

## Palladium-Catalyzed $\alpha$ -Arylation of Indolin-3-ones

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### Supporting Information

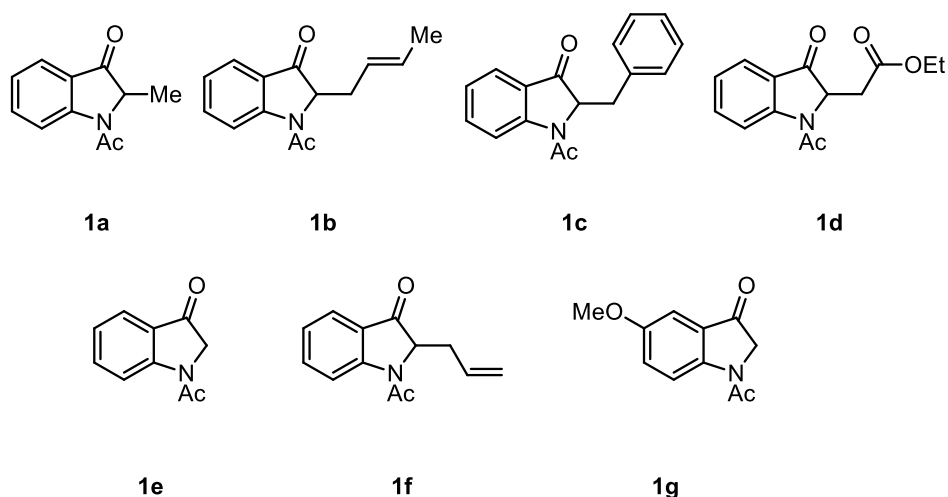
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## General Information

All air-sensitive reactions were carried out using flame-dried glassware under N<sub>2</sub> atmosphere with standard Schlenk line technique. Toluene, 1,4-dioxane, tetrahydrofuran, dichloromethane were purified by passage over activated alumina using a commercial solvent purification system. All other solvents (ACS grade) and commercially obtained reagents were used as received. Aluminum heating blocks were applied to all thermal reactions. Reactions were monitored by thin layer chromatography (TLC) on silica gel 60 Å F254 plates, visualized by UV (254 nm) and KMnO<sub>4</sub> staining solution. Flash chromatography was performed on silica gel (230-400 mesh) with indicated eluents. Melting points were uncorrected. NMR spectra were measured at 400 or 600 MHz for <sup>1</sup>H spectra and 100 or 150 MHz for <sup>13</sup>C spectra and calibrated from residual solvent signals (chloroform at 7.26 ppm for <sup>1</sup>H spectra; chloroform at 77.16 ppm for <sup>13</sup>C spectra; trifluoroacetic acid as internal standard at -76.55 ppm for <sup>19</sup>F spectra). Chemical shifts were denoted in ppm (δ), and the following abbreviations were used to explain the multiplicities: s = singlet, br = broad, br s = broad singlet, br d = broad doublet, d = doublet, t = triplet, q = quartet, p = pentate, dd = doublet doublet, td = triple doublet, dt = double triplet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Infrared (IR) spectra were measured on KBr salt plates. Mass spectra were recorded by using EI or ESI as specified in each case.

## Synthesis of Previously Known Compounds



Compounds **1a-g** were prepared by following previously described procedures:

- For synthesis of compound **1a**, see: Matsumoto, S.; Samata, D.; Akazome, M.; Ogura, K. *Tetrahedron Lett.* **2009**, *50*, 111-114.
- For synthesis of compound **1b**, see: Kawasaki, T.; Masuda, K.; Baba, Y.; Terashima, R.; Takada, K.; Sakamoto, M. *J. Chem. Soc., Perkin Trans. 1* **1996**, 729-733.
- For synthesis of compound **1c**, see: Buzas, A.; Mérour, J. Y. *Synthesis* **1989**, *6*, 458-461.
- For synthesis of compound **1d**, see: Mérour, J. Y.; Chichereau, L.; Desarbre, E.; Gadonneix, P. *Synthesis* **1996**, 519-524.
- For synthesis of compounds **1e** and **1g**, see: Bourlot, A. S.; Desarbre, E.; Mérour, J. Y. *Synthesis* **1993**, 411-416.
- For synthesis of compound **1f**, see: Kawasaki, T.; Masuda, K.; Baba, Y.; Takada, K.; Sakamoto, M. *Chem. Pharm. Bull.* **1994**, *42*, 1974-1976.

## Synthesis and Characterization Data

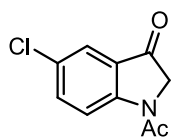
### General Procedure for the Synthesis of **S1**, **S2**, and **1h**.

To a solution of a substituted indole-3-carboxaldehyde (1.0 mmol) in THF (2.0 mL) at 0 °C was added Ac<sub>2</sub>O (2.0 mmol) and DMAP (0.2 mmol). The reaction mixture was stirred overnight at room temperature. The reaction mixture was diluted with ethyl acetate (10 mL x 2). The resulting solution were sequentially washed with NaHCO<sub>3(aq)</sub> (10 mL x 2) and water (15 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and then concentrated under reduced pressure.

To the thus obtained crude product in DCM (5 mL), *m*-CPBA (1.3 mmol) and AcOH (5 mL) were added. The reaction mixture was stirred overnight at 0 °C. The reaction mixture was diluted with DCM (20 mL) and quenched with 10% Na<sub>2</sub>SO<sub>3(aq)</sub> (10 mL). The organic layers were sequentially washed with NaHCO<sub>3(aq)</sub> (10 mL) and water (15 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and then concentrated under reduced

pressure. The resulting crude was dissolved in DCM (5 ml) and MeOH (5 ml). Na<sub>2</sub>SO<sub>3</sub> (1.2 mmol) and H<sub>2</sub>O (1.5 mL) were added. The reaction mixture was stirred for 3 h at room temperature. After the reaction was completed as judged by TLC, solvents were removed using a rotary evaporator. The residue was dissolved in DCM (15 mL x 2), washed with H<sub>2</sub>O (15 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and then concentrated under reduced pressure. The crude compound was purified by flash column chromatography to give the indolin-3-one product.

### 1-Acetyl-5-chloroindolin-3-one (S1)



**S1**

The reaction was conducted with 1.0 mmol of 5-chloro-1H-indole-3-carbaldehyde following the General Procedure. The crude product was purified by flash column chromatography (hexanes/EtOAc = 2/1 to 0/1) to afford **S1** (99 mg, 47% over 3 steps) as white solid (m.p. 163-165 °C). R<sub>f</sub> = 0.5 (hexanes/EtOAc = 1:1).

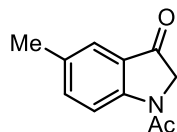
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.45 (d, *J* = 8.8 Hz, 1H), 7.61 (br s, 1H), 7.54 (dd, *J* = 8.9, 2.2 Hz, 1H), 4.29 (s, 2H), 2.29 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 193.44, 168.18, 152.11, 137.10, 130.02, 126.18, 123.22, 119.87, 56.46, 24.19.

IR (cast): 3029, 2919, 2861, 1711, 1667 cm<sup>-1</sup>

HRMS (EI, [M]<sup>+</sup>) for C<sub>10</sub>H<sub>8</sub>ClNO<sub>2</sub> calcd. 209.0244, found: 209.0249.

### 1-Acetyl-5-methylindolin-3-one (S2)



**S2**

The reaction was conducted with 1.0 mmol of 5-methyl-1H-indole-3-carbaldehyde following the General Procedure. The crude product was purified by flash column chromatography (hexanes/EtOAc = 2/1 to 0/1) to afford **S2** (100 mg, 53% over 3 steps) as white solid (m.p. 163-165 °C). R<sub>f</sub> = 0.5 (hexanes/EtOAc = 1:1).

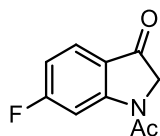
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.37 (m, 2H), 4.22 (s, 2H), 2.35 (s, 3H), 2.26 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 194.83, 168.01, 151.96, 138.49, 134.25, 125.05, 123.31, 118.34, 56.40, 24.21, 20.83.

IR (cast): 3066, 2928, 2866, 1719, 1673  $\text{cm}^{-1}$

HRMS (EI,  $[\text{M}]^+$ ) for  $\text{C}_{11}\text{H}_{11}\text{NO}_2$  calcd. 189.0790, found: 189.0793.

### 1-Acetyl-6-fluoroindolin-3-one (1h)



1h

The reaction was conducted with 1.0 mmol of 6-fluoro-1H-indole-3-carbaldehyde following the General Procedure. The crude product was purified by flash column chromatography (hexanes/EtOAc = 5/1 to 0/1) to afford **S1** (77 mg, 40% over 3 steps) as white solid (m.p. 115-116  $^{\circ}\text{C}$ ).  $R_f$  = 0.3 (hexanes/EtOAc = 3 :1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.13 (d,  $J$  = 8.9 Hz, 1H), 7.74 – 7.52 (m, 1H), 6.83 (t,  $J$  = 8.4 Hz, 1H), 4.29 – 4.18 (br s, 2H), 2.26 (s, 3H).

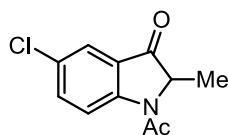
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.89, 169.71, 167.78 (d,  $J_{\text{C-F}}$  = 124.6 Hz), 155.17 (d,  $J_{\text{C-F}}$  = 14.5 Hz), 125.70 (d,  $J_{\text{C-F}}$  = 11.8 Hz), 121.32, 112.44 (d,  $J_{\text{C-F}}$  = 24.4 Hz), 106.02 (d,  $J_{\text{C-F}}$  = 28.9 Hz), 56.59, 24.12.

$^{19}\text{F NMR}$  (375 MHz,  $\text{CDCl}_3$ ): -97.44.

IR (cast): 3244, 3127, 2361, 1729, 1684  $\text{cm}^{-1}$

HRMS (EI,  $[\text{M}]^+$ ) for  $\text{C}_{10}\text{H}_8\text{NO}_2\text{F}$  calcd. 193.0534, found: 193.0536.

### 1-Acetyl-5-chloro-2-methylindolin-3-one (1i)



1i

The reaction was conducted with 0.24 mmol of **S1** following the procedure for the synthesis of **1a**. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 2/1) to afford **1i** (41 mg, 77%) as red solid (m.p. 138-140 $^{\circ}\text{C}$ ).  $R_f$  = 0.3 (hexanes/EtOAc = 2:1).

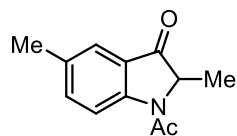
$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.52 (br s, 1H), 7.70 (s, 1H), 7.60 (dd,  $J$  = 8.9, 2.3 Hz, 1H), 4.30 (br s, 1H), 2.36 (s, 3H), 1.60 (d,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.62, 168.51, 151.33, 137.24, 130.23, 129.64, 123.67, 120.48, 62.41, 23.96, 18.43.

IR (cast): 2956, 2917, 2848, 1725, 1677  $\text{cm}^{-1}$

HRMS (EI,  $[\text{M}]^+$ ) for  $\text{C}_{11}\text{H}_{10}\text{ClNO}_2$  calcd. 223.0400, found: 223.0397.

### 1-Acetyl-2,5-dimethylindolin-3-one (**1j**)



**1j**

The reaction was conducted with 2.7 mmol of **S2** following the procedure for the synthesis of **1a**. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 2/1) to afford **1j** (238 mg, 42%) as a red solid (m.p. 127 °C).  $R_f$  = 0.3 (hexanes/EtOAc = 2 : 1).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 8.37 (s, 1H), 7.46 (s, 1H), 7.42 (d,  $J$  = 8.5 Hz, 1H), 4.20 (br s, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.53 (d,  $J$  = 6.8 Hz, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 198.79, 168.26, 151.05, 138.46, 134.37, 124.82, 123.57, 118.78, 62.08, 23.84, 20.75, 18.34.

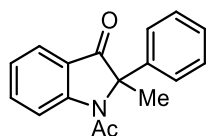
**IR** (cast): 3337, 2923, 2850, 1718, 1672 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub> calcd. 203.0946, found: 203.0947.

### General Procedure A for the Arylation of **1a-d**.

To a stirring mixture of indolin-3-one (0.2 mmol) in anhydrous co-solvent of THF (1.05 mL) and 1,4-dioxane (1.05 mL) was added Cs<sub>2</sub>CO<sub>3</sub> (83 mg, 0.25 mmol), bromoarene (2 equiv), Pd<sub>2</sub>(dba)<sub>3</sub> (7.5 mg, 6 mol %), PAd<sub>3</sub> (7.4 mg, 8 mol %). The resulting mixture was brought up to 120 °C (temperature of the aluminum heating block) and then stirred for 20 h. After indolin-3-one was completely consumed as indicated by TLC analysis, 1 M of aqueous hydrochloric acid solution (15 mL) was added to quench the reaction at room temperature. The reaction mixture was filtered through a pad of celite. The filtrate was extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with water (15 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography to give the corresponding arylated product.

### 1-Acetyl-2-methyl-2-phenylindolin-3-one (**2a**)



**2a**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2a** (46 mg, 67%) as a brown solid (m.p. 125-127 °C).  $R_f = 0.5$  (hexanes/EtOAc = 3:1).

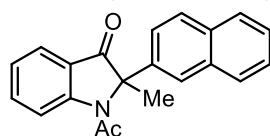
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.80 (br s, 1H), 7.80 – 7.71 (m, 2H), 7.38 – 7.23 (m, 6H), 2.04 (s, 3H), 1.98 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.14, 170.02, 153.63, 138.03, 137.77, 129.45, 128.39, 125.20, 125.12, 124.88, 121.37, 119.05, 71.90, 25.33, 22.56.

**IR** (cast): 3025, 2955, 2853, 1725, 1675  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{17}\text{H}_{15}\text{NO}_2$  calcd. 265.1097, found: 265.1092.

### 1-Acetyl-2-methyl-2-(naphthalen-2-yl)indolin-3-one (**2b**)



**2b**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2b** (63 mg, 94%) as a white solid (m.p. 139-140 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1). [Note: The reaction conducted with 1 mmol of **1a** gave product **2b** in 99% yield.]

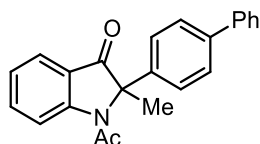
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.86 (br s, 1H), 7.88 – 7.74 (m, 6H), 7.55 – 7.45 (m, 2H), 7.30 (t,  $J = 7.5$  Hz, 1H), 7.20 (dd,  $J = 8.7, 1.9$  Hz, 1H), 2.16 (s, 3H), 2.00 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.13, 170.13, 153.74, 137.90, 135.51, 133.56, 133.02, 129.55, 128.34, 127.74, 126.81, 126.80, 125.23, 125.01, 124.90, 122.52, 121.57, 119.20, 72.14, 25.37, 22.69.

**IR** (cast): 3056, 2953, 1724, 1674, 1507  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{21}\text{H}_{17}\text{NO}_2$  calcd. 315.1253, found: 315.1247.

### 1-Acetyl-2-methyl-2-(naphthalen-2-yl)indolin-3-one (**2c**)



**2c**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2c** (66 mg, 91%) as a white solid (m.p. 161-162 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

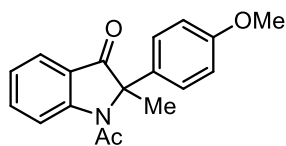
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.82 (br s, 1H), 7.81 – 7.74 (m, 2H), 7.61 – 7.51 (m, 4H), 7.46 – 7.39 (m, 2H), 7.38 – 7.27 (m, 4H), 2.08 (s, 3H), 2.05 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 198.16, 170.06, 153.70, 141.30, 140.17, 137.85, 136.96, 128.93, 128.13, 127.72, 127.13, 125.68, 125.21, 124.93, 121.41, 119.14, 71.75, 25.46, 22.63.

**IR** (cast): 3957, 2924, 2870, 1724, 1674 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub> calcd. 341.1410, found: 341.1418.

### 1-Acetyl-2-(4-methoxyphenyl)-2-methylindolin-3-one (**2d**)



**2d**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2d** (63 mg, 99%) as a white solid (m.p. 114-115 °C).  $R_f = 0.7$  (hexanes/EtOAc = 3/1).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.77 (br s, 1H), 7.80 – 7.68 (m, 2H), 7.31 – 7.23 (m, 1H), 7.19 – 7.10 (m, 2H), 6.86 (d,  $J = 9.0$  Hz, 2H), 3.77 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H).

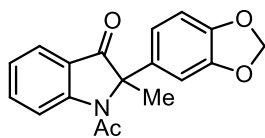
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 198.55, 170.16, 159.65, 153.54, 137.74, 129.99, 126.52, 125.14, 124.85, 121.45, 119.10, 114.85, 71.56, 55.41, 25.31, 22.54.

**IR** (cast): 2956, 2919, 2850, 1722, 1674 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub> calcd. 295.1202, found: 295.1200.

### 1-Acetyl-2-(benzo[d][1,3]dioxol-5-yl)-2-methylindolin-3-one (**2e**)





**2e**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2e** (29 mg, 44%) as a brown solid (m.p. 105-106 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

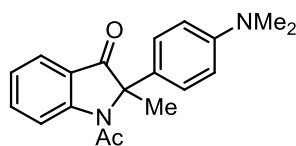
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.77 (br s, 1H), 7.80 – 7.68 (m, 2H), 7.31 – 7.21 (m, 1H), 6.80 – 6.70 (m, 2H), 6.66 (d,  $J = 1.7$  Hz, 1H), 5.95 – 5.93 (m, 2H), 2.04 (s, 3H), 1.97 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.20, 169.96, 153.55, 148.77, 147.85, 137.84, 131.80, 125.20, 124.92, 121.37, 118.88, 108.99, 105.85, 101.60, 71.63, 25.30, 22.58 [One aromatic carbon signal is missing due to peak overlap.]

**IR** (cast): 2955, 2924, 1723, 1674, 1607  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{18}\text{H}_{15}\text{NO}_4$  calcd. 309.0996, found: 309.0994.

### 1-Acetyl-2-(4-(dimethylamino)phenyl)-2-methylindolin-3-one (**2f**)



**2f**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2f** (67 mg, 99%) as a yellow solid (m.p. 116-117 °C).  $R_f = 0.7$  (hexanes/EtOAc = 3/1).

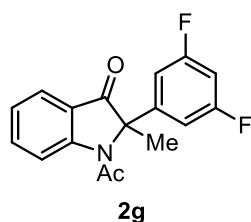
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.77 (br s, 1H), 7.79 – 7.66 (m, 2H), 7.24 (t,  $J = 7.2$  Hz, 1H), 7.06 (d,  $J = 8.7$  Hz, 2H), 6.65 (d,  $J = 8.8$  Hz, 2H), 2.91 (s, 6H), 2.00 (s, 3H), 1.98 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.80, 170.25, 153.42, 150.20, 137.39, 125.91, 124.90, 124.84, 124.54, 121.54, 118.89, 112.82, 71.56, 40.28, 25.14, 22.22.

**IR** (cast): 2955, 2923, 1724, 1672, 1608  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$  calcd. 308.1524, found: 308.1519.

### 1-Acetyl-2-(3,5-difluorophenyl)-2-methylindolin-3-one (**2g**)



The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2g** (30 mg, 46%) as a yellow oil.  $R_f = 0.5$  (hexanes/EtOAc = 3/1).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.78 (br s, 1H), 7.77 (t,  $J = 7.2$  Hz, 2H), 7.30 (t,  $J = 7.5$  Hz, 1H), 6.79 – 6.75 (m, 3H), 2.06 (s, 3H), 2.06 (s, 3H).

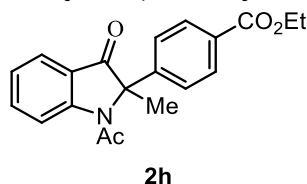
**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.86, 169.33, 163.71 (dd,  $J_{\text{C-F}} = 249, 13.0$  Hz), 153.39, 142.28 (t,  $J_{\text{C-F}} = 8.6$  Hz), 138.23, 125.37, 125.23, 121.08, 119.12, 108.69 (dd,  $J_{\text{C-F}} = 19.0, 7.6$  Hz), 103.86 (t,  $J_{\text{C-F}} = 28.4$  Hz), 71.33, 25.46, 22.58.

**$^{19}\text{F}$  NMR** (375 MHz,  $\text{CDCl}_3$ ): -107.75.

**IR** (film): 2956, 2923, 1723, 1680, 1607  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{17}\text{H}_{13}\text{NO}_2\text{F}_2$  calcd. 301.0909, found: 301.0907.

### Ethyl 4-(1-acetyl-2-methyl-3-oxoindolin-2-yl)benzoate (**2h**)



The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2h** (61 mg, 86%) as a brown solid (m.p. 107-109 °C).  $R_f = 0.4$  (hexanes/EtOAc = 3/1).

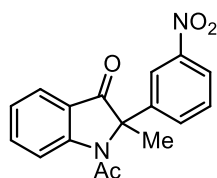
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.77 (br s, 1H), 8.00 (d,  $J = 8.4$  Hz, 2H), 7.79 – 7.69 (m, 2H), 7.35 – 7.23 (m, 3H), 4.39 – 4.28 (m, 2H), 2.04 (s, 3H), 1.95 (s, 3H), 1.34 (dd,  $J = 9.4, 4.9$  Hz, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.30, 169.67, 165.88, 153.49, 142.87, 137.97, 130.59, 128.74, 128.53, 125.30, 125.04, 121.28, 119.05, 71.82, 61.18, 25.33, 22.69, 14.35.

**IR** (cast): 2980, 2957, 2926, 1722, 1677  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{20}\text{H}_{19}\text{NO}_4$  calcd. 337.1309, found: 337.1306.

### 1-Acetyl-2-methyl-2-(3-nitrophenyl)indolin-3-one (**2i**)



**2i**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2i** (41 mg, 63%) as a yellow solid (m.p. 150-151 °C).  $R_f = 0.4$  (hexanes/EtOAc = 3/1).

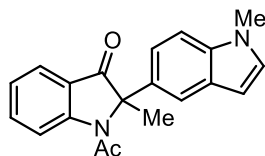
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.78 (br s, 1H), 8.18 (br s, 2H), 7.81 – 7.77 (m, 2H), 7.55 – 7.53 (m, 2H), 7.31 (t,  $J = 7.8$  Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 196.92, 169.42, 153.78, 148.99, 140.61, 138.32, 131.32, 130.42, 130.21, 125.29, 123.40, 120.64, 119.32, 118.56, 71.41, 25.64, 22.65.

**IR** (cast): 2956, 2925, 1724, 1531, 1369 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub> calcd. 310.0948, found: 310.0949.

### 1-Acetyl-2-methyl-2-(1-methyl-1H-indol-5-yl)indolin-3-one (**2j**)



**2j**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2j** (46 mg, 69%) as a yellow oil.  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

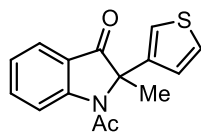
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.83 (br s, 1H), 7.83 – 7.69 (m, 2H), 7.56 (s, 1H), 7.30 – 7.22 (m, 2H), 7.05 (d,  $J = 3.0$  Hz, 1H), 7.02 – 6.95 (m, 1H), 6.45 (br s, 1H), 3.77 (s, 3H), 2.10 (s, 3H), 1.98 (br s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 199.00, 170.59, 153.75, 137.66, 136.56, 130.07, 129.15, 128.90, 125.22, 124.86, 121.77, 119.18, 118.57, 118.05, 110.39, 101.61, 72.37, 33.11, 25.39, 22.83.

**IR** (film): 2957, 2924, 2855, 1720, 1670 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> calcd. 318.1363, found: 318.1365.

### 1-Acetyl-2-methyl-2-(thiophen-3-yl)indolin-3-one (**2k**)



**2k**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2k** (41 mg, 71%) as a yellow solid (m.p. 127-129 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

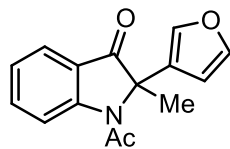
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.74 (br s, 1H), 7.78 – 7.69 (m, 2H), 7.31 – 7.22 (m, 3H), 6.79 (dd,  $J = 5.1, 1.4$  Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H).

**$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.25, 169.95, 153.18, 139.45, 137.82, 127.72, 125.11, 124.83, 124.81, 122.05, 121.32, 119.15, 70.21, 25.02, 22.99.

**IR** (cast): 3100, 2956, 2923, 1724, 1672  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{15}\text{H}_{13}\text{NO}_2\text{S}$  calcd. 271.0662, found: 271.0658.

### 1-Acetyl-2-(furan-3-yl)-2-methylindolin-3-one (**2l**)



**2l**

The reaction was conducted with 0.2 mmol of **1a** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2l** (41 mg, 45%) as a white solid (m.p. 93-94 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

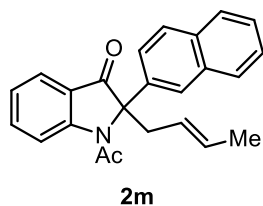
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.70 (br s, 1H), 7.77 (d,  $J = 7.7$  Hz, 1H), 7.72 (t,  $J = 7.9$  Hz, 1H), 7.49 (s, 1H), 7.37 (s, 1H), 7.25 (t,  $J = 7.4$  Hz, 1H), 6.10 (s, 1H), 2.18 (s, 3H), 1.91 (s, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.82, 169.87, 153.02, 144.51, 140.05, 137.93, 125.07, 124.97, 124.83, 121.32, 119.15, 107.94, 67.32, 25.12, 22.54.

**IR** (cast): 3137, 3080, 2936, 1721, 1367  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{15}\text{H}_{13}\text{NO}_2\text{S}$  calcd. 255.0890, found: 255.0893.

### (E)-1-Acetyl-2-(but-2-en-1-yl)-2-(naphthalen-2-yl)indolin-3-one (**2m**)



The reaction was conducted with 0.2 mmol of **1b** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2m** (32 mg, 45%) as a colorless oil.  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

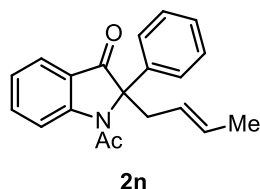
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.85 (d,  $J = 8.1$  Hz, 1H), 7.85 – 7.71 (m, 6H), 7.56 – 7.46 (m, 2H), 7.30 – 7.25 (m, 1H), 7.20 (d,  $J = 8.8$  Hz, 1H), 5.68 – 5.59 (m, 1H), 5.14 – 5.04 (m, 1H), 3.71– 3.68 (m, 1H), 3.30 – 3.14 (m, 1H), 1.99 (s, 3H), 1.70 – 1.48 (m, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 197.95, 170.25, 137.79, 137.66, 135.39, 133.64, 133.10, 131.52, 129.52, 129.44, 128.41, 128.33, 127.74, 127.65, 126.79, 124.88, 124.74, 122.61, 121.83, 119.05, 68.98, 39.19, 29.71, 18.03.

**IR** (film): 2923, 2853, 1720, 1672, 1601 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub> calcd. 355.1567, found: 355.1571.

### **(E)-1-Acetyl-2-(but-2-en-1-yl)-2-phenylindolin-3-one (2n)**



The reaction was conducted with 0.4 mmol of **1b** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 15/1 to 5/1) to afford **2n** (60 mg, 49%) as a white solid (m.p. 56-57 °C).  $R_f = 0.5$  (hexanes/EtOAc = 2/1).

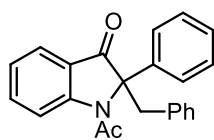
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 8.81 (br s, 1H), 7.71 (t,  $J = 7.5$  Hz, 2H), 7.38 – 7.19 (m, 6H), 5.61 – 5.56 (m, 1H), 5.05 – 5.00 (m, 1H), 3.58 (br s, 1H), 3.07 (br s, 1H), 1.97 (s, 3H), 1.46 (d,  $J = 6.4$  Hz, 3H).

**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 198.00, 170.13, 154.69, 137.86, 137.66, 131.38, 129.49, 128.45, 125.20, 124.70, 124.59, 122.51, 121.88, 118.92, 75.03, 39.12, 25.18, 17.97.

**IR** (cast): 3059, 3025, 2957, 2924, 1724 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub> calcd. 305.1410, found: 355.1411.

### **1-Acetyl-2-benzyl-2-(naphthalen-2-yl)indolin-3-one (2o)**



**2o**

The reaction was conducted with 0.2 mmol of **1c** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2o** (35 mg, 49%) as a white solid (m.p. 229-230 °C).  $R_f = 0.5$  (hexanes/EtOAc = 3/1).

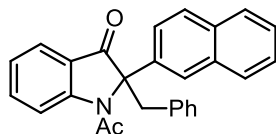
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.53 (d,  $J = 6.5$  Hz, 1H), 7.62 – 7.56 (m, 1H), 7.55 – 7.48 (m, 1H), 7.45 – 7.28 (m, 6H), 7.10 – 7.05 (m, 5H), 4.20 (d,  $J = 14.4$  Hz, 1H), 3.64 (d,  $J = 14.4$  Hz, 1H), 2.11 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.20, 169.90, 154.72, 138.18, 137.45, 133.30, 129.71, 128.65, 128.29, 128.09, 127.40, 125.40, 124.61, 124.24, 122.78, 118.68, 75.69, 40.96, 25.75.

**IR** (cast): 3030, 2924, 1719, 1672, 1607  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{23}\text{H}_{19}\text{NO}_2$  calcd. 341.1410, found: 341.1404.

### 1-Acetyl-2-benzyl-2-(naphthalen-2-yl)indolin-3-one (**2p**)



**2p**

The reaction was conducted with 0.2 mmol of **1c** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2p** (51 mg, 63%) as a yellow solid (m.p. 204-205 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

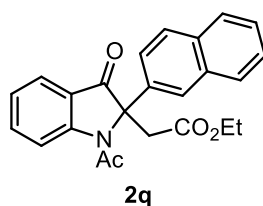
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.58 (d,  $J = 8.2$  Hz, 1H), 7.97 (s, 1H), 7.89 – 7.83 (m, 3H), 7.62 – 7.53 (m, 4H), 7.23 (d,  $J = 7.6$  Hz, 1H), 7.13 – 7.06 (m, 6H), 4.33 (d,  $J = 13.4$  Hz, 1H), 3.78 (d,  $J = 13.4$  Hz, 1H), 2.12 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.13, 169.97, 154.80, 137.54, 135.65, 133.67, 133.30, 133.11, 129.78, 129.64, 128.43, 128.32, 127.77, 127.44, 127.05, 126.94, 125.10, 124.69, 124.28, 123.05, 122.68, 118.78, 75.91, 41.10, 25.73.

**IR** (cast): 2956, 2925, 1719, 1673, 1601  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{27}\text{H}_{21}\text{NO}_2$  calcd. 391.1567, found: 391.1568.

### Ethyl 2-(1-acetyl-2-(naphthalen-2-yl)-3-oxoindolin-2-yl)acetate (**2q**)



The reaction was conducted with 0.8 mmol of **1d** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2q** (268 mg, 98%) as a yellow solid (m.p. 60-61 °C).  $R_f = 0.6$  (hexanes/EtOAc = 2/1).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.88 (br s, 1H), 7.79 – 7.67 (m, 6H), 7.47 – 7.35 (m, 2H), 7.27 – 7.10 (m, 2H), 4.17 (br s, 1H), 3.96 – 3.88 (m, 2H), 3.58 (br s, 1H), 2.07 (s, 3H), 0.81 (br s, 3H).

**$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.81, 169.63, 167.92, 154.10, 137.13, 133.91, 133.18, 133.03, 132.73, 129.50, 128.02, 127.38, 126.64, 125.11, 124.67, 124.33, 122.49, 121.69, 118.49, 71.99, 60.94, 41.87, 24.89, 13.32.

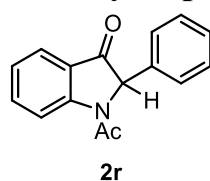
**IR** (cast): 3028, 2928, 1714, 1667, 1604  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{24}\text{H}_{21}\text{NO}_4$  calcd. 387.1465, found: 387.1468.

### General Procedure B for the Arylation of **1e**.

To a stirring mixture of indolin-3-one **1e** (0.3 mmol) in anhydrous co-solvent of THF (1.05 mL) and 1,4-dioxane (1.05 mL) was added  $\text{Cs}_2\text{CO}_3$  (205.3 mg, 0.63 mmol), a bromoarene (2 equiv.),  $\text{Pd}_2(\text{dba})_3$  (10.4 mg, 6 mol %),  $\text{PAd}_3$  (10.5 mg, 8 mol %). The resulting mixture was brought up to 120 °C (temperature of the aluminum heating block) and then stirred for 2 h. After completion of the reaction as indicated by TLC analysis, 1 M of aqueous hydrochloric acid solution (15 mL) was added to quench the reaction at room temperature. The reaction mixture was filtered through a pad of celite. The filtrate extracted with ethyl acetate (15 mL x 2). The combined organic layers were with water (15 mL), dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography.

### 1-Acetyl-2-phenylindolin-3-one (**2r**)



The reaction was conducted with 0.2 mmol of **1e** following the General Procedure B.

The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2r** (42 mg, 83%) as a yellow solid (m.p. 126-128 °C).  $R_f = 0.5$  (hexanes/EtOAc = 3/1).

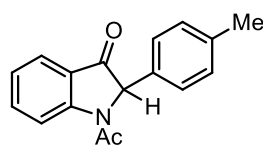
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.68 (br s, 1H), 7.74 – 7.37 (m, 2H), 7.36 – 7.32 (m, 3H), 7.28 – 7.23 (m, 3H), 5.19 (s, 1H), 2.06 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.08, 169.41, 153.99, 137.72, 134.67, 129.64, 128.91, 125.92, 124.94, 124.87, 122.98, 118.66, 69.76, 24.73.

**IR** (cast): 3029, 2925, 1720, 1671, 1603  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{16}\text{H}_{13}\text{NO}_2$  calcd. 251.0941, found: 251.0934.

### 1-Acetyl-2-(p-tolyl)indolin-3-one (**2s**)



**2s**

The reaction was conducted with 0.2 mmol of **1e** following the General Procedure B. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2s** (40 mg, 76%) as a white solid (m.p. 115-116 °C).  $R_f = 0.5$  (hexanes/EtOAc = 3/1).

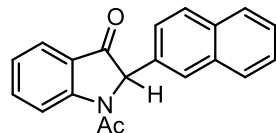
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.64 (br s, 1H), 7.68 – 7.66 (m, 2H), 7.22 – 7.13 (m, 5H), 5.14 (s, 1H), 2.30 (s, 3H), 2.04 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.20, 169.34, 153.80, 138.62, 137.45, 131.62, 130.14, 125.70, 124.68, 124.61, 122.87, 118.42, 69.43, 24.56, 21.11.

**IR** (cast): 3018, 2930, 1721, 1673, 1605  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{17}\text{H}_{15}\text{NO}_2$  calcd. 265.1097, found: 265.1094.

### 1-Acetyl-2-(naphthalen-2-yl)indolin-3-one (**2t**)



**2t**

The reaction was conducted with 0.3 mmol of **1e** following the General Procedure B. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2t** (89 mg, 98%) as a white solid (m.p. 130-131 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1).



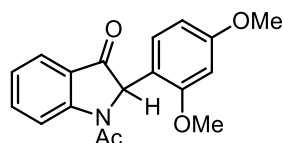
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.76 (d, *J* = 7.2 Hz, 1H), 7.87 – 7.79 (m, 3H), 7.79 – 7.72 (m, 3H), 7.53 – 7.45 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 5.36 (s, 1H), 2.09 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 195.02, 169.51, 154.02, 137.77, 133.54, 133.42, 132.07, 129.79, 128.06, 127.93, 126.88, 126.75, 125.38, 124.96, 124.93, 123.06, 118.71, 69.87, 24.78.

**IR** (cast): 3017, 2924, 1725, 1673, 1604 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>20</sub>H<sub>15</sub>NO<sub>2</sub> calcd. 301.1097, found: 301.1094.

### 1-Acetyl-2-(2,4-dimethoxyphenyl)indolin-3-one (2u)



**2u**

The reaction was conducted with 0.3 mmol of **1e** following the General Procedure B. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2u** (89 mg, 95%) as a white solid (m.p. 142-143 °C). *R<sub>f</sub>* = 0.6 (hexanes/EtOAc = 3/1).

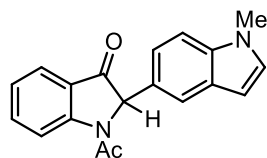
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.58 (br s, 1H), 7.68 – 7.63 (m, 2H), 7.19 – 7.17 (m, 1H), 6.83 (s, 1H), 6.46 – 6.37 (m, 2H), 5.52 (s, 1H), 3.71 (s, 6H), 1.99 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 196.68, 169.36, 161.16, 158.14, 153.76, 136.98, 128.14, 124.13, 123.98, 123.53, 118.22, 116.07, 105.20, 99.26, 64.26, 55.79, 55.31, 24.25.

**IR** (cast): 3008, 2937, 1719, 1672, 1607 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>18</sub>H<sub>17</sub>NO<sub>4</sub> calcd. 311.1152, found: 311.1155.

### 1-acetyl-2-(1-methyl-1H-indol-5-yl)indolin-3-one (2v)



**2v**

The reaction was conducted with 0.2 mmol of **1e** following the general procedure B. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2v** (168 mg, 97%) as white oil (m.p. 142-143 °C). *R<sub>f</sub>* = 0.6 (hexanes/EtOAc = 2/1).

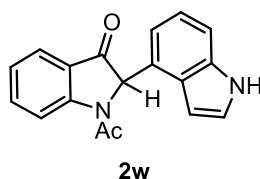
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.73 (d, *J* = 6.7 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.51 (s, 1H), 7.33 – 7.20 (m, 2H), 7.11 – 7.01 (m, 2H), 6.43 (s, 1H), 5.26 (s, 1H), 3.73 (s, 3H), 2.06 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 195.88, 169.72, 153.91, 137.37, 136.77, 130.01, 129.01, 125.46, 124.77, 124.59, 123.10, 119.11, 118.45, 118.41, 110.42, 101.21, 70.18, 32.93, 24.71.

**IR** (film): 2955, 2922, 1720, 1678, 1606 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> calcd. 304.1206, found: 304.1204.

### 1-Acetyl-2-(1H-indol-4-yl)indolin-3-one (2w)



The reaction was conducted with 0.2 mmol of **1e** following the General Procedure B. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2w** (32 mg, 55%) as a brown solid (m.p. 259-260 °C). *R<sub>f</sub>* = 0.5 (hexanes/EtOAc = 2/1).

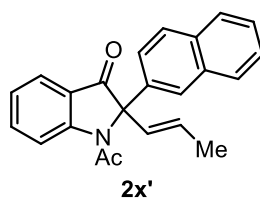
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.74 (d, *J* = 6.4 Hz, 1H), 8.34 (s, 1H), 7.76 – 7.74 (m, 2H), 7.38 (d, *J* = 9.9 Hz, 1H), 7.28 – 7.14 (m, 3H), 6.97 (br s, 1H), 6.46 (br s, 1H), 5.58 (s, 1H), 2.01 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 195.49, 169.87, 154.03, 147.28, 137.64, 136.68, 126.35, 125.32, 124.77, 124.72, 123.46, 122.50, 118.67, 111.84, 100.91, 69.26, 29.85, 24.63.

**IR** (cast): 3007, 2916, 1718, 1661, 1604 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> calcd. 290.1049, found: 290.1045.

### (*E*)-1-Acetyl-2-(naphthalen-2-yl)-2-(prop-1-en-1-yl)indolin-3-one (2x')



The reaction was conducted with 0.2 mmol of **1f** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 8/1 to 3/1) to afford **2x'** (25 mg, 32%) as a brown solid (m.p. 174-175 °C). *R<sub>f</sub>* = 0.7 (hexanes/EtOAc = 3/1).

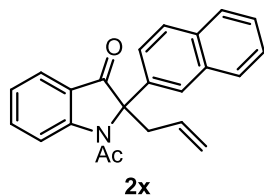
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.63 (d, *J* = 7.5 Hz, 1H), 7.80 (m, 5H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.24 (t, *J* = 7.7 Hz, 1H), 5.67 (d, *J* = 8.8 Hz, 1H), 5.18 (d, *J* = 8.7 Hz, 1H), 2.50 (s, 3H), 2.35 (br s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 195.69, 169.05, 153.37, 142.40, 138.93, 137.64, 133.31, 133.03, 132.72, 128.30, 128.12, 127.63, 126.50, 126.30, 124.93, 124.55, 124.39, 123.95, 121.59, 118.94, 65.99, 24.33, 17.27.

**IR** (cast): 2958, 2925, 1722, 1679, 1606 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub> calcd. 341.1410, found: 341.1407.

### 1-Acetyl-2-allyl-2-(naphthalen-2-yl)indolin-3-one (**2x**)



To a stirring mixture of **1f** (0.2 mmol) in anhydrous co-solvent of THF (1.05 mL) and 1,4-dioxane (1.05 mL) was added Cs<sub>2</sub>CO<sub>3</sub> (82.7 mg, 0.25 mmol), 2-bromonaphthalene (86.6 mg, 0.42 mmol), Pd<sub>2</sub>(OAc)<sub>3</sub> (2.9 mg, 6 mol %), PAd<sub>3</sub> (7.4 mg, 8 mol %). The resulting mixture was brought up to 120 °C (temperature of the aluminum heating block) and then stirred for 20 h. After completion of the reaction as indicated by TLC analysis, 1 M of aqueous hydrochloric acid solution (15 mL) was added to quench the reaction at room temperature. The reaction mixture was filtered through a pad of celite. The filtrate extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with water (15 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 8/1 to 3/1) to afford **2x** (84 mg, 99%) as a white solid (m.p. 74-75 °C). R<sub>f</sub> = 0.6 (hexanes/ EtOAc = 3/1).

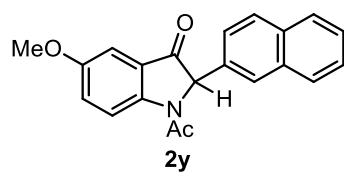
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.85 (br s, 1H), 7.83 (s, 2H), 7.80 – 7.75 (m, 4H), 7.50 – 7.45 (m, 2H), 7.30 – 7.24 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 5.51 – 5.41 (m, 1H), 5.23 (d, *J* = 16.8 Hz, 1H), 5.04 (d, *J* = 9.8 Hz, 1H), 3.79 (d, *J* = 9.5 Hz, 1H), 3.28 (s, 1H), 2.00 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 197.70, 170.14, 154.81, 137.92, 137.74, 135.13, 133.59, 133.08, 129.71, 129.66, 129.60, 128.37, 127.73, 126.84, 124.91, 124.82, 122.62, 122.45, 120.71, 119.11, 74.85, 40.43, 25.21.

**IR** (cast): 3050, 3014, 2928, 1720, 1668 cm<sup>-1</sup>

**HRMS** (CI, [M+H]<sup>+</sup>) for C<sub>23</sub>H<sub>20</sub>NO<sub>2</sub> calcd. 342.1489, found: 342.1493.

### 1-Acetyl-5-methoxy-2-(naphthalen-2-yl)indolin-3-one (2y)



The reaction was conducted with 0.4 mmol of **1g** following the General Procedure B. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2y** (63 mg, 45%) as white solid (m.p. 145-146 °C).  $R_f = 0.6$  (hexanes/EtOAc = 3/1).

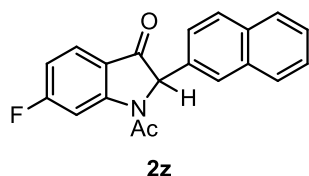
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.68 (d,  $J = 9.0$  Hz, 1H), 7.91 – 7.72 (m, 4H), 7.54 – 7.43 (m, 2H), 7.40 – 7.29 (m, 2H), 7.13 (br s, 1H), 5.35 (s, 1H), 3.80 (s, 3H), 2.04 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 194.86, 168.81, 157.05, 148.84, 133.46, 133.31, 132.11, 129.66, 127.97, 127.84, 126.77, 126.64, 126.43, 125.36, 123.83, 123.00, 119.82, 105.44, 70.20, 55.79, 24.41.

**IR** (cast): 3064, 3010, 2942, 1717, 1671 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>21</sub>H<sub>17</sub>NO<sub>3</sub> calcd. 331.1203, found:331.1207 .

### 1-Acetyl-6-fluoro-2-(naphthalen-2-yl)indolin-3-one (2z)



The reaction was conducted with 0.3 mmol of **1h** following the General Procedure B. The crude product was purified by flash column chromatography (hexanes/EtOAc = 6/1 to 3/1) to afford **2z** (51 mg, 53%) as white solid (m.p. 138-139 °C).  $R_f = 0.7$  (hexanes/EtOAc = 3/1).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.46 (d,  $J = 8.7$  Hz, 1H), 7.90 – 7.69 (m, 5H), 7.50 (s, 2H), 7.32 (d,  $J = 8.2$  Hz, 1H), 6.97 (t,  $J = 7.4$  Hz, 1H), 5.37 (s, 1H), 2.07 (s, 3H).

