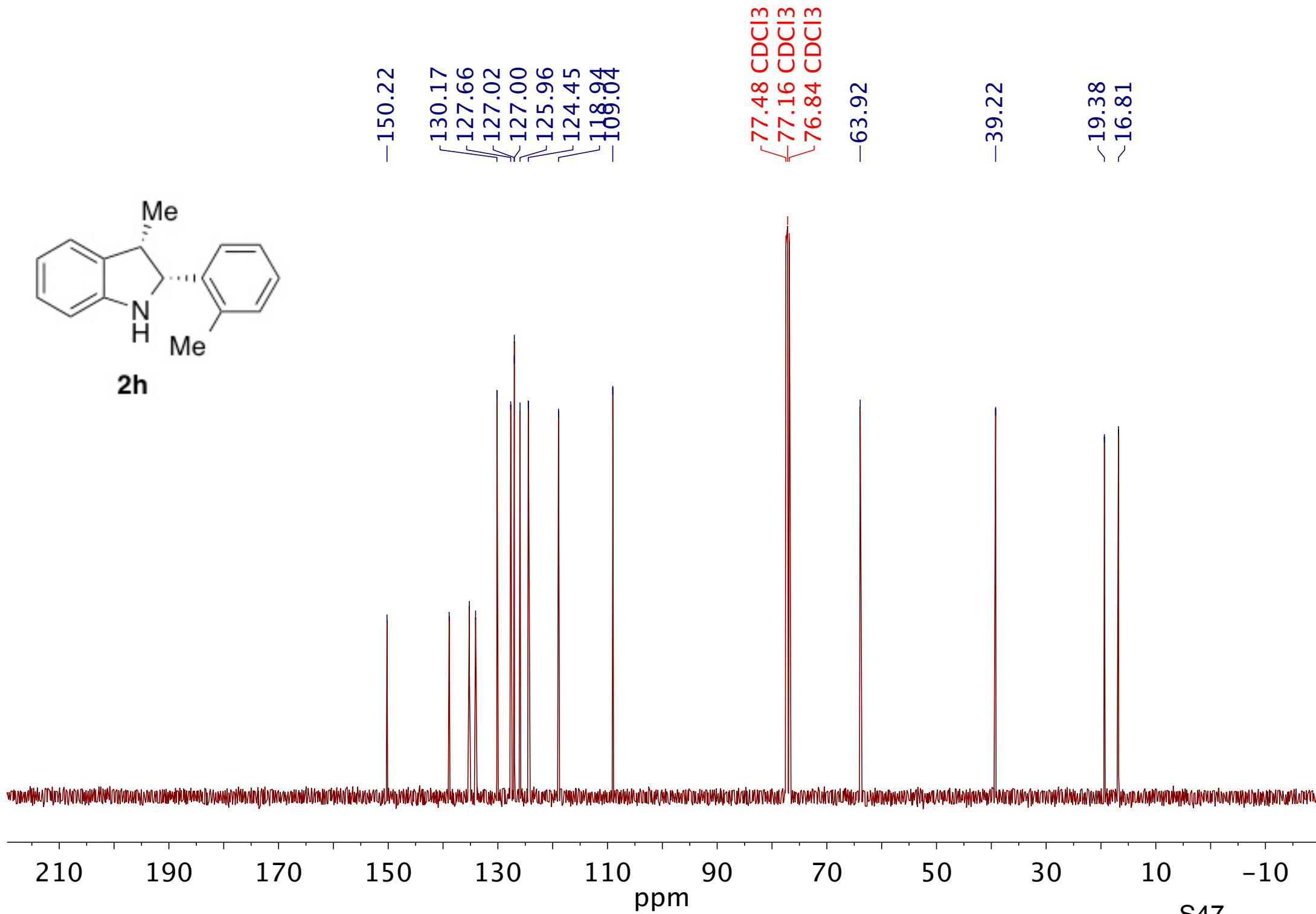
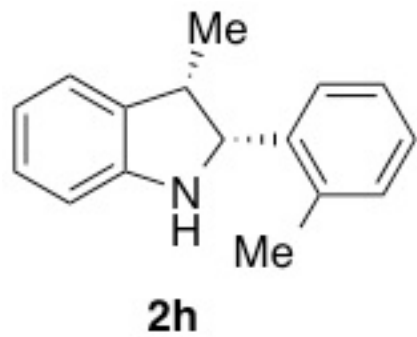


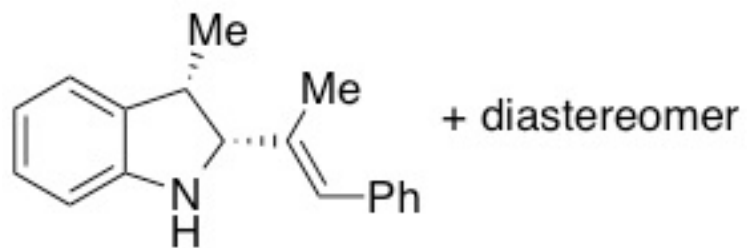
**2h**

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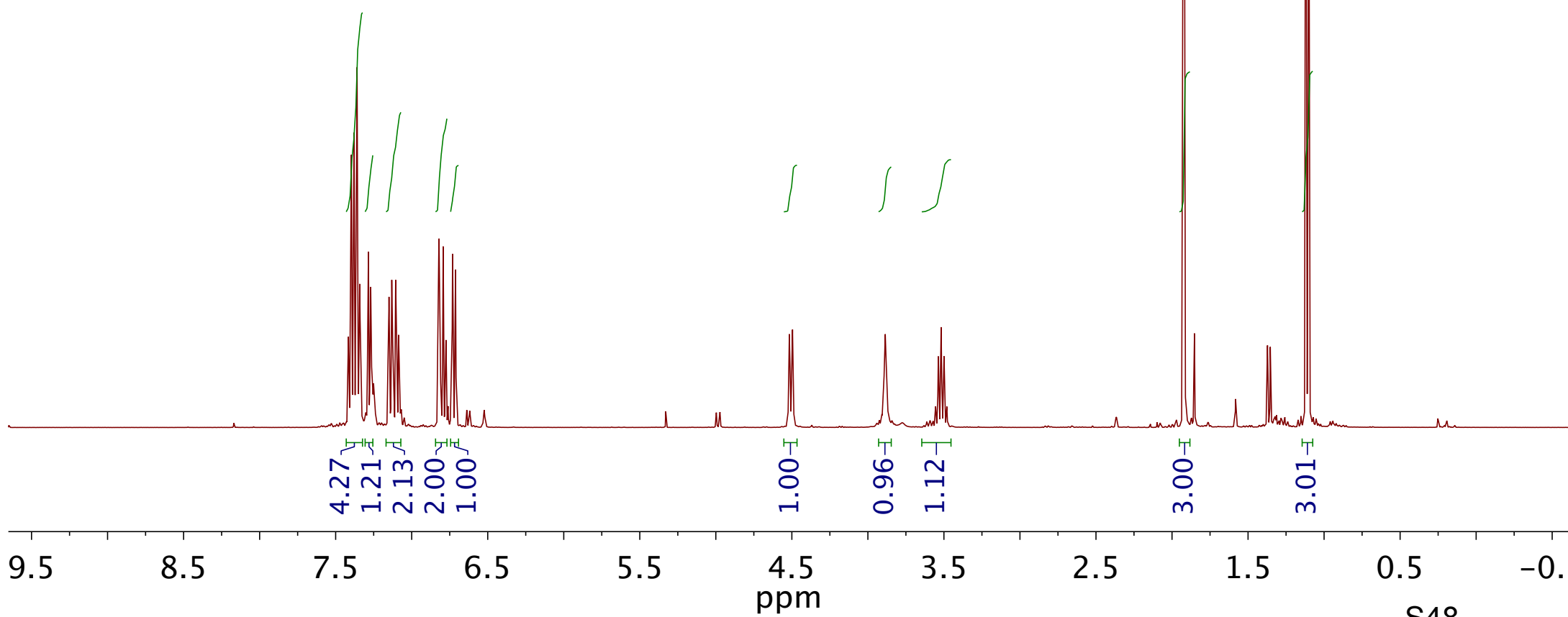


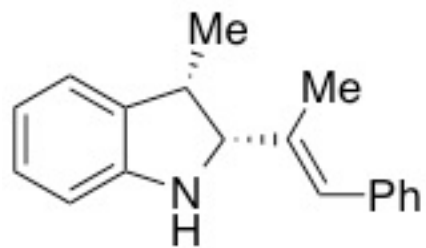
S46





**2i** (11:1 dr)  
in  $\text{CDCl}_3$





+ diastereomer

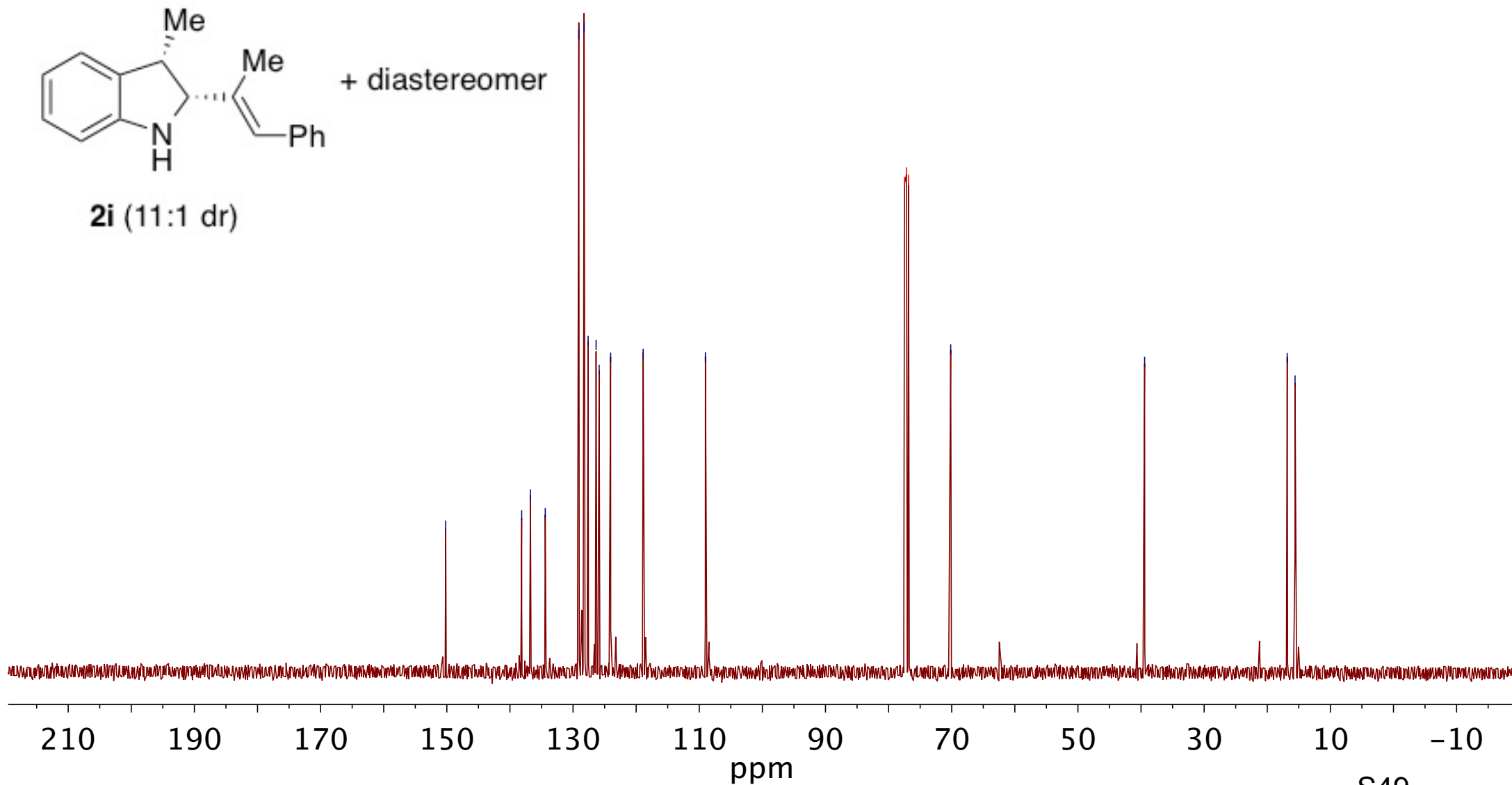
**2i** (11:1 dr)

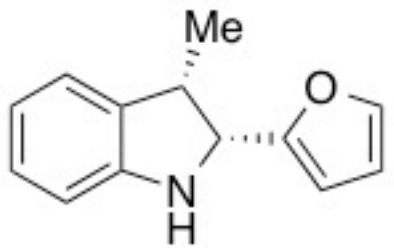
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129.09  
128.25  
127.61  
126.35  
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124.05  
118.89

77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>  
70.16

39.43

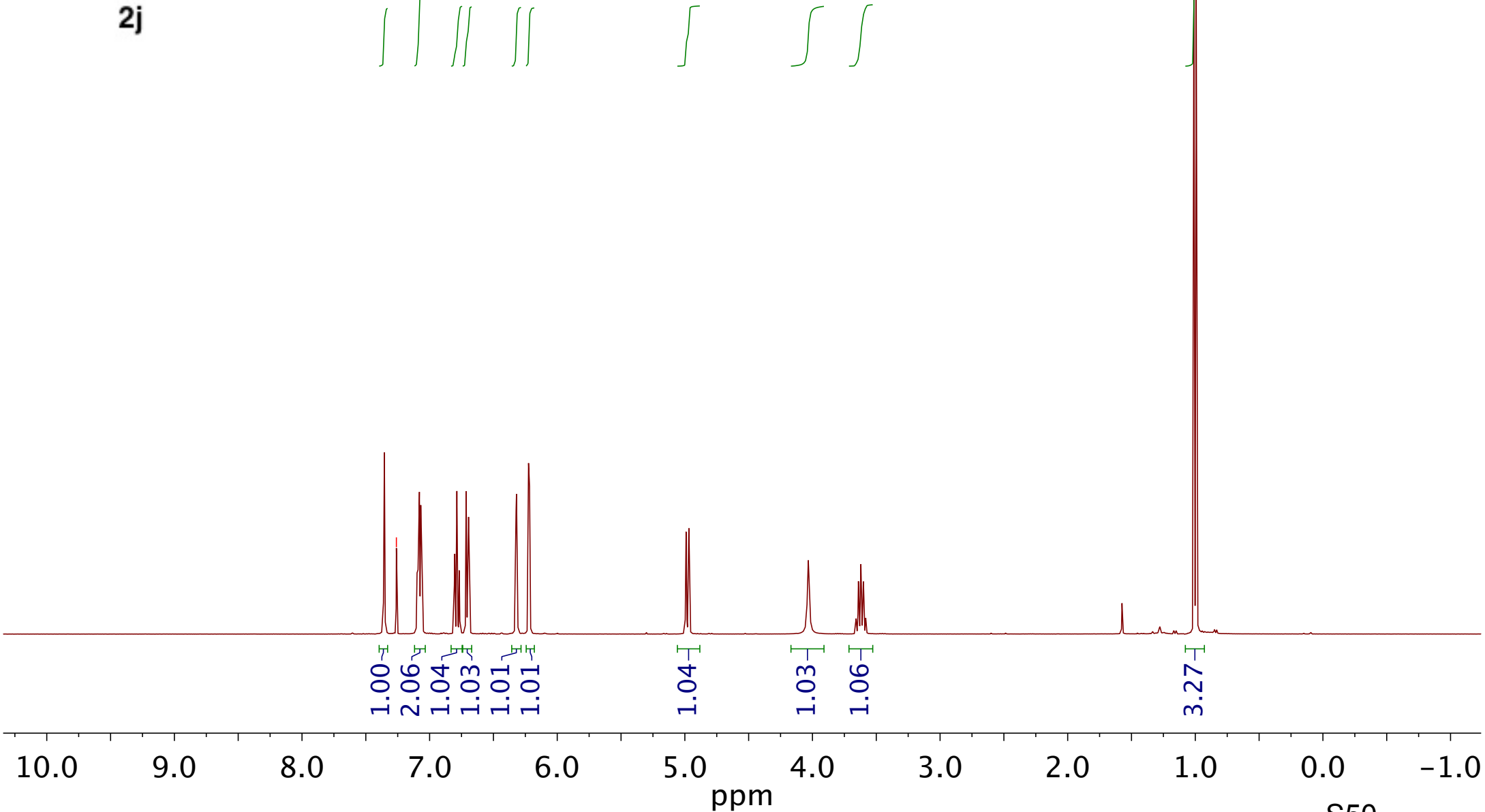
16.84  
15.60

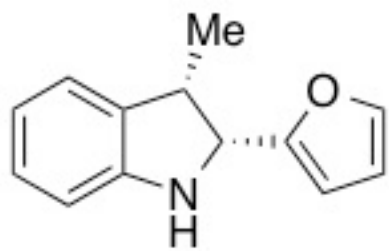




2j

-7.26 CDCl<sub>3</sub>





2j

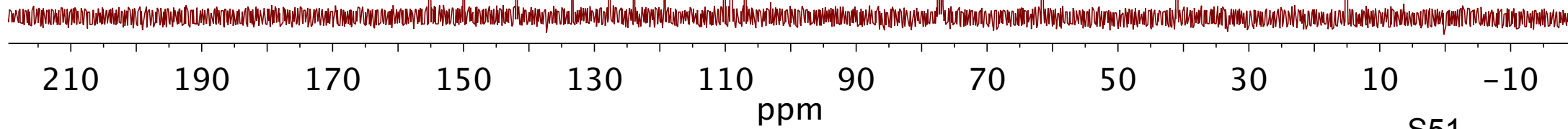
155.25  
150.04  
141.88  
133.37  
127.61  
123.91  
119.29  
110.15  
109.22  
106.92

77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

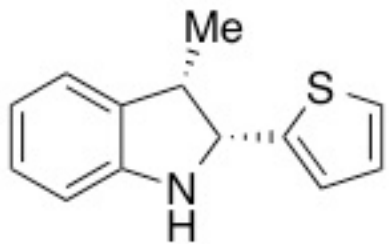
-61.56

-41.01

-15.17

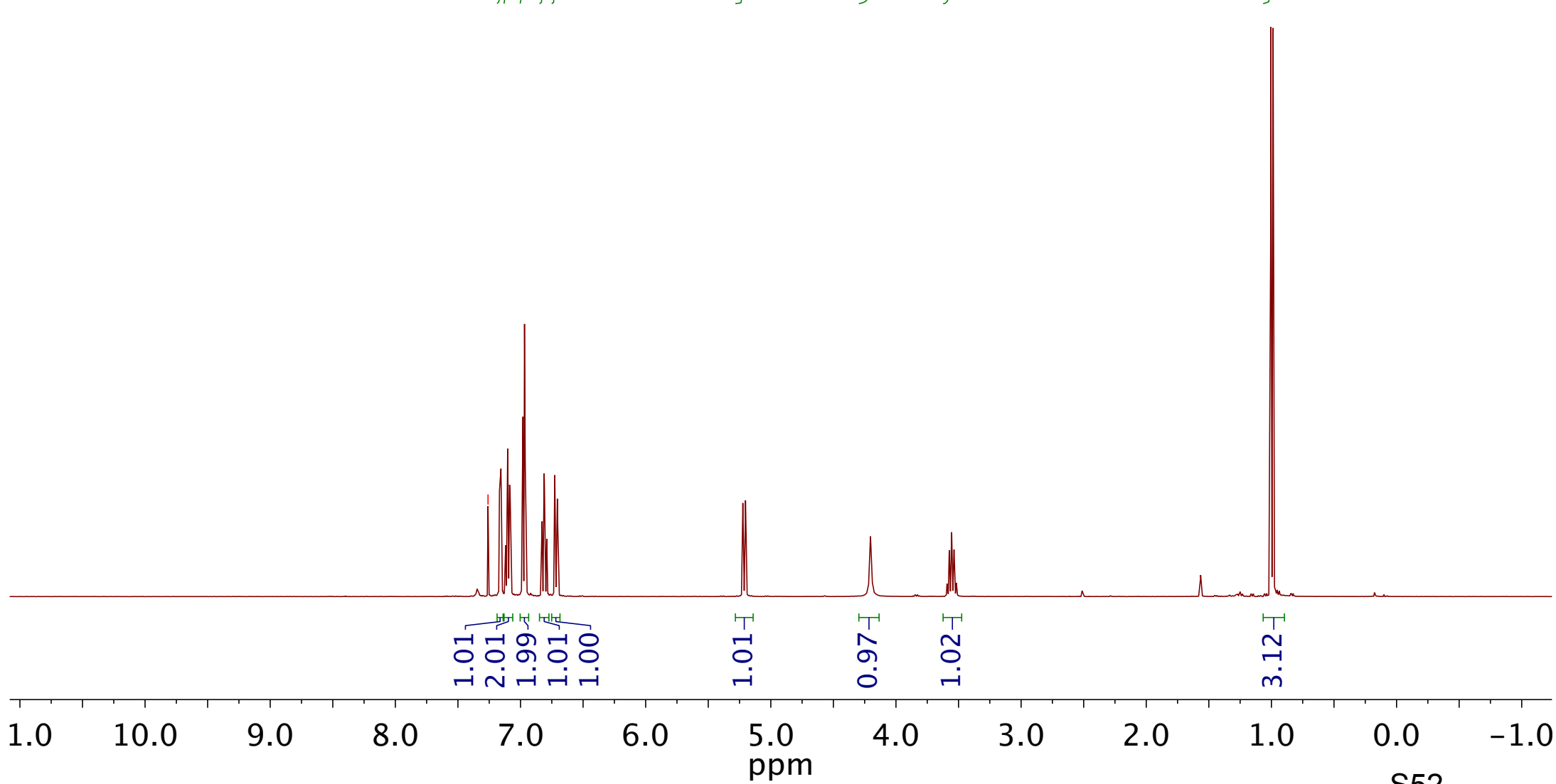


S51

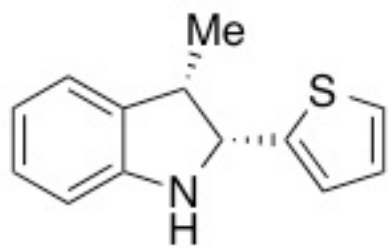


2k

-7.26 CDCl<sub>3</sub>







2k

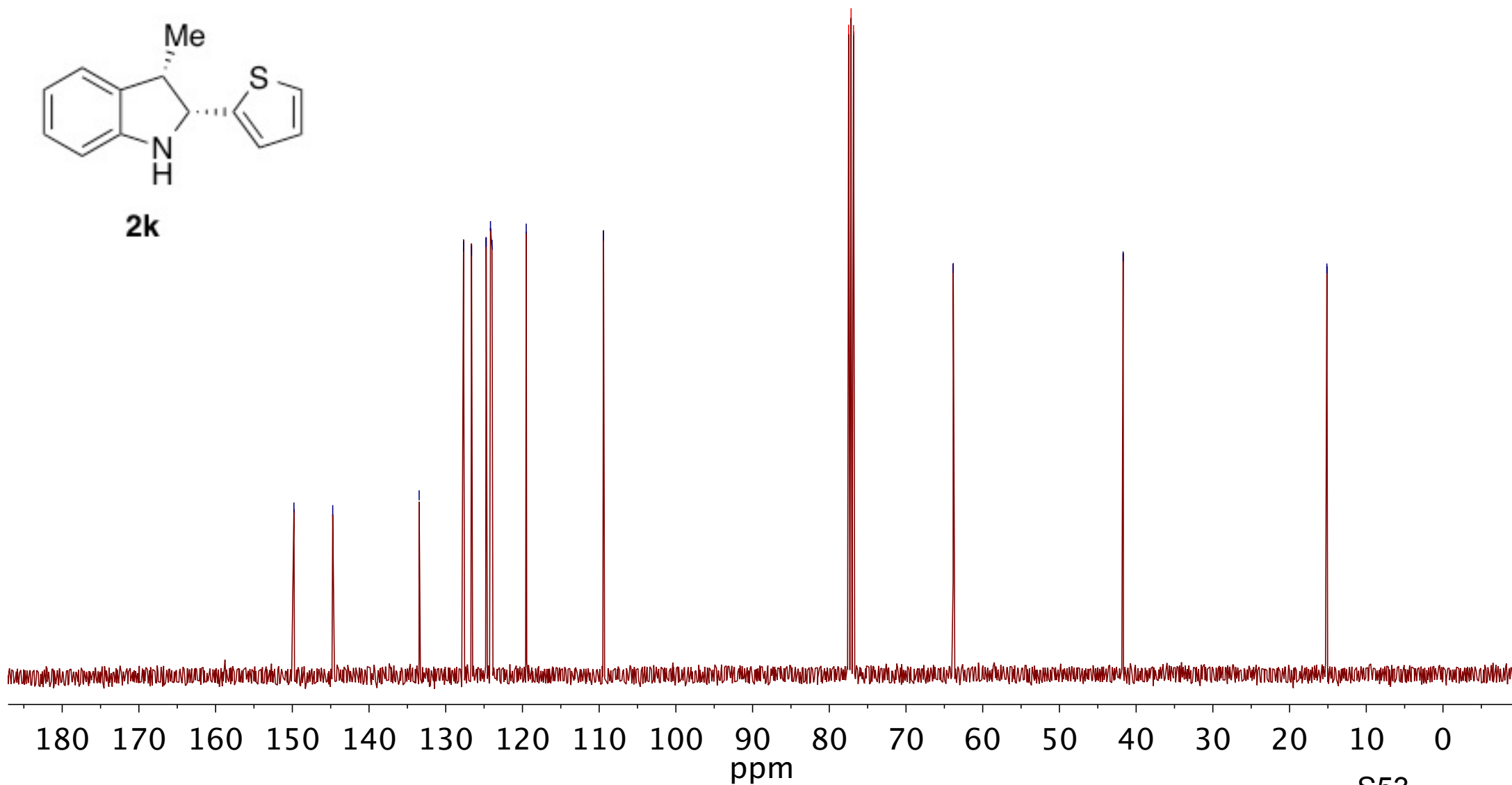
—149.79  
—144.73  
133.47  
127.68  
126.64  
124.73  
124.17  
123.97  
119.51  
—109.43

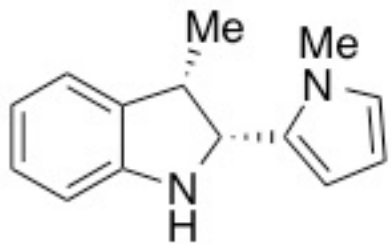
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

—63.85

—41.69

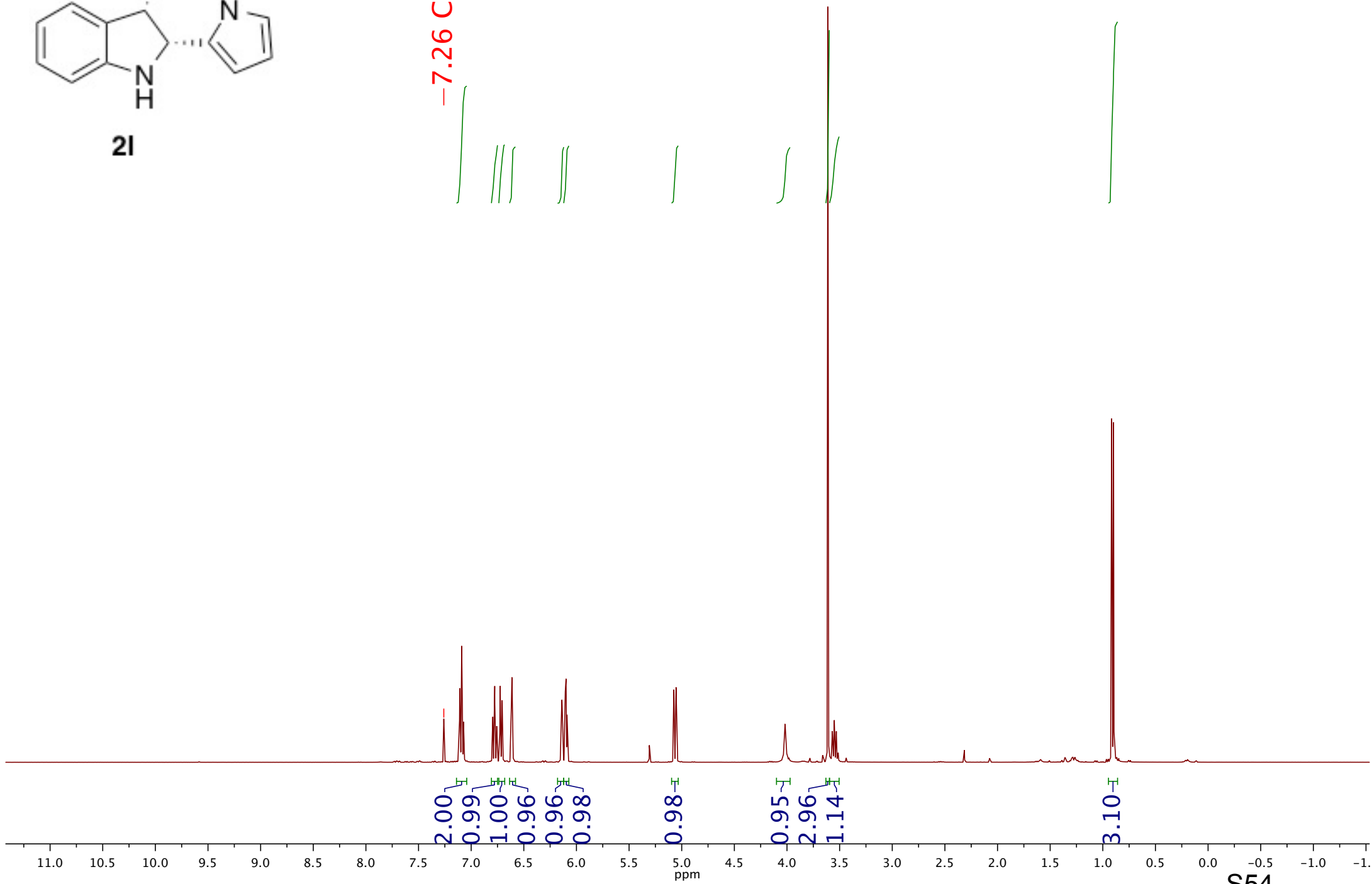
—15.14



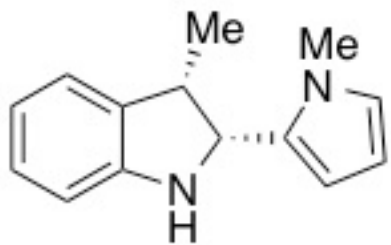


21

-7.26 CDCl<sub>3</sub>



S54



2l

—150.09

133.67

132.45

127.62

124.23

122.23

118.96

109.02

107.41

106.93

77.48 CDCl<sub>3</sub>

77.16 CDCl<sub>3</sub>

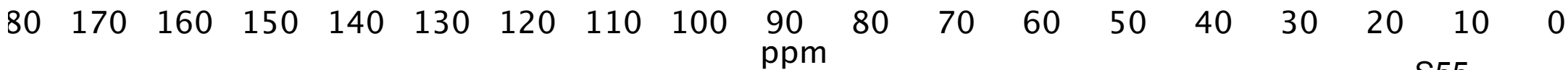
76.84 CDCl<sub>3</sub>

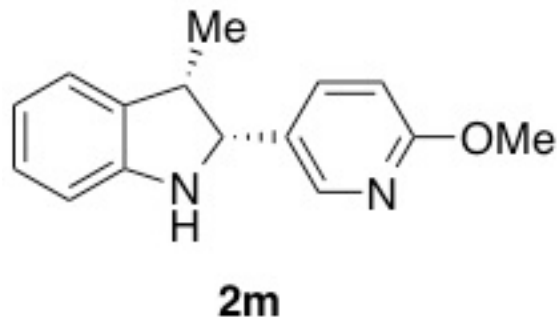
—60.53

—40.68

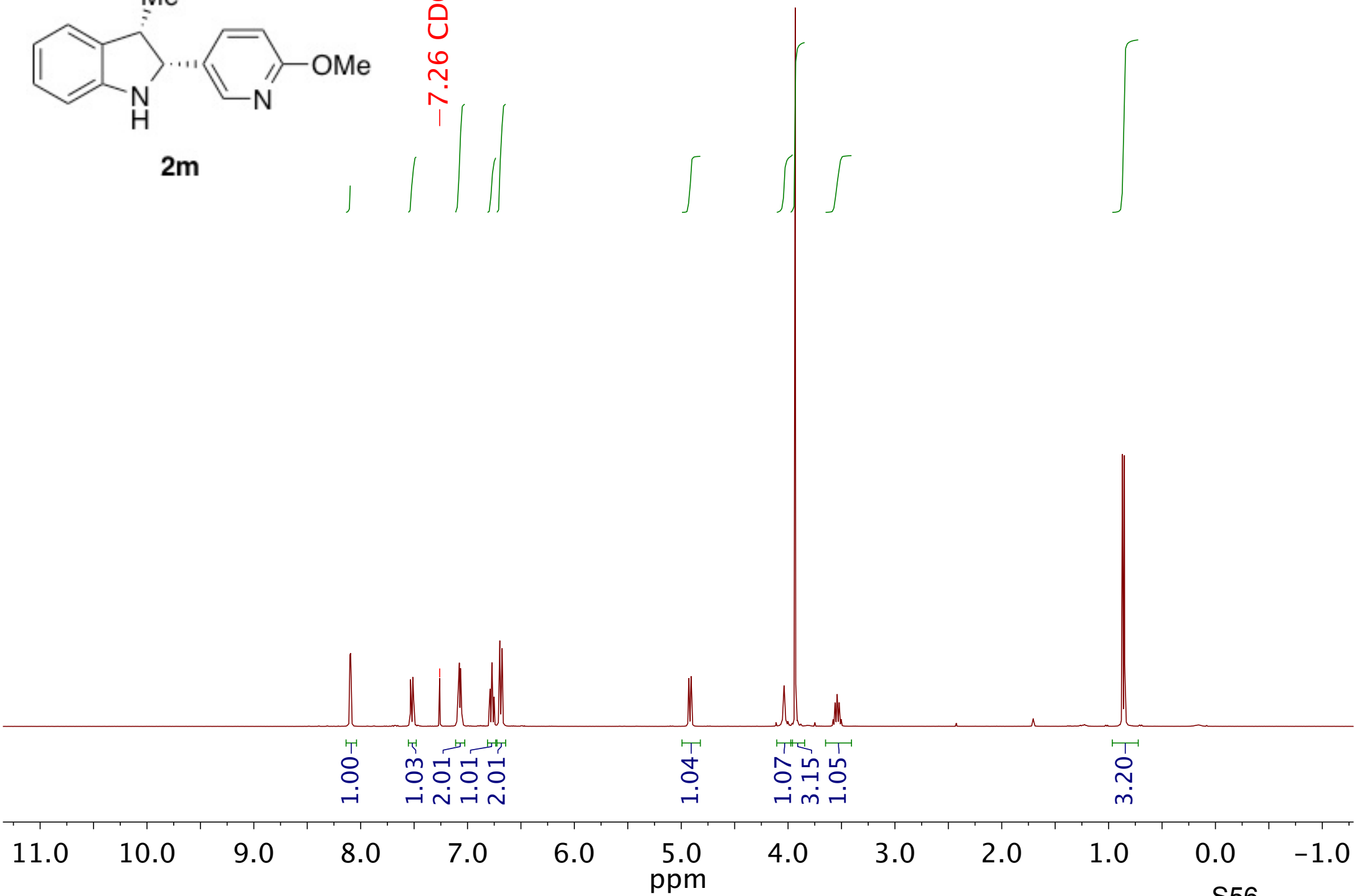
—34.07

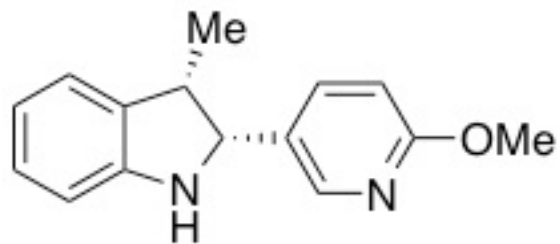
—15.85



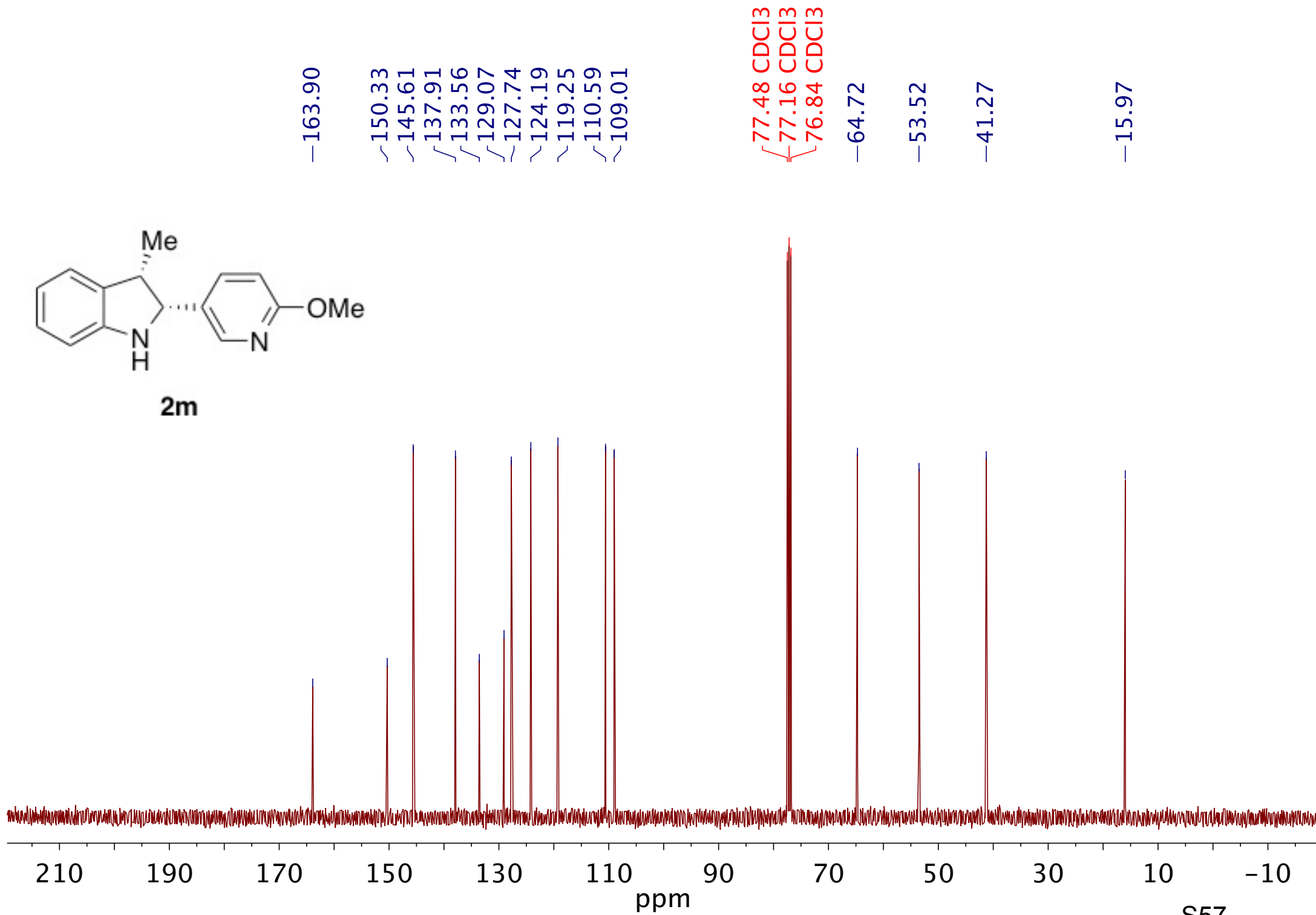


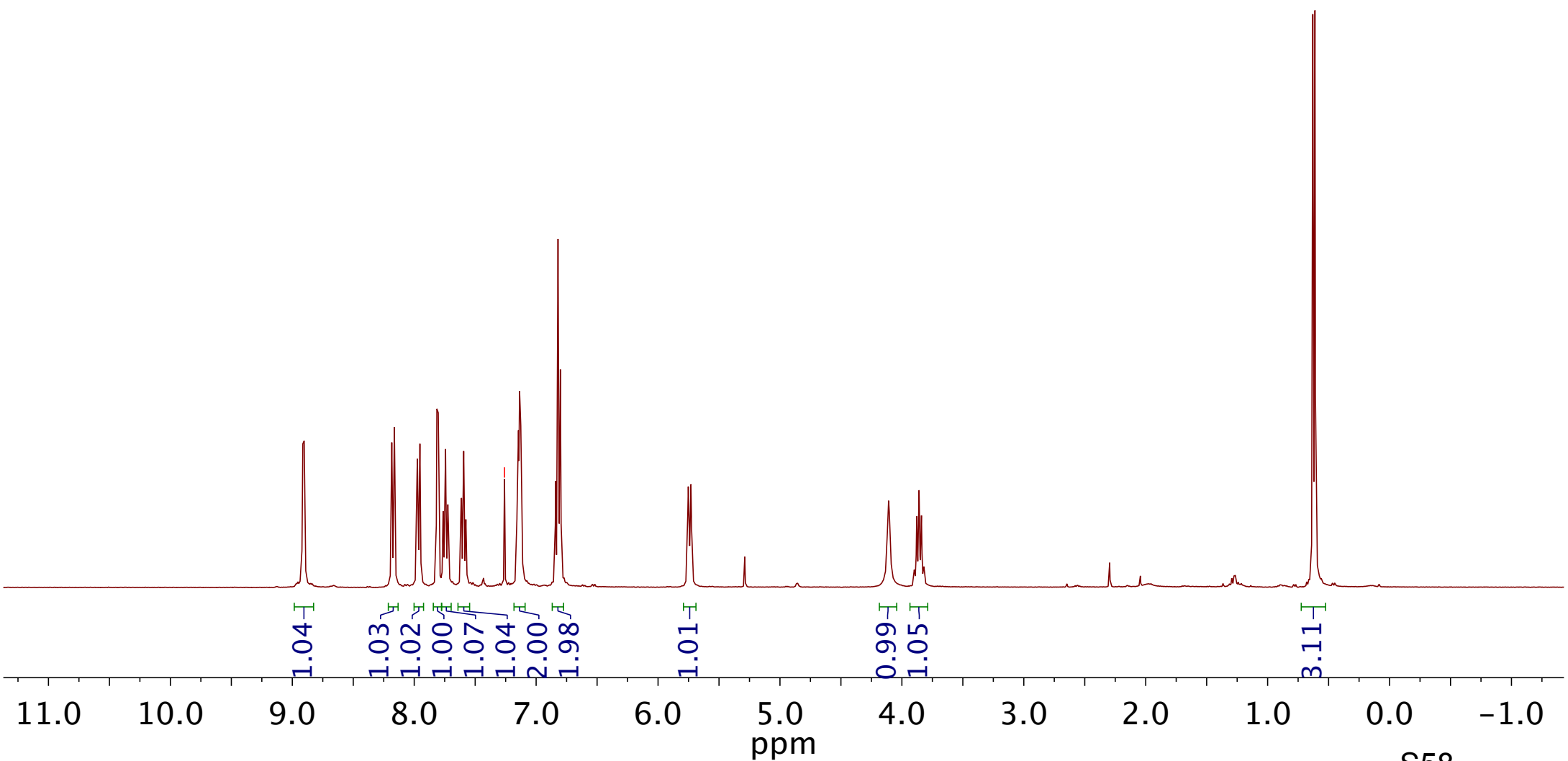
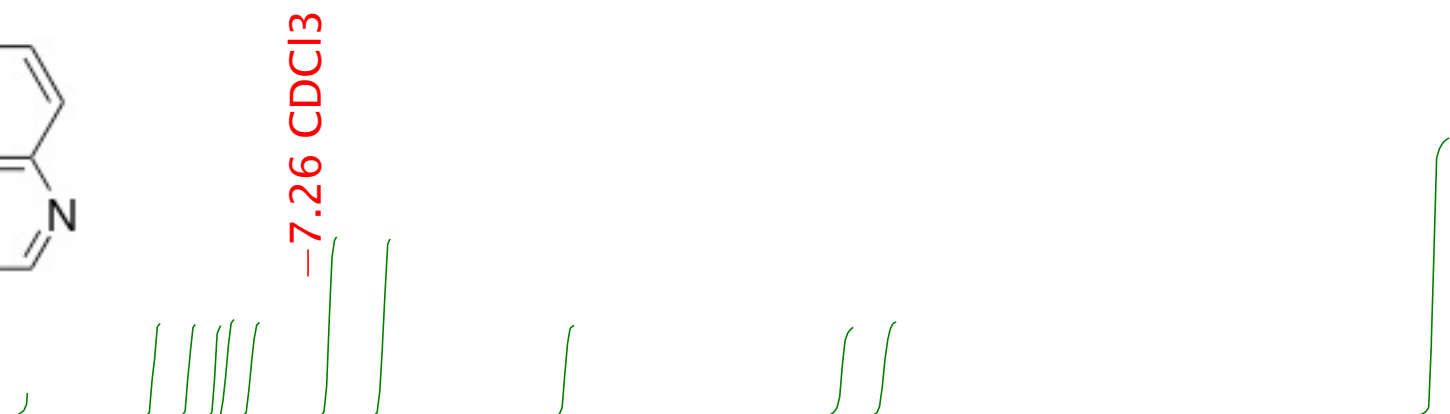
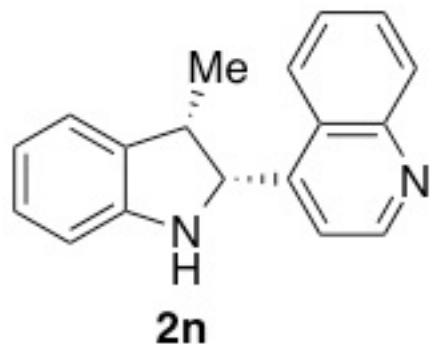
-7.26 CDCl<sub>3</sub>

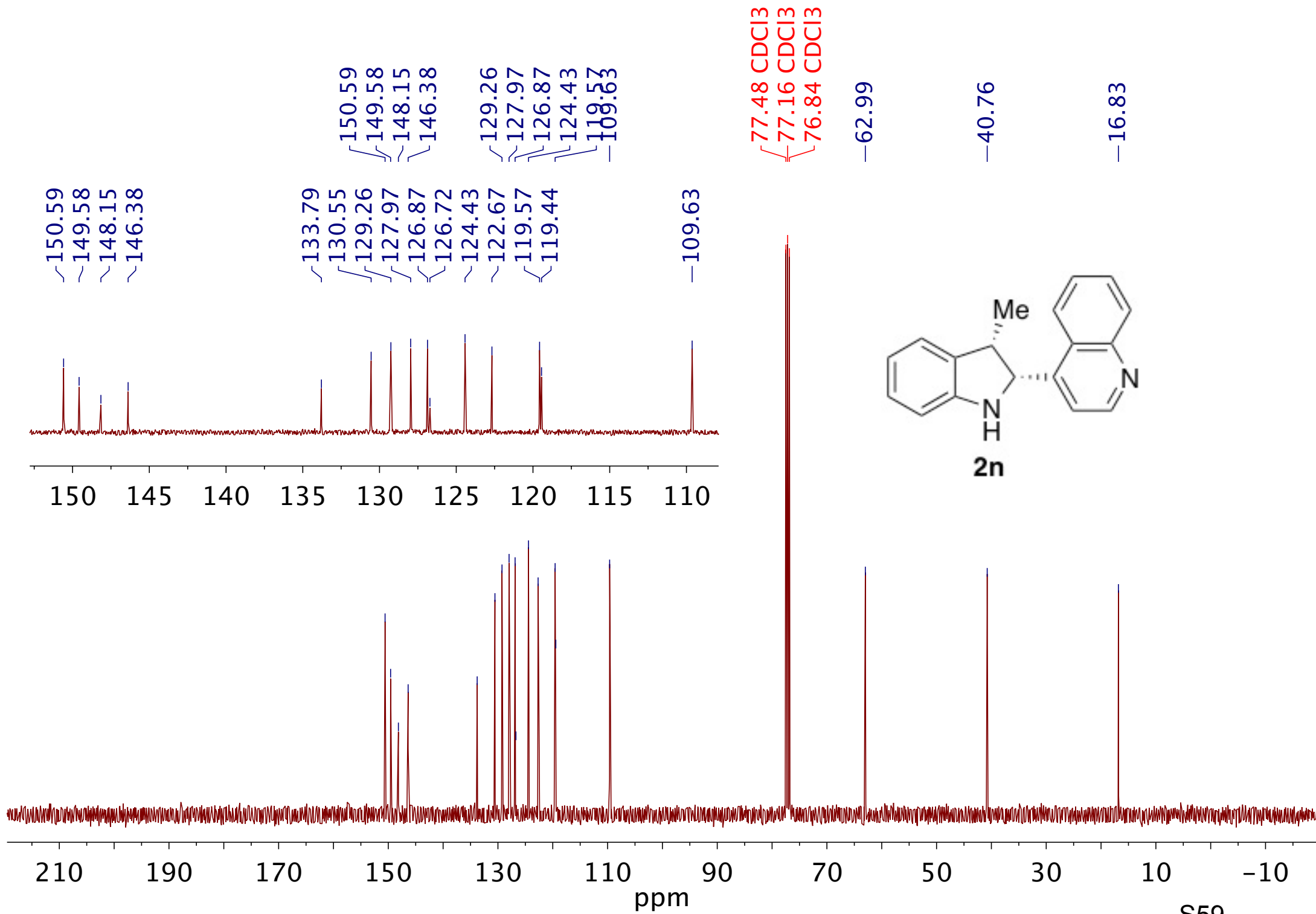


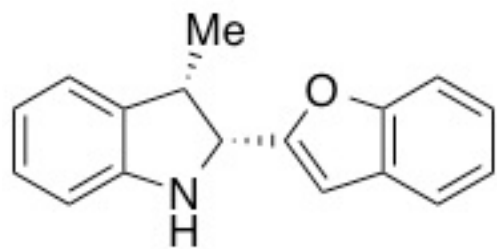


2m

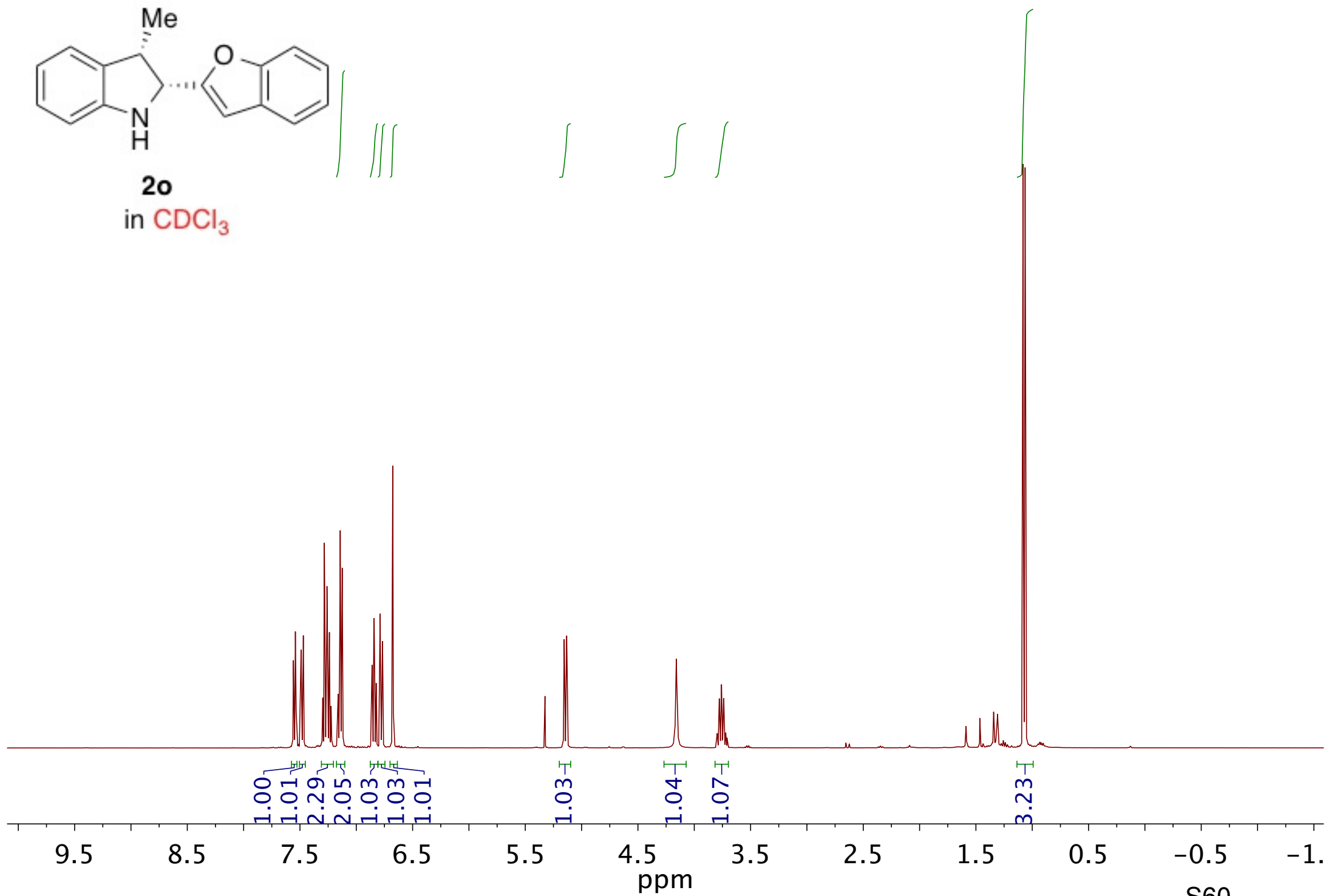




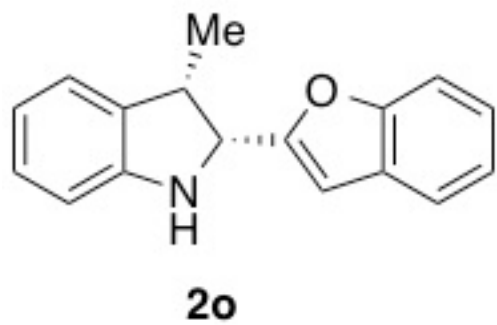




**2o**  
in  $\text{CDCl}_3$







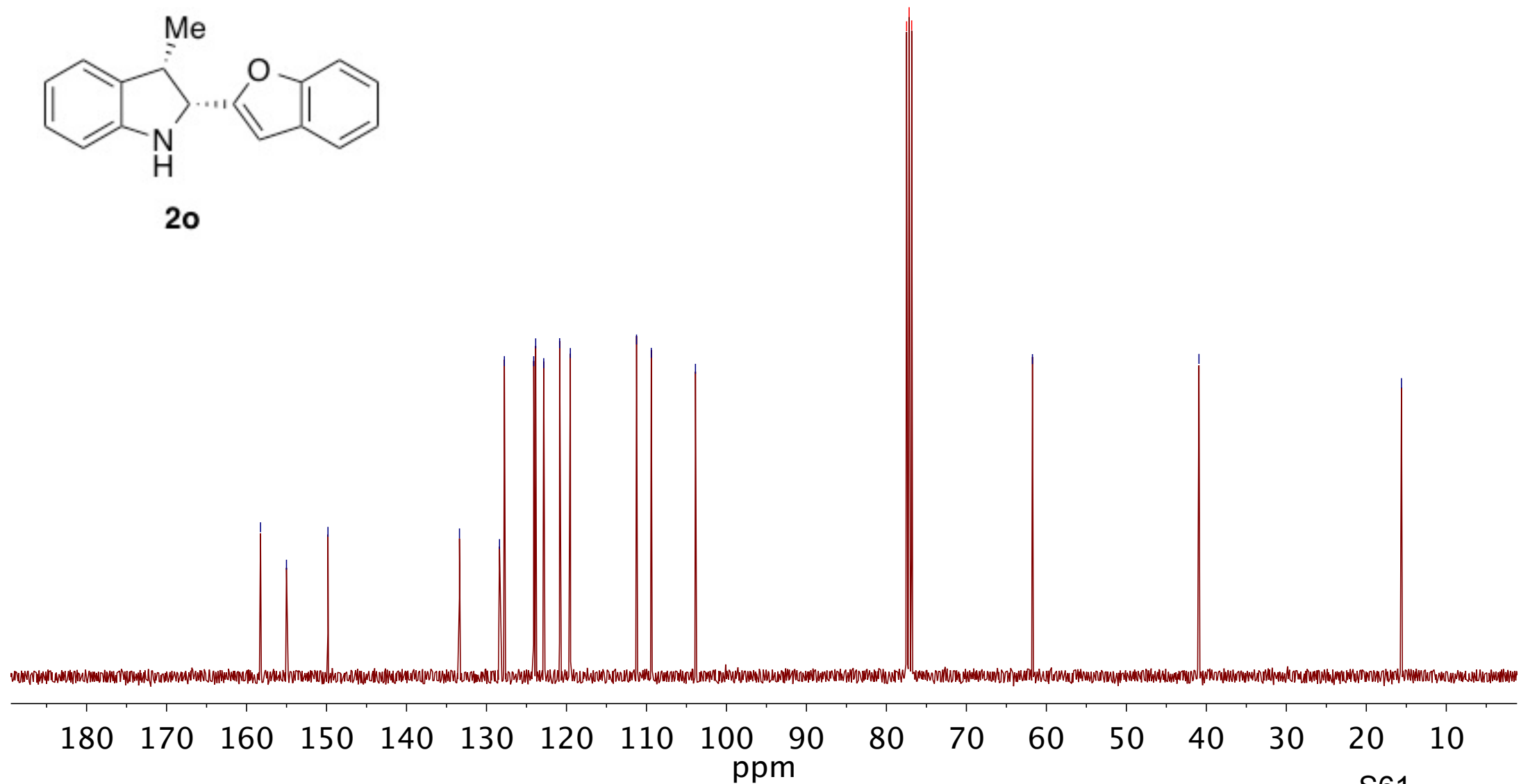
~158.26  
~155.01  
~149.82  
133.38  
128.37  
127.77  
124.10  
123.85  
122.84  
120.86  
119.52  
111.24  
109.40  
103.88

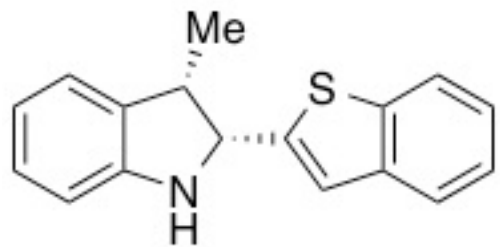
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

