

SUPPORTING INFORMATION

**Brønsted acid catalyzed Ficini [2 + 2] cycloaddition of ynamides with enones**

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## Part I Experimental Part

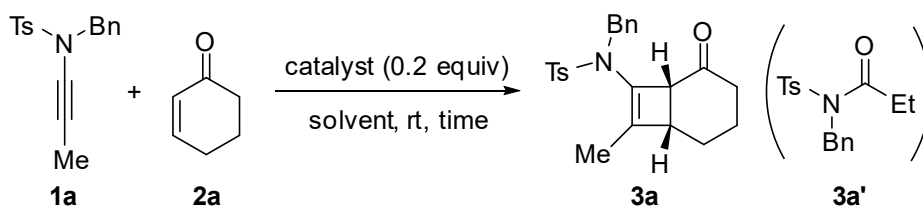
### General Information

Unless otherwise indicated, all starting materials were obtained from commercial supplies and used as received. Ynamides **1a**,<sup>1</sup> **1b**,<sup>2</sup> **1c**,<sup>3</sup> **1d**,<sup>4</sup> **1e**,<sup>5</sup> **1f**,<sup>6</sup> **1g**,<sup>7</sup> **1h**,<sup>6</sup> **1i**,<sup>8</sup> **1j**,<sup>8</sup> **1k**,<sup>1</sup> **1l**,<sup>1</sup> **1m**,<sup>9</sup> **1n**,<sup>1</sup> **1o**,<sup>10</sup> **1p**,<sup>11</sup> **1q**,<sup>1</sup> **1r**,<sup>12</sup> and **1s**<sup>13</sup> were known compounds and synthesized according to the literature, and the data were matched with the reported values. All reactions were performed in oven-dried glassware under a nitrogen atmosphere unless otherwise stated. All catalysts were added in the glove box. Solvents were distilled prior to use. Chromatographic separations were performed using 200~300 mesh silica gel. <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained on a Bruker's Ascend<sup>TM</sup> 400 NMR spectrometer using CDCl<sub>3</sub> as the solvent with TMS or residual solvent as standard unless otherwise noted. ABq represents the splitting of two hydrogens on the same carbon. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz) spectra were reported in ppm with the internal chloroform signal at 77.2 ppm as the standard. Infrared spectra were obtained on a PerkinElmer FT/IR spectrophotometer and relative intensities are expressed qualitatively as s (strong), m (medium), and w (weak). TLC analysis was performed using 254 nm polyester-backed plates and visualized using UV and KMnO<sub>4</sub> stain. High-resolution mass spectra (HRMS) were performed on a Bruker MicrOTOF-Q II mass spectrometer.

### 1.1 Optimization of the Reaction Conditions.

Entry 13 (1.0 mmol synthetic method): To an oven-dried tube was added ynamide **1a**<sup>1</sup> (358.9 mg, 1.20 mmol), cyclohexenone **2a** (96.13 mg, 1.00 mmol), DCE (5.0 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (56.2 mg, 0.20 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was filtered through a short pad of silica gel. Then the filtrate was concentrated in vacuo and purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether/EtOAc] to afford cyclobutenamide **3a** (356.1 mg, 0.90 mmol) in 90% yield.