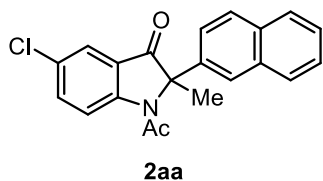
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 193.15, 170.10, 168.56 (d,  $J_{C-F} = 203.9$  Hz), 155.53 (d,  $J_{C-F} = 14.4$  Hz), 133.46 (d,  $J_{C-F} = 6.5$  Hz), 131.75, 129.86, 128.03, 127.92, 127.02, 126.95, 126.91, 126.83, 125.34, 122.87, 119.35, 113.14 (d,  $J_{C-F} = 24.3$  Hz), 106.31 (d,  $J_{C-F} = 29.1$  Hz), 70.40, 24.66.

**<sup>19</sup>F NMR** (375 MHz, CDCl<sub>3</sub>): -96.96.

**IR** (cast): 3126, 3019, 2925, 1725, 1684 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>20</sub>H<sub>14</sub>NO<sub>2</sub>F calcd. 319.1003, found: 319.1006.

### 1-Acetyl-5-chloro-2-methyl-2-(naphthalen-2-yl)indolin-3-one (2aa)



The reaction was conducted with 0.3 mmol of **1i** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1 to 0/1) to afford **2aa** (45 mg, 46%) as yellow solid (m.p. 201-203 °C).  $R_f = 0.3$  (hexanes/EtOAc = 3/1).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.83 (br s, 1H), 7.87 – 7.83 (m, 1H), 7.83 – 7.78 (m, 3H), 7.77 – 7.67 (m, 2H), 7.51 (m, 2H), 7.17 (d,  $J = 8.6$  Hz, 1H), 2.15 (s, 3H), 1.98 (s, 3H).

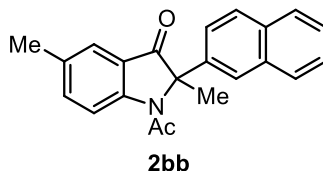
$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.94, 169.99, 152.08, 137.58, 134.95, 133.51, 133.05, 130.51, 129.69, 128.31, 127.75, 126.93, 124.89, 124.47, 122.91, 122.29, 120.47, 72.59, 25.19, 22.65.

[One aromatic carbon signal is missing due to peak overlap.]

**IR** (cast): 3058, 2925, 2855, 1725, 1673  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{21}\text{H}_{16}\text{ClNO}_2$  calcd. 349.0870, found: 349.0868.

### 1-Acetyl-2,5-dimethyl-2-(naphthalen-2-yl)indolin-3-one (2bb)



The reaction was conducted with 0.6 mmol of **1j** following the General Procedure A. The crude product was purified by flash column chromatography (hexanes/EtOAc = 20/1 to 0/1) to afford **2bb** (158 mg, 83%) as white solid (m.p. 190-191 °C).  $R_f = 0.3$  (hexanes/EtOAc = 5/1).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.76 (br s, 1H), 7.83 (d,  $J = 7.2$  Hz, 2H), 7.79 (t,  $J = 9.1$  Hz, 2H), 7.64 – 7.56 (m, 2H), 7.54 – 7.44 (m, 2H), 7.19 (d,  $J = 8.5$  Hz, 1H), 2.41 (s, 3H), 2.14 (s, 3H), 1.96 (s, 3H).

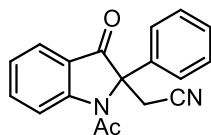
$^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.08, 169.83, 151.97, 139.01, 135.65, 135.02, 133.53, 132.97, 129.48, 128.30, 127.70, 126.75, 124.84, 124.68, 122.54, 121.63, 118.99, 72.25, 25.16, 22.65, 20.83.

[One aromatic carbon signal is missing due to peak overlap.]

**IR** (cast): 2654, 2917, 2849, 1723, 1672  $\text{cm}^{-1}$

**HRMS** (EI,  $[\text{M}]^+$ ) for  $\text{C}_{10}\text{H}_8\text{NO}_2\text{F}$  calcd. 329.1416, found: 329.1413.

### 2-(1-Acetyl-3-oxo-2-phenylindolin-2-yl)acetonitrile (3)



**3**

To a stirring mixture of **2r** (100 mg, 0.4 mmol) in anhydrous THF (4 mL) was added Cs<sub>2</sub>CO<sub>3</sub> (156.4 mg, 0.48 mmol) and bromoacetonitrile (57.6 mg, 0.48 mmol). The mixture was stirred for 20 h at room temperature. After completion of the reaction as indicated by TLC analysis, H<sub>2</sub>O (1 mL) was added to quench the reaction at room temperature. The resulting mixture was extracted with ethyl acetate (5 mL x 2). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 8/1 to 5/1) to afford **3** (90 mg, 78%) as a yellow oil. R<sub>f</sub> = 0.6 (hexanes/EtOAc = 3/1).

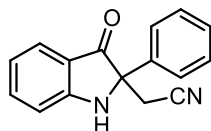
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.82 (br s, 1H), 7.91 – 7.72 (m, 2H), 7.32 – 7.26 (m, 4H), 7.16 (d, *J* = 7.5 Hz, 2H), 3.73 (br s, 2H), 2.66 (br s, 3H).

**<sup>13</sup>C NMR** (100 MHz, d<sup>6</sup>-DMSO): δ 195.42, 168.57, 153.13, 138.87, 135.01, 129.34, 128.55, 125.25, 125.05, 124.77, 120.99, 117.01, 116.11, 71.66, 25.65, 23.91.

**IR** (film): 3022, 2990, 2253, 1720, 1607 cm<sup>-1</sup>

**HRMS** (EI, [M]<sup>+</sup>) for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> calcd. 290.1038, found: 290.1049.

### 2-(3-Oxo-2-phenylindolin-2-yl)acetonitrile (**4**)



**4**

To a stirring mixture of **3** (0.2 mmol) in EtOH (2 mL) and 1,4-dioxane (1.05 mL) was added 2 M NaOH<sub>(aq)</sub> (0.13 mL, 0.23 mmol). The resulting mixture was brought up to 80 °C (temperature of the aluminum heating block) and then stirred for 1 h. After completion of the reaction as indicated by TLC analysis, H<sub>2</sub>O (1 mL) was added to quench the reaction at room temperature. The resulting mixture was extracted with ethyl acetate (5 mL x 2). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 5/1 to 2/1) to afford **4** (48 mg, 99%) as a yellow oil. R<sub>f</sub> = 0.6 (hexanes/EtOAc = 3/2).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.63 – 7.52 (m, 2H), 7.50 – 7.48 (m, 2H), 7.43 – 7.31 (m, 3H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 5.43 (s, 1H), 3.31 (d, *J* = 16.7 Hz, 1H), 2.93 (d, *J* = 16.7 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 198.06, 160.25, 138.53, 135.90, 129.42, 129.02, 126.02, 125.32, 120.52, 118.51, 116.66, 112.48, 68.14, 27.32.

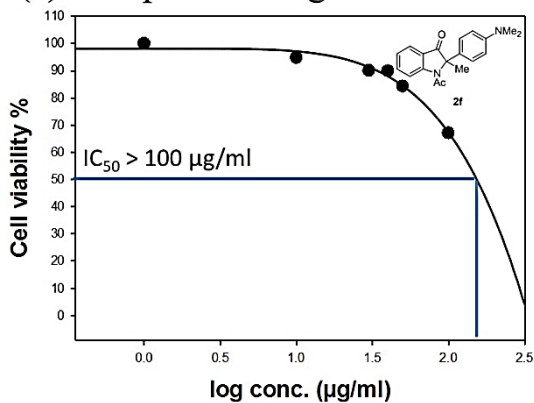
IR (film): 3343, 2923, 2259, 1615, 1487 cm<sup>-1</sup>

HRMS (EI, [M]<sup>+</sup>) for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O calcd. 248.0944, found: 248.0940.

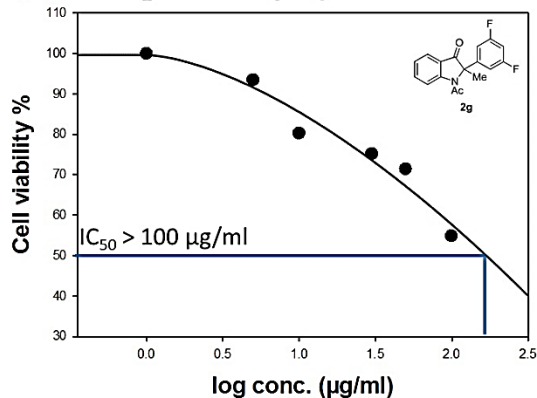
### **Cytotoxic Activities of 2f-j, 2q, 2v, and 2w.**

The cytotoxic activities of these compounds were preliminarily evaluated against HCT-116 (human colorectal carcinoma cells) and MCF-7 (human breast adenocarcinoma cells) cell lines by the MTT assay. HCT-116 and MCF-7 (all purchased from BCRC, Hsinchu, Taiwan) grown in DMEM (Dulbecco Modified Eagle Medium) supplemented with 10% fetal bovine serum and 1% (w/v) penicillin/strepto-mycin were seeded as 100 μL aliquots into a sterile 96 well microtiter plate at a titer of approximately 10000 cells per well and incubated (24 h, 37 °C, 5% CO<sub>2</sub>). Compounds **2f-j**, **2q**, **2v** and **2w** resuspended in DMSO and a compound-free DMSO control were diluted in fresh medium and added to the appropriate wells at final concentrations of 100, 50, 40, 30, 10 and 5 μg/mL. These plates were then cultured for an additional 24 h. MTT assay was used to assess the cytotoxicity of compound **2f-j**, **2q**, **2v** and **2w** against the cells. Briefly, 10 μL MTT solution (5 mg/ml) was added to each well and the 96-well plate was continuously incubated at 37 °C for 2 h. The OD value for each well was read at a 570 nm wavelength to determine the cell viability on a microplate reader (Thermo Scftware, Multiskan GO). The assay was repeated three times. An IC<sub>50</sub> value was calculated using SigmaPlot 14.0 software.

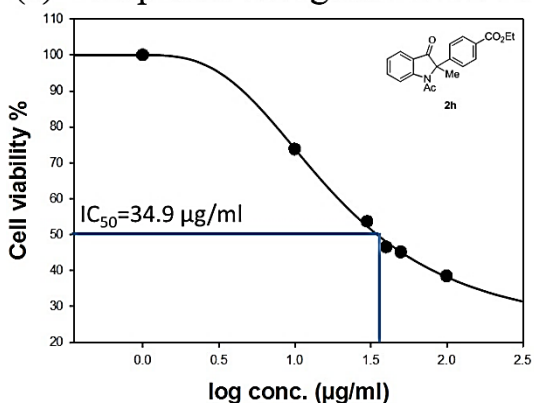
(a) Compound **2f** against HCT-116



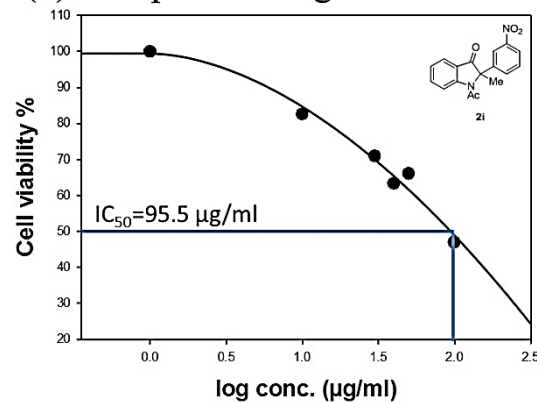
(b) Compound **2g** against HCT-116



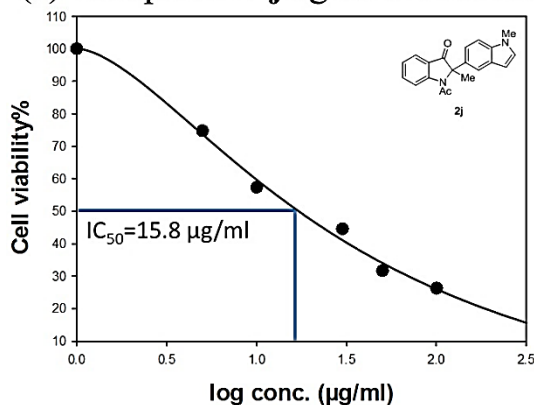
(c) Compound **2h** against HCT-116



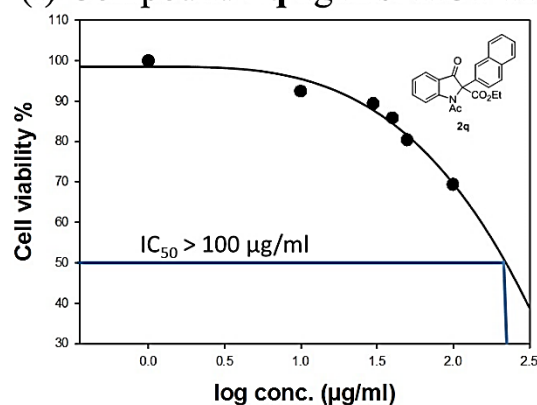
(d) Compound **2i** against HCT-116



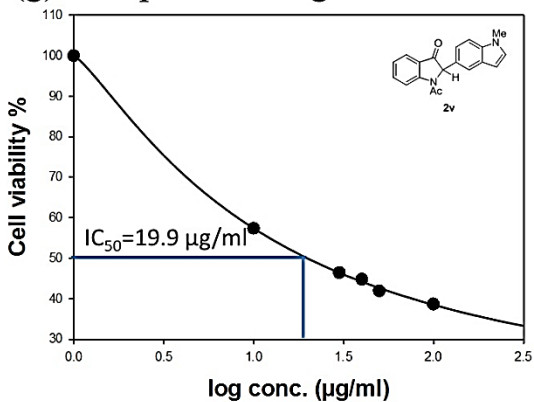
(e) Compound **2j** against HCT-116



(f) Compound **2q** against HCT-116



(g) Compound **2v** against HCT-116



(h) Compound **2w** against HCT-116

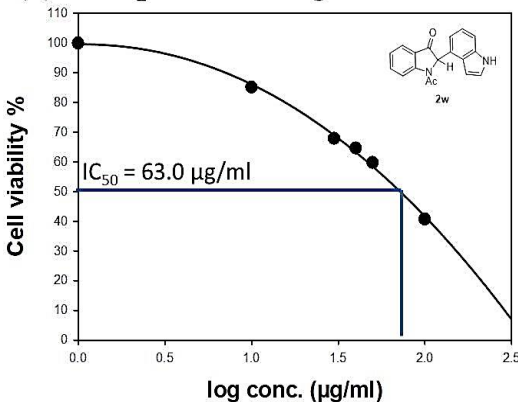


Figure S1. Cytotoxicity Results.



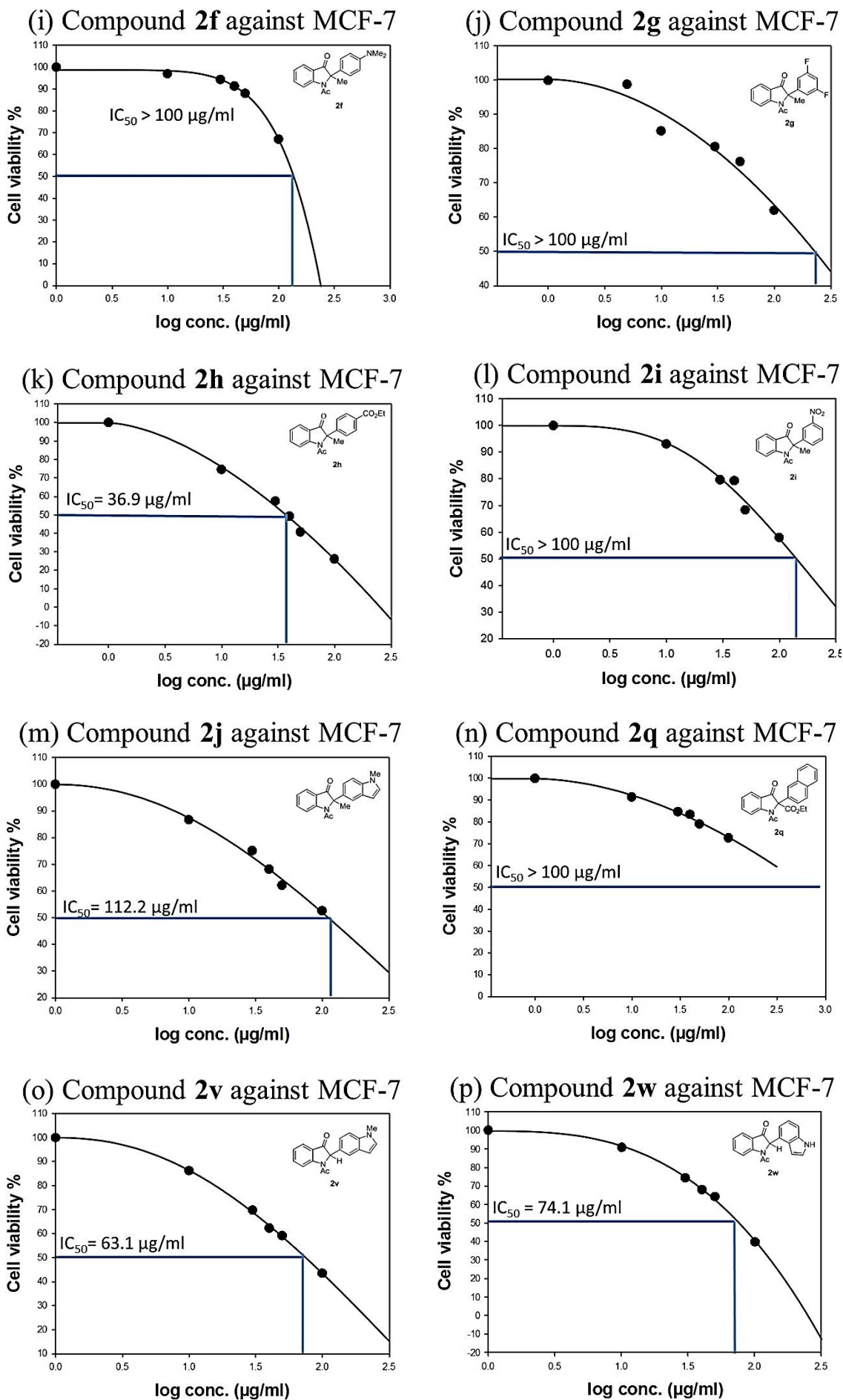
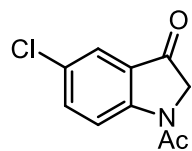


Figure S1. Cytotoxicity Results. (continued)

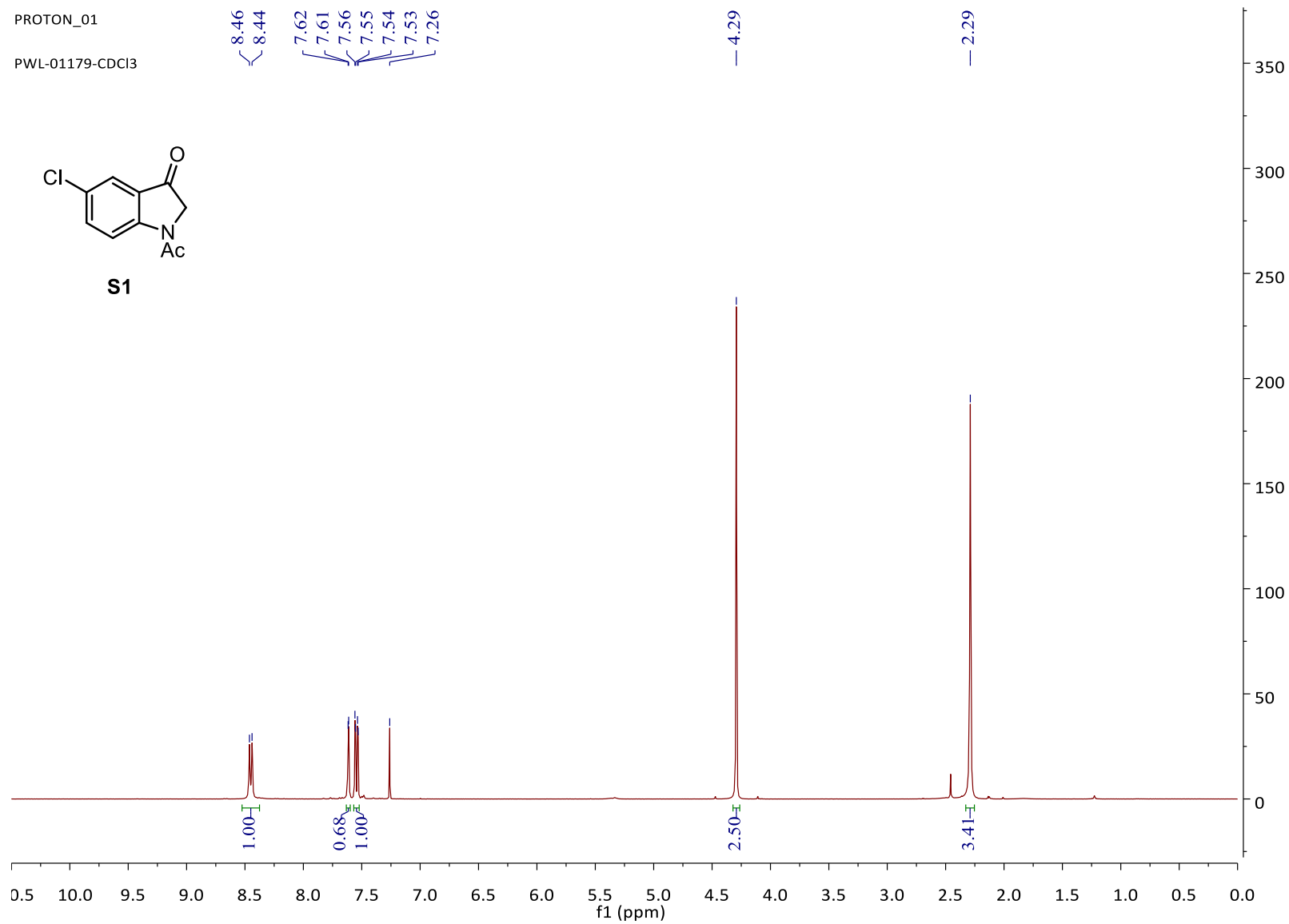
## **$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra**

PROTON\_01

PWL-01179-CDCl3



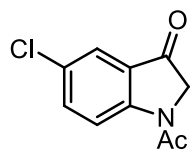
**S1**



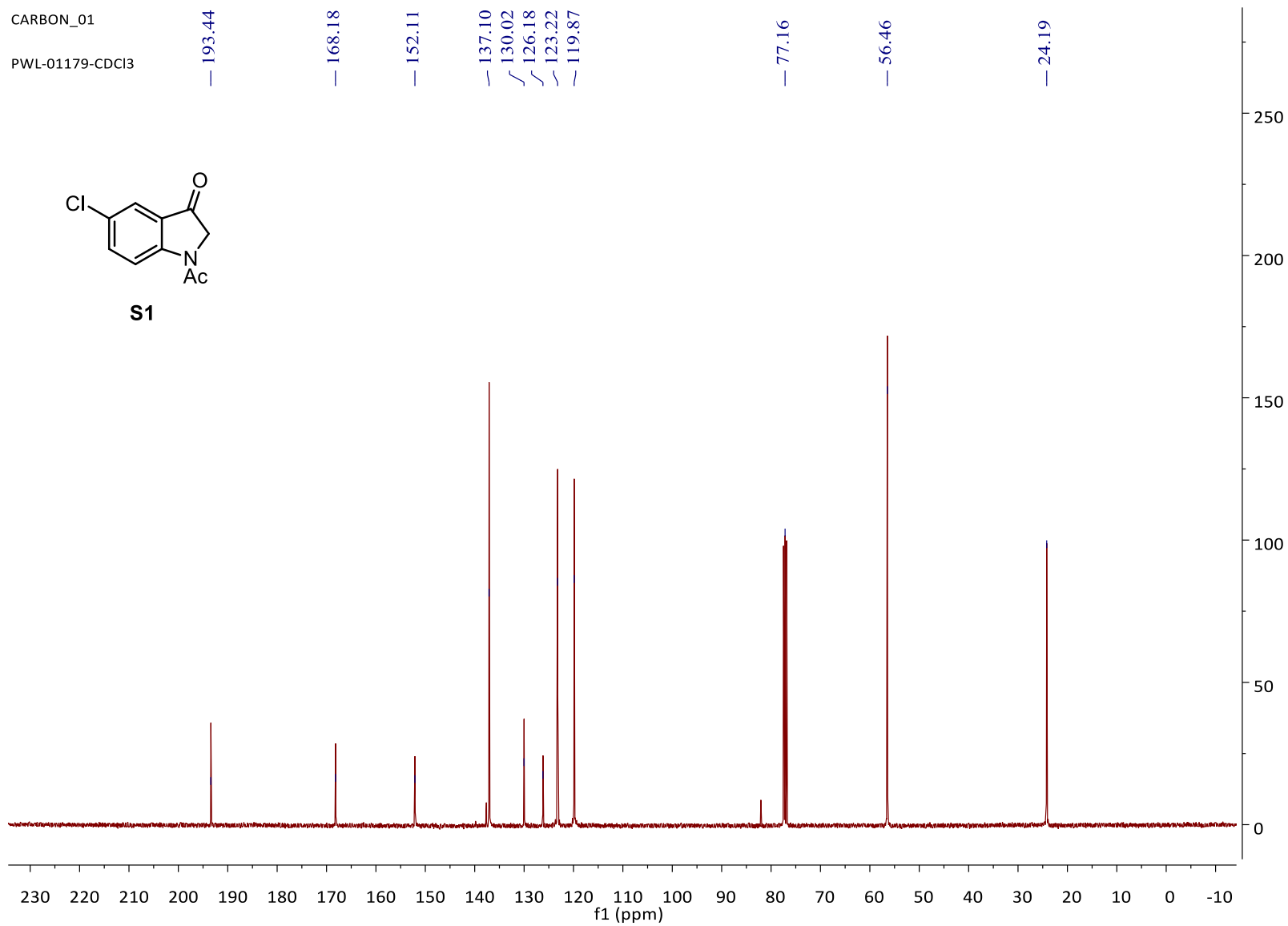
**<sup>1</sup>H NMR spectrum of compound S1**

CARBON\_01  
PWL-01179-CDCl3

— 193.44 — 168.18 — 152.11 — 137.10 — 77.16 — 56.46 — 24.19  
/ 130.02 / 126.18 / 123.22 / 119.87

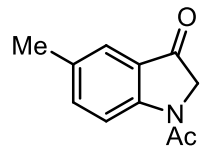


S1

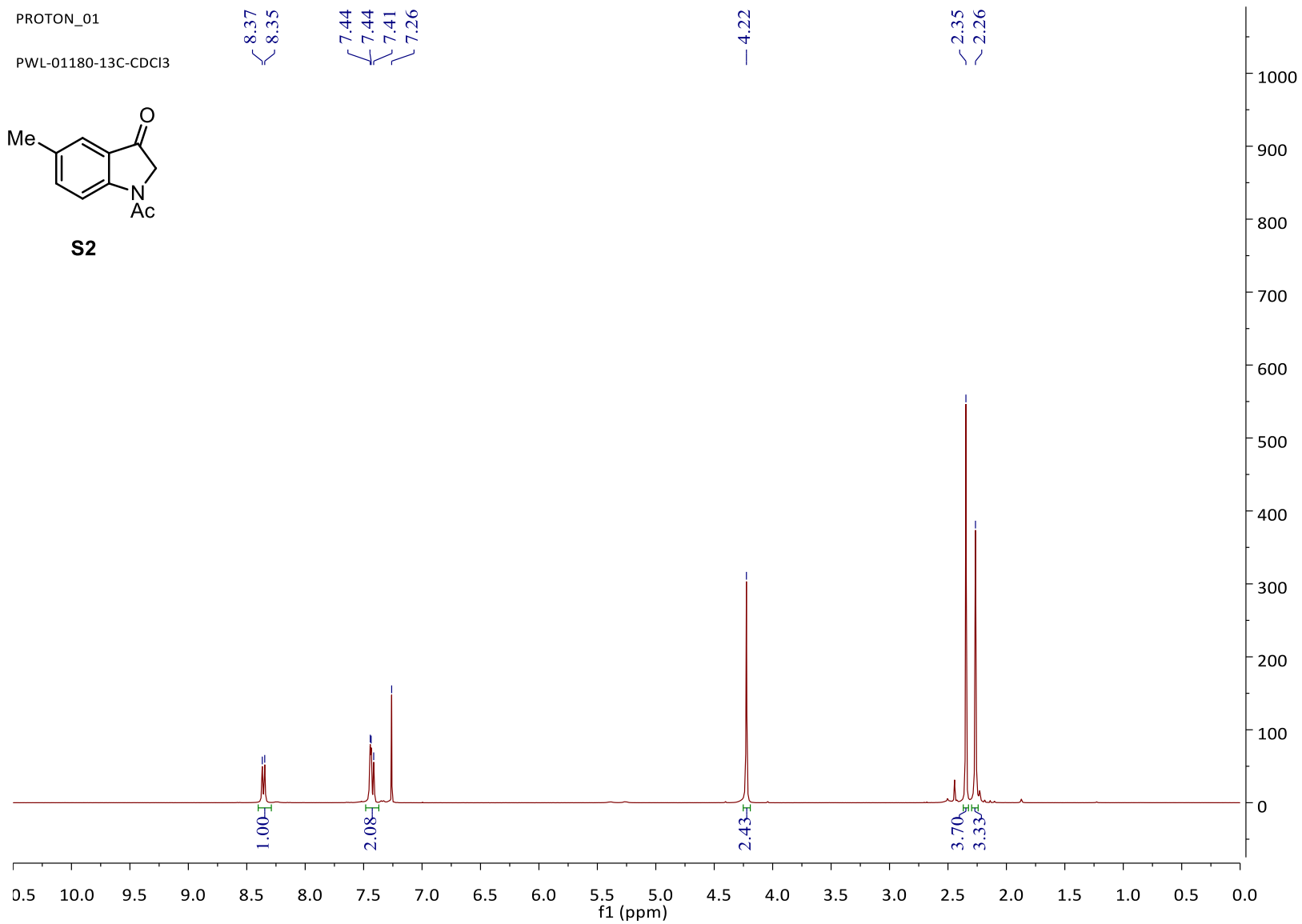


<sup>13</sup>C NMR spectrum of compound S1

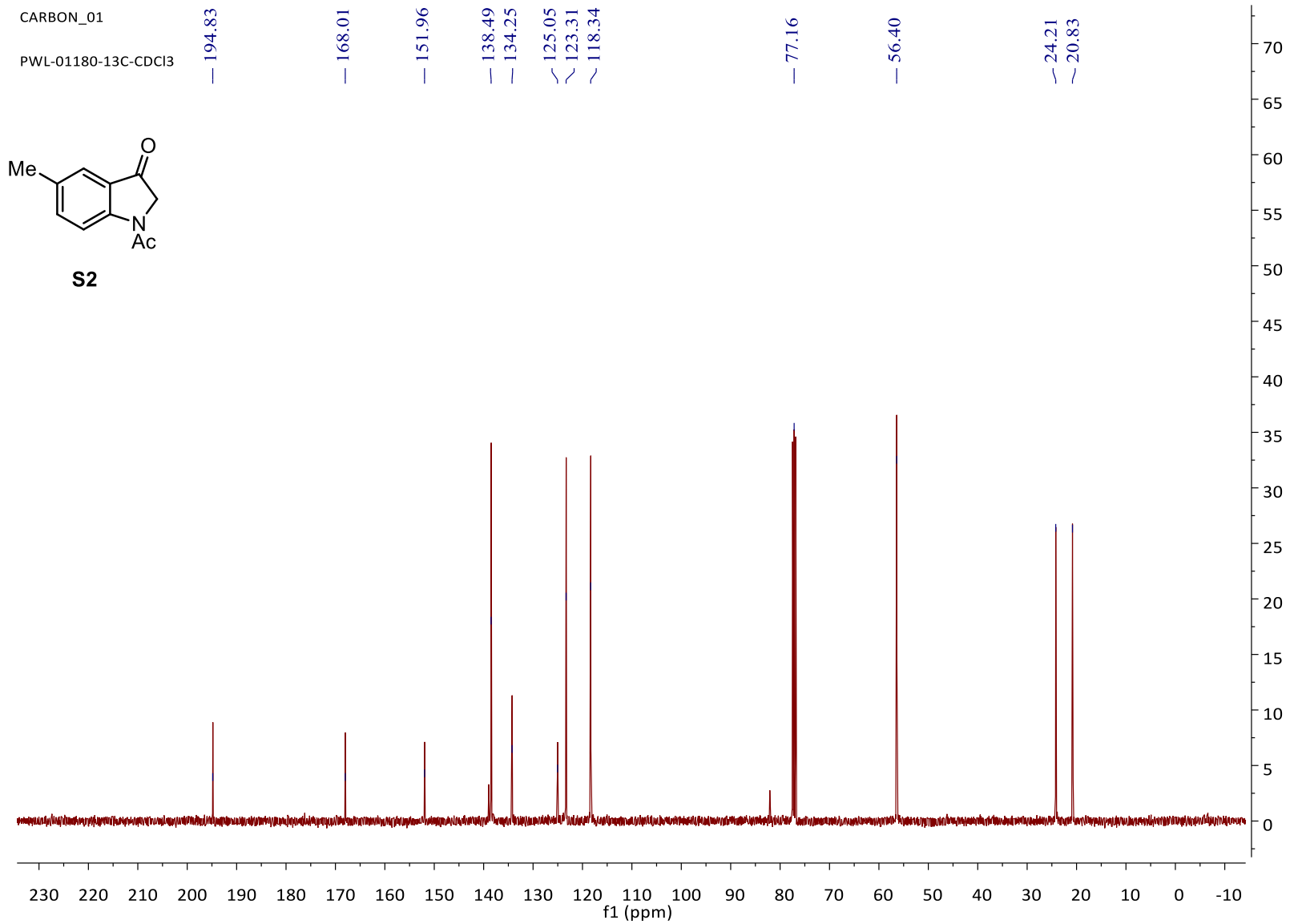
PROTON\_01  
PWL-01180-13C-CDCl3



**S2**



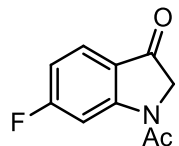
**<sup>1</sup>H NMR spectrum of compound S2**



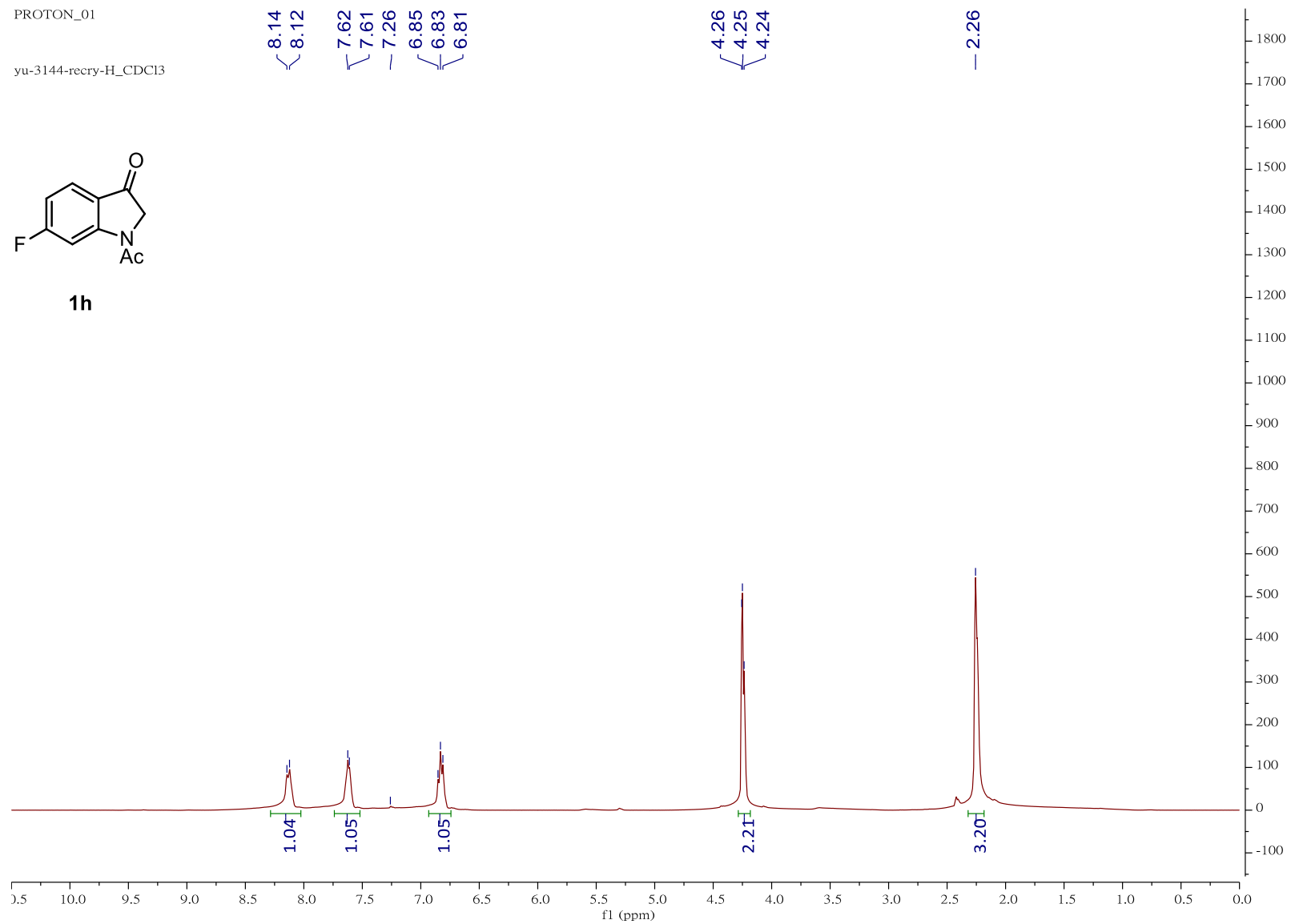
<sup>13</sup>C NMR spectrum of compound S2