-61.74

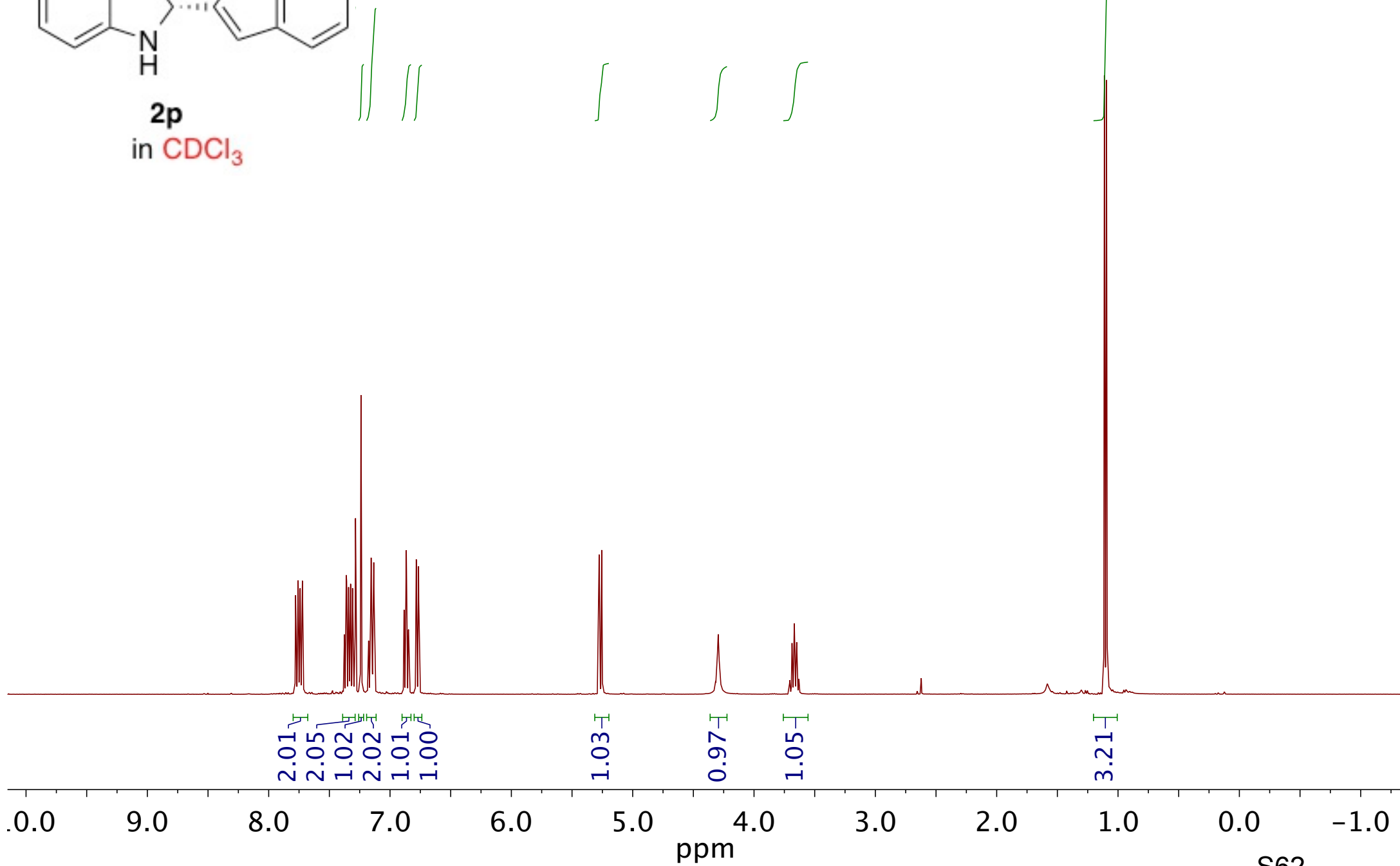
-40.92

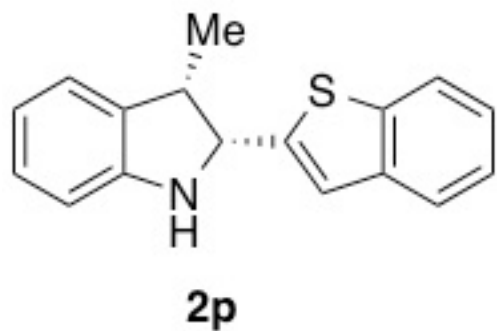
-15.60





**2p**  
in  $\text{CDCl}_3$





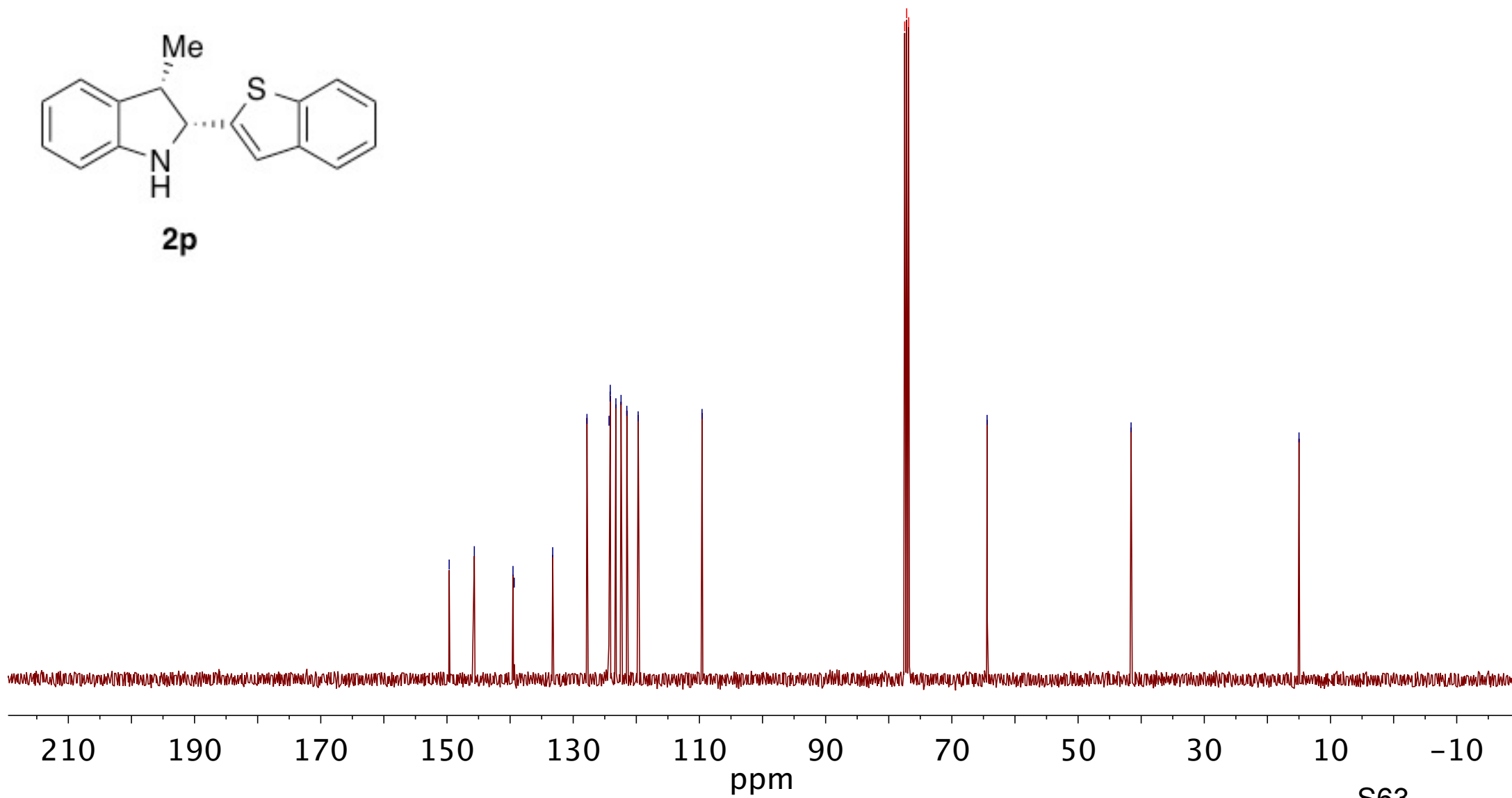
149.65  
145.67  
139.54  
139.35  
133.25  
127.82  
124.33  
124.16  
124.13  
123.24  
122.42  
121.50  
119.71  
109.58

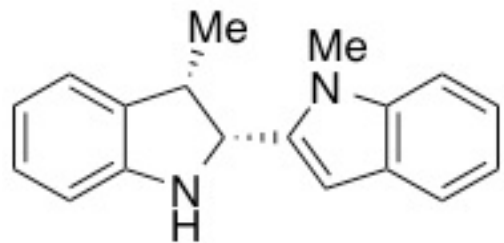
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

64.42

41.60

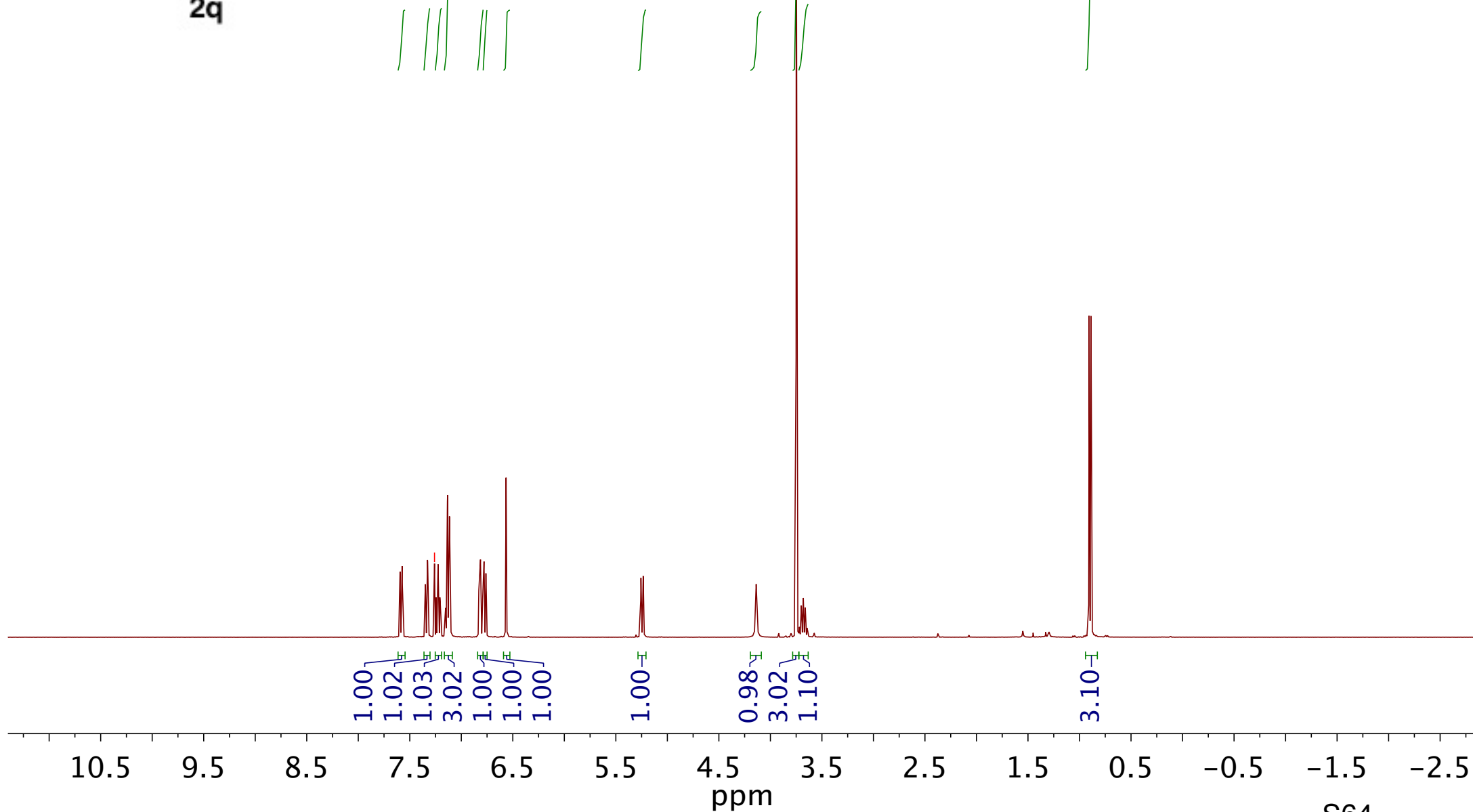
14.99

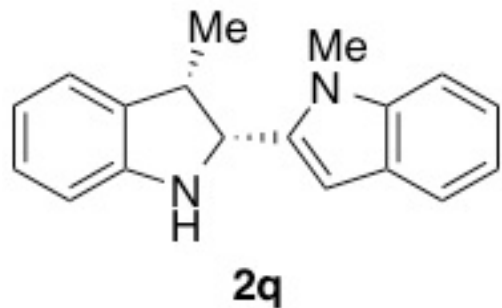




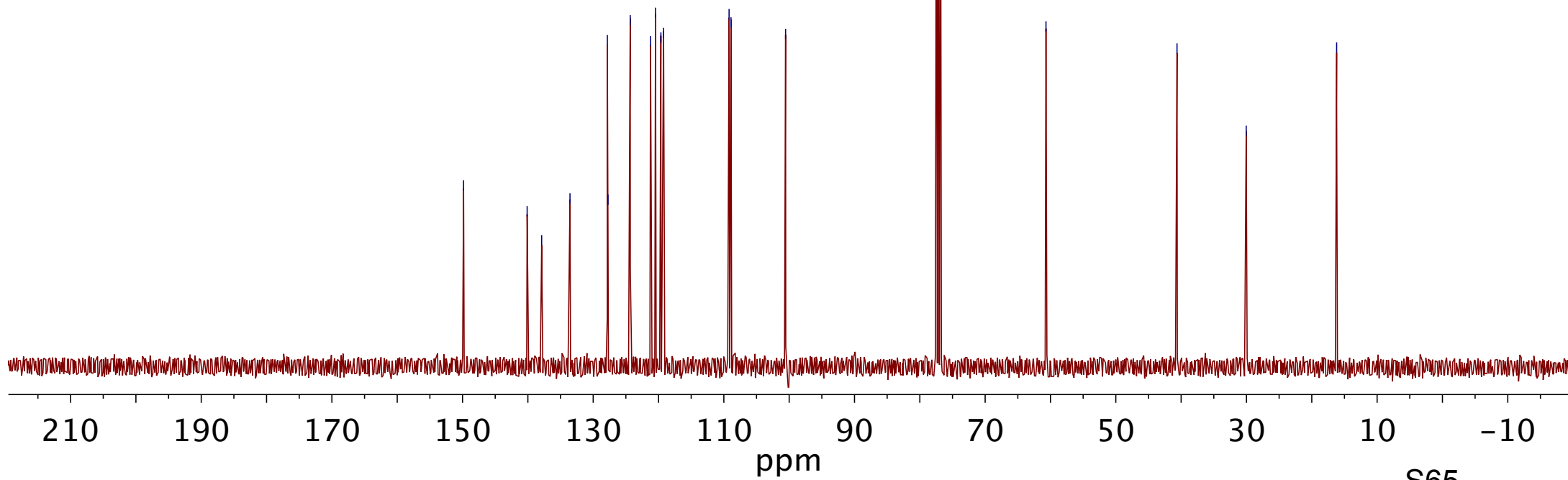
2q

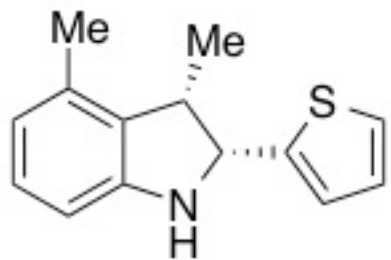
-7.26 CDCl<sub>3</sub>



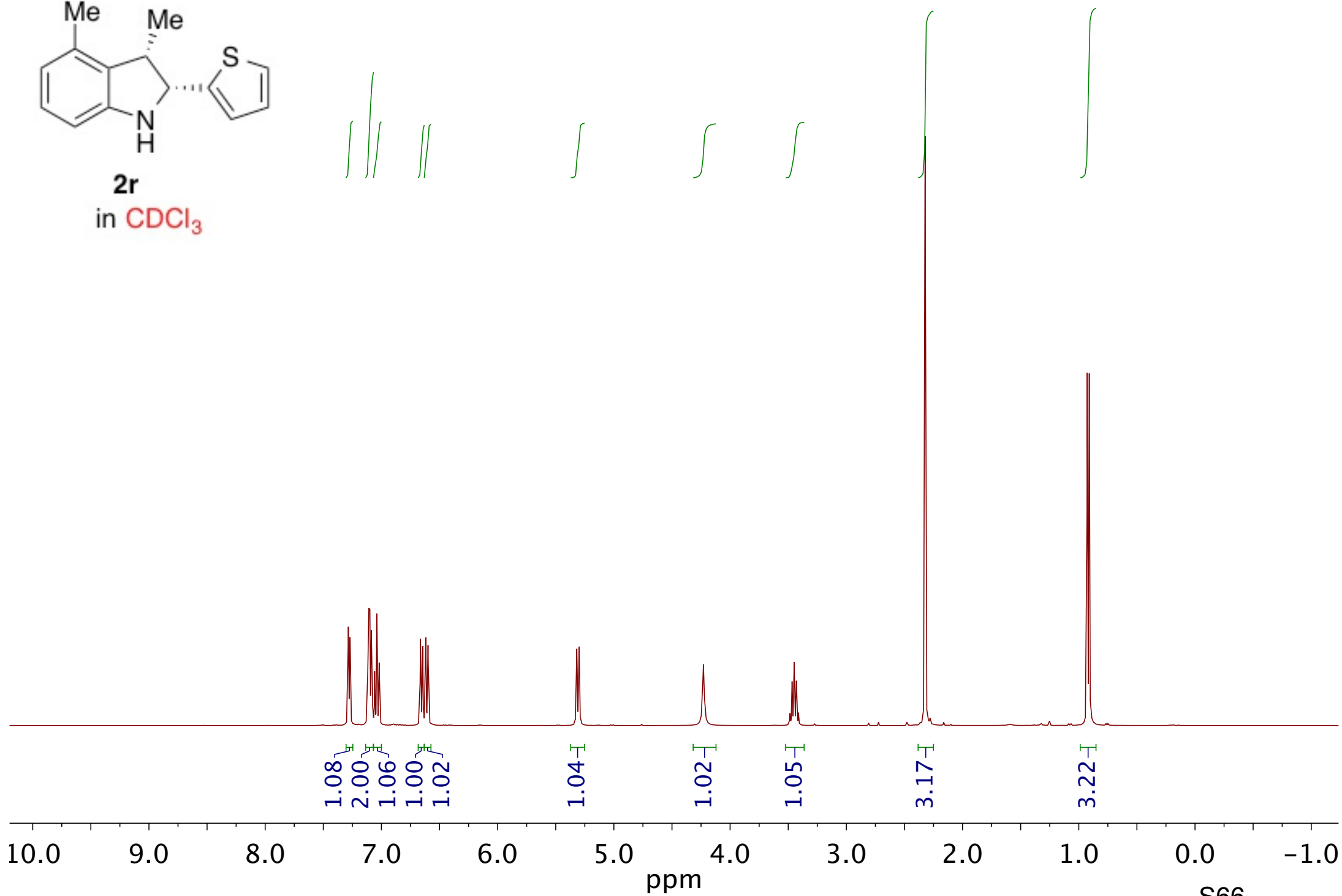


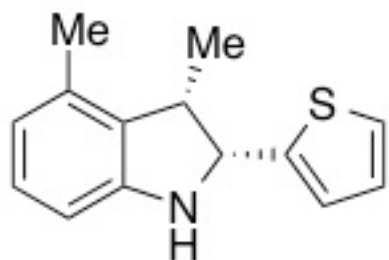
-149.84  
 133.55  
 127.83  
 124.33  
 121.22  
 120.46  
 119.64  
 109.23  
 108.91  
 ~100.55  
 77.48 CDCl<sub>3</sub>  
 77.16 CDCl<sub>3</sub>  
 76.84 CDCl<sub>3</sub>  
 -60.69  
 -40.63  
 -30.04  
 -16.20





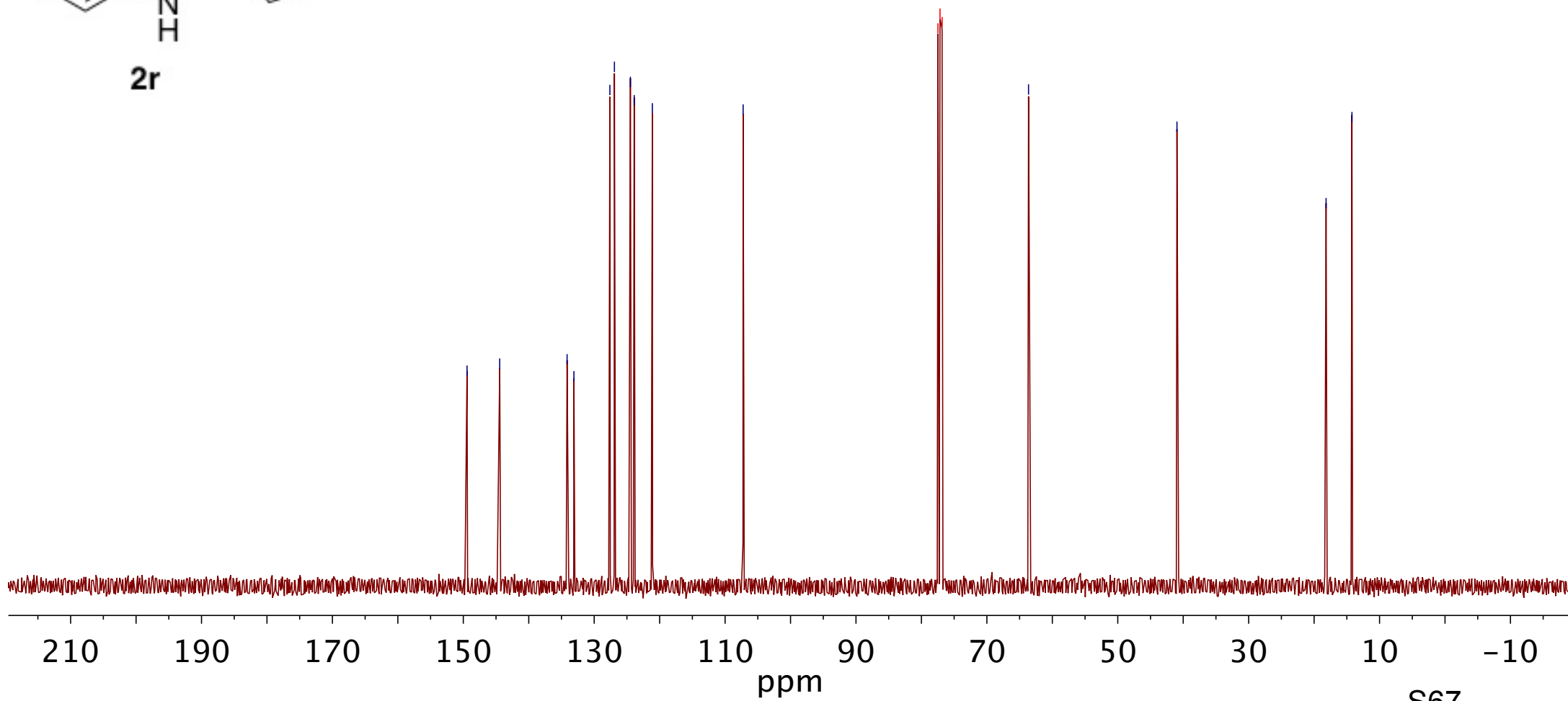
**2r**  
in  $\text{CDCl}_3$



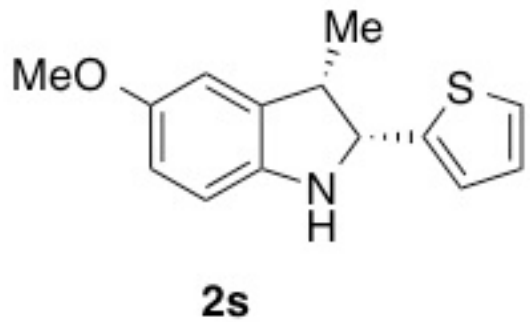


2r

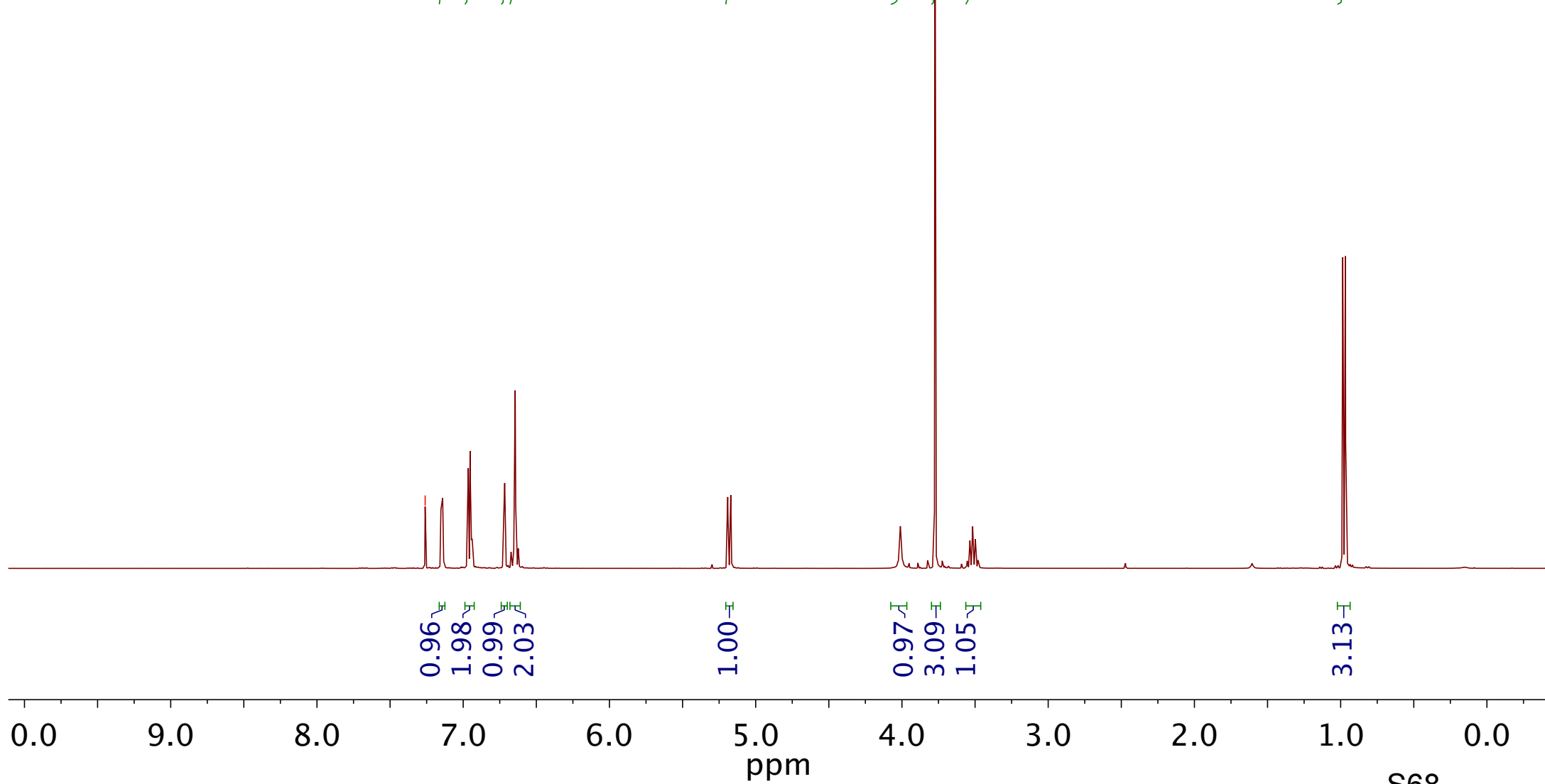
149.43  
144.44  
134.14  
127.60  
126.91  
124.47  
123.89  
121.13  
117.25  
77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3  
63.64  
40.96  
18.17  
14.22



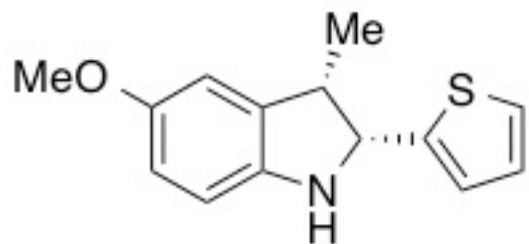
S67



-7.26 CDCl<sub>3</sub>







2s

154.13  
144.82  
143.58  
135.17  
126.59  
124.71  
123.94  
112.31  
111.24  
109.93

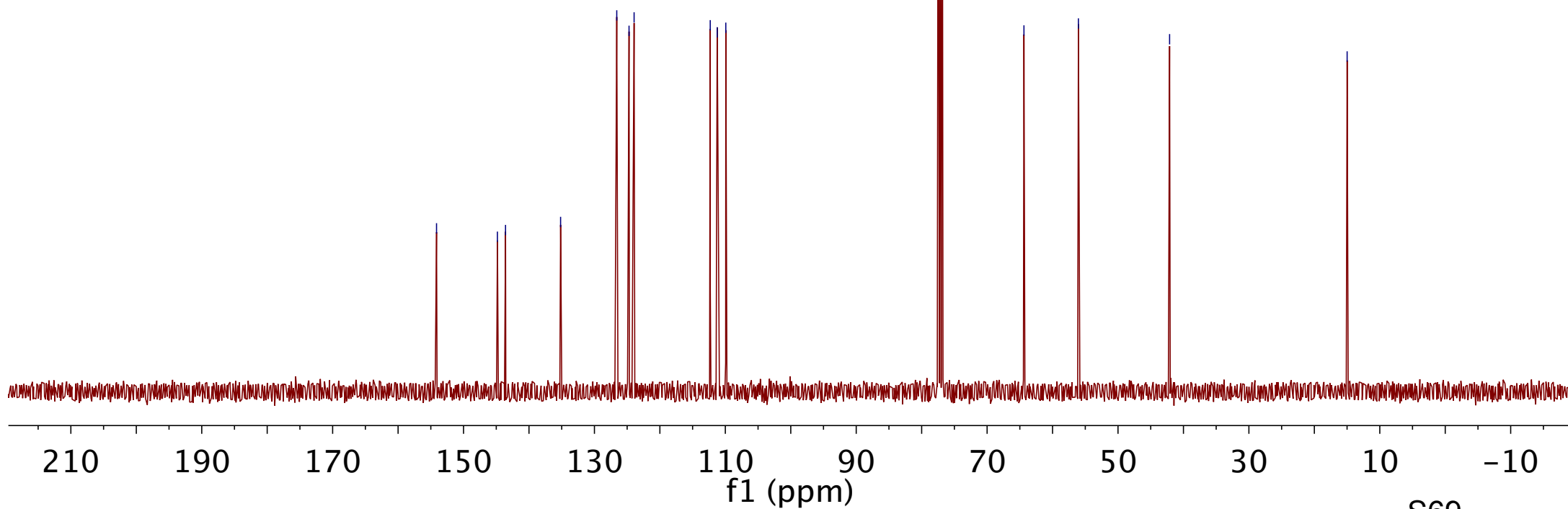
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

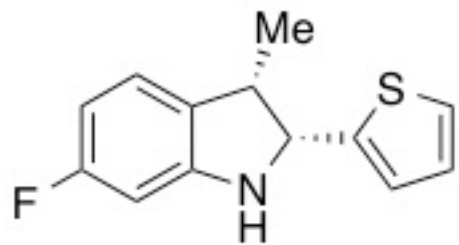
64.37

56.05

42.12

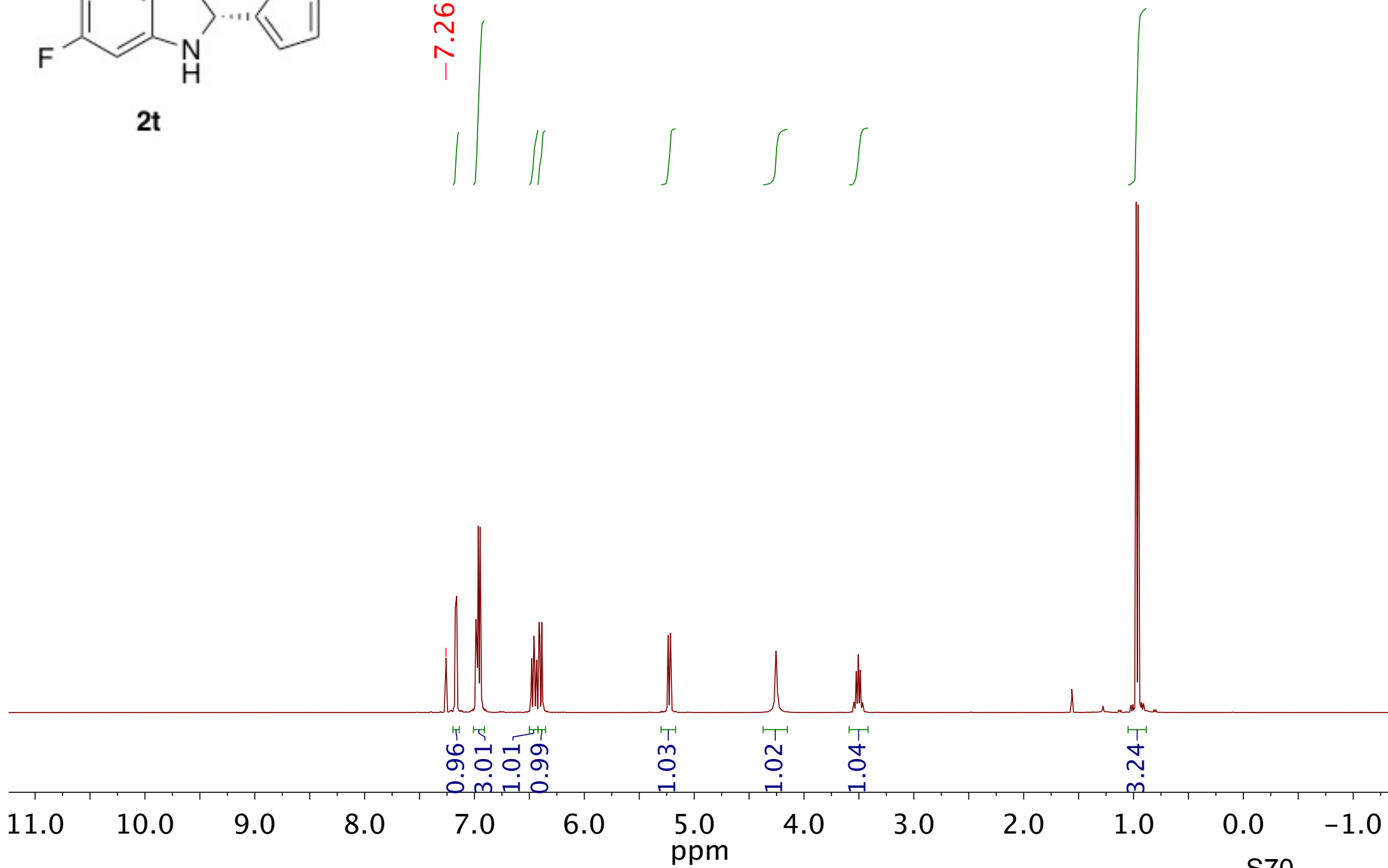
14.99

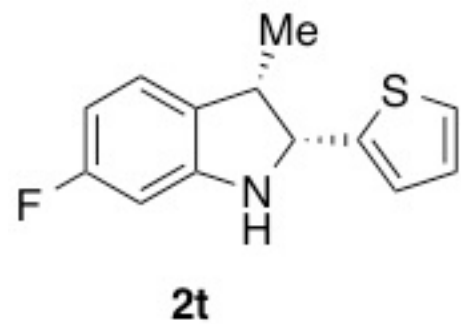




**2t**

-7.26 CDCl<sub>3</sub>





~164.51  
~162.11

151.26  
151.14  
144.20

128.78  
128.76  
126.70  
124.88  
124.61  
124.50  
124.16

105.50  
105.28

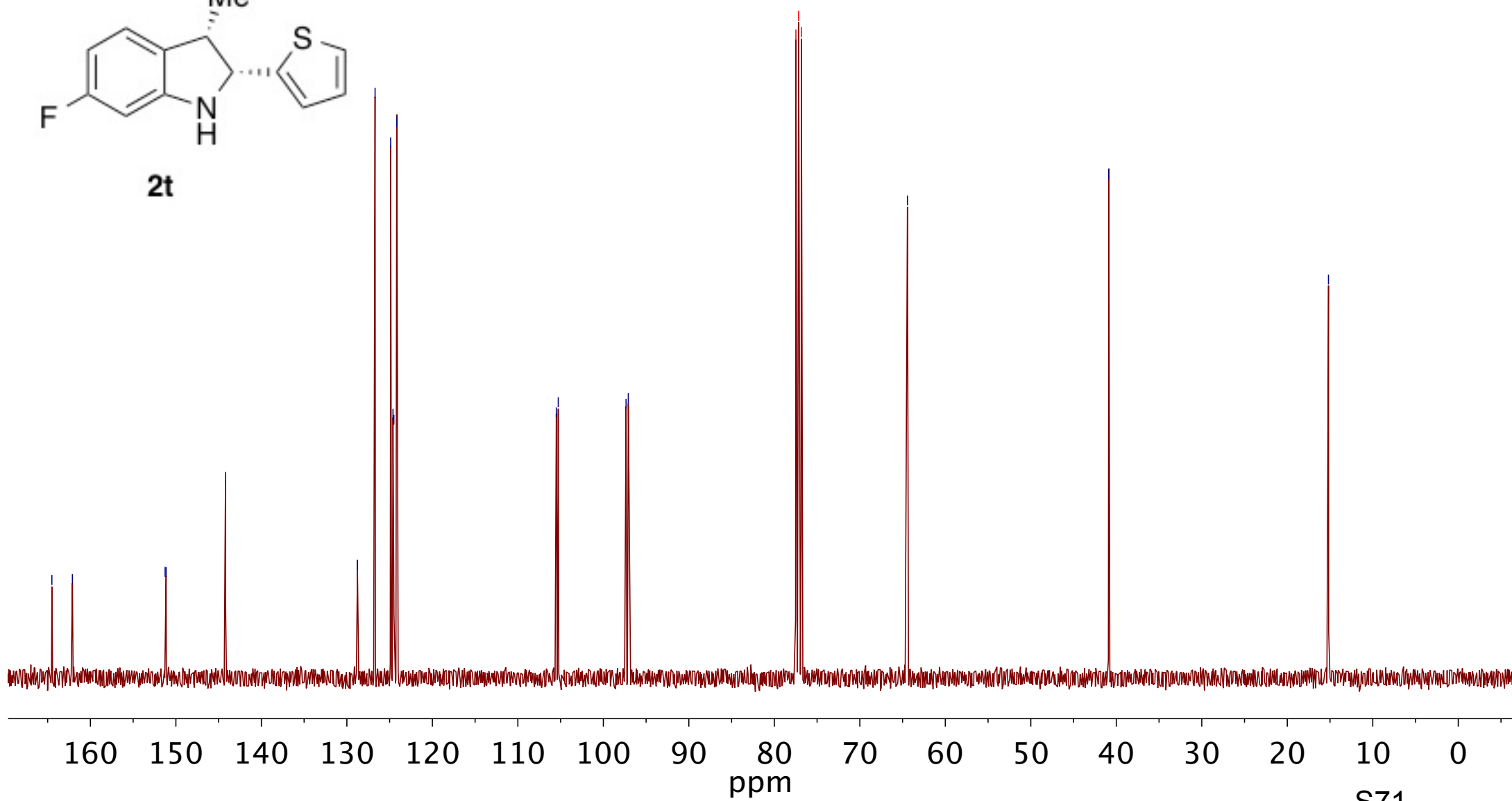
97.34  
97.08

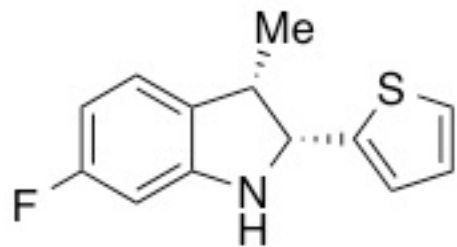
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

64.43

40.88

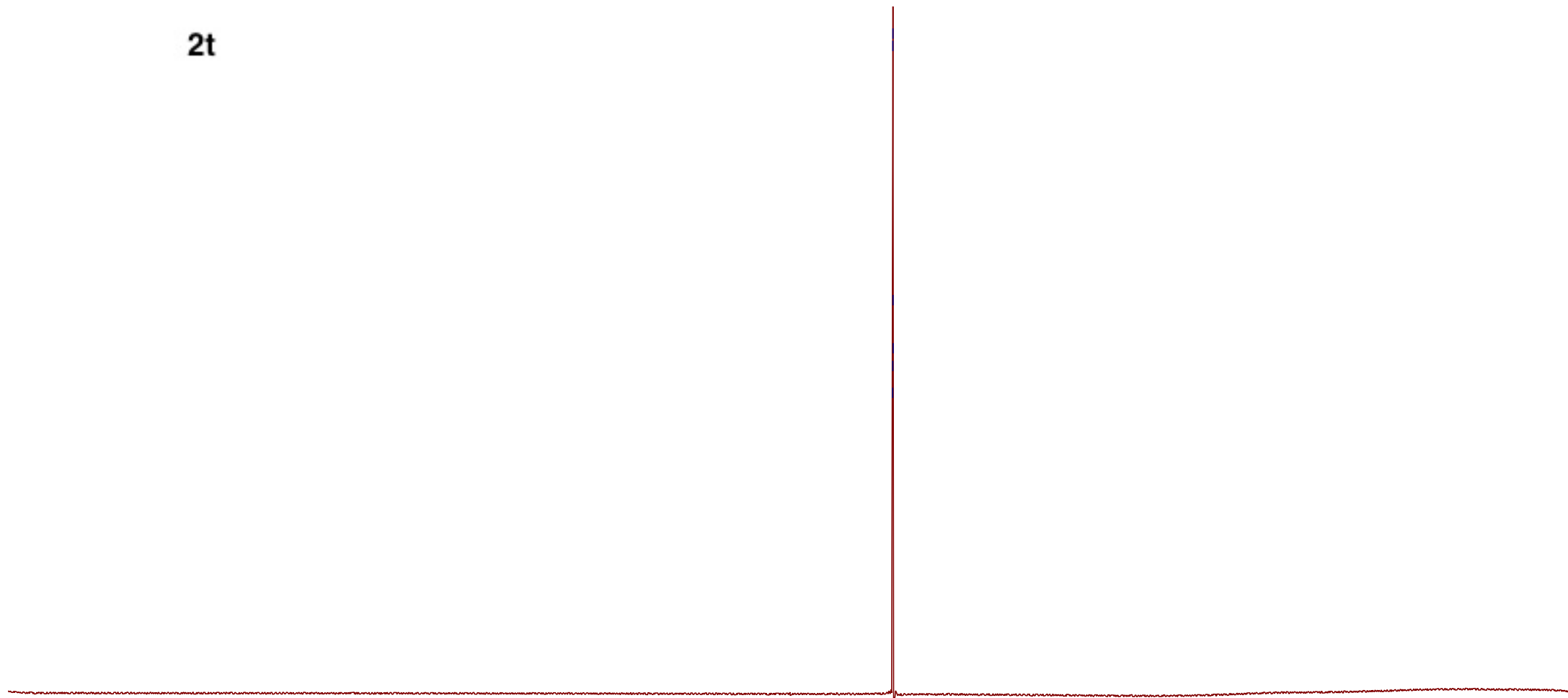
15.18



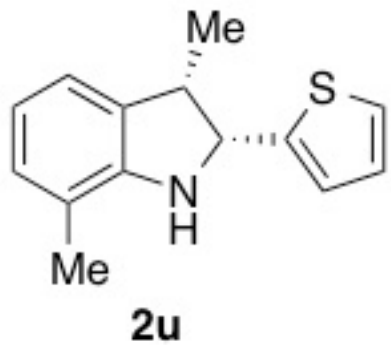


2t

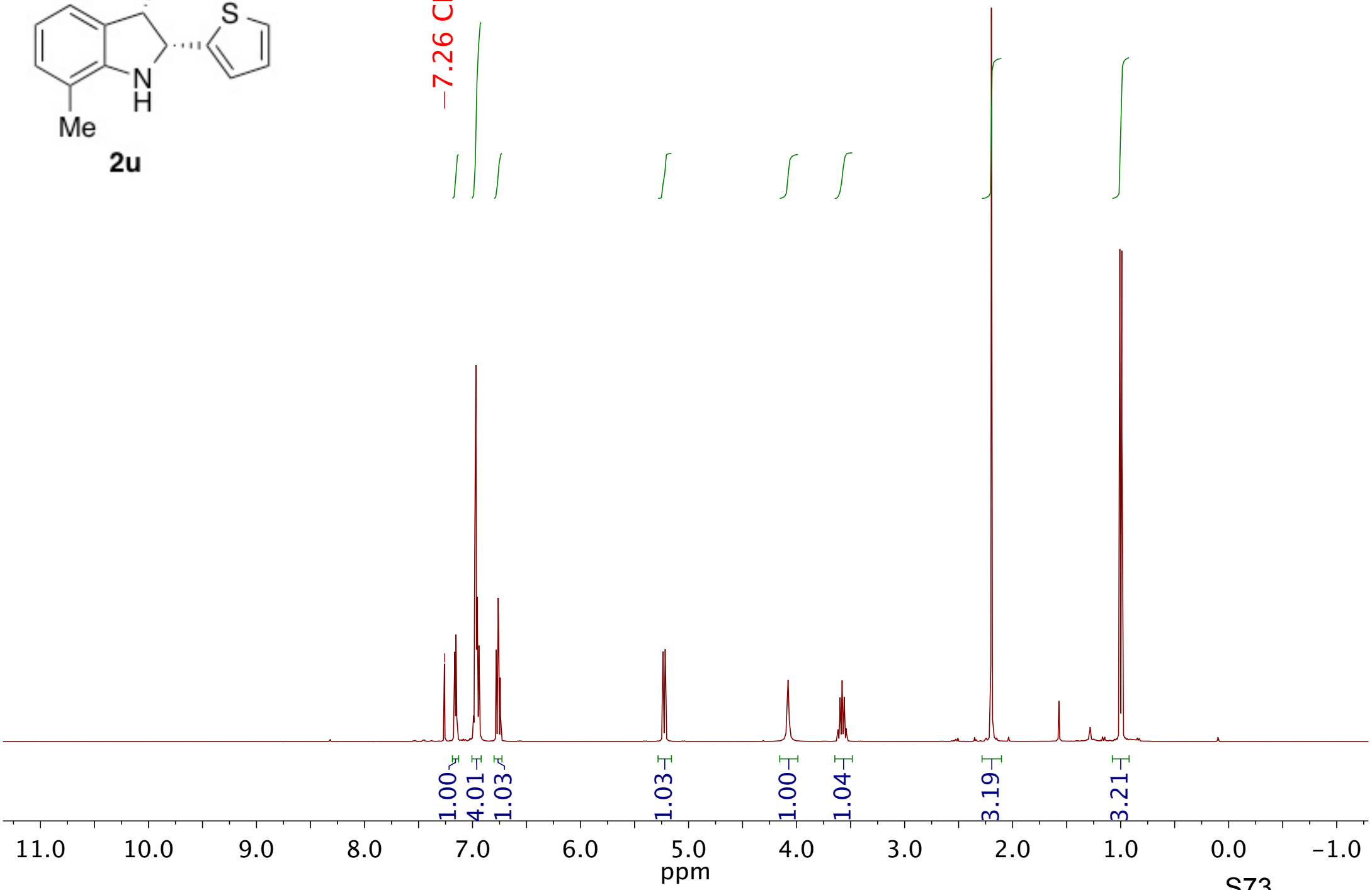
115.57  
115.58  
115.59  
115.61  
115.62  
115.63

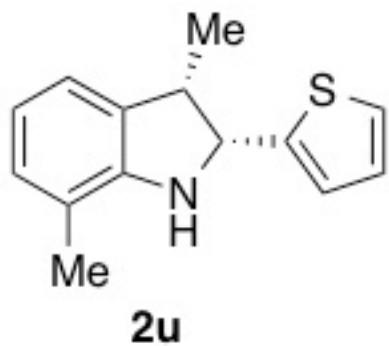


10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210  
ppm



-7.26 CDCl3





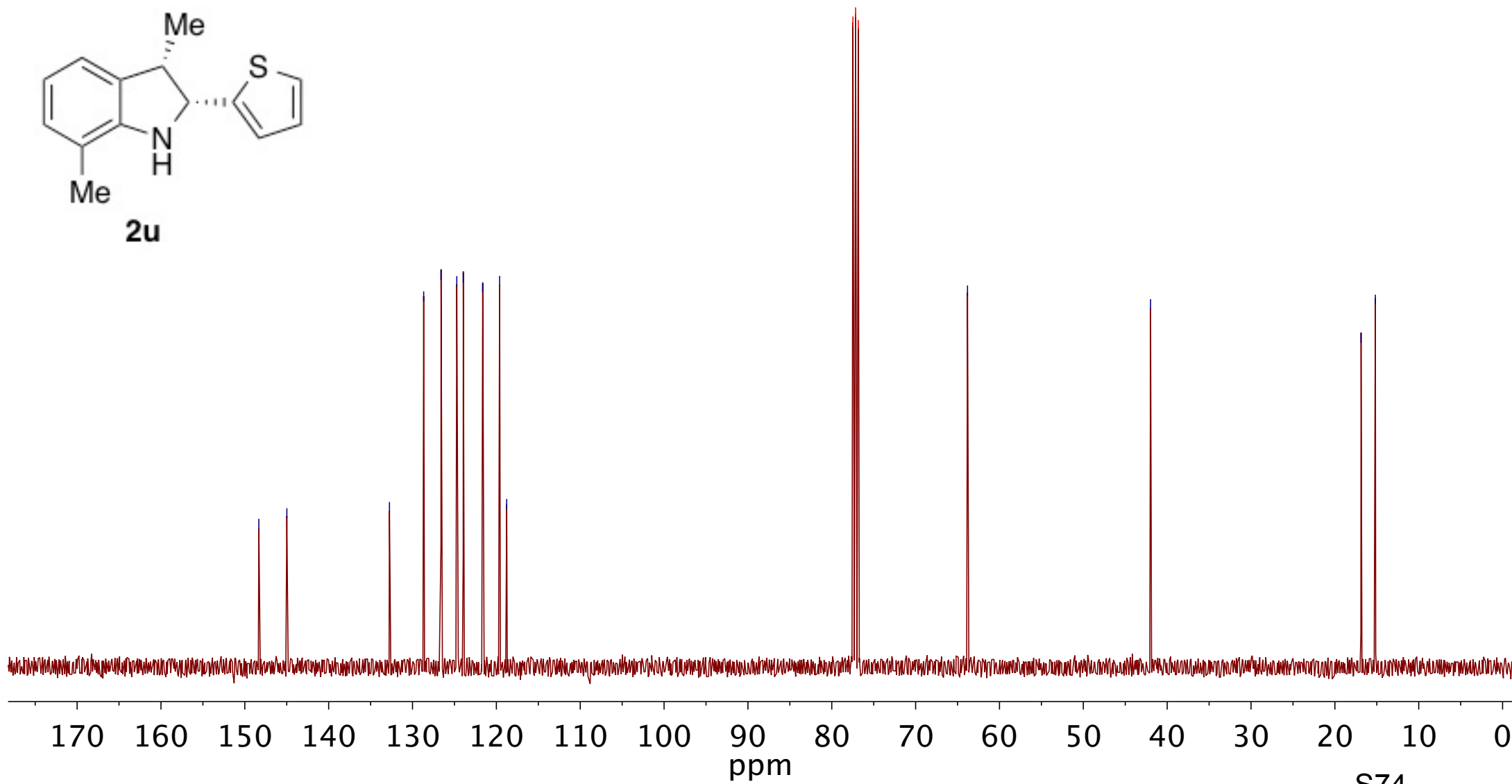
148.33  
144.99  
132.75  
128.67  
126.60  
124.72  
123.95  
121.63  
119.61  
118.77

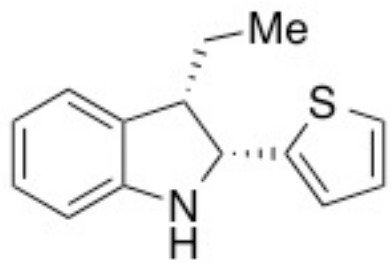
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

63.82

41.98

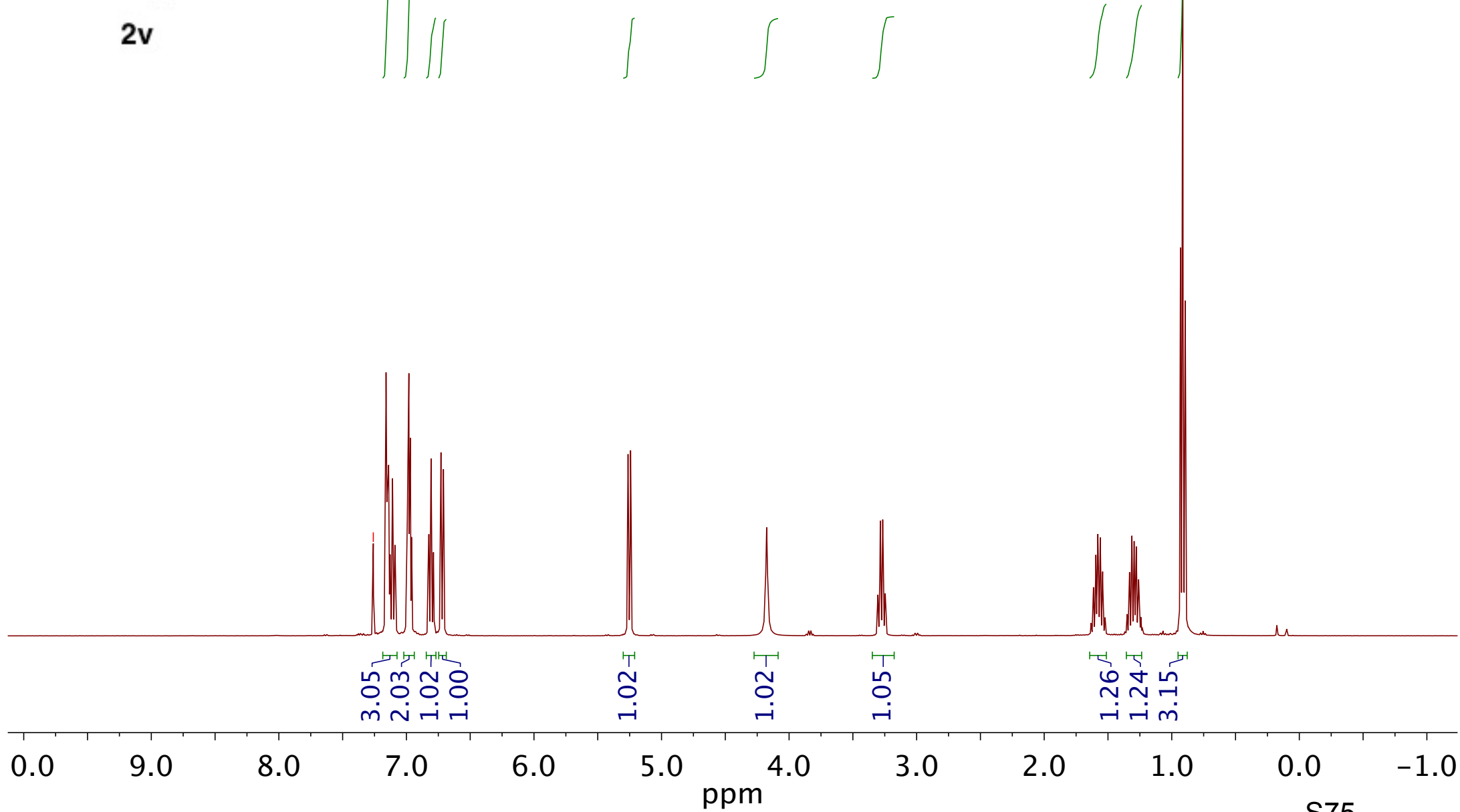
16.88  
15.17



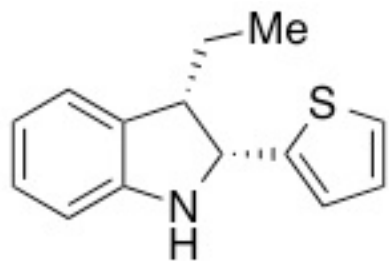


2v

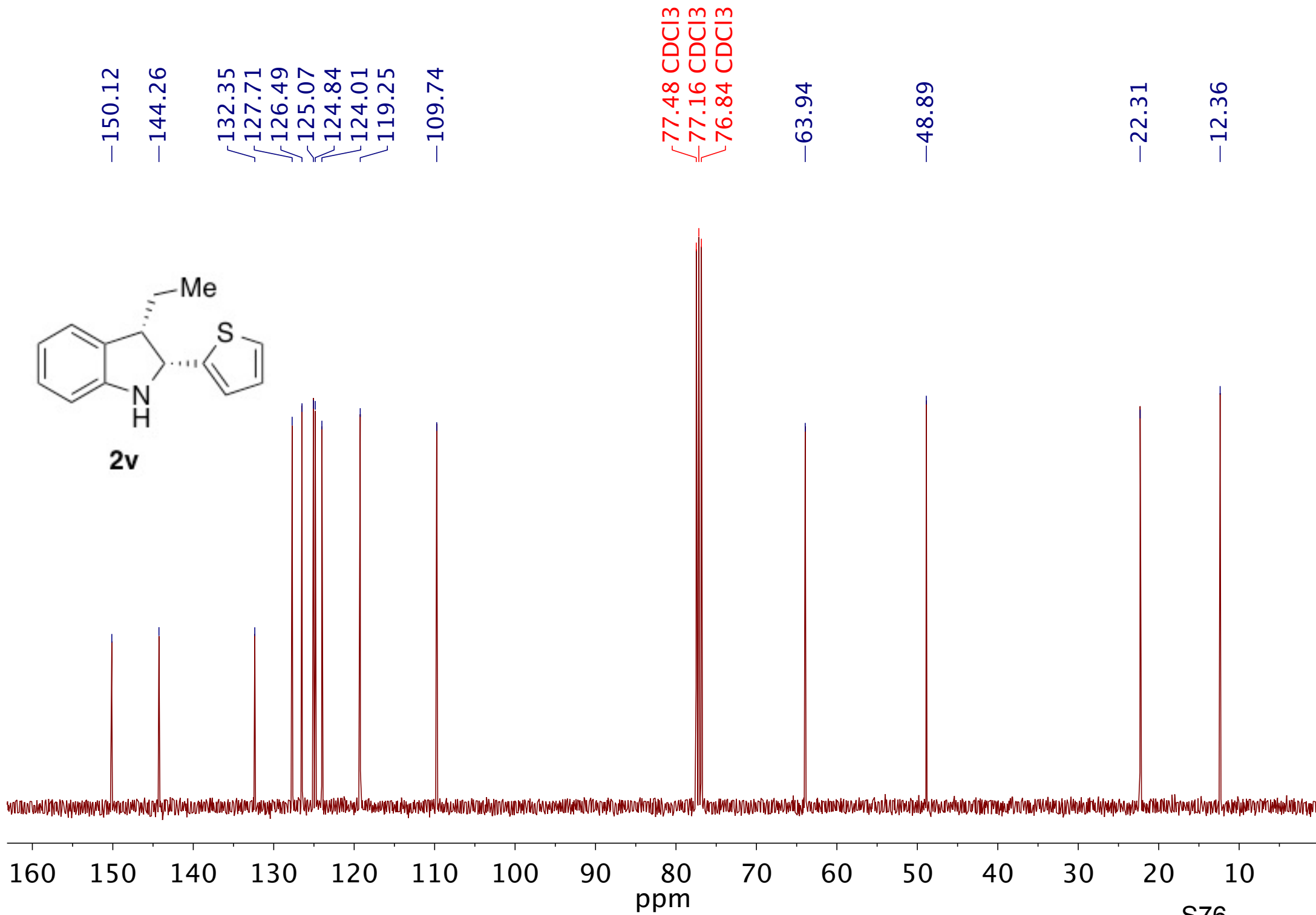
-7.26 CDCl<sub>3</sub>



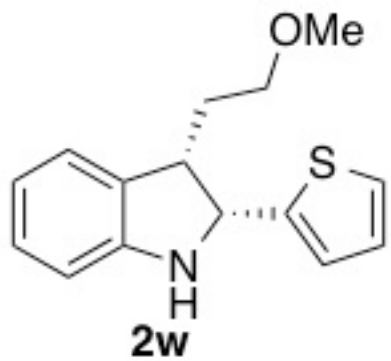
S75



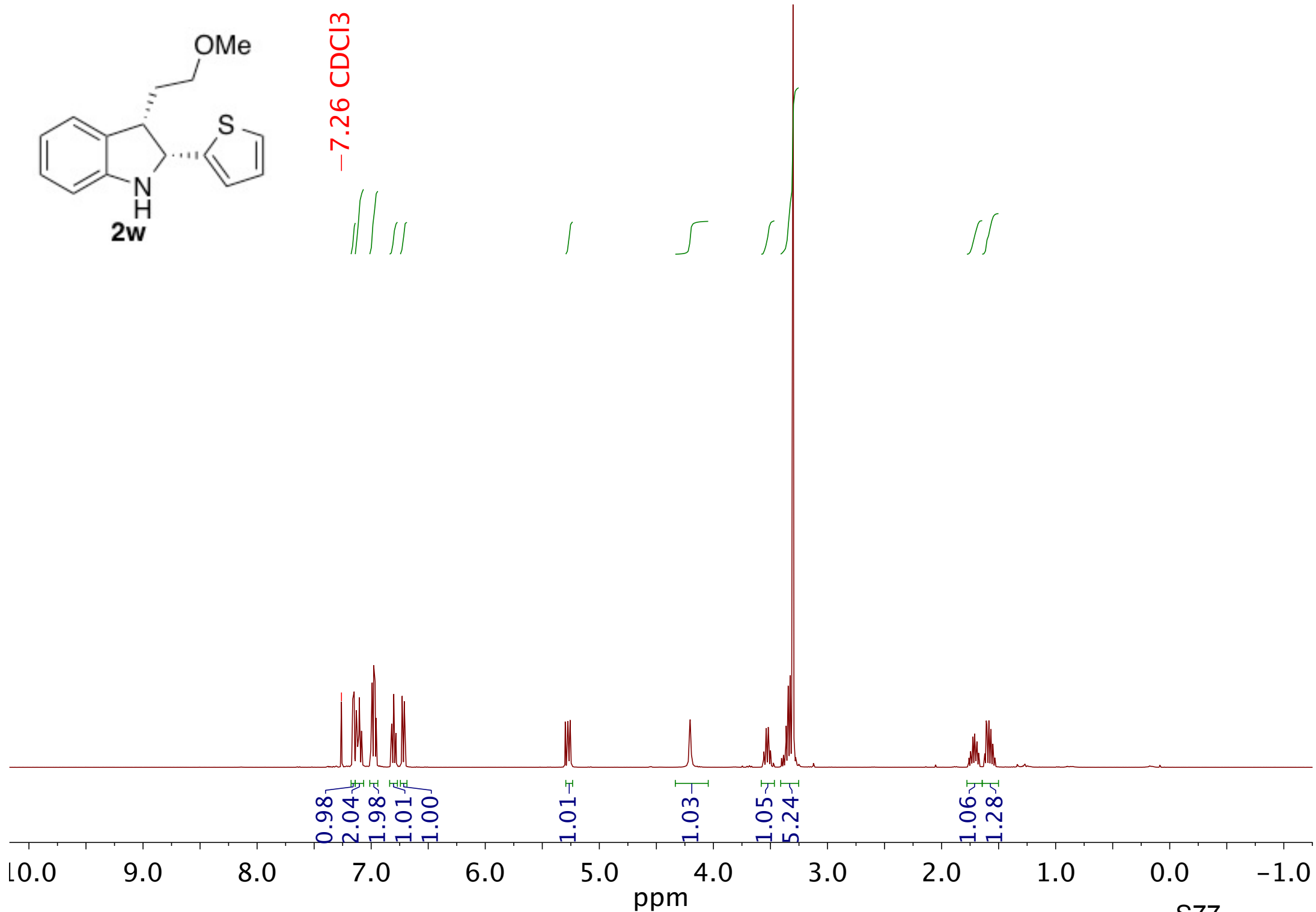
2v

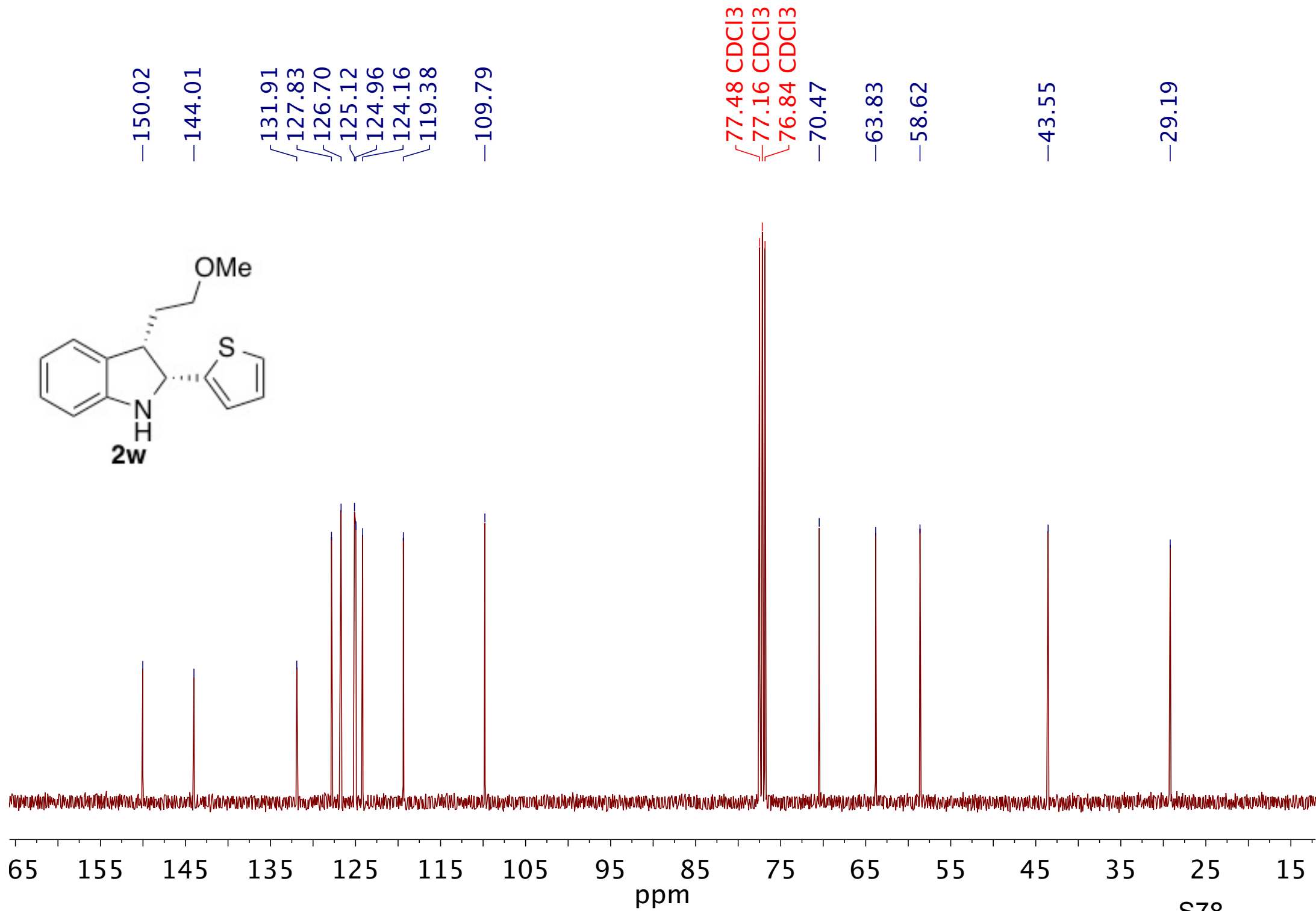
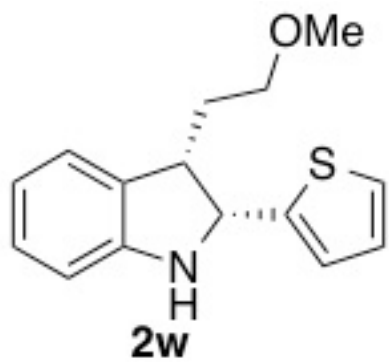