**Table S1. Optimization of the Reaction Conditions**

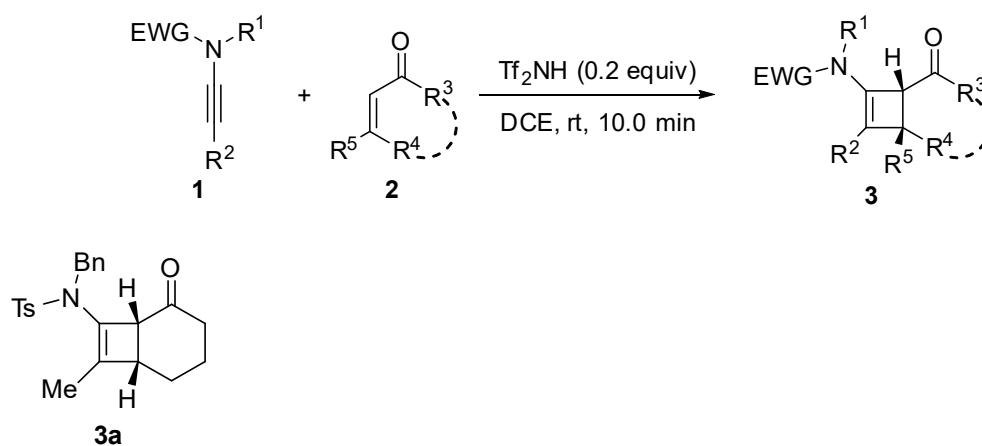


entry <sup>a</sup>	catalyst	solvent	time (min)	yield <sup>b</sup> (%)	
				<b>3a</b>	<b>3a'</b>
1	Tf <sub>2</sub> O	CH <sub>2</sub> Cl <sub>2</sub>	10.0	55	30
2	TfOMe	CH <sub>2</sub> Cl <sub>2</sub>	10.0	70	0
3	TMSOTf	CH <sub>2</sub> Cl <sub>2</sub>	10.0	75	20
4	TBSOTf	CH <sub>2</sub> Cl <sub>2</sub>	10.0	75	12
5	TIPSOTf	CH <sub>2</sub> Cl <sub>2</sub>	10.0	74	18
6	TfOH	CH <sub>2</sub> Cl <sub>2</sub>	10.0	64	28
7	Tf <sub>2</sub> NH	CH <sub>2</sub> Cl <sub>2</sub>	10.0	90	trace
8	BF <sub>3</sub> •Et <sub>2</sub> O	CH <sub>2</sub> Cl <sub>2</sub>	5.0	87	10
9	Tf <sub>2</sub> NH	toluene	10.0	85	9
10	Tf <sub>2</sub> NH	1,4-dioxane	10.0	63	13
11	Tf <sub>2</sub> NH	THF	25.0	18	22
12	Tf <sub>2</sub> NH	DCE	10.0	93	trace
13 <sup>c</sup>	Tf <sub>2</sub> NH	DCE	10.0	90	trace

<sup>a</sup>Unless otherwise noted, reactions were carried out using **1a** (0.36 mmol) and **2a** (0.30 mmol) with catalyst (0.06 mmol) in solvent (1.5 mL) under N<sub>2</sub>. <sup>b</sup>Isolated yields. <sup>c</sup>**1a** (1.20 mmol) and **2a** (1.00 mmol) were added.

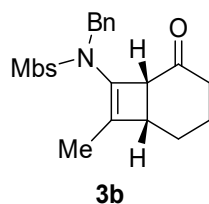
## 1.2 Reaction Scope of the [2 + 2] Cycloaddition.

Cyclobutenamides **3a**,<sup>2</sup> **3b**,<sup>2</sup> **3d**,<sup>2</sup> **3e**,<sup>2</sup> **3u**,<sup>14</sup> and **3z**<sup>2</sup> were known compounds, the data were matched with reported values. Cyclobutenamides **3c**, **3f**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, **3m**, **3n**, **3o-3t**, **3v-3y**, **3aa**, and **3ab** were new compounds.



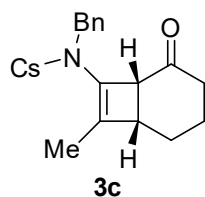
To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3a** (110.1 mg, 0.28 mmol) in 93% yield.

**3a**: *R<sub>f</sub>* = 0.19 [6:1 petroleum ether/EtOAc]; white solid; mp = 114–115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (d, 2H, *J* = 8.3 Hz), 7.34-7.27 (m, 7H), 4.63, 4.56 (ABq, 2H, *J<sub>AB</sub>* = 15.0 Hz), 3.18 (dq, 1H, *J* = 4.6, 2.3 Hz), 2.75 (br, 1H), 2.45 (s, 3H), 1.81-1.77 (m, 2H), 1.68-1.67 (m, 3H), 1.45-1.39 (m, 2H), 1.33-1.22 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 210.7, 144.1, 144.0, 136.6, 136.5, 129.9, 128.6, 127.9, 127.7, 127.6, 126.7, 53.9, 51.3, 40.5, 38.6, 23.8, 21.8, 17.1, 12.6. Spectral data are in agreement with literature values<sup>2</sup>.



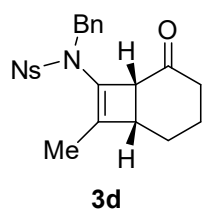
To an oven-dried tube was added ynamide **1b**<sup>2</sup> (113.5 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3b** (114.7 mg, 0.28 mmol) in 93% yield.

**3b**: *R<sub>f</sub>* = 0.23 [5:1 petroleum ether/EtOAc]; white solid; mp = 128–129 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.79 (d, 2H, *J* = 8.9 Hz), 7.33-7.27 (m, 5H), 7.00 (d, 2H, *J* = 8.9 Hz), 4.61, 4.55 (ABq, 2H, *J<sub>AB</sub>* = 15.0 Hz), 3.89 (s, 3H), 3.19 (dq, 1H, *J* = 4.7, 2.3 Hz), 2.75 (br, 1H), 1.88-1.75 (m, 3H), 1.68-1.67 (m, 3H), 1.48-1.39 (m, 2H), 1.28-1.22 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 210.7, 163.3, 144.0, 136.5, 131.2, 129.7, 128.6, 127.9, 127.7, 126.9, 114.4, 55.8, 54.0, 51.3, 40.5, 38.6, 23.8, 17.1, 12.6. Spectral data are in agreement with literature values<sup>2</sup>.



To an oven-dried tube was added ynamide **1c**<sup>3</sup> (114.8 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3c** (103.8 mg, 0.25 mmol) in 83% yield.