PROTON\_01

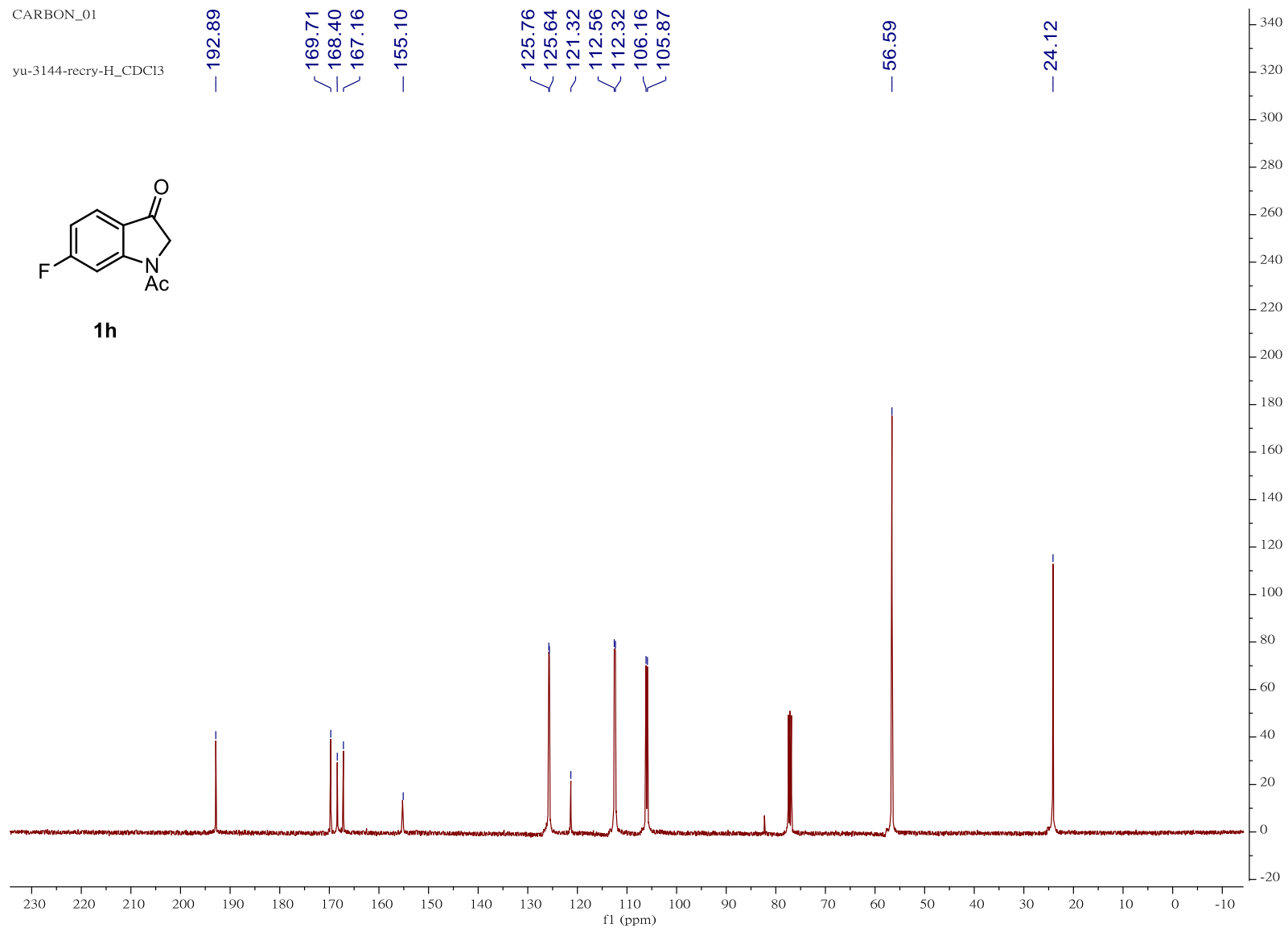
yu-3144-recry-H\_CDCI3



**1h**



**<sup>1</sup>H NMR spectrum of compound 1h**

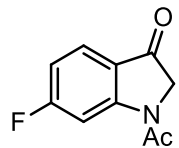


**$^{13}\text{C}$  NMR spectrum of compound 1h**

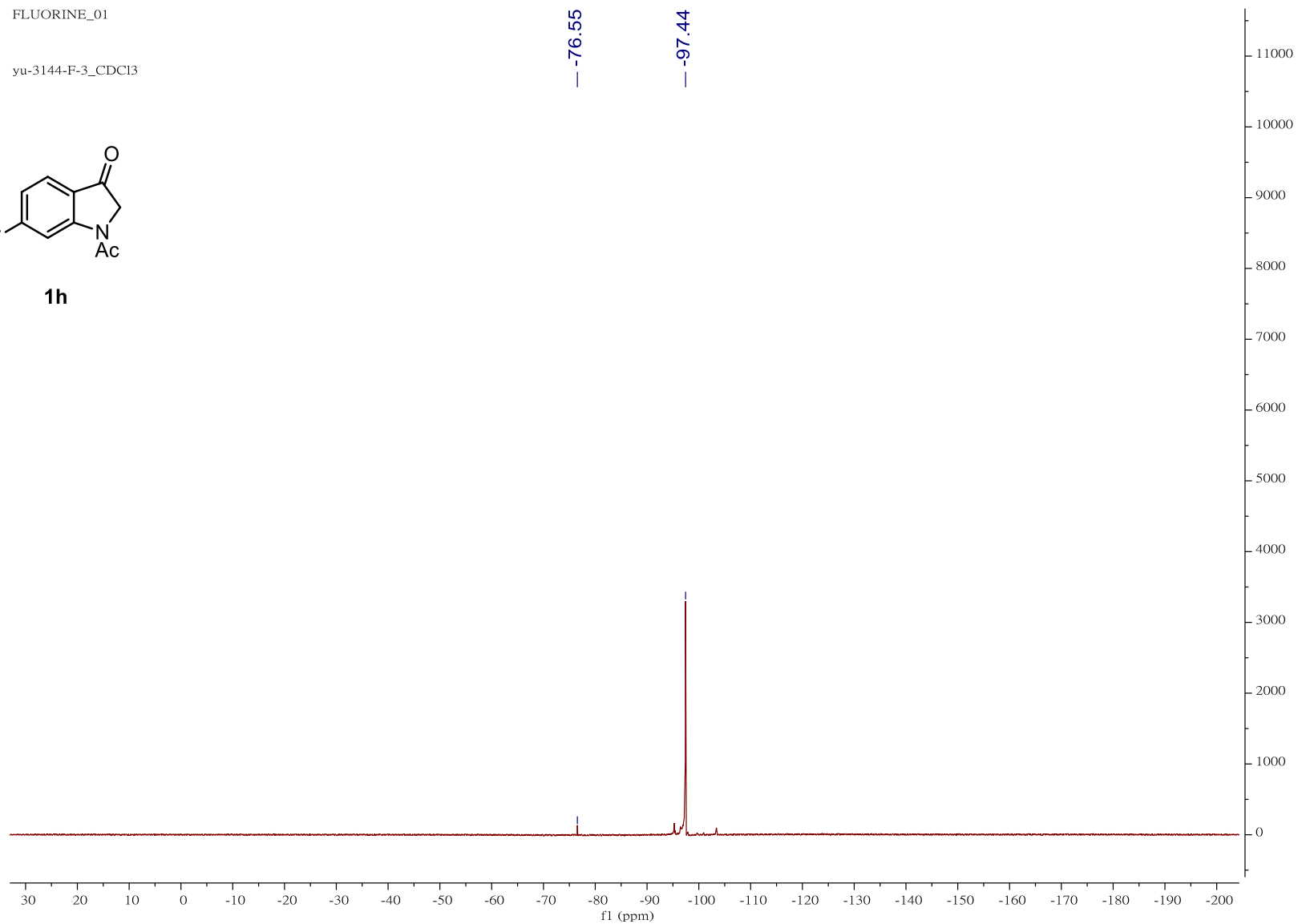


FLUORINE\_01

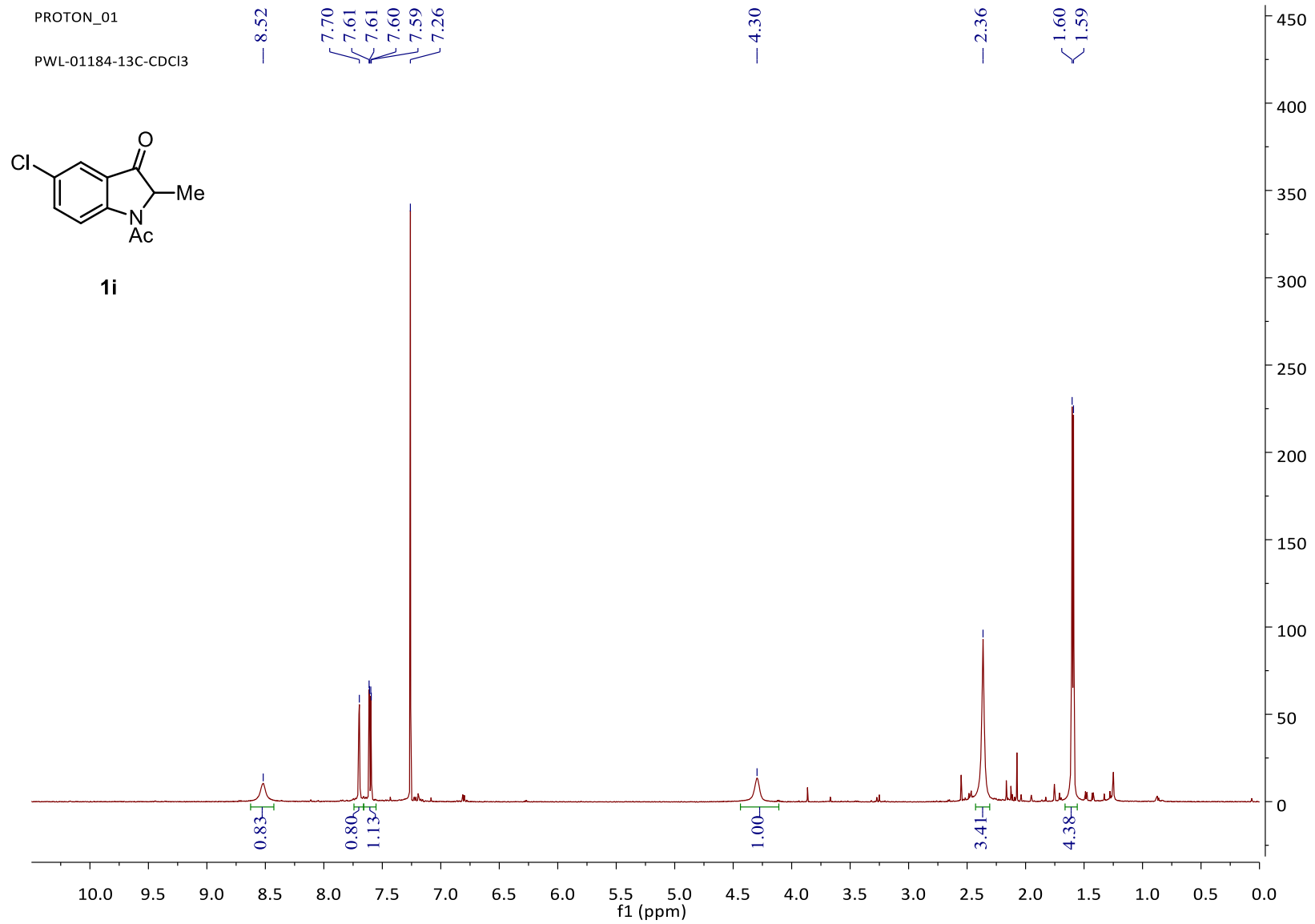
yu-3144-F-3\_CDCl3



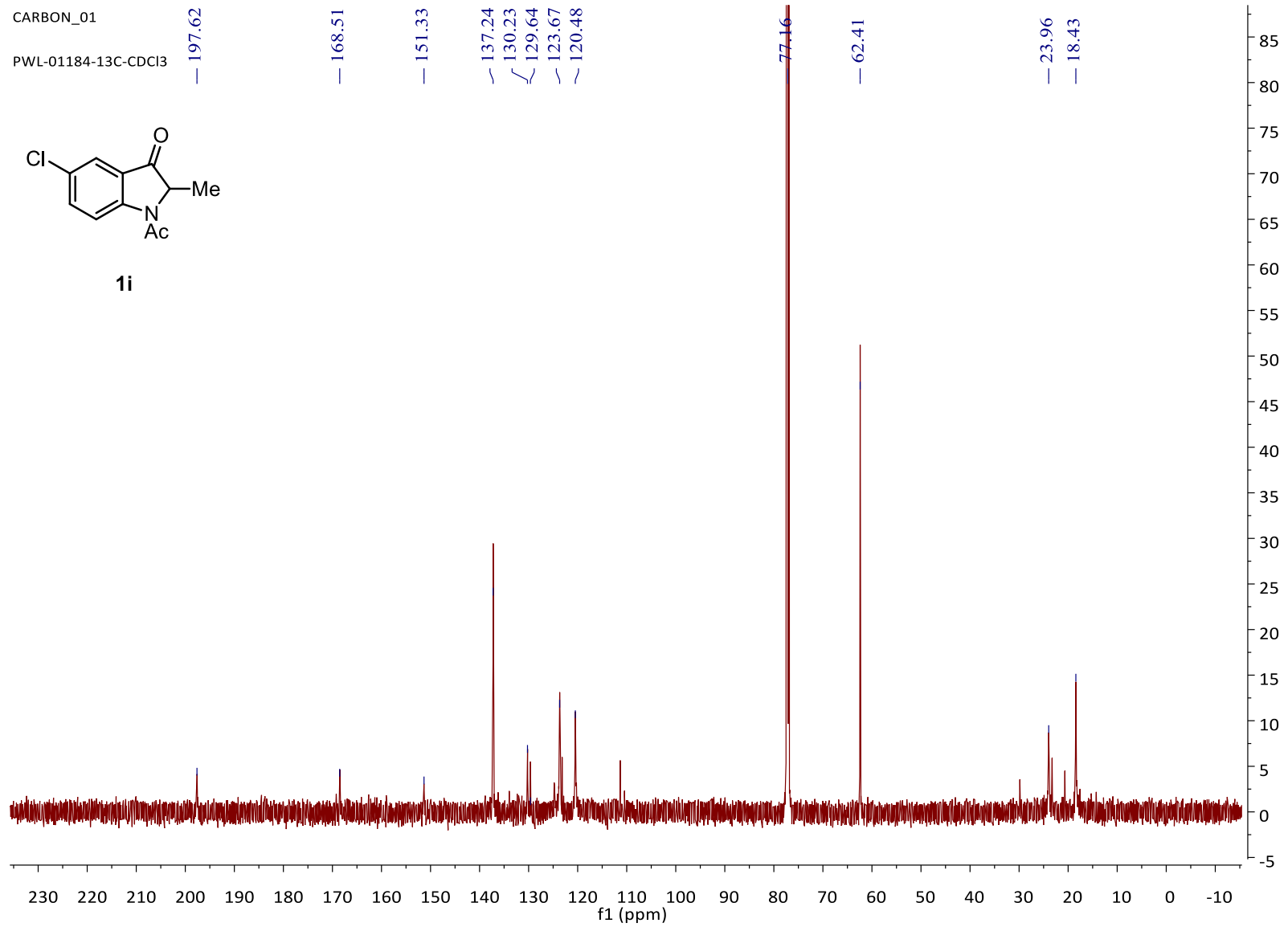
**1h**



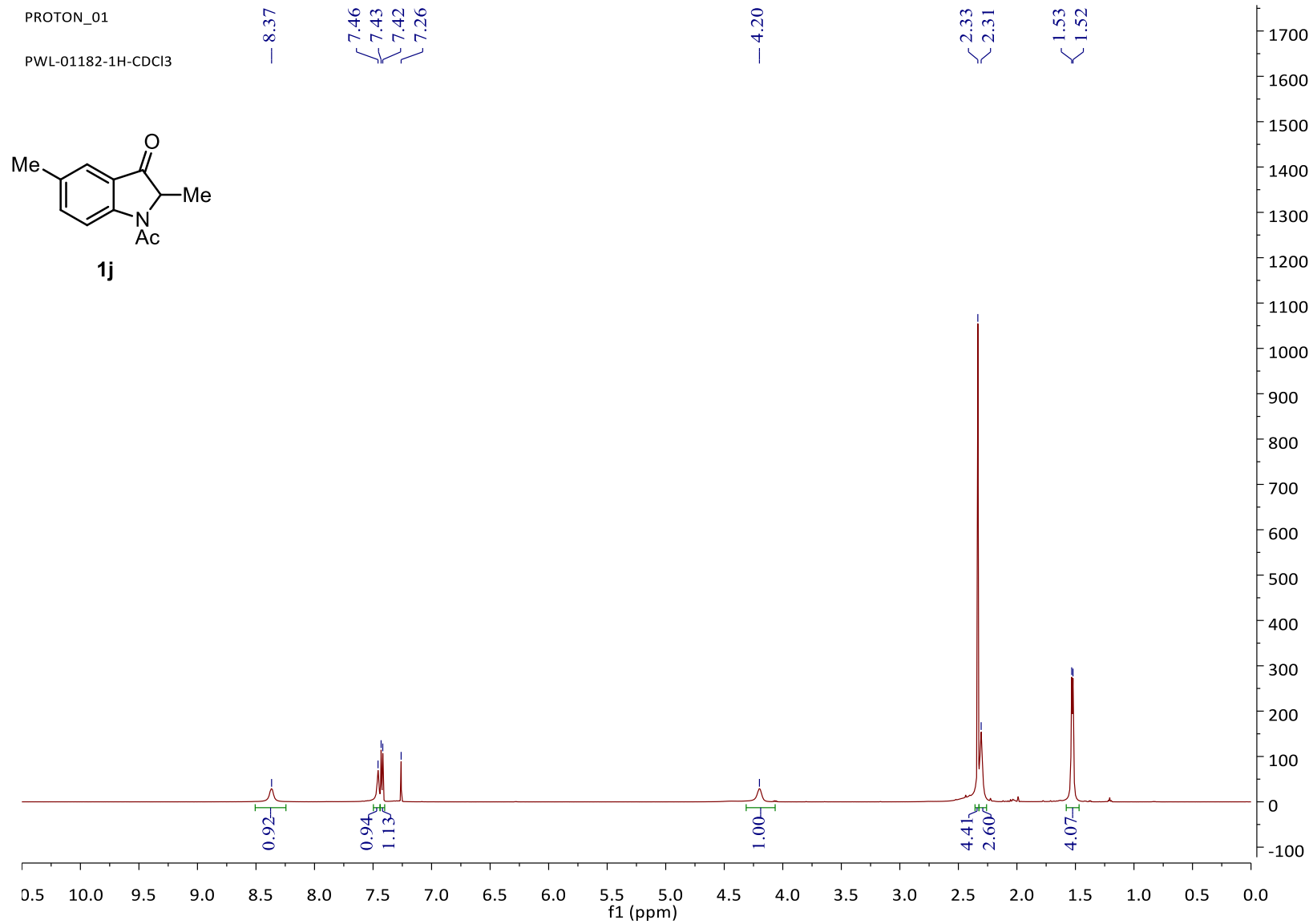
$^{19}\text{F}$  NMR spectrum of compound 1h



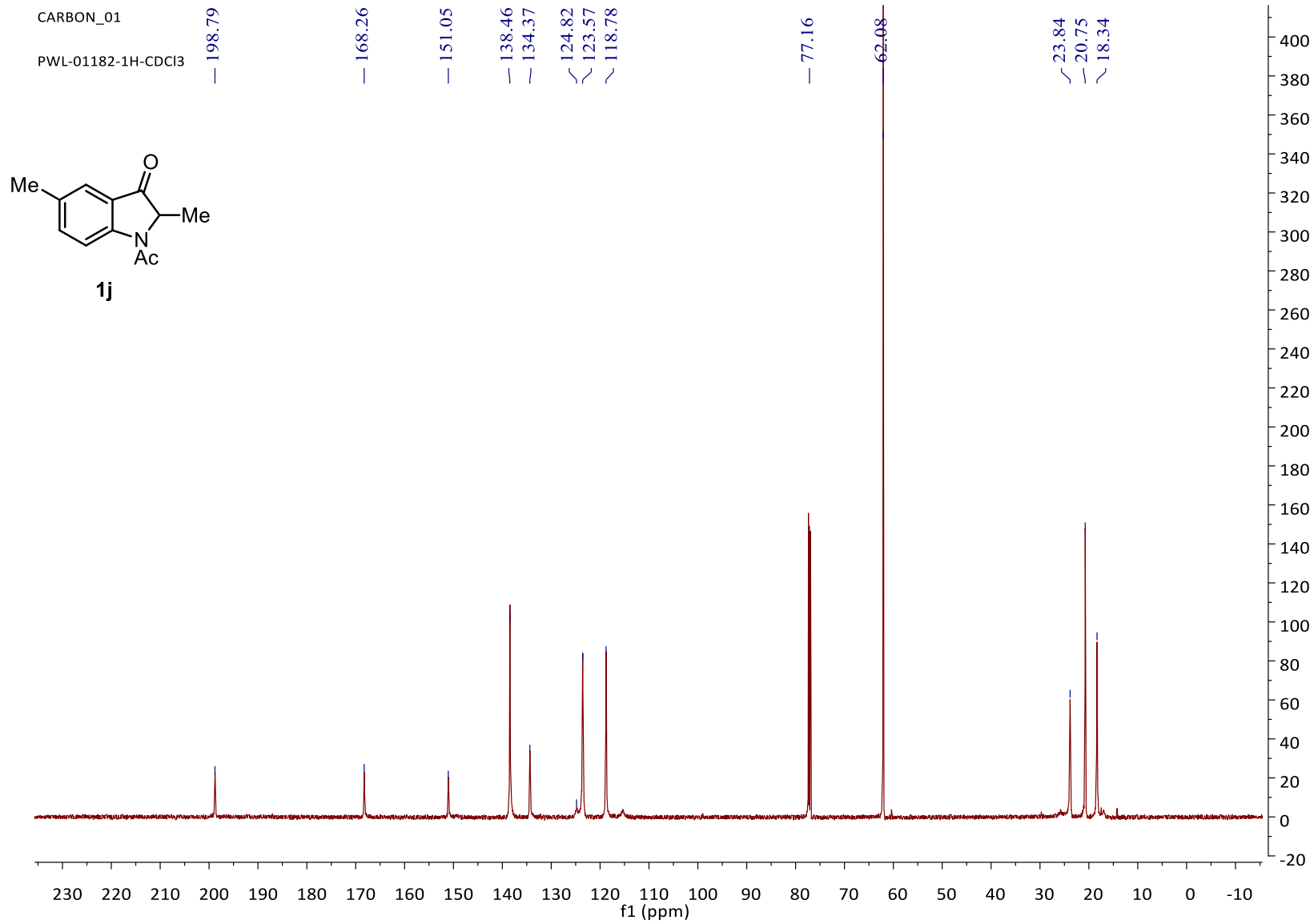
**<sup>1</sup>H NMR spectrum of compound 1i**



<sup>13</sup>C NMR spectrum of compound **1i**

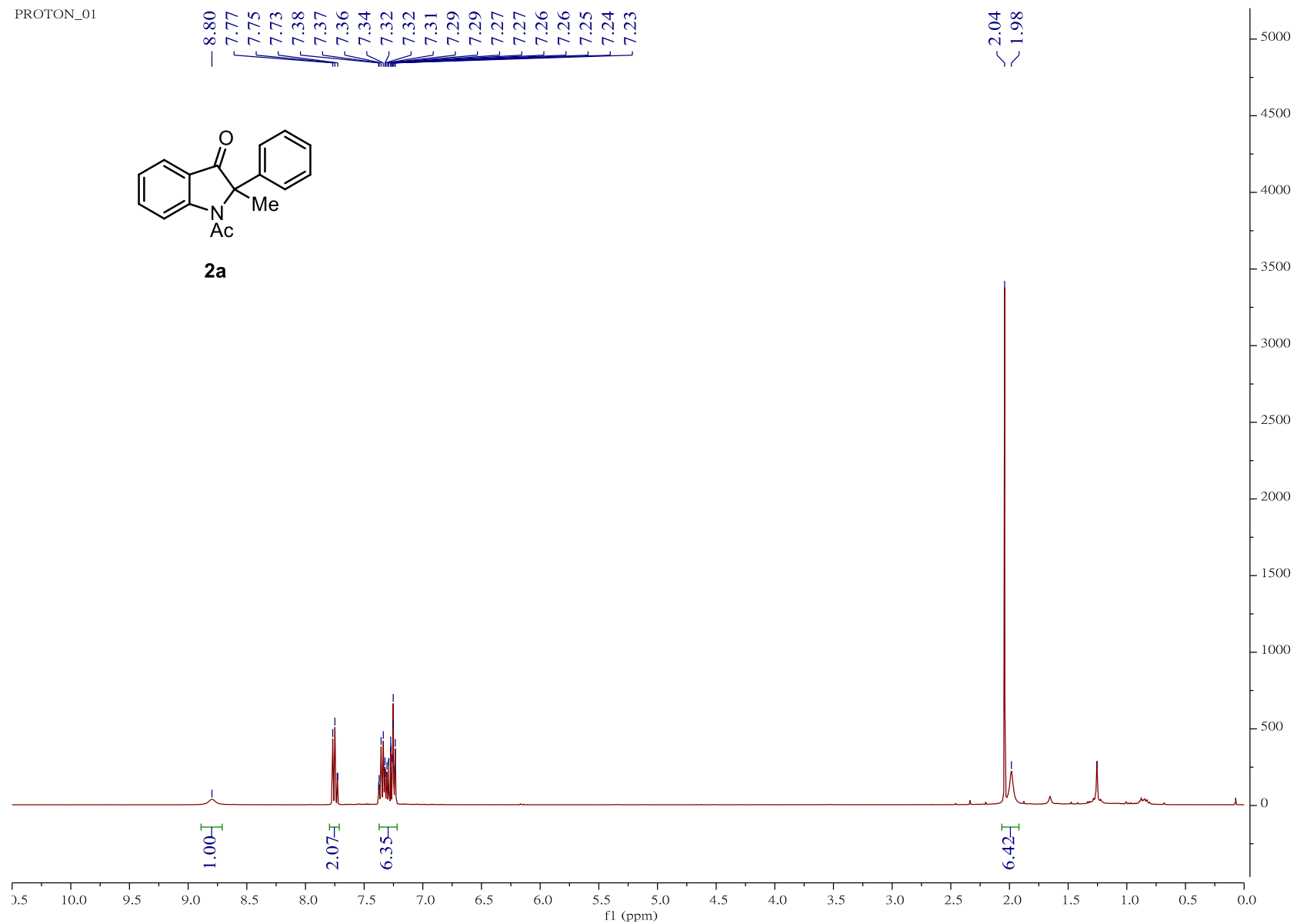


**<sup>1</sup>H NMR spectrum of compound 1j**

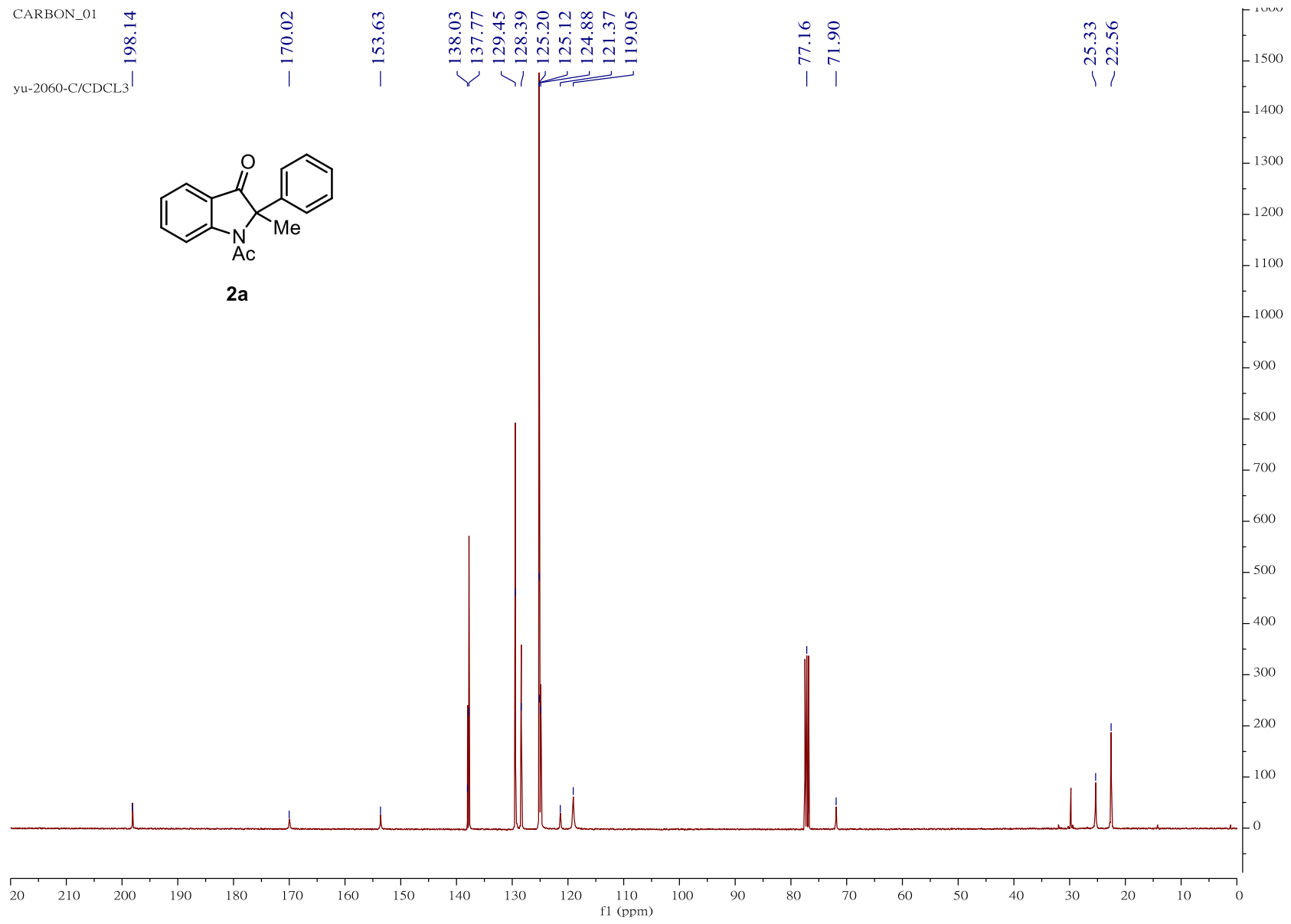


<sup>13</sup>C NMR spectrum of compound 1j

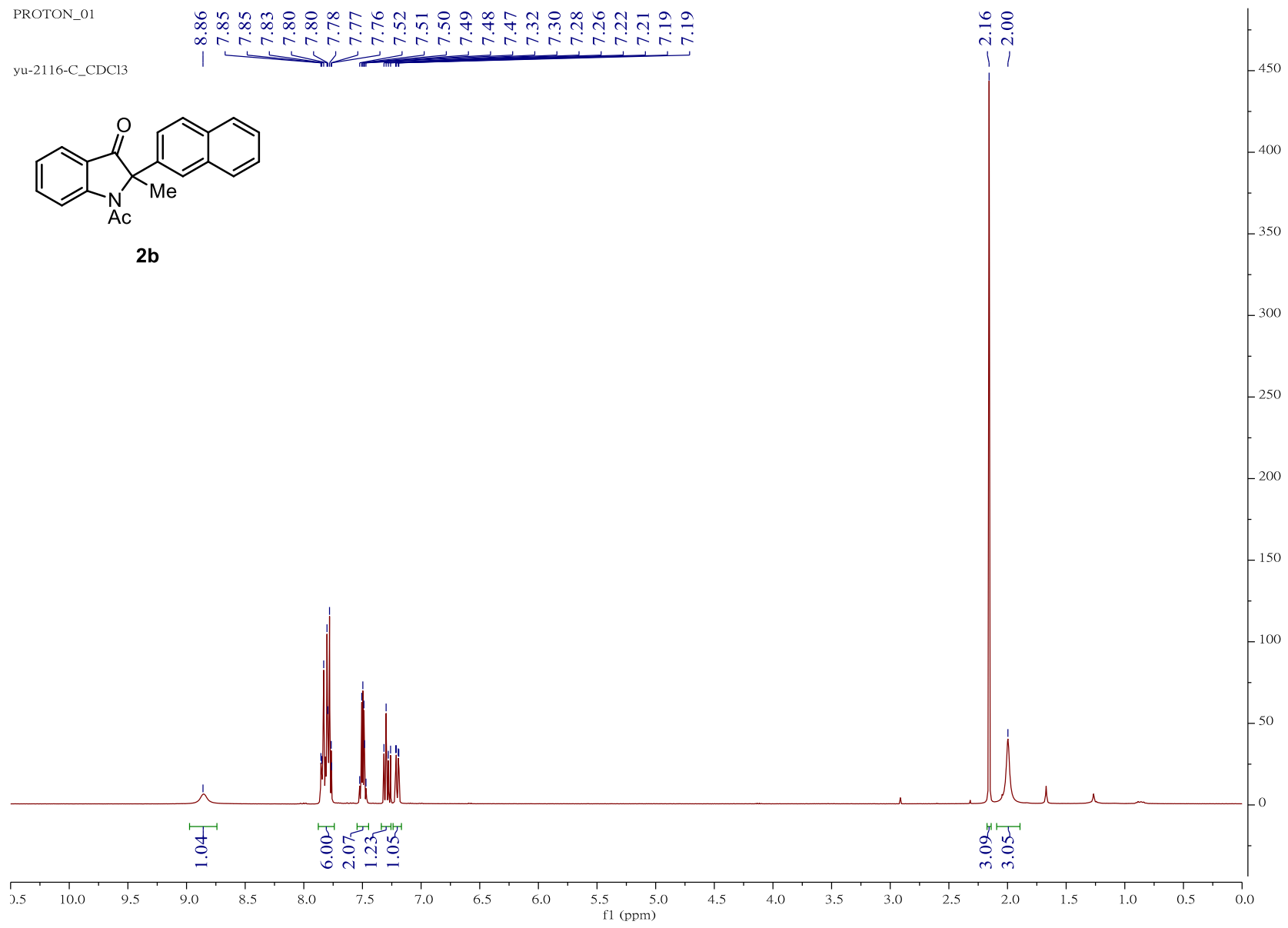
PROTON\_01



<sup>1</sup>H NMR spectrum of compound 2a



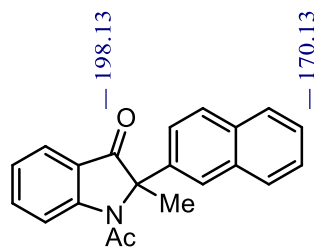
**<sup>13</sup>C NMR spectrum of compound 2a**  
S-39



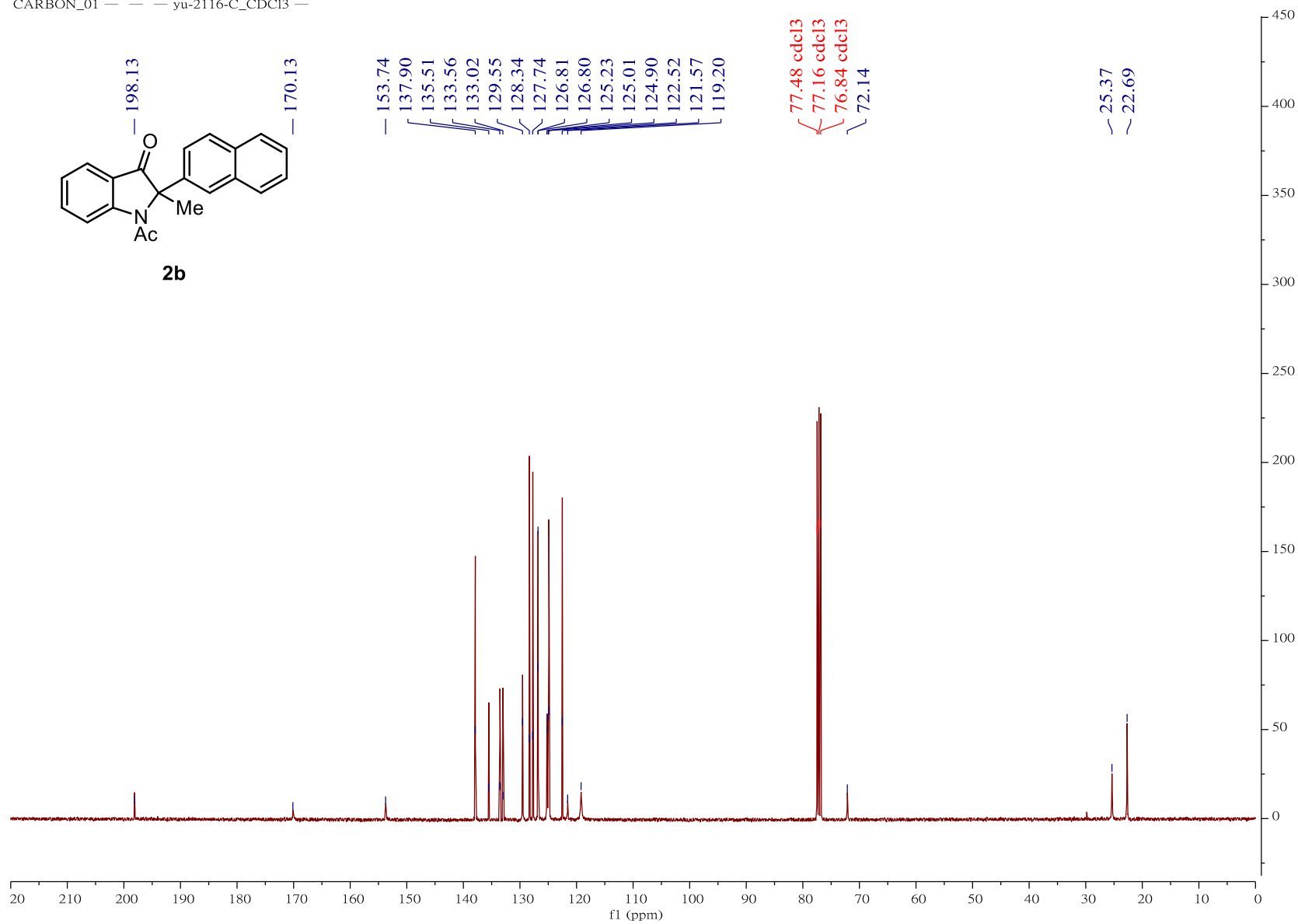
<sup>1</sup>H NMR spectrum of compound **2b**



CARBON\_01 -- -- yu-2116-C\_CDC13 --



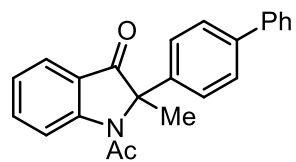
2b



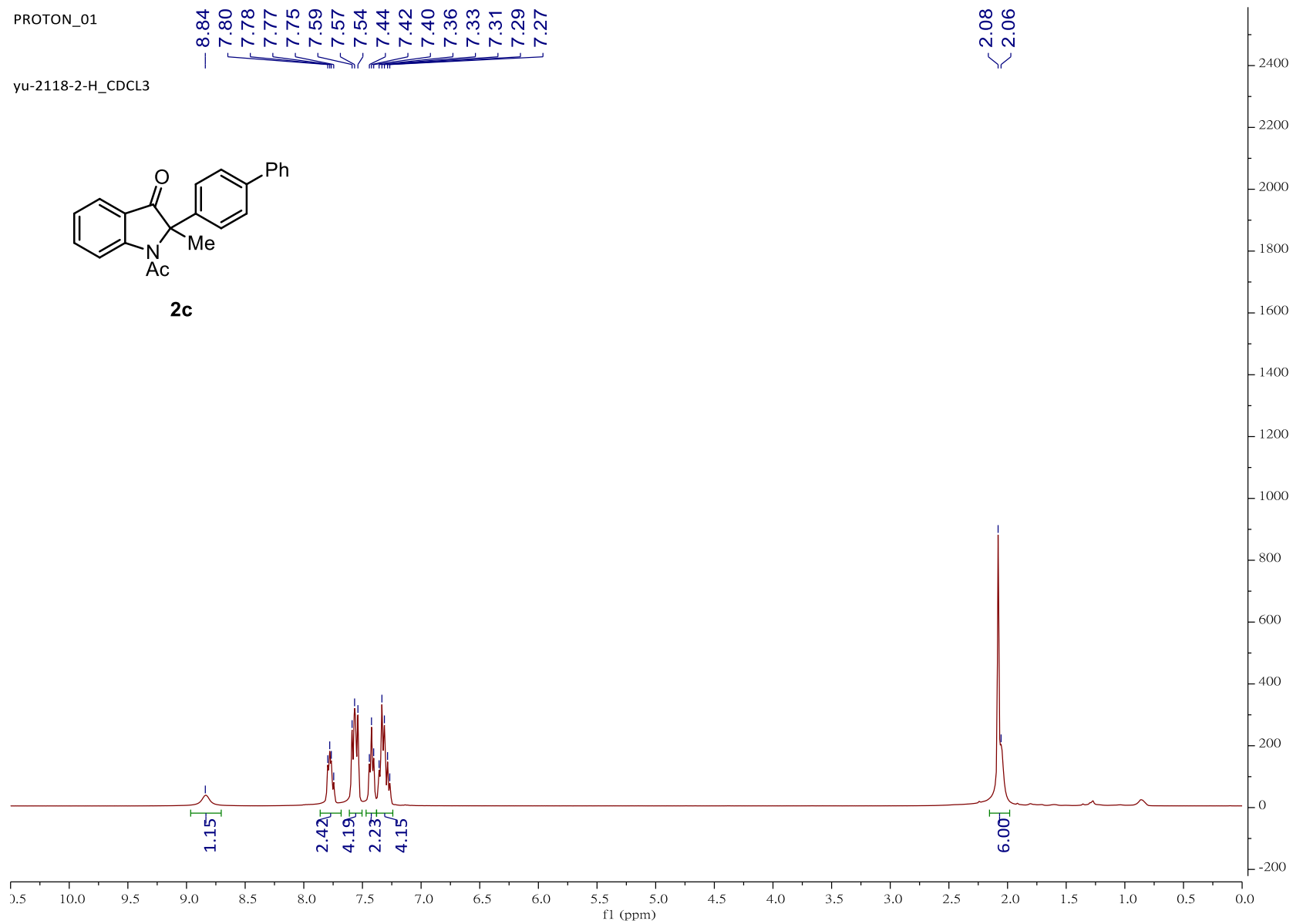
$^{13}\text{C}$  NMR spectrum of compound 2b