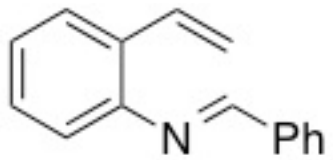




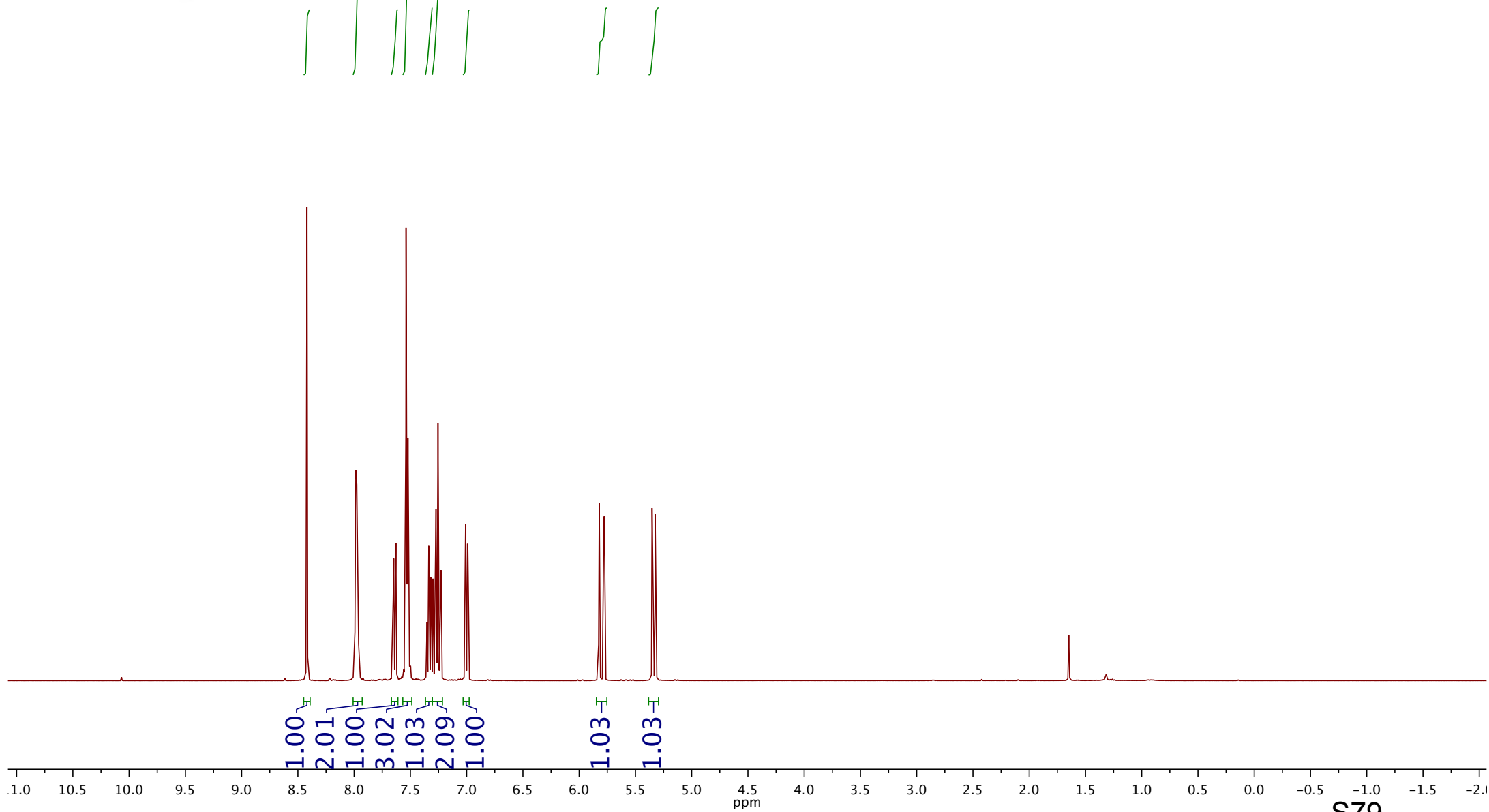
-7.26 CDCl<sub>3</sub>

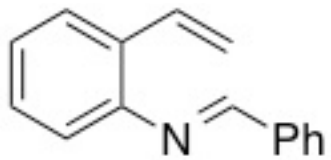






**1a**  
in CDCl<sub>3</sub>





**1a**

—160.25

—149.98

136.43

133.45

131.51

131.36

128.97

128.91

128.89

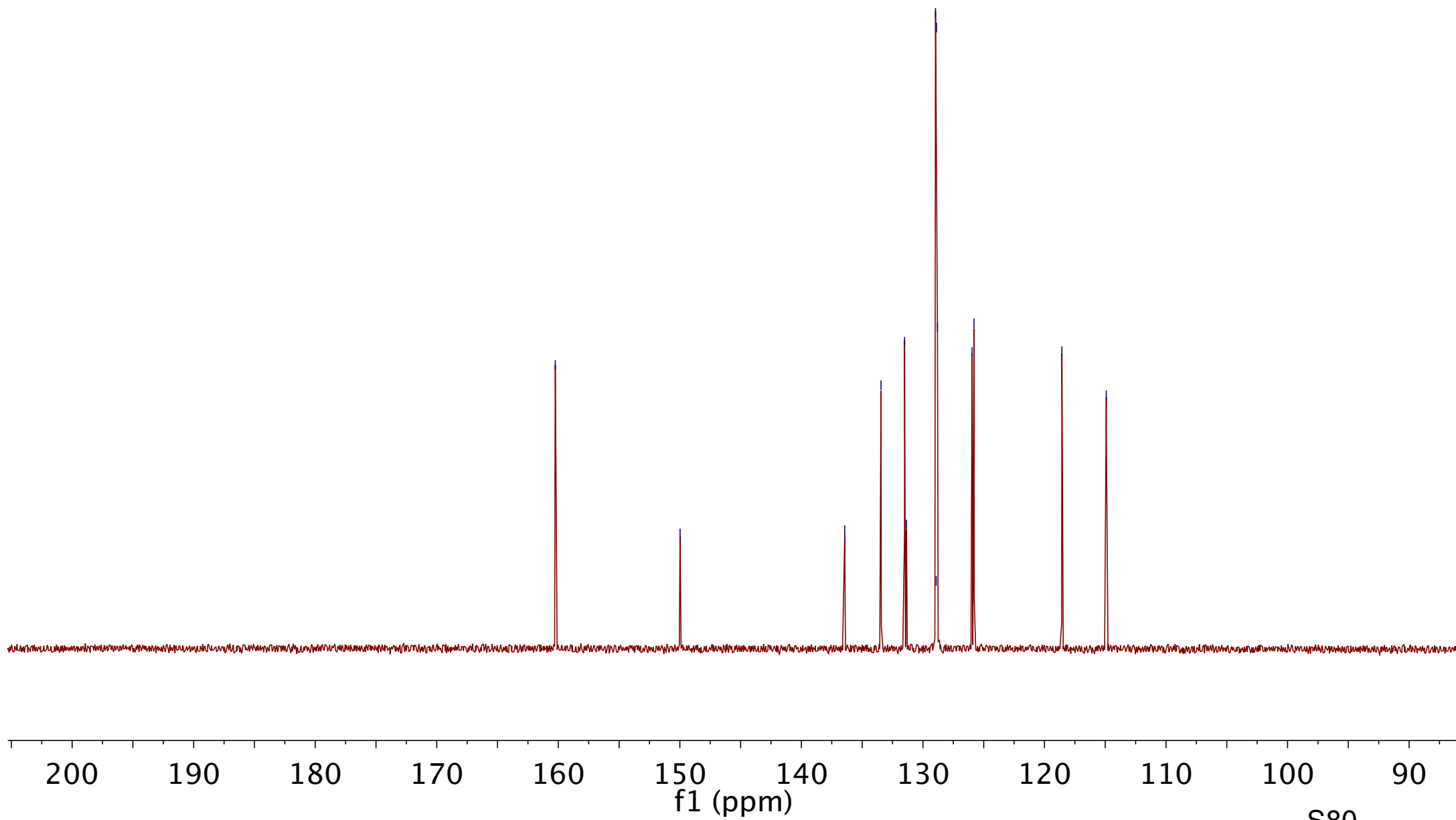
128.81

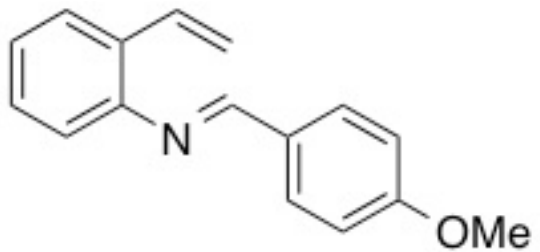
125.96

125.80

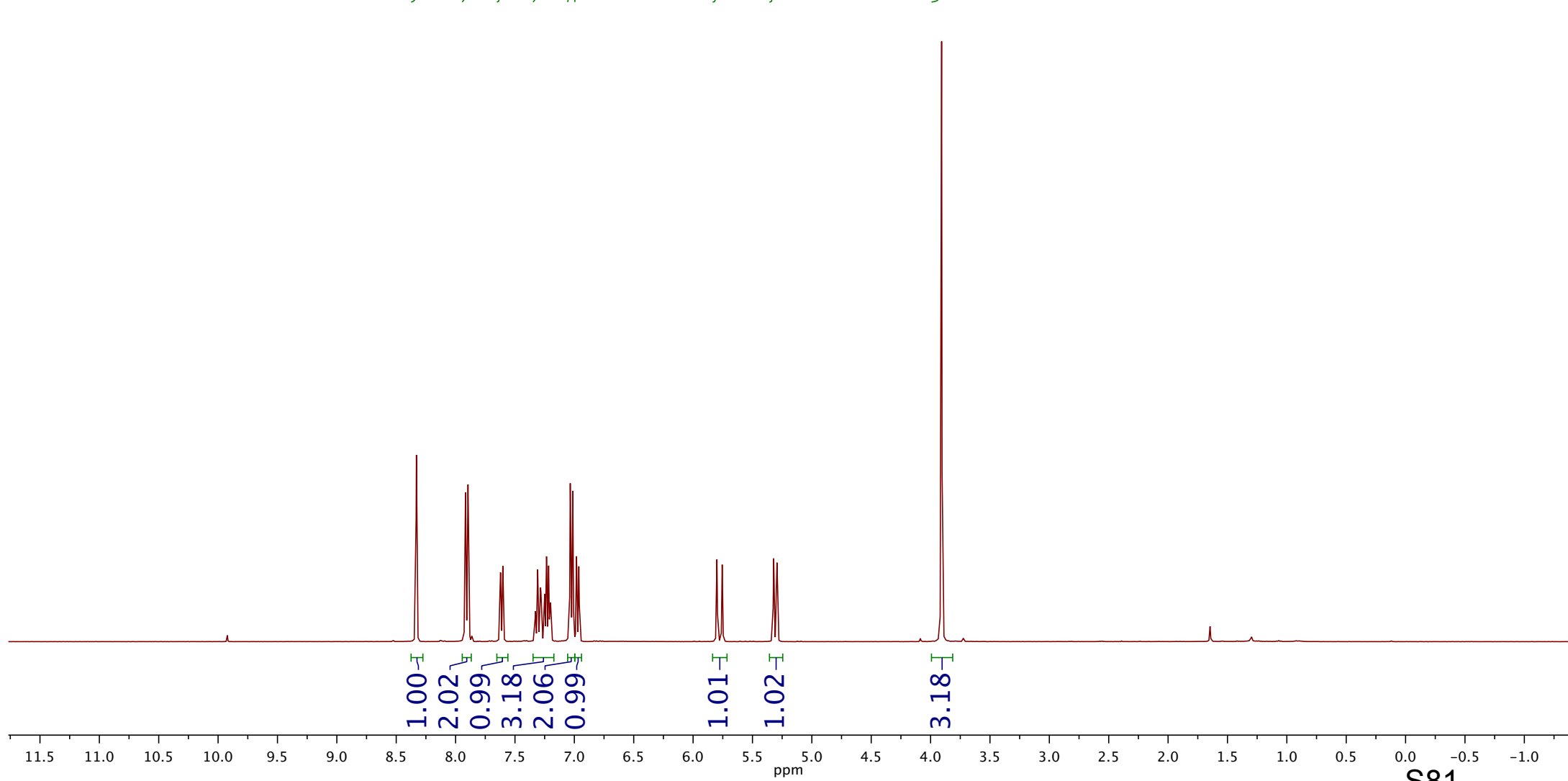
118.57

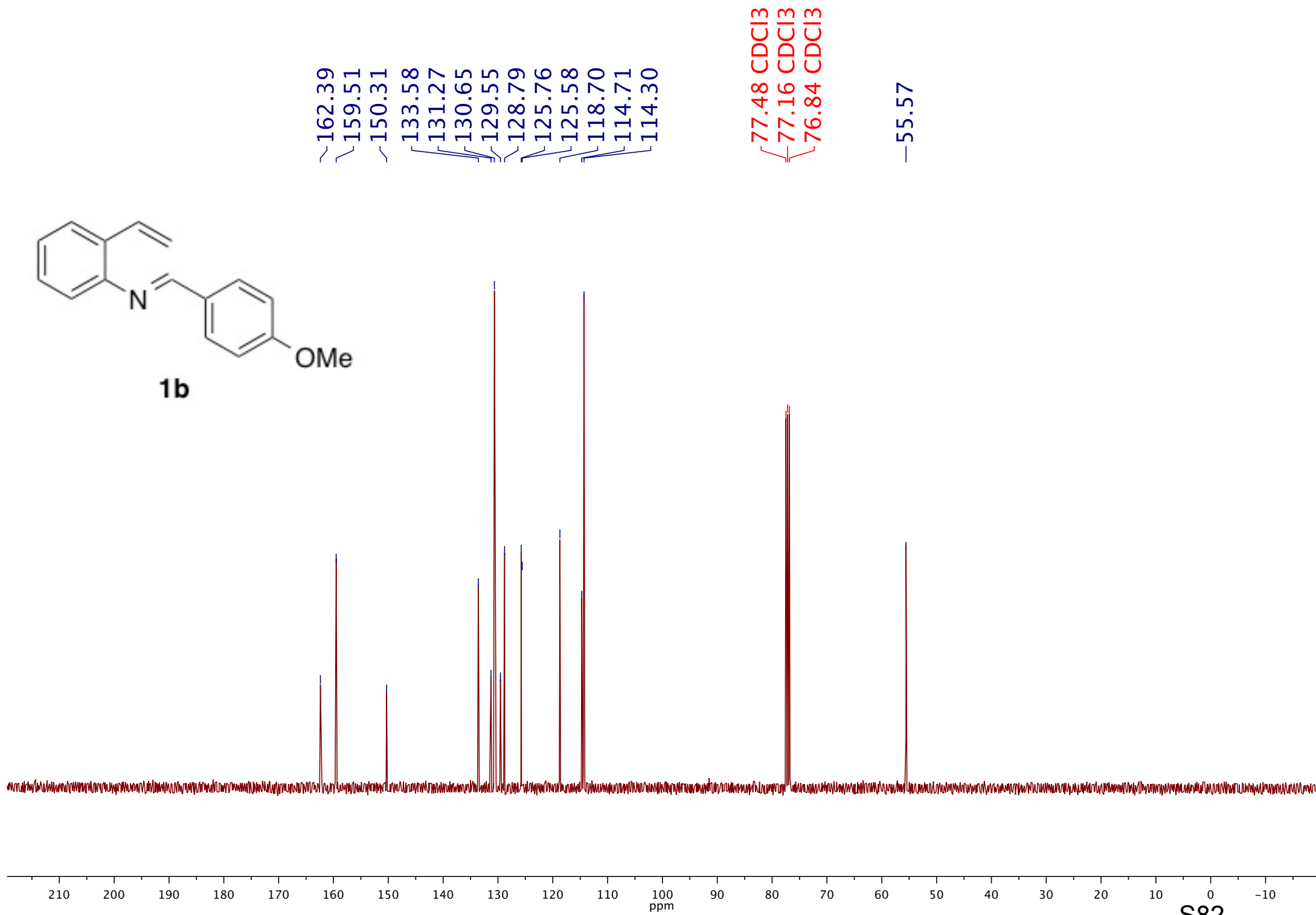
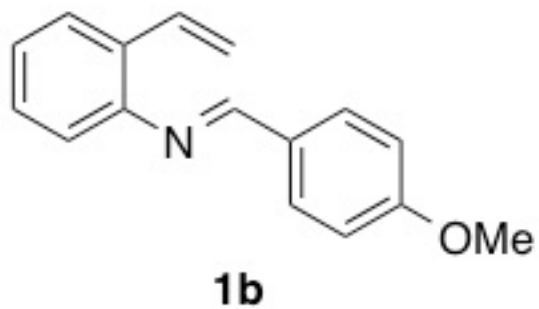
—114.92

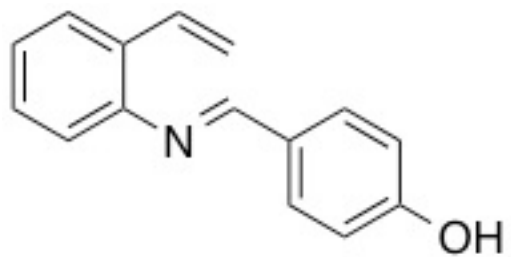




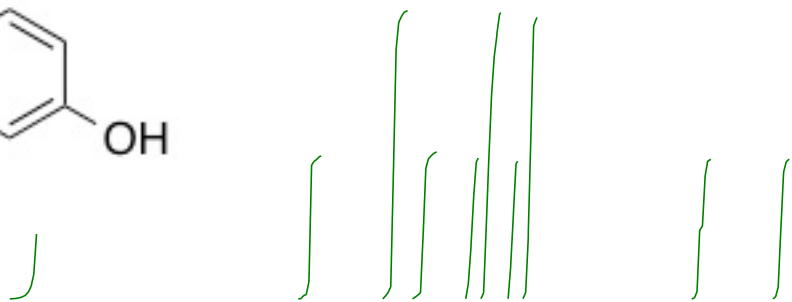
**1b**  
in CDCl<sub>3</sub>



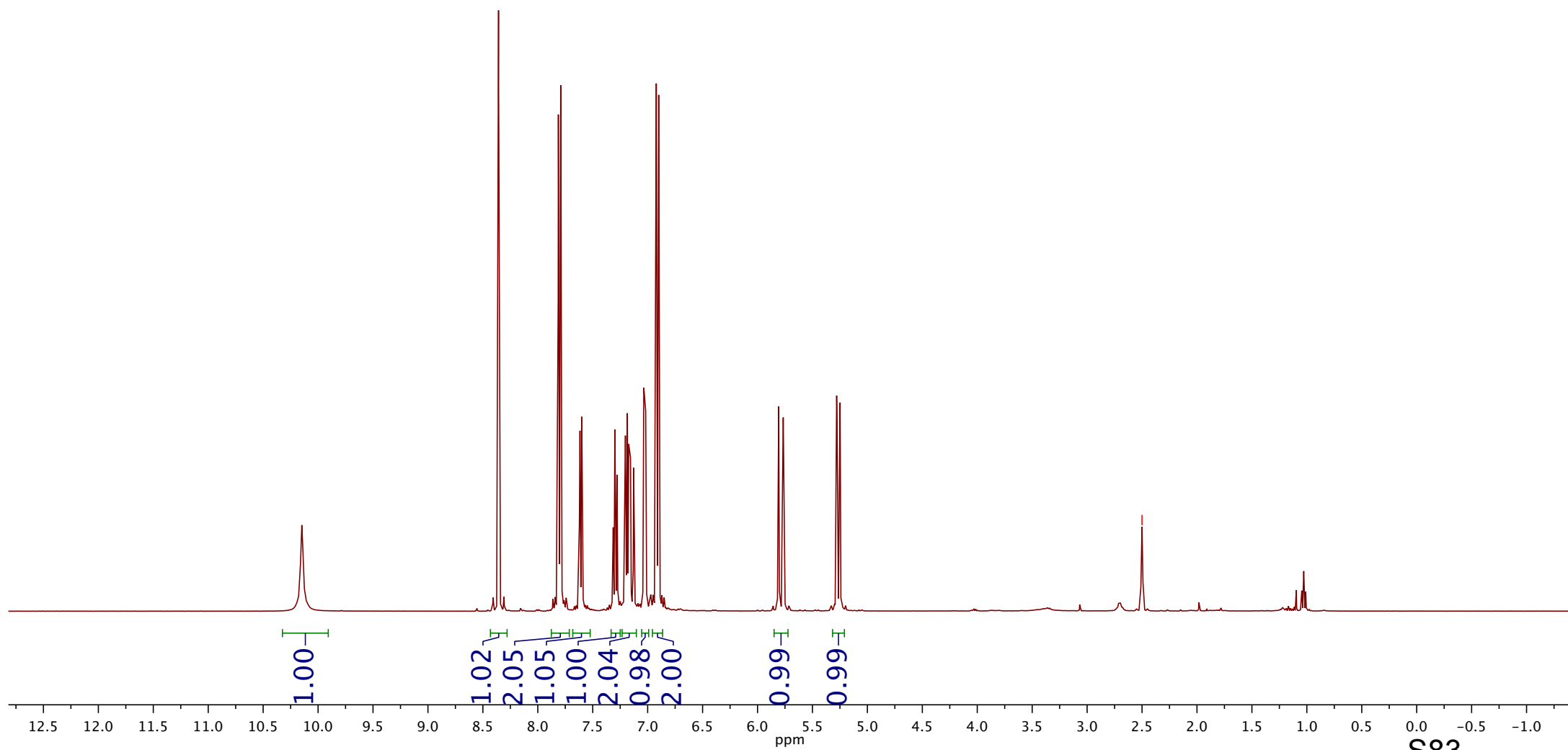




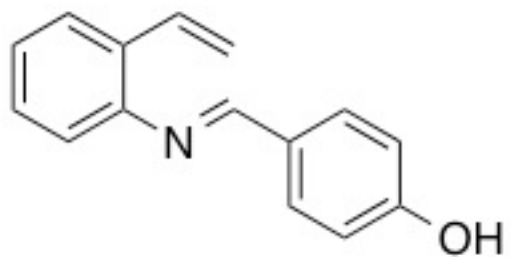
1c



-2.50 DMSO



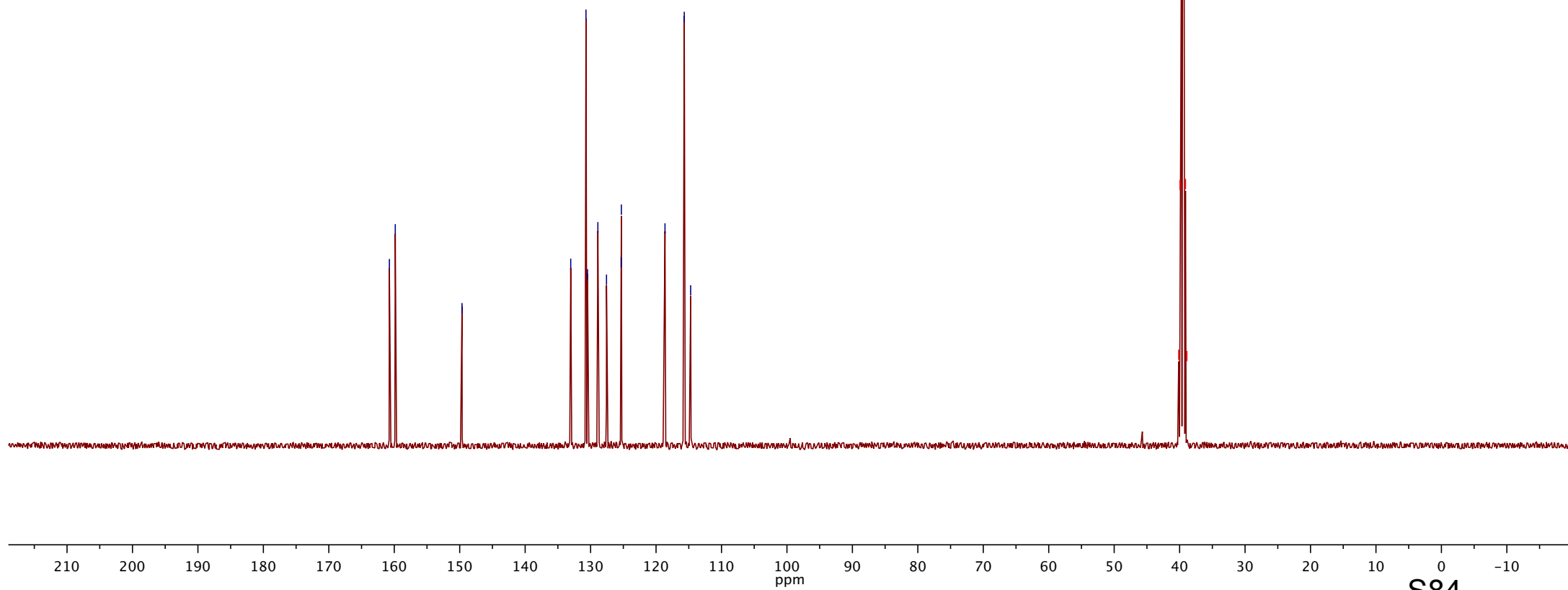
S83



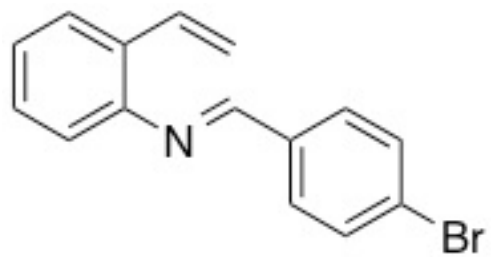
1c

160.75  
159.85  
149.65  
133.04  
130.71  
130.47  
128.89  
127.57  
125.33  
125.30  
118.63  
115.69  
114.71

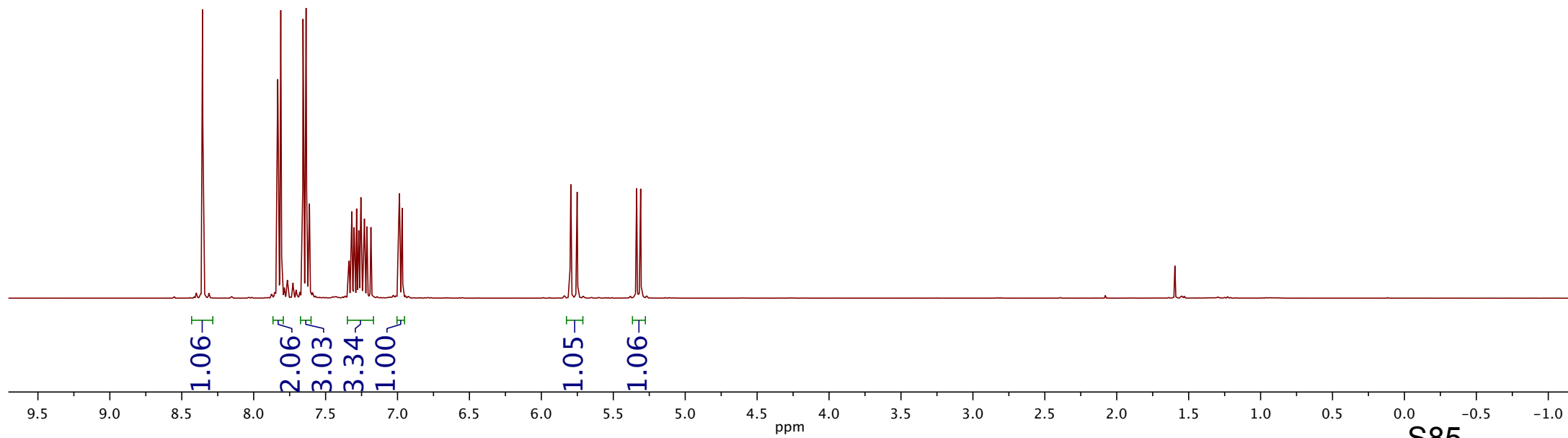
40.15 DMSO  
39.94 DMSO  
39.73 DMSO  
39.52 DMSO  
39.31 DMSO  
39.10 DMSO  
38.89 DMSO

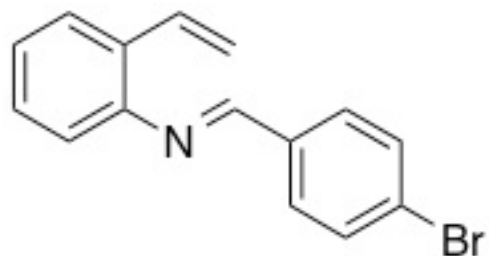




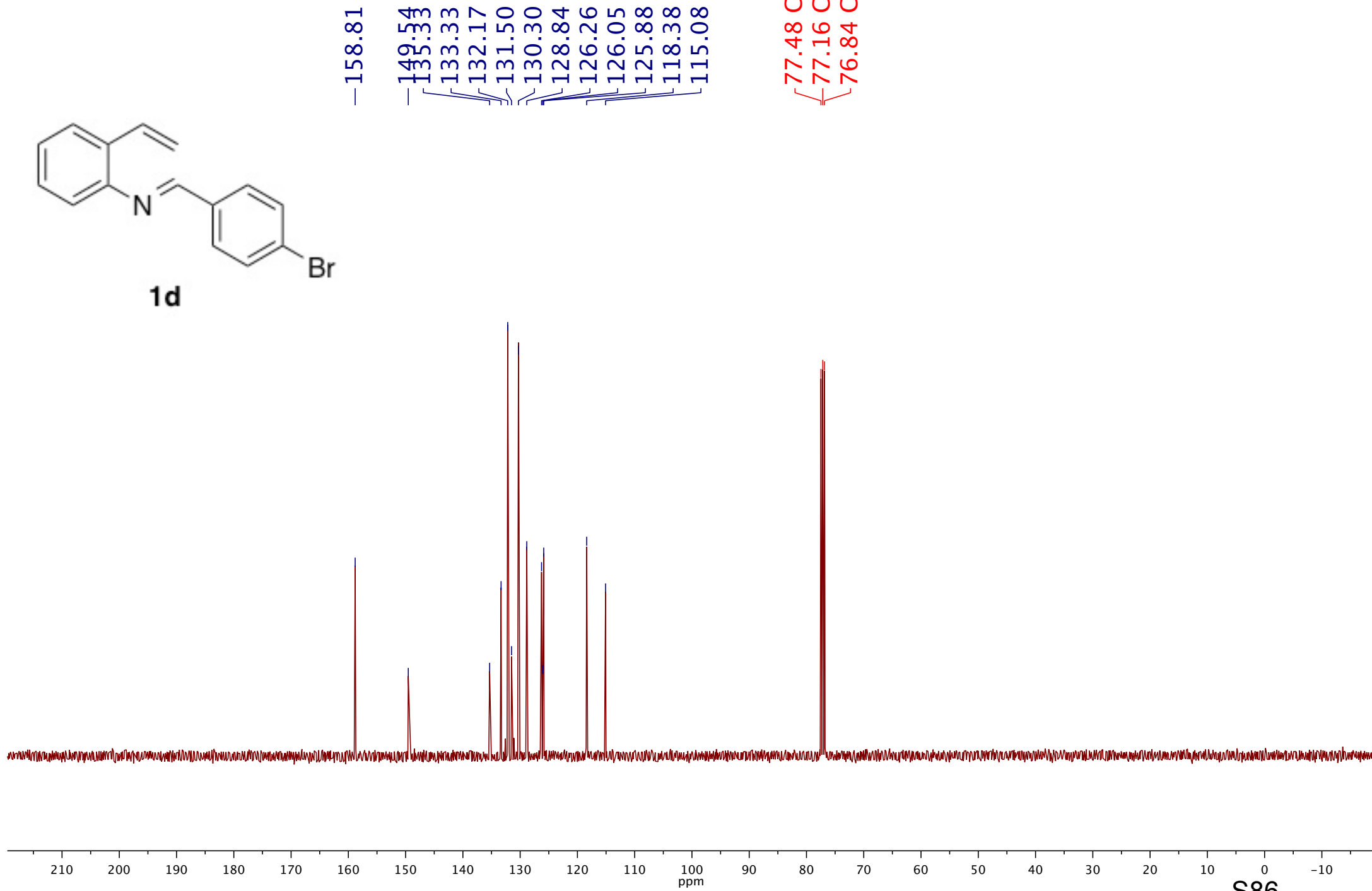


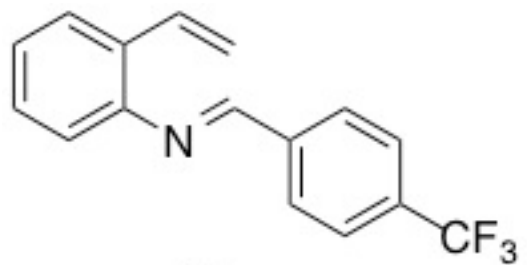
**1d**  
in CDCl<sub>3</sub>



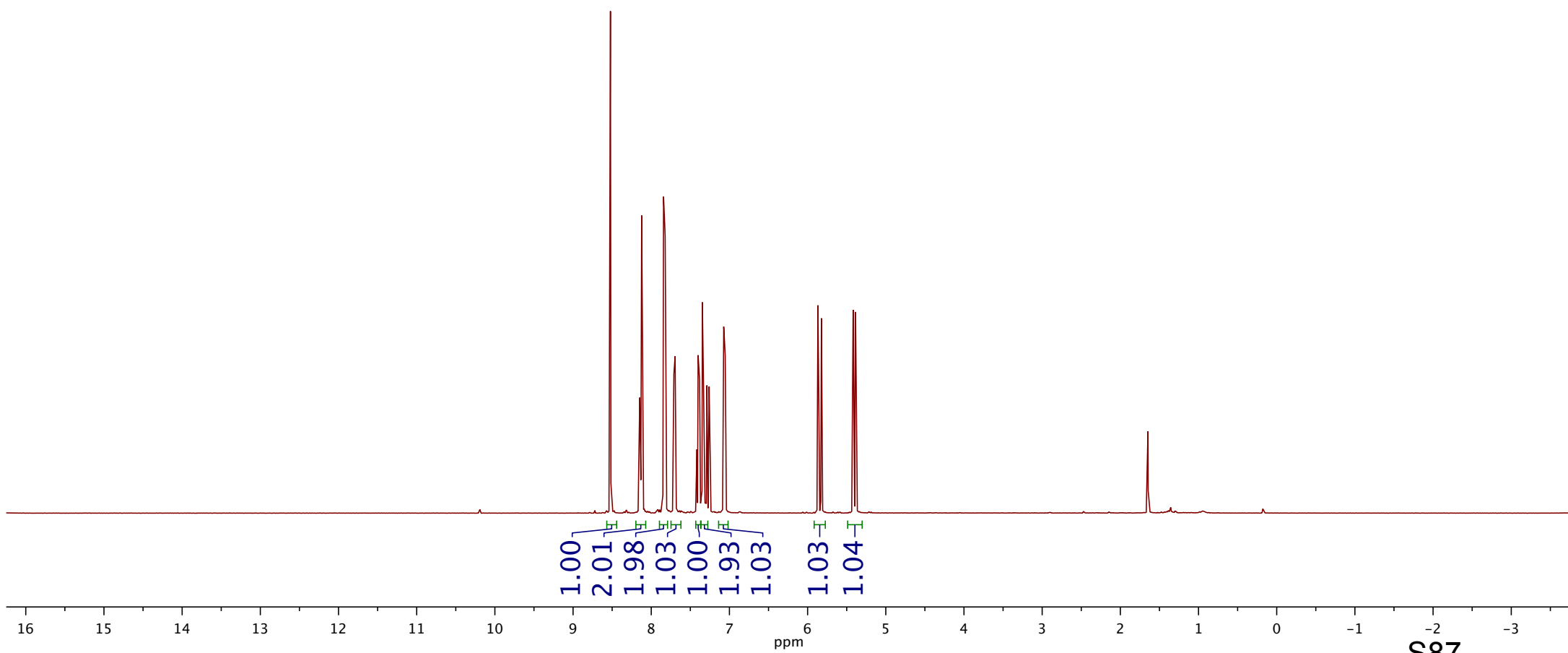
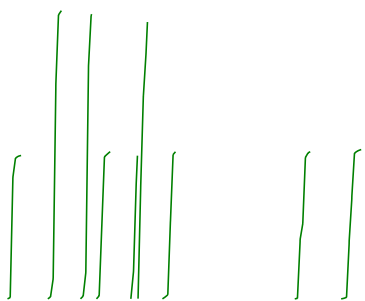


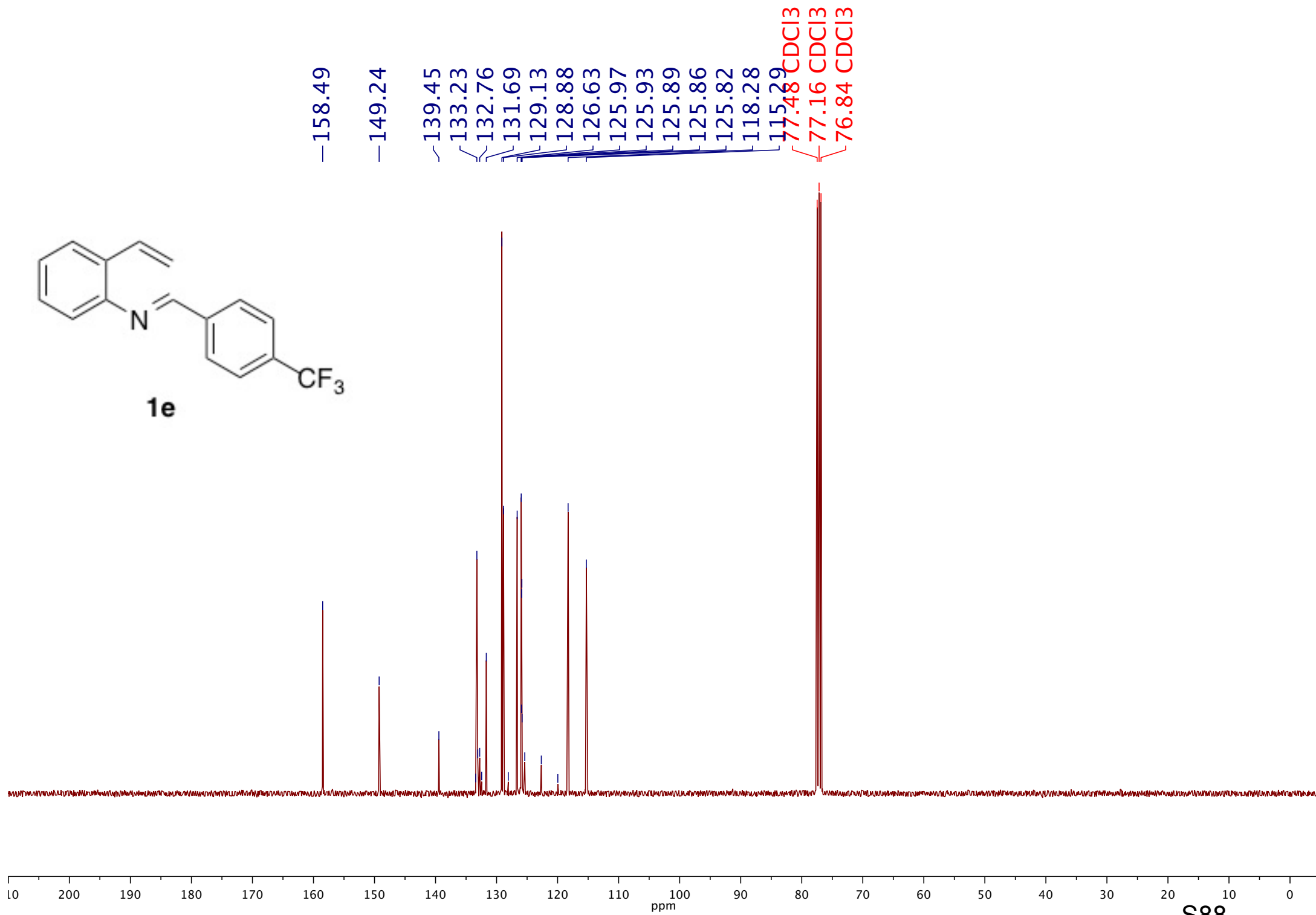
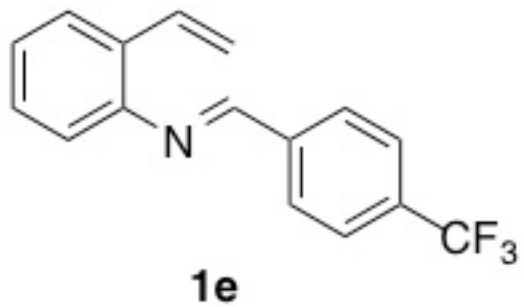
**1d**

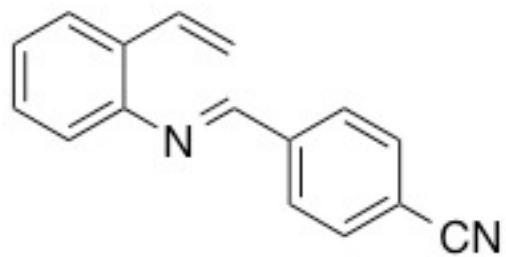




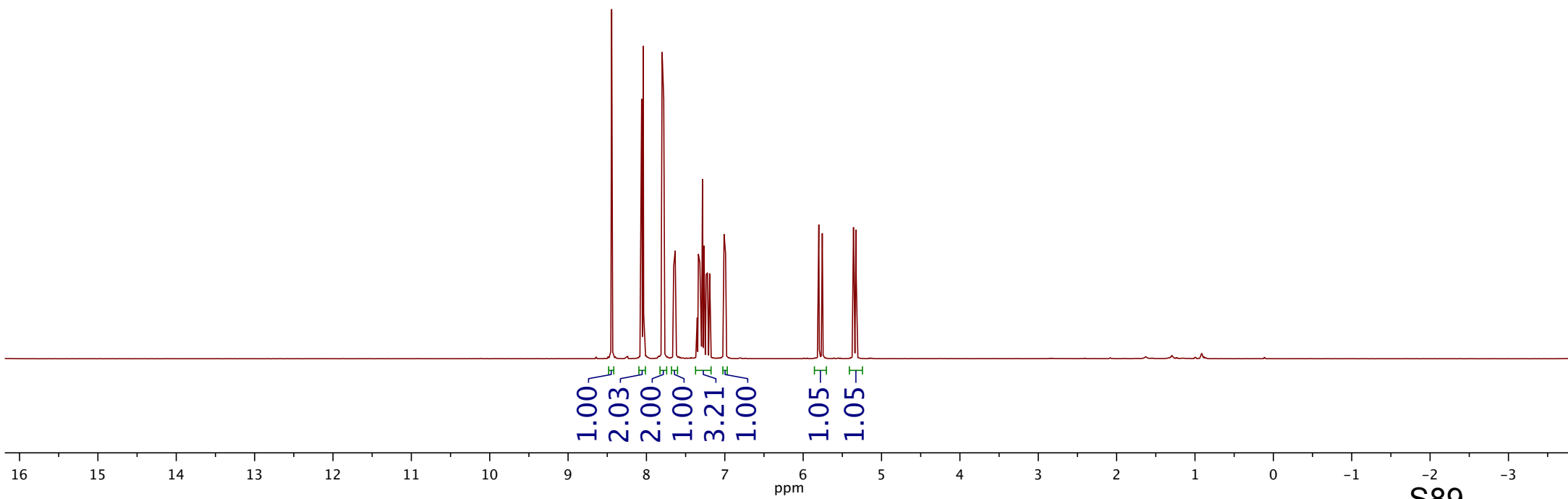
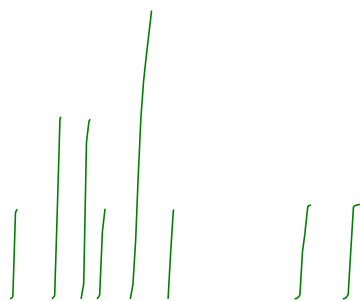
**1e**  
in CDCl<sub>3</sub>

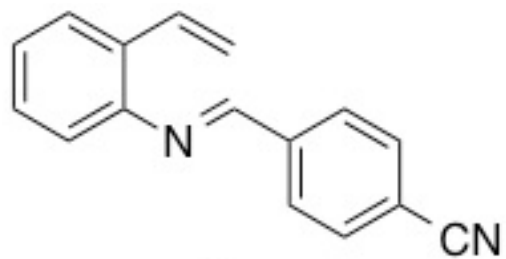






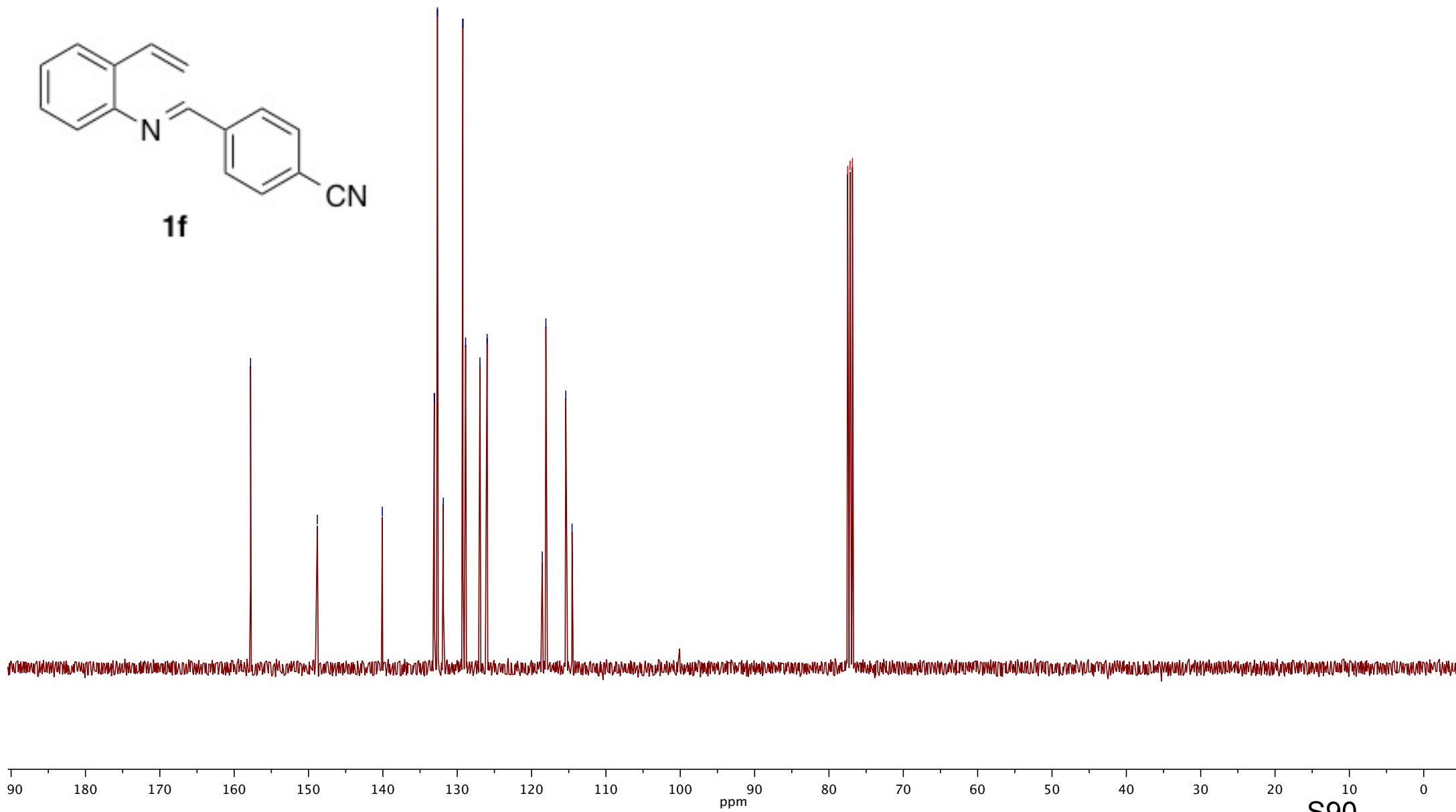
**1f**  
in CDCl<sub>3</sub>

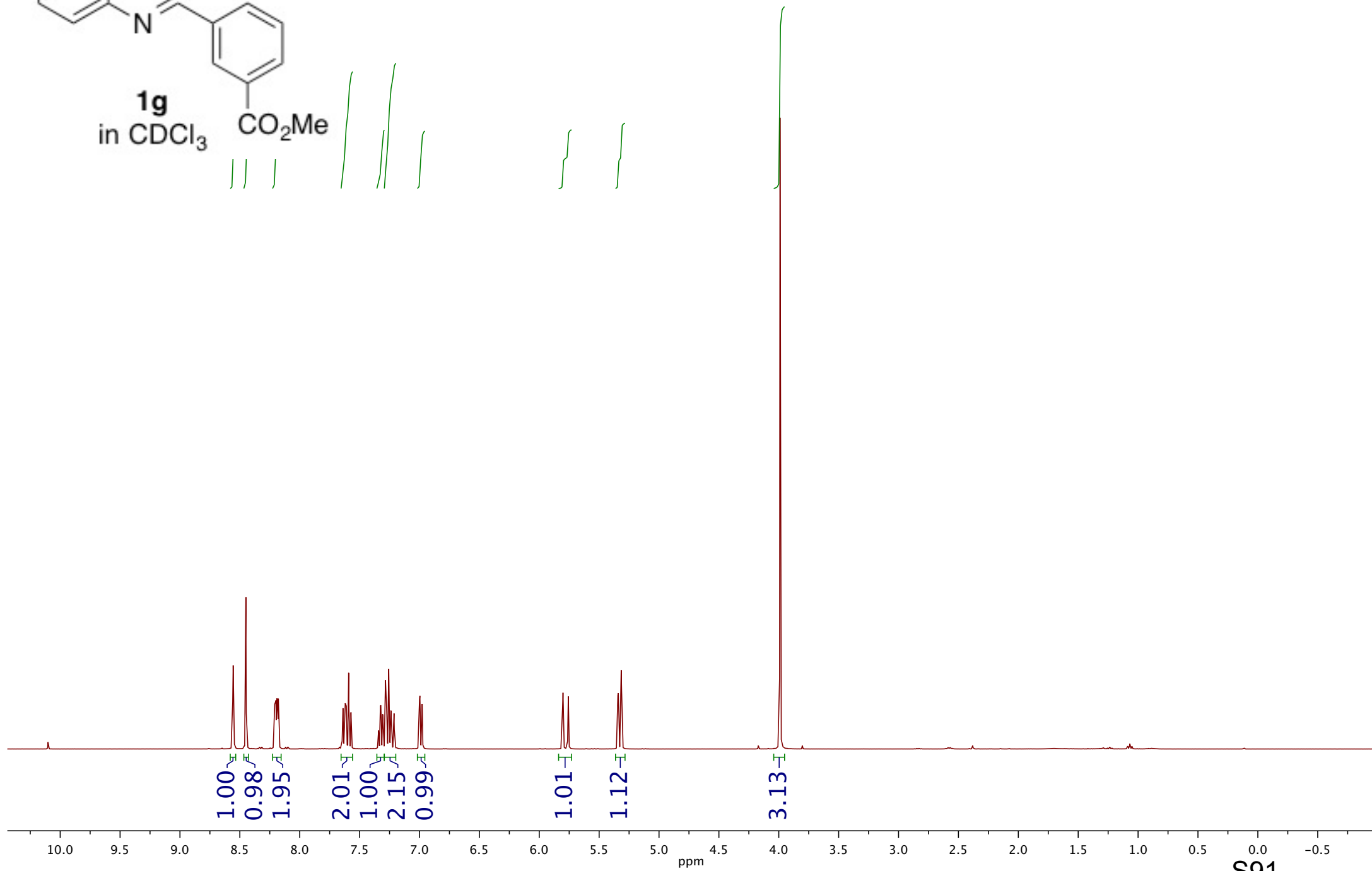
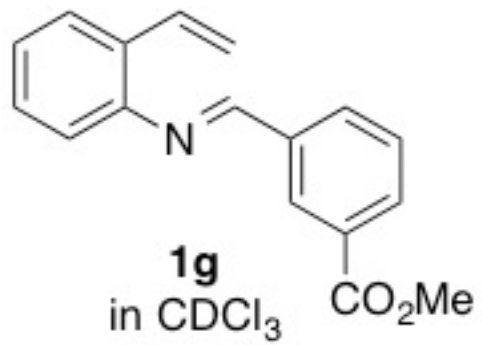


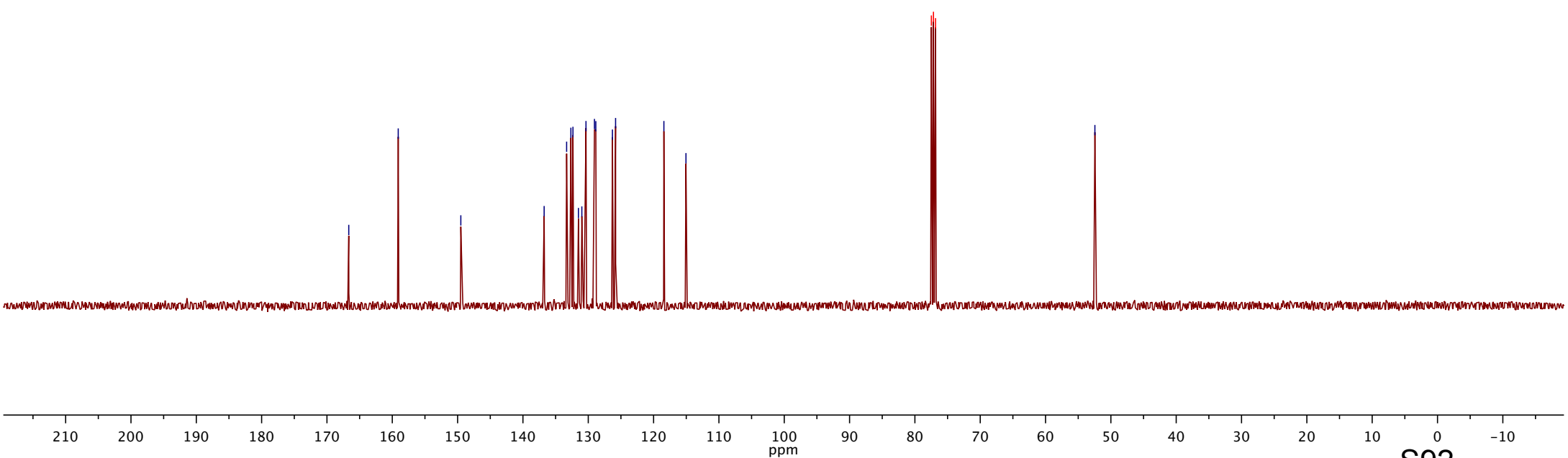
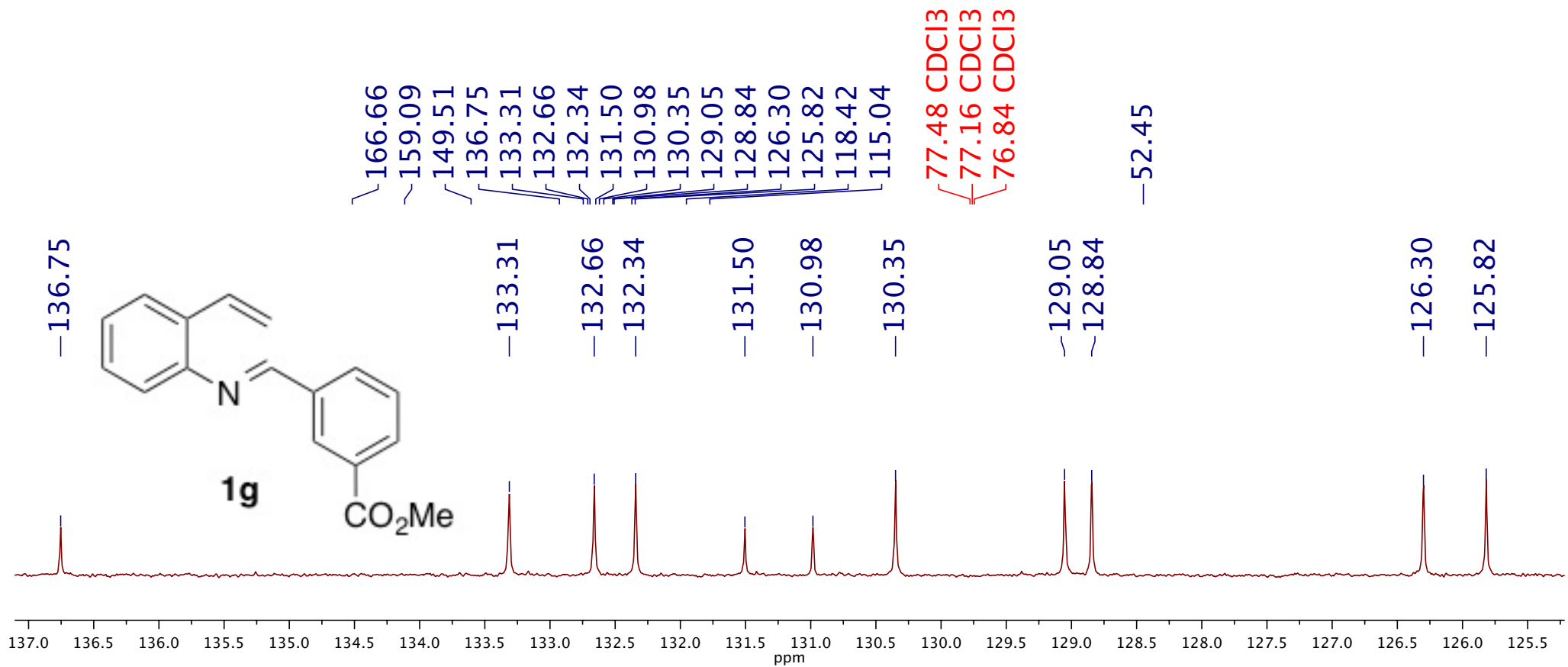


157.79  
148.81  
140.08  
133.09  
132.66  
131.87  
129.24  
128.87  
126.94  
125.98  
118.56  
118.07  
115.40  
114.55

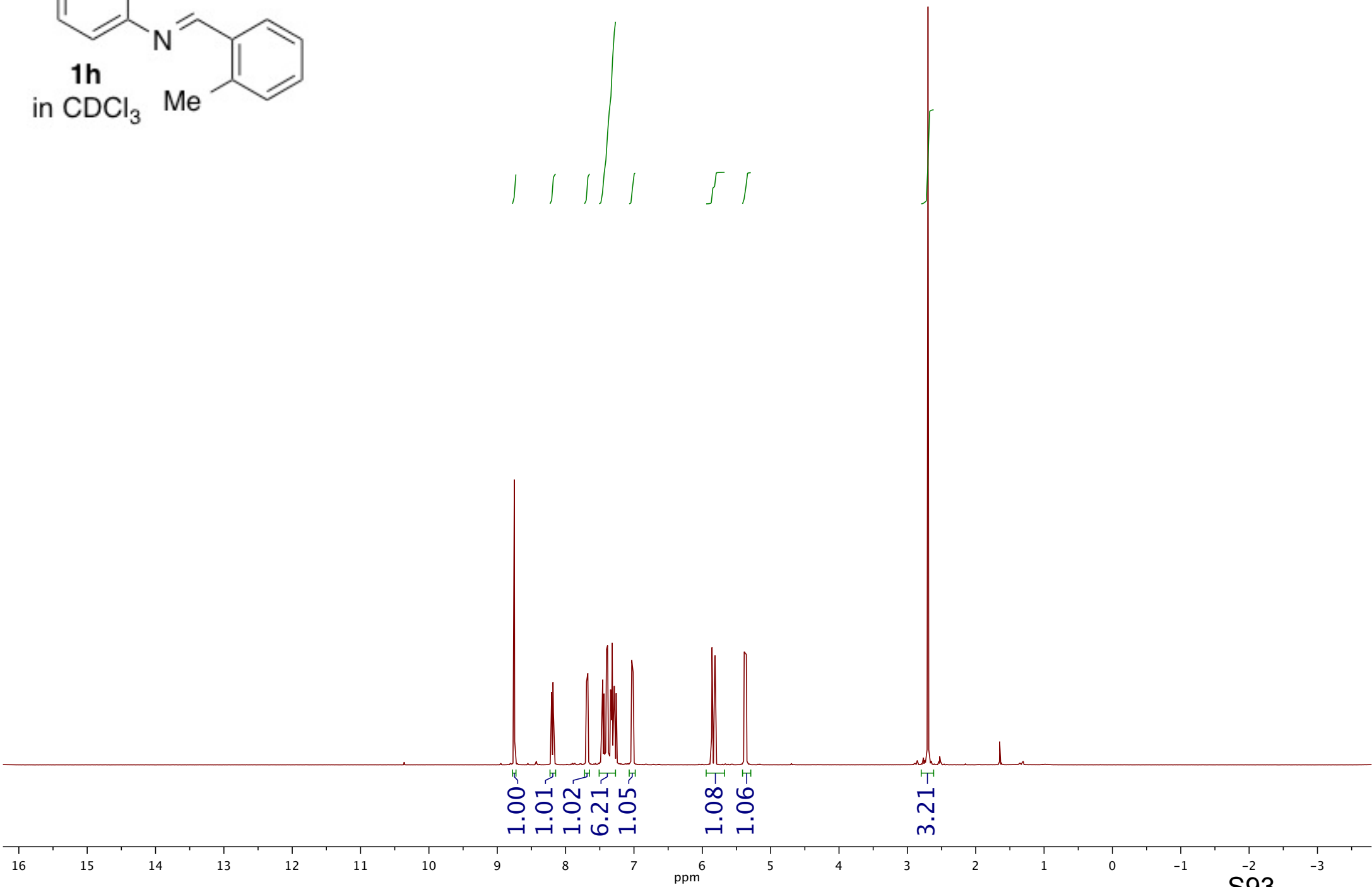
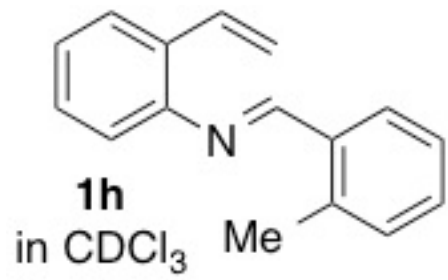
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

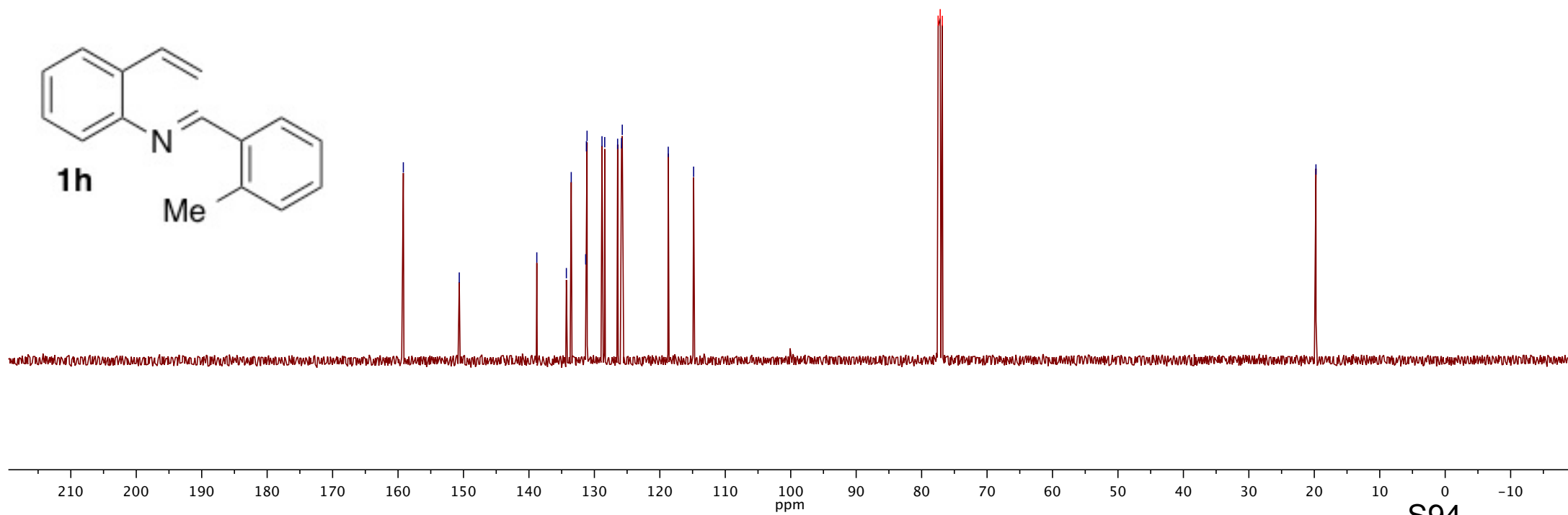
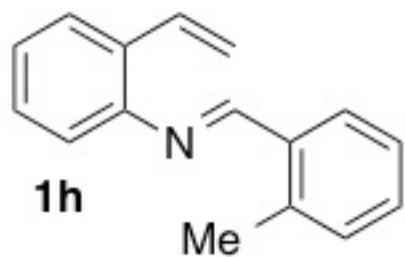
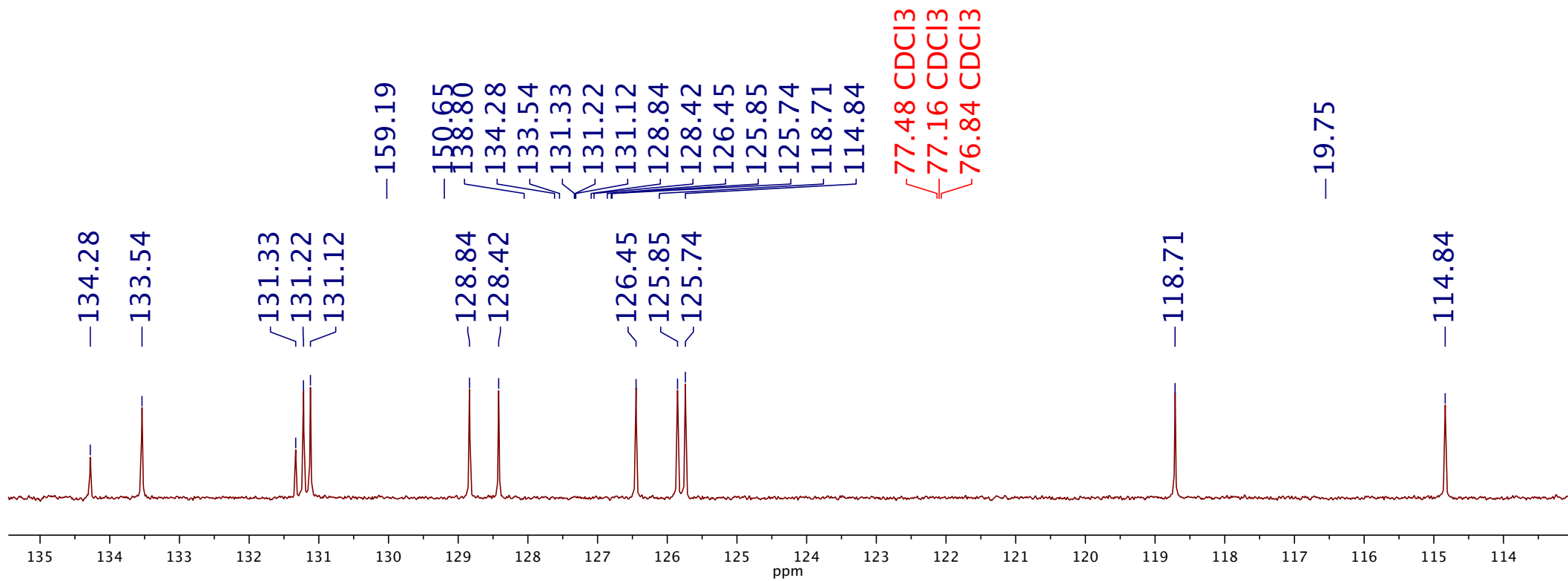


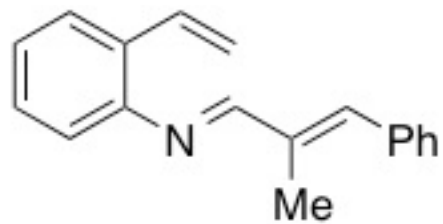




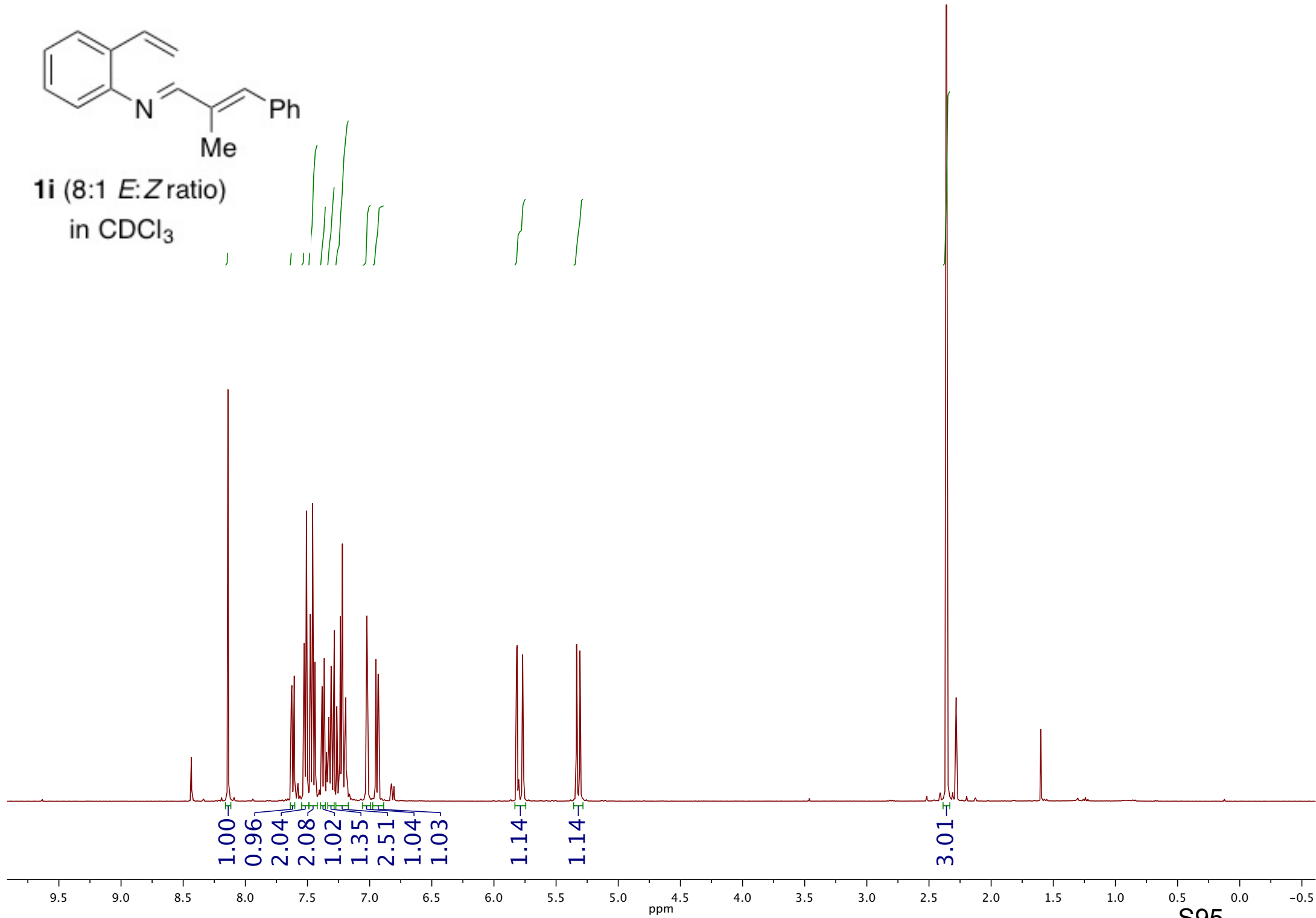


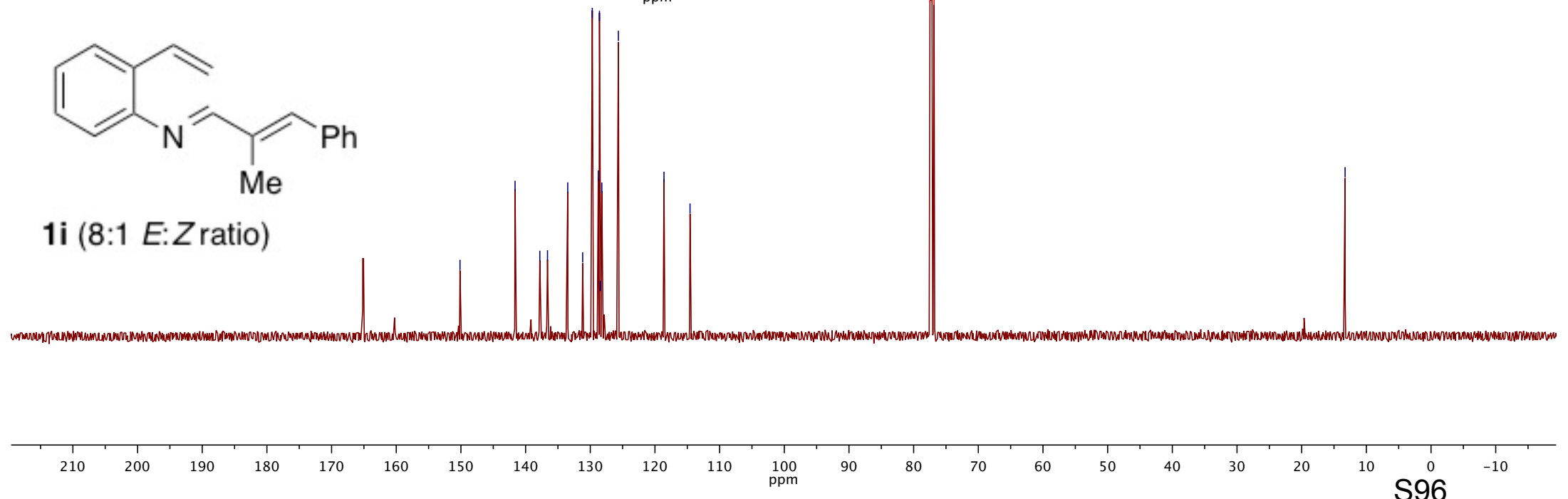
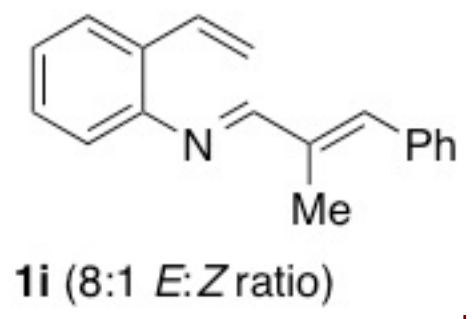
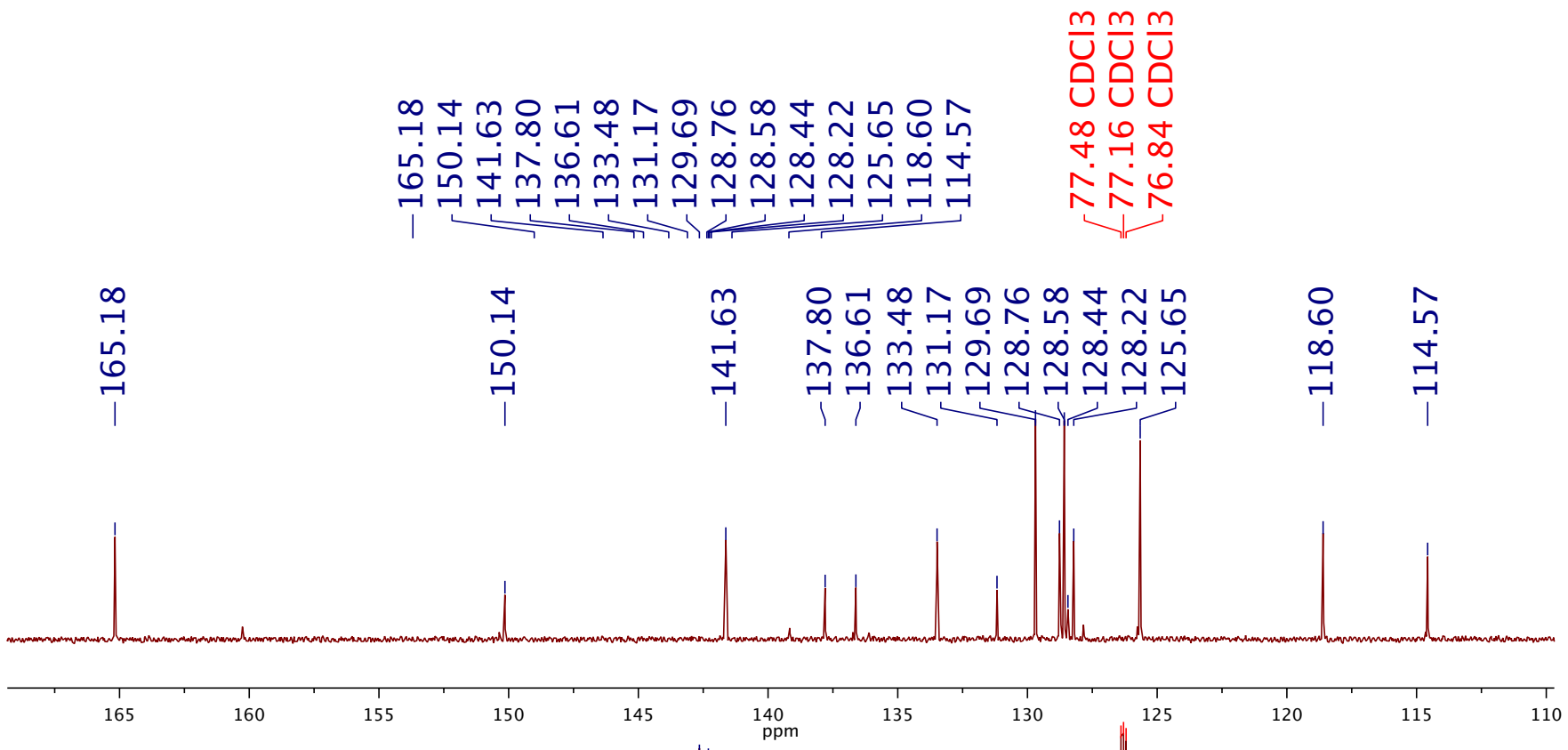


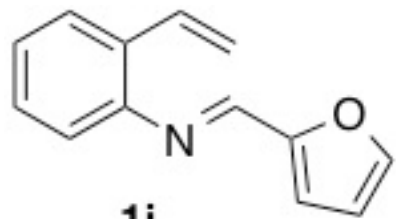




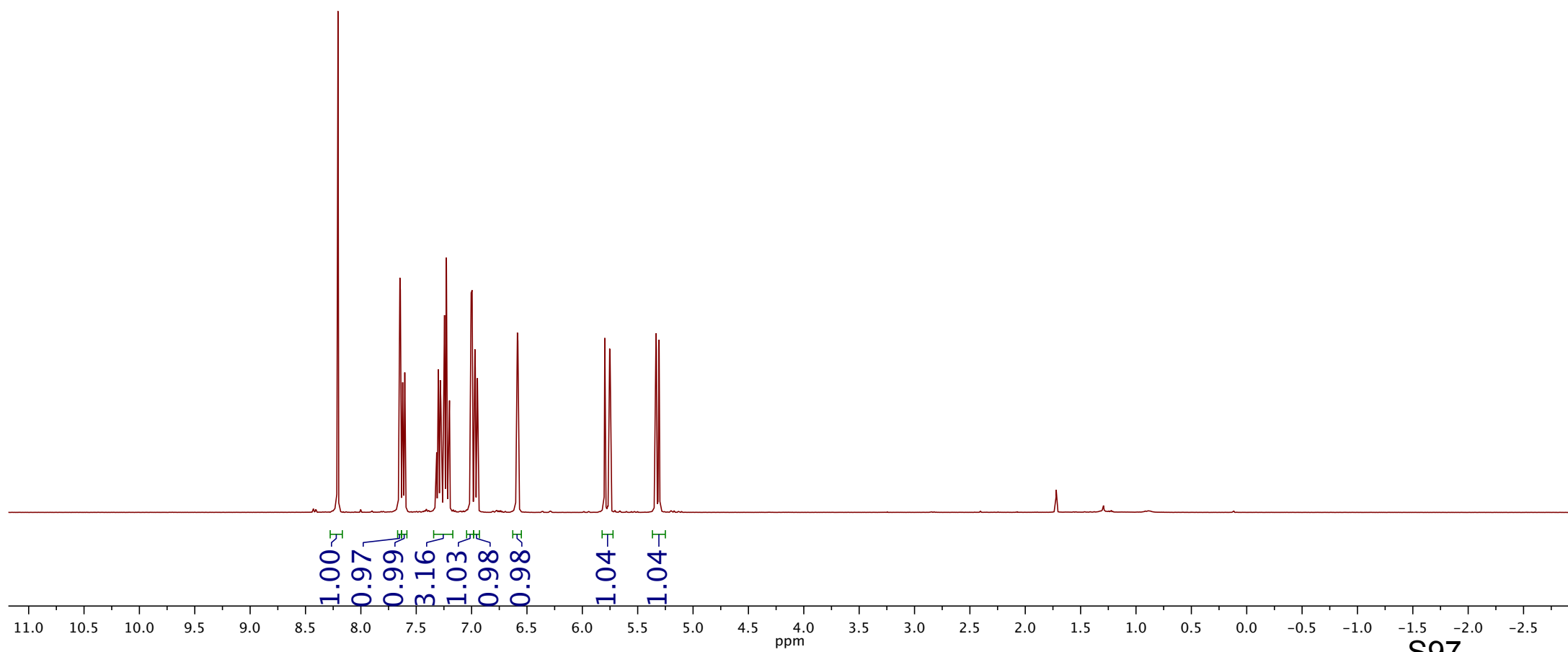
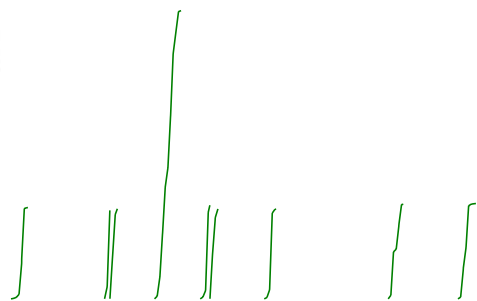
**1i** (8:1 *E*:*Z* ratio)  
in CDCl<sub>3</sub>

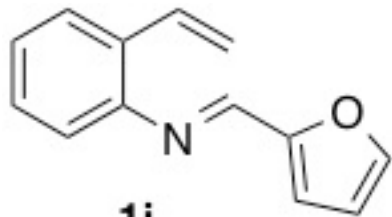






**1j**  
in CDCl<sub>3</sub>

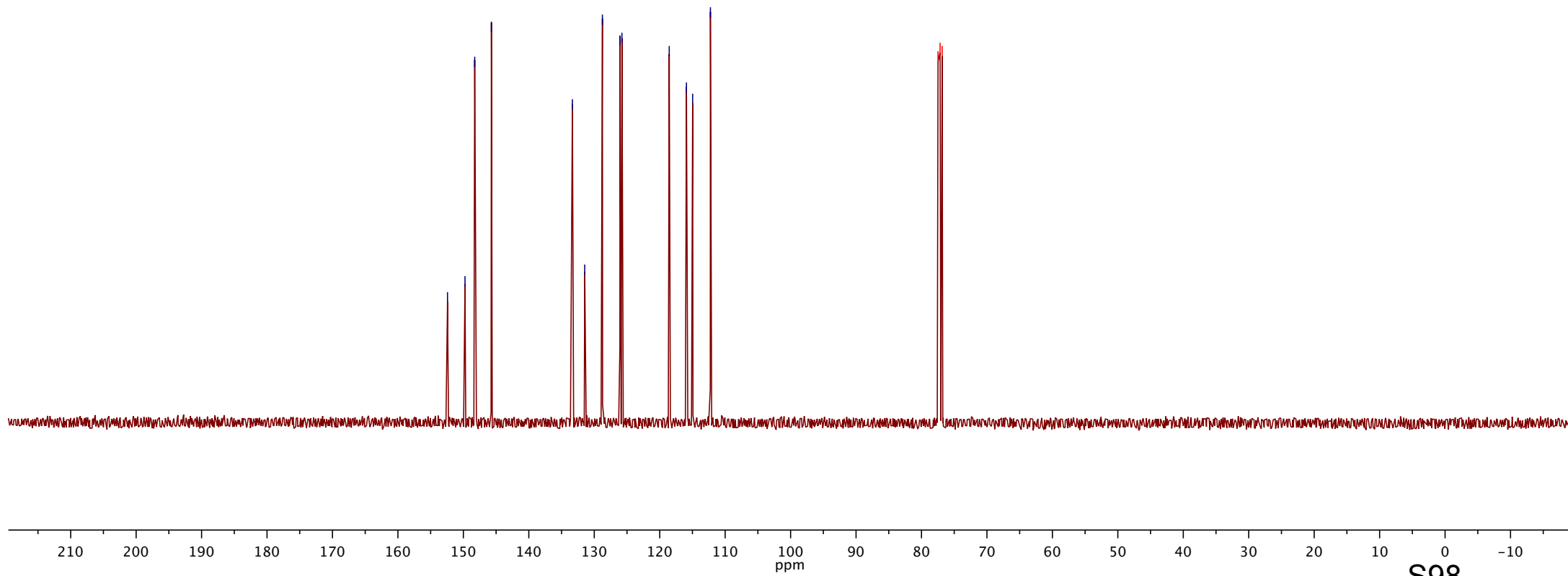


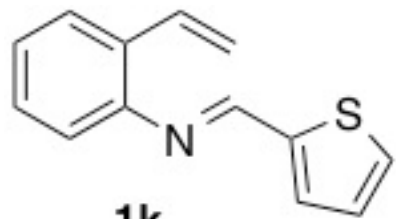


1j

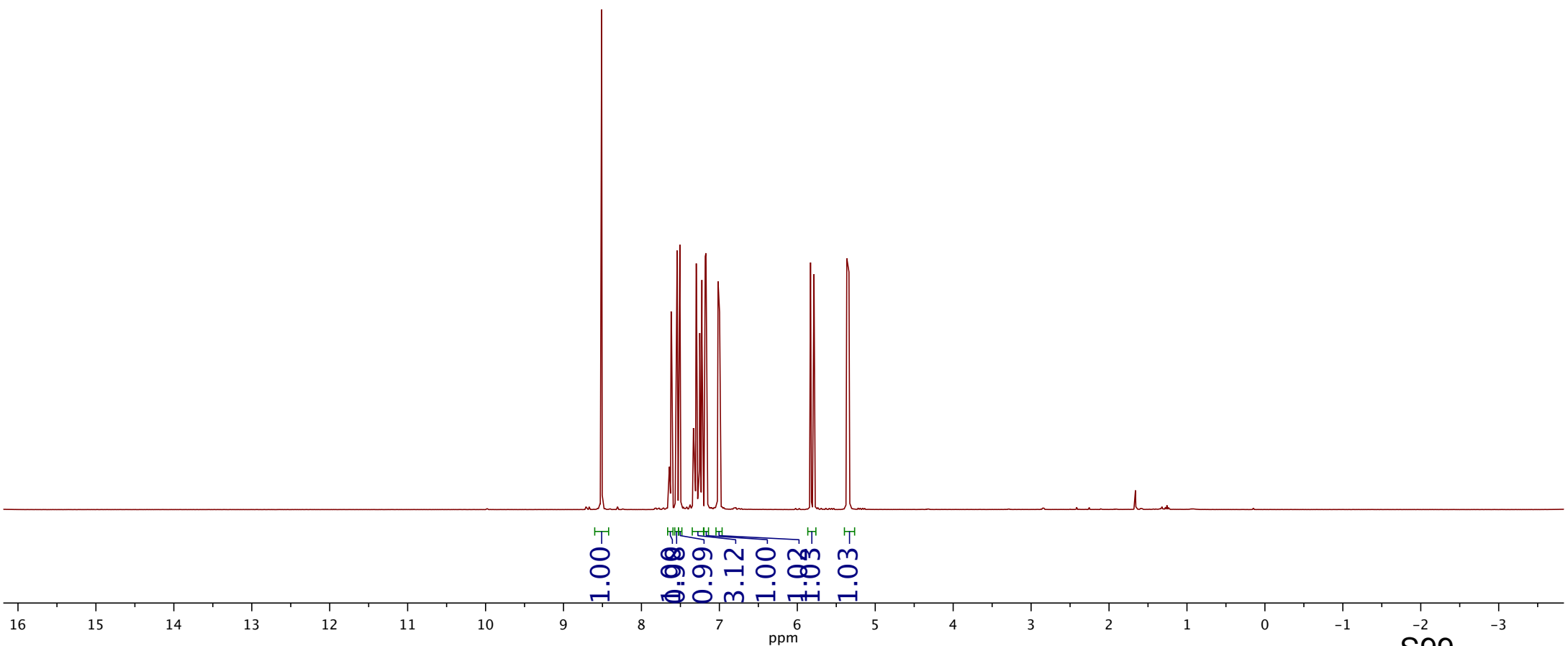
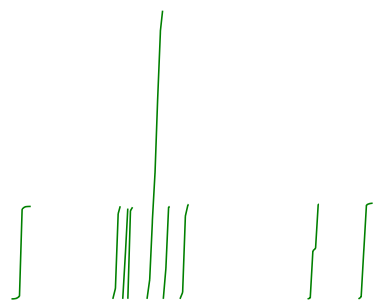
152.42  
149.75  
148.27  
145.72  
133.34  
131.46  
128.75  
126.07  
125.77  
118.55  
115.91  
114.97  
112.25

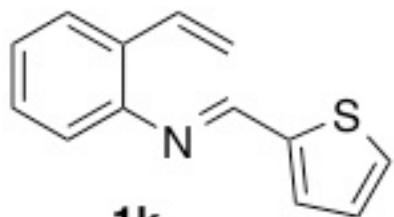
77.48 CDCI3  
77.16 CDCI3  
76.84 CDCI3





**1k**  
in CDCl<sub>3</sub>

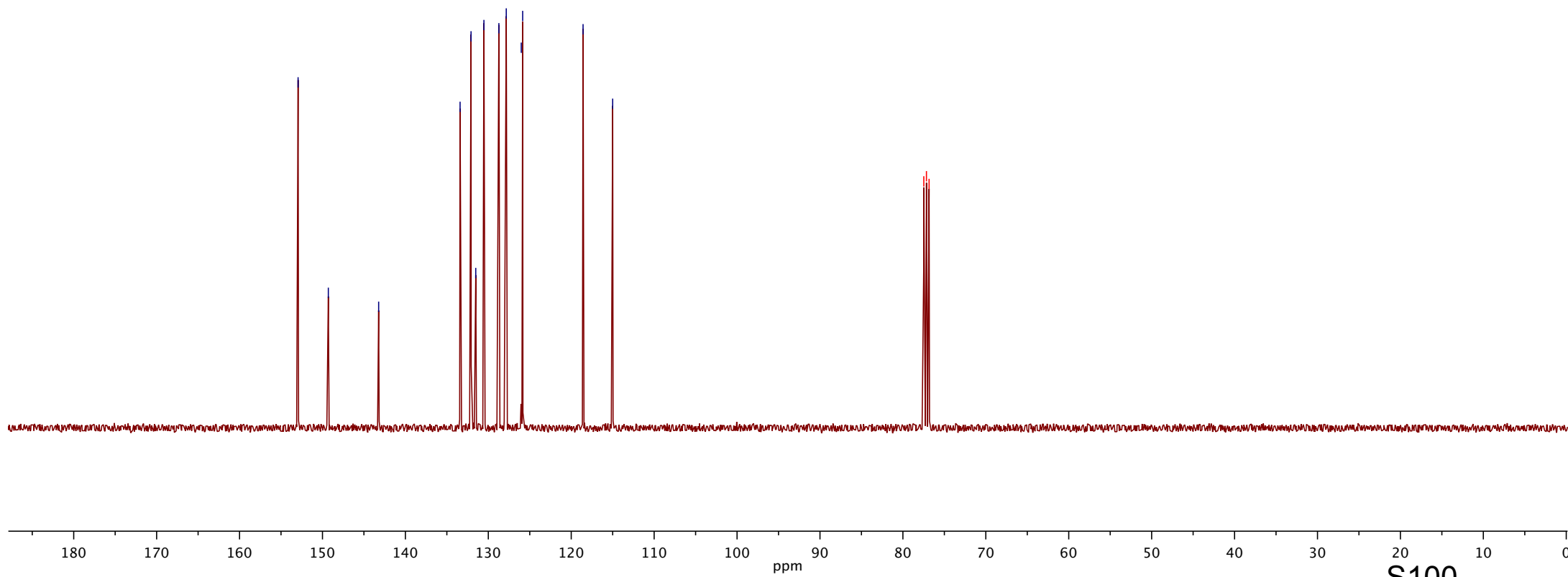




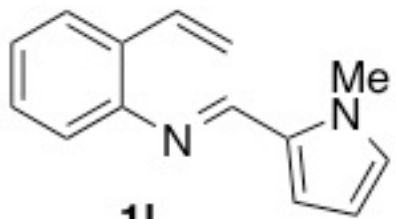
1k

152.94  
149.29  
143.22  
133.40  
132.08  
131.51  
130.53  
128.73  
127.83  
126.03  
125.86  
118.57  
115.00

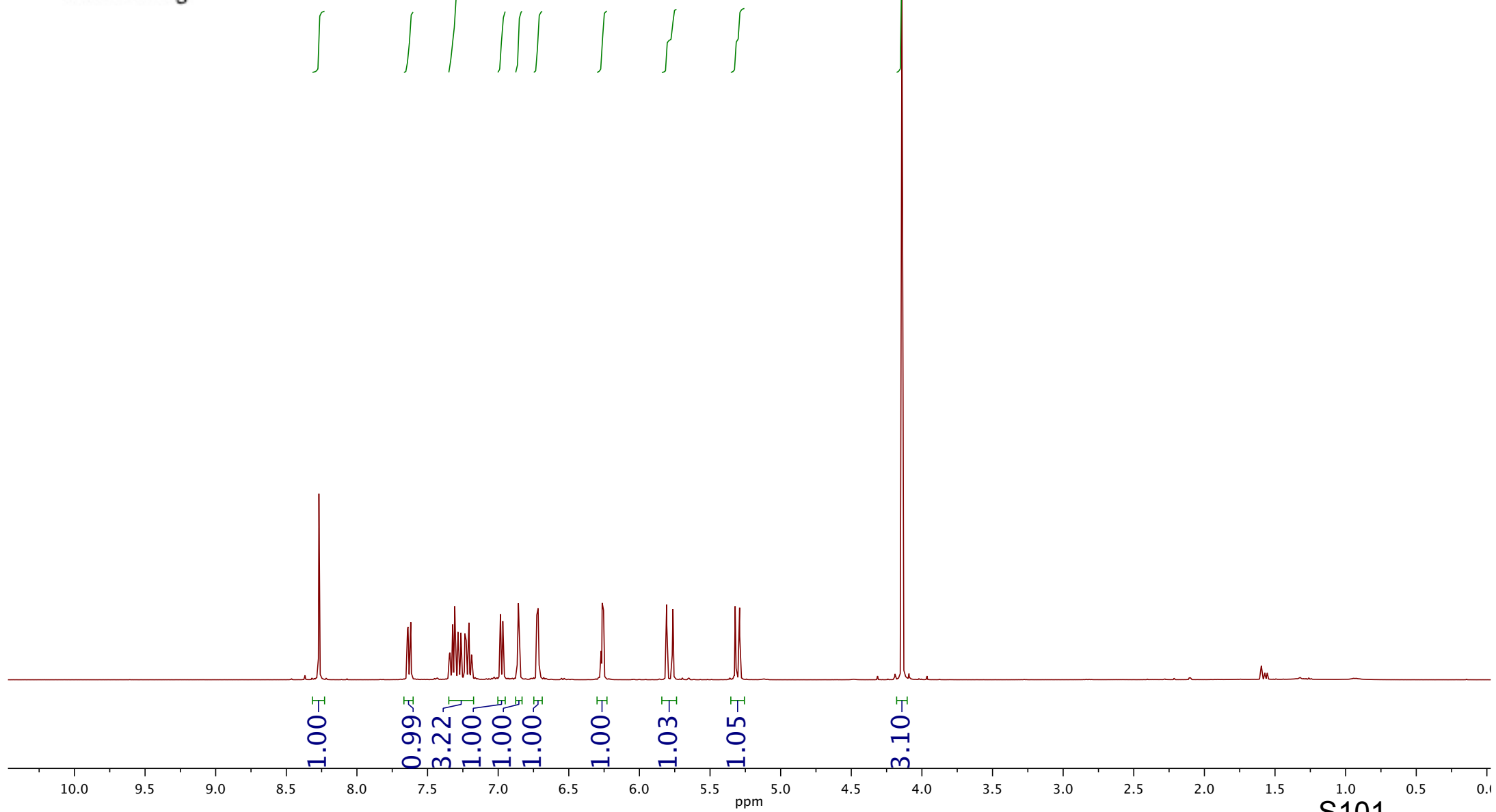
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

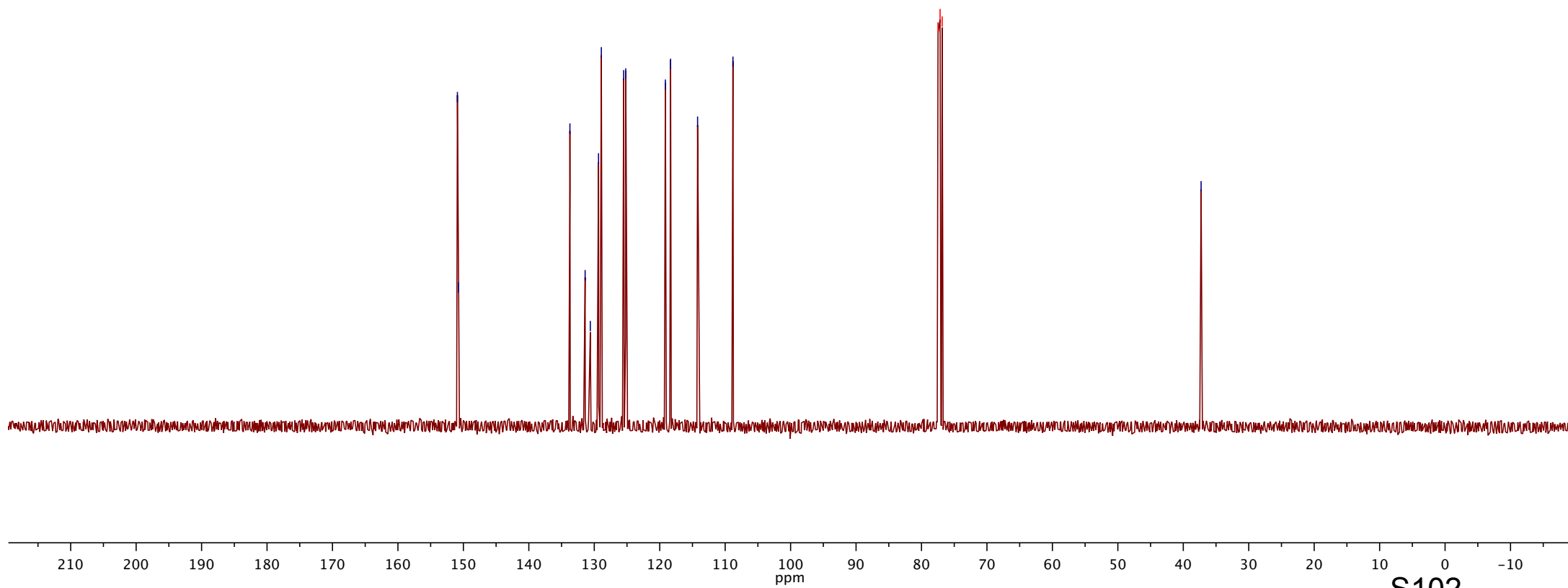
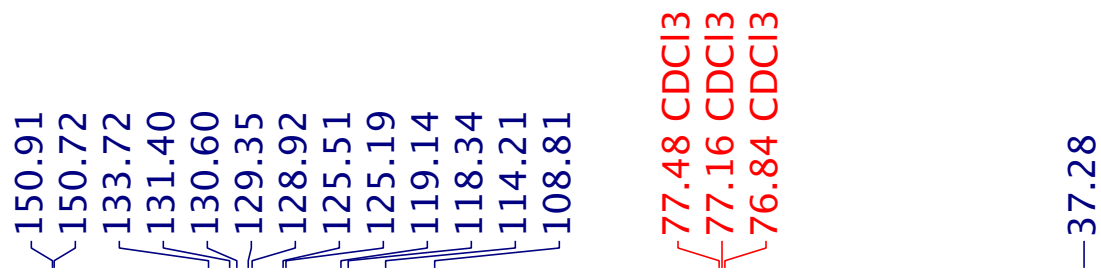
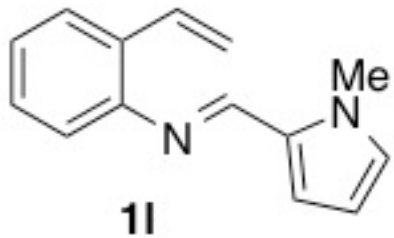


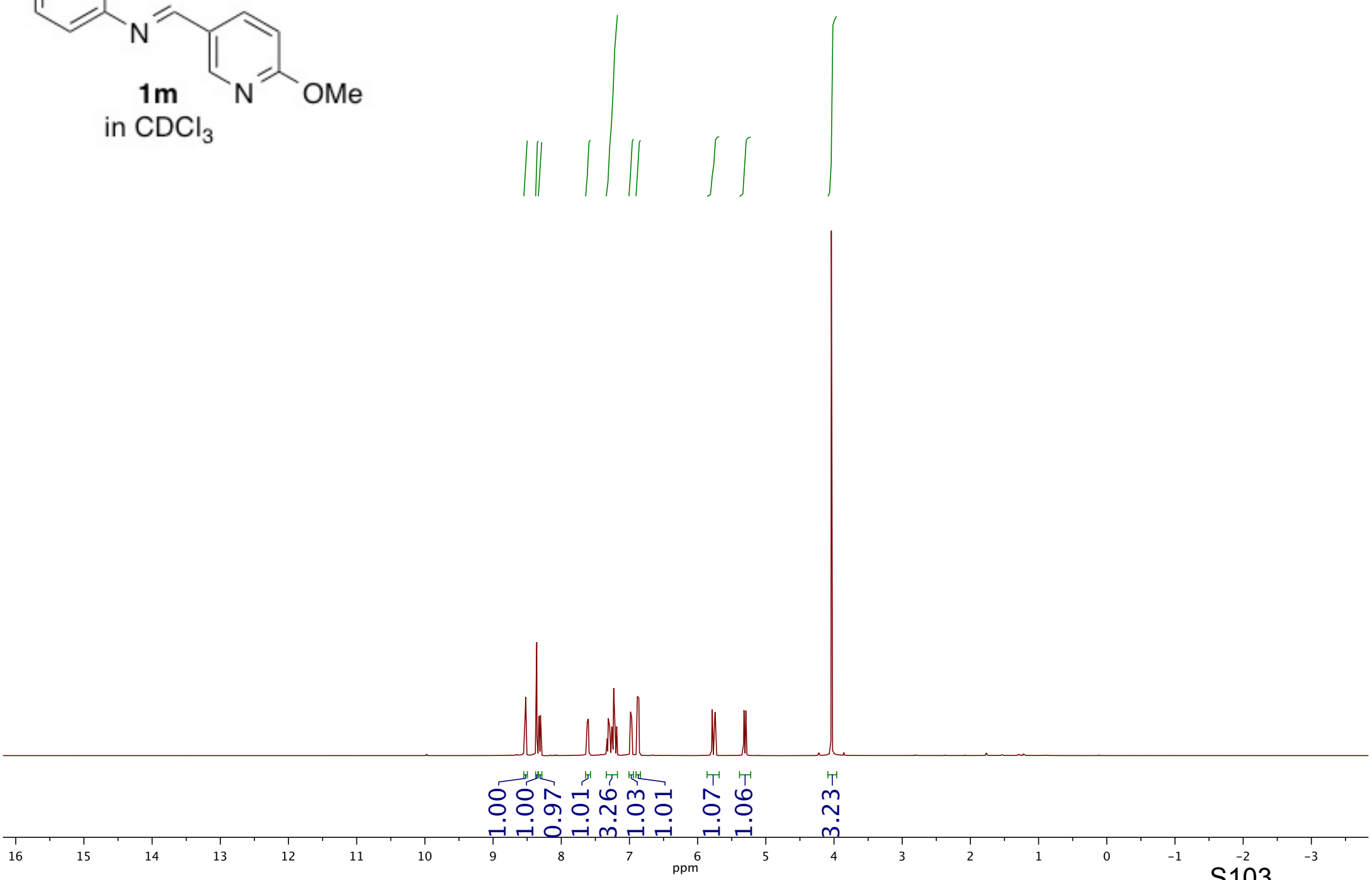
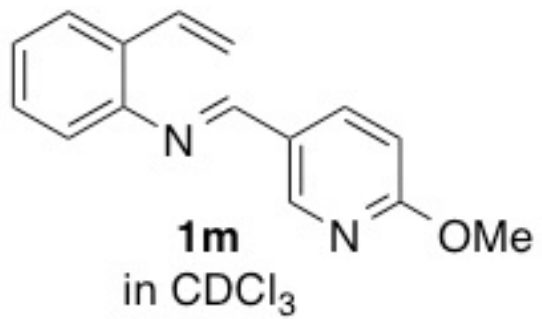


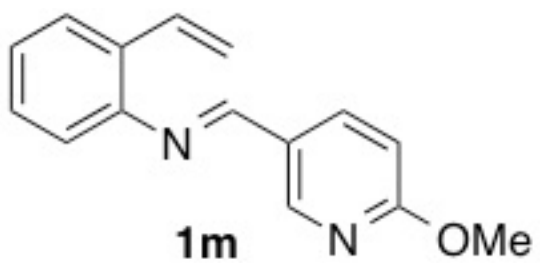


**11**  
in CDCl<sub>3</sub>





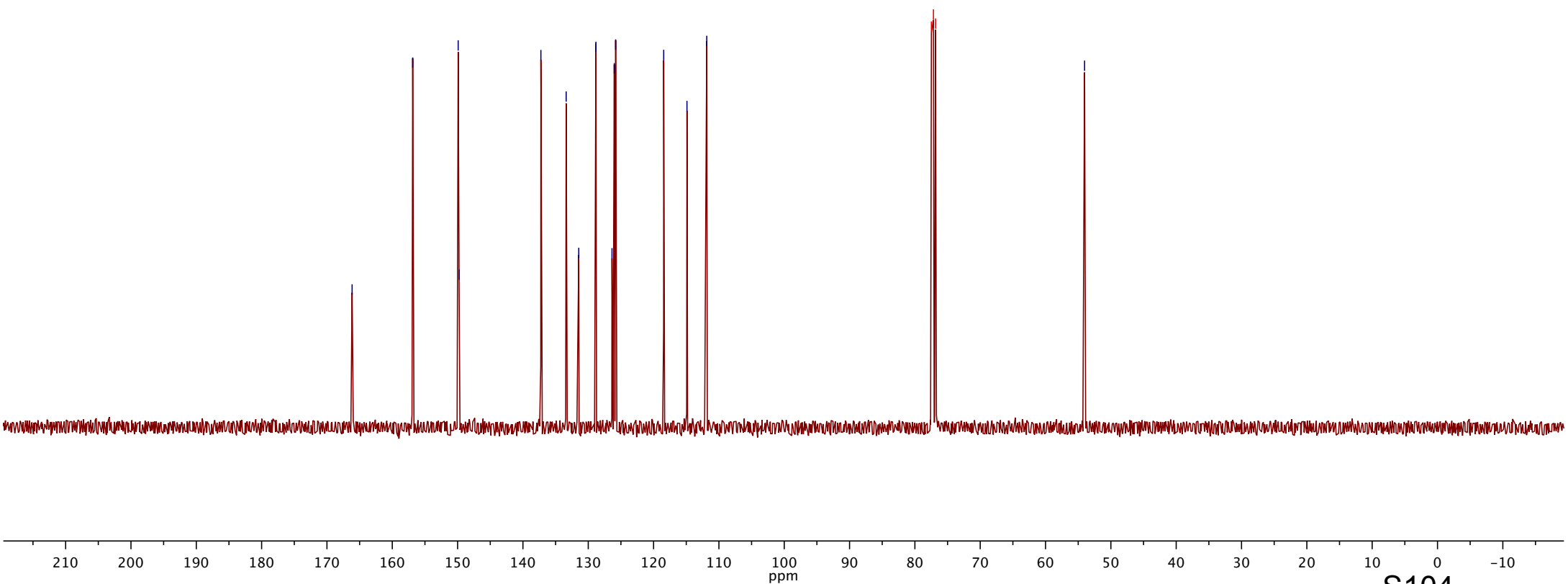


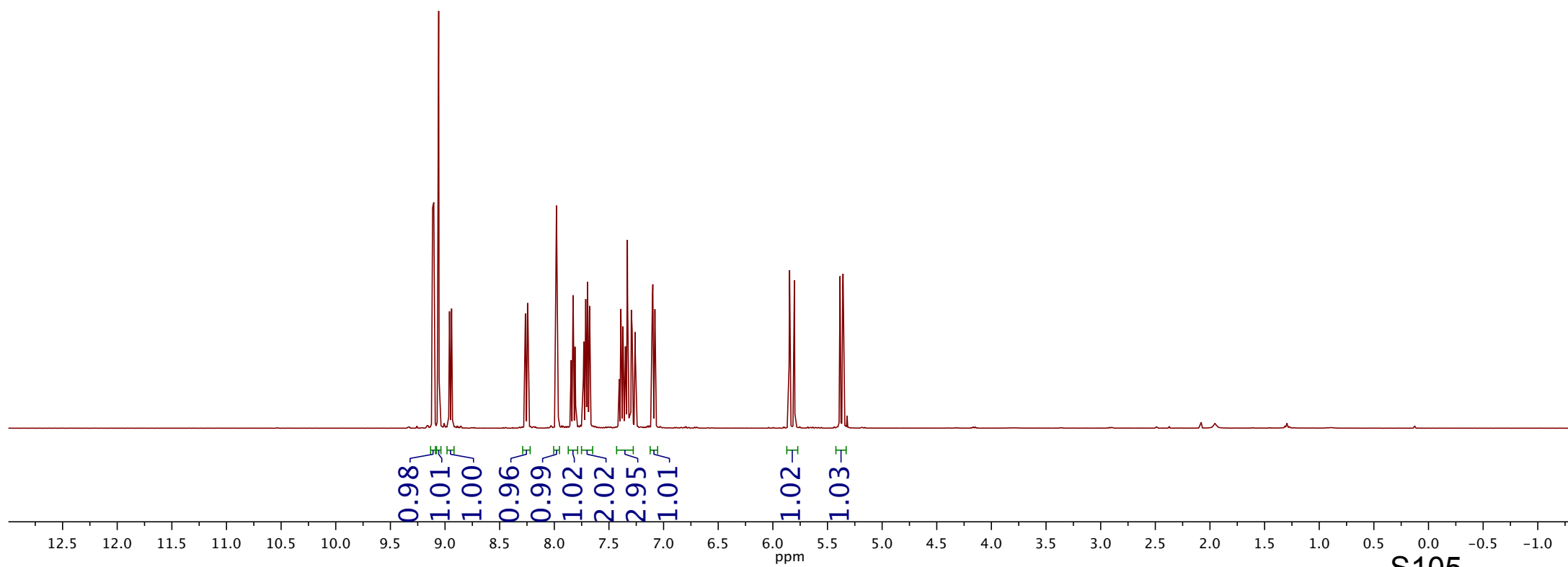
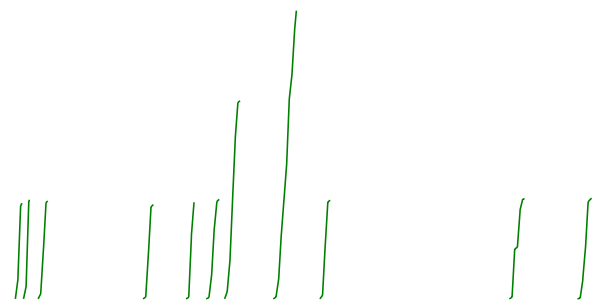
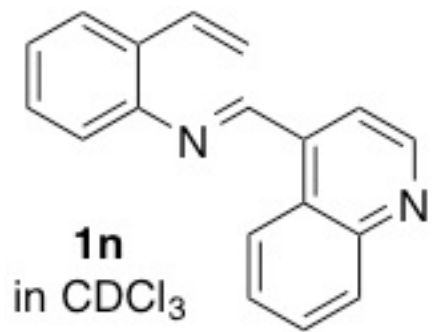