PROTON\_01

yu-2118-2-H\_CDCl3

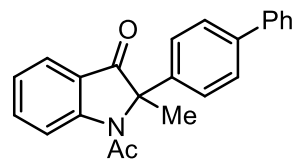


2c

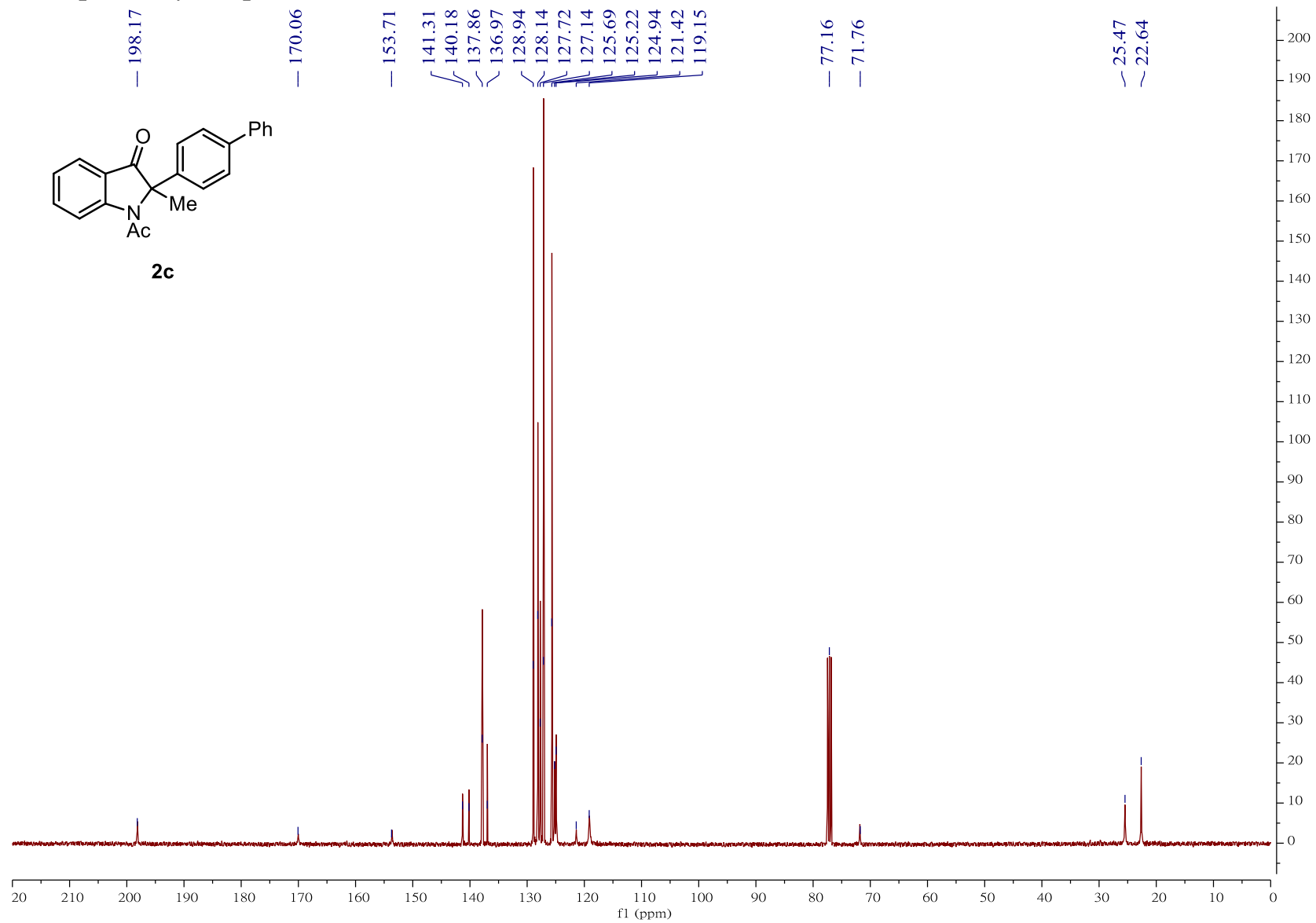


<sup>1</sup>H NMR spectrum of compound 2c

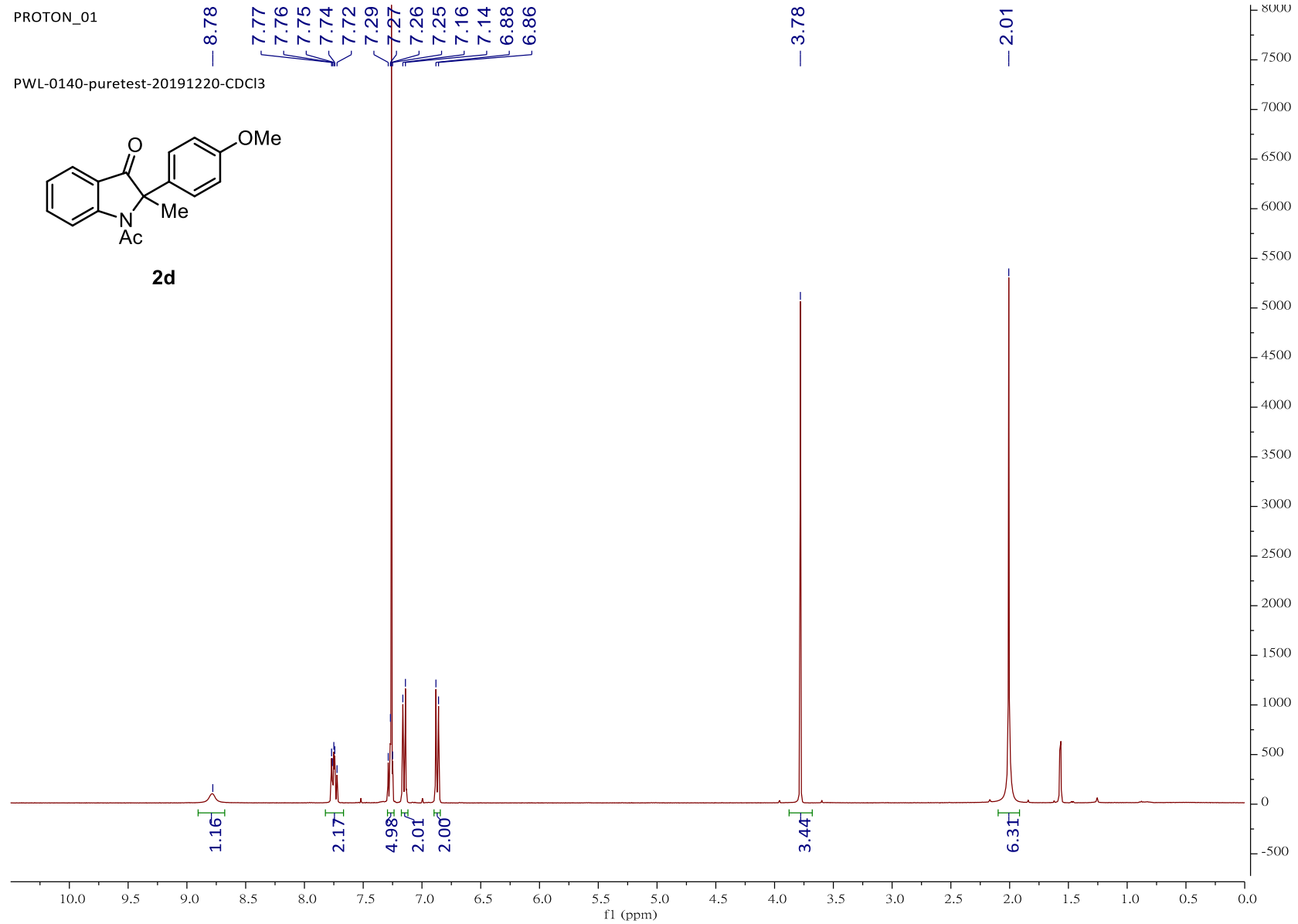
CARBON\_01 — — — yu-2118-C\_CDCL3 —



**2c**

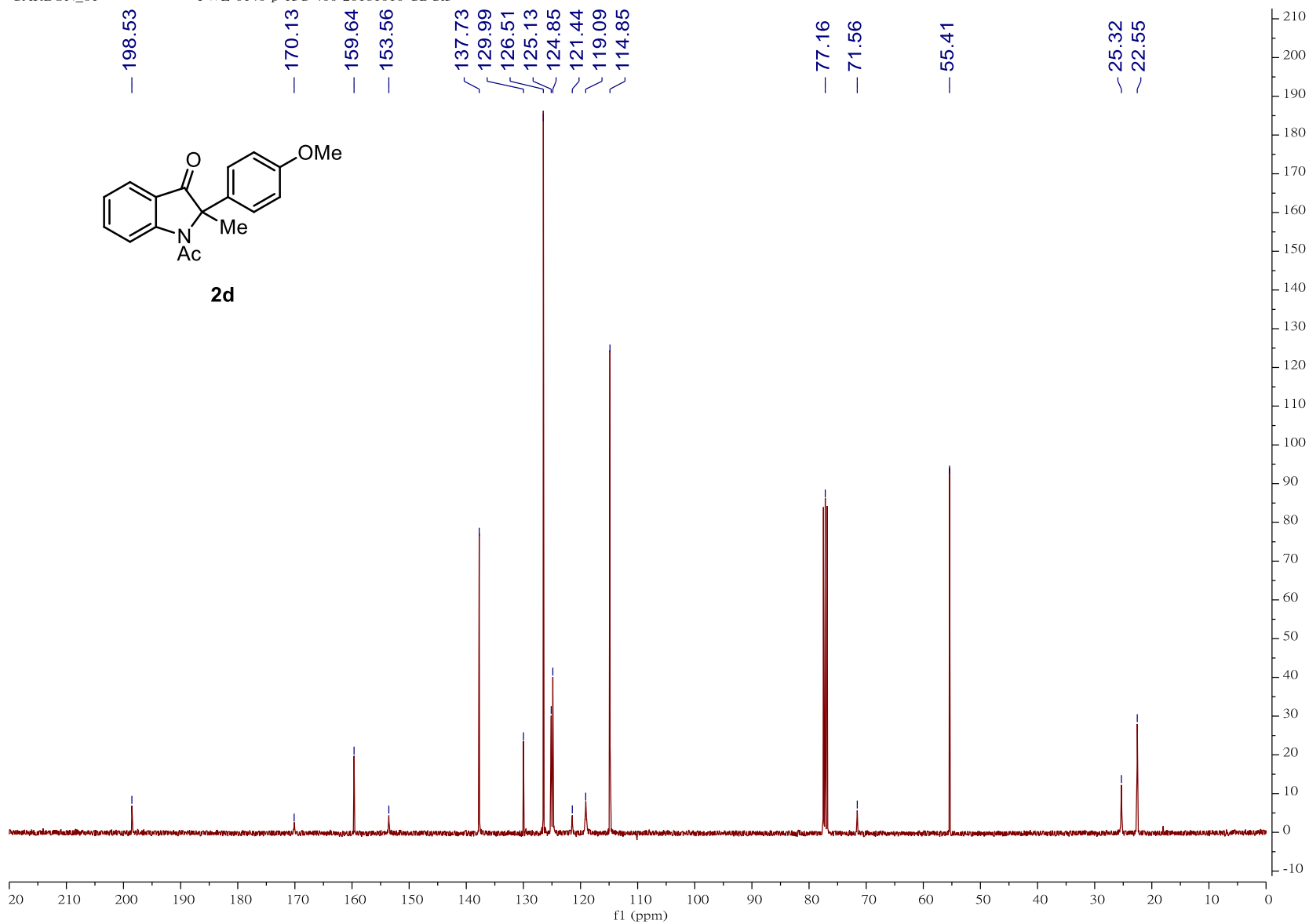


$^{13}\text{C}$  NMR spectrum of compound 2c

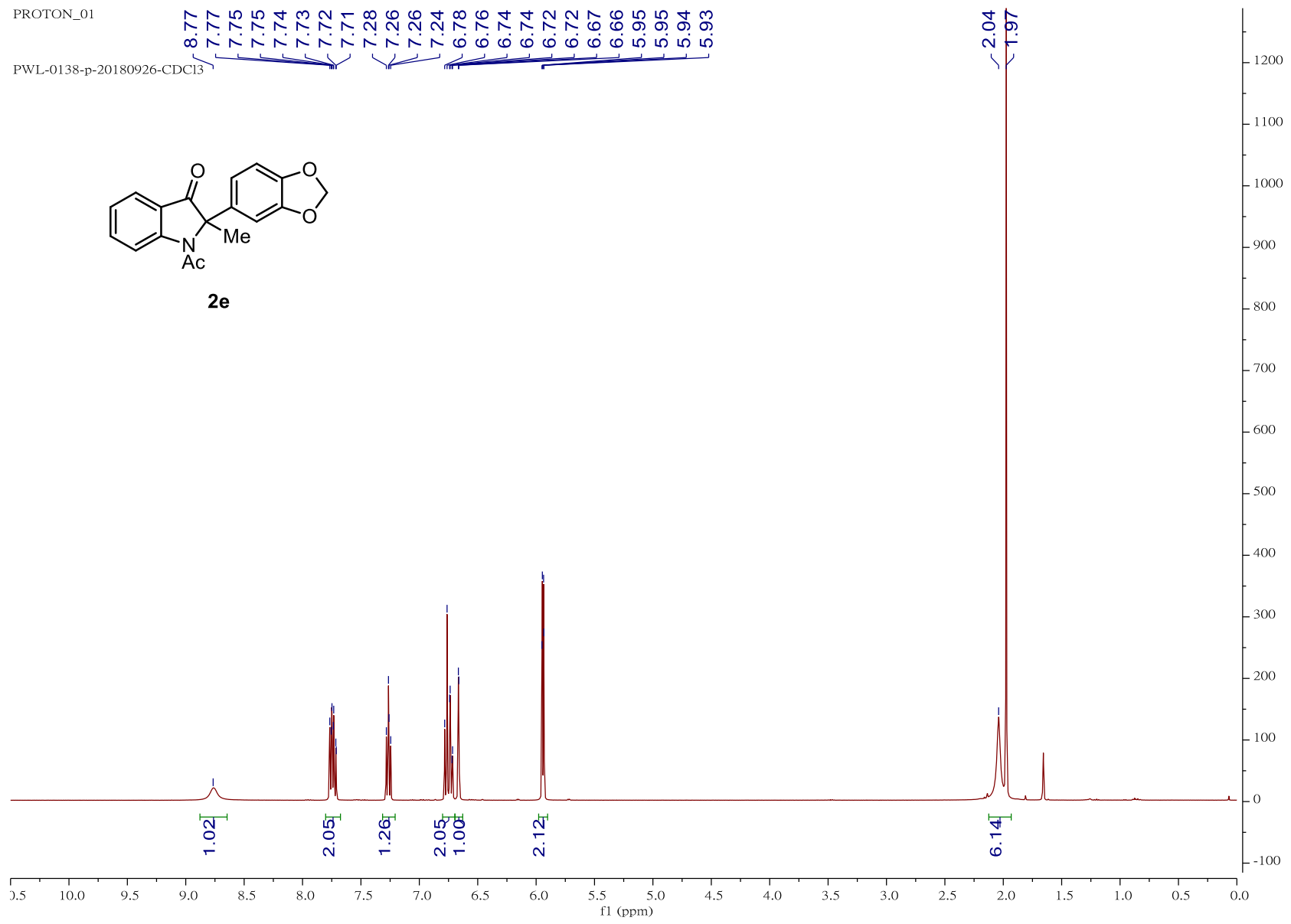


**<sup>1</sup>H NMR spectrum of compound 2d**

CARBON\_01 — — — PWL-0140-p-13C-400-20181010-CDCl3 —

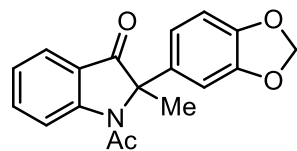


<sup>13</sup>C NMR spectrum of compound 2d

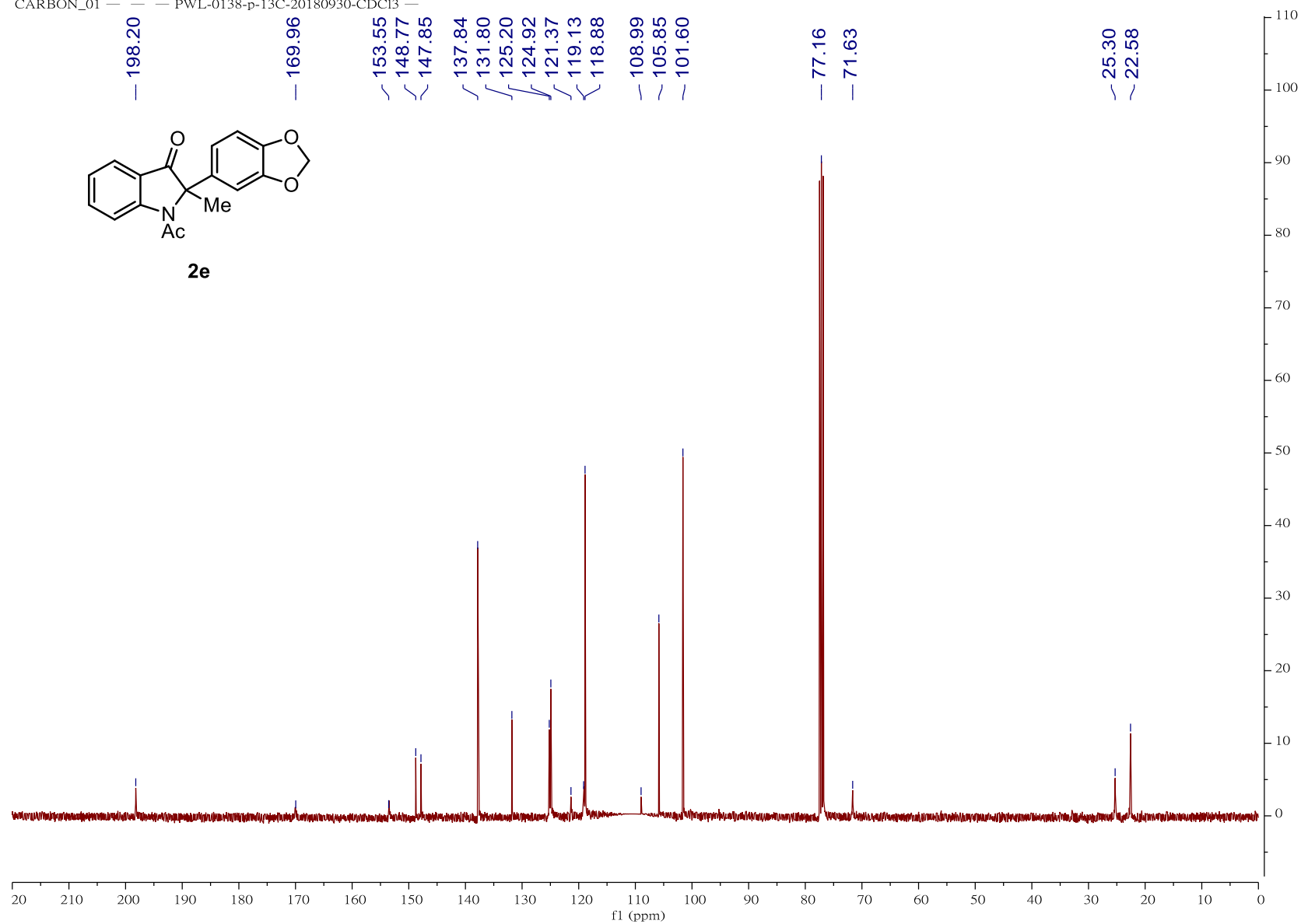


**<sup>1</sup>H NMR spectrum of compound 2e**  
S-46

CARBON\_01 — — PWL-0138-p-13C-20180930-CDCl3 —



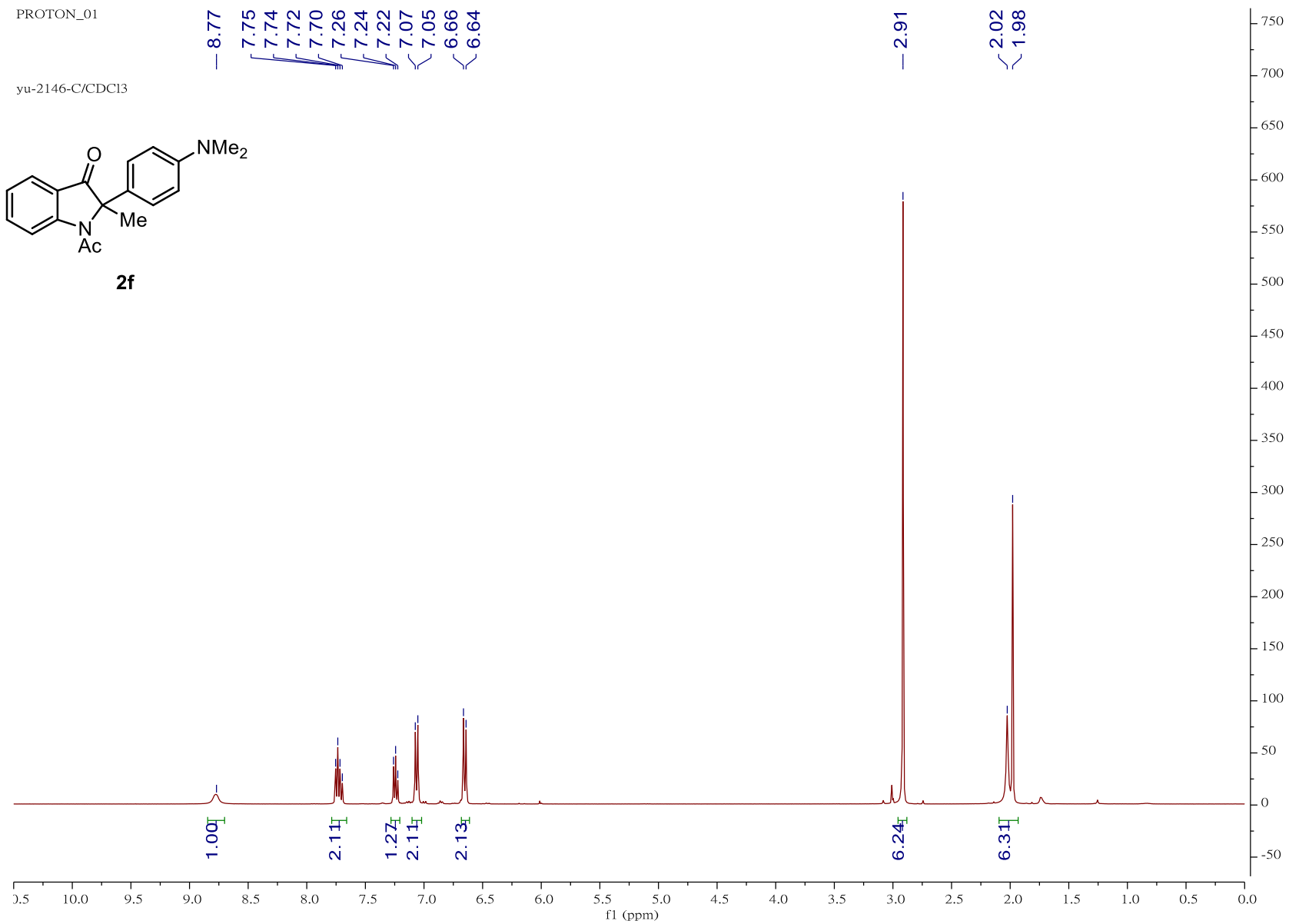
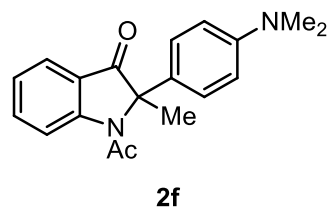
**2e**



$^{13}\text{C}$  NMR spectrum of compound 2e

PROTON\_01

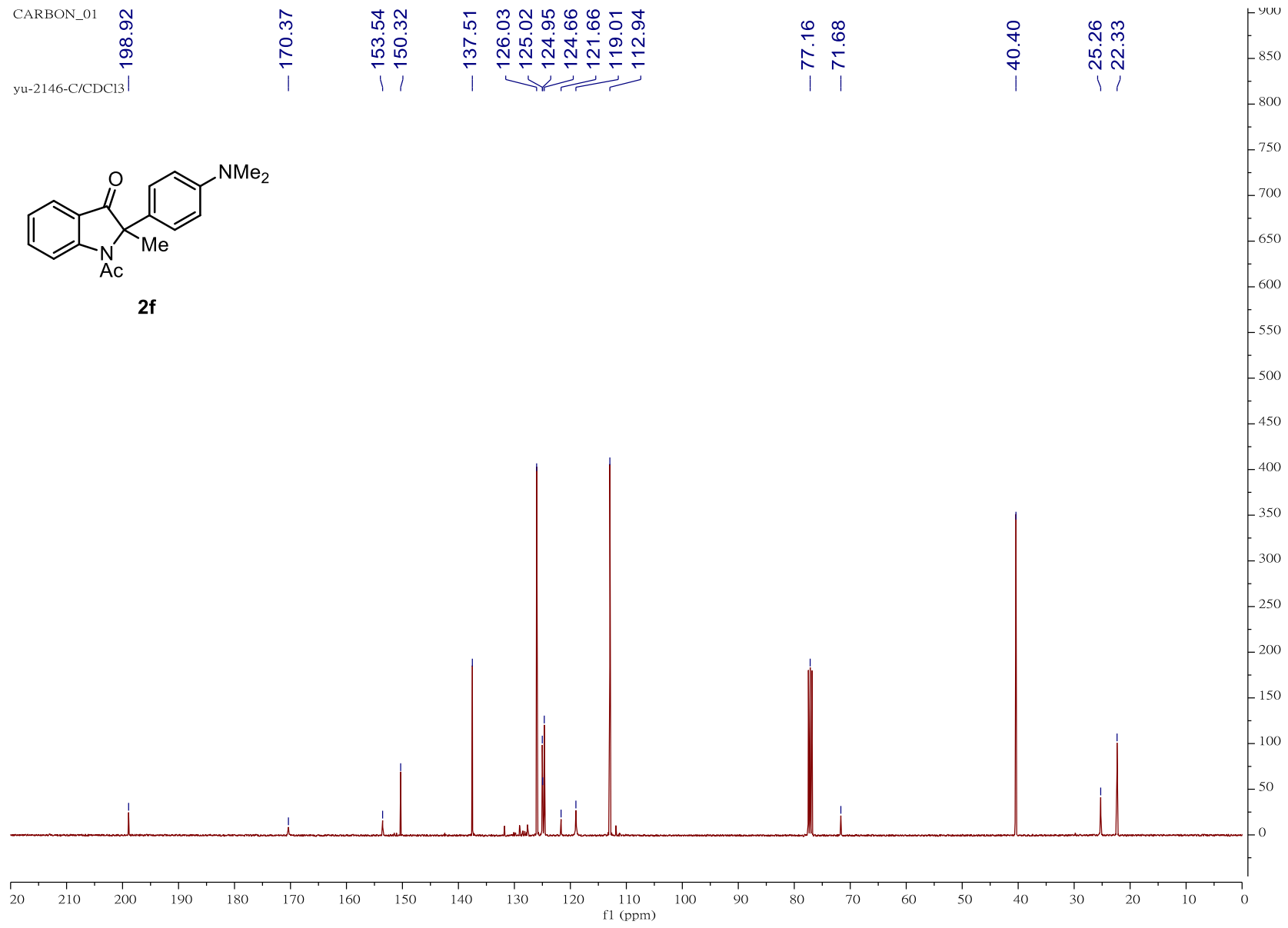
yu-2146-C/CDC13



**<sup>1</sup>H NMR spectrum of compound 2f**

S-48

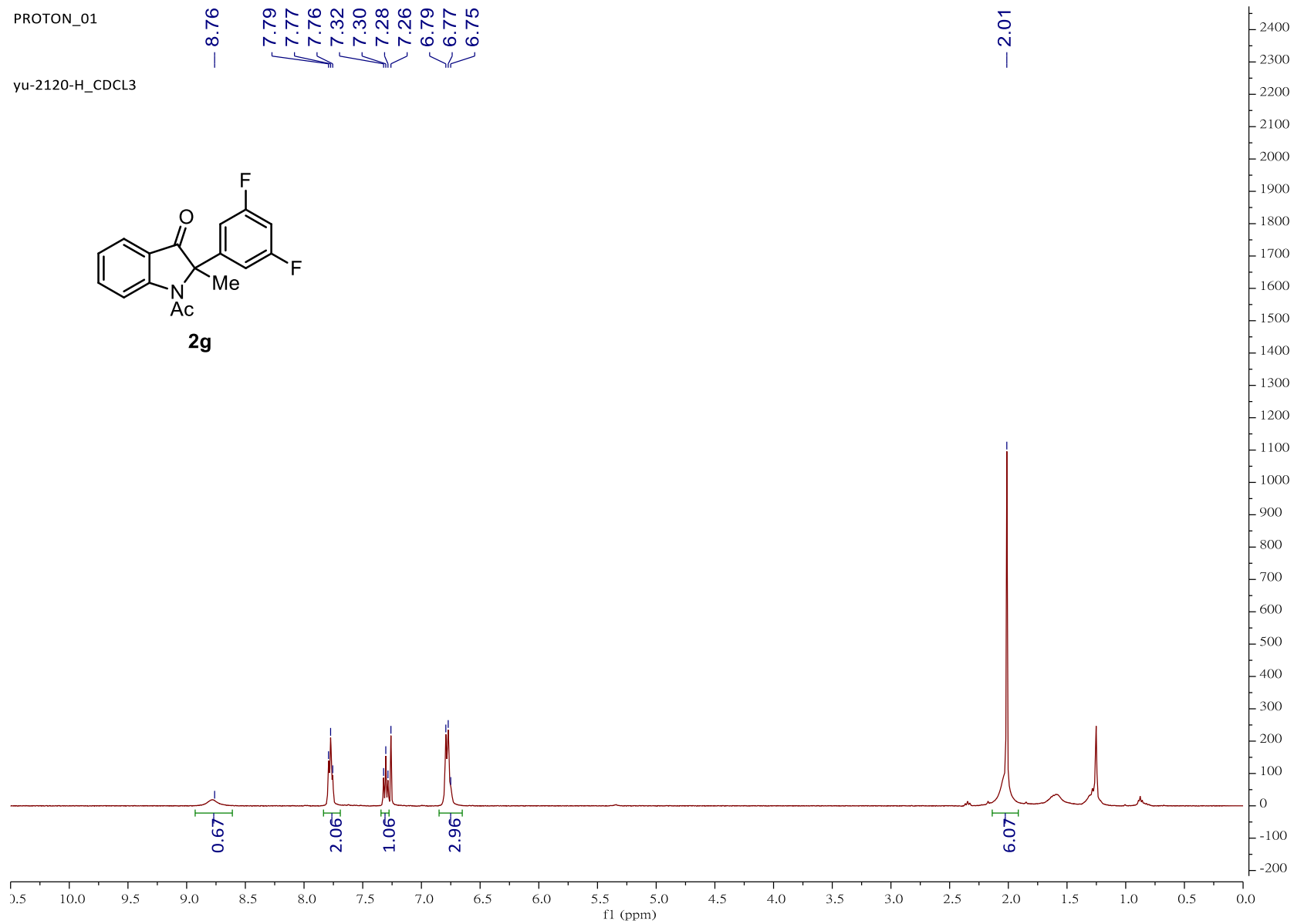
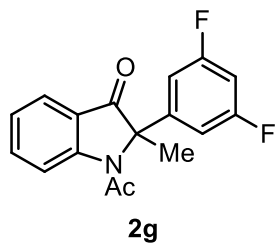




<sup>13</sup>C NMR spectrum of compound 2f

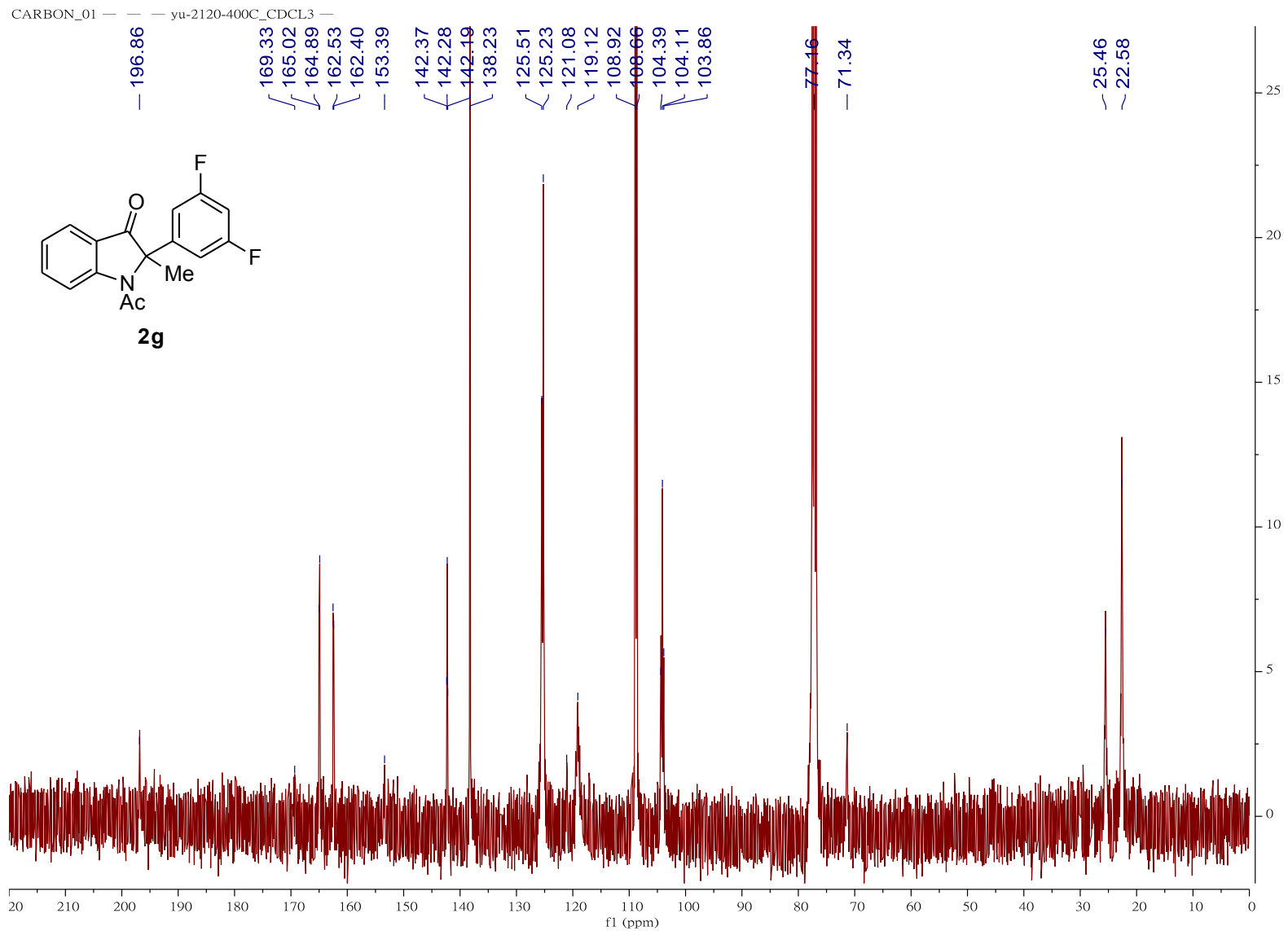
PROTON\_01

yu-2120-H\_CDCL3



**<sup>1</sup>H NMR spectrum of compound 2g**

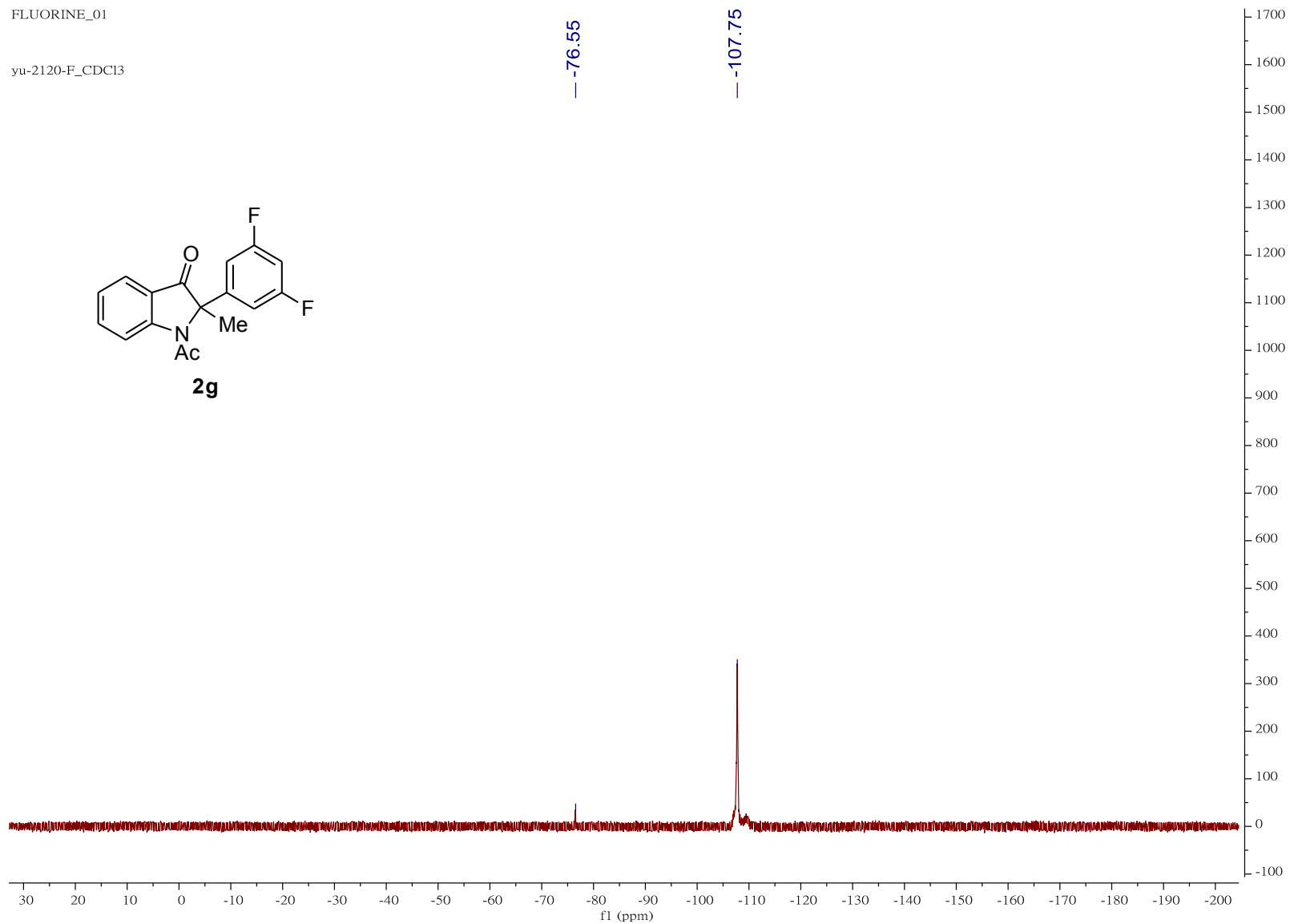
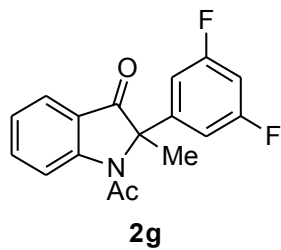
S-50



**<sup>13</sup>C NMR spectrum of compound 2g**

FLUORINE\_01

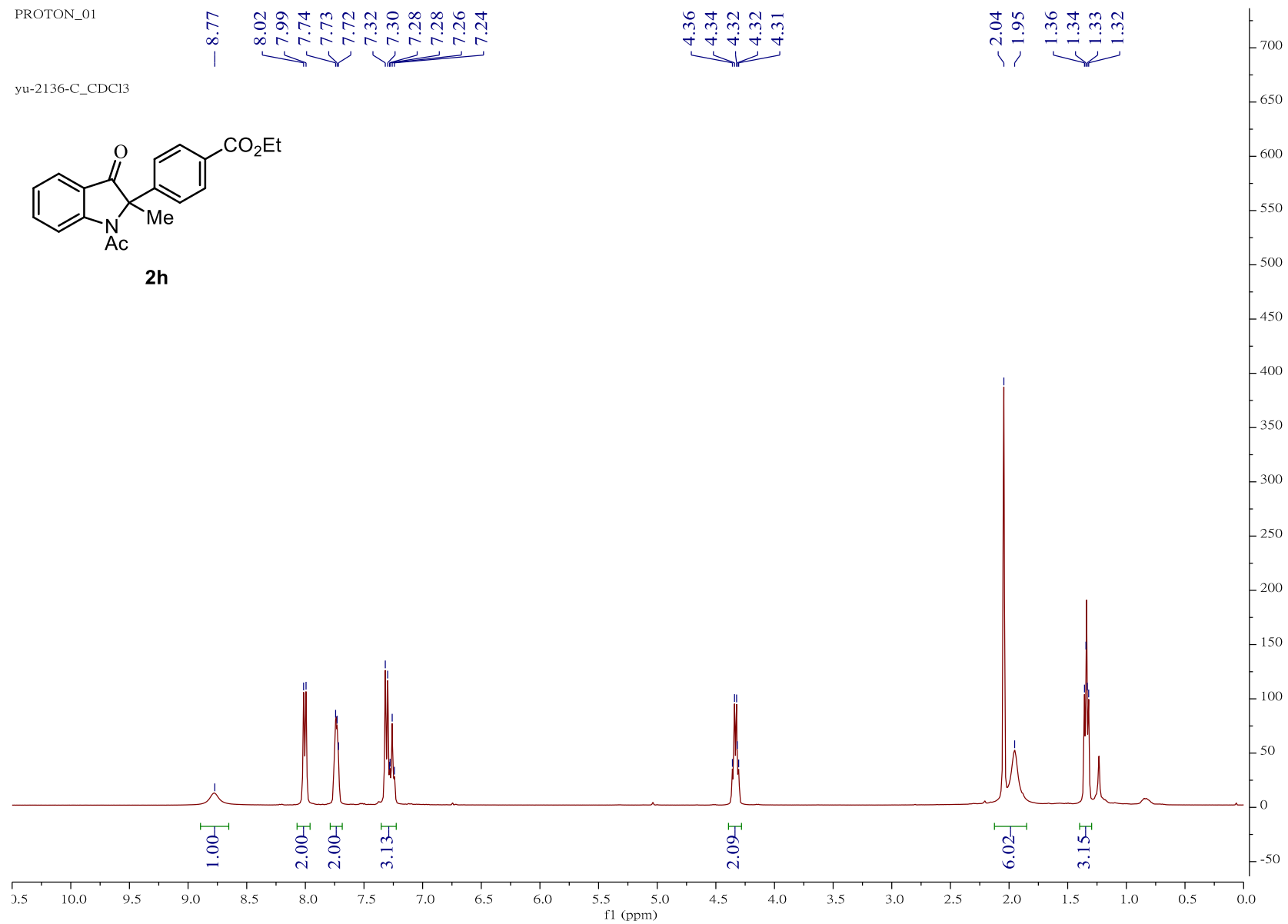
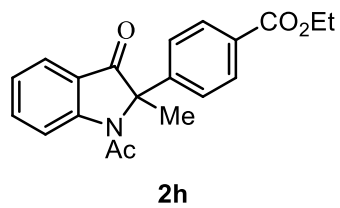
yu-2120-F\_CDCl3



$^{19}\text{F}$  NMR spectrum of compound **2g**

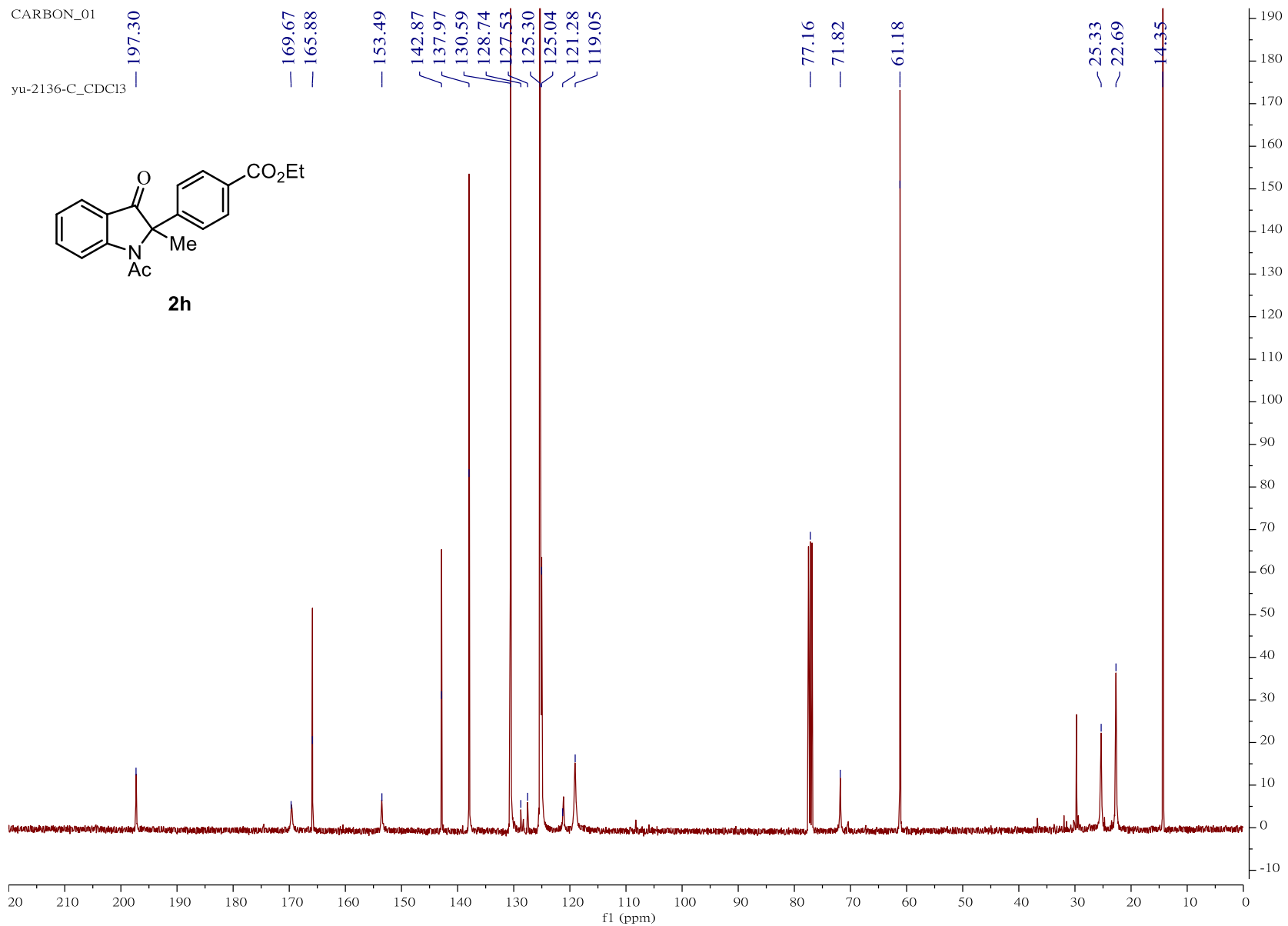
PROTON\_01

yu-2136-C-CDCl3



**<sup>1</sup>H NMR spectrum of compound 2g**

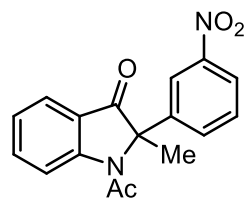
S-53



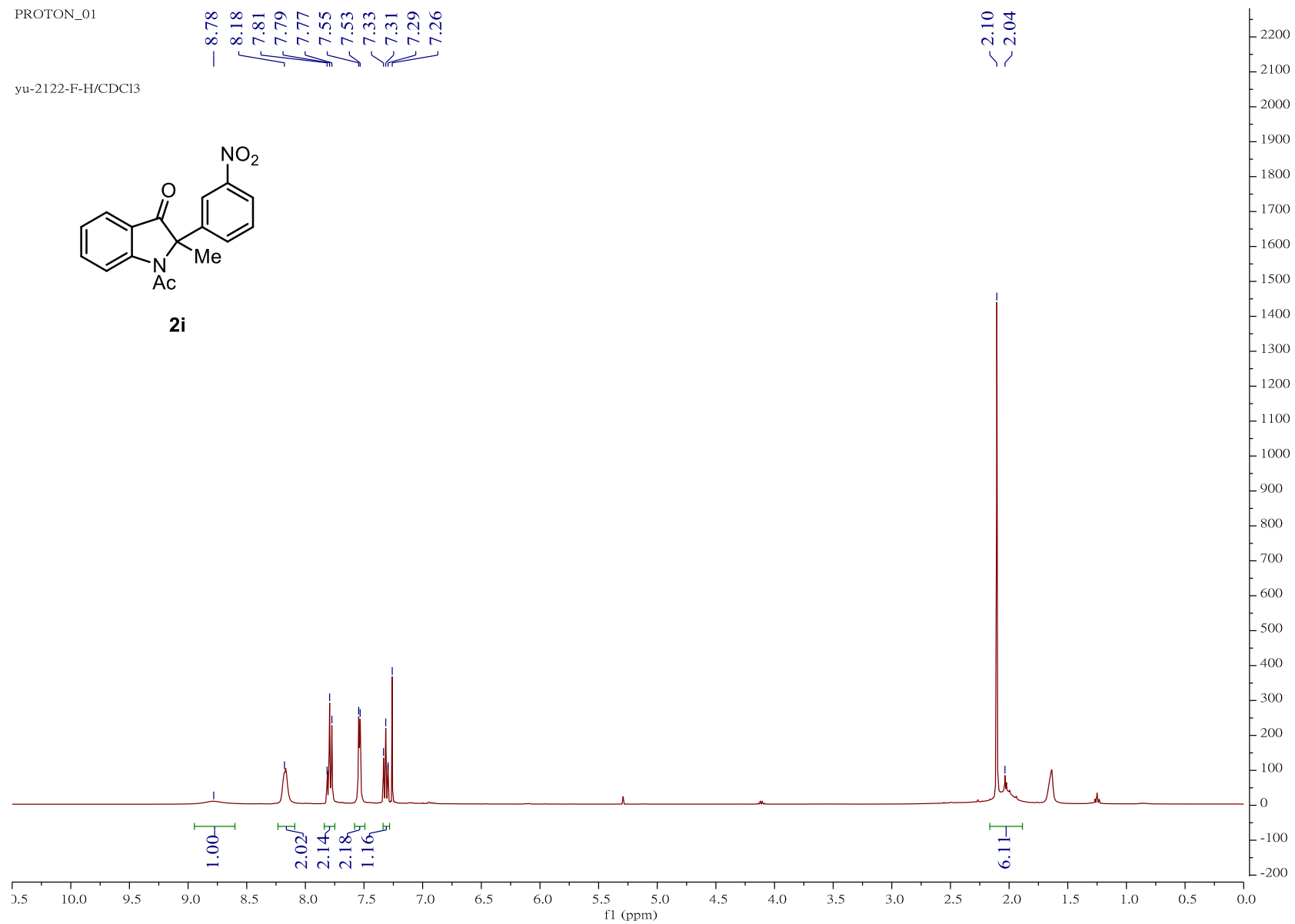
<sup>13</sup>C NMR spectrum of compound 2h

PROTON\_01

yu-2122-F-H/CDC13

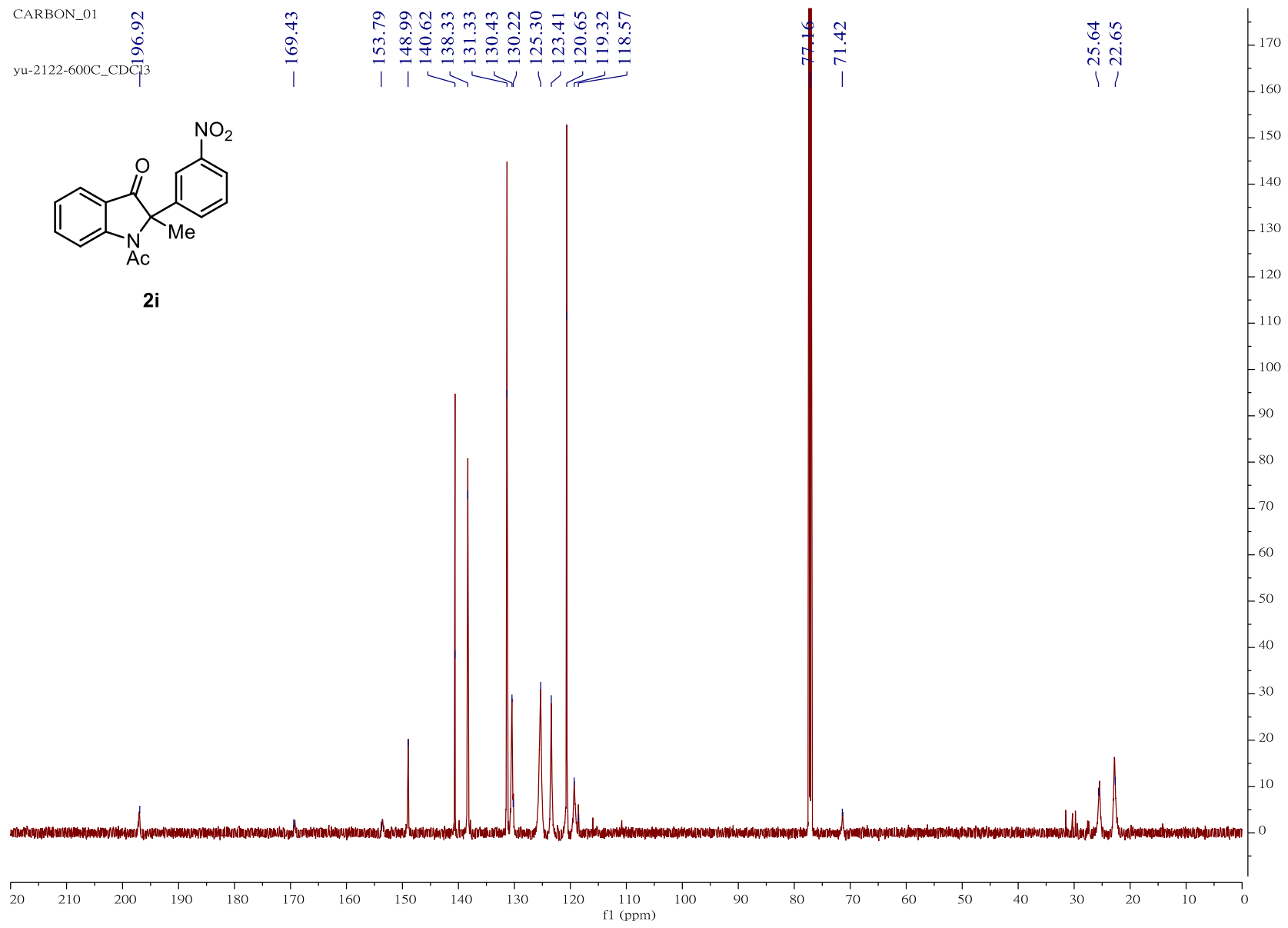


2i



<sup>1</sup>H NMR spectrum of compound 2i

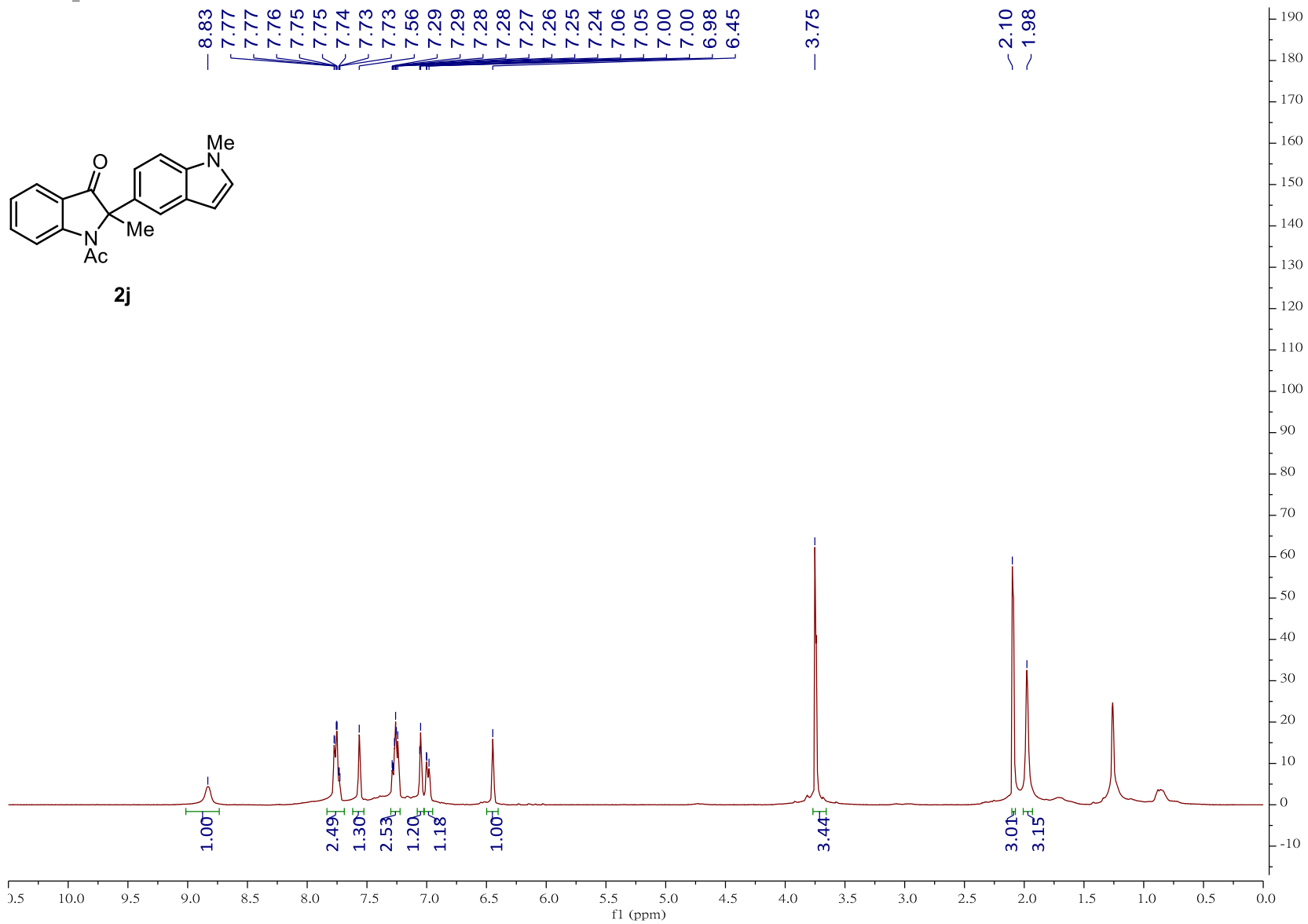
S-55



**<sup>13</sup>C NMR spectrum of compound 2i**

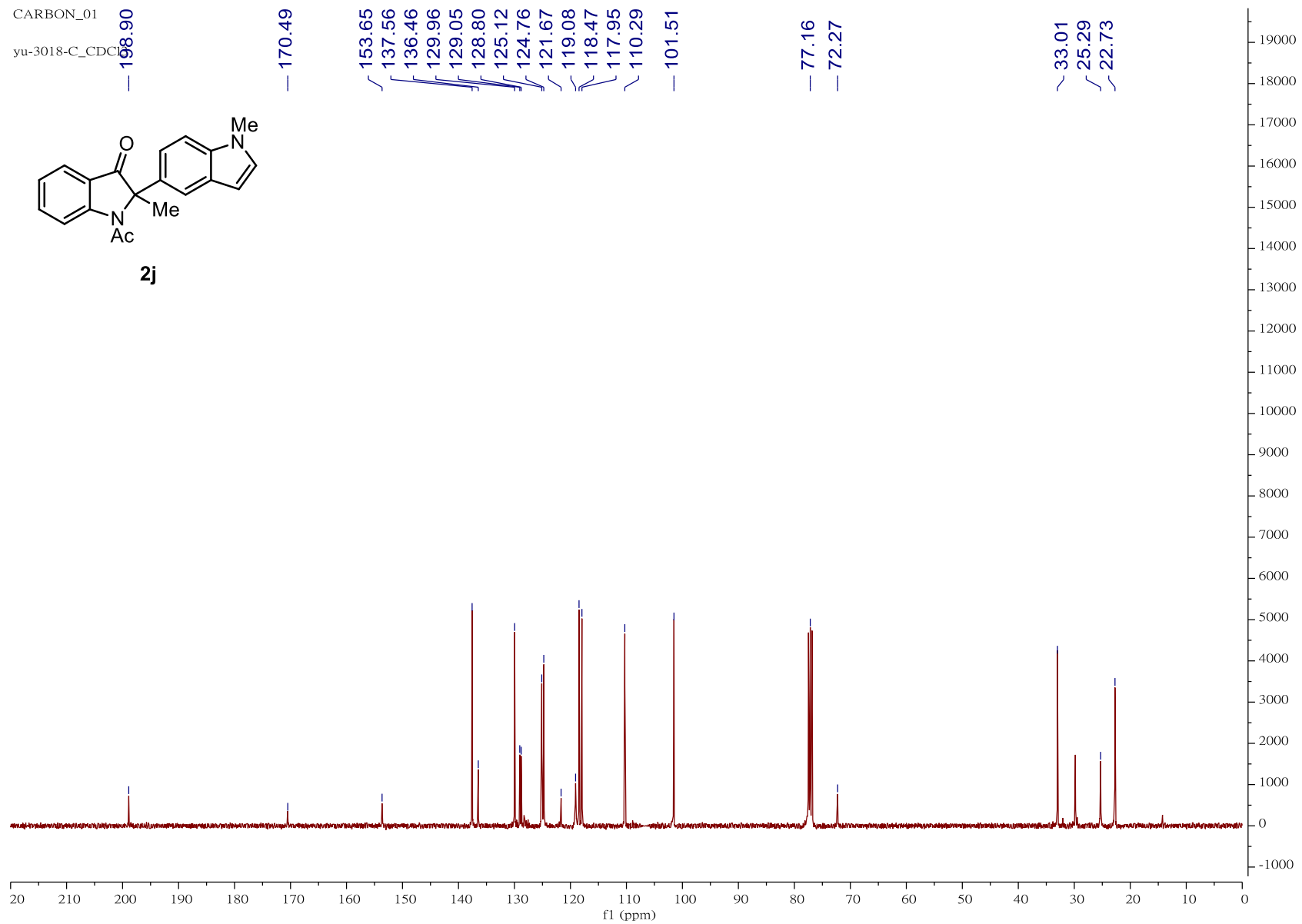


PROTON\_01



**<sup>1</sup>H NMR spectrum of compound 2j**

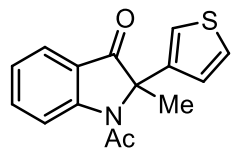
S-57



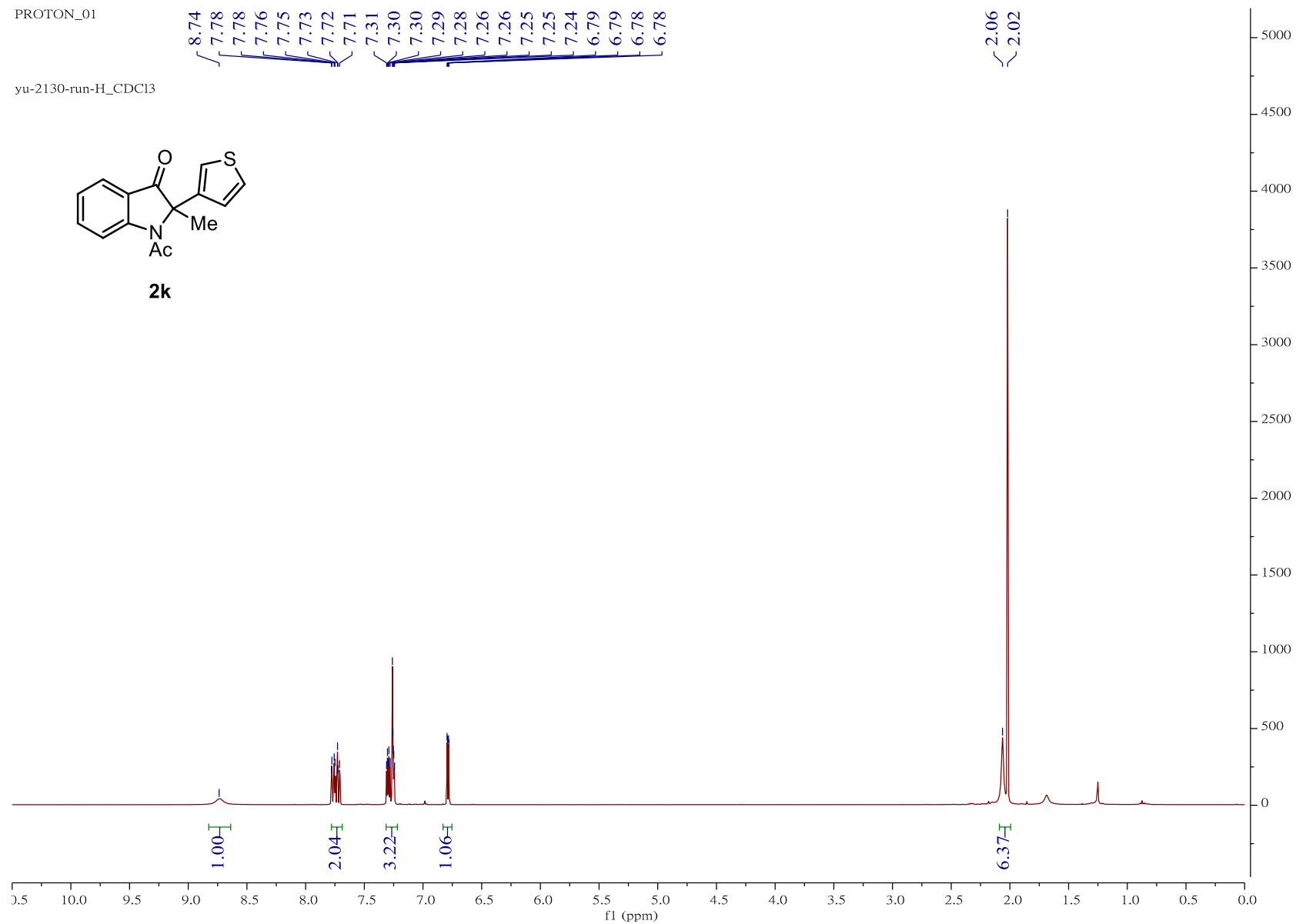
<sup>13</sup>C NMR spectrum of compound **2j**

PROTON\_01

yu-2130-run-H\_CDCI3

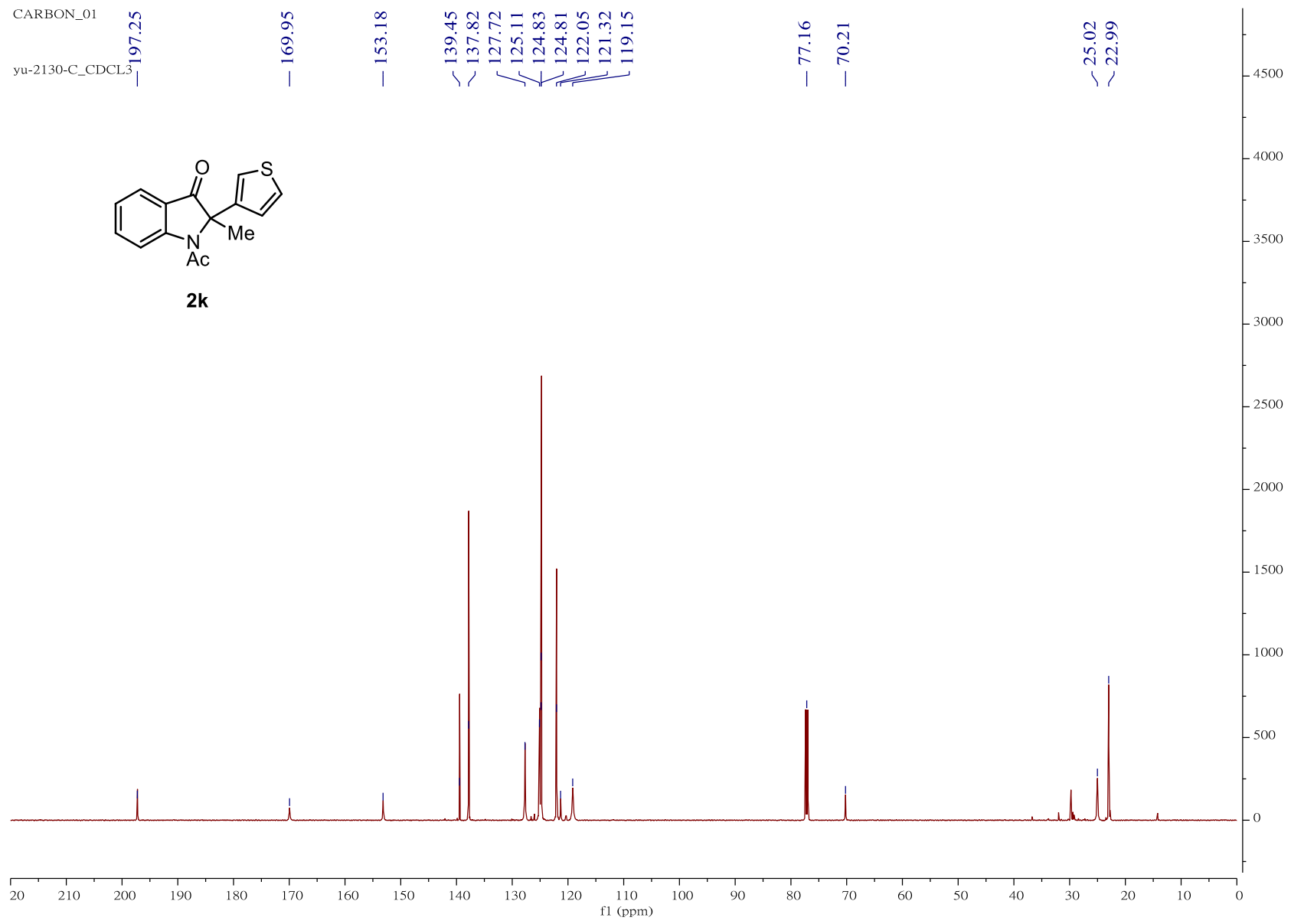


**2k**

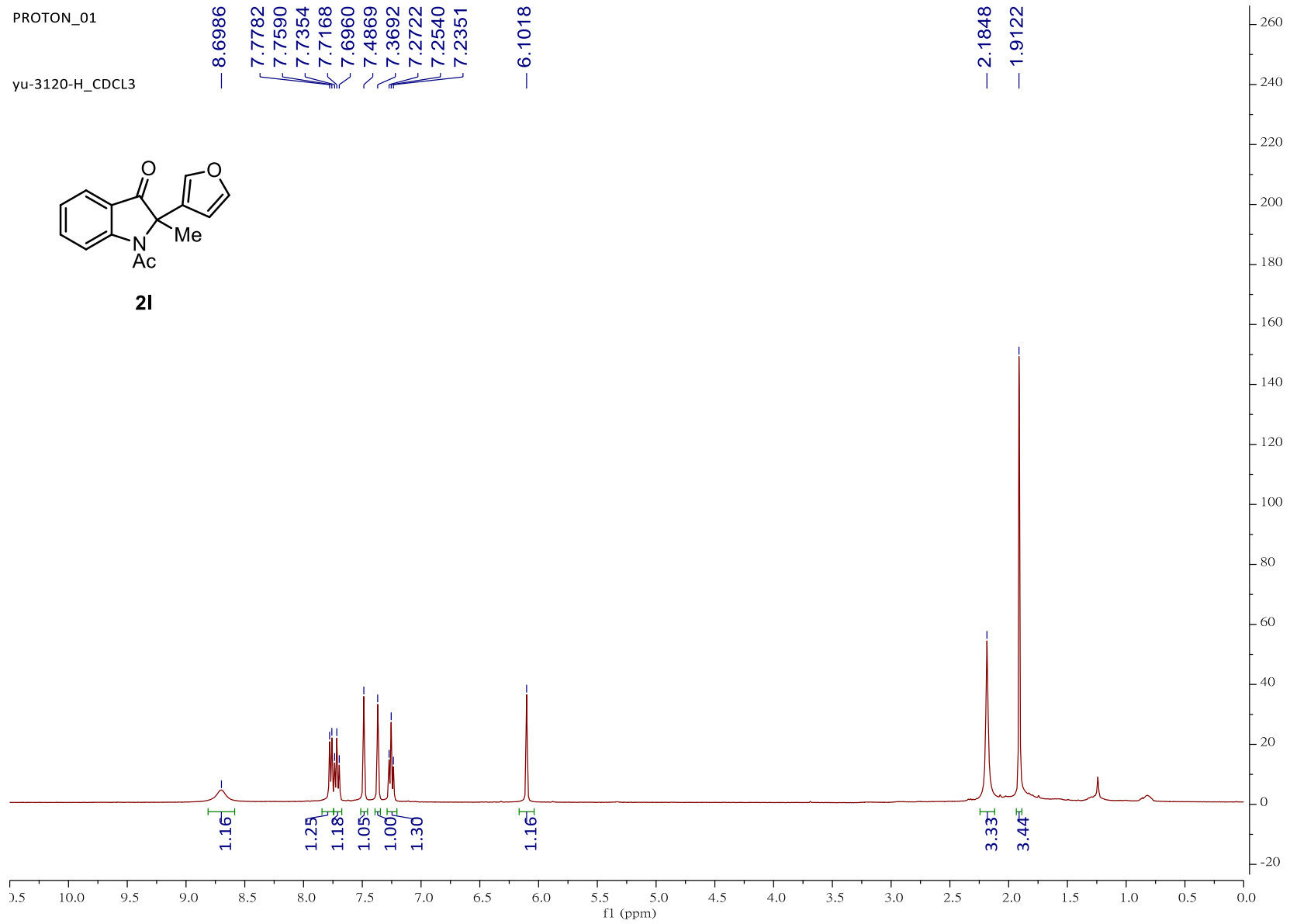


**<sup>1</sup>H NMR spectrum of compound 2k**

S-59

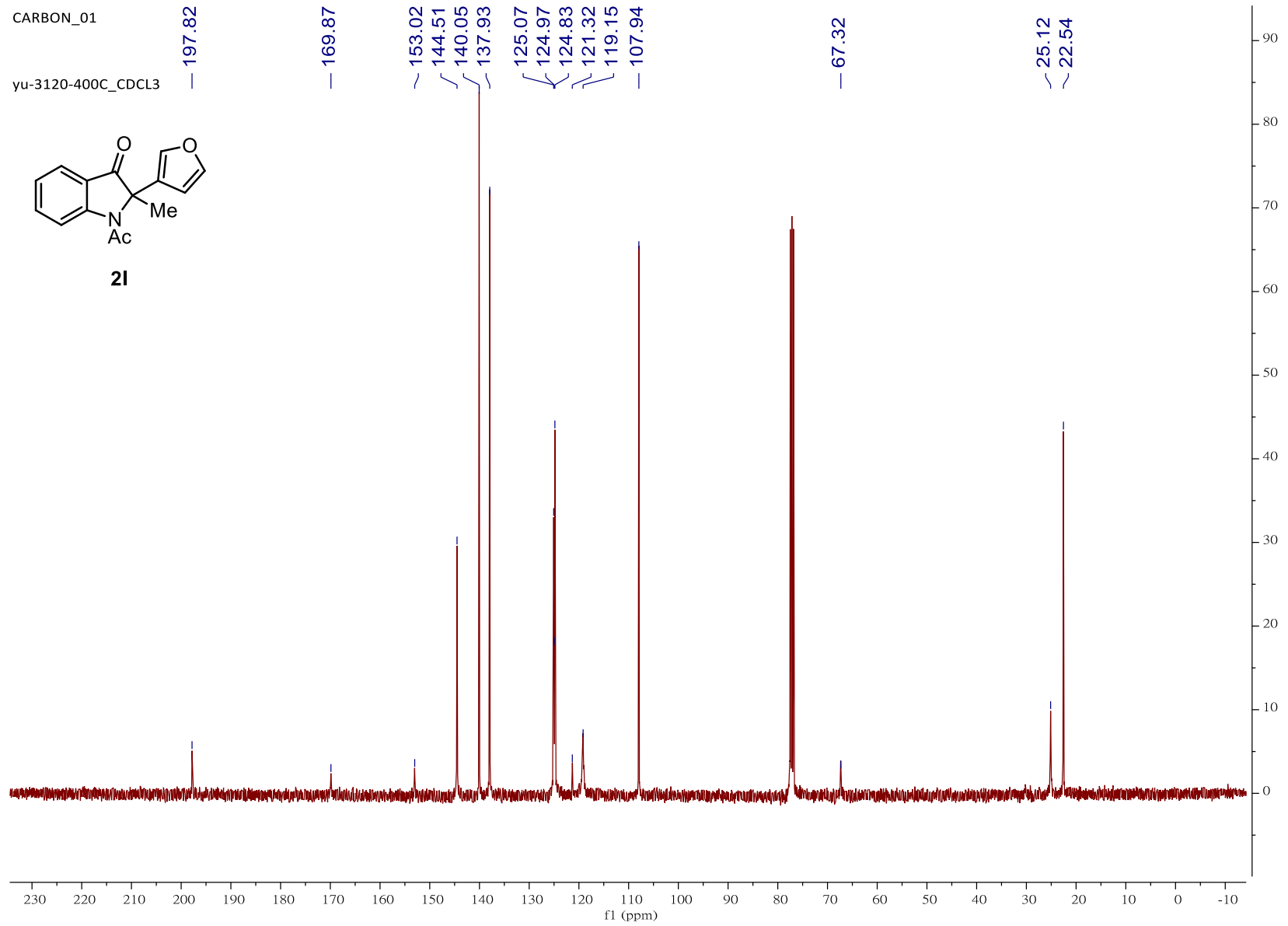


<sup>13</sup>C NMR spectrum of compound 2k

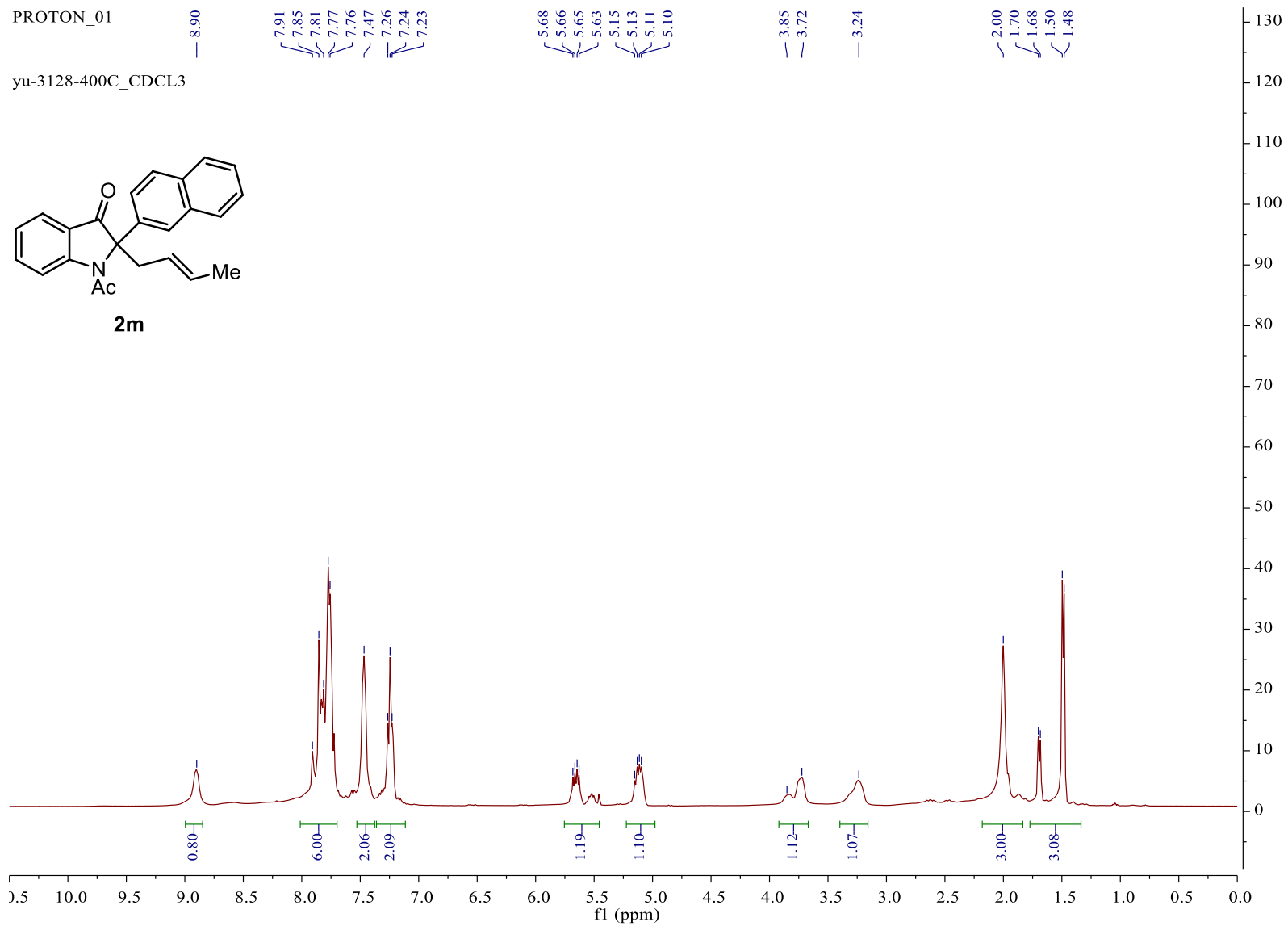


**<sup>1</sup>H NMR spectrum of compound 2l**

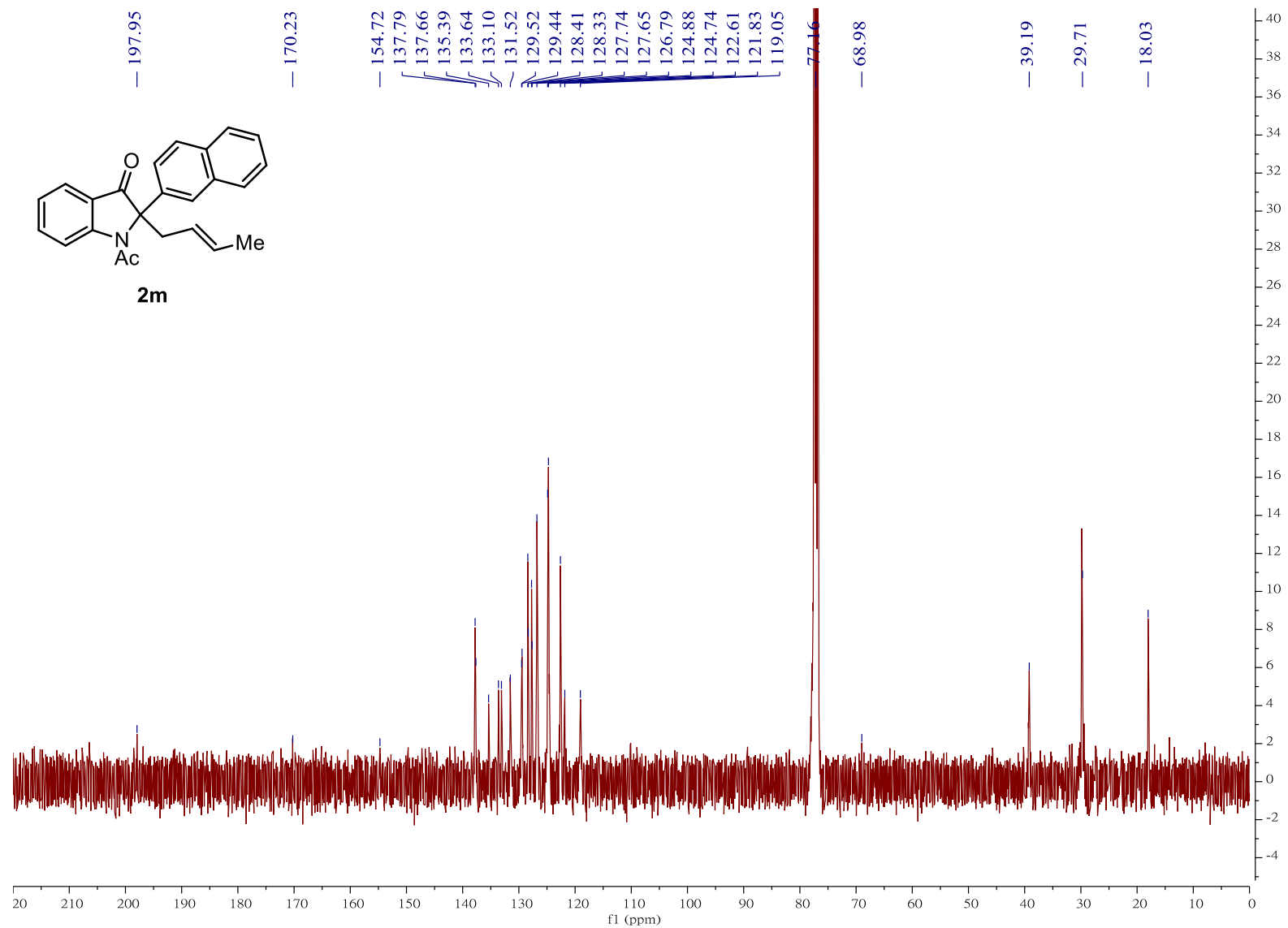
S-61



<sup>13</sup>C NMR spectrum of compound 2l

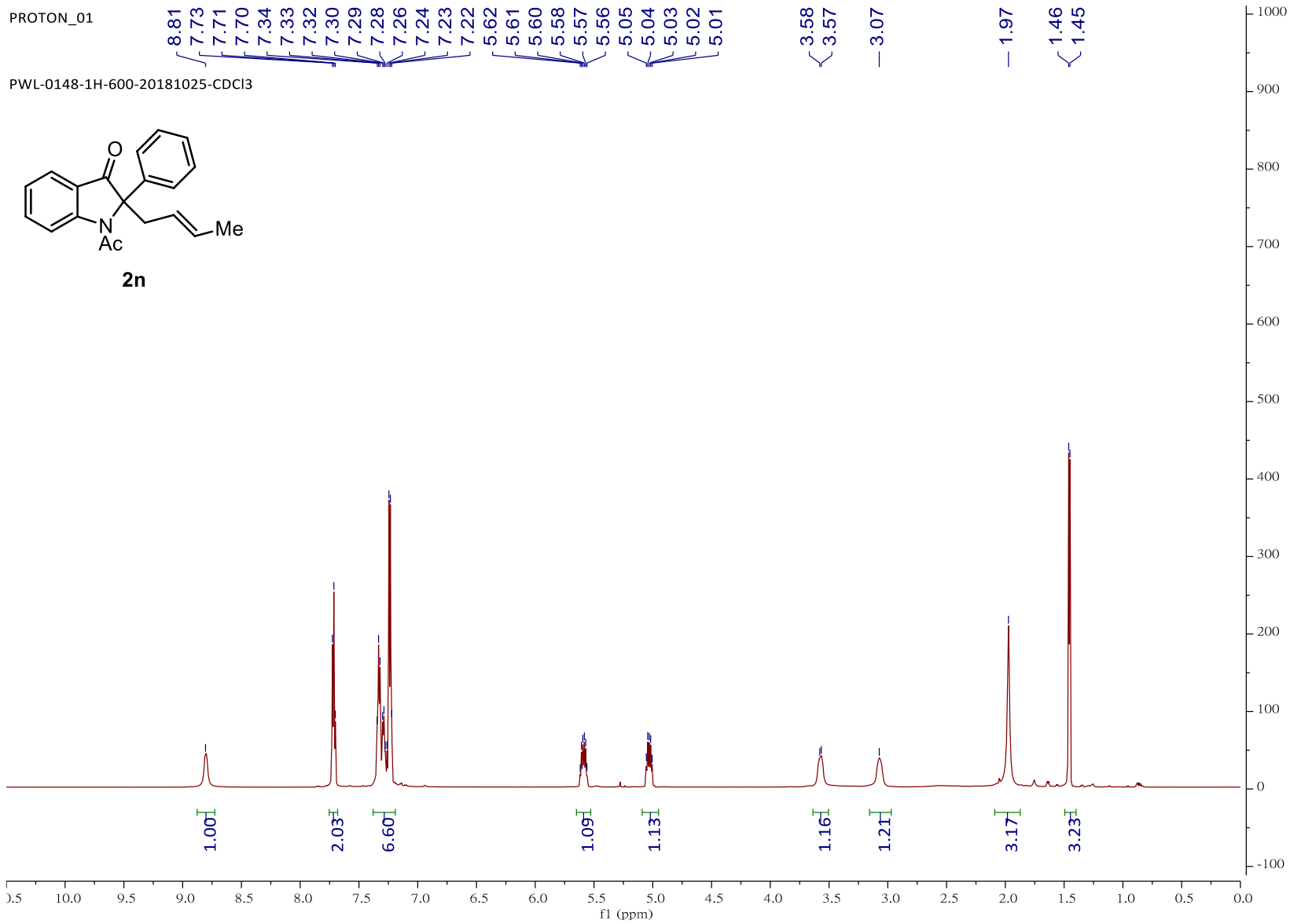


**$^1\text{H}$  NMR spectrum of compound 2m**

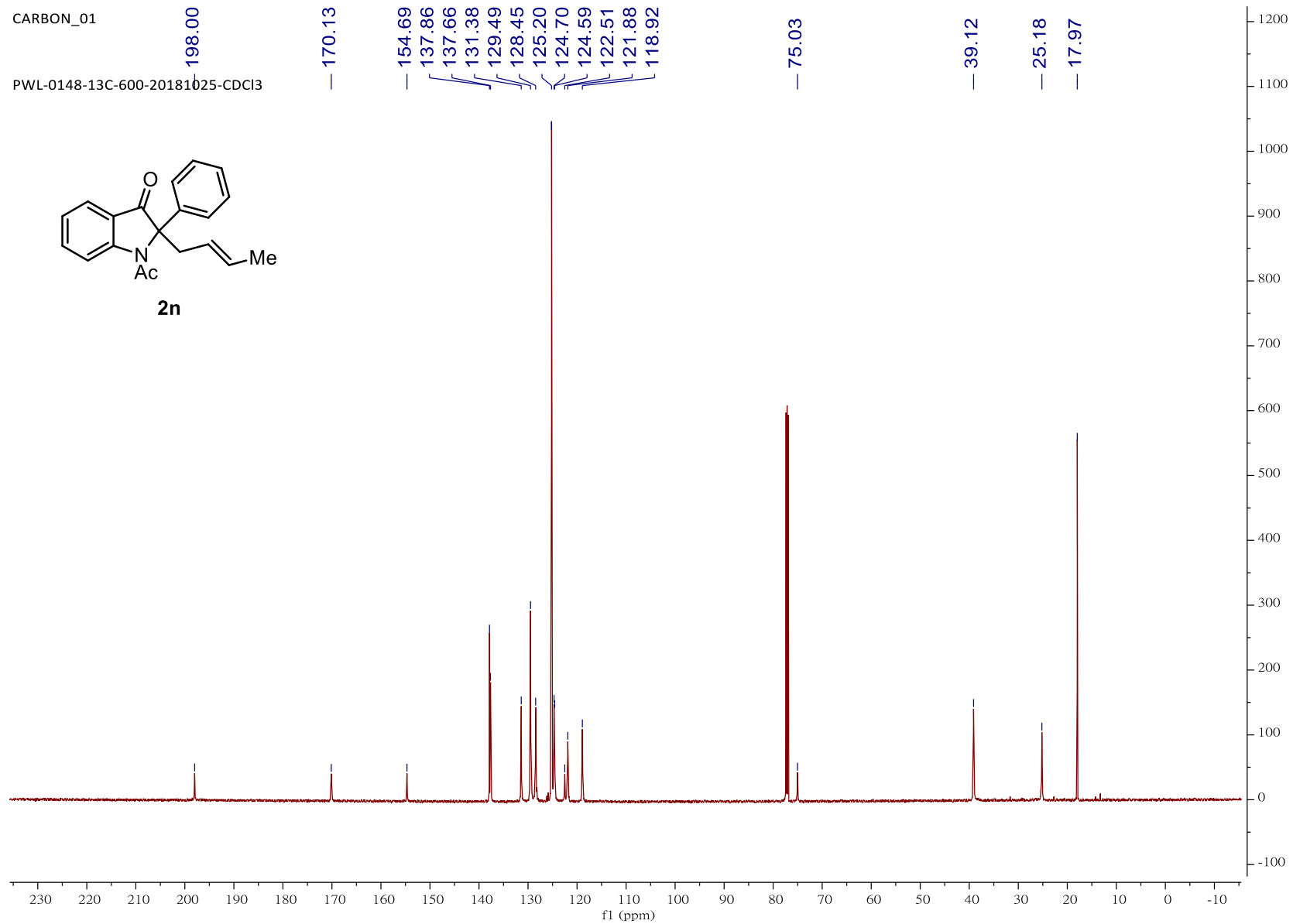


**<sup>13</sup>C NMR spectrum of compound 2m**



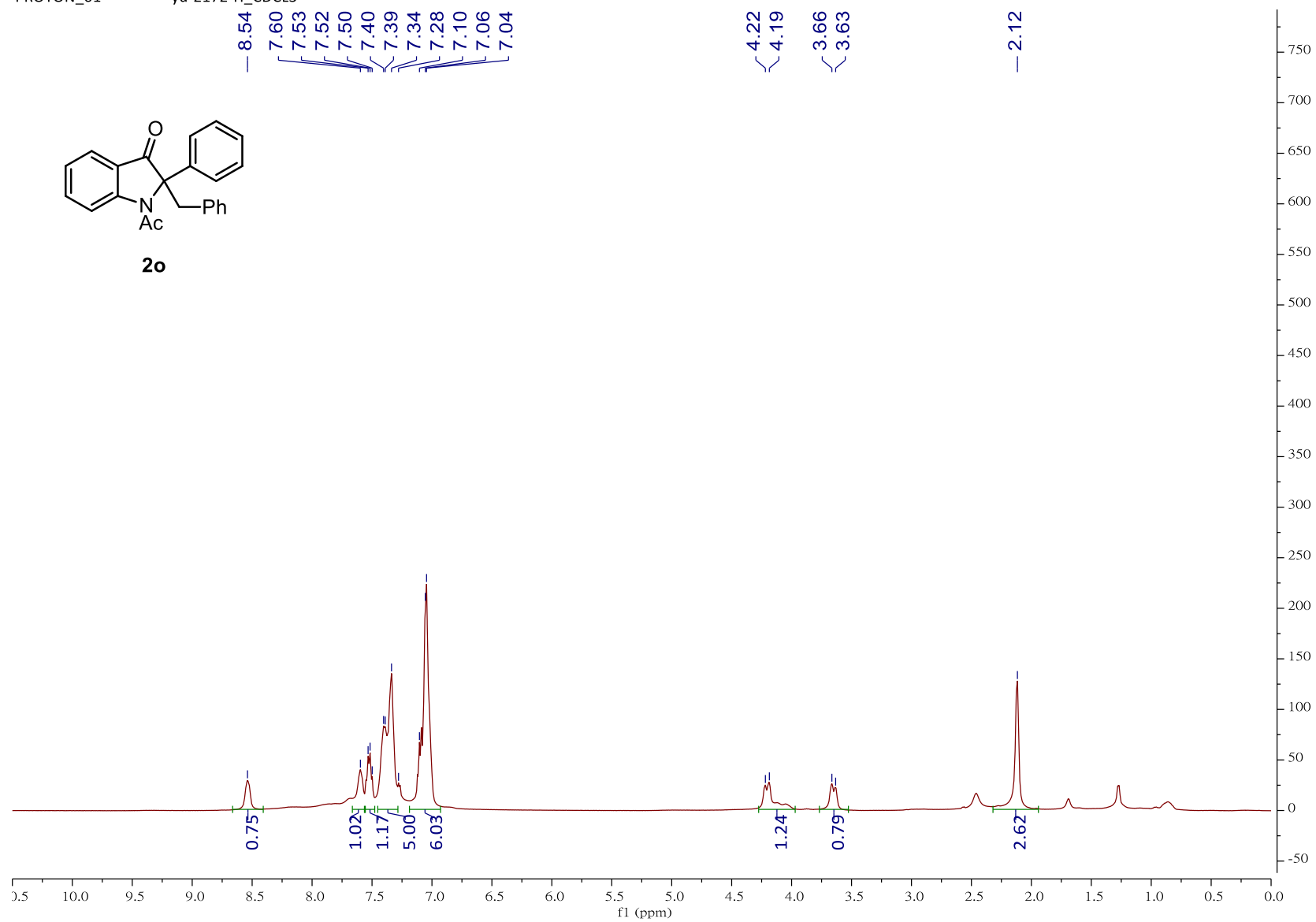
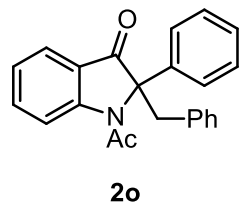