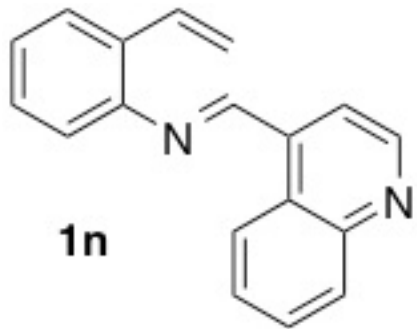
166.15  
156.87  
149.91  
149.78  
137.25  
133.38  
131.46  
128.83  
126.37  
126.02  
125.81  
118.45  
114.89  
111.86

77.48 CDCI3  
77.16 CDCI3  
76.84 CDCI3

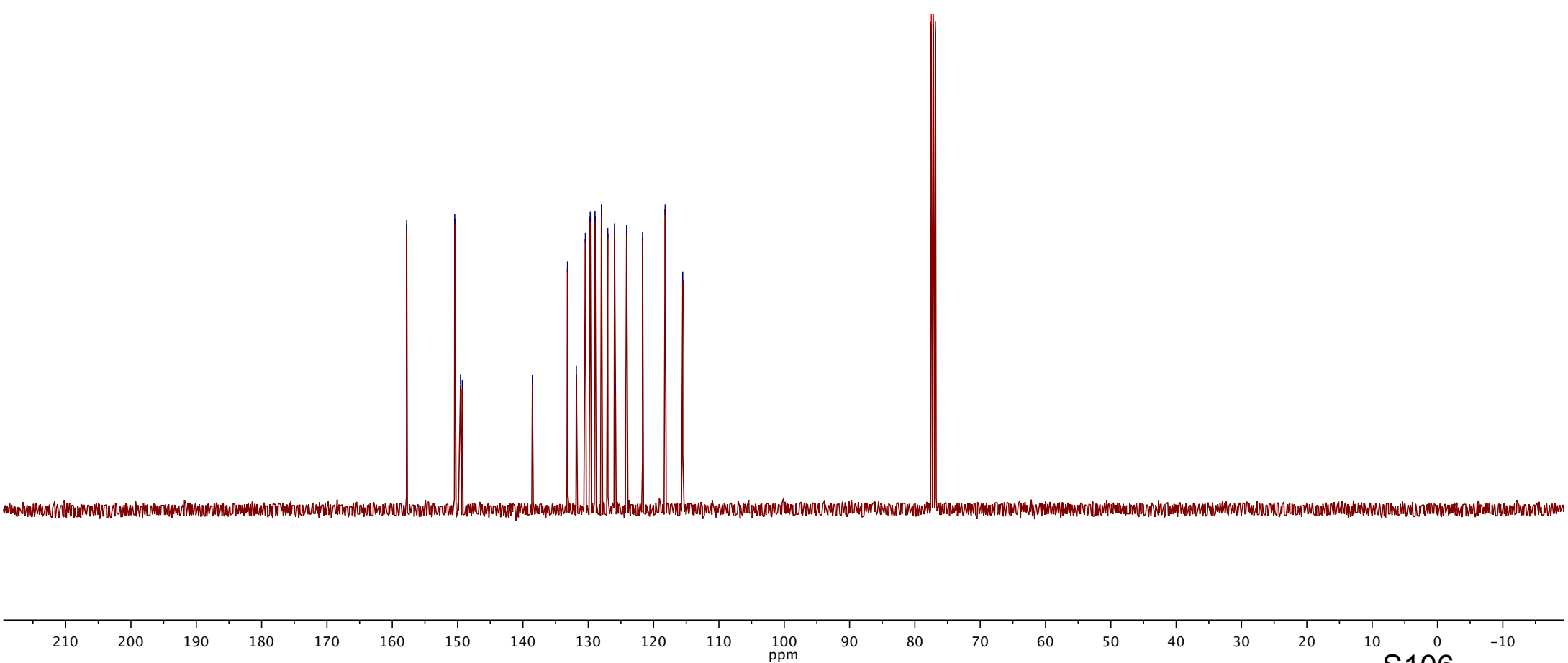
54.02

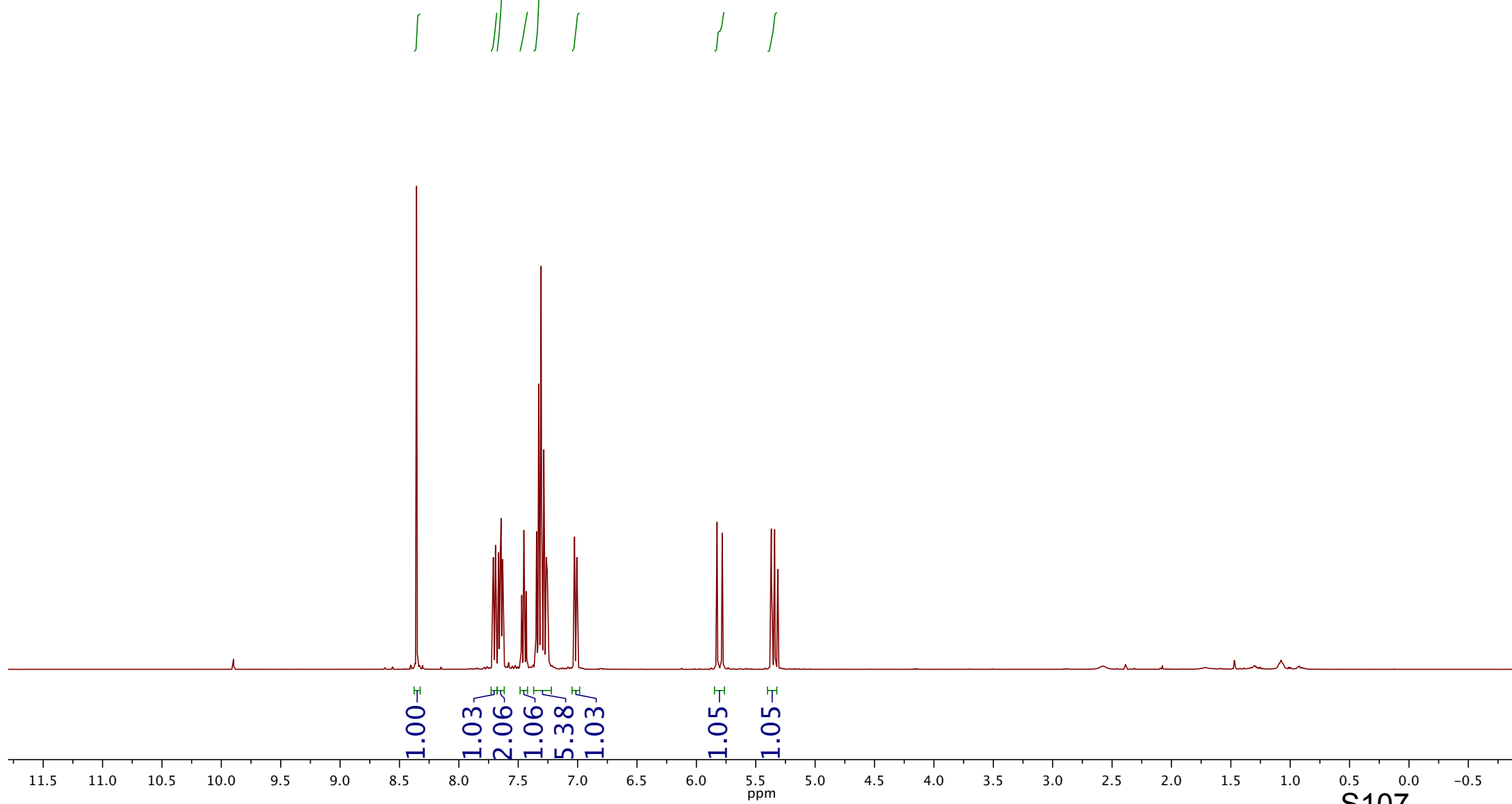
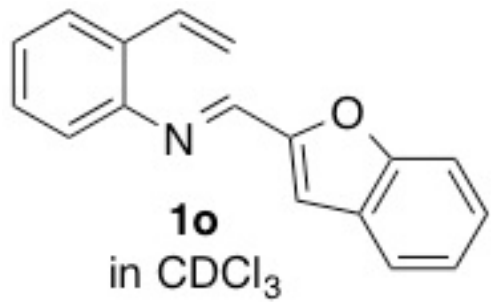


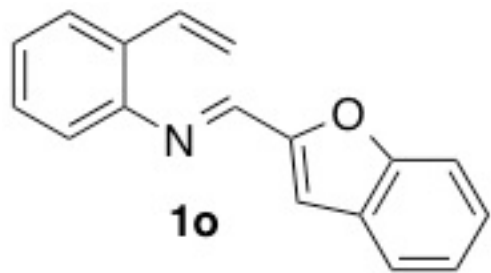




- 157.79
- 150.44
- 149.55
- 149.28
- 133.18
- 131.83
- 130.44
- 129.69
- 128.96
- 127.98
- 127.01
- 125.98
- 124.13
- 121.68
- 118.22
- 115.54
- 77.48 CDCl3
- 77.16 CDCl3
- 76.84 CDCl3

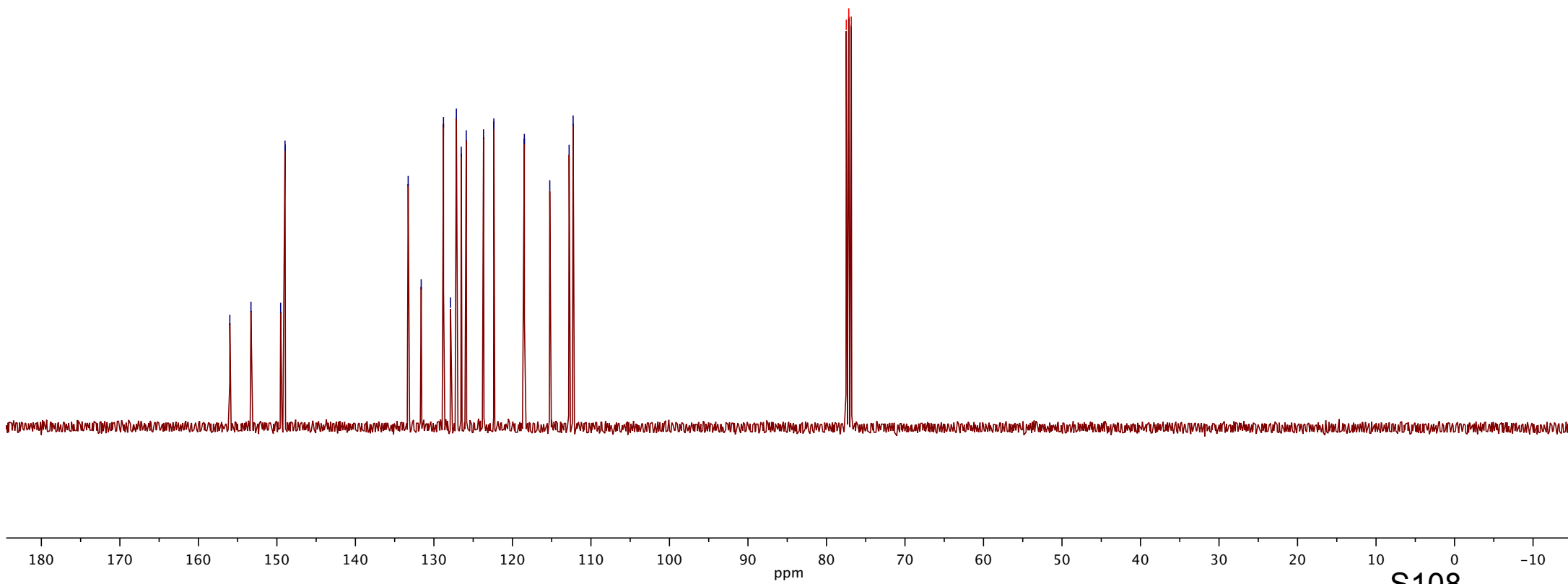




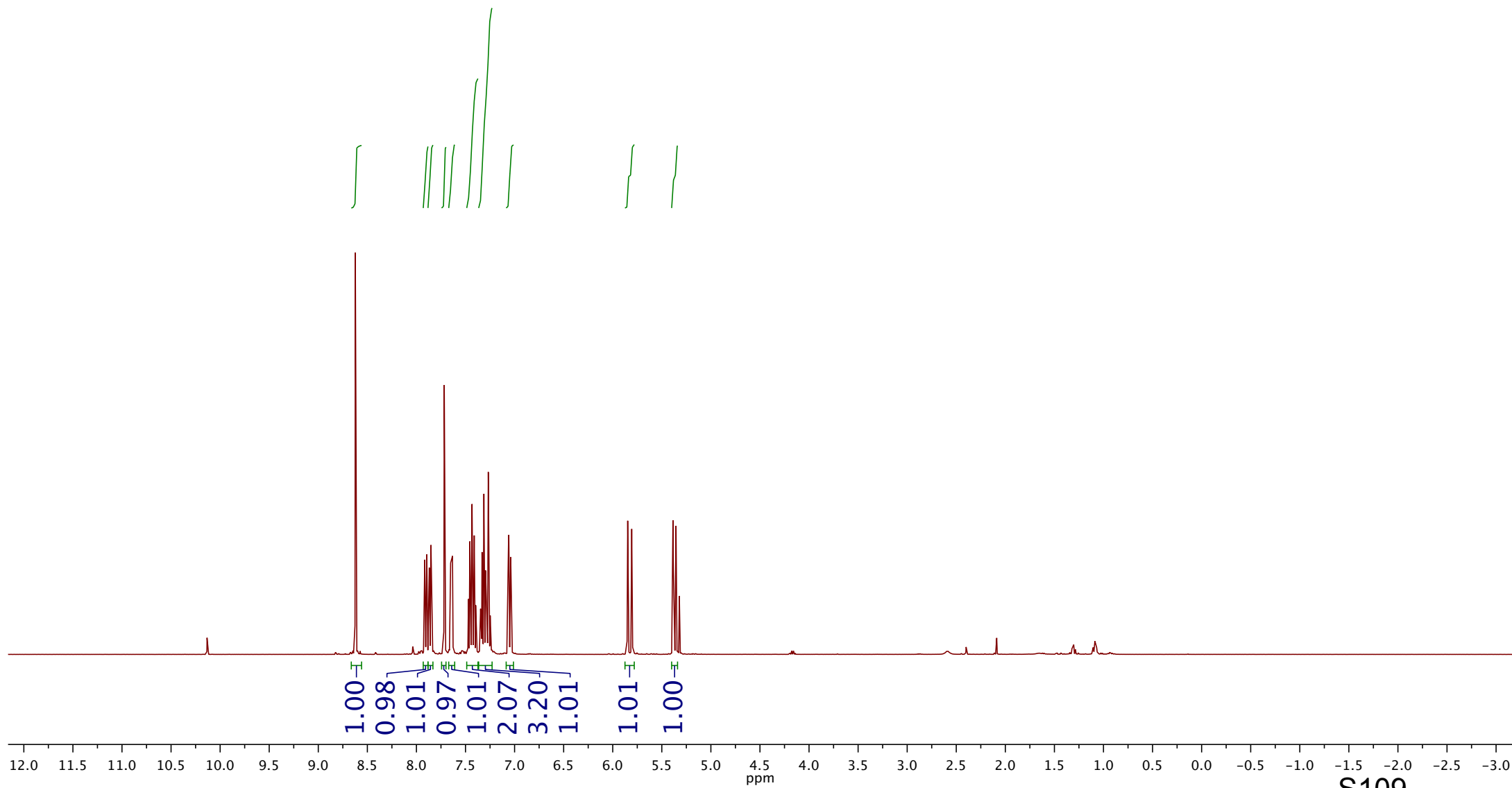
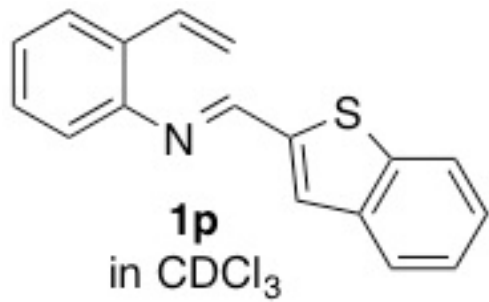


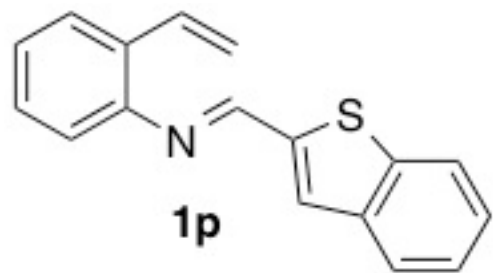
155.99  
153.30  
149.52  
148.97  
133.28  
131.62  
128.78  
127.88  
127.14  
126.52  
125.88  
123.68  
122.36  
118.48  
115.24  
112.78  
112.27

77.48 CDCI3  
77.16 CDCI3  
76.84 CDCI3



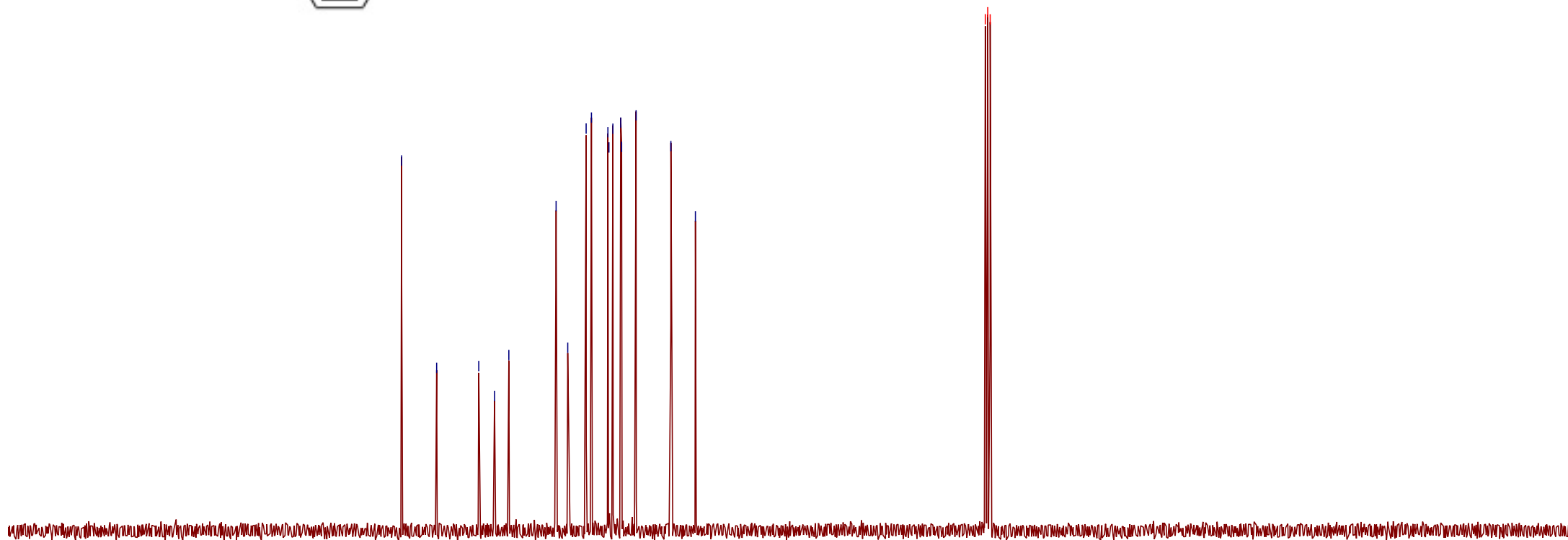


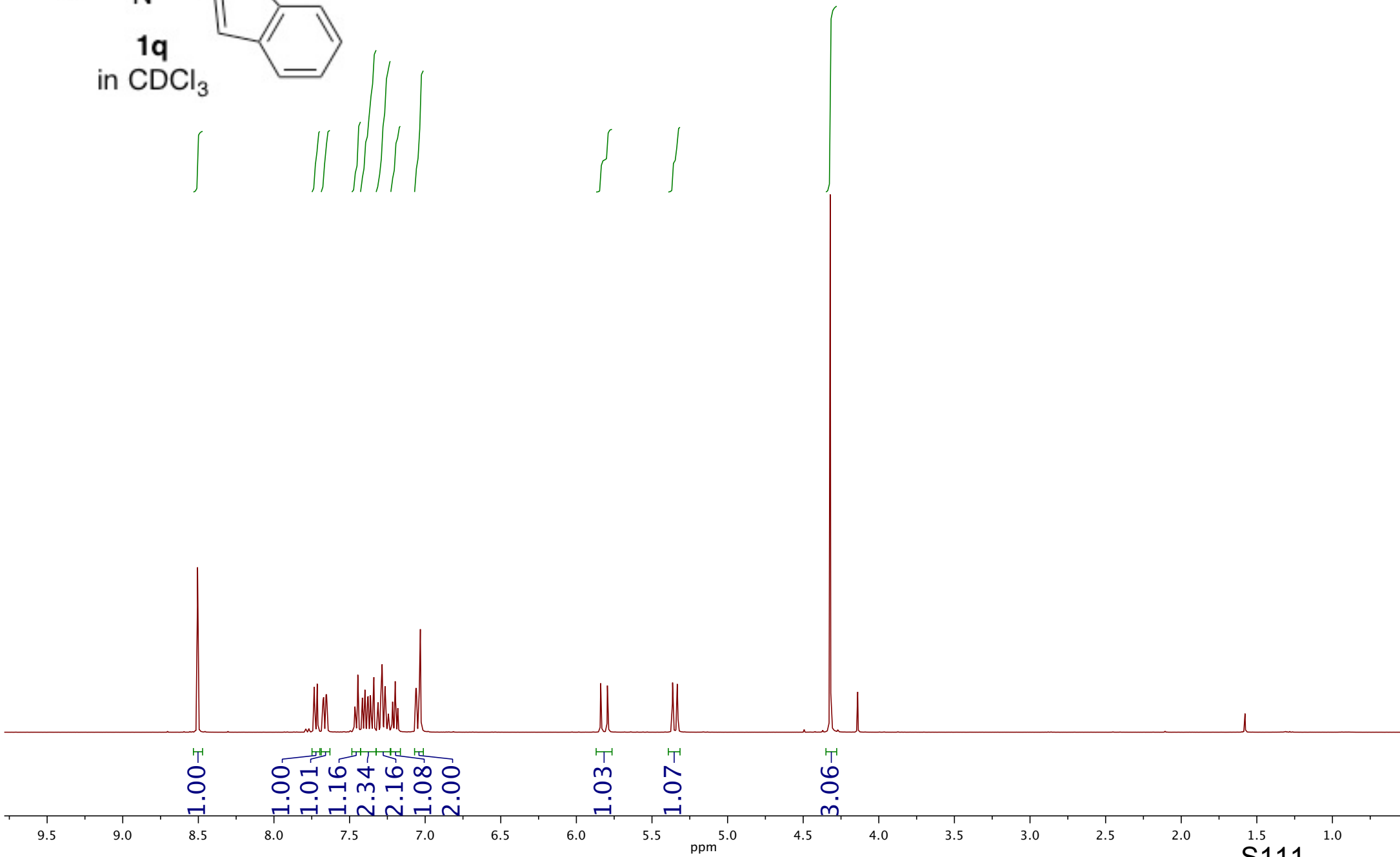
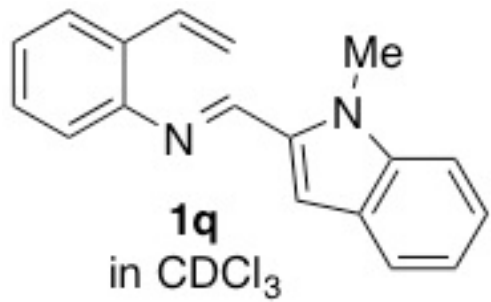


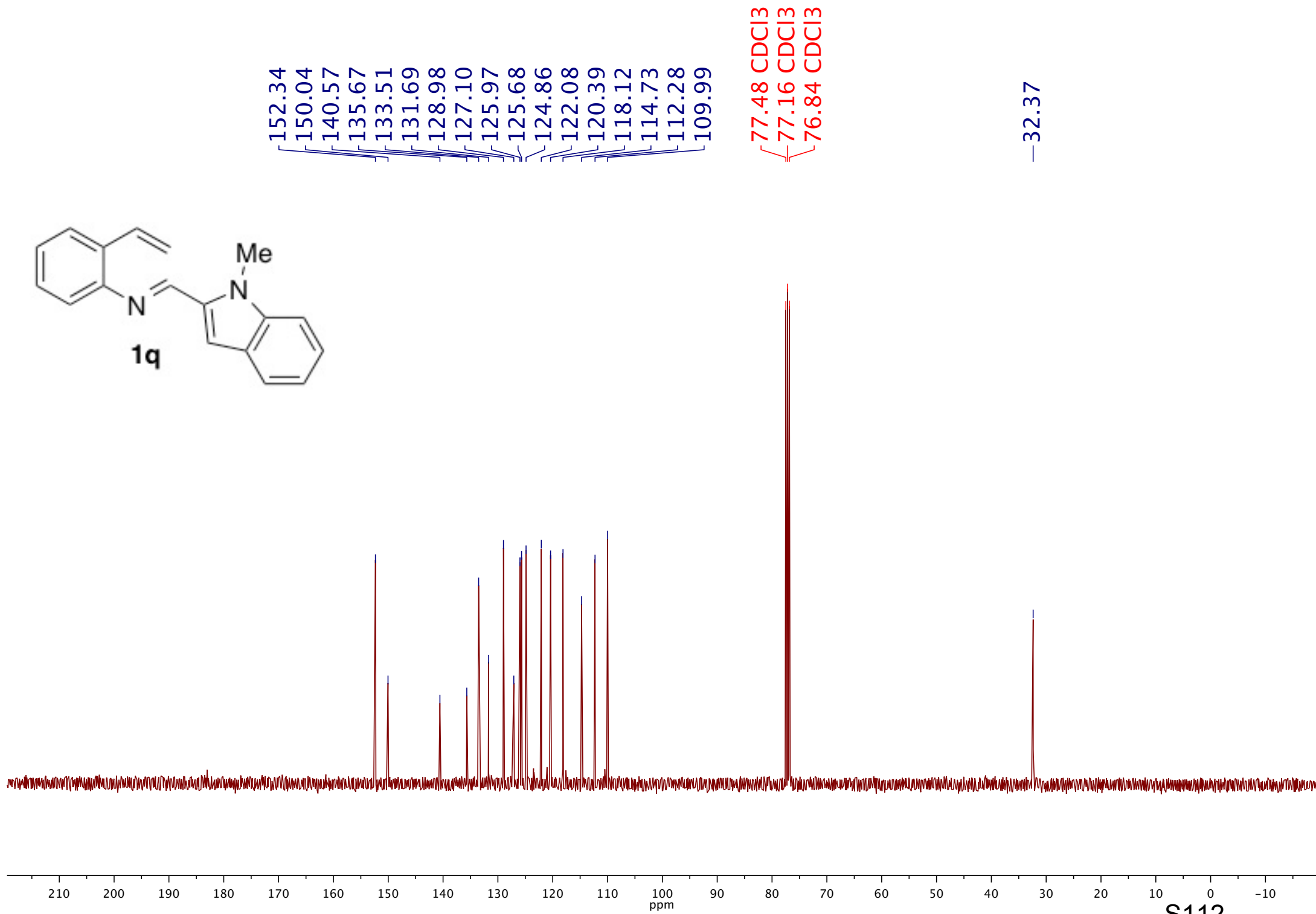
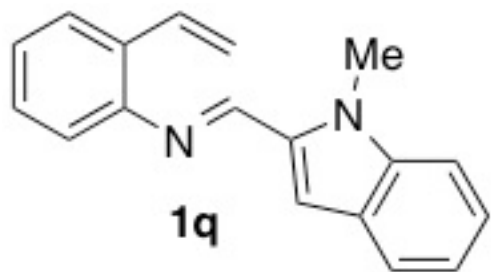


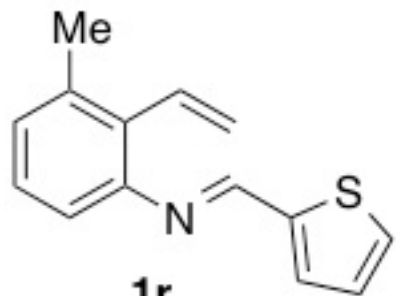
153.45  
148.89  
143.41  
141.35  
139.49  
133.34  
131.82  
129.43  
128.74  
126.60  
126.47  
125.95  
124.93  
124.81  
122.93  
118.40  
115.21

77.48 CDCI3  
77.16 CDCI3  
76.84 CDCI3

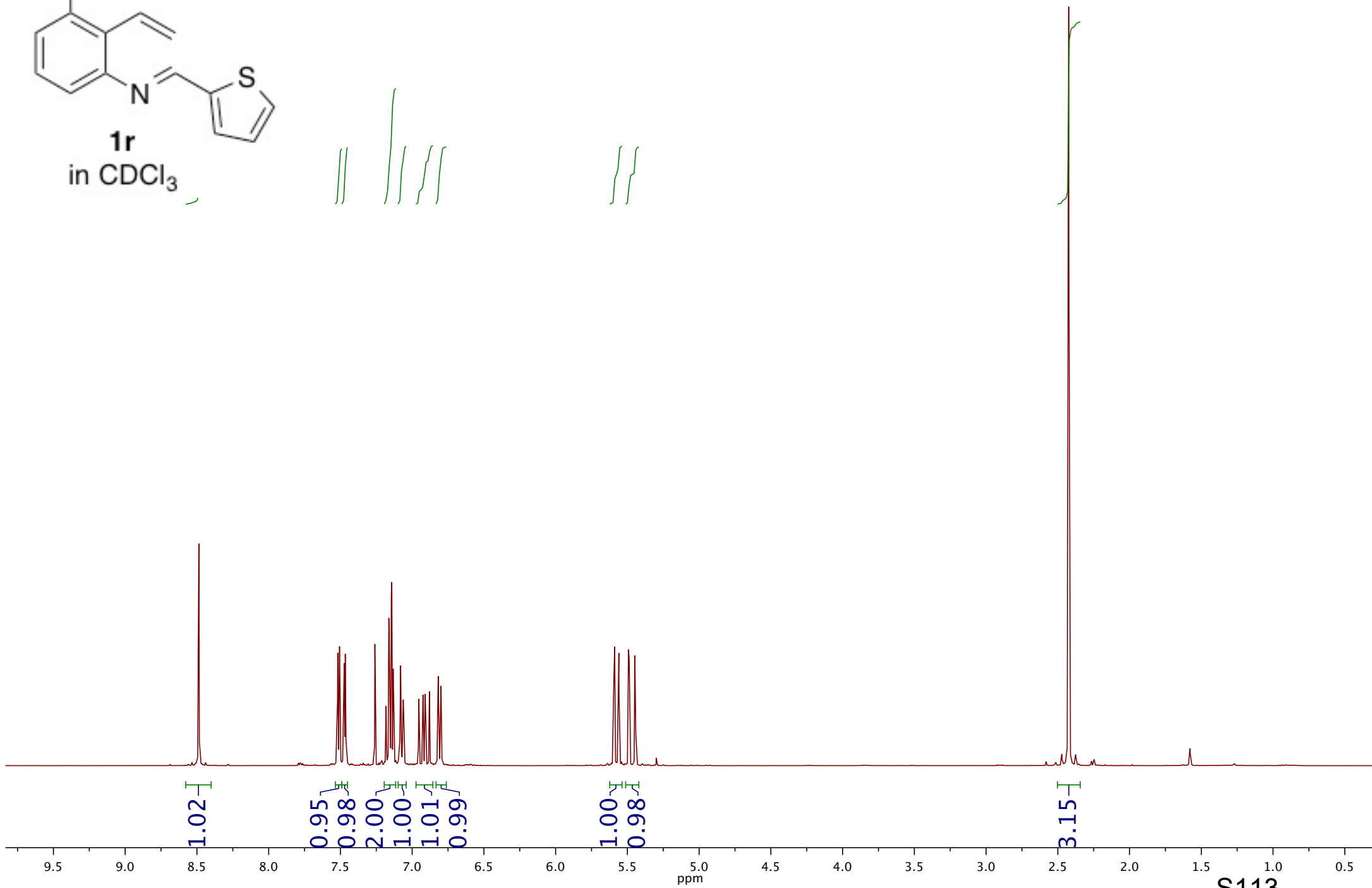




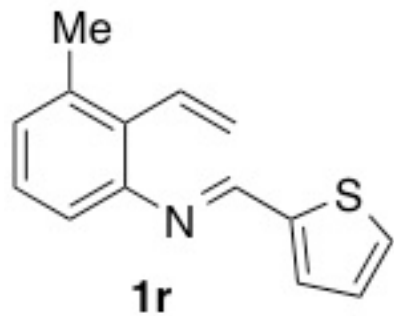




**1r**  
in CDCl<sub>3</sub>



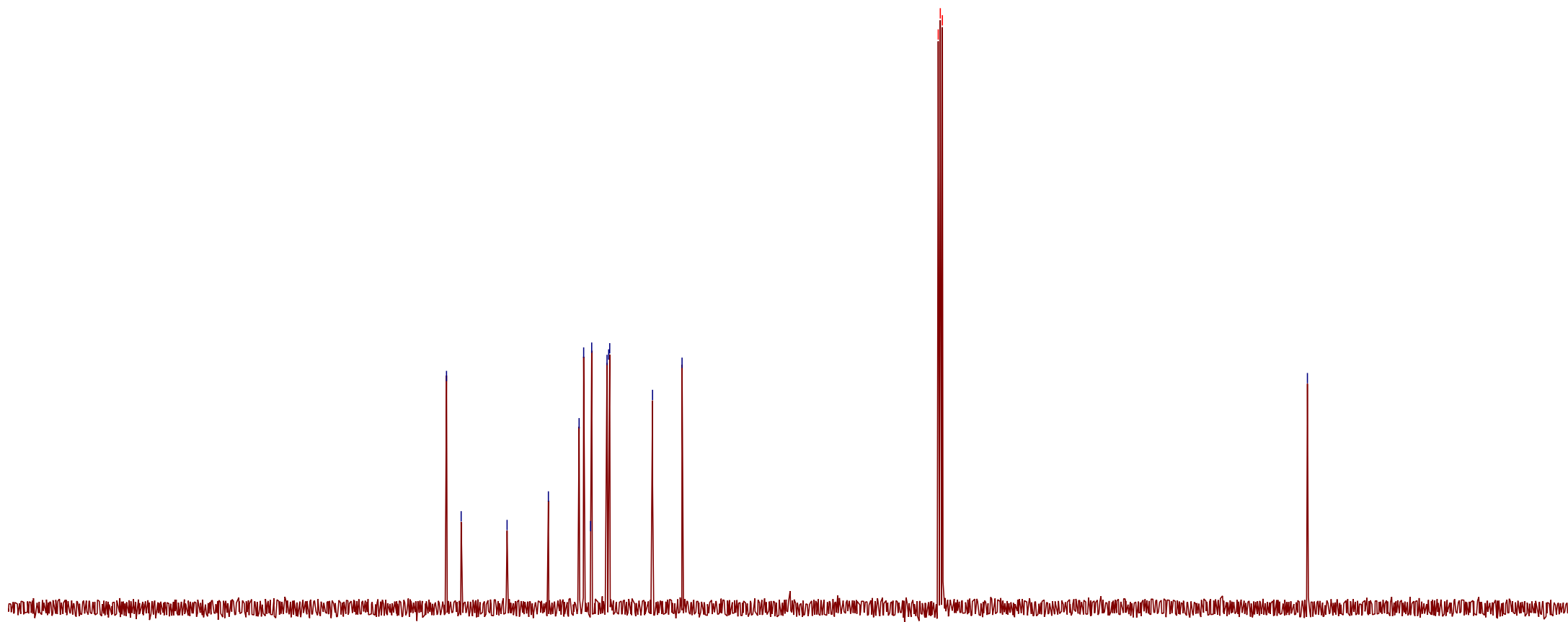
S113



152.61  
150.37  
143.36  
137.04  
132.35  
131.65  
130.59  
130.42  
128.08  
127.83  
127.67  
121.13  
116.62

77.48 CDCI3  
77.16 CDCI3  
76.84 CDCI3

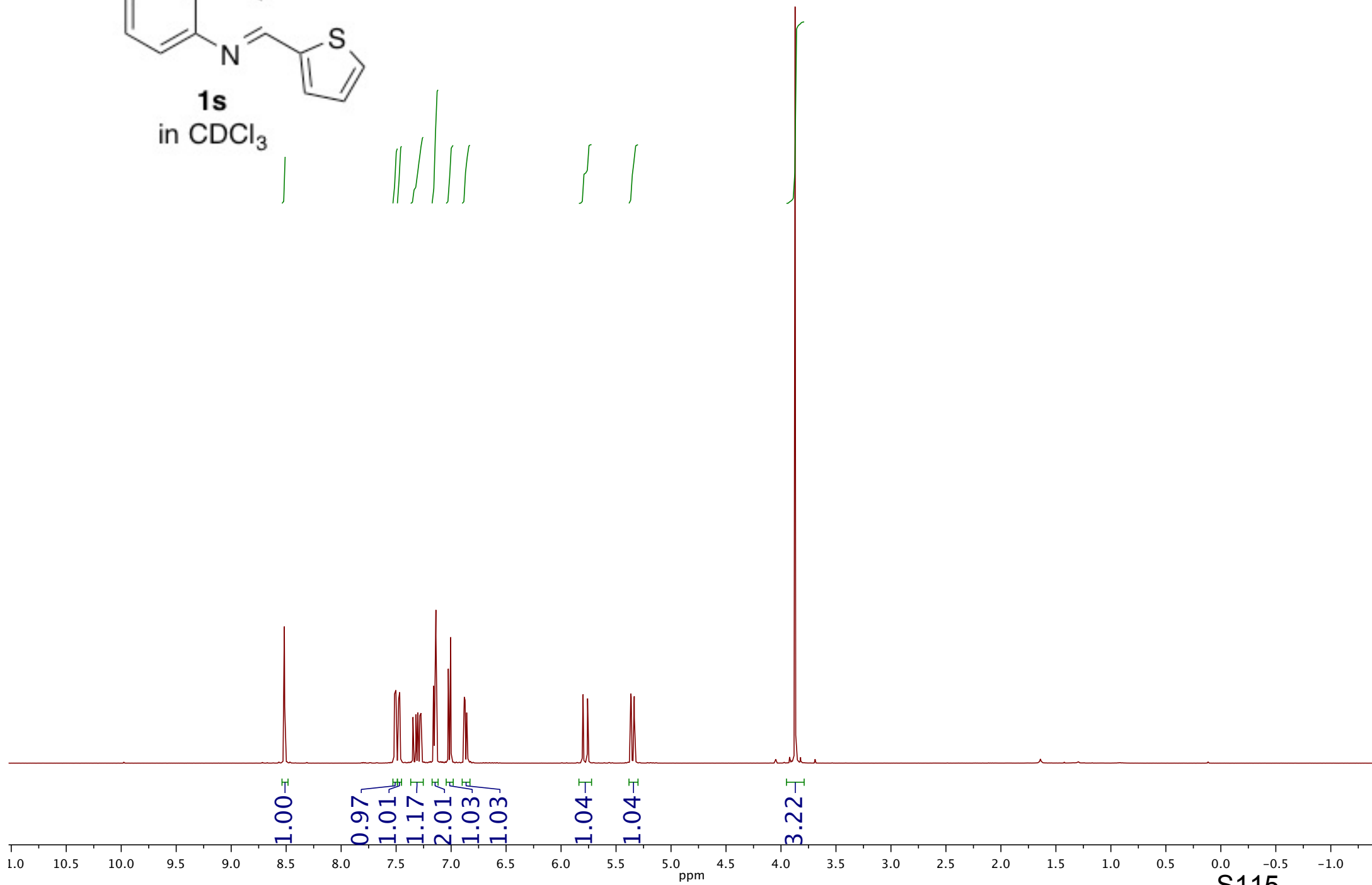
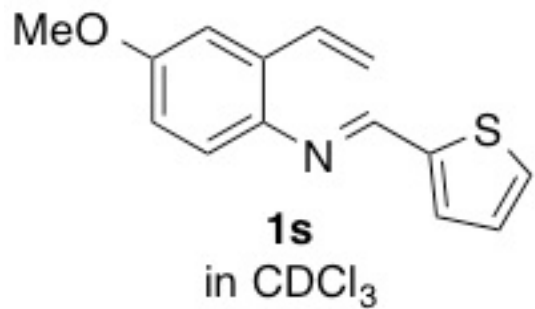
-21.07

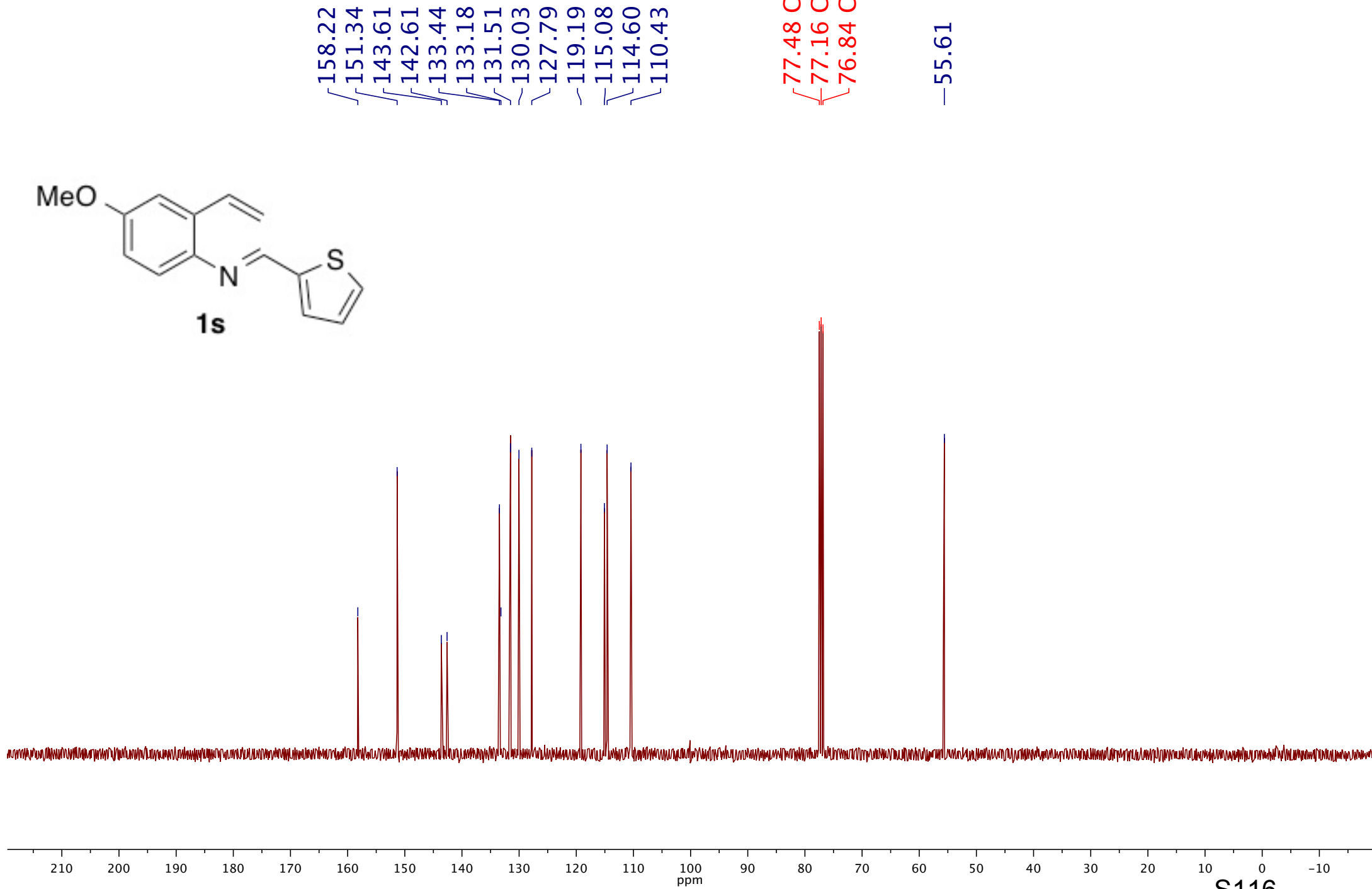
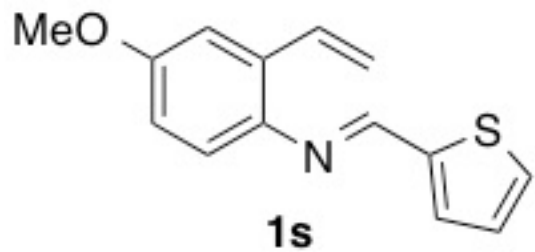


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

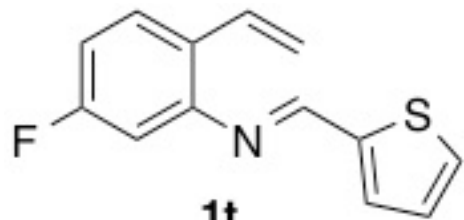
ppm

S114

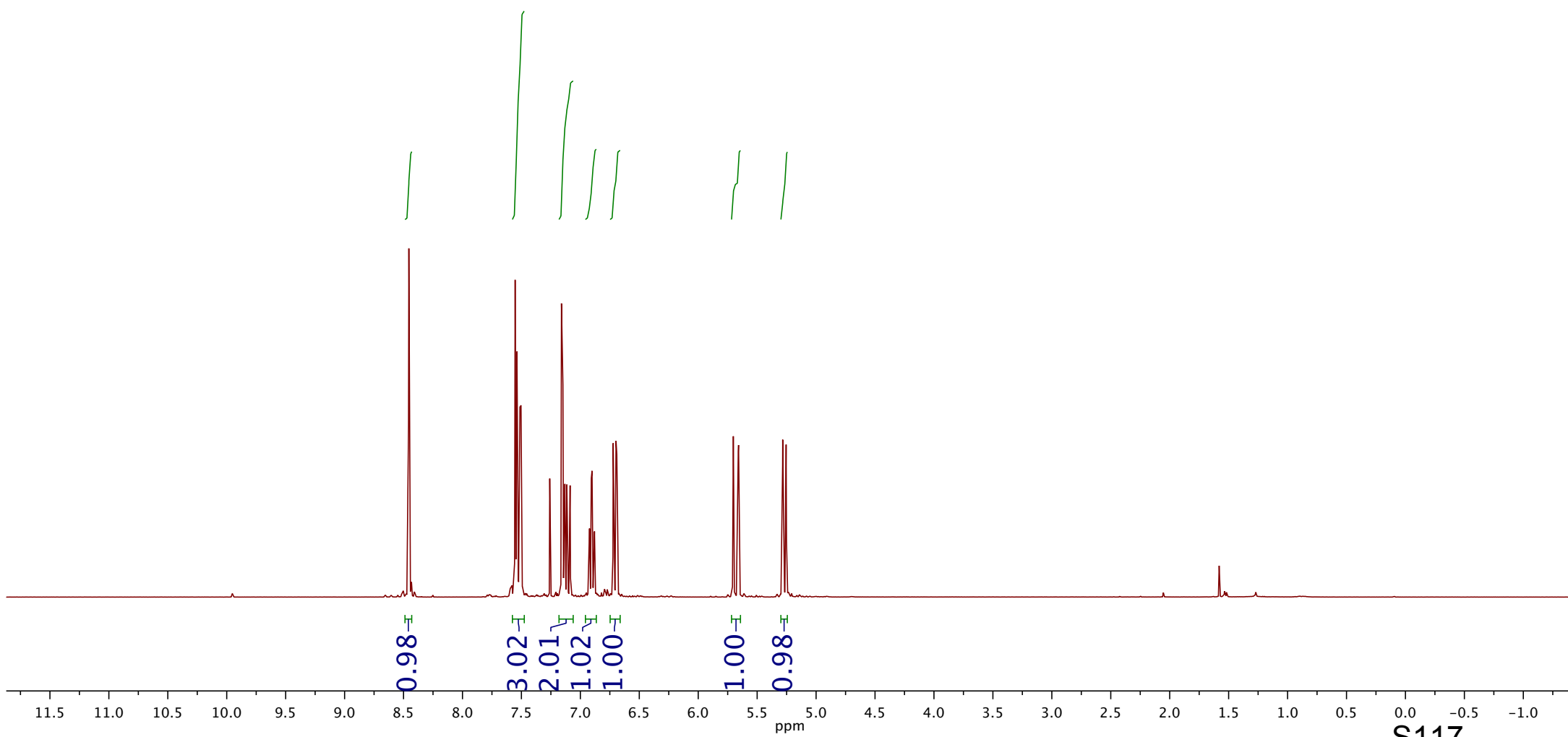


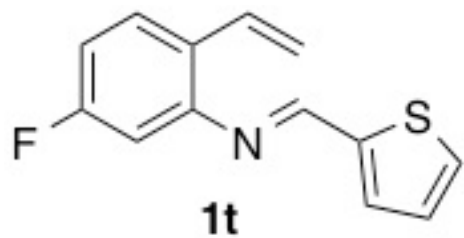






**1t**  
in CDCl<sub>3</sub>

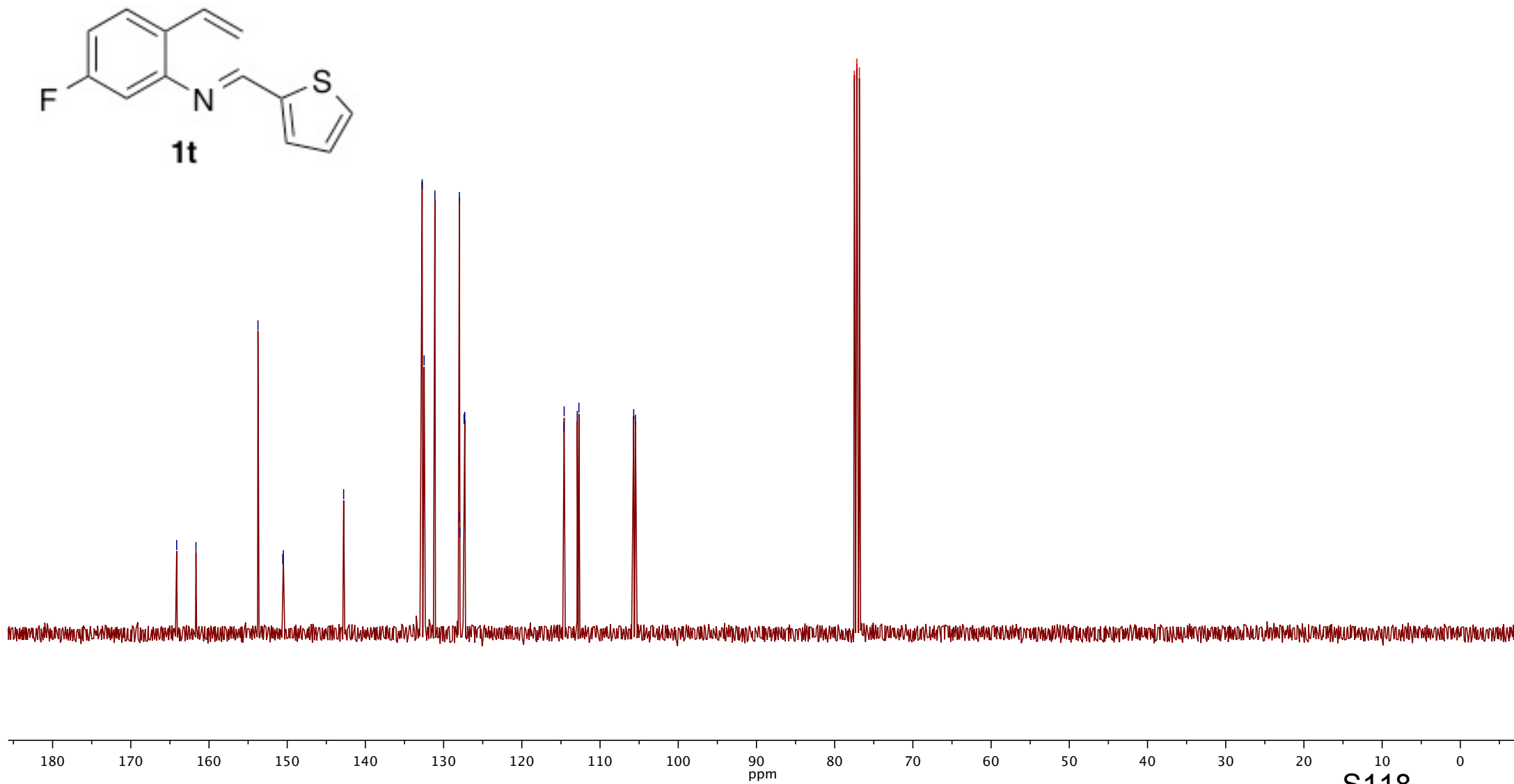


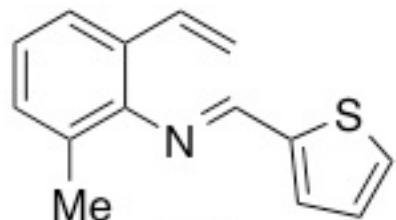


~ 164.13  
~ 161.67  
~ 153.74  
~ 150.57  
~ 150.49  
~ 142.78

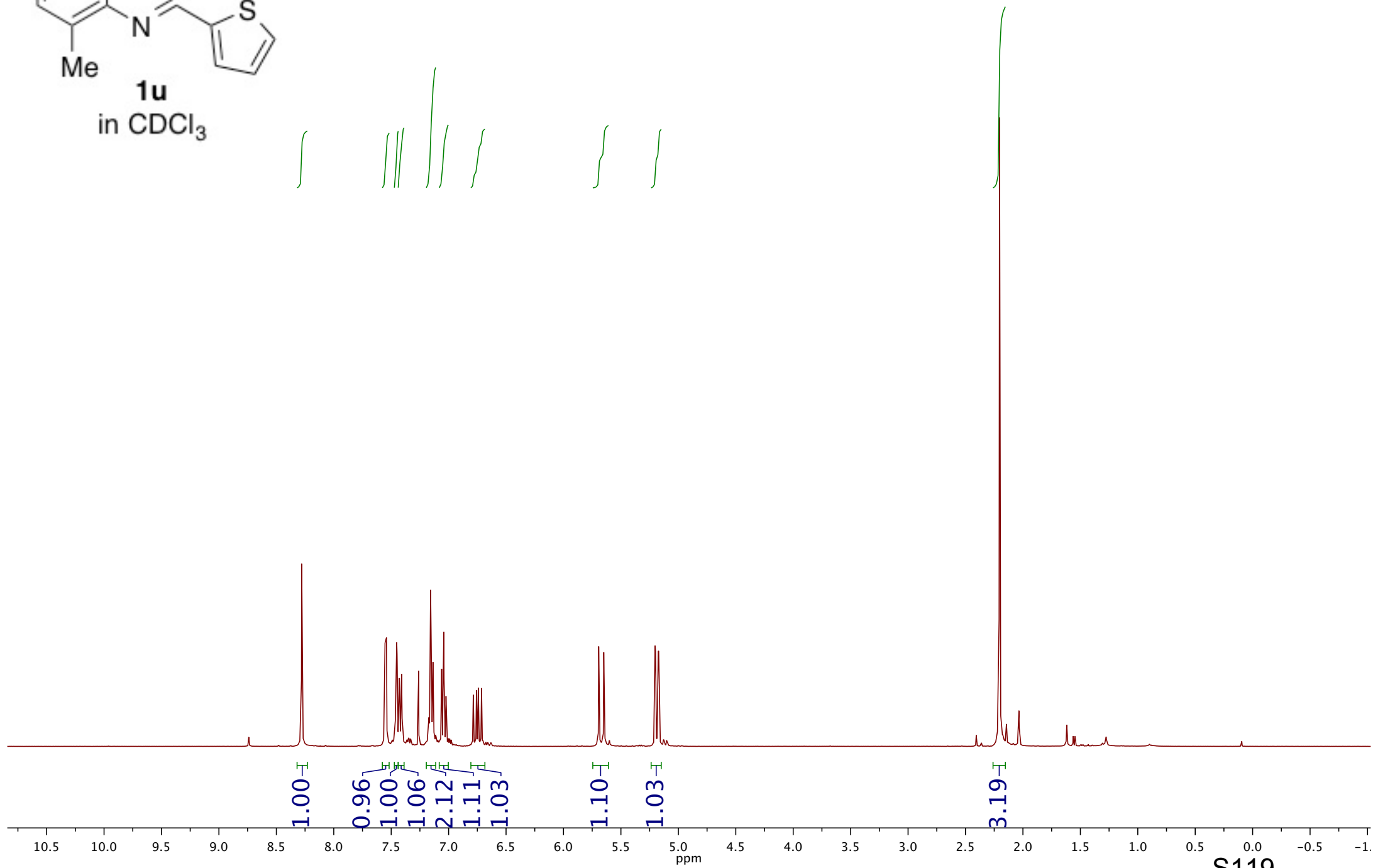
132.75  
132.49  
131.12  
127.99  
114.61  
114.59  
112.92  
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105.70  
105.47

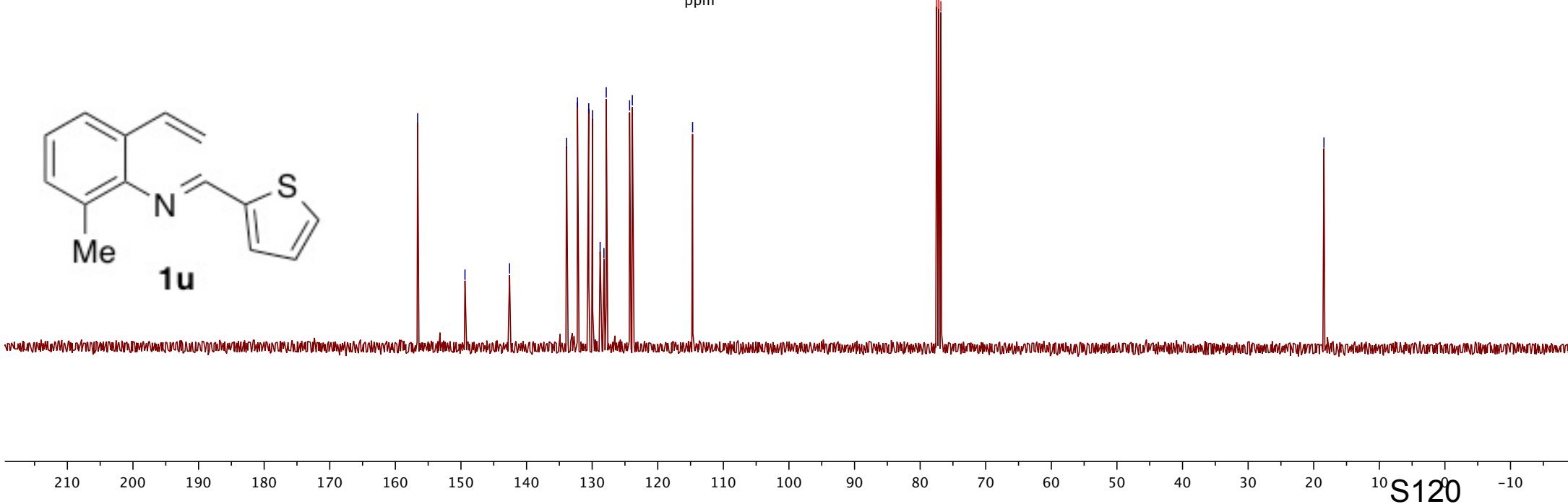
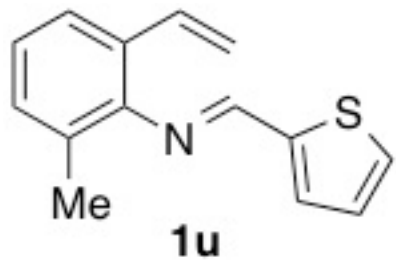
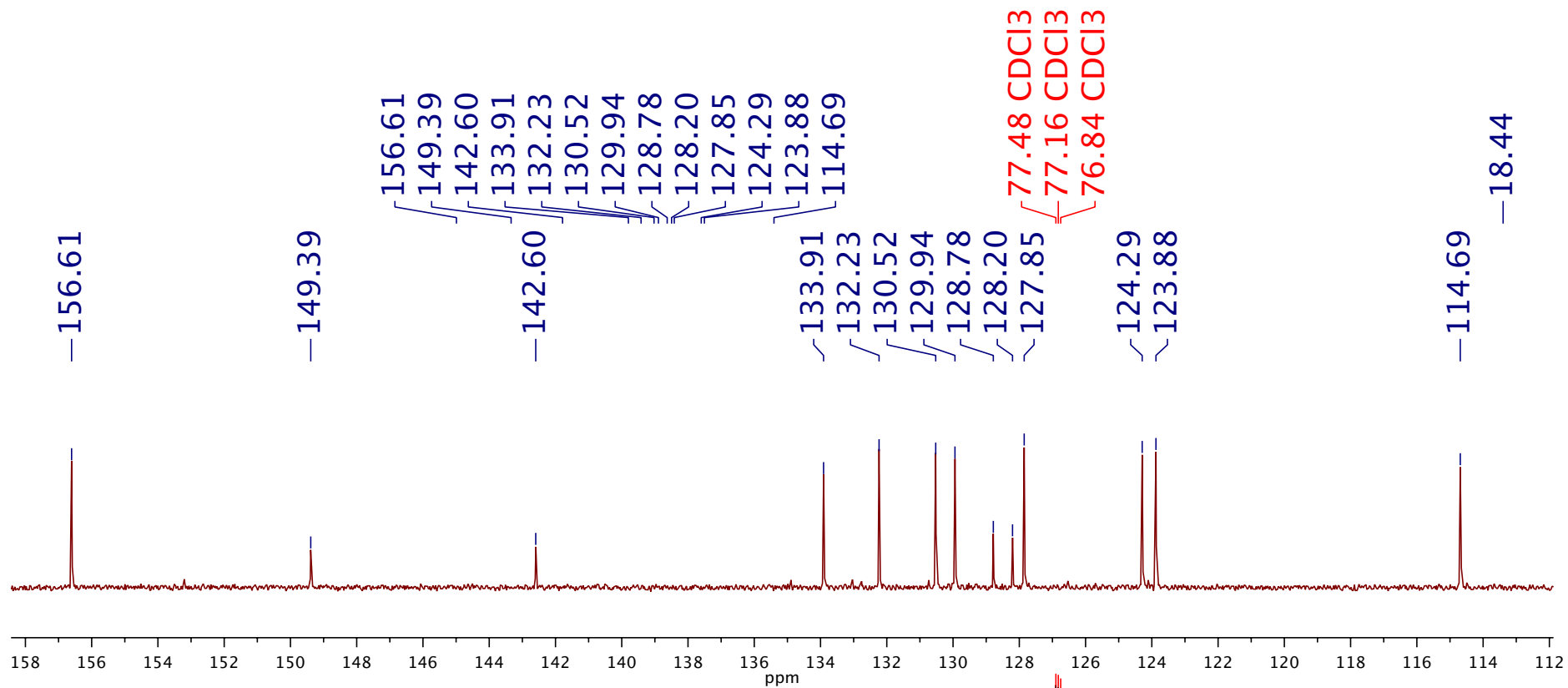
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

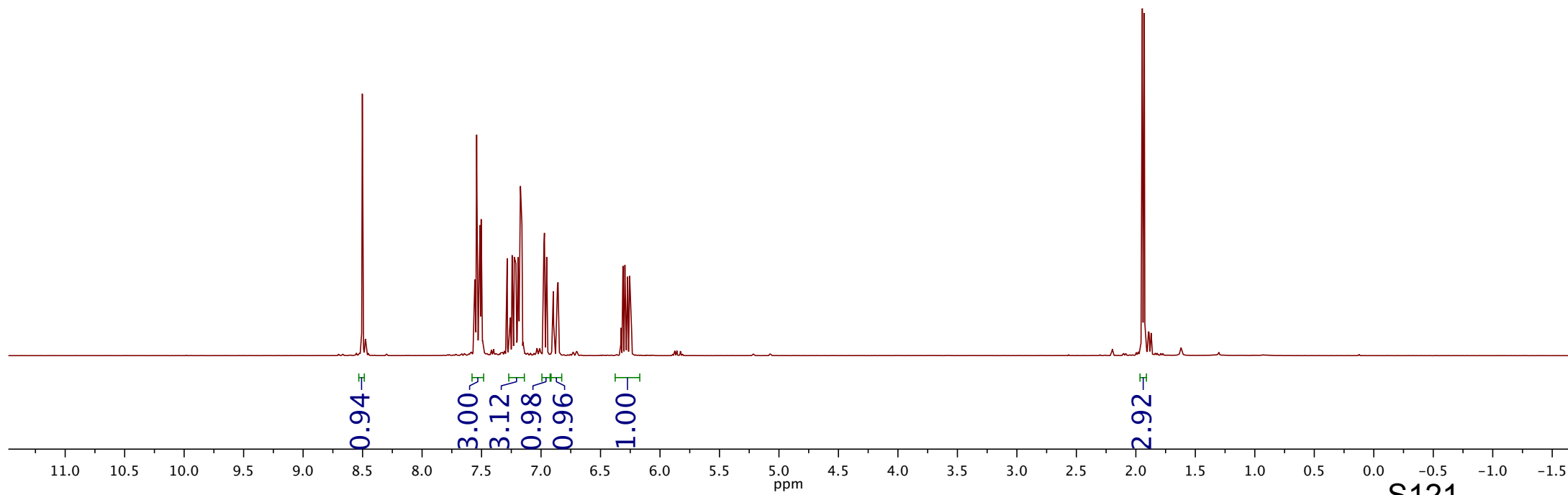
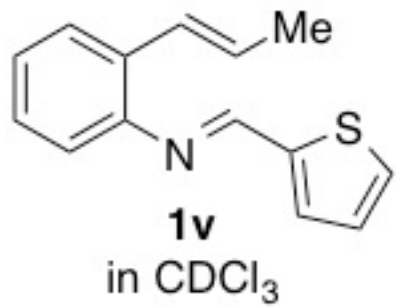


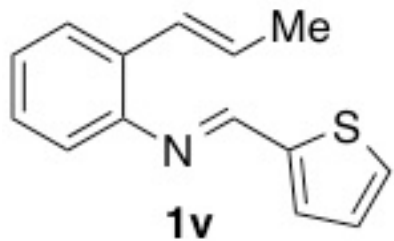


**1u**  
in CDCl<sub>3</sub>









152.69  
148.76  
143.38  
131.91  
131.86  
130.40  
127.83  
127.65  
127.47  
127.21  
126.05  
125.87  
118.54

77.48 CDCl3  
77.16 CDCl3  
76.84 CDCl3

19.16

131.91  
131.86

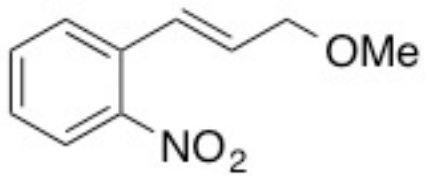
130.40

127.83  
127.65  
127.47  
127.21  
126.05  
125.87

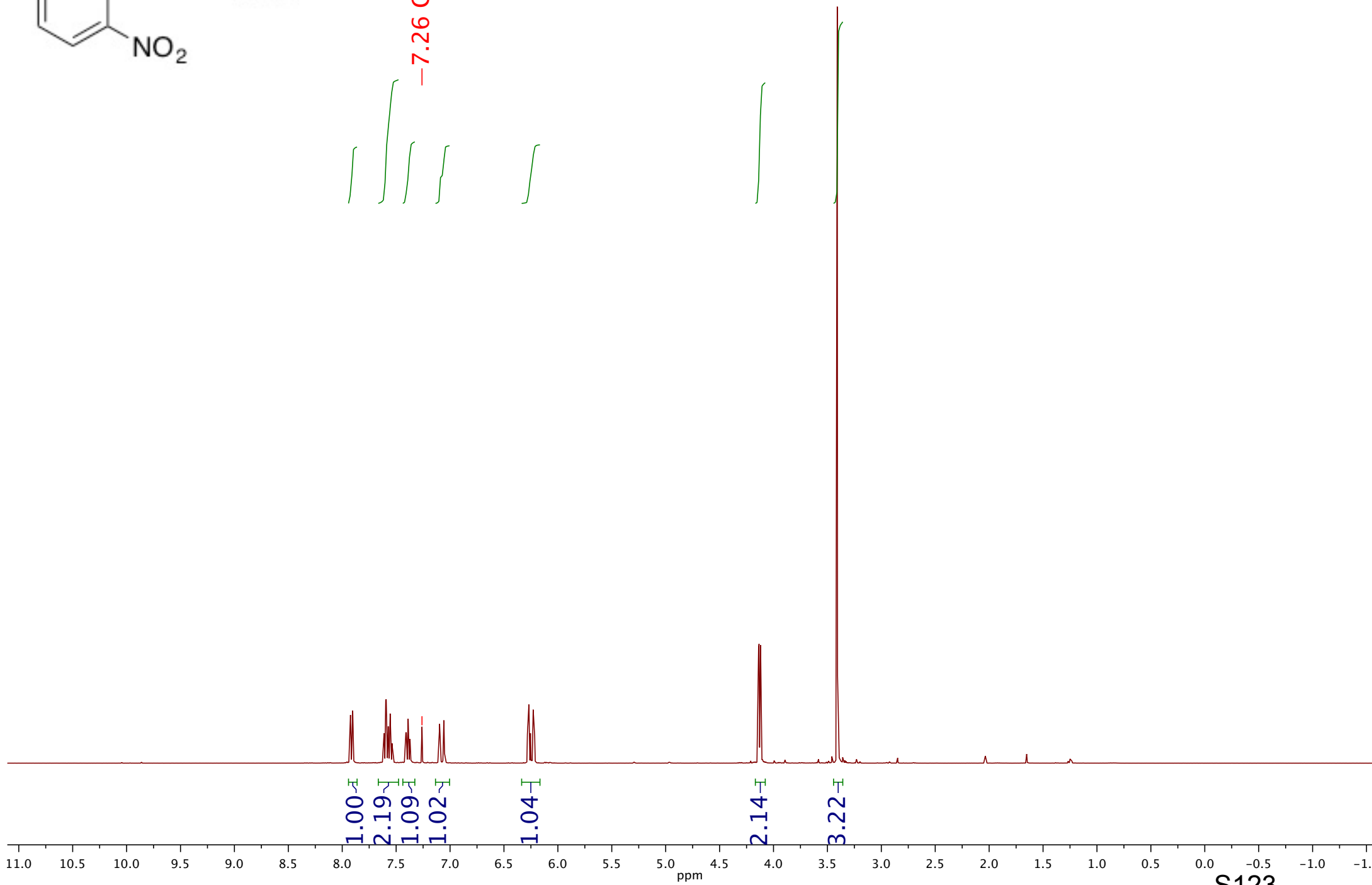
118.54

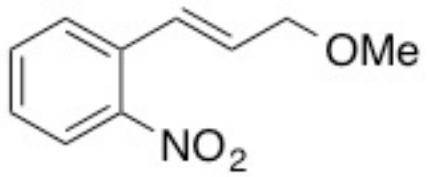
135 134 133 132 131 130 129 128 127 126 (ppm) 125 124 123 122 121 120 119 118 117 116

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



—7.26 CDCl<sub>3</sub>

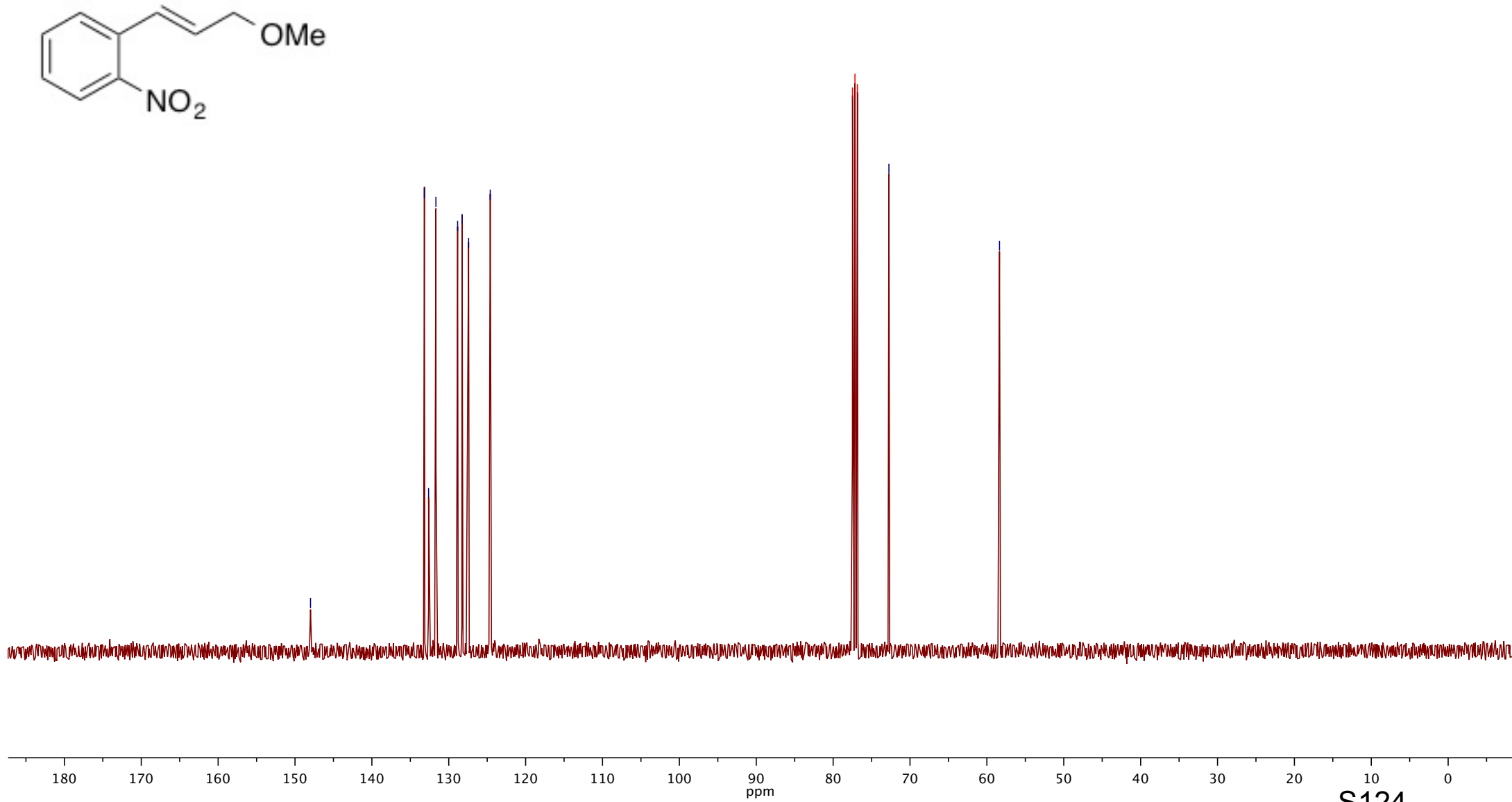




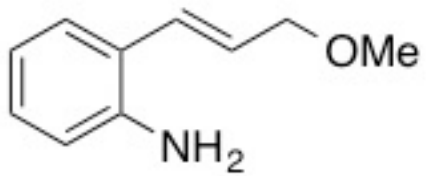
147.98  
133.17  
132.62  
131.67  
128.85  
128.27  
127.42  
124.61

77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>  
72.74

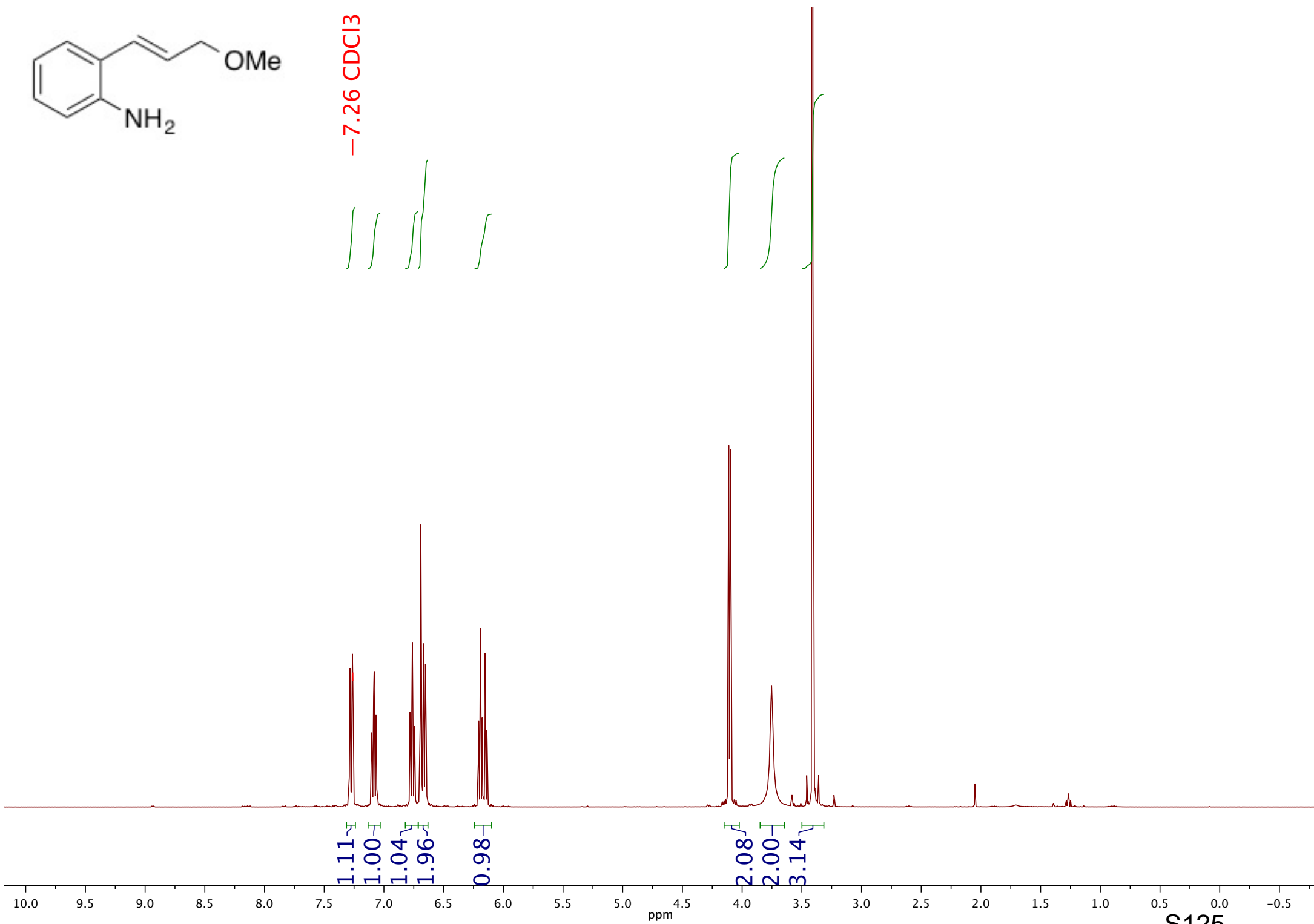
58.36

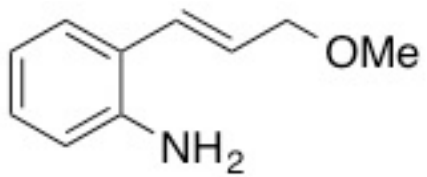




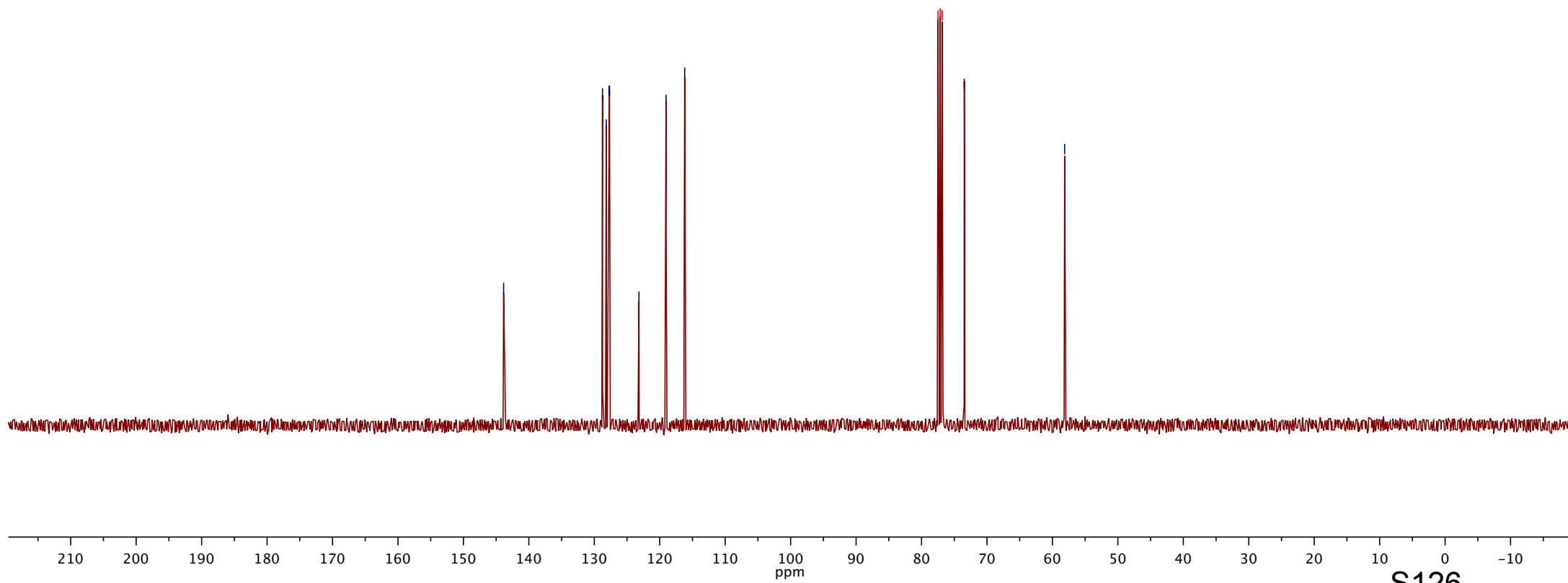


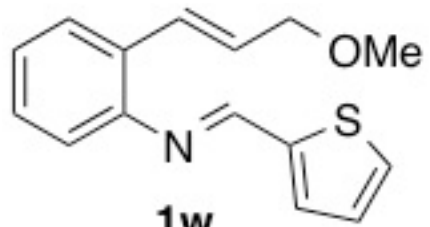
-7.26 CDCI3



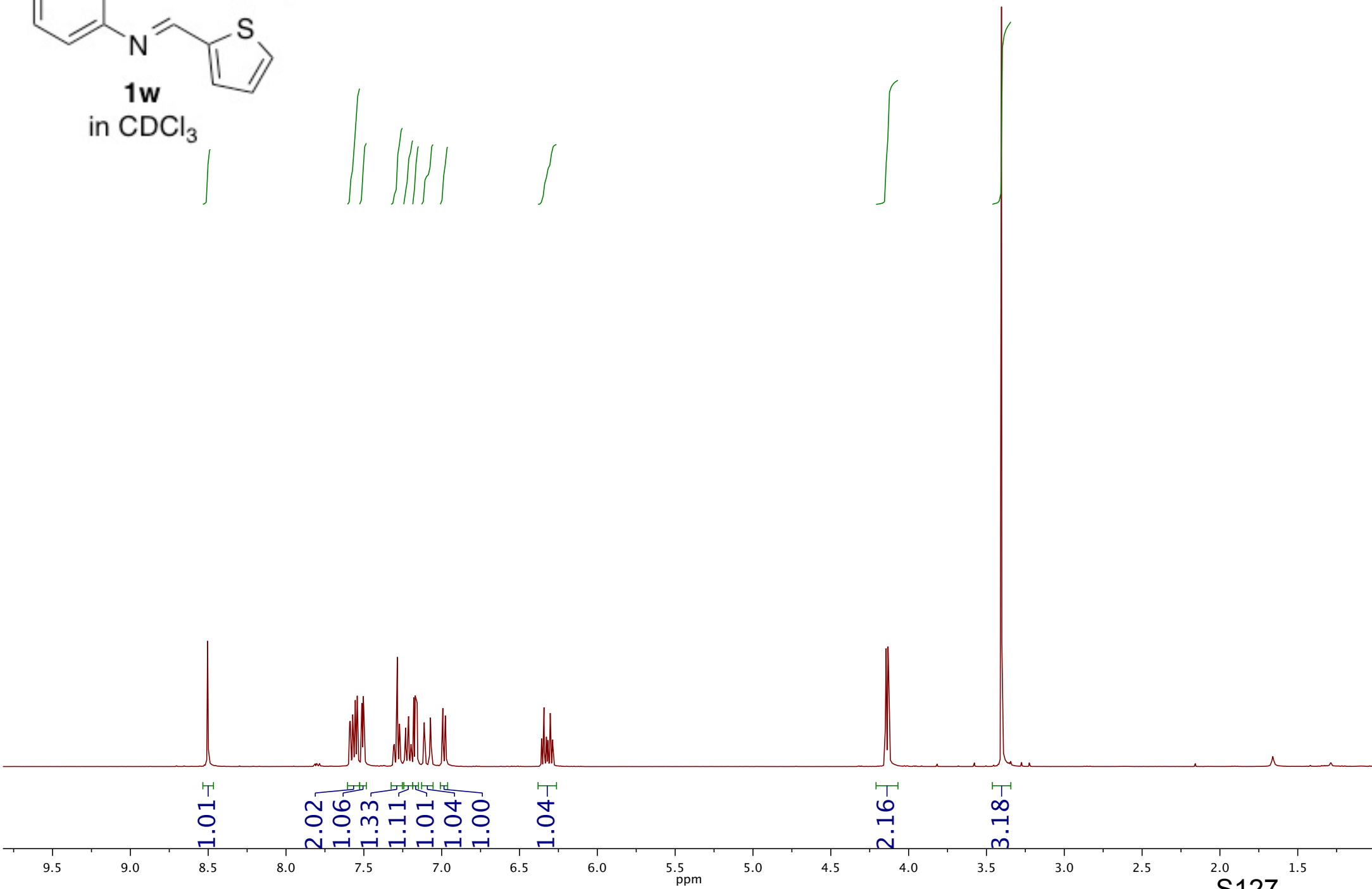


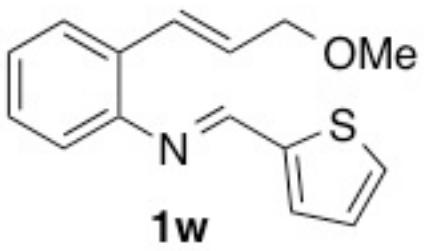
—143.85  
128.75  
128.17  
127.75  
127.68  
123.18  
119.04  
116.19  
77.48 CDCI3  
77.16 CDCI3  
76.84 CDCI3  
73.47  
—58.13





**1w**  
in CDCl<sub>3</sub>





—152.94

—149.35

—152.94

—149.35

—143.27

—132.11

—130.70

—130.59

—129.35

—128.65

—127.88

—127.32

—126.43

—126.10

—118.60

77.48 CDCl<sub>3</sub>

77.16 CDCl<sub>3</sub>

76.84 CDCl<sub>3</sub>

73.75

—57.99

—132.11

—130.70

—130.59

—129.35

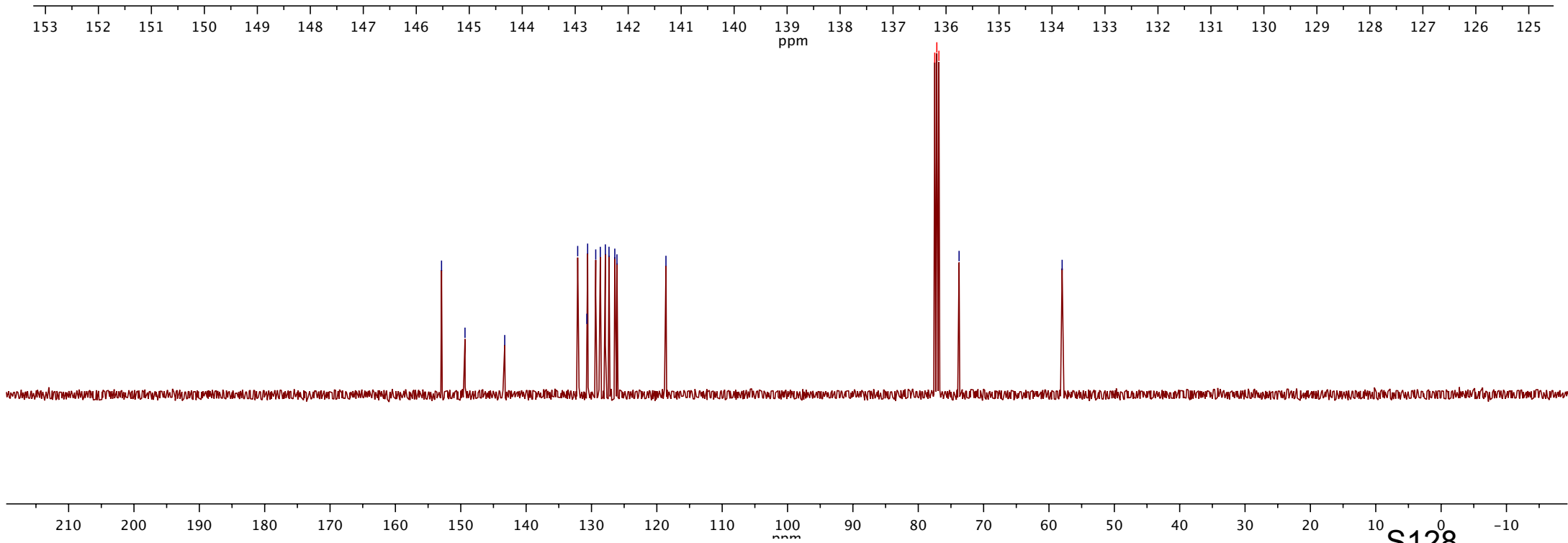
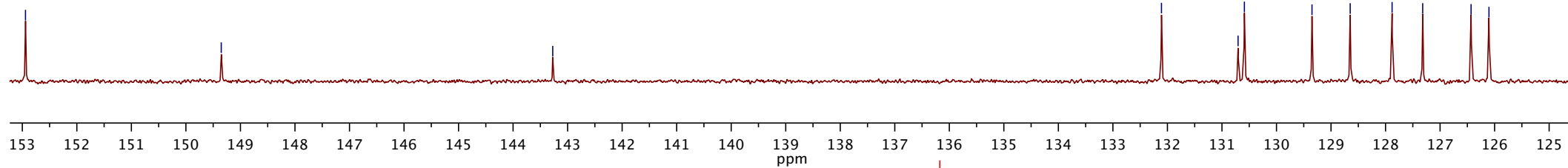
—128.65

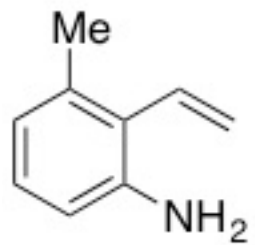
—127.88

—127.32

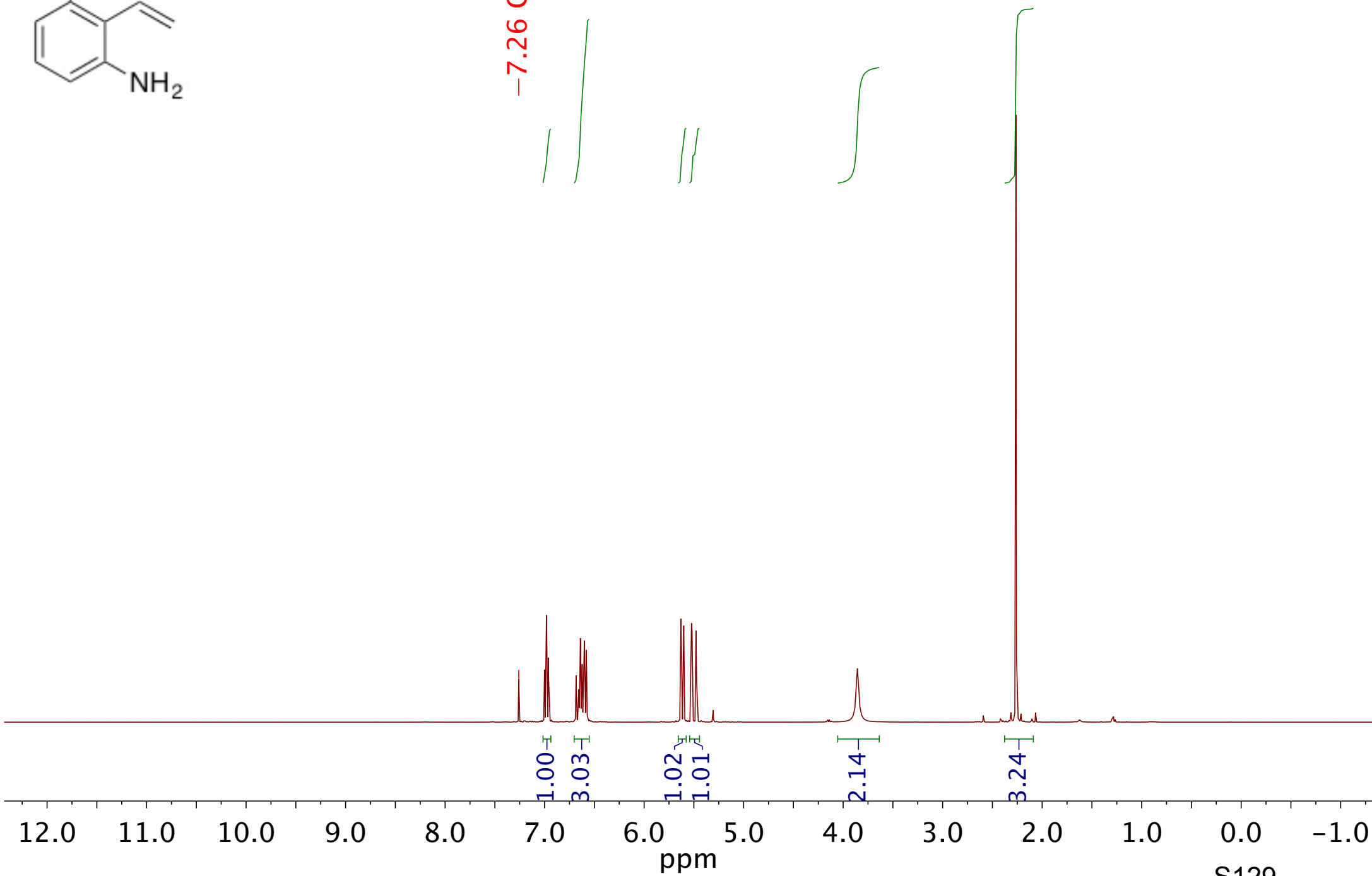
—126.43

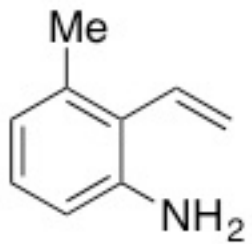
—126.10





-7.26 CDCl<sub>3</sub>

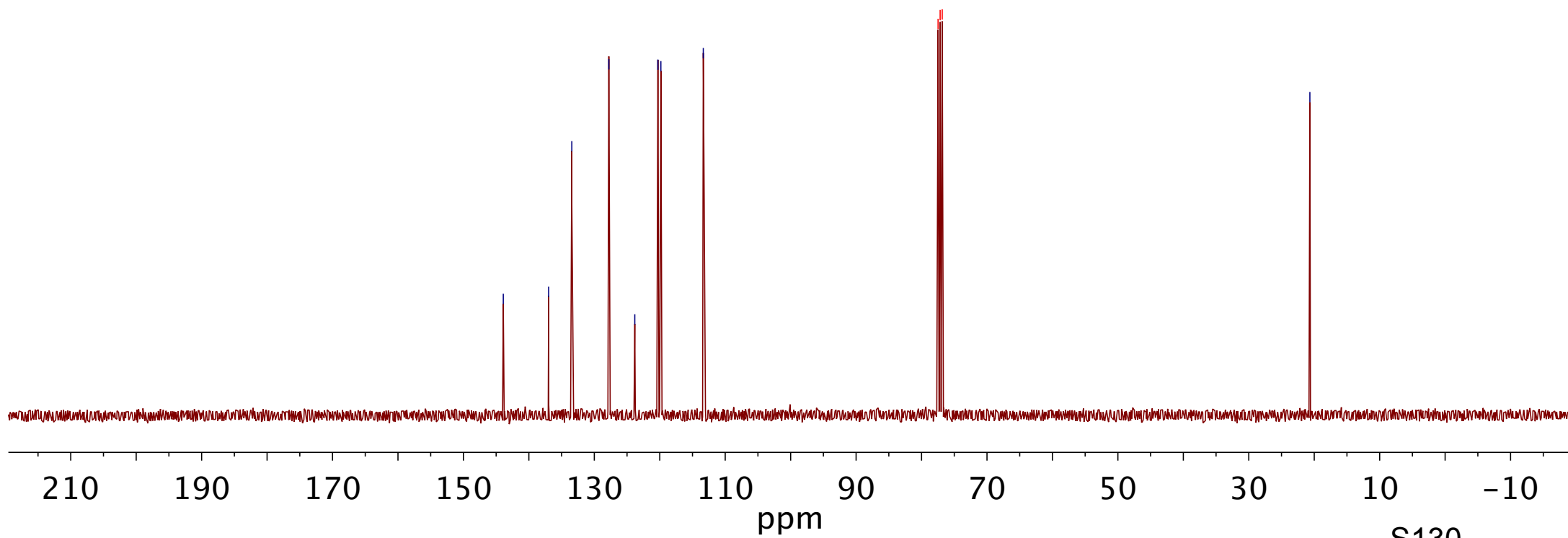




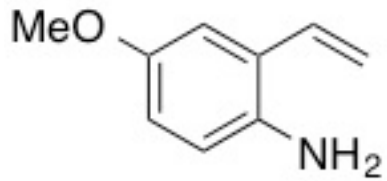
143.91  
136.98  
133.44  
127.78  
123.81  
120.28  
119.83  
113.35

77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>

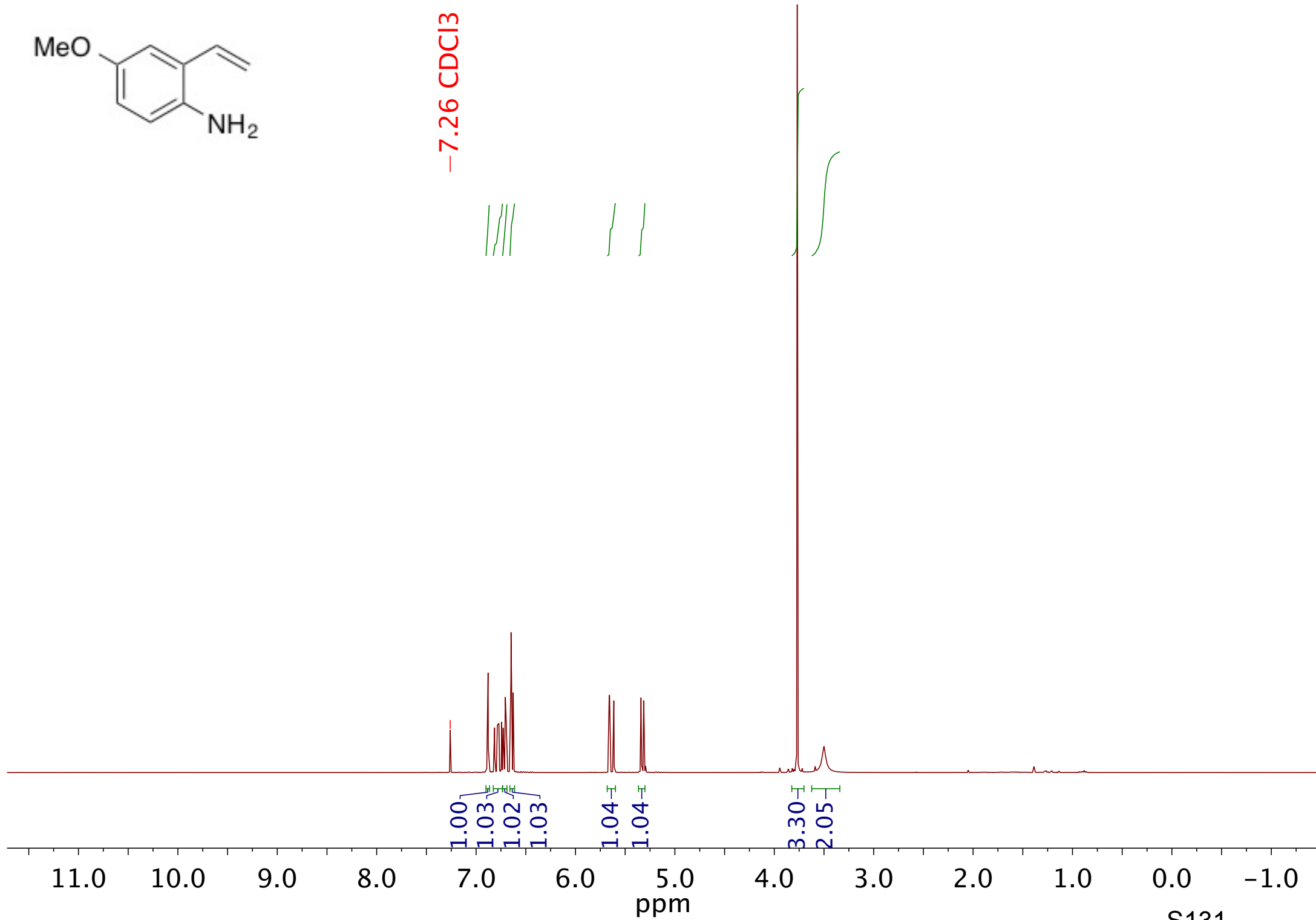
-20.66

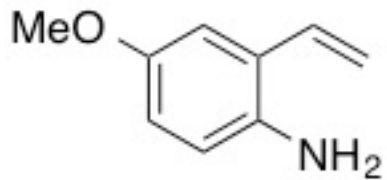


S130



-7.26 CDCl<sub>3</sub>





153.09

137.58

132.77

125.30

117.62

115.87

115.09

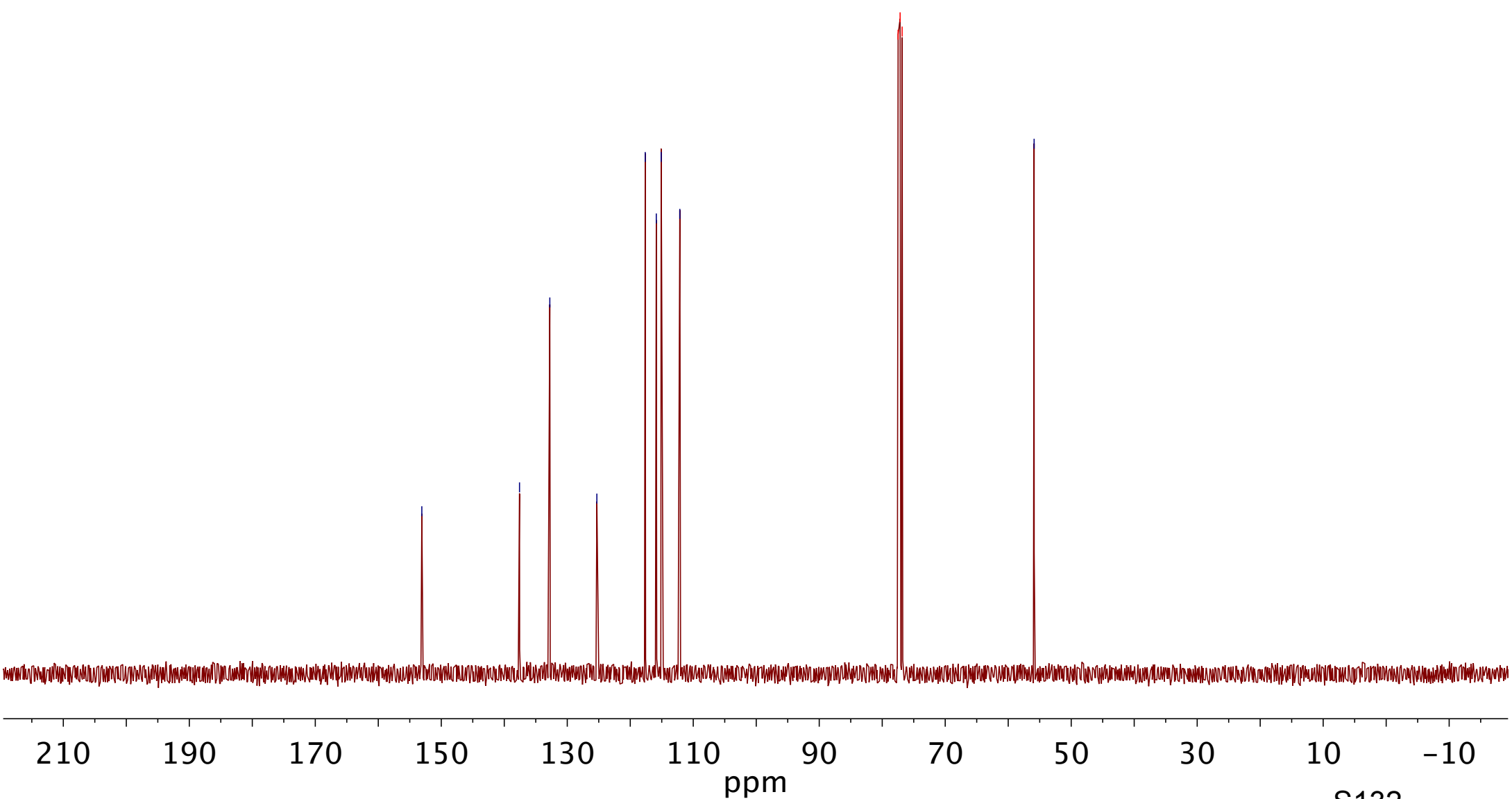
112.13

77.48 CDCl<sub>3</sub>

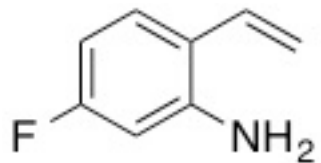
77.16 CDCl<sub>3</sub>

76.84 CDCl<sub>3</sub>

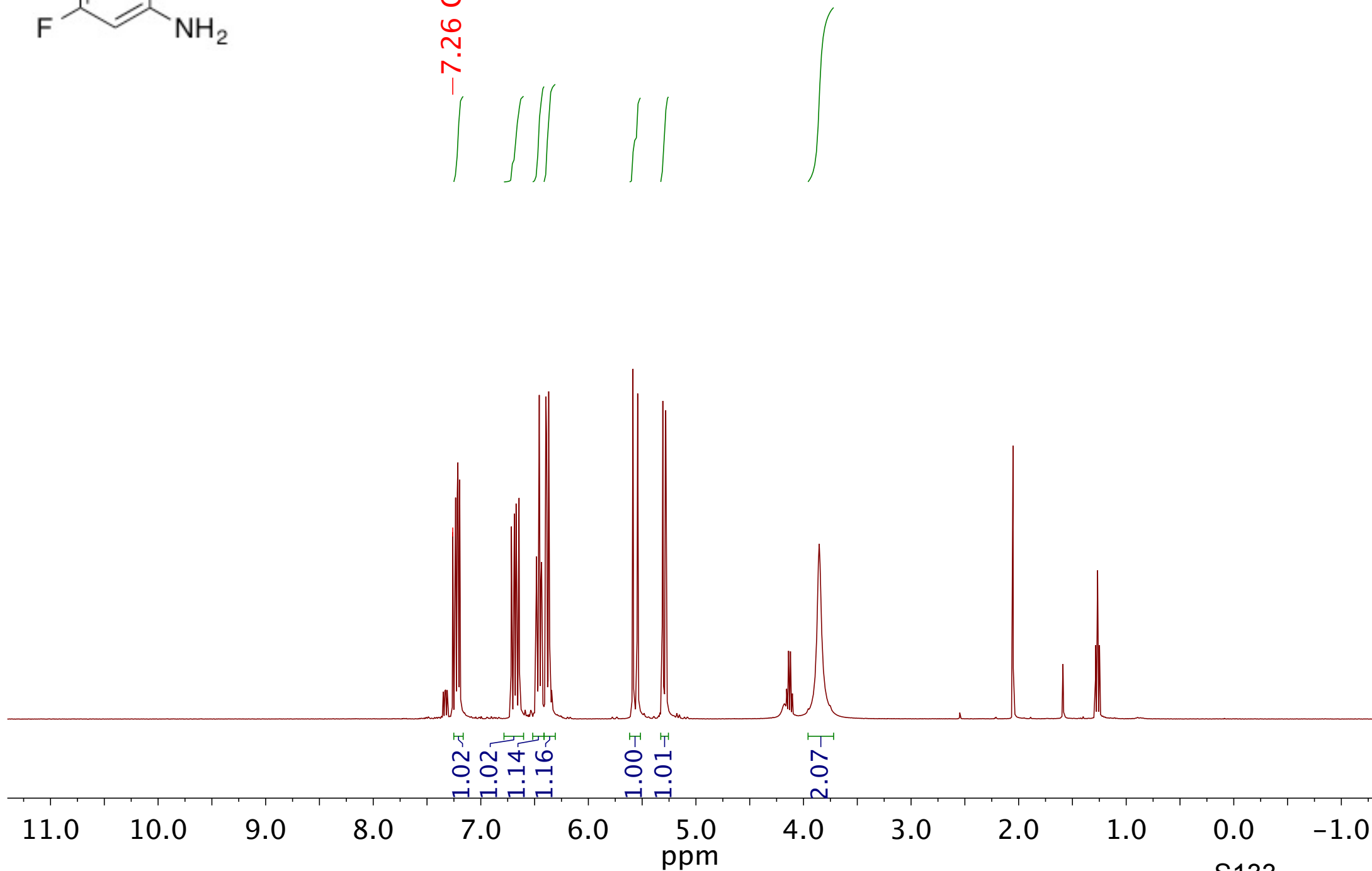
55.89

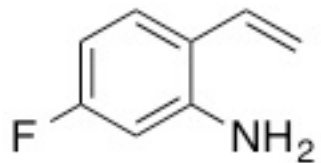






-7.26 CDCl3





164.61  
162.18

145.39  
145.28

131.98  
128.98  
128.88

120.23

115.65

115.64

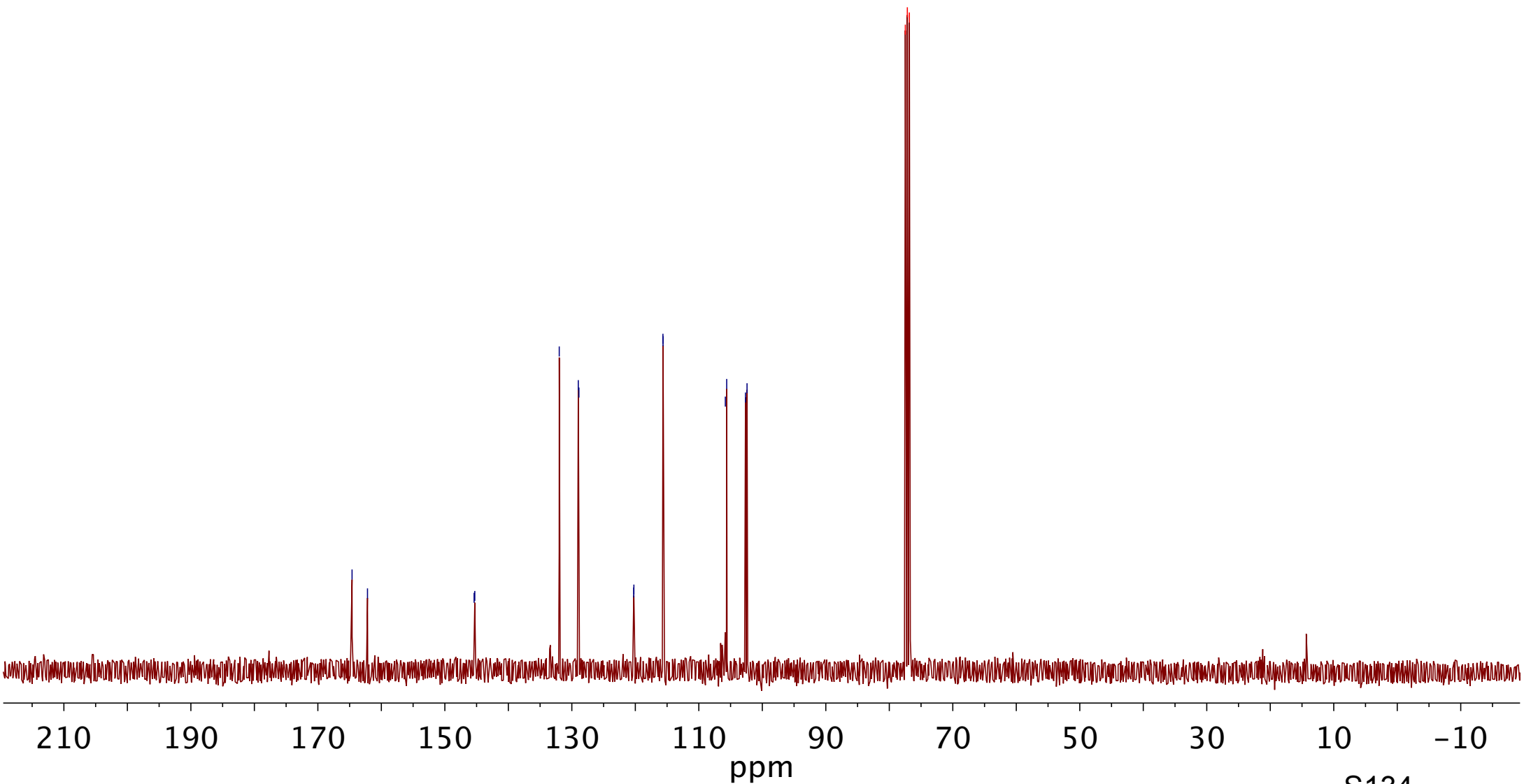
105.82

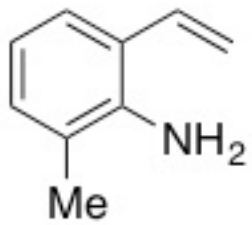
105.61

102.65

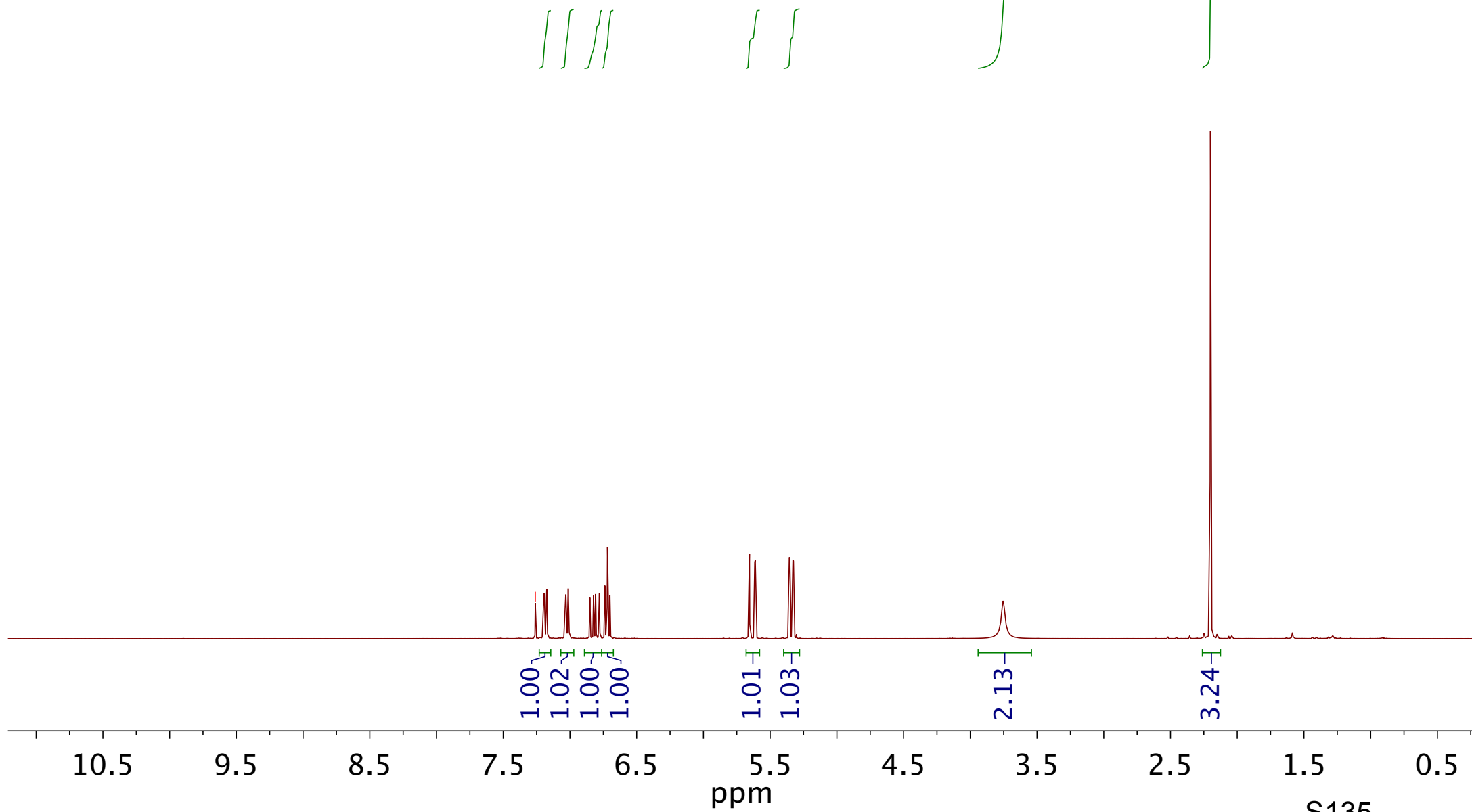
102.41

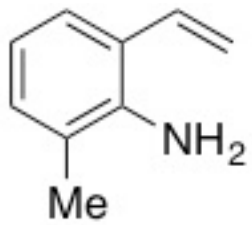
77.48 CDCl<sub>3</sub>  
77.16 CDCl<sub>3</sub>  
76.84 CDCl<sub>3</sub>