**<sup>1</sup>H NMR spectrum of compound 2n**  
S-65

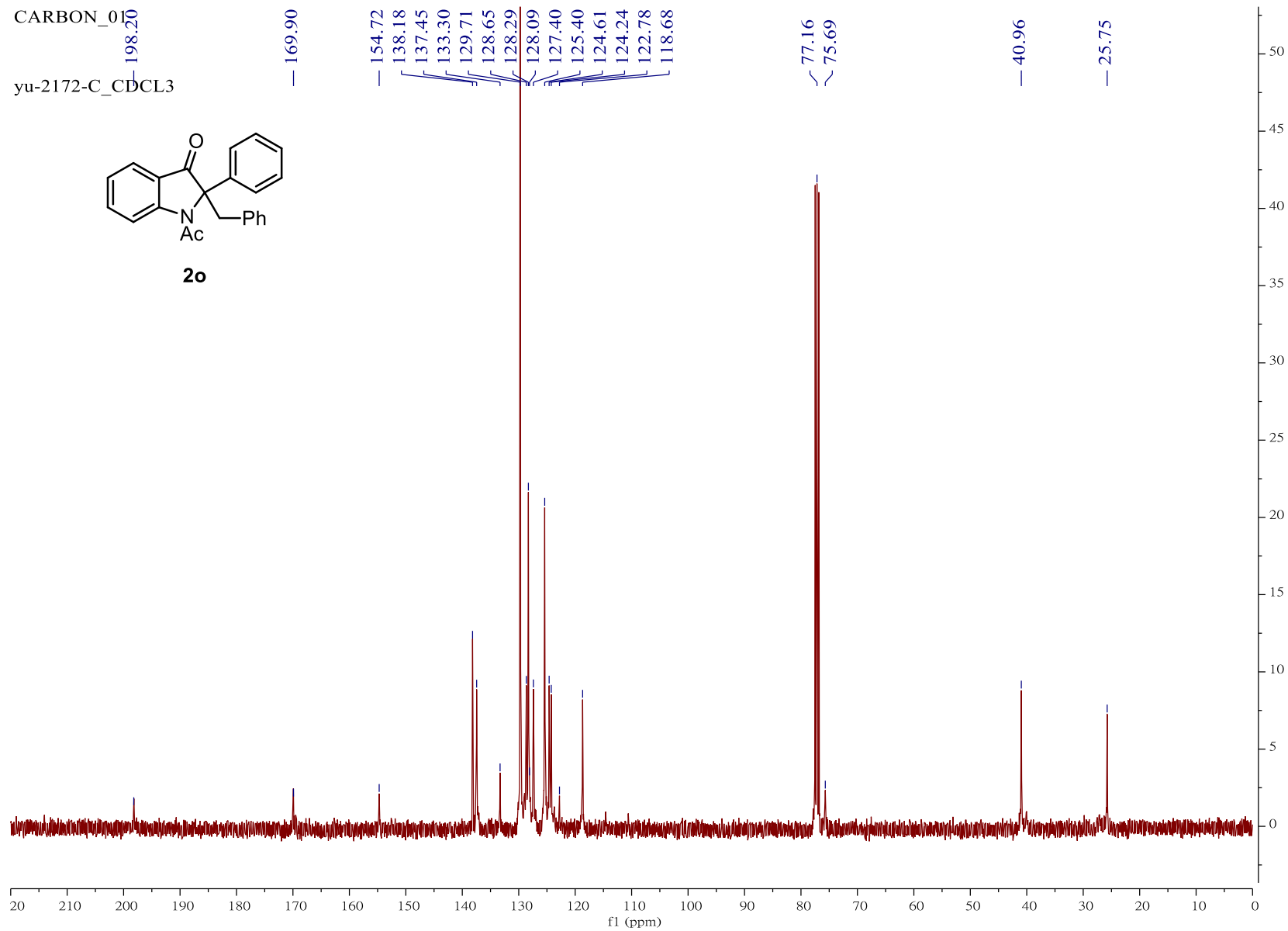


**<sup>13</sup>C NMR spectrum of compound 2n**

PROTON\_01 -- -- yu-2172-H\_CDCL3 --

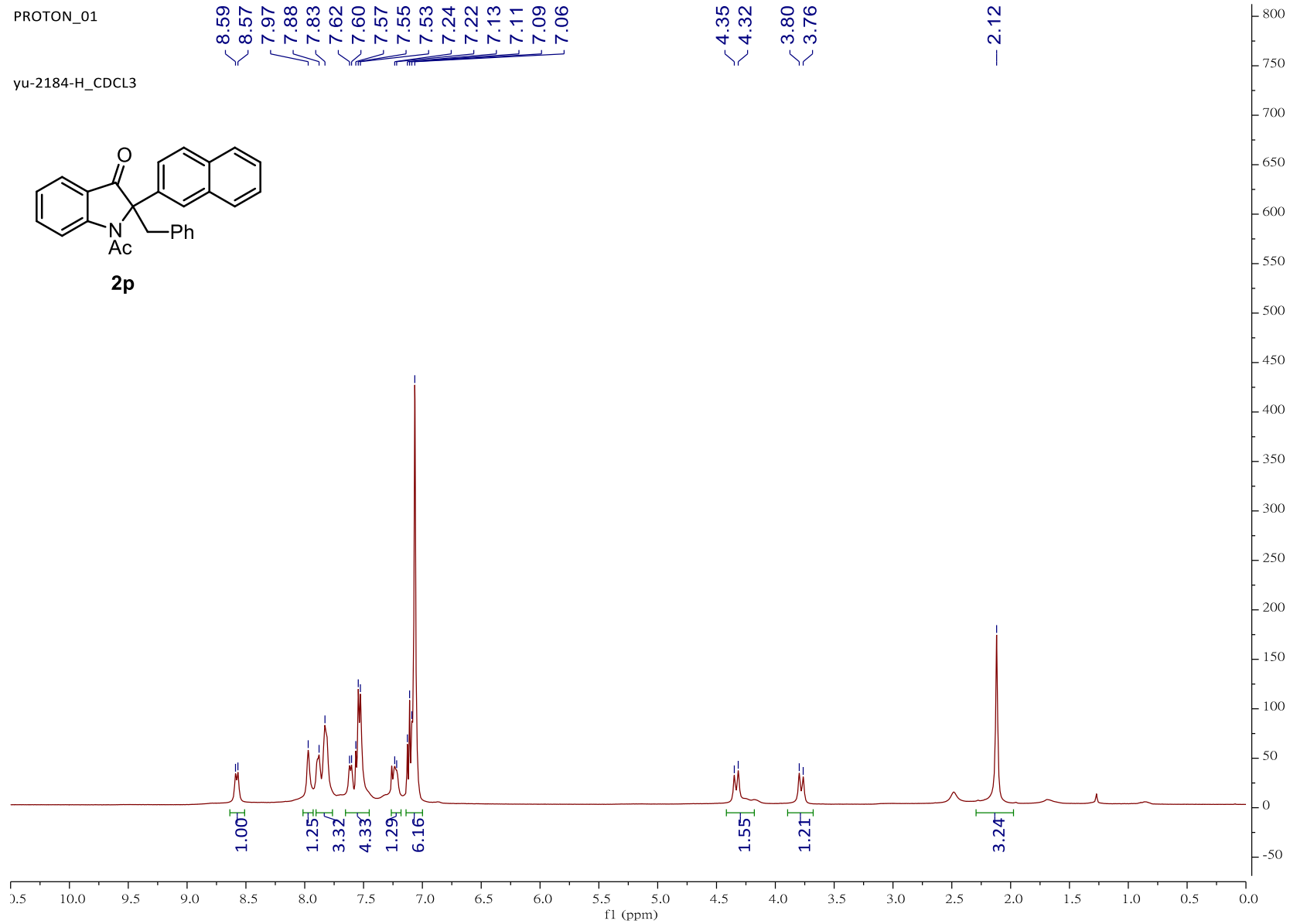


**<sup>1</sup>H NMR spectrum of compound 2o**

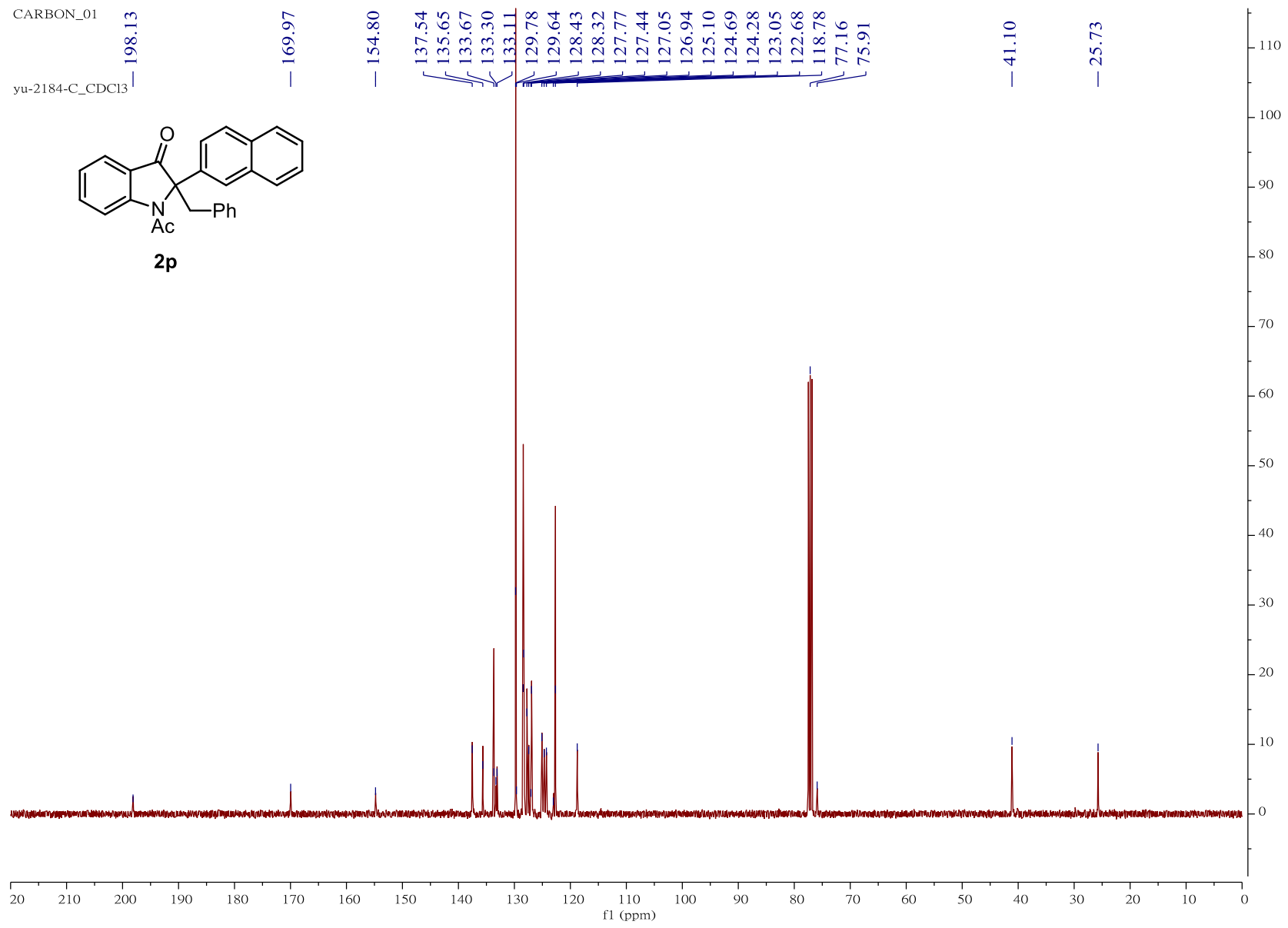


**<sup>13</sup>C NMR spectrum of compound 2o**

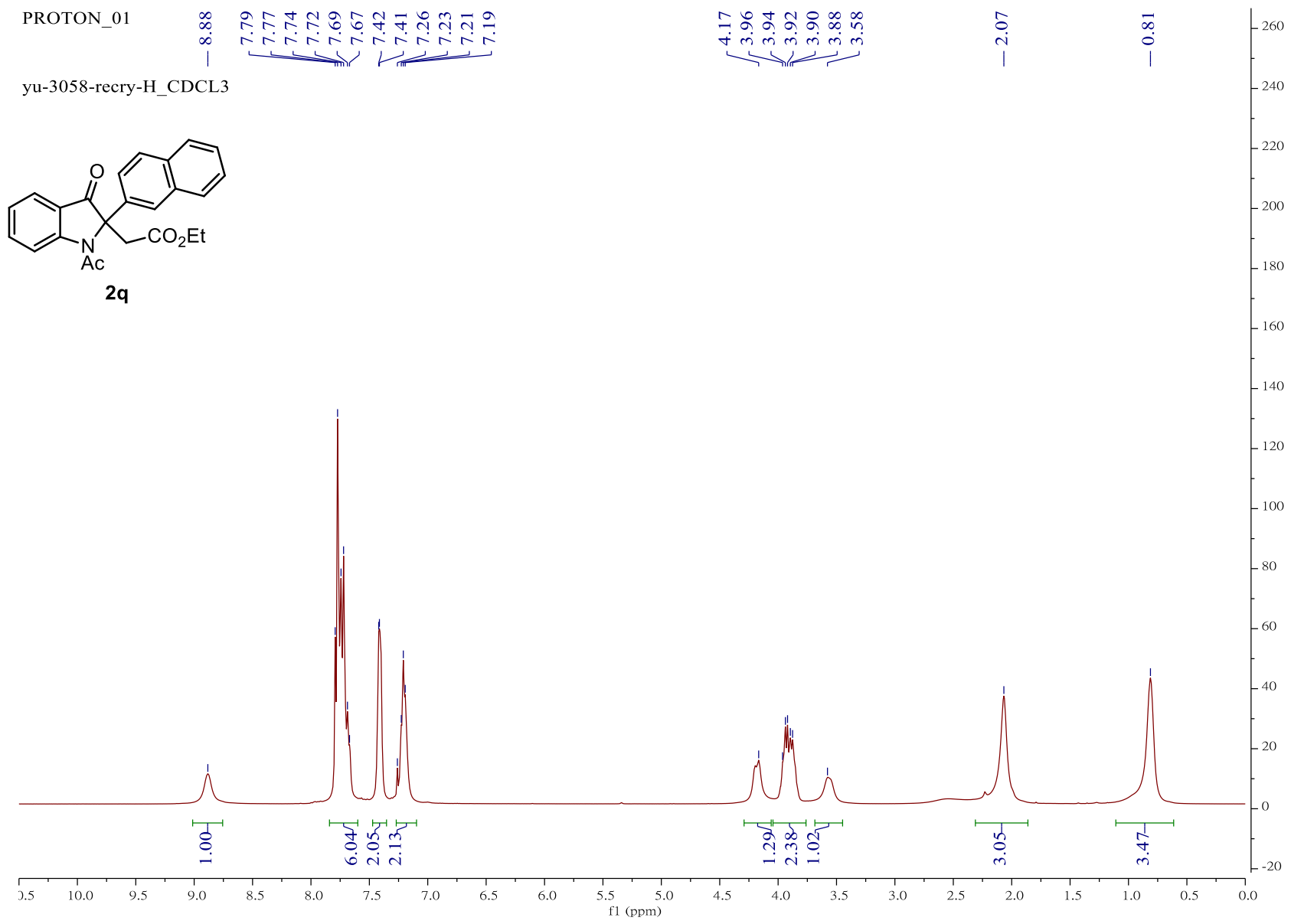
S-68



**<sup>1</sup>H NMR spectrum of compound 2p**



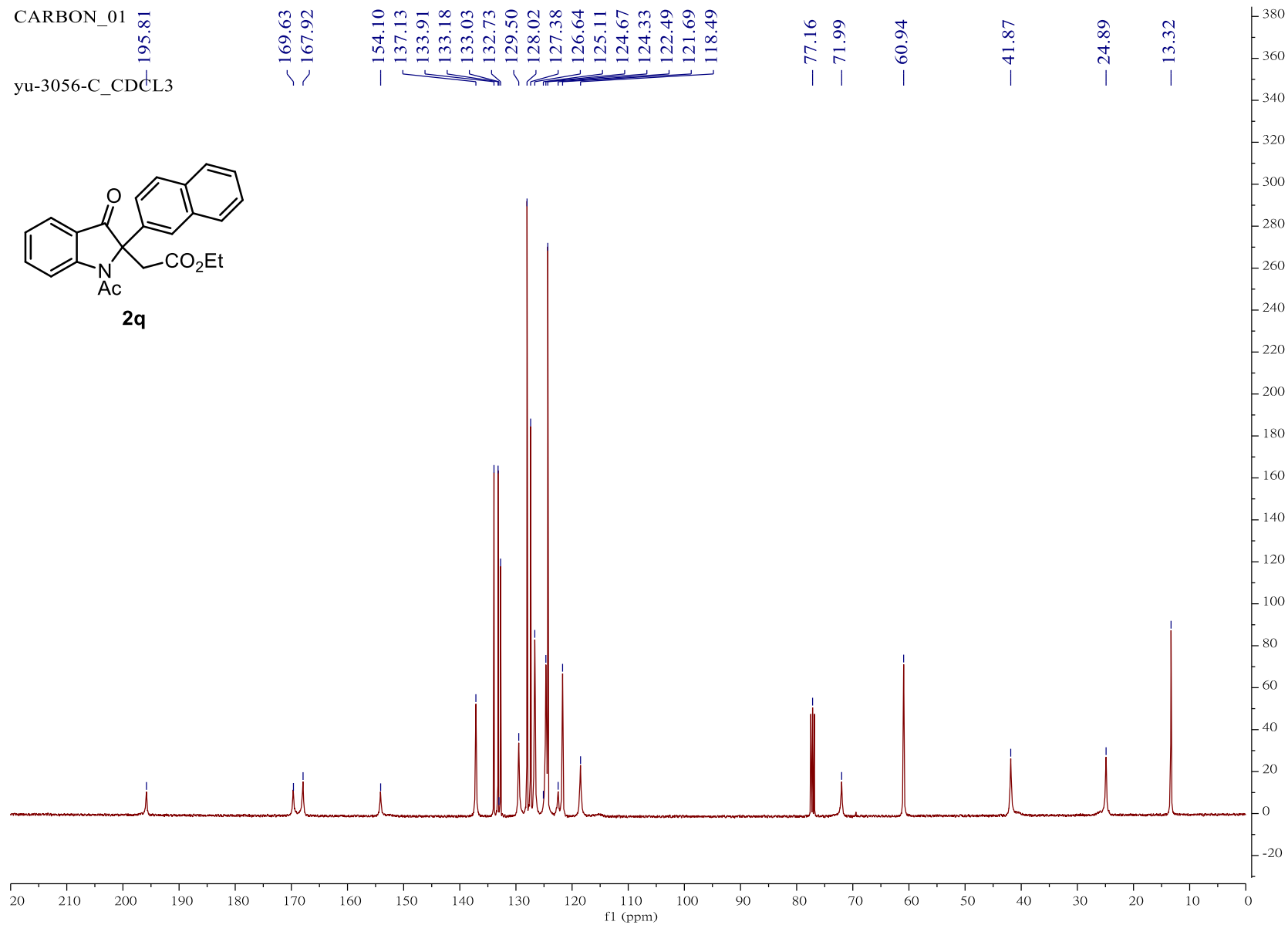
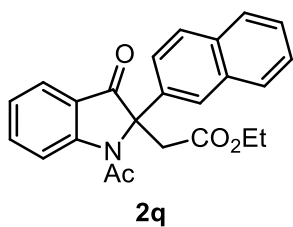
**<sup>13</sup>C NMR spectrum of compound 2p**  
S-70



**<sup>1</sup>H NMR spectrum of compound 2q**

S-71

CARBON\_01  
yu-3056-C\_CDCL3

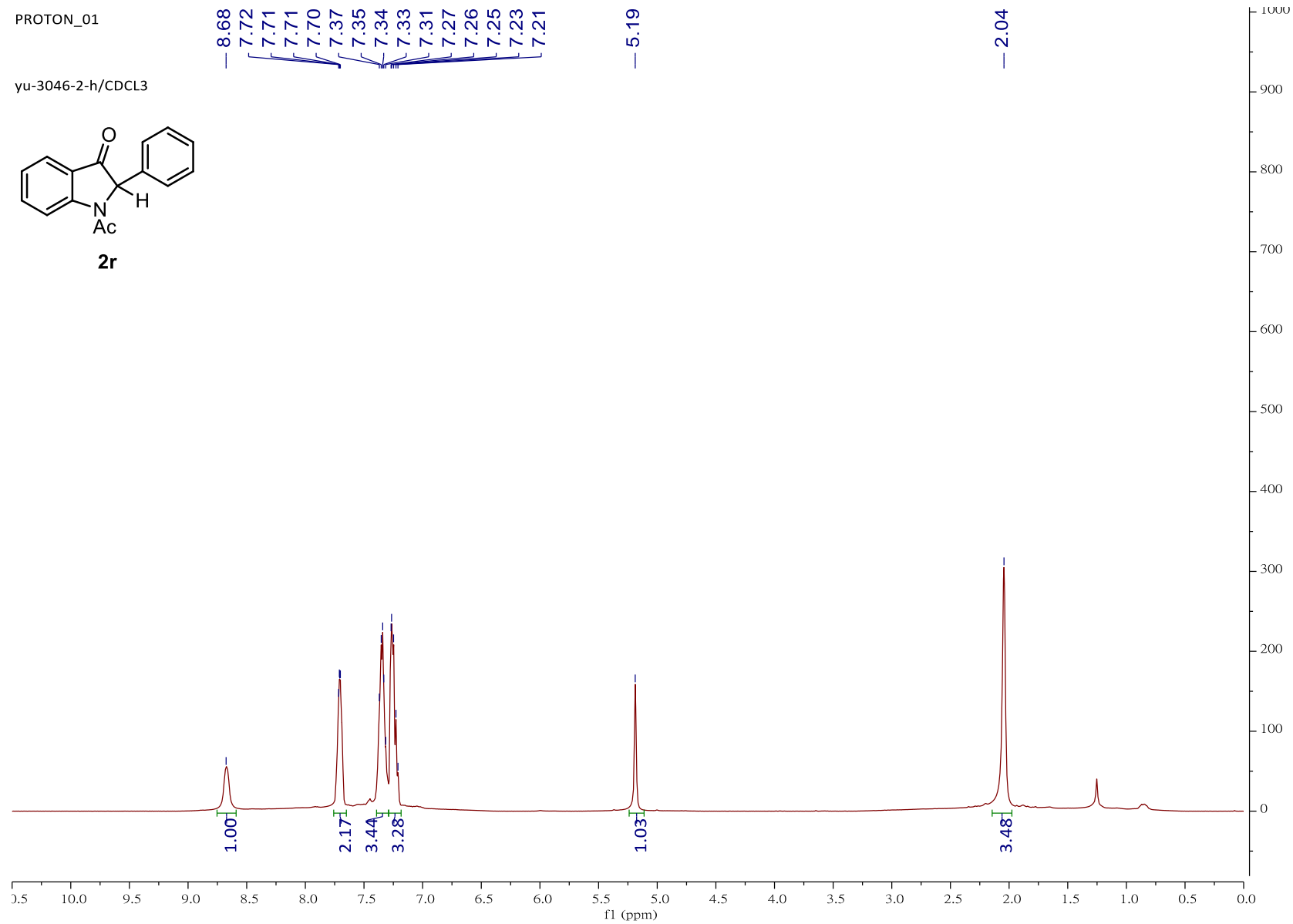
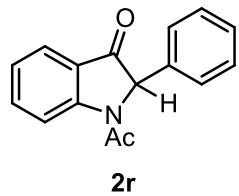


**<sup>13</sup>C NMR spectrum of compound 2q**



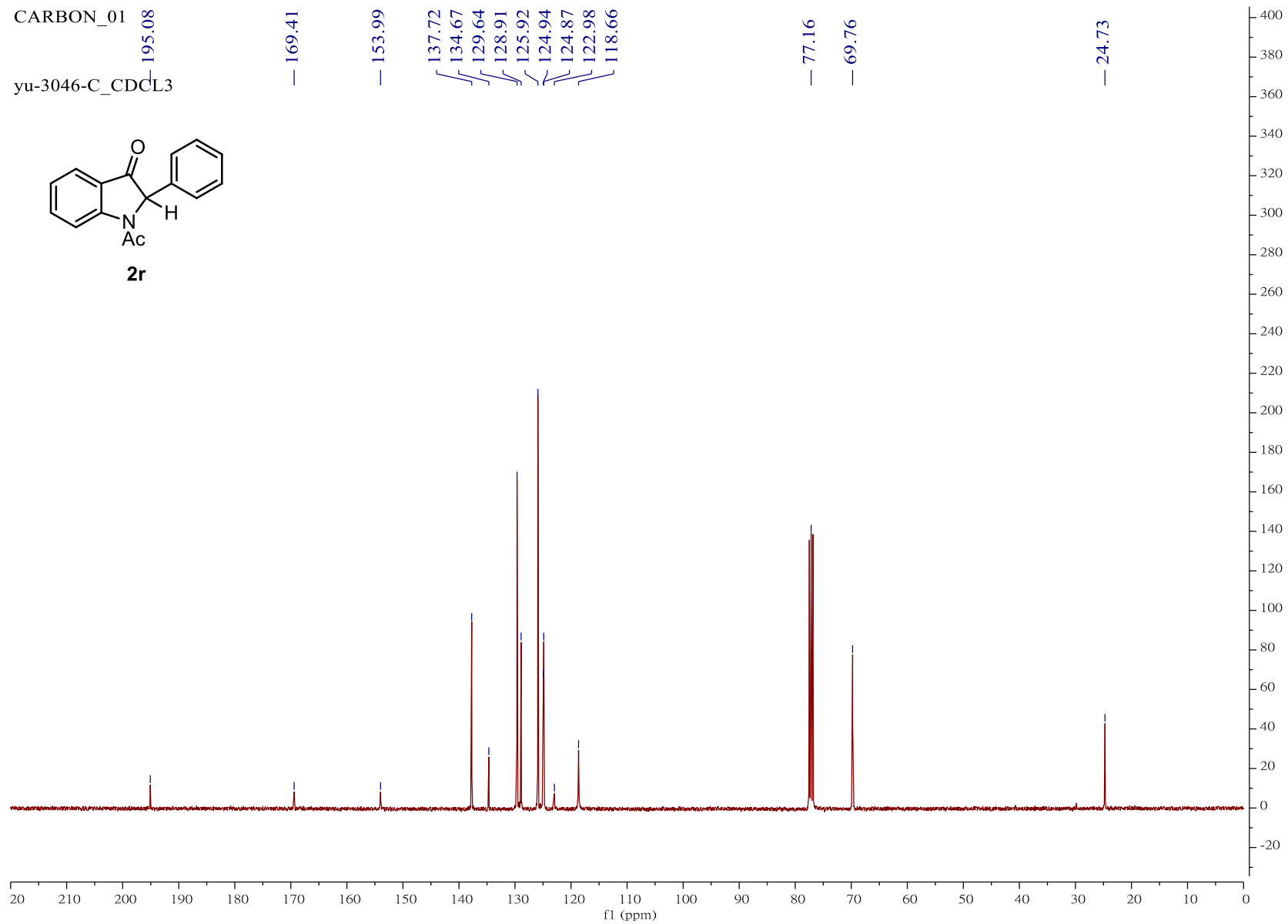
PROTON\_01

yu-3046-2-h/CDCl3



**<sup>1</sup>H NMR spectrum of compound 2r**

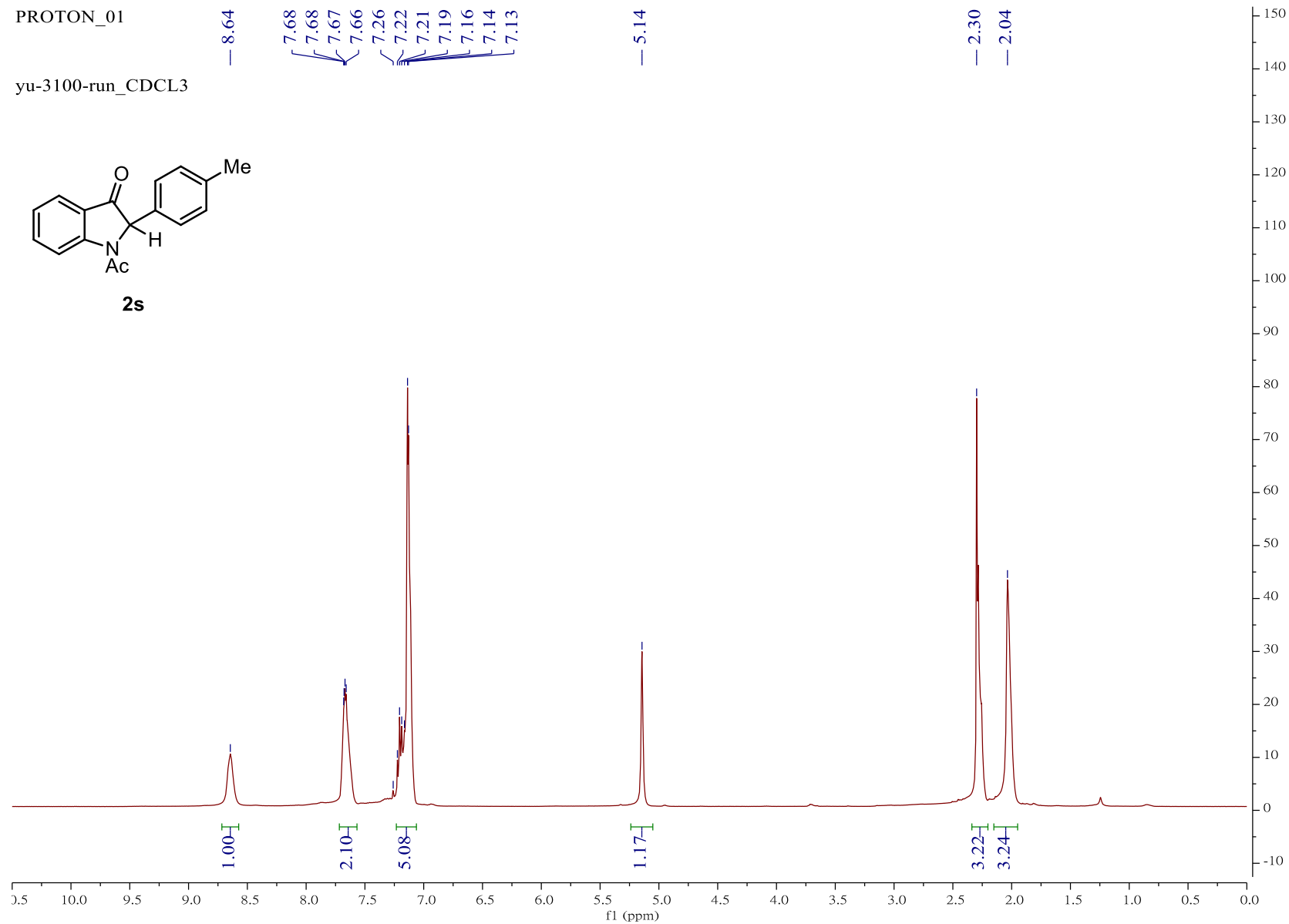
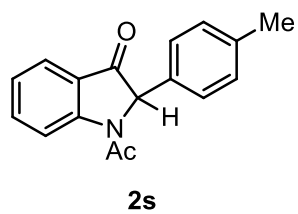
S-73



<sup>13</sup>C NMR spectrum of compound 2r

PROTON\_01

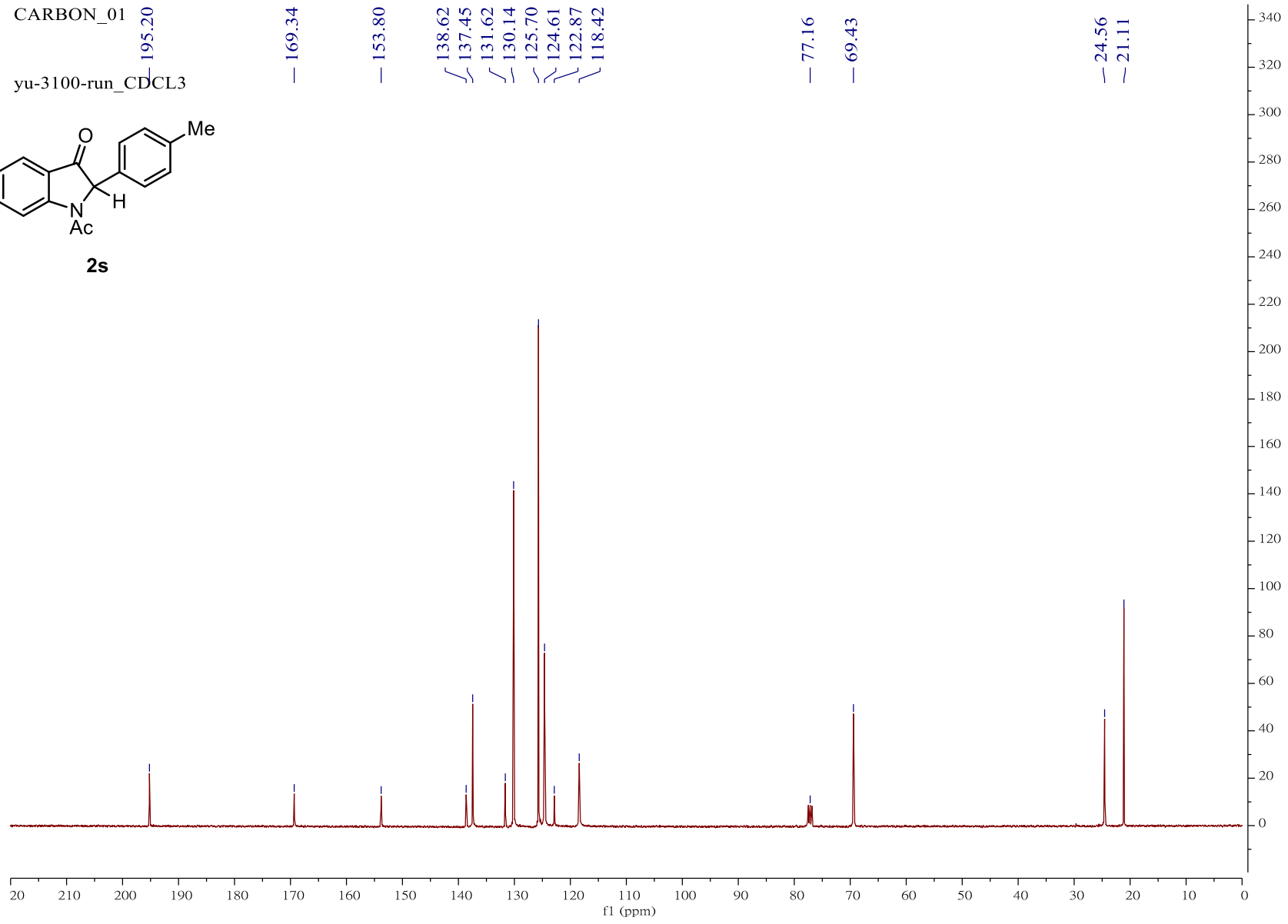
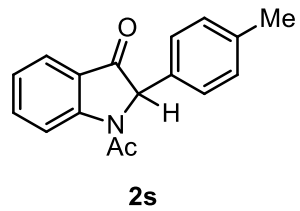
yu-3100-run\_CDCL3



**<sup>1</sup>H NMR spectrum of compound 2s**

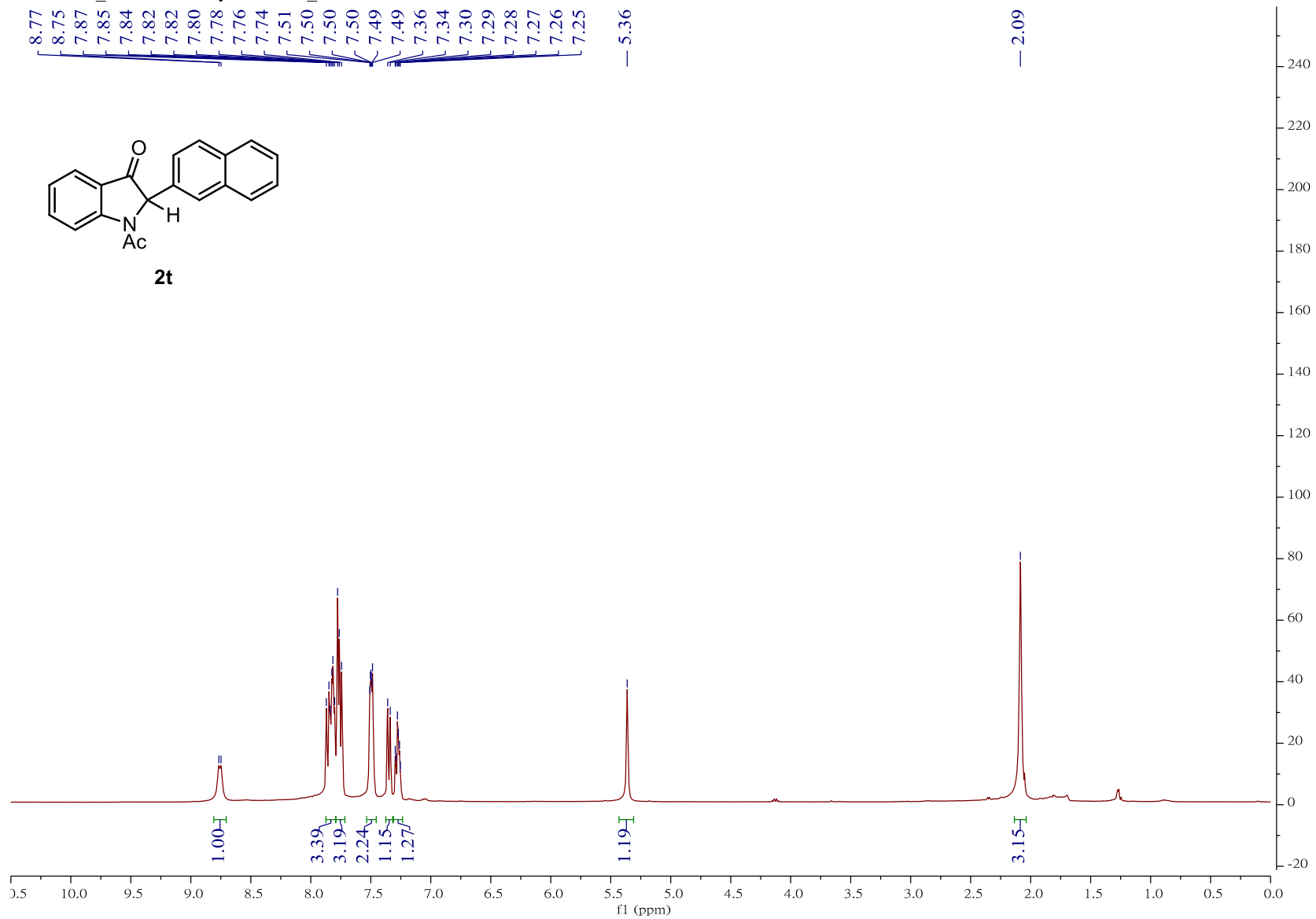
S-75

CARBON\_01  
yu-3100-run\_CDCL3



<sup>13</sup>C NMR spectrum of compound 2r  
S-76

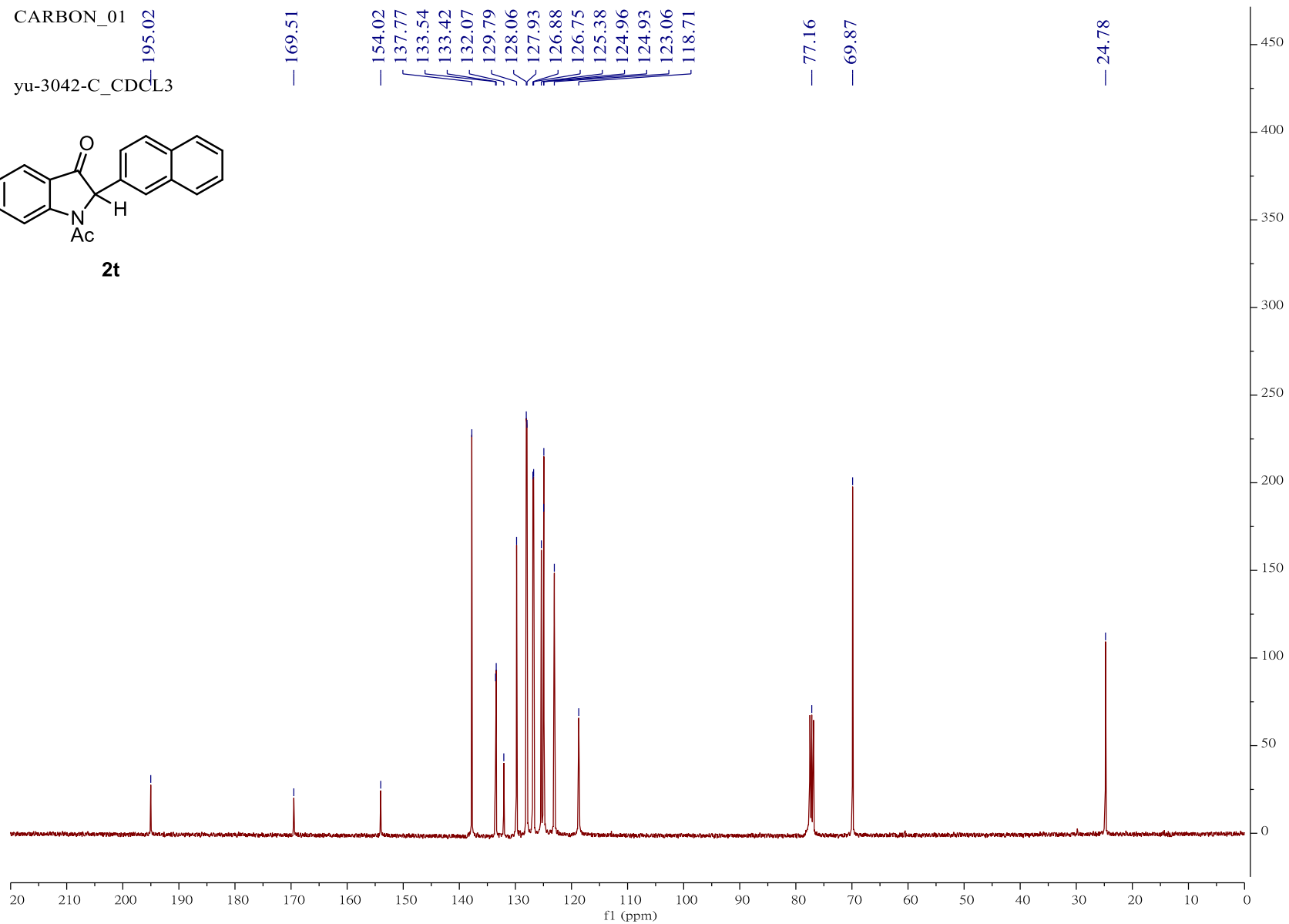
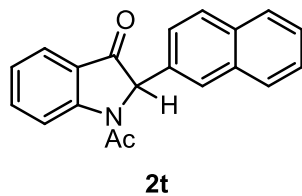
PROTON\_01 — — — yu-3042-C\_CDCL3 —