-7.26 CDCl<sub>3</sub>





-141.98

133.27

130.04

125.46

123.91

122.62

118.38

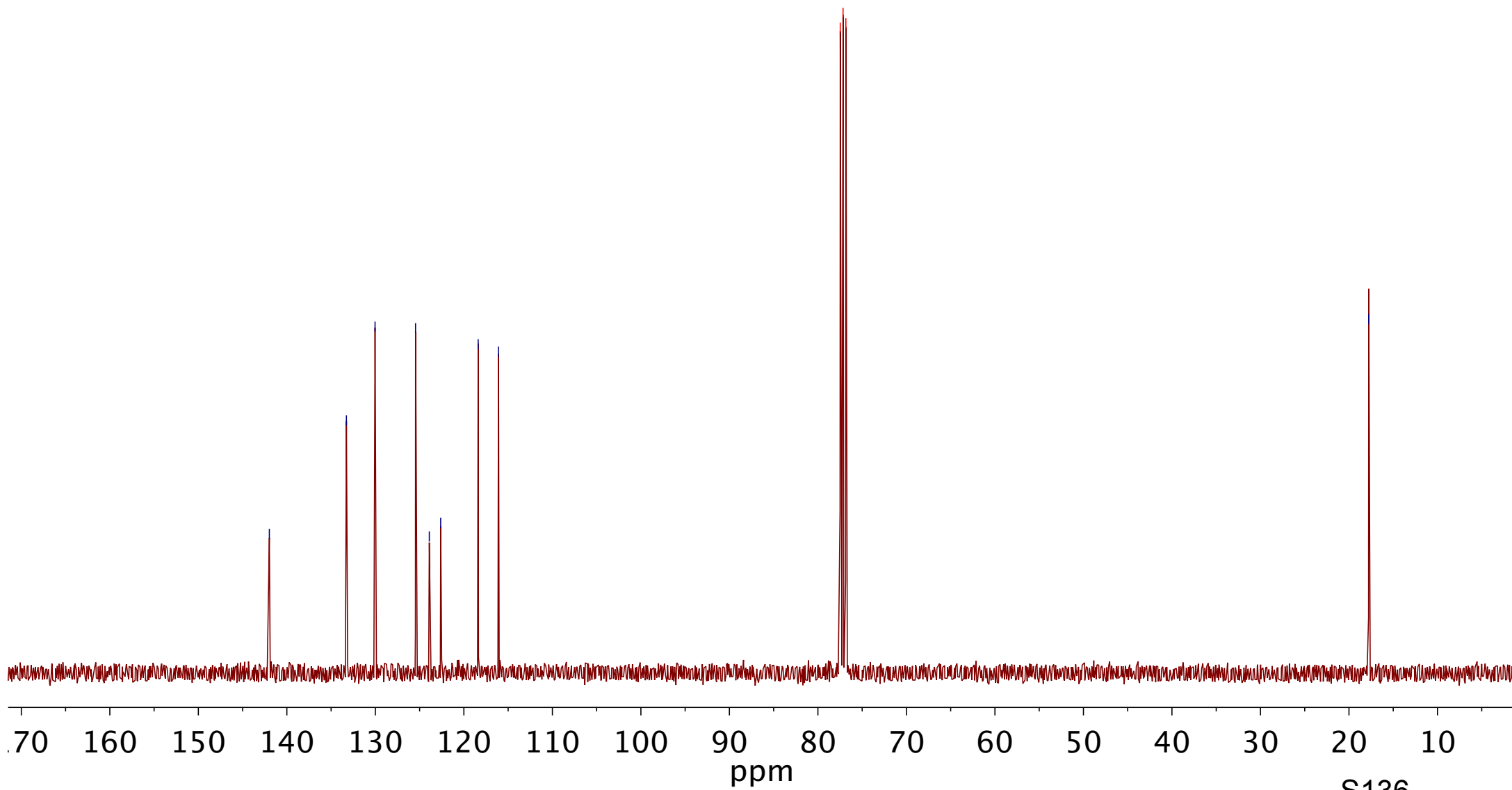
116.09

77.48 CDCl<sub>3</sub>

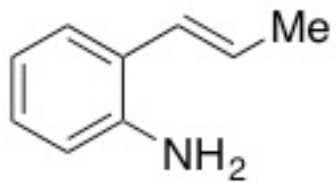
77.16 CDCl<sub>3</sub>

76.84 CDCl<sub>3</sub>

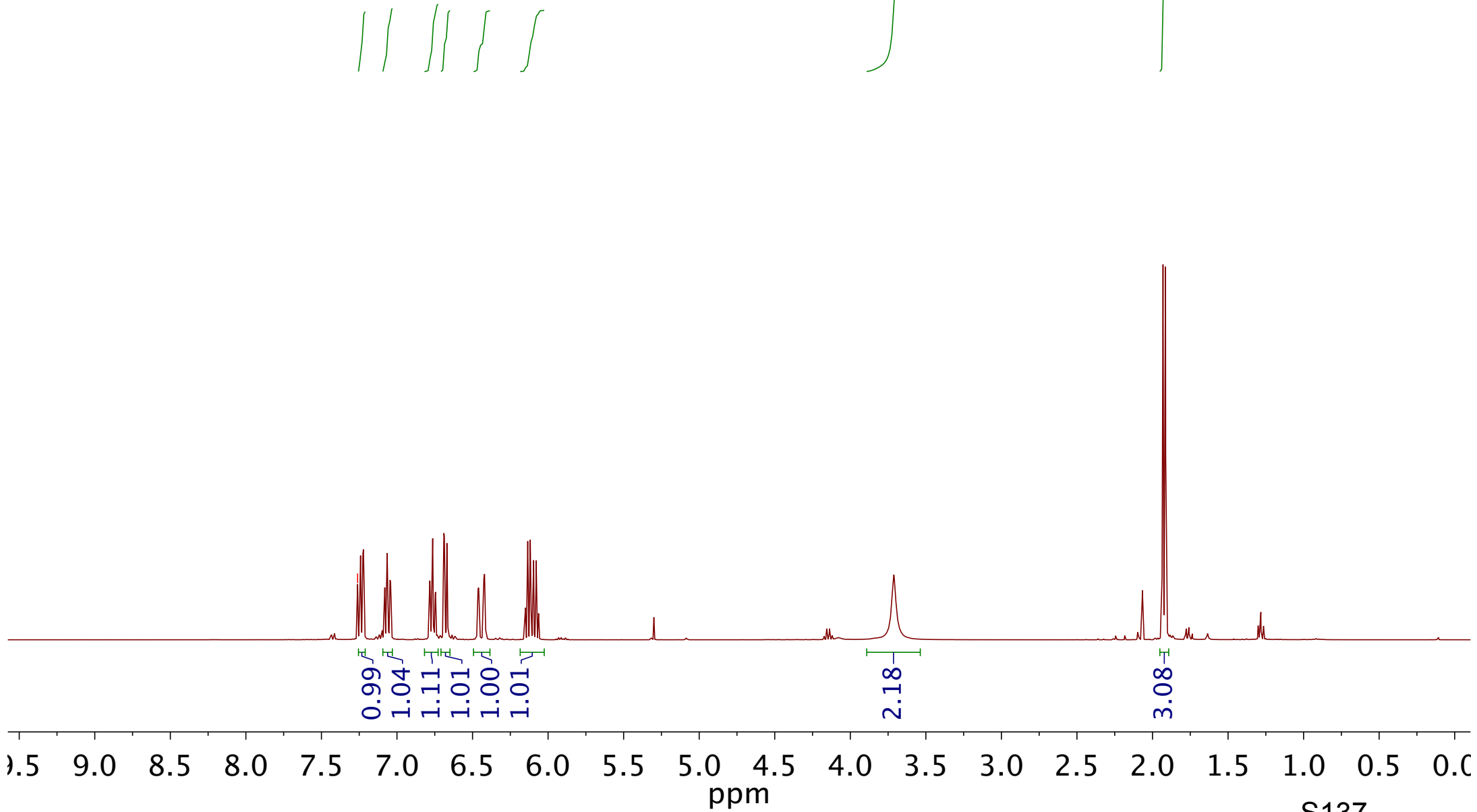
-17.77

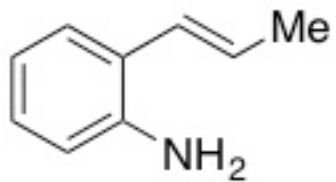


S136



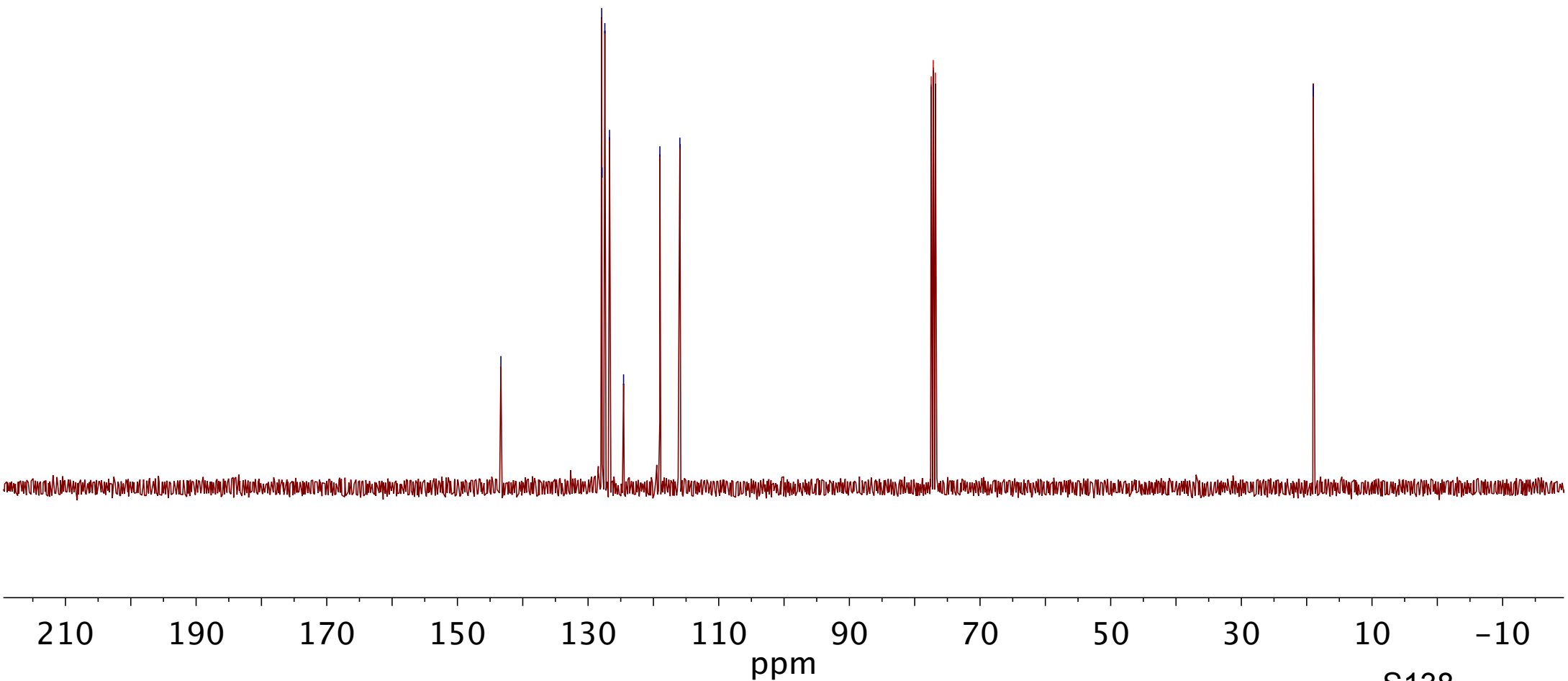
-7.26 CDCl<sub>3</sub>



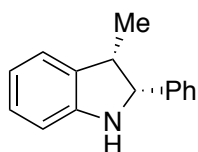


Chemical shift values (ppm):

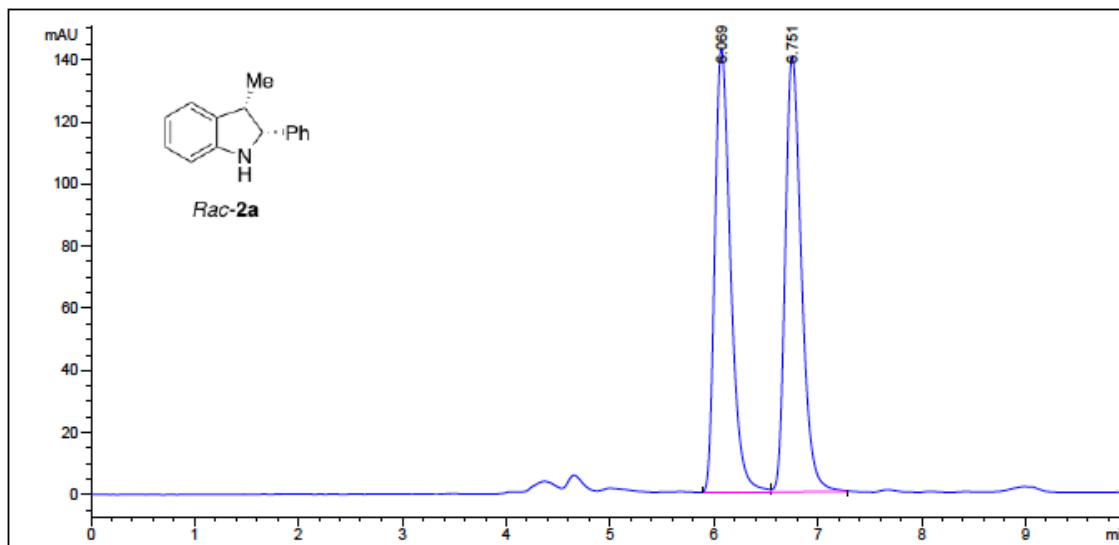
- 143.35
- 127.92
- 127.86
- 127.43
- 126.72
- 124.57
- 119.01
- 115.95
- 77.48 CDCl<sub>3</sub>
- 77.16 CDCl<sub>3</sub>
- 76.84 CDCl<sub>3</sub>
- 19.00



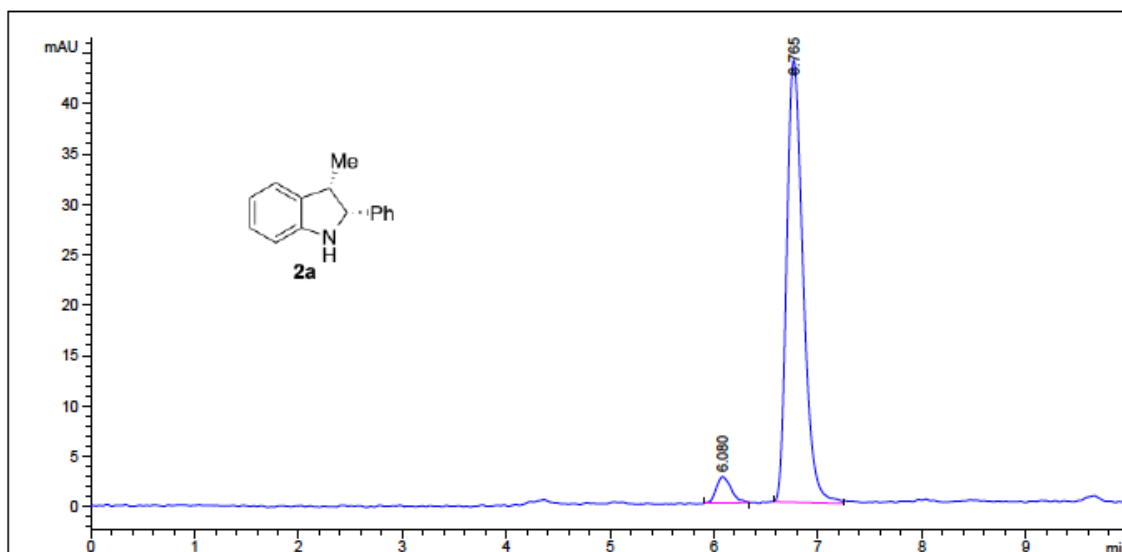
## **IV. Chiral HPLC Chromatograms**



**(2R,3S)-3-Methyl-2-phenylindoline** (Table 2, entry **2 a**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 90% ee:  $t_R$  (major) = 6.7 min,  $t_R$  (minor) = 6.0 min.

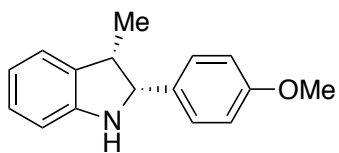


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.069	BV	0.1626	1501.54565	142.94022	49.7341
2	6.751	VB	0.1660	1517.59875	140.48648	50.2659

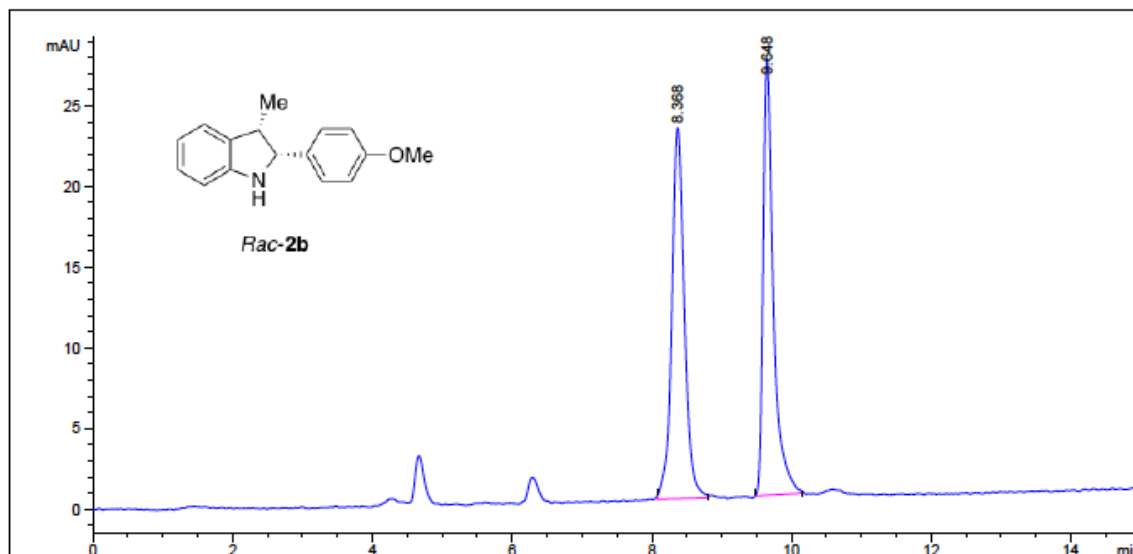


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.080	BB	0.1493	26.45265	2.63124	5.2100
2	6.765	MM T	0.1827	481.27982	43.89272	94.7900

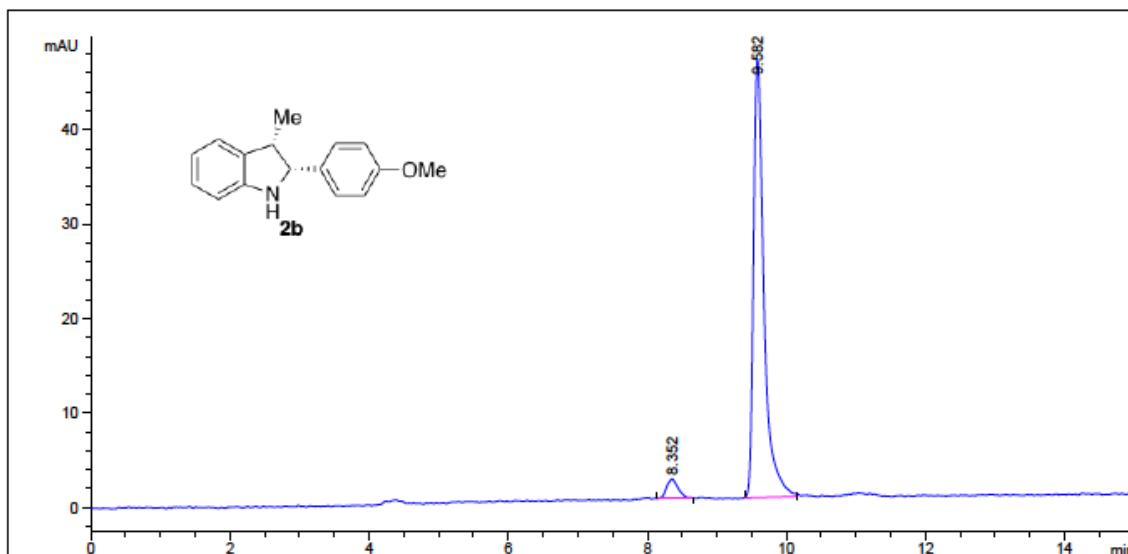




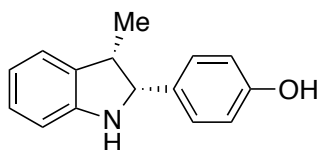
**(2R,3S)-2-(4-Methoxyphenyl)-3-methylindoline**  
 (Table 2, **2b**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 91% ee:  $t_R$  (major) = 9.6 min,  $t_R$  (minor) = 8.3 min.



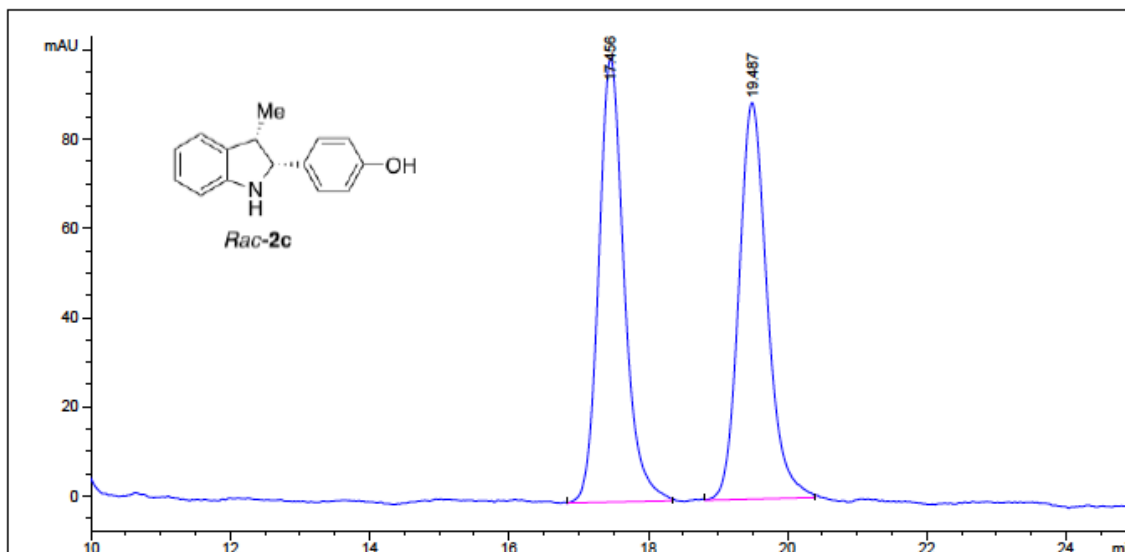
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.368	BB	0.1883	288.61670	23.01538	51.0982
2	9.648	BB	0.1531	276.21091	27.05328	48.9018



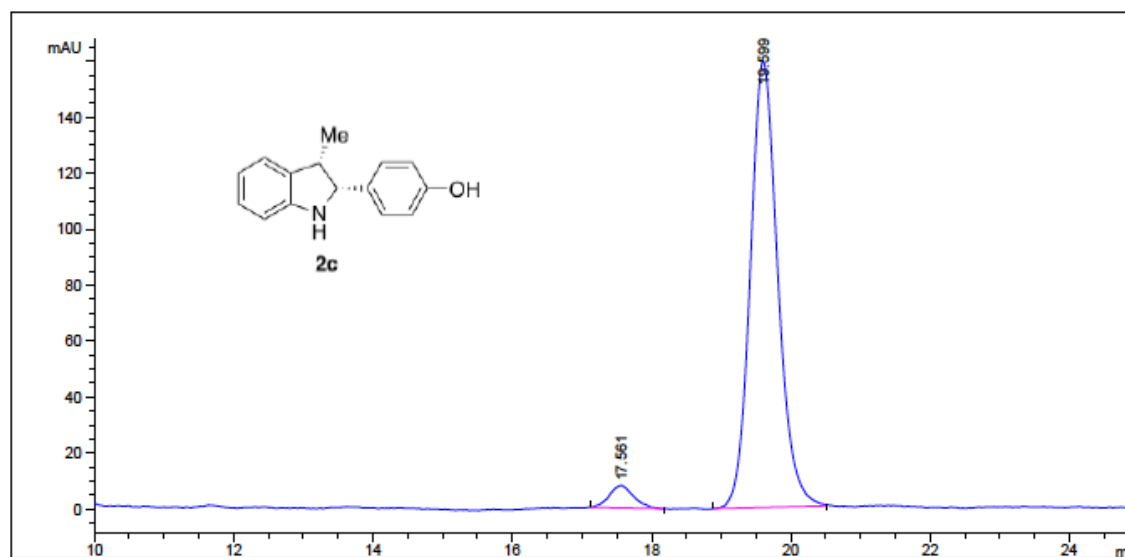
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.352	BB	0.1822	23.75406	2.06513	4.6626
2	9.582	BB	0.1580	485.70135	46.43272	95.3374



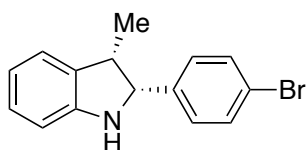
**4-((2R,3S)-3-Methylindolin-2-yl)phenol** (Table 2, **2c**):  
 HPLC analysis (IA, 10% IPA/hexane, 0.8 mL/min, 230 nm)  
 indicated 91% ee:  $t_R$  (major) = 19.5 min,  $t_R$  (minor) = 17.5 min.



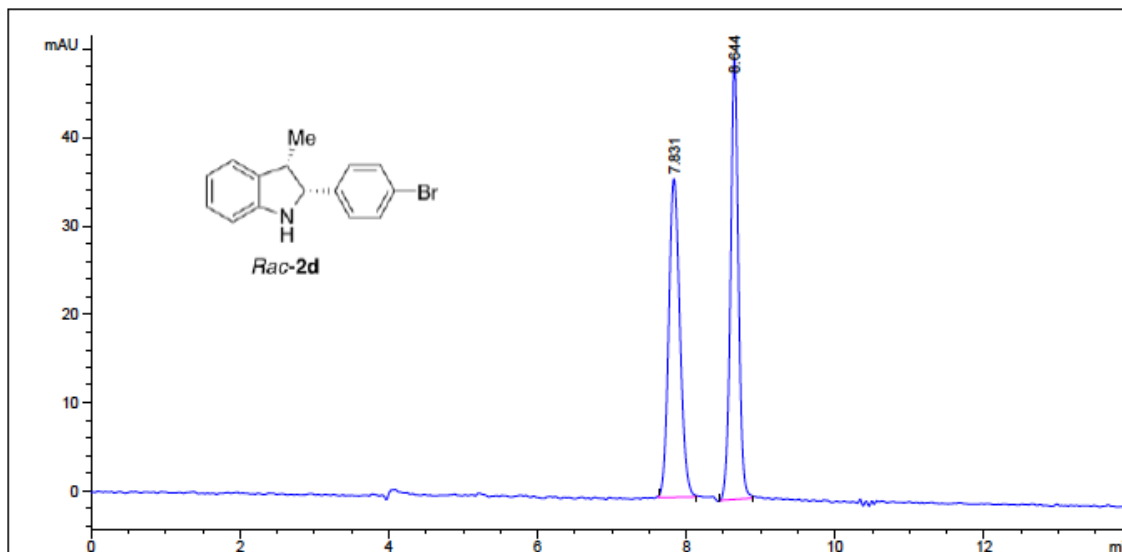
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.456	VB	0.3787	2533.02246	99.59955	50.2658
2	19.487	VB	0.4285	2506.23608	89.02036	49.7342



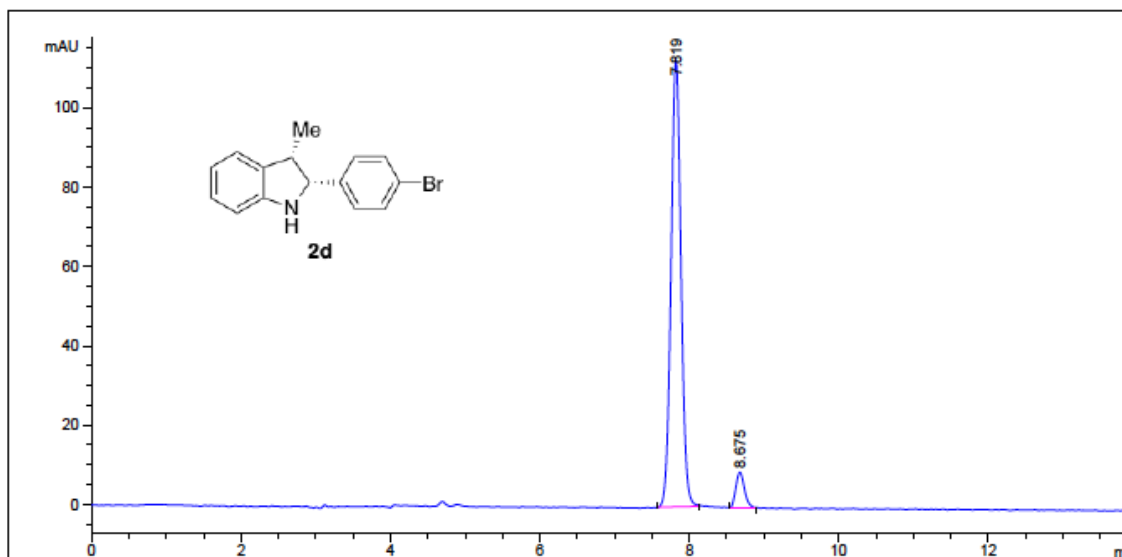
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.561	BB	0.2991	198.67110	8.12918	4.3487
2	19.599	BB	0.4197	4369.82080	159.48055	95.6513



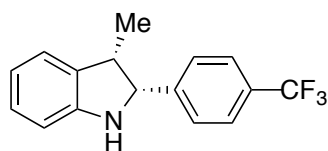
**(2R,3S)-2-(4-Bromophenyl)-3-methylindoline** (Table 2, **2d**): HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 87% ee:  $t_R$  (major) = 7.8 min,  $t_R$  (minor) = 8.6 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.831	BB	0.1619	377.26584	36.10504	50.5610
2	8.644	BB	0.1101	368.89420	50.00888	49.4390

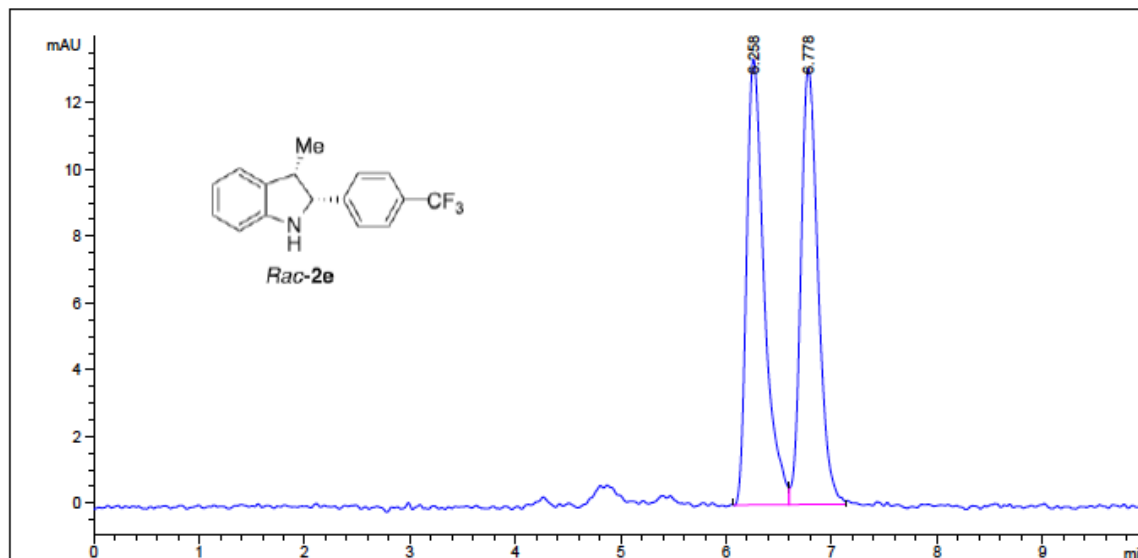


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.819	BB	0.1440	1042.72266	112.67705	93.5406
2	8.675	BB	0.1258	72.00418	8.96011	6.4594

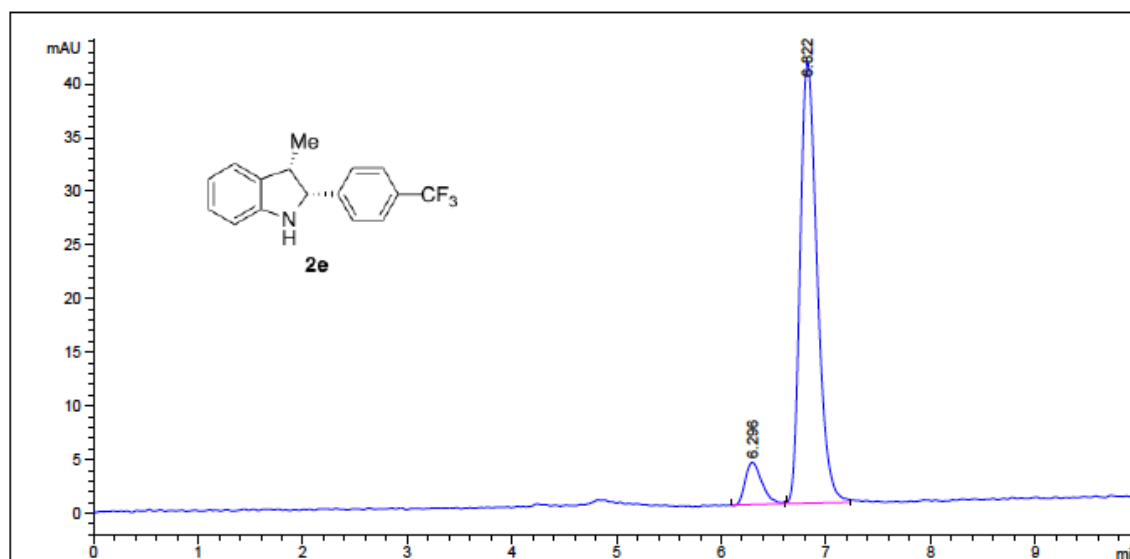


**(2R,3S)-3-Methyl-2-(4-(trifluoromethyl)phenyl)indoline**

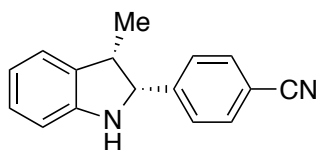
(Table 2, **2e**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 83% ee:  $t_R$  (major) = 6.8 min,  $t_R$  (minor) = 6.2 min.



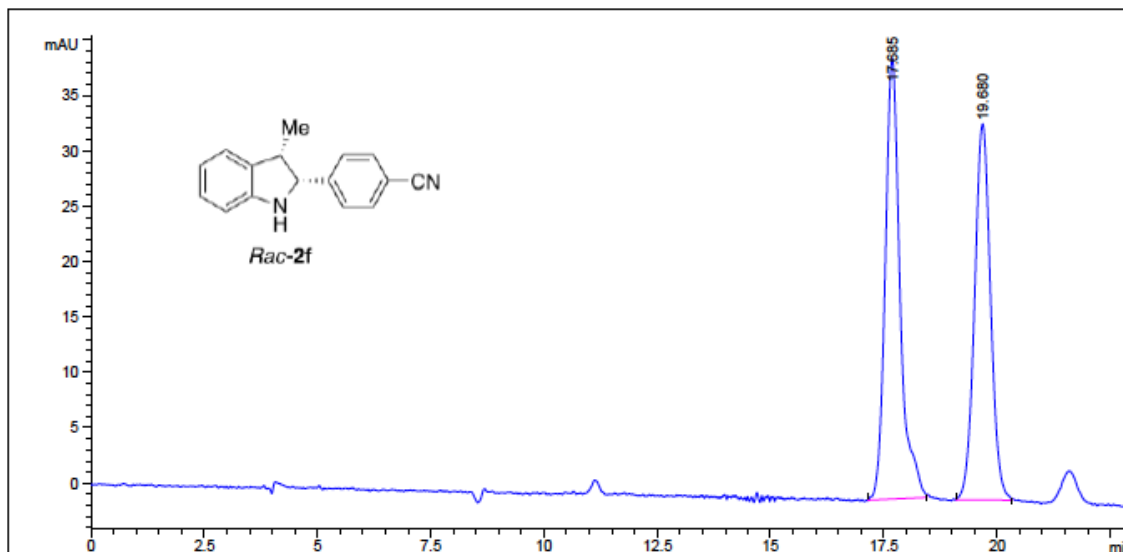
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.258	BV	0.1758	155.59216	13.36831	51.2022
2	6.778	VB	0.1763	148.28574	13.07544	48.7978



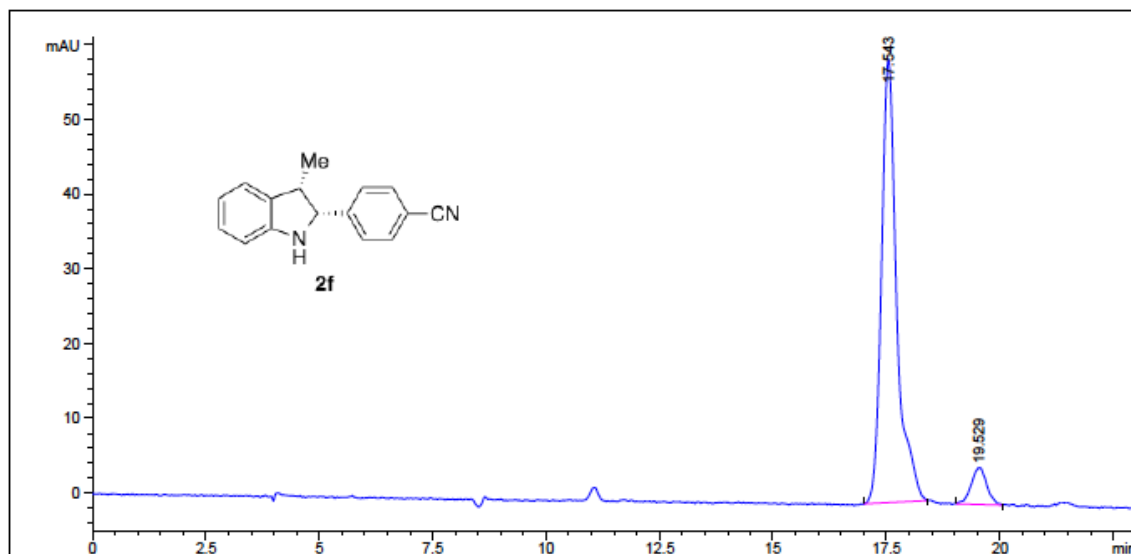
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.296	BB	0.1693	43.82582	3.95301	8.5895
2	6.822	BB	0.1761	466.40164	41.19452	91.4105



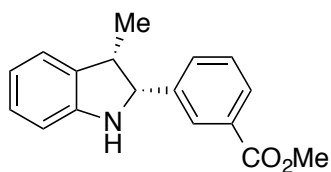
**4-((2R,3S)-3-Methylindolin-2-yl)benzonitrile** (Table 2, **2f**): HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 84% ee:  $t_R$  (major) = 17.6 min,  $t_R$  (minor) = 19.6 min.



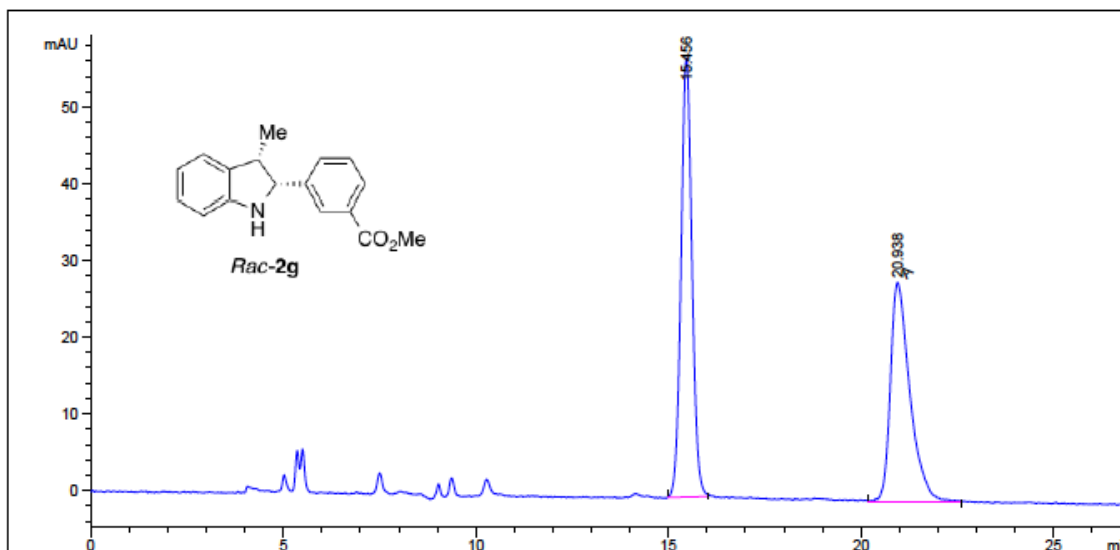
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.685	BB	0.3401	907.43475	39.77752	52.1491
2	19.680	BB	0.3581	832.64325	33.95079	47.8509



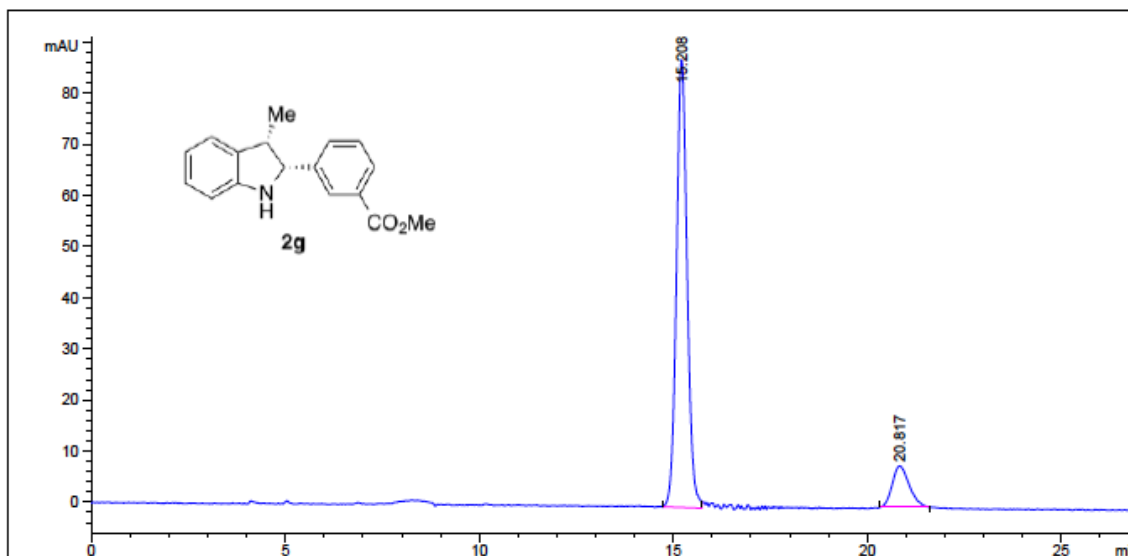
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.543	BB	0.3392	1389.14563	59.31224	92.1360
2	19.529	BV	0.2909	118.56622	4.92407	7.8640



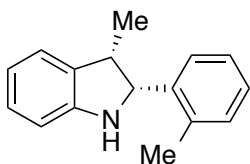
**Methyl 3-((2R,3S)-3-methylindolin-2-yl)benzoate**  
 (Table 2, **2g**): HPLC analysis (IA, 5 % IPA/hexane, 0.8 mL/min, 230 nm) indicated 74% ee:  $t_R$  (major) = 15.2 min,  $t_R$  (minor) = 20.8 min.



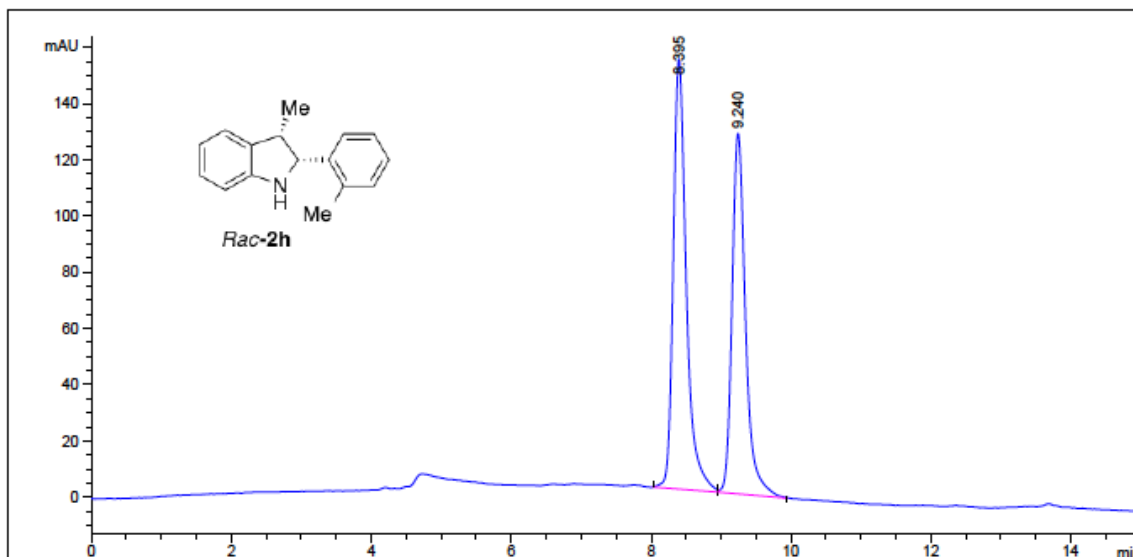
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.456	BB	0.2998	1127.83081	57.26651	52.7320
2	20.938	MM T	0.6587	1010.96692	28.68095	47.2680



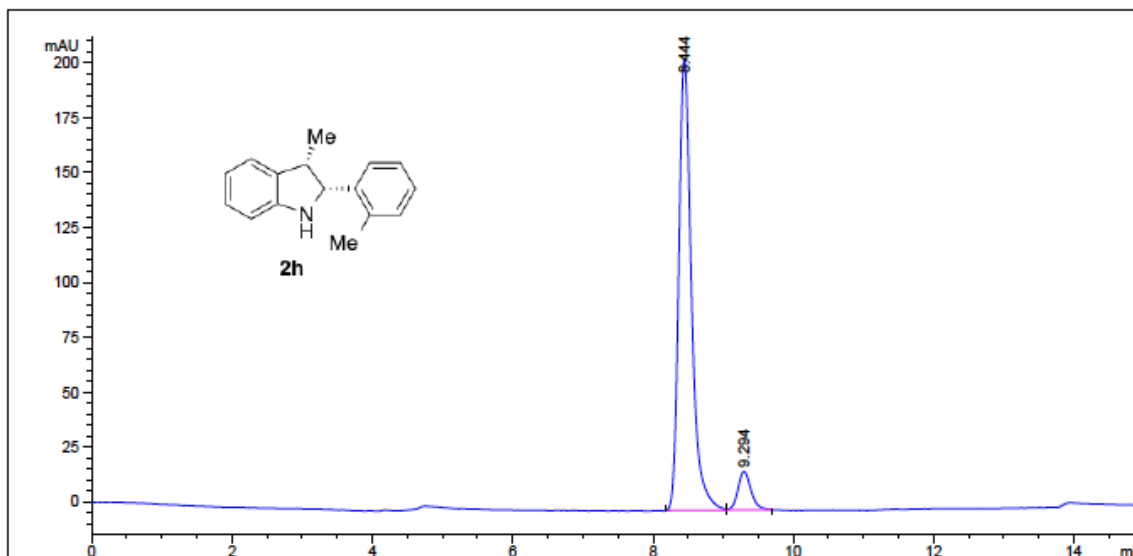
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.208	BB	0.2824	1668.93555	87.56011	87.0091
2	20.817	BB	0.3755	249.17949	8.13181	12.9909



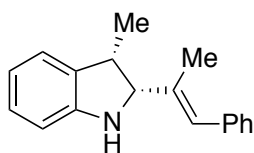
**(2R,3S)-3-Methyl-2-(o-tolyl)indoline** (Table 2, **2h**): HPLC analysis (IA, 2 % IPA/hexane, 0.8 mL/min, 230 nm) indicated 84% ee:  $t_R$  (major) = 8.4 min,  $t_R$  (minor) = 9.2 min.



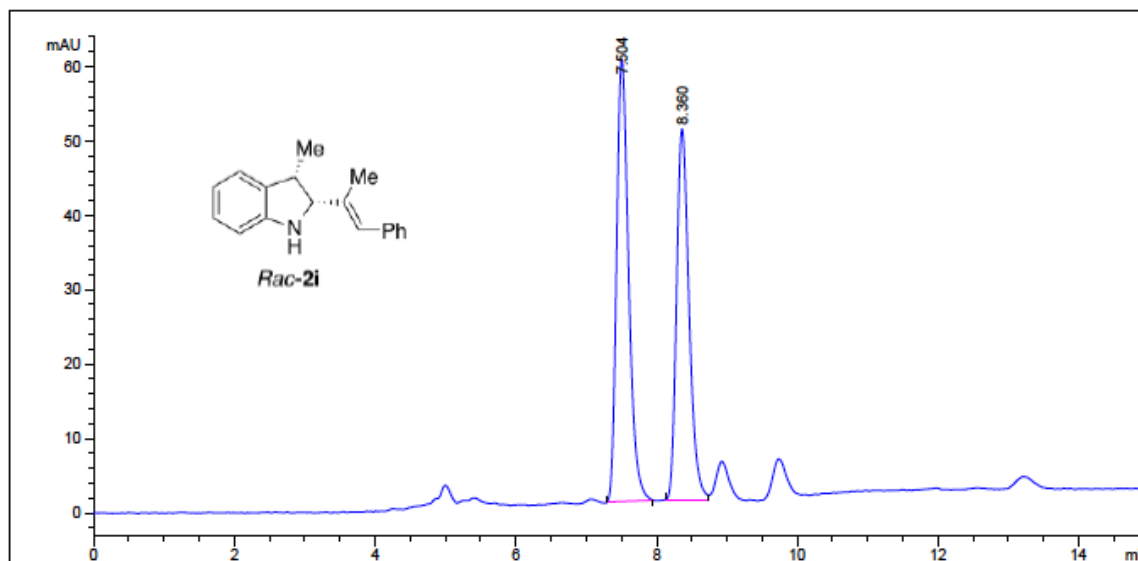
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.395	BV	0.1952	1981.90442	152.94885	53.7012
2	9.240	VB	0.2013	1708.71362	128.32768	46.2988



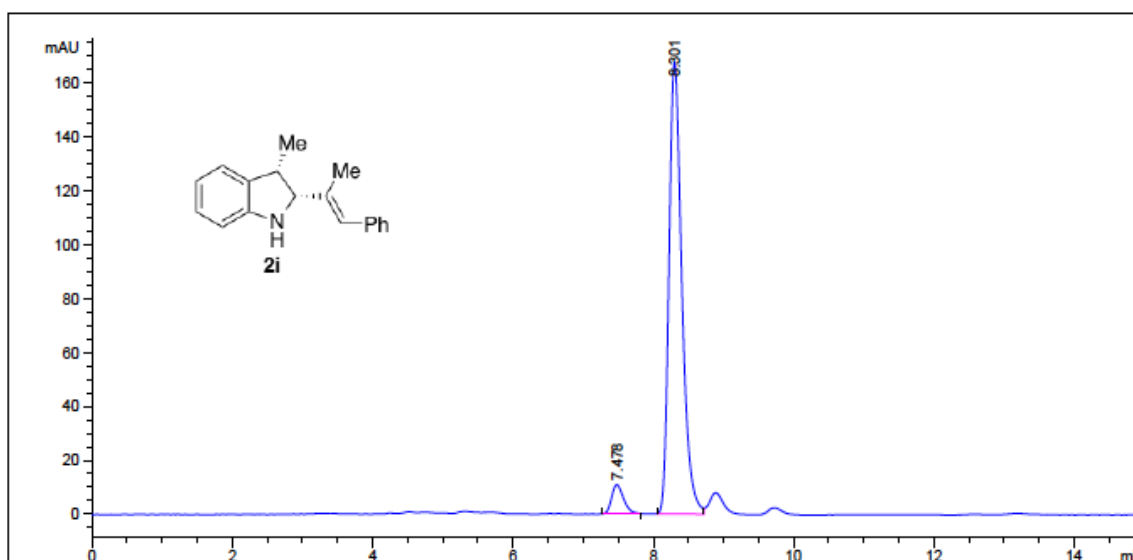
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.444	BB	0.1907	2587.82861	205.81415	91.7850
2	9.294	BB	0.2010	231.61855	17.66512	8.2150



**(2R,3S)-3-Methyl-2-((E)-1-phenylprop-1-en-2-yl)indoline**  
 (Table 2, **2i**): HPLC analysis (IC, 1% IPA/hexane, 0.8 mL/min, 230 nm) indicated 89% ee:  $t_R$  (major) = 8.3 min,  $t_R$  (minor) = 7.5 min.

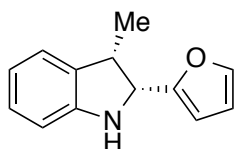


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.504	BB	0.1810	708.23541	59.46534	53.4194
2	8.360	BV	0.1903	617.56653	49.91759	46.5806

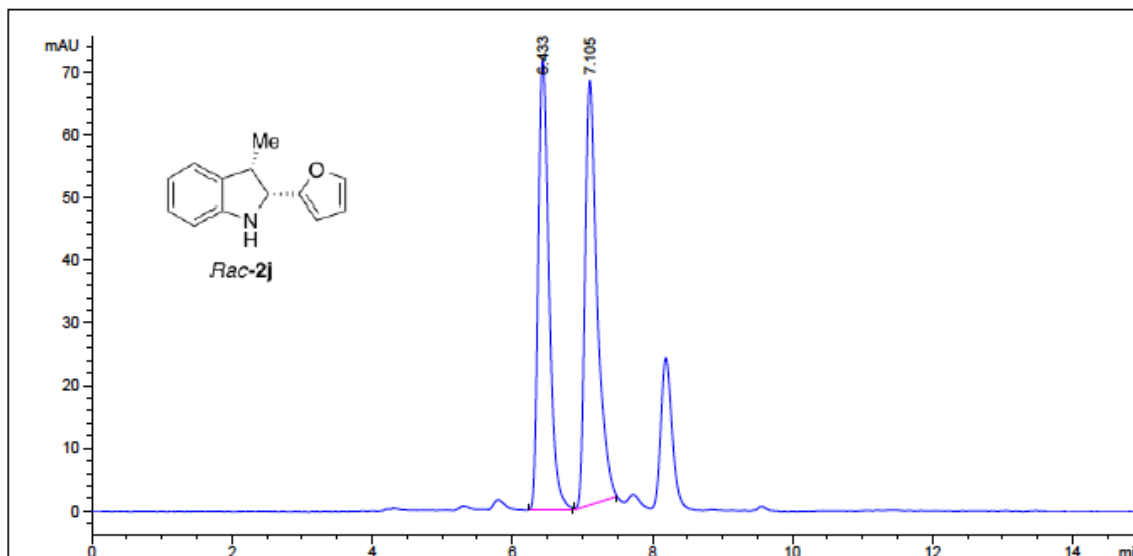


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.478	BB	0.1831	129.66144	10.87425	5.7304
2	8.301	BV	0.1945	2133.04761	167.56821	94.2696

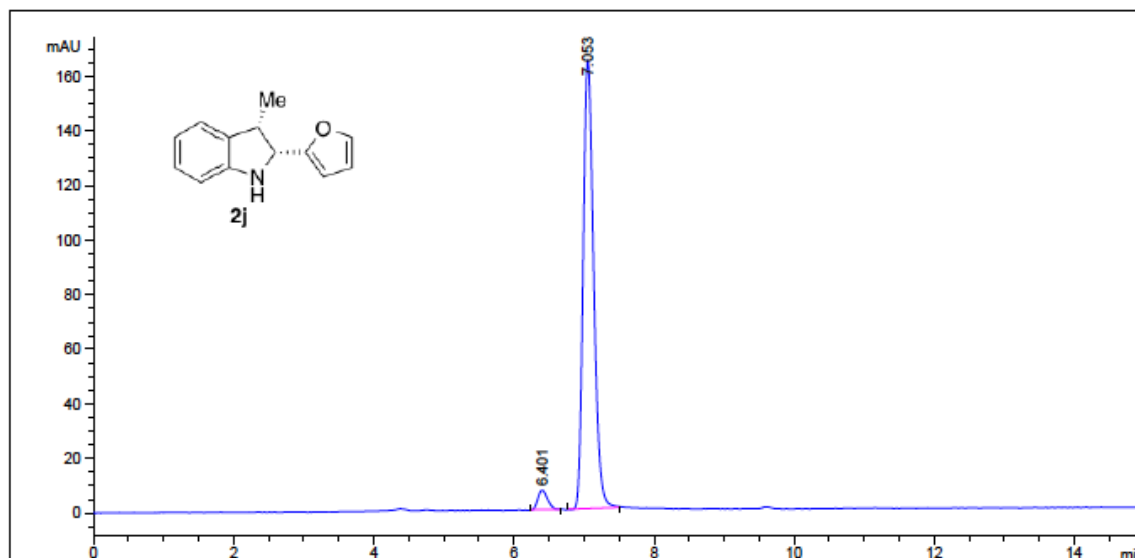




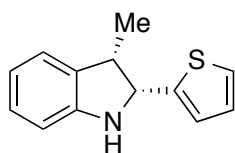
**(2R,3S)-2-(Furan-2-yl)-3-methylindoline** (Table 2, **2j**): HPLC analysis (IC, 5 % IPA/hexane, 0.8 mL/min, 230 nm) indicated 92% ee:  $t_R$  (major) = 7.0 min,  $t_R$  (minor) = 6.4 min.