**<sup>1</sup>H NMR spectrum of compound 2t**

S-77

CARBON\_01  
yu-3042-C\_CDCL3

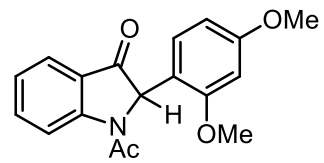


<sup>13</sup>C NMR spectrum of compound 2s

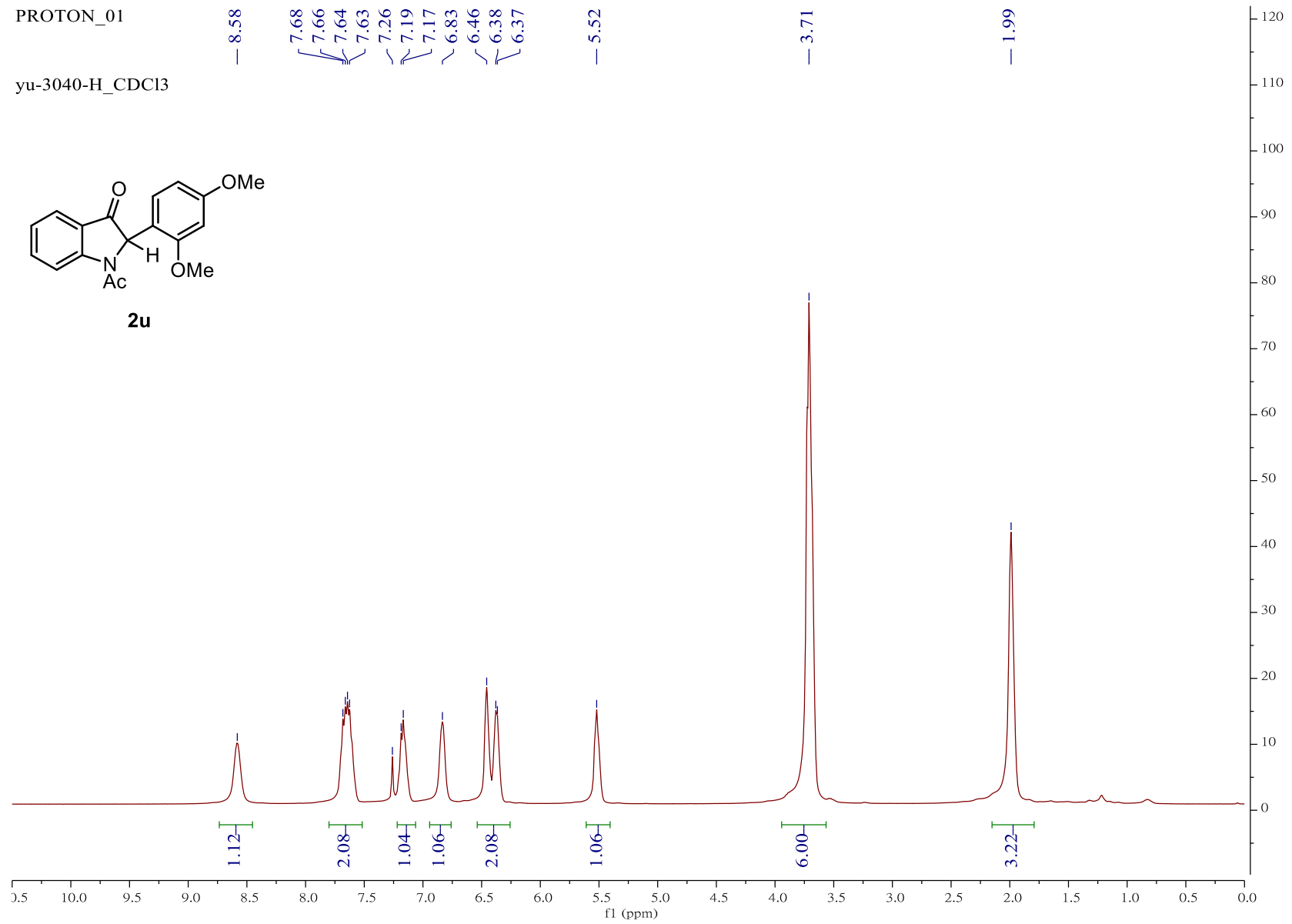
S-78

PROTON\_01

yu-3040-H\_CDCI3

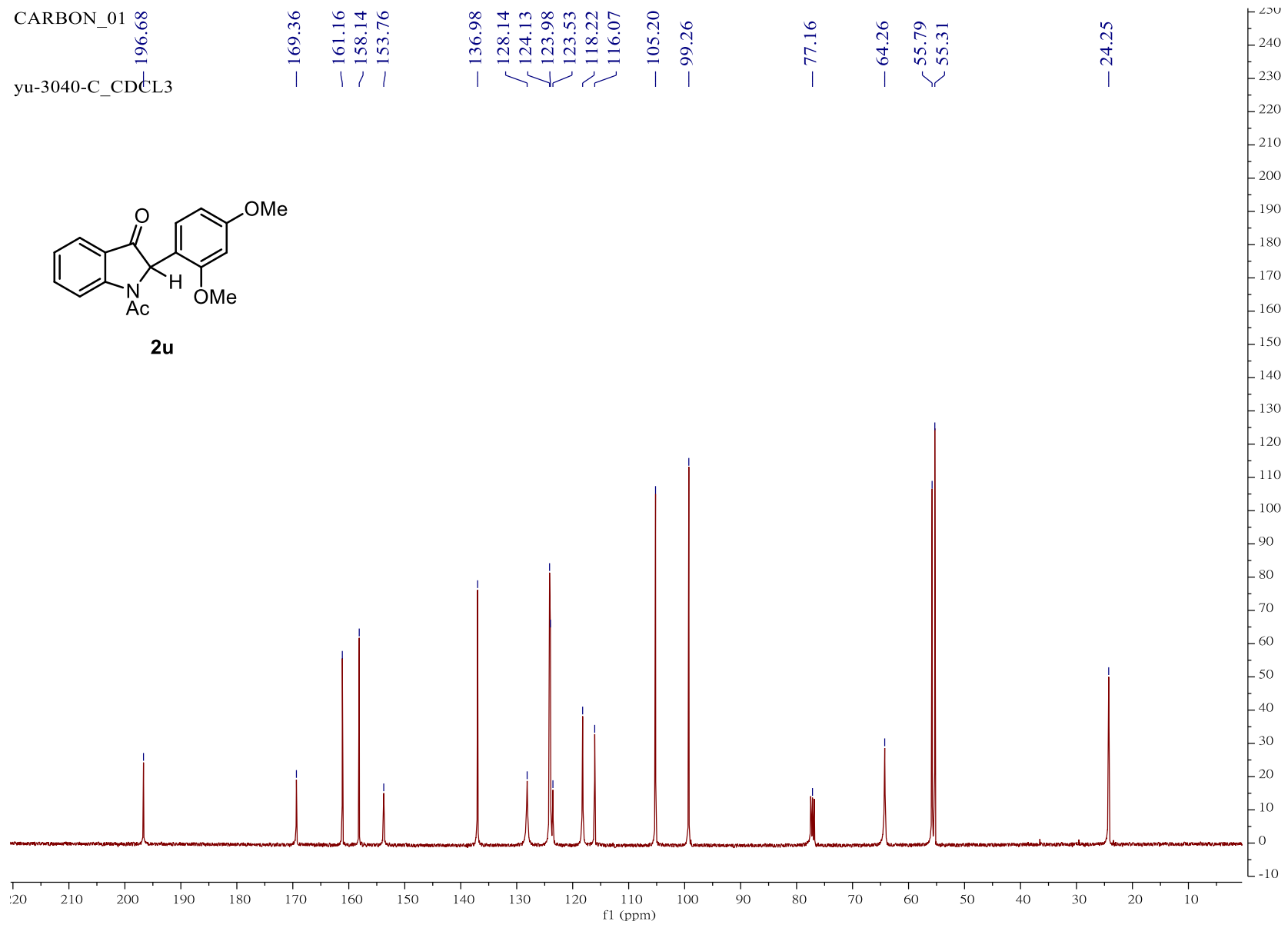


2u



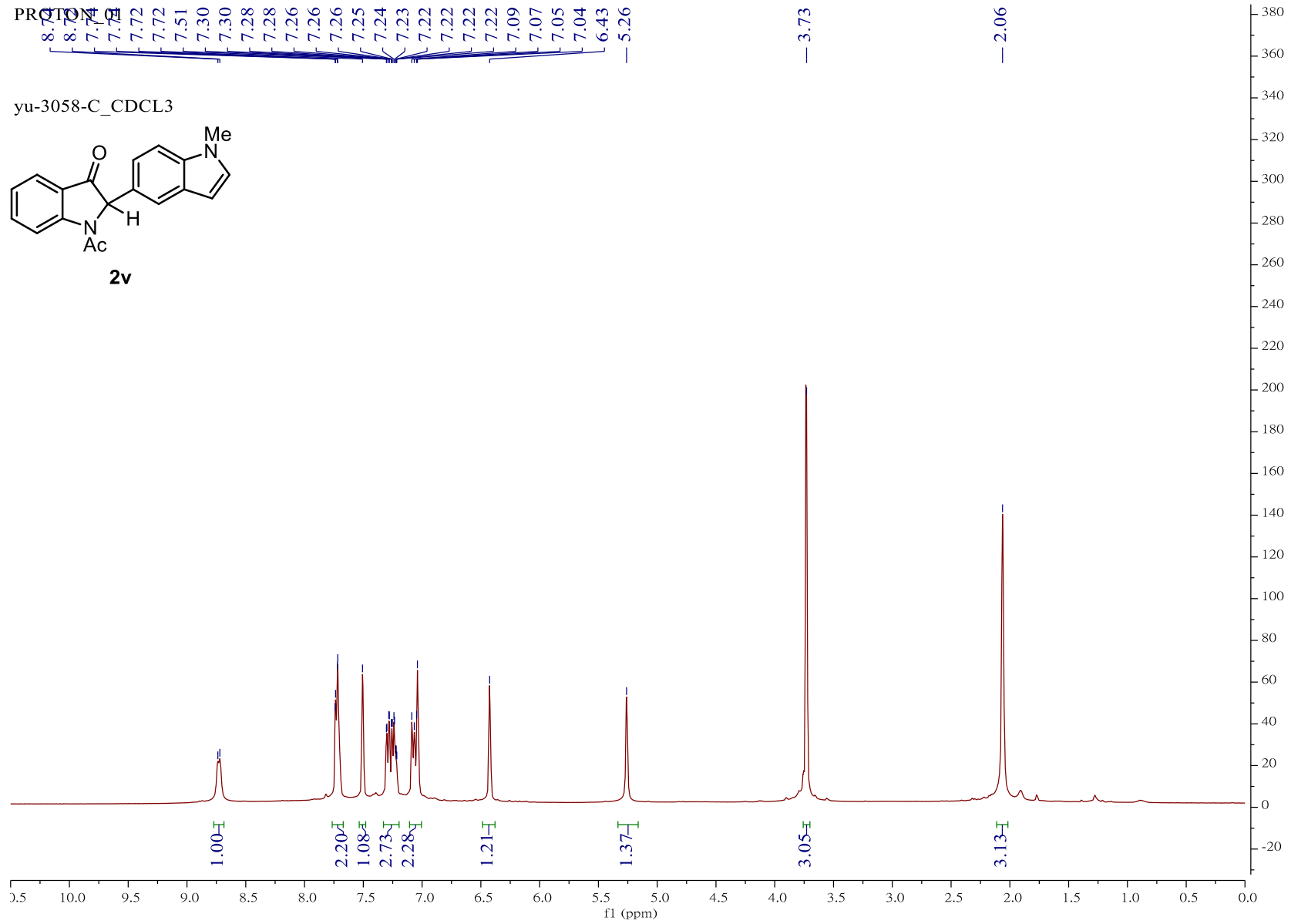
<sup>1</sup>H NMR spectrum of compound 2u

S-79



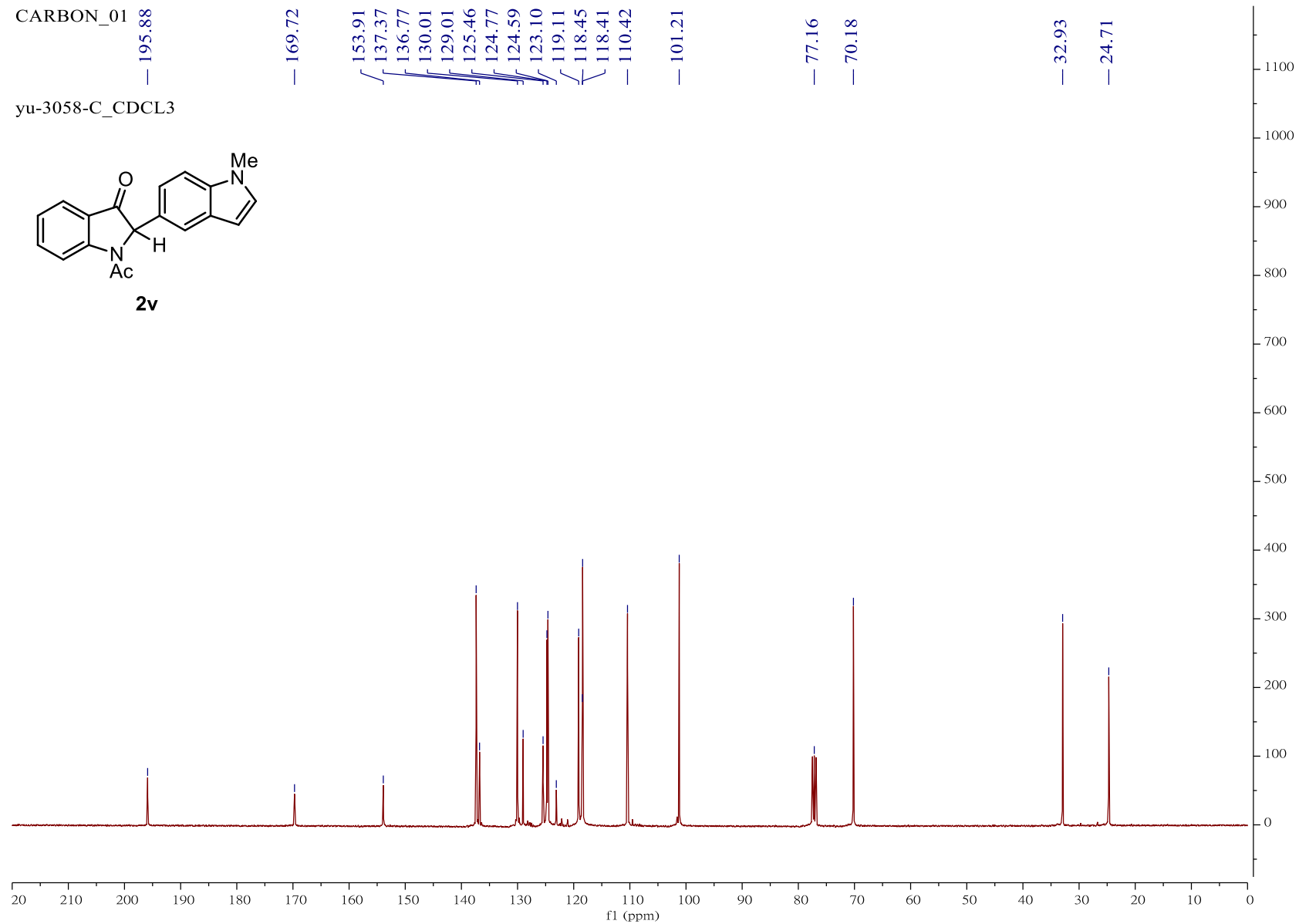
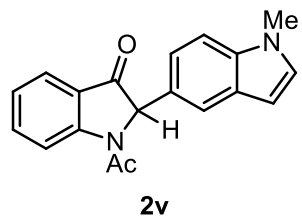
**<sup>13</sup>C NMR spectrum of compound 2u**  
S-80





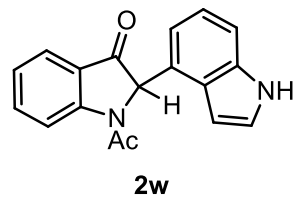
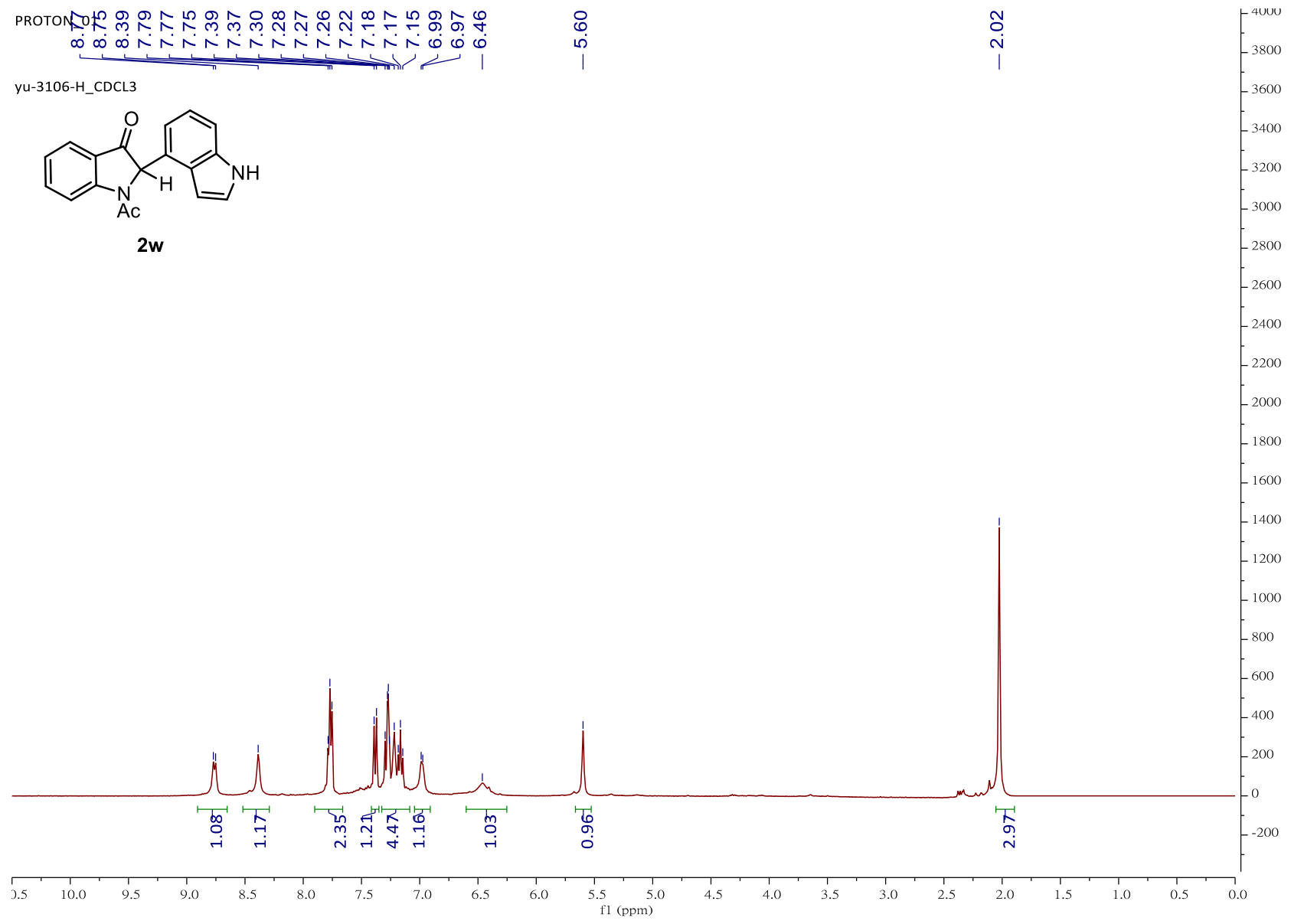
**<sup>1</sup>H NMR spectrum of compound 2v**

CARBON\_01  
yu-3058-C\_CDCL3



**<sup>13</sup>C NMR spectrum of compound 2v**

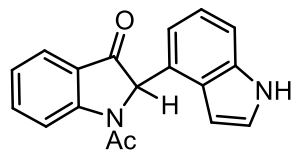
S-82



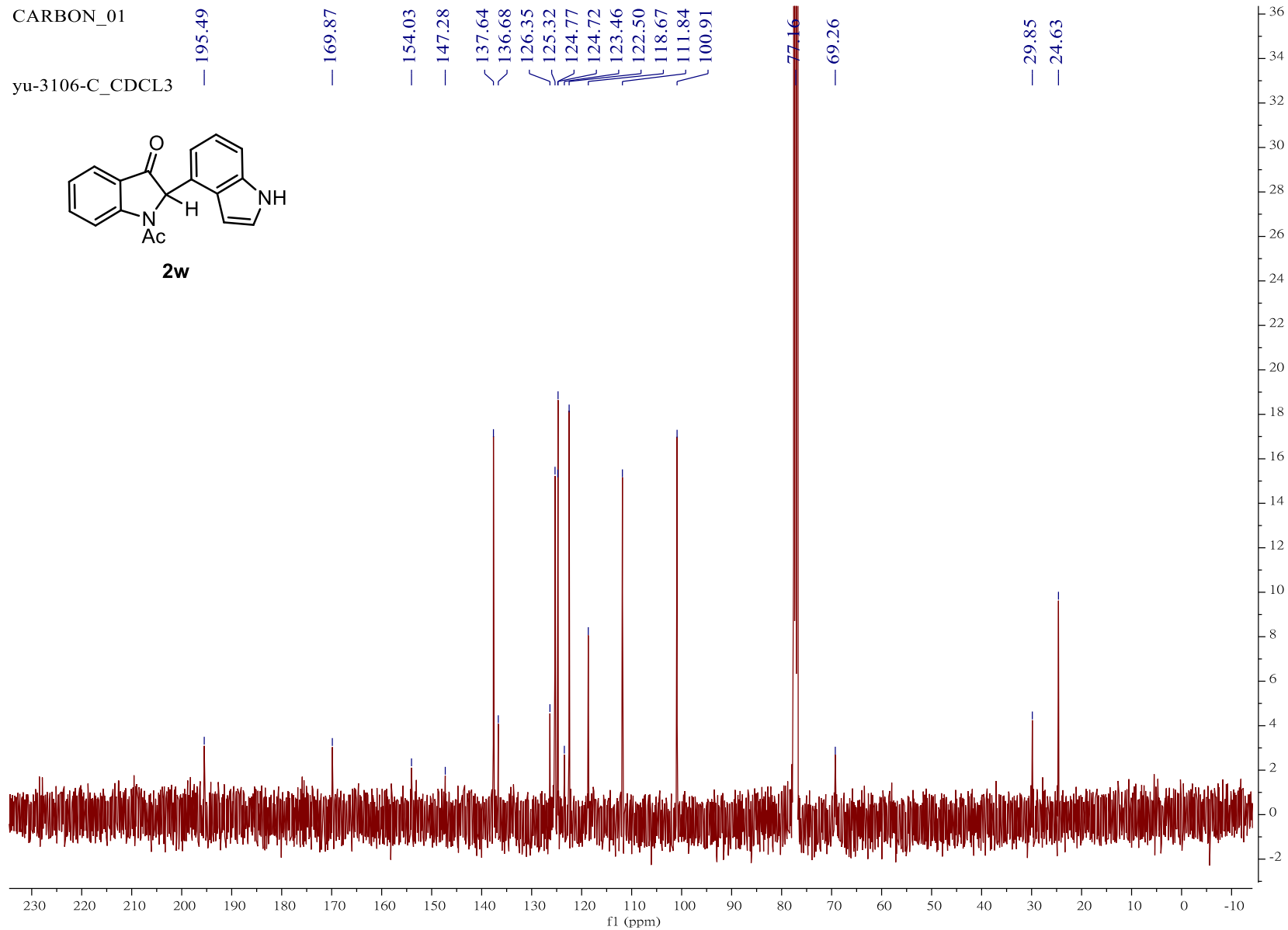
**<sup>1</sup>H NMR spectrum of compound 2w**  
S-83

CARBON\_01

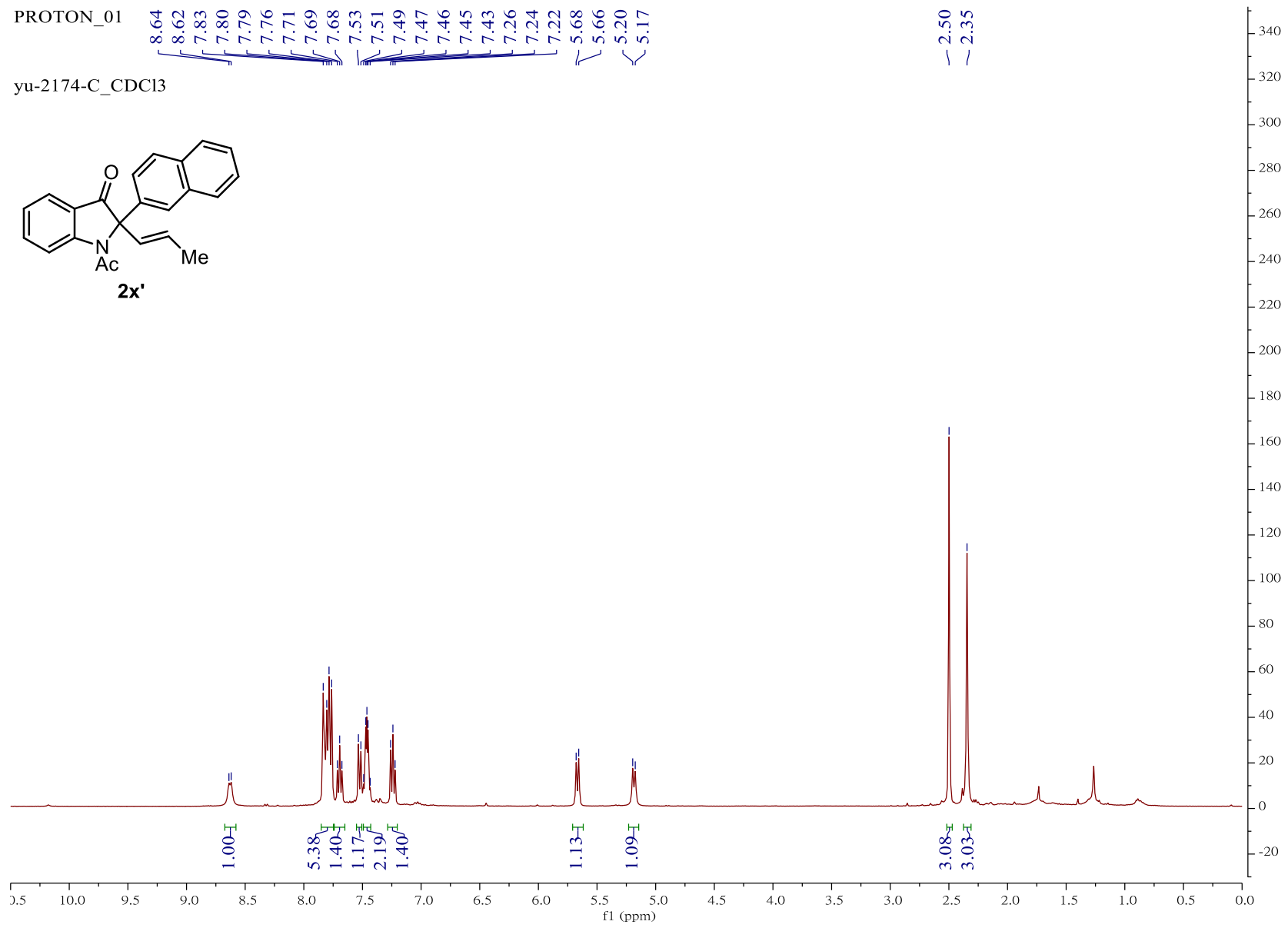
yu-3106-C\_CDCL3



**2w**

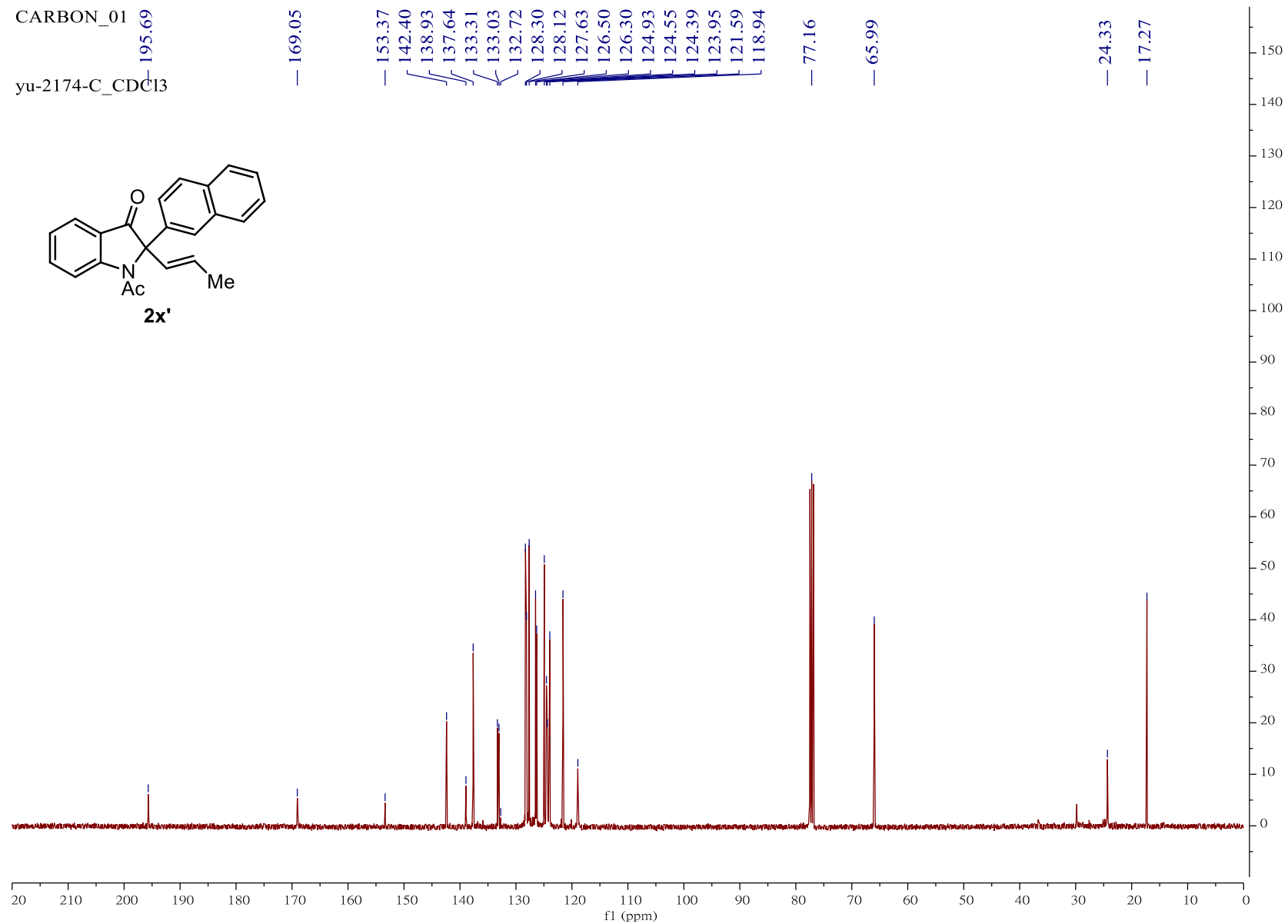
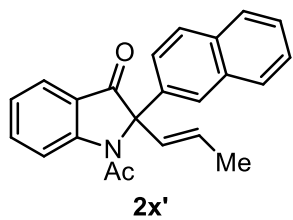


**<sup>13</sup>C NMR spectrum of compound 2w**

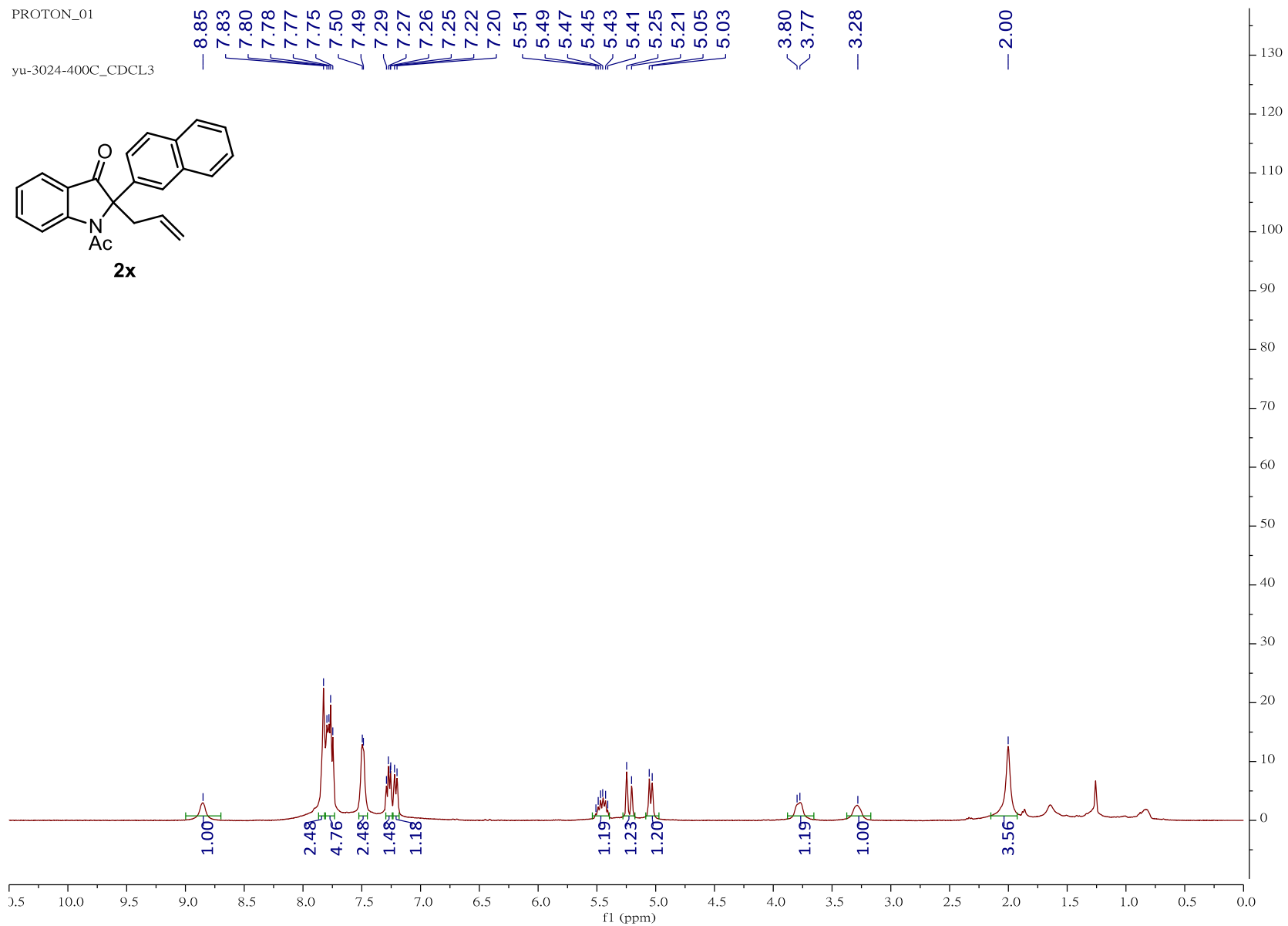


**$^1\text{H}$  NMR spectrum of compound **2x'****  
S-85

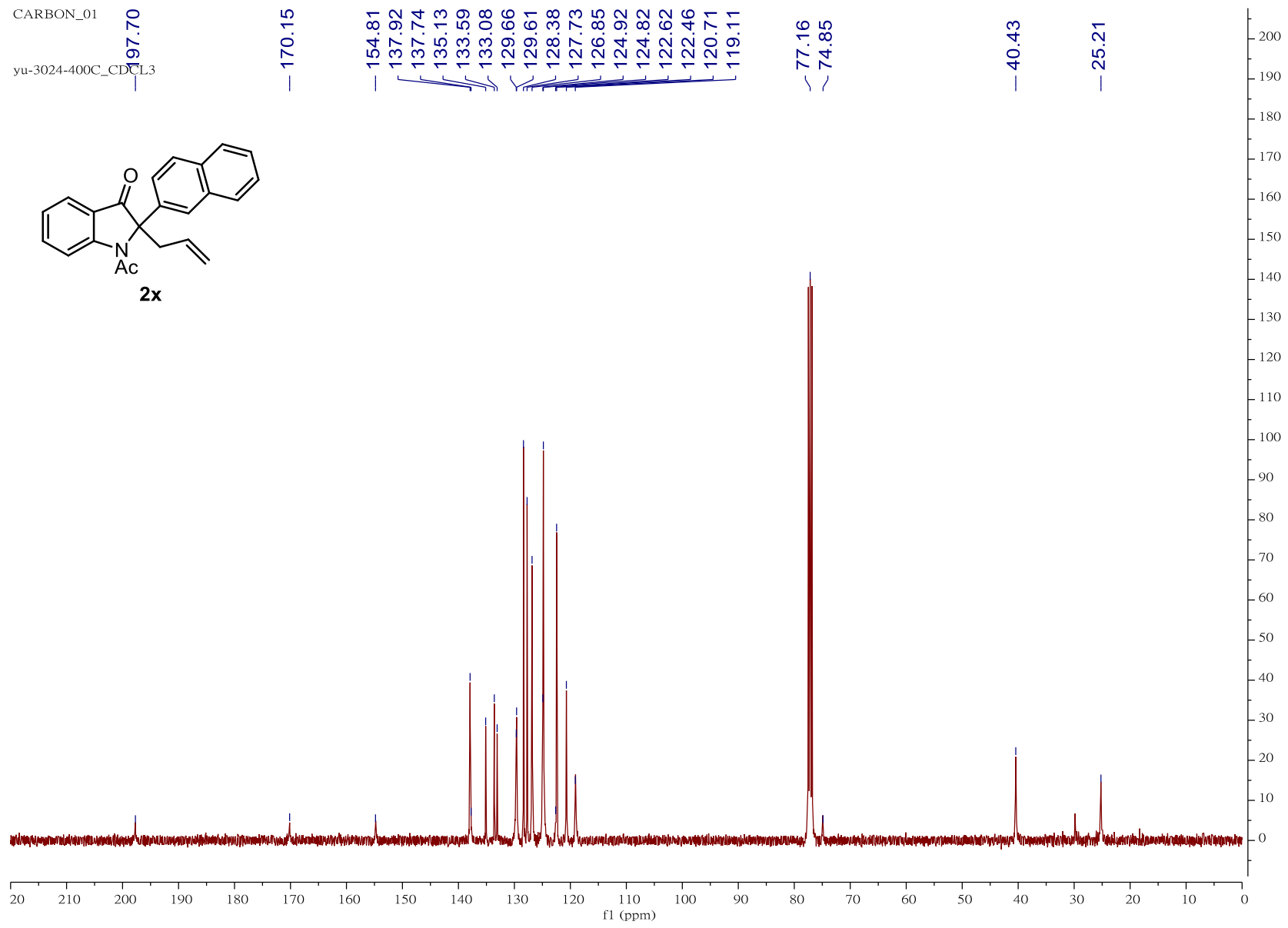
CARBON\_01  
yu-2174-C\_CDC13



**<sup>13</sup>C NMR spectrum of compound 2x'**

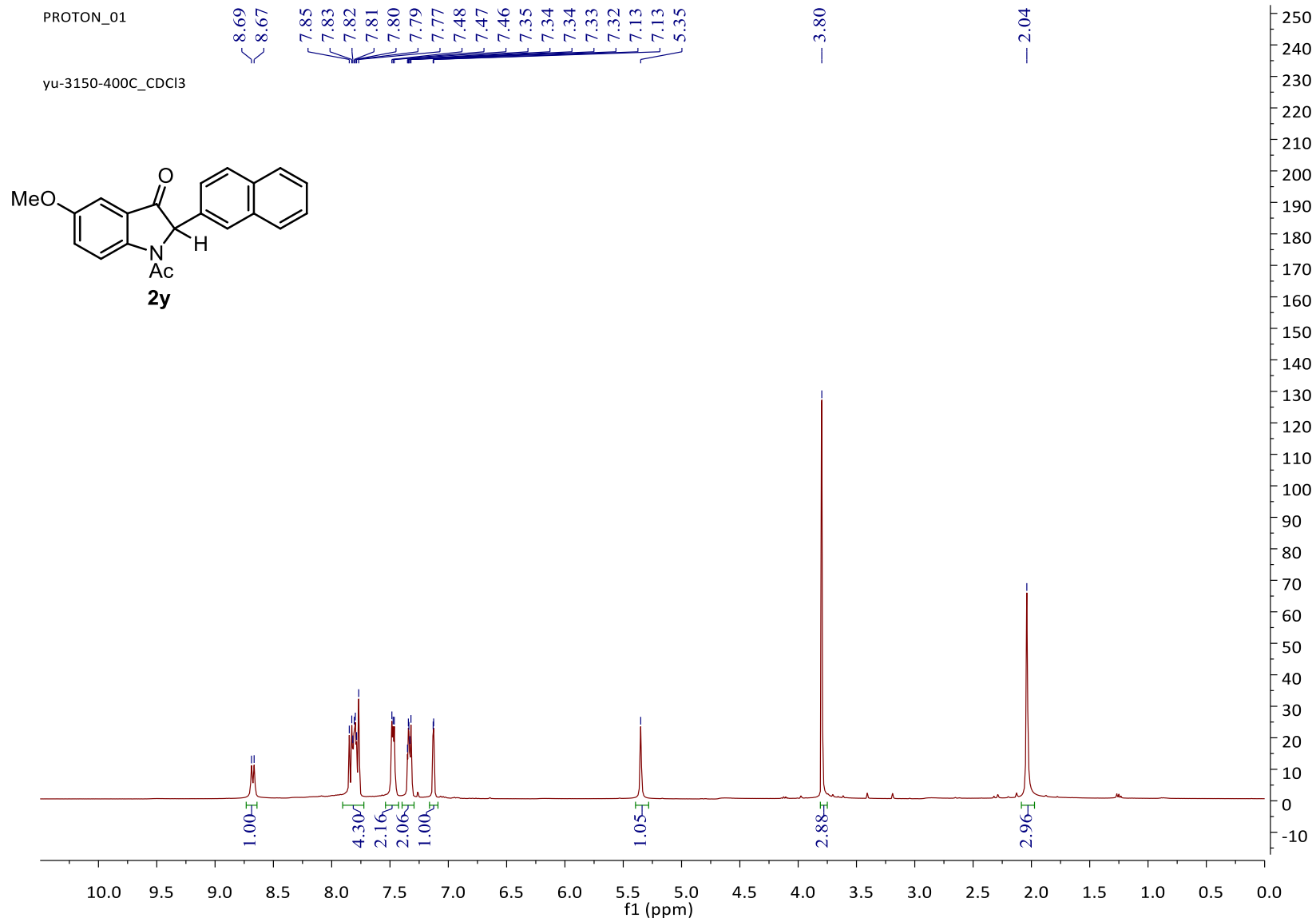


**<sup>1</sup>H NMR spectrum of compound 2x**

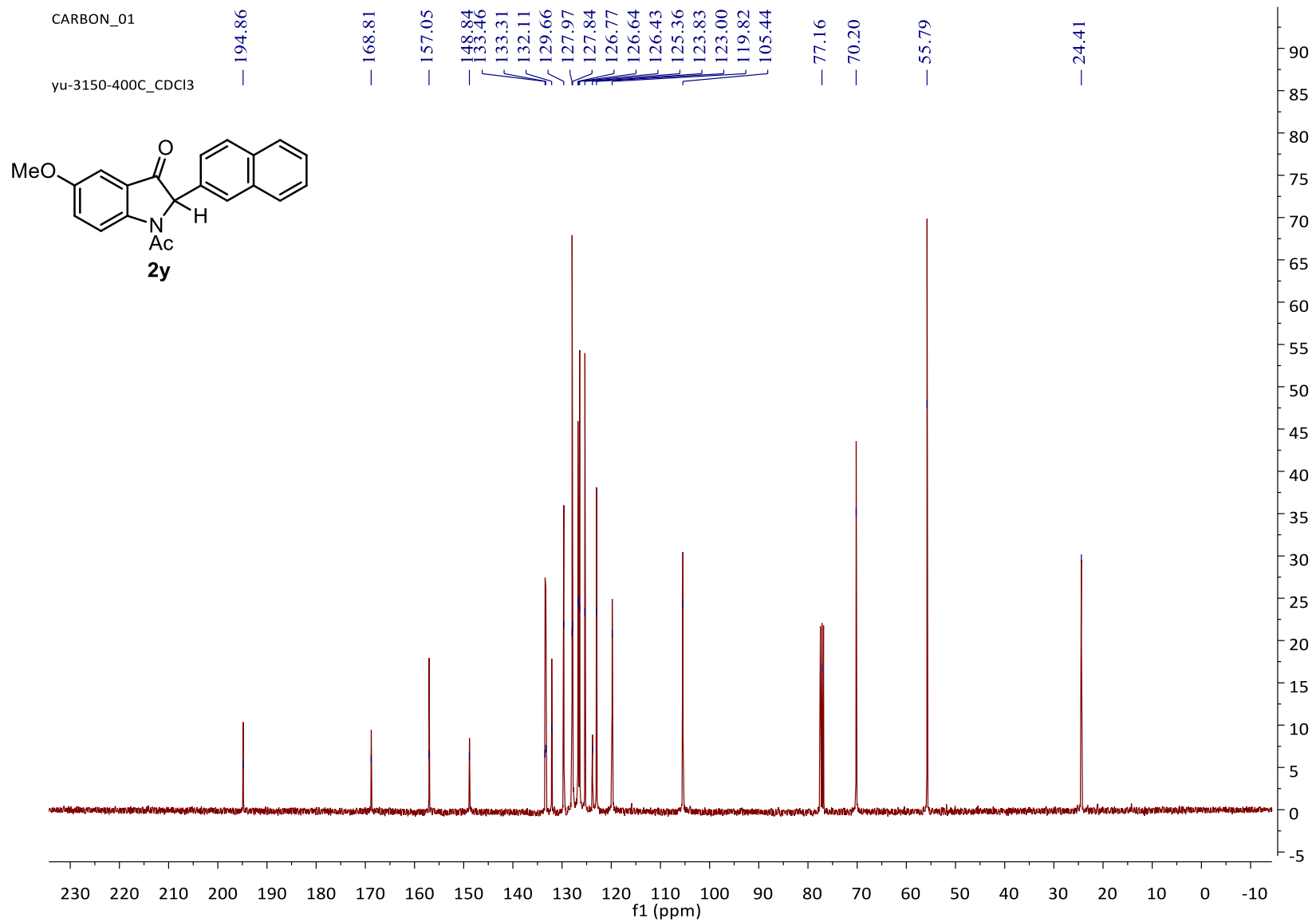


<sup>13</sup>C NMR spectrum of compound 2x

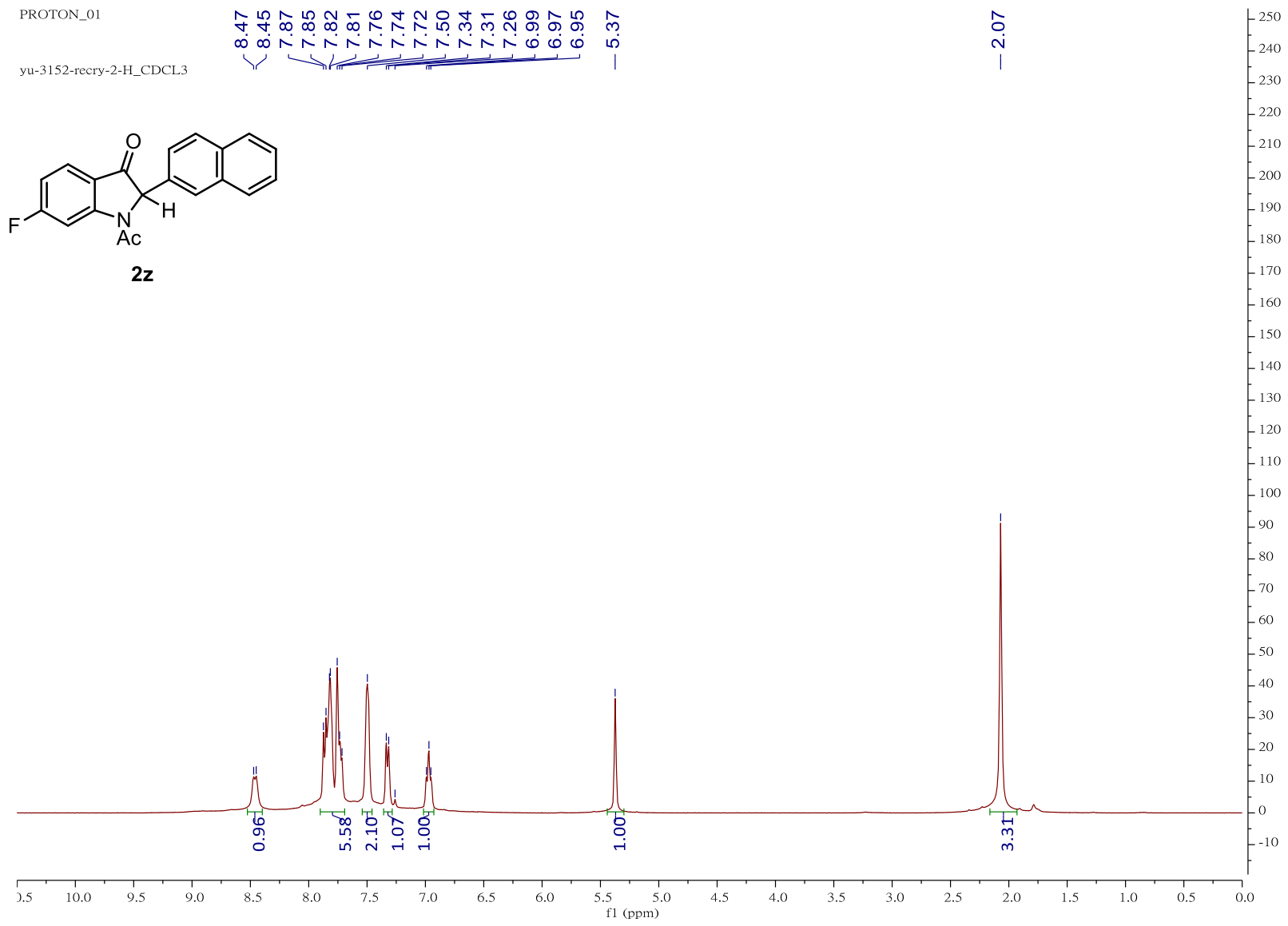




**<sup>1</sup>H NMR spectrum of compound 2y**



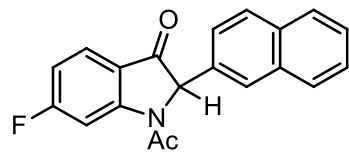
$^{13}\text{C}$  NMR spectrum of compound 2y