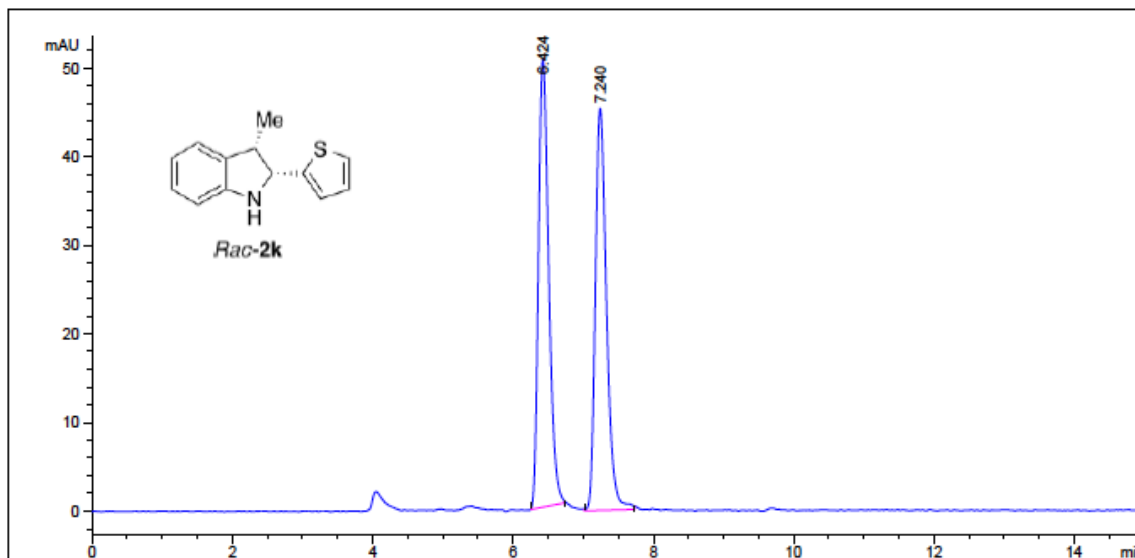
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.433	BB	0.1650	771.47119	71.99957	48.5127
2	7.105	MM T	0.2011	818.77625	67.87449	51.4873



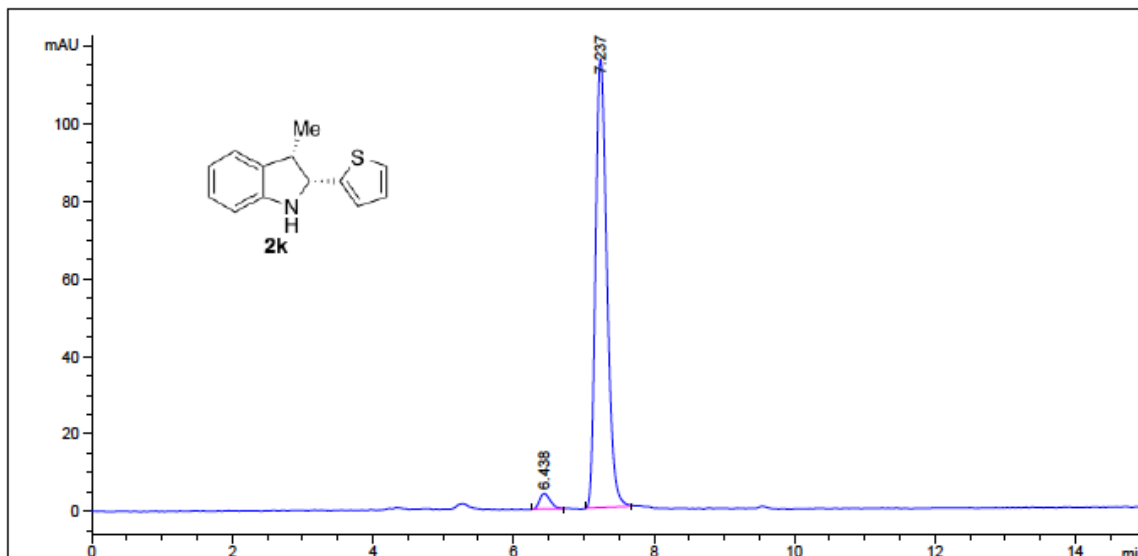
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.401	BB	0.1483	70.77338	7.22207	3.9790
2	7.053	BB	0.1611	1707.90710	164.51382	96.0210



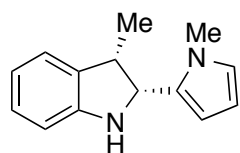
**(2R,3S)-3-Methyl-2-(thiophen-2-yl)indoline** (Table 2, **2k**):  
 HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 94% ee:  $t_R$  (major) = 7.2 min,  $t_R$  (minor) = 6.4 min.



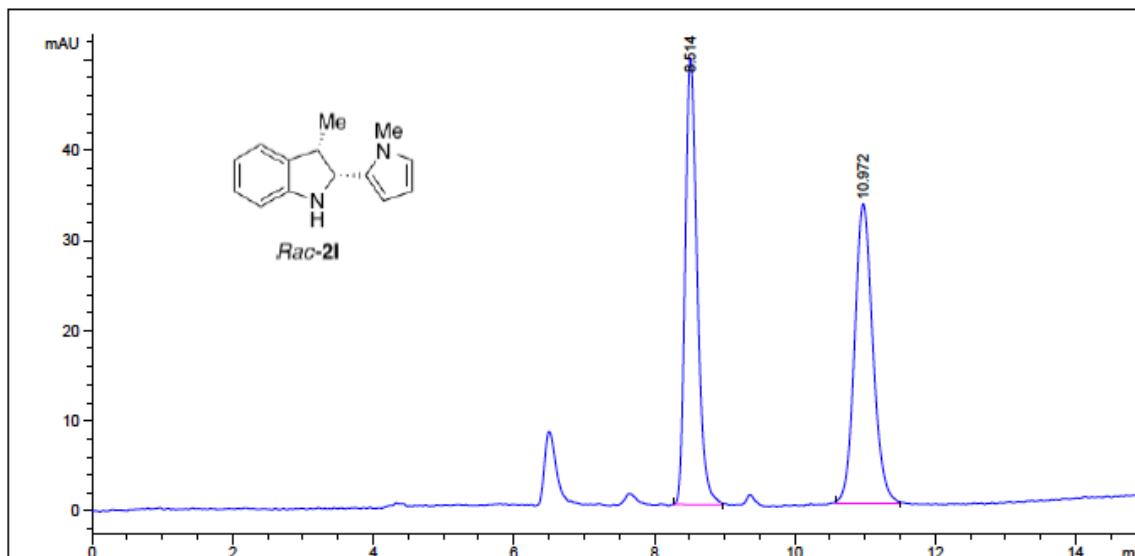
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.424	MM T	0.1687	512.79095	50.64674	50.4875
2	7.240	MM T	0.1845	502.88766	45.43791	49.5125



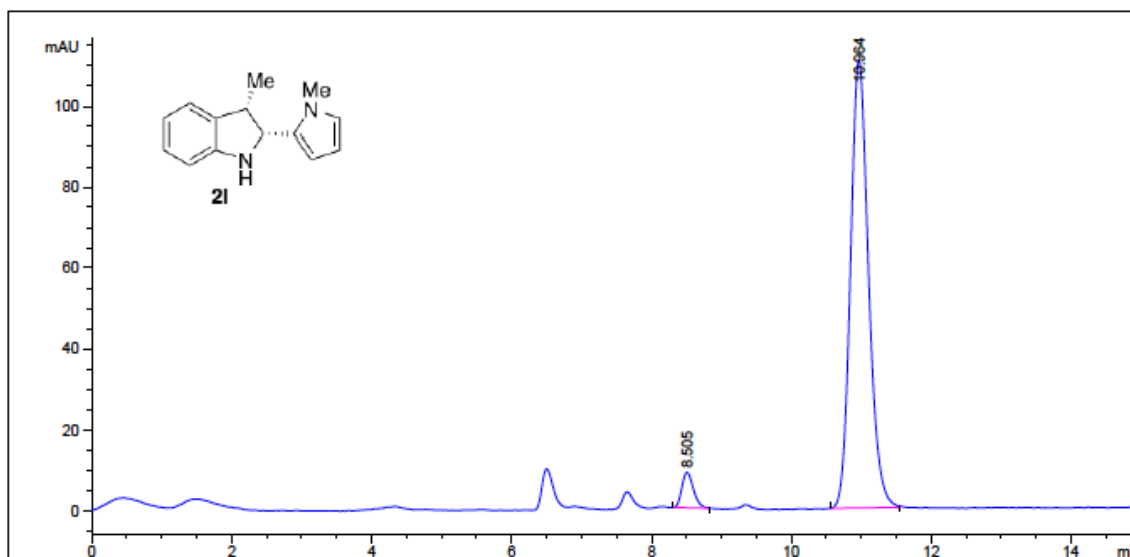
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.438	BB	0.1641	43.60040	4.03511	3.2400
2	7.237	BB	0.1732	1302.07617	115.81172	96.7600



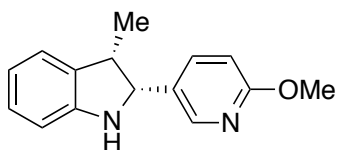
**(2R,3S)-3-Methyl-2-(1-methyl-1H-pyrrol-2-yl)indoline**  
 (Table 2, **2I**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 90% ee:  $t_R$  (major) = 10.9 min,  $t_R$  (minor) = 8.5 min.



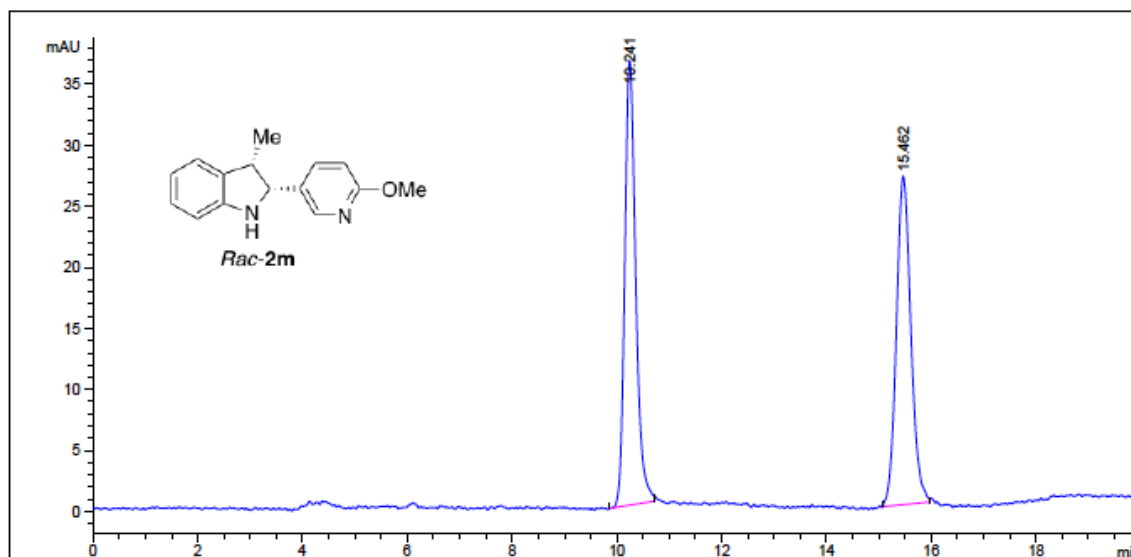
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.514	BB	0.1828	589.22015	49.51160	49.5238
2	10.972	BB	0.2729	600.55109	33.22447	50.4762



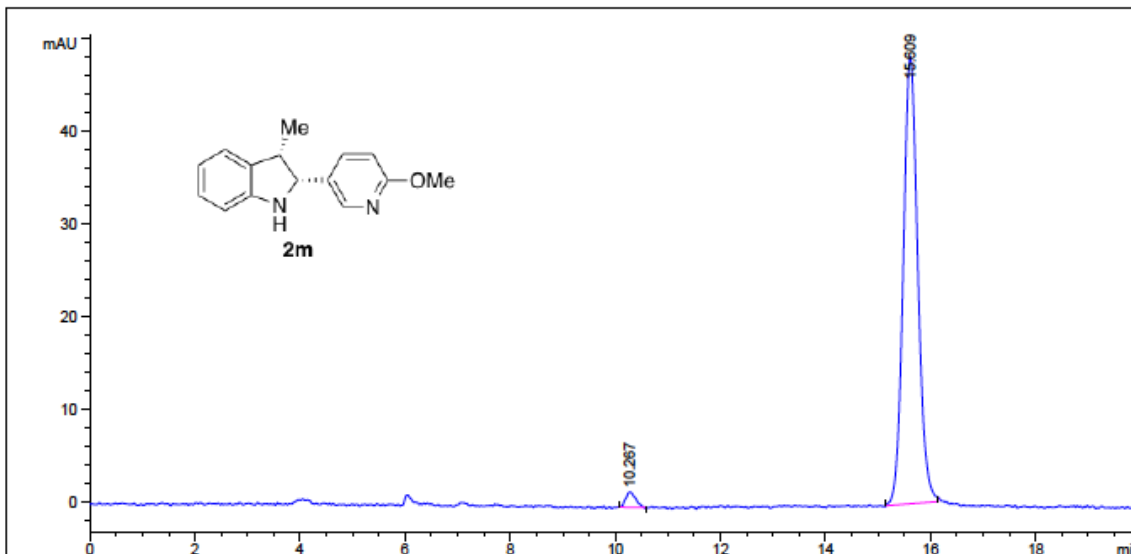
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.505	BB	0.1755	102.35625	8.81191	4.9113
2	10.964	BB	0.2746	1981.72949	110.82069	95.0887



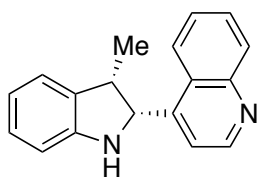
**(2R,3S)-2-(6-Methoxypyridin-3-yl)-3-methylindoline**  
 (Table 2, **2m**): HPLC analysis (IA, 10% IPA/hexane, 0.8 mL/min, 230 nm) indicated 95% ee:  $t_R$  (major) = 15.6 min,  $t_R$  (minor) = 10.2 min.



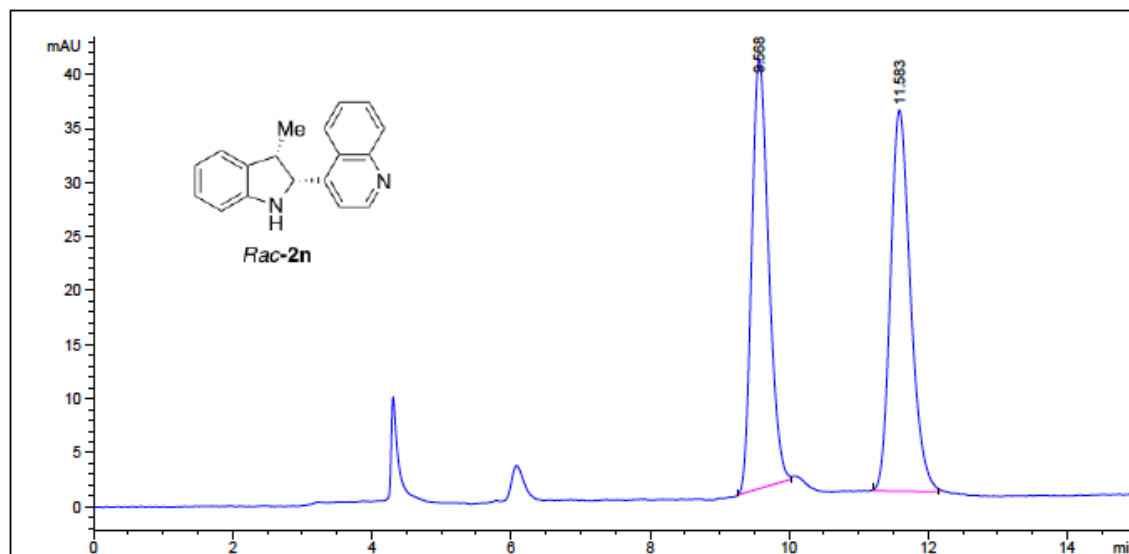
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.241	BB	0.2234	529.69904	36.47078	50.5664
2	15.462	BB	0.2943	517.83234	26.93490	49.4336



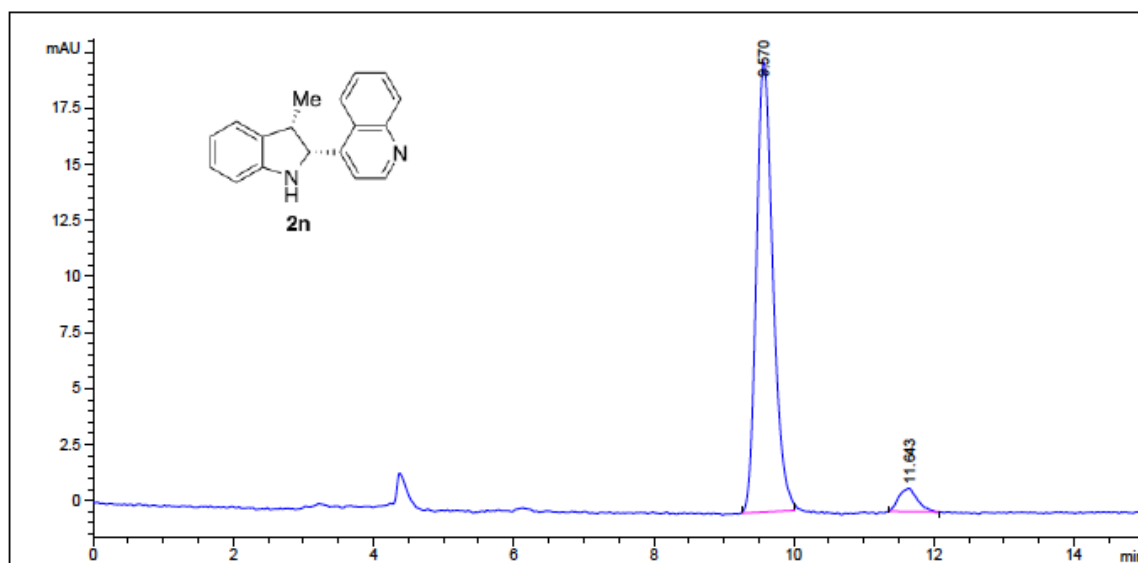
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.267	BB	0.1678	21.92513	1.64231	2.3104
2	15.609	BB	0.2943	927.06445	48.20953	97.6896



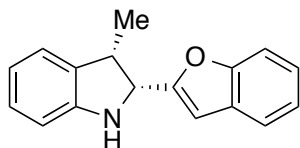
**4-((2*R*,3*S*)-3-Methylindolin-2-yl)quinoline** (Table 2, **2n**):  
 HPLC analysis (IC, 20% IPA/hexane, 0.8 mL/min, 280 nm)  
 indicated 89% ee:  $t_R$  (major) = 9.6 min,  $t_R$  (minor) = 11.6 min.



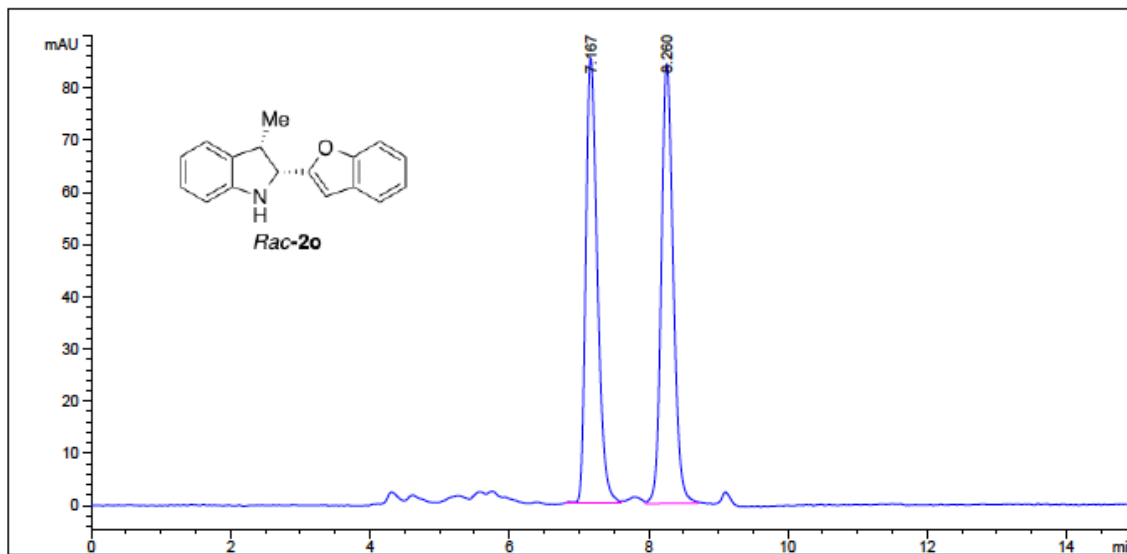
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.568	BB	0.2612	672.45734	39.78879	48.8106
2	11.583	BB	0.3092	705.22870	35.28518	51.1894



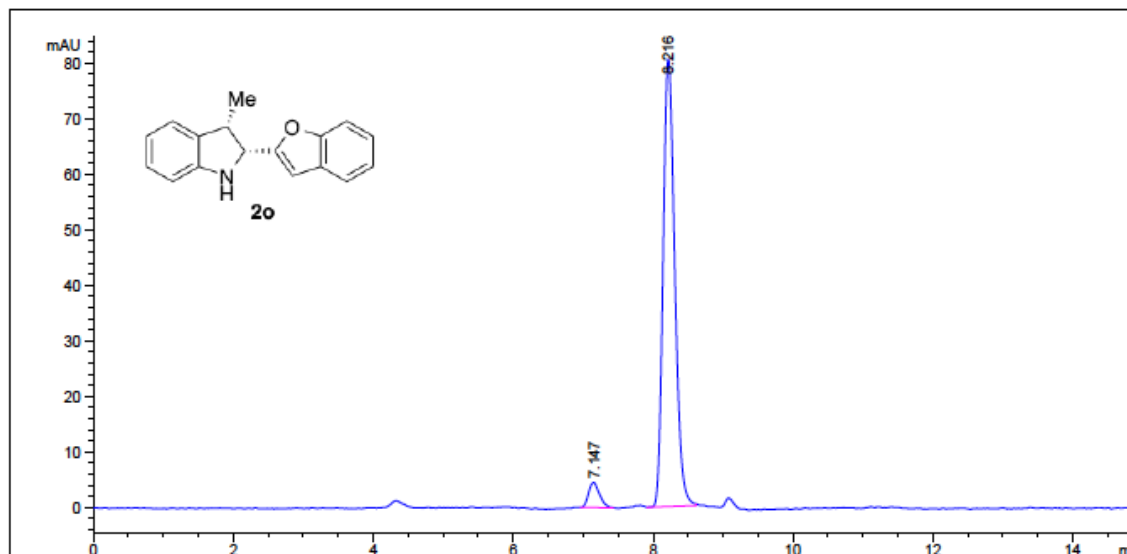
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.570	BB	0.2542	330.37662	20.05817	94.4772
2	11.643	BB	0.2404	19.31261	1.04141	5.5228



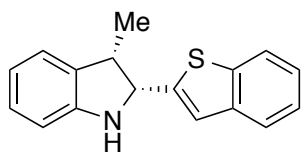
**(2R,3S)-2-(Benzofuran-2-yl)-3-methylindoline** (Table 2, **2o**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 90% ee:  $t_R$  (major) = 8.2 min,  $t_R$  (minor) = 7.1 min.



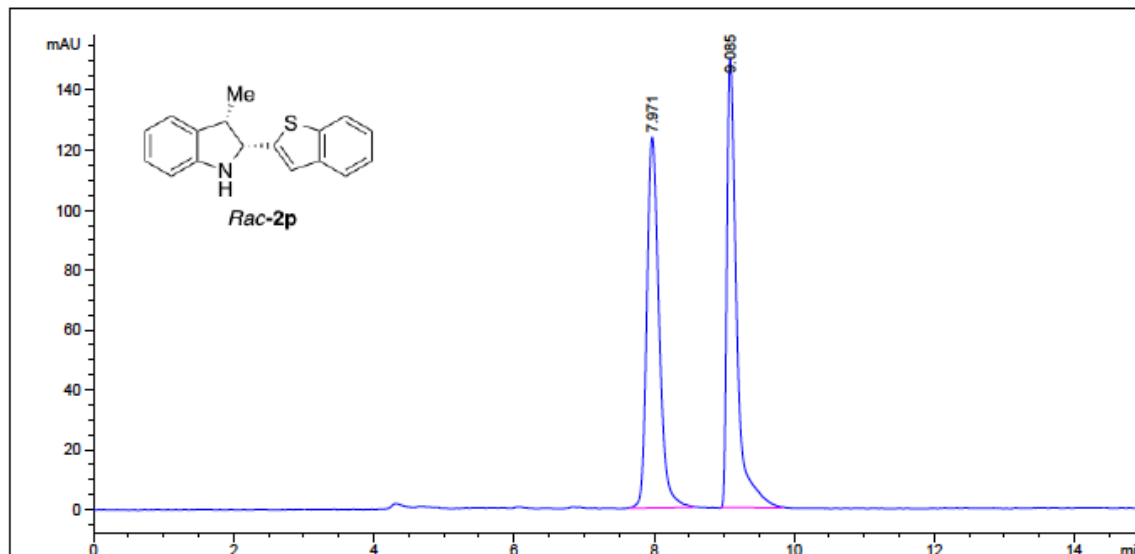
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.167	BB	0.1773	991.35449	85.46016	49.6634
2	8.260	VB	0.1831	1004.79303	84.28996	50.3366



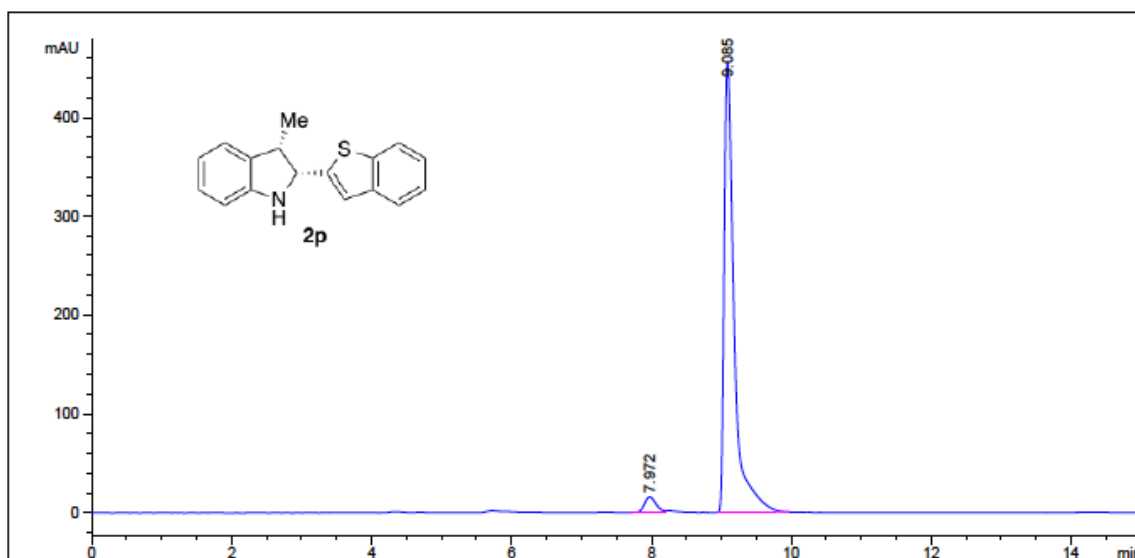
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.147	BB	0.1653	50.40735	4.54982	5.1298
2	8.216	VB	0.1788	932.22943	80.68486	94.8702



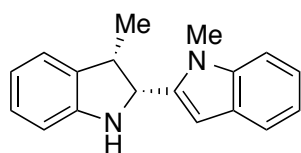
**(2R,3S)-2-(Benzo[b]thiophen-2-yl)-3-methylindoline**  
 (Table 2, **2p**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 92% ee:  $t_R$  (major) = 9.0 min,  $t_R$  (minor) = 7.9 min.



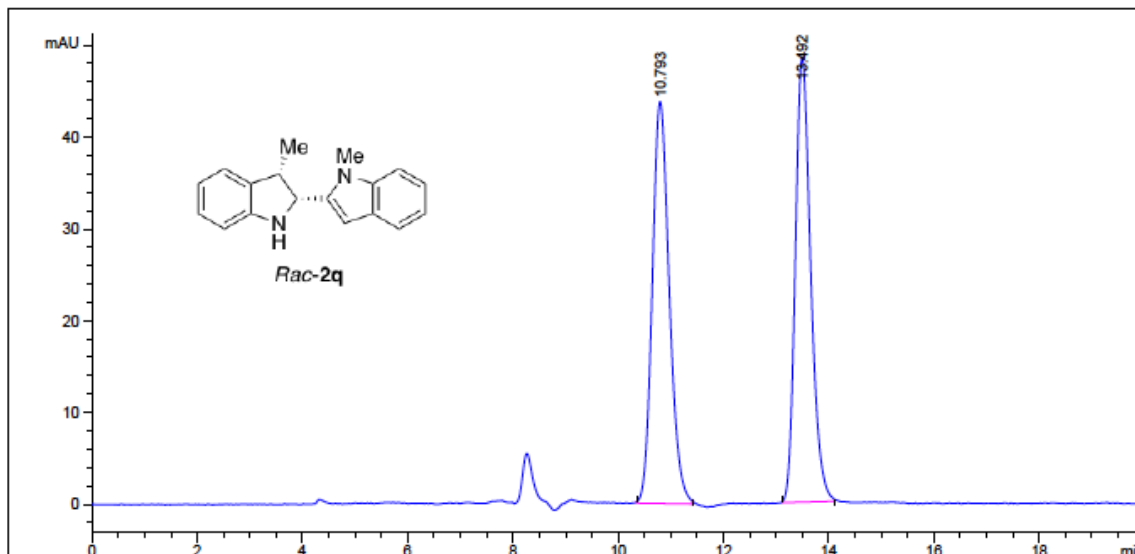
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.971	BB	0.1854	1501.85596	123.90401	50.7286
2	9.085	BB	0.1472	1458.71729	150.35445	49.2714



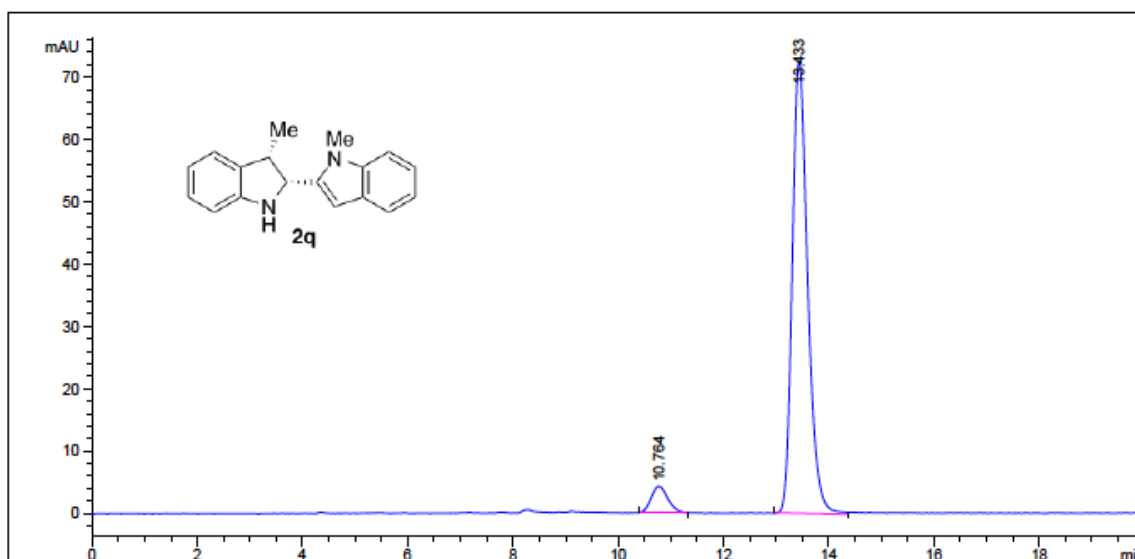
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.972	BV	0.1832	185.20247	15.75048	3.9238
2	9.085	BB	0.1479	4534.76172	456.51361	96.0762



**1-Methyl-2-((2R,3S)-3-methylindolin-2-yl)-1H-indole**  
 (Table 2, **2q**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 280 nm) indicated 88% ee:  $t_R$  (major) = 13.4 min,  $t_R$  (minor) = 10.7 min.

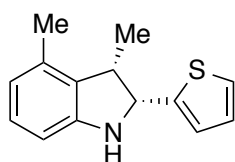


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.793	BB	0.3460	983.48895	43.79112	49.9827
2	13.492	BB	0.3109	984.17041	48.47686	50.0173

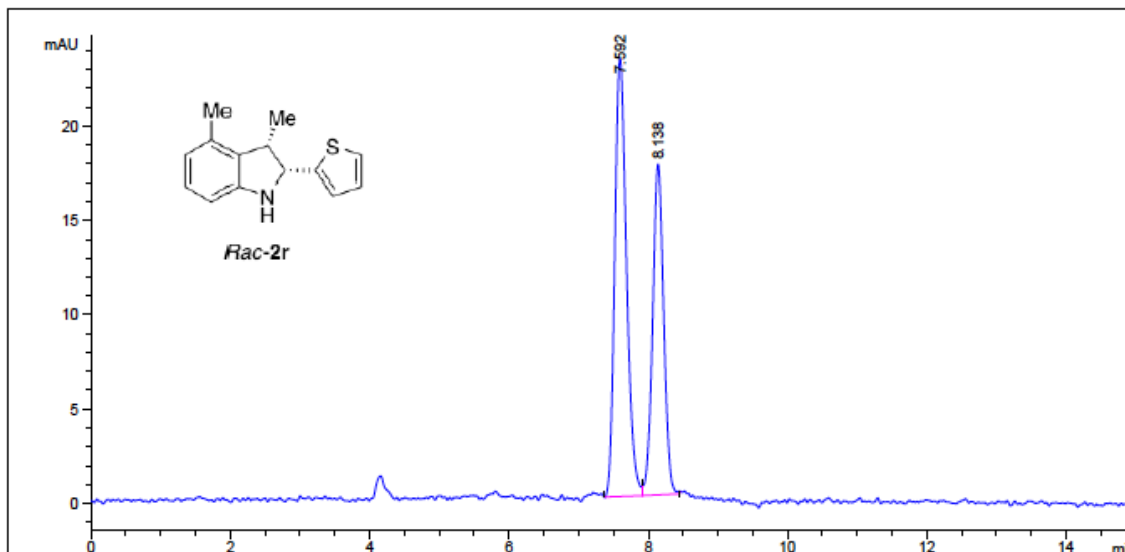


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.764	BB	0.3126	93.07466	4.23257	5.9177
2	13.433	MM T	0.3398	1479.74170	72.58424	94.0823

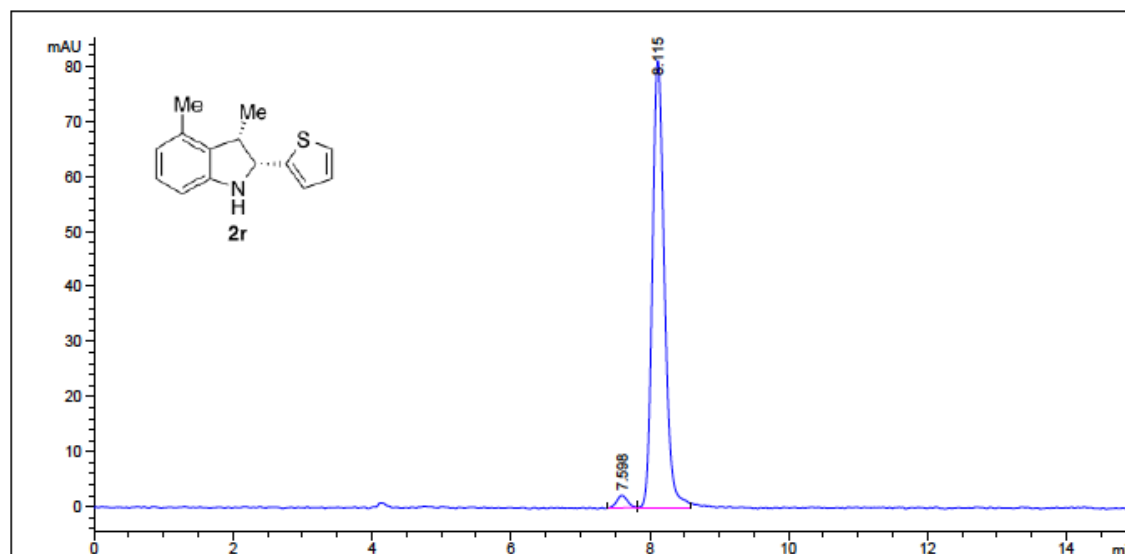




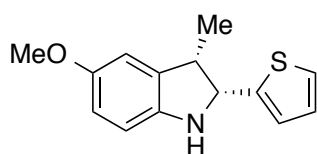
**(2R,3S)-3,4-Dimethyl-2-(thiophen-2-yl)indoline** (Table 2, **2r**): HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 95% ee:  $t_R$  (major) = 8.1 min,  $t_R$  (minor) = 7.6 min.



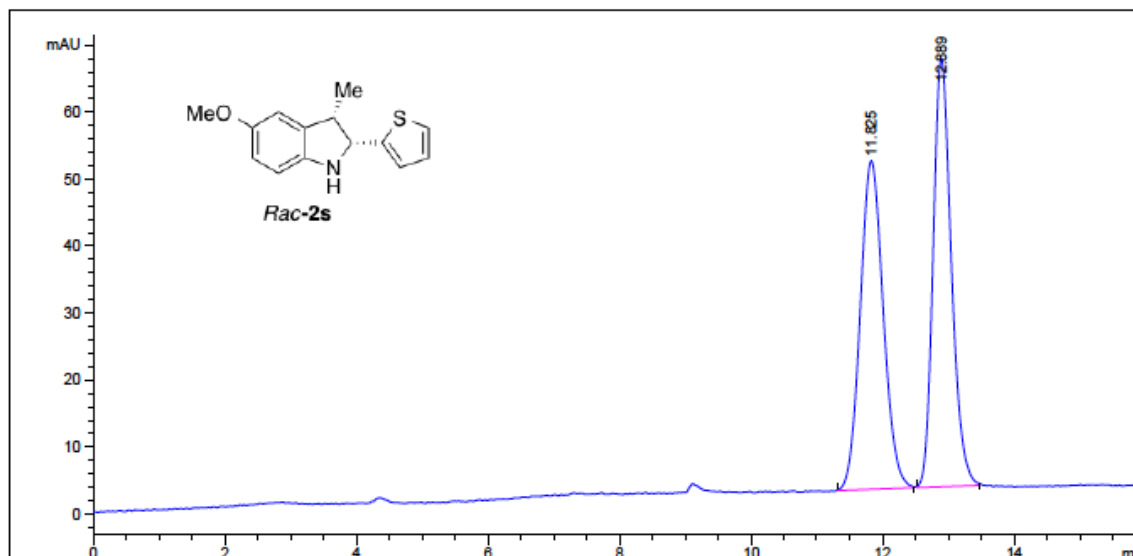
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.592	BB	0.1828	272.64493	23.25183	58.5687
2	8.138	BB	0.1662	192.86813	17.55733	41.4313



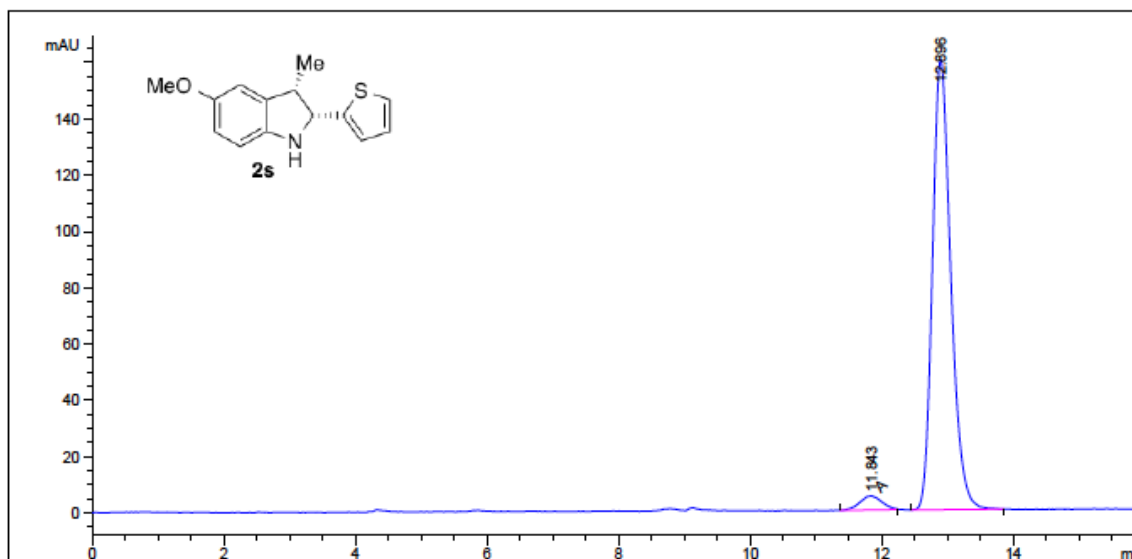
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.598	BV	0.1556	25.75121	2.31839	2.5640
2	8.115	VB	0.1844	978.57861	81.29505	97.4360



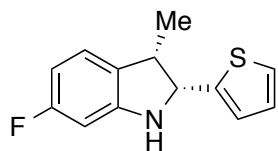
**(2R,3S)-5-Methoxy-3-methyl-2-(thiophen-2-yl)indoline**  
 (Table 2, **2s**): HPLC analysis (IC, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_R$  (major) = 12.8 min,  $t_R$  (minor) = 11.8 min.



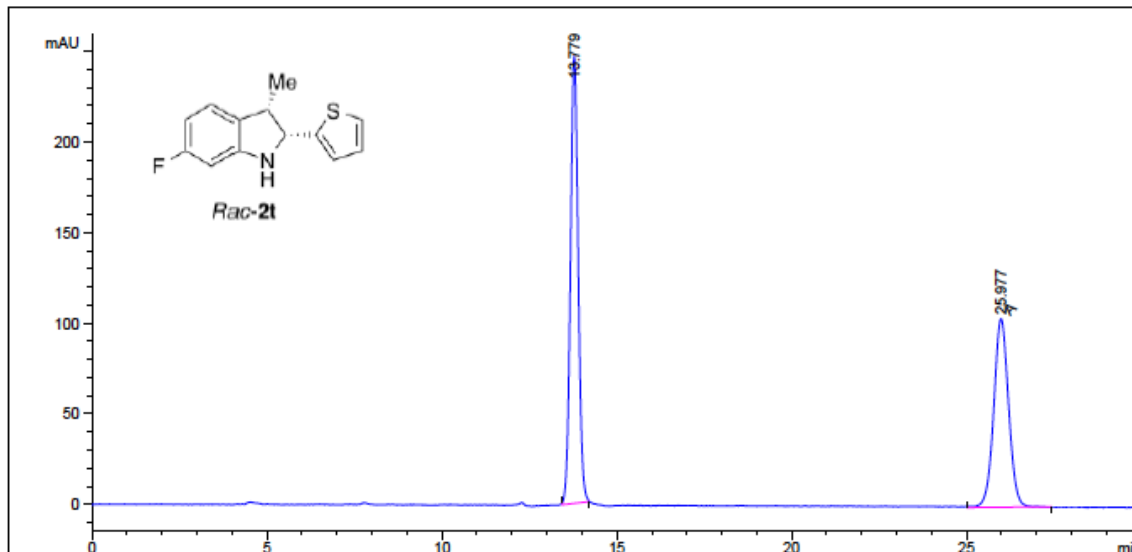
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.825	BB	0.3716	1193.60486	49.11028	49.2861
2	12.889	BB	0.2960	1228.18396	63.95902	50.7139



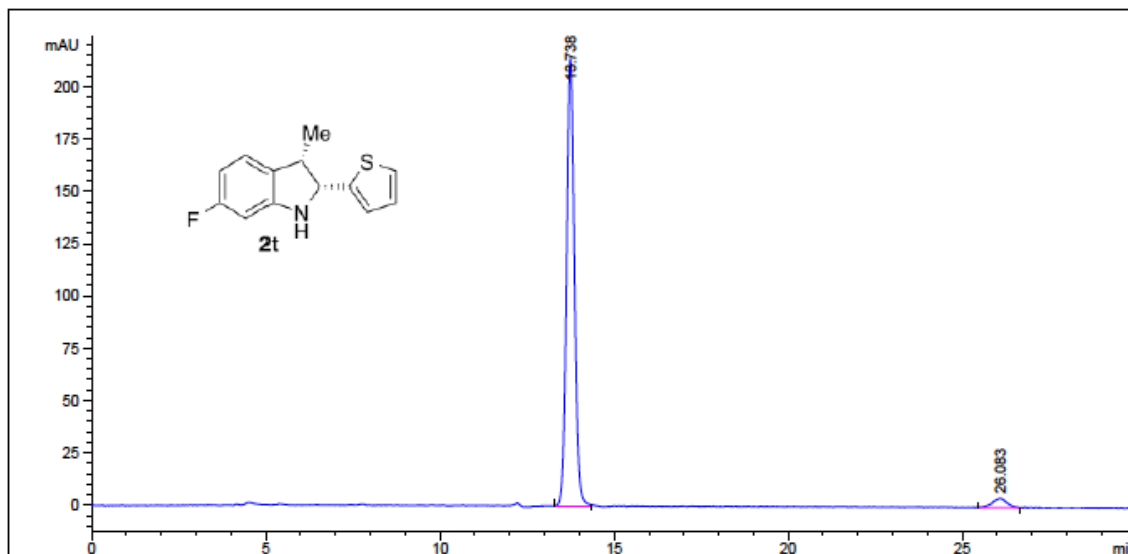
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.843	MM T	0.3923	118.09015	5.01756	3.6685
2	12.896	MM T	0.3231	3100.91357	159.94656	96.3315



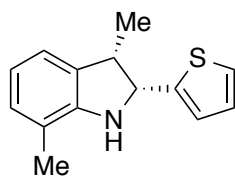
**(2R,3S)-6-Fluoro-3-methyl-2-(thiophen-2-yl)indoline** (Table 2, **2t**): HPLC analysis (IA, 2% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_R$  (major) = 13.7 min,  $t_R$  (minor) = 26.0 min.



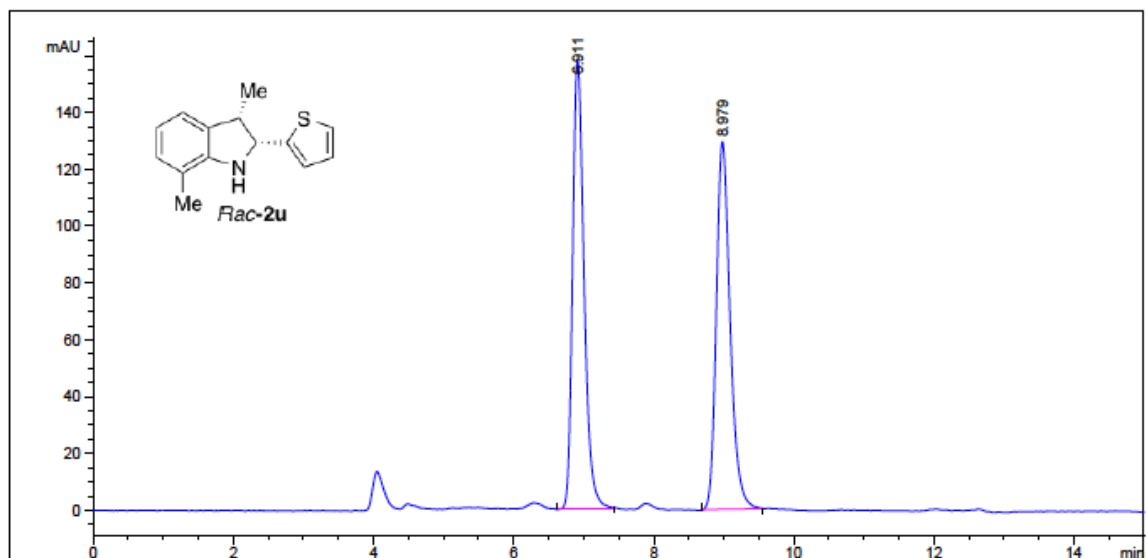
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.779	MM T	0.2567	3805.73389	247.06081	55.1424
2	25.977	MM T	0.4955	3095.90723	104.12977	44.8576



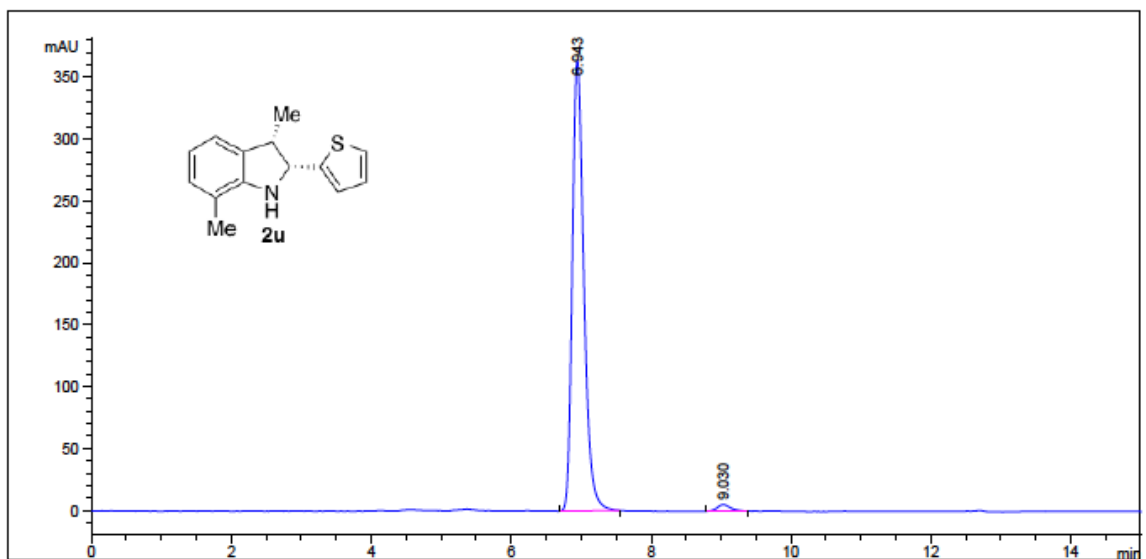
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.738	BB	0.2407	3350.34595	213.95082	96.1244
2	26.083	VV	0.3538	135.08267	4.53108	3.8756



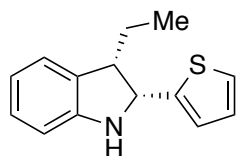
**(2R,3S)-3,7-Dimethyl-2-(thiophen-2-yl)indoline** (Table 2, **2u**): HPLC analysis (IA, 2% IPA/hexane, 0.8 mL/min, 230 nm) indicated 97% ee:  $t_R$  (major) = 6.9 min,  $t_R$  (minor) = 9.0 min.



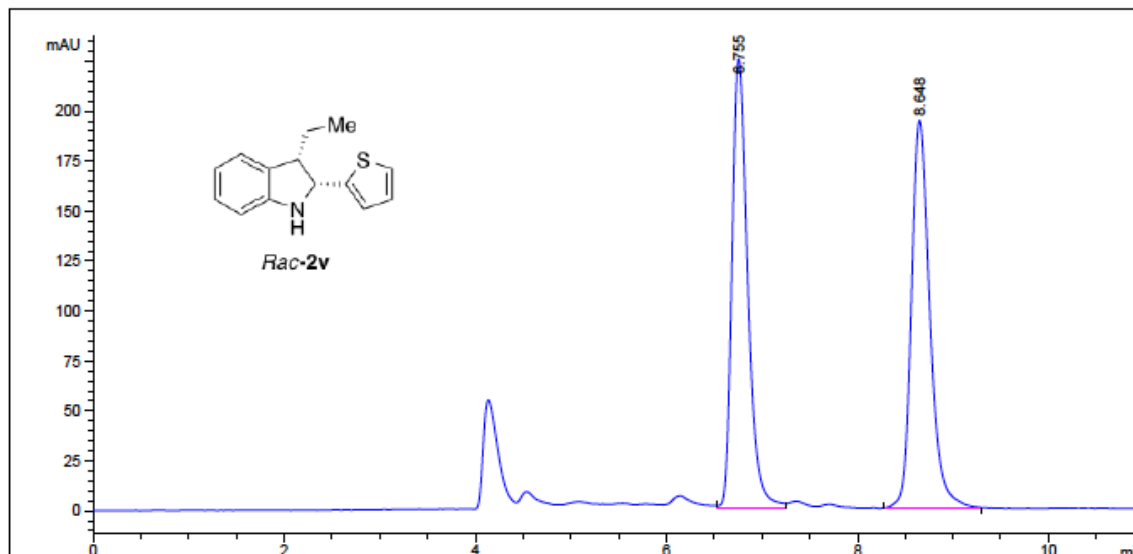
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.911	VB	0.1729	1803.68420	158.35460	50.4698
2	8.979	BB	0.2076	1770.10376	129.38274	49.5302



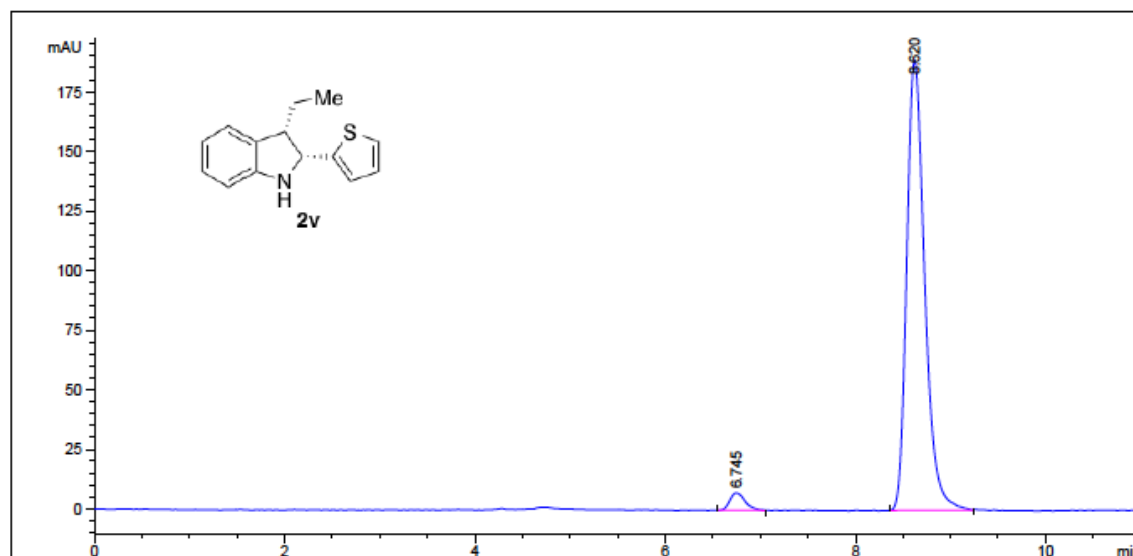
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.943	BB	0.1761	4189.36377	364.44171	98.3179
2	9.030	BB	0.1962	71.67686	5.28551	1.6821



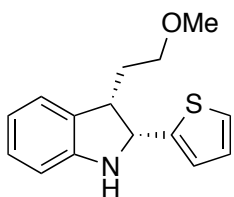
**(2R,3S)-3-ethyl-2-(Thiophen-2-yl)indoline** (Table 2, **2v**):  
 HPLC analysis (IC, 2% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_R$  (major) = 8.6 min,  $t_R$  (minor) = 6.7 min.



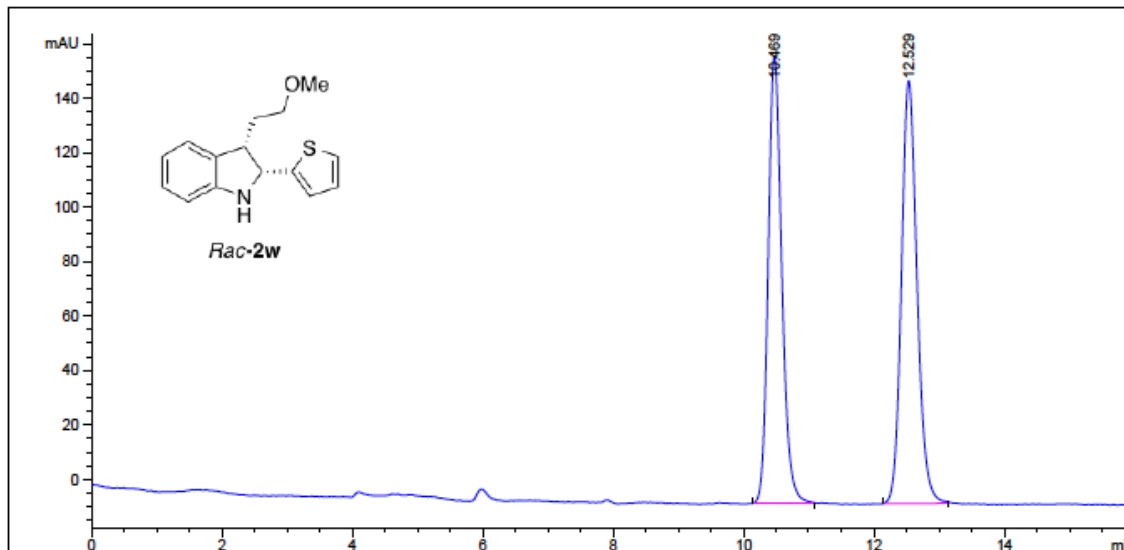
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.755	VV	0.1760	2587.56982	225.22086	49.8016
2	8.648	BB	0.2047	2608.18481	194.17400	50.1984



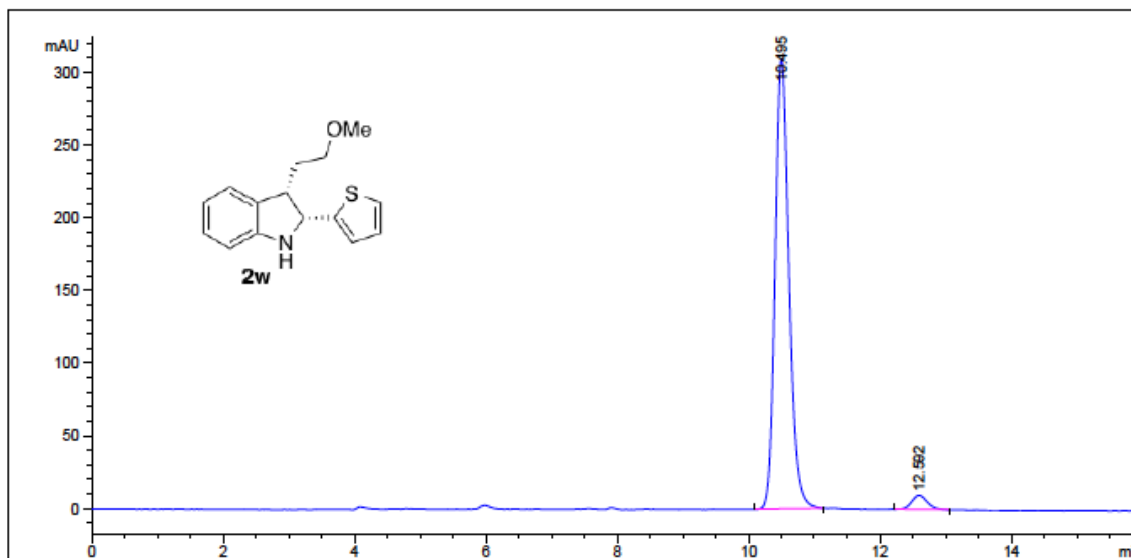
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.745	VB	0.1761	83.45827	7.36972	3.2650
2	8.620	BB	0.2007	2472.71558	188.89276	96.7350



**(2R,3S)-3-(2-Methoxyethyl)-2-(thiophen-2-yl)indoline** (Table 2, **2w**): HPLC analysis (IA, 5% IPA/hexane, 0.8 mL/min, 230 nm) indicated 93% ee:  $t_R$  (major) = 10.4 min,  $t_R$  (minor) = 12.5 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.469	BB	0.2235	2390.12842	164.48709	48.0574
2	12.529	BB	0.2538	2583.36255	155.54547	51.9426



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.495	VB	0.2250	4539.31396	309.63953	96.4914
2	12.592	VB	0.2440	165.05675	9.82729	3.5086