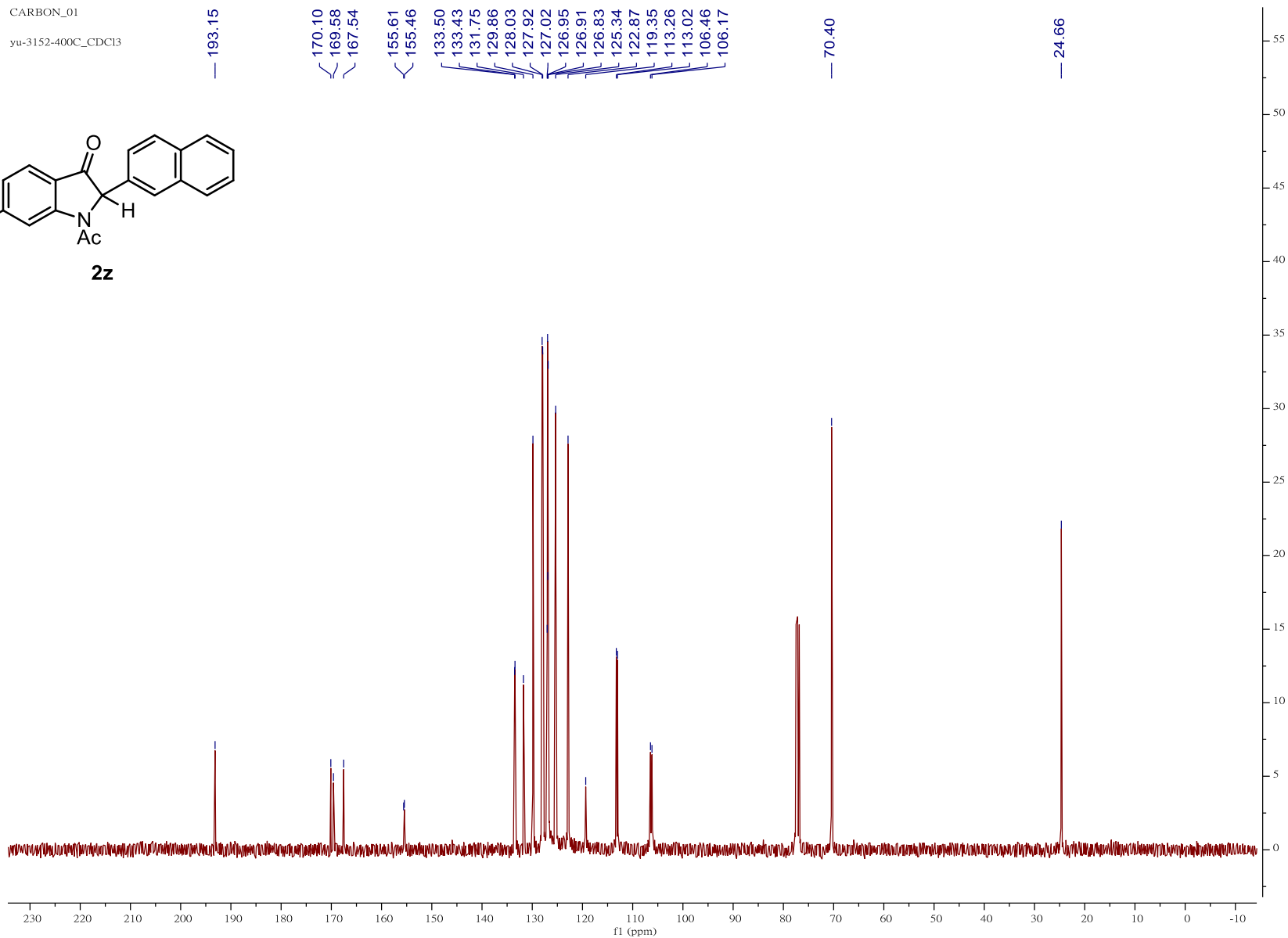
**<sup>1</sup>H NMR spectrum of compound 2z**

CARBON\_01

yu-3152-400C\_CDCl3



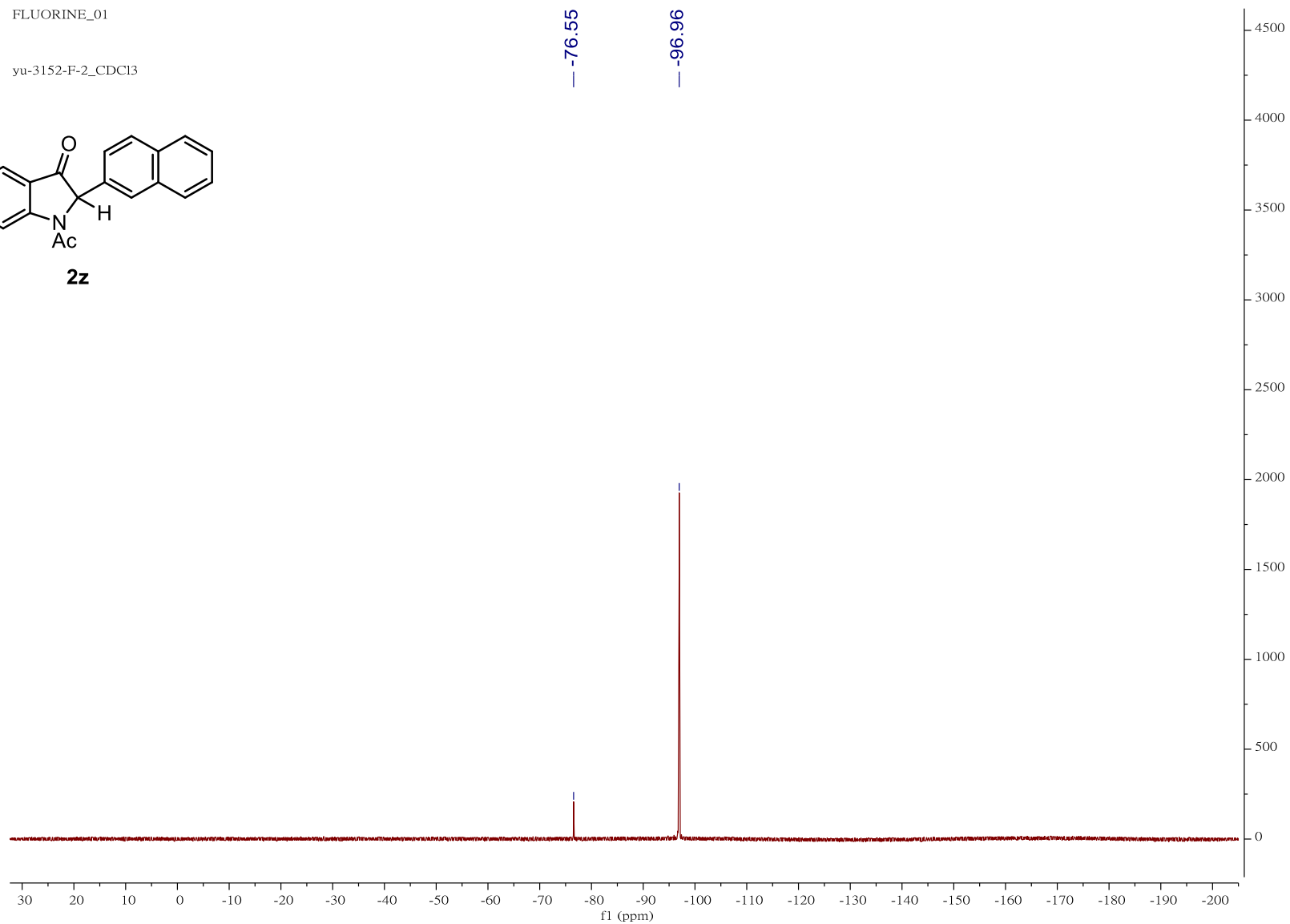
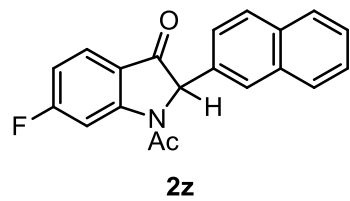
**2z**



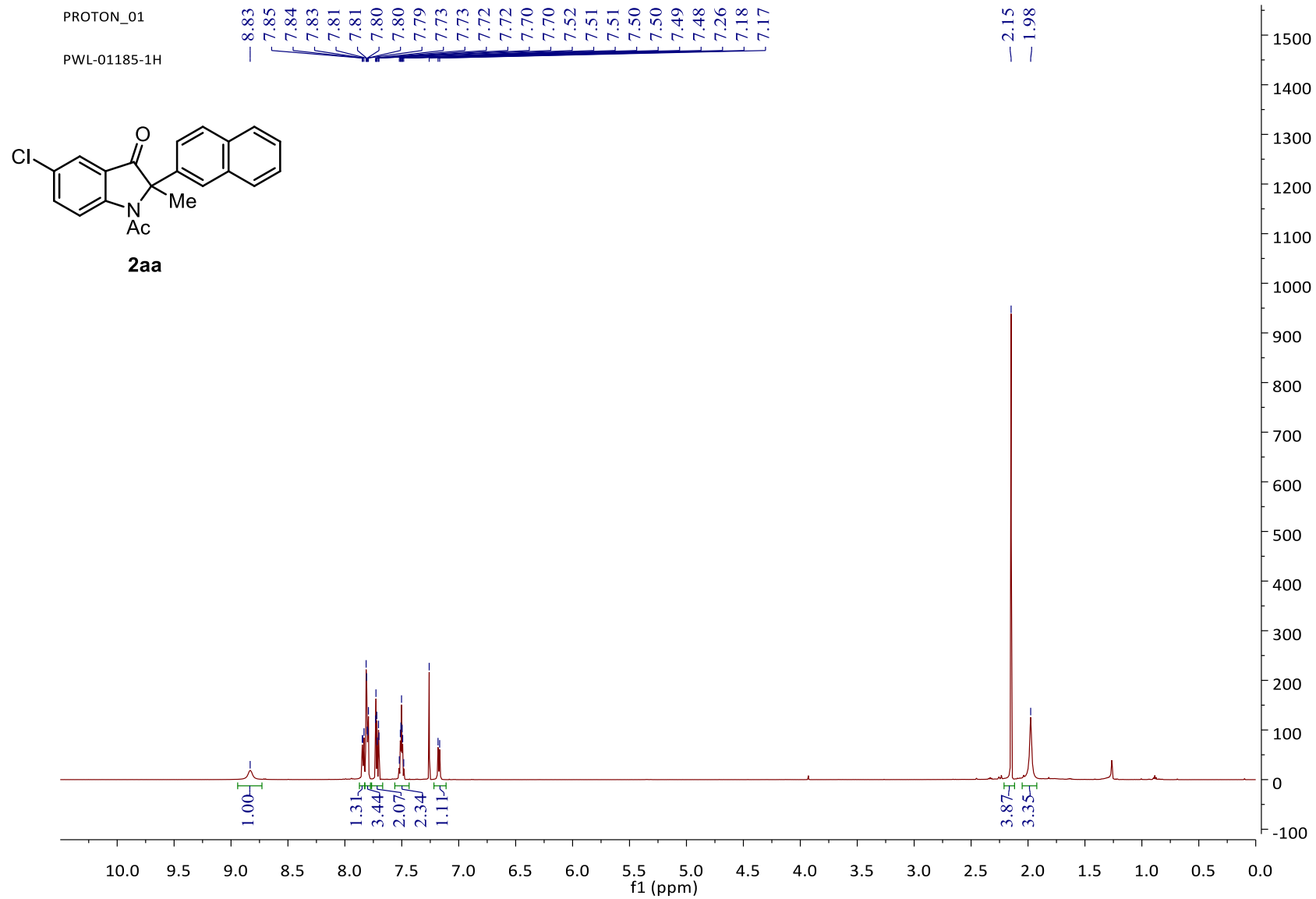
<sup>13</sup>C NMR spectrum of compound 2z

FLUORINE\_01

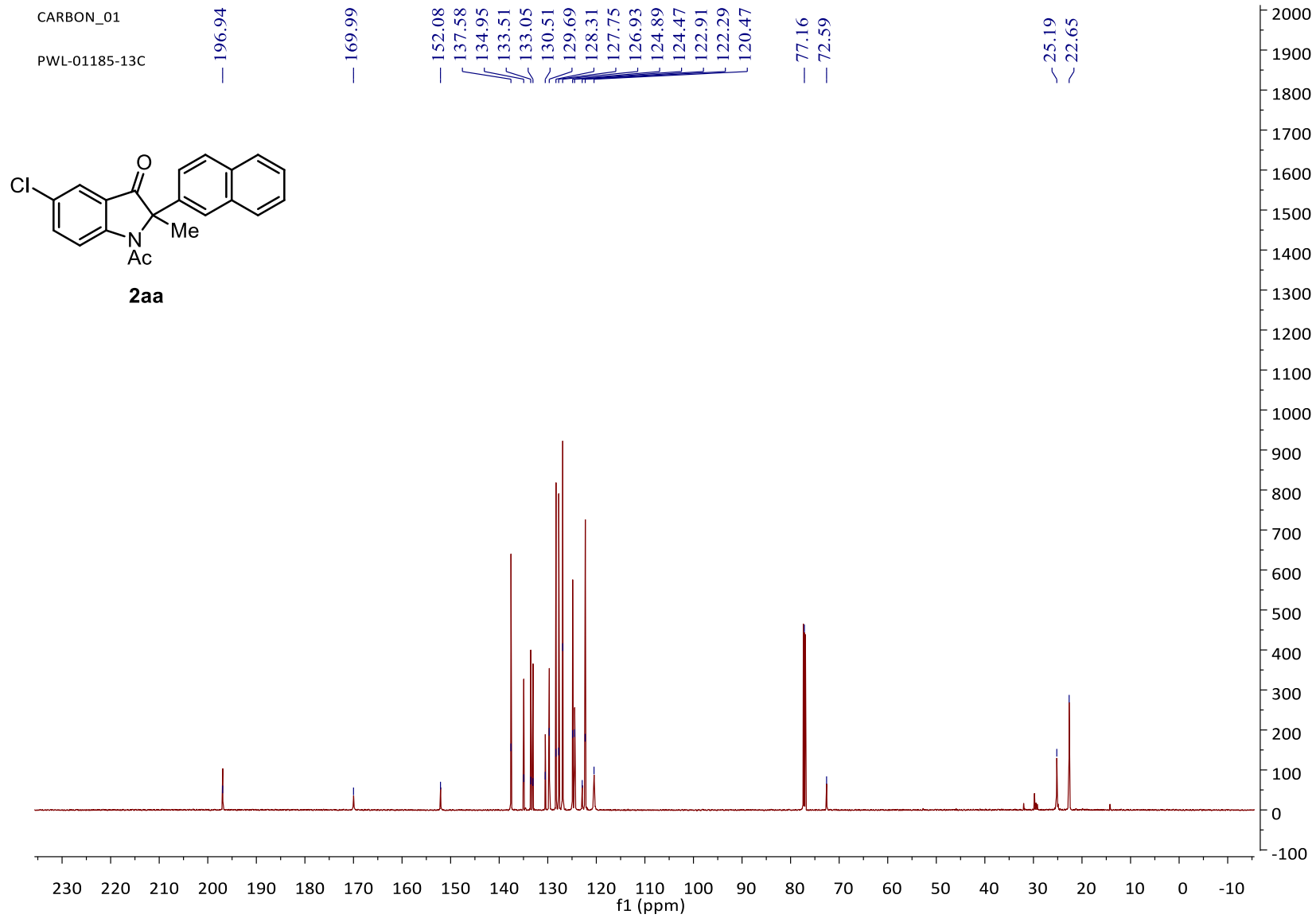
yu-3152-F-2\_CDCl3



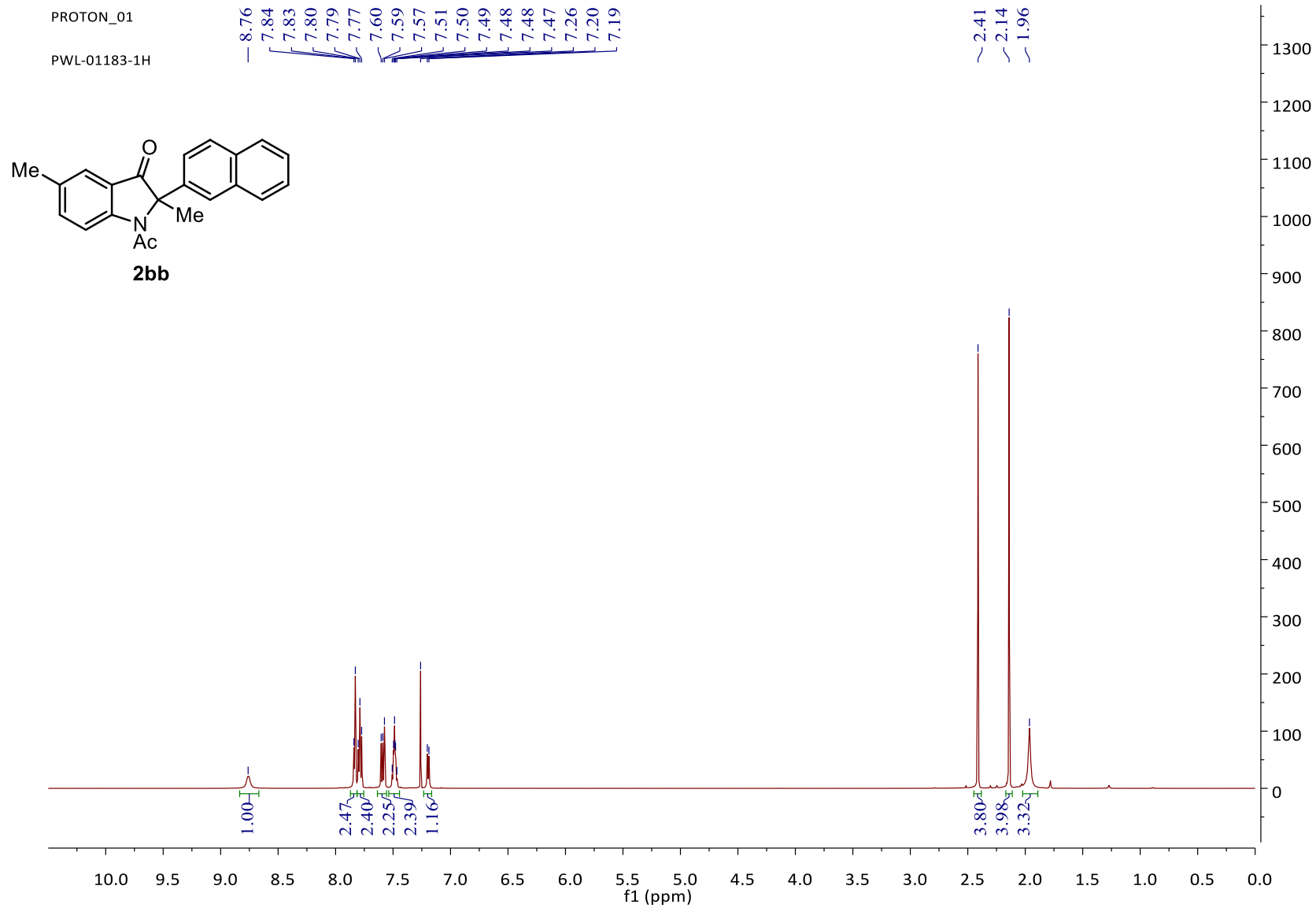
$^{19}\text{F}$  NMR spectrum of compound **2z**



**<sup>1</sup>H NMR spectrum of compound 2aa**

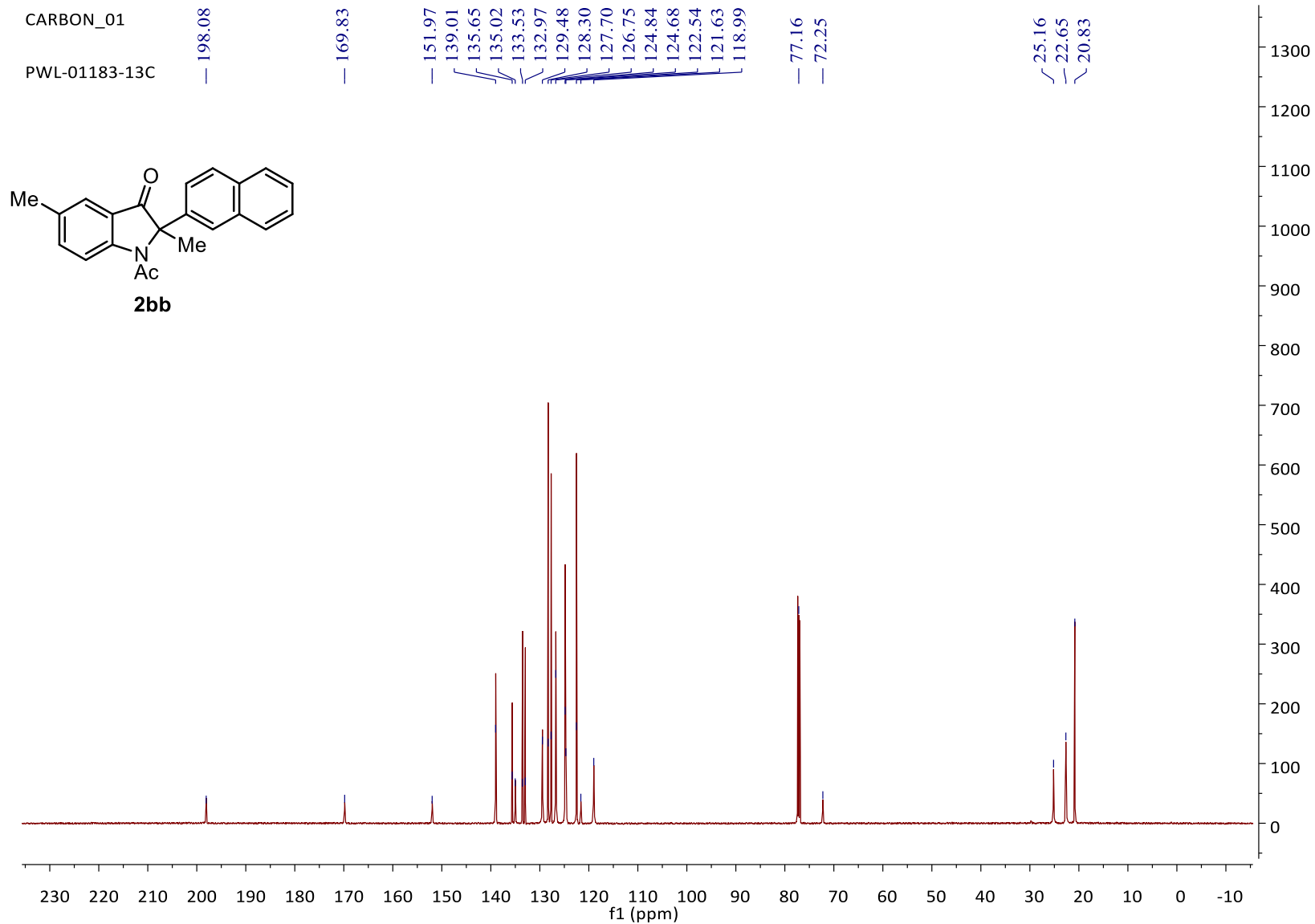


<sup>13</sup>C NMR spectrum of compound 2aa



$^1\text{H}$  NMR spectrum of compound **2bb**

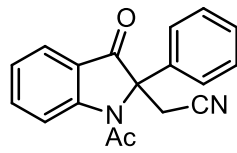




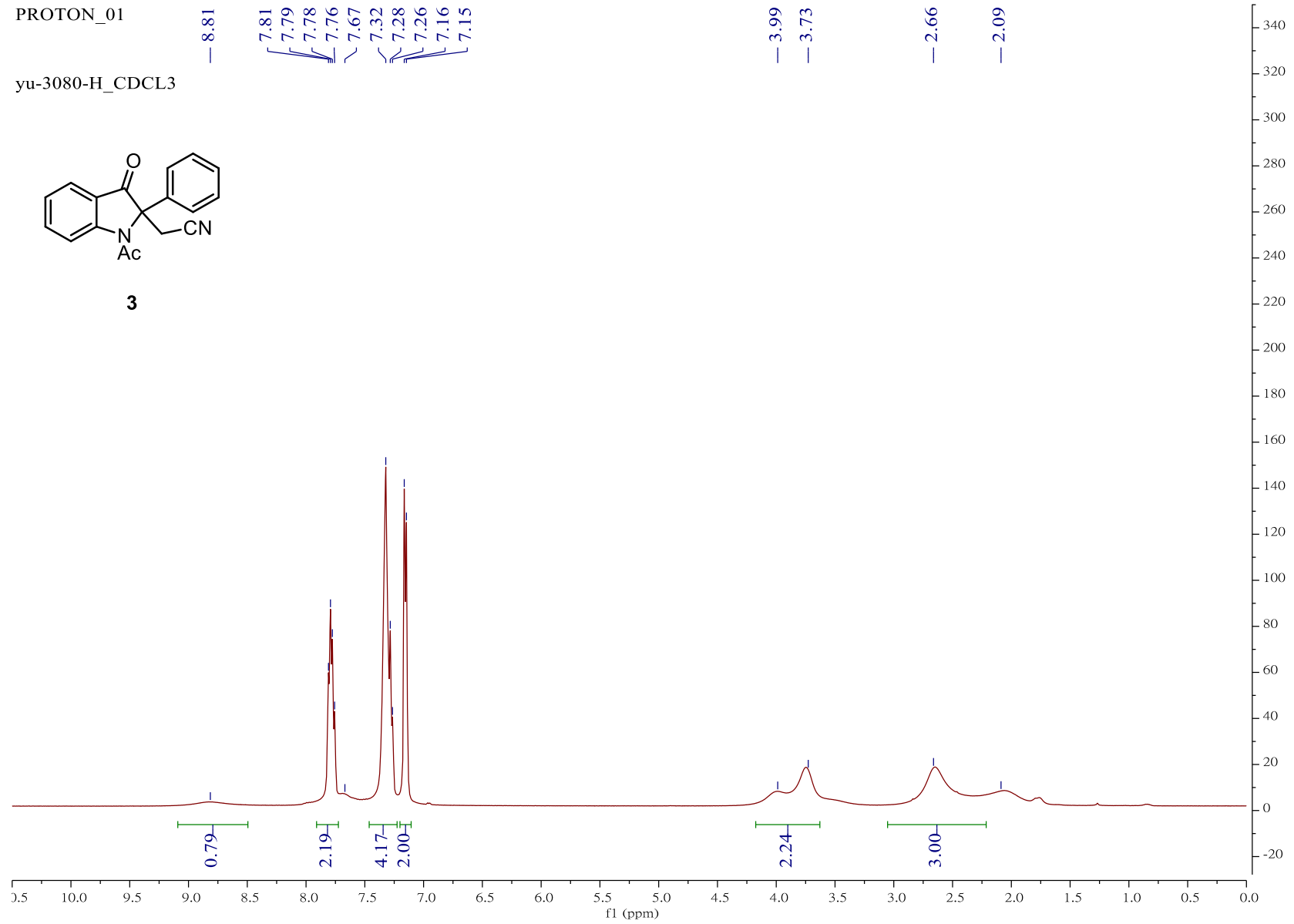
<sup>13</sup>C NMR spectrum of compound 2bb

PROTON\_01

yu-3080-H\_CDCL3

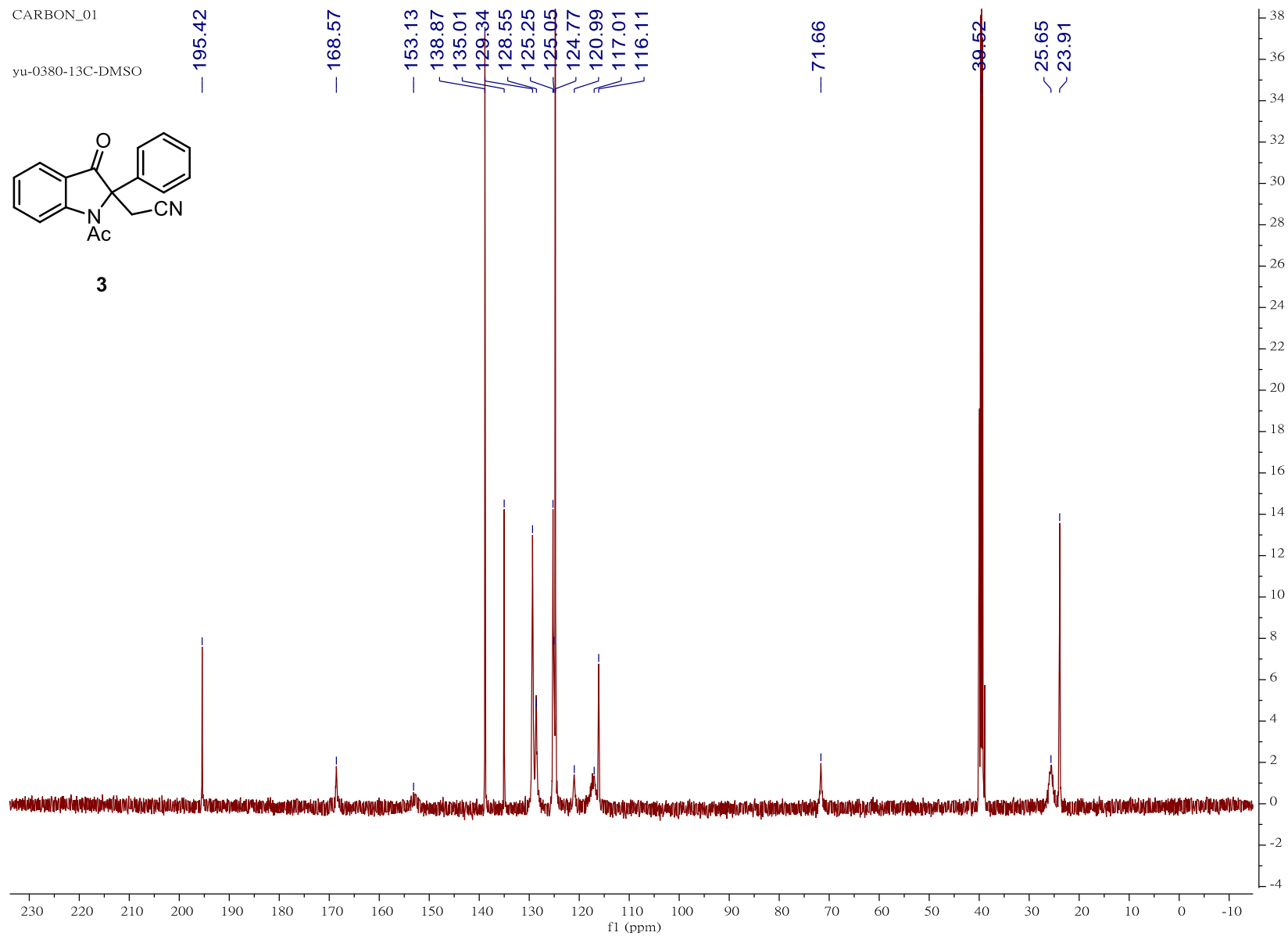


**3**



**<sup>1</sup>H NMR spectrum of compound 3**

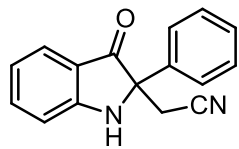
S-98



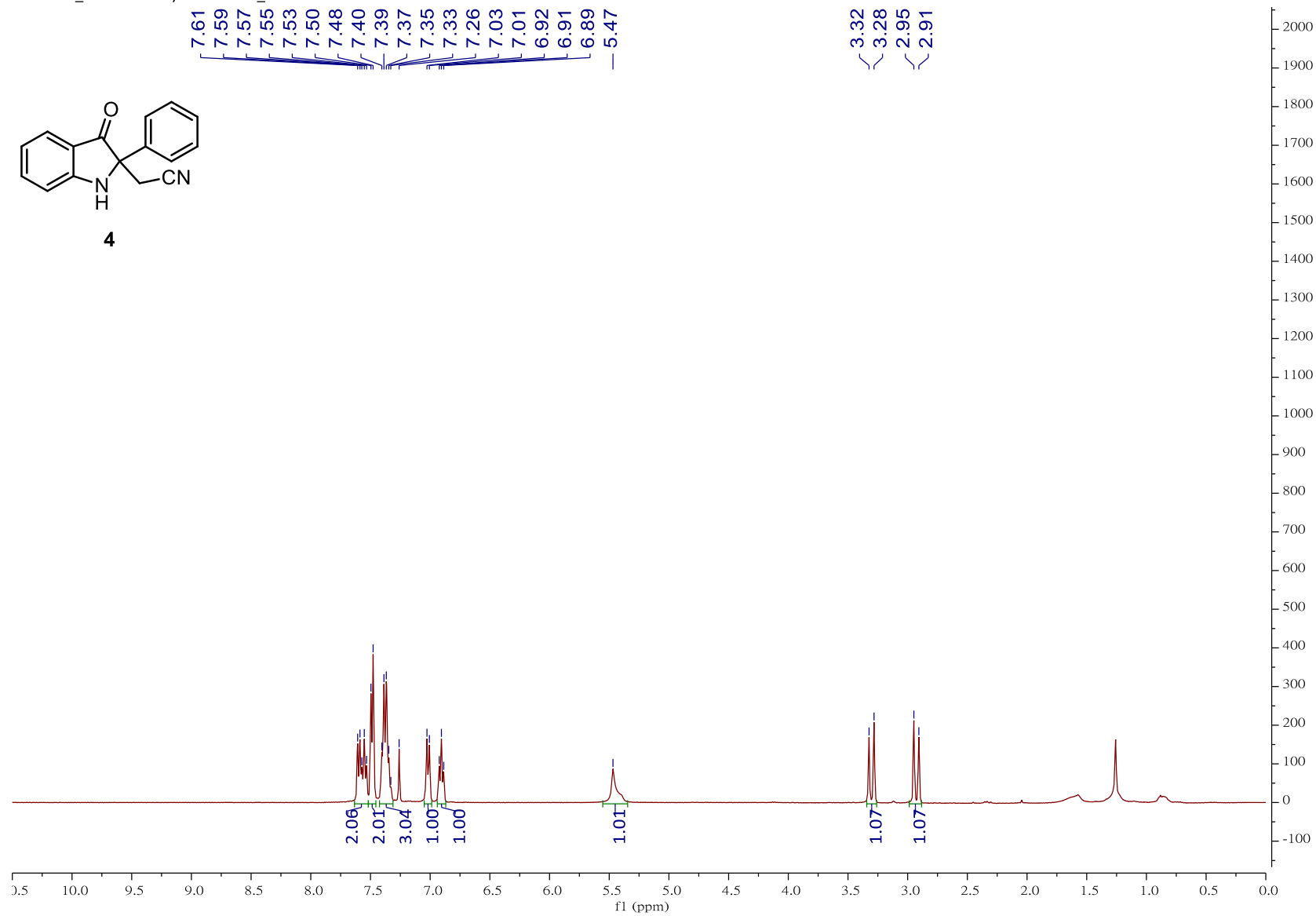
**<sup>13</sup>C NMR spectrum of compound 3**

S-99

PROTON\_01 -- -- yu-3076-4-H\_CDCL3 --



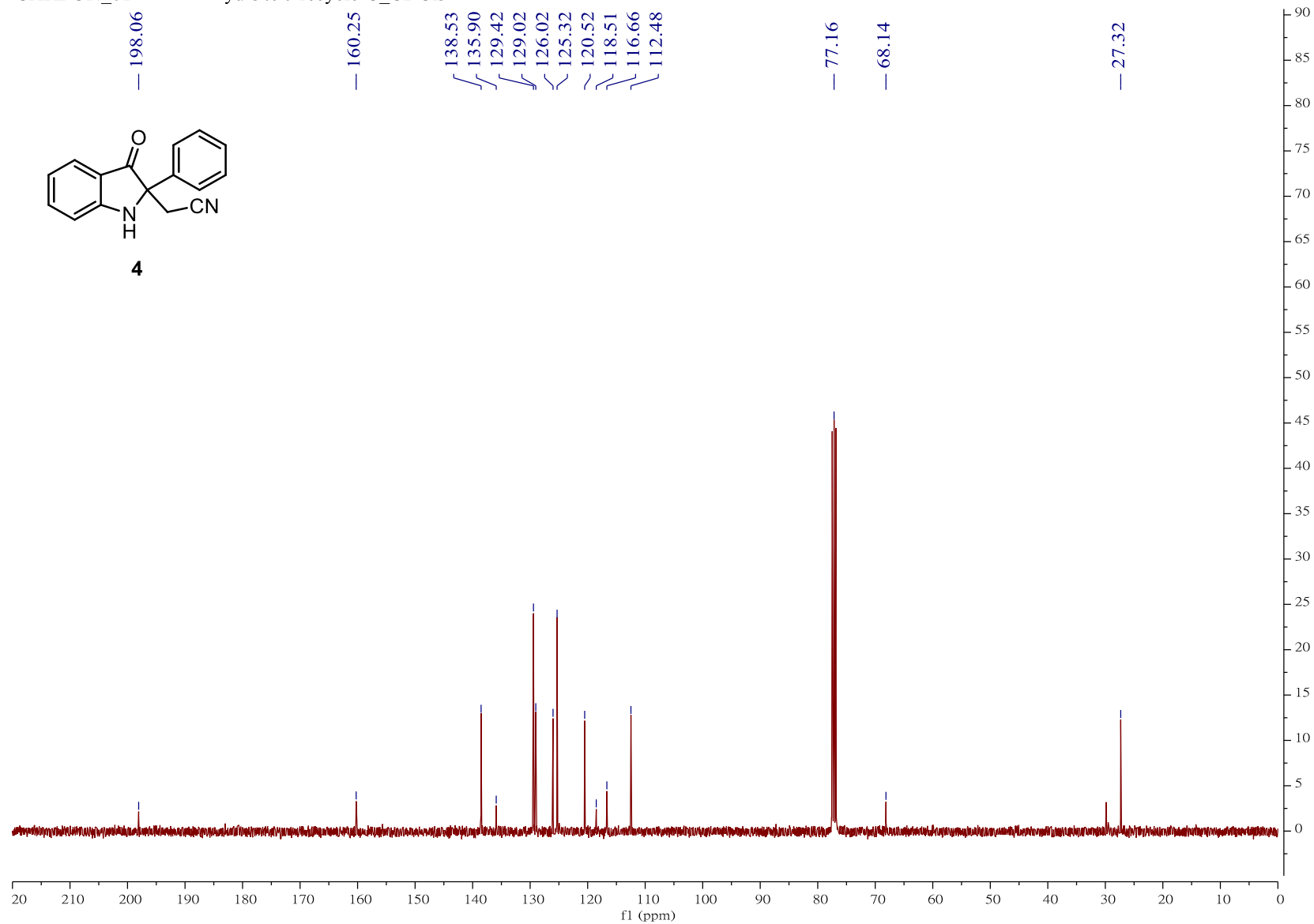
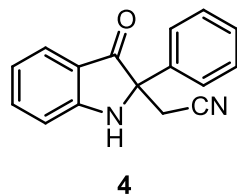
4



**<sup>1</sup>H NMR spectrum of compound 4**

S-100

CARBON\_01 — — — yu-3096-recycle-C\_CDCI3 —



**<sup>13</sup>C NMR spectrum of compound 4**