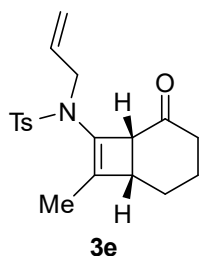
**3c**:  $R_f$  = 0.33 [5:1 petroleum ether/EtOAc]; white solid; mp = 114–115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (d, 2H,  $J$  = 8.6 Hz), 7.51 (d, 2H,  $J$  = 8.6 Hz), 7.34-7.27 (m, 5H), 4.63, 4.56 (ABq, 2H,  $J_{AB}$  = 14.9 Hz), 3.19 (dq, 1H,  $J$  = 4.6, 2.4 Hz), 2.76 (br, 1H), 1.86-1.77 (m, 3H), 1.66-1.65 (m, 3H), 1.50-1.43 (m, 2H), 1.31-1.22 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 210.4, 144.9, 139.7, 138.1, 136.1, 129.5, 129.1, 128.7, 128.0, 127.9, 126.3, 53.7, 51.5, 40.7, 38.6, 23.8, 17.2, 12.6; IR (neat) (cm<sup>-1</sup>) 2928m, 2865w, 1686s, 1521m, 1294w, 626s; HRMS (ESI):  $m/z$  calcd for C<sub>22</sub>H<sub>23</sub>ClNO<sub>3</sub>S [M + H]<sup>+</sup> 416.1082, found 416.1080.



To an oven-dried tube was added ynamide **1d**<sup>4</sup> (118.9 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3d** (98.2 mg, 0.23 mmol) in 77% yield.

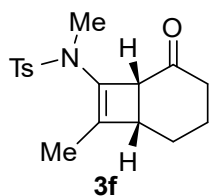
**3d**:  $R_f$  = 0.29 [5:1 petroleum ether/EtOAc]; white solid; mp = 115–116 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.39 (d, 2H,  $J$  = 8.8 Hz), 8.04 (d, 2H,  $J$  = 8.8 Hz), 7.35-7.28 (m,

5H), 4.66, 4.58 (ABq, 2H,  $J_{AB} = 14.8\text{Hz}$ ), 3.19 (br, 1H), 2.79 (br, 1H), 1.96-1.79 (m, 3H), 1.67-1.66 (m, 3H), 1.55-1.47 (m, 2H), 1.32-1.25 (m, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.1, 150.4, 146.1, 145.5, 135.6, 128.9, 128.8, 128.2, 128.1, 125.8, 124.5, 53.4, 51.8, 41.0, 38.7, 23.8, 17.2, 12.6. Spectral data are in agreement with literature values<sup>2</sup>.



To an oven-dried tube was added ynamide **1e**<sup>5</sup> (89.8 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3e** (95.1 mg, 0.28 mmol) in 92% yield.

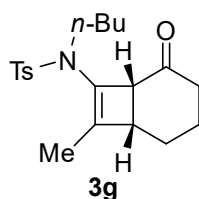
**3e**:  $R_f = 0.17$  [5:1 petroleum ether/EtOAc]; white solid; mp = 100–101 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.67 (d, 2H,  $J = 8.3$  Hz), 7.29 (d, 2H,  $J = 8.0$  Hz), 5.82-5.72 (m, 1H), 5.26-5.14 (m, 2H), 4.13-3.97 (m, 2H), 3.28 (br, 1H), 2.88 (br, 1H), 2.43 (s, 3H), 2.15-2.09 (m, 1H), 1.97-1.87 (m, 2H), 1.74-1.73 (m, 3H), 1.65-1.53 (m, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.5, 143.9, 143.2, 136.8, 133.7, 129.8, 127.6, 126.9, 117.8, 53.9, 50.3, 40.6, 38.6, 23.9, 21.8, 17.3, 12.6. Spectral data are in agreement with literature values<sup>2</sup>.



To an oven-dried tube was added ynamide **1f**<sup>6</sup> (80.38 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic

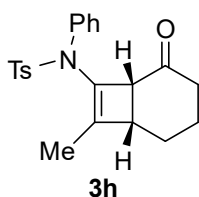
eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3f** (80.8 mg, 0.25 mmol) in 84% yield.

**3f**:  $R_f = 0.25$  [5:1 petroleum ether/EtOAc]; colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.66 (d, 2H,  $J = 8.3$  Hz), 7.30 (d, 2H,  $J = 8.0$  Hz), 3.32 (br, 1H), 3.02 (s, 3H), 2.88 (br, 1H), 2.43 (s, 3H), 2.19-2.14 (m, 1H), 2.01-1.88 (m, 2H), 1.77-1.76 (m, 3H), 1.73-1.53 (m, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.7, 144.0, 139.6, 135.8, 129.7, 128.2, 127.6, 53.8, 40.2, 38.7, 35.5, 24.0, 21.8, 17.4, 12.7; IR (neat) ( $\text{cm}^{-1}$ ) 2932m, 2855w, 1595m, 1402w, 1013w, 887m, 675s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{21}\text{NNaO}_3\text{S}$   $[\text{M} + \text{Na}]^+$  342.1134, found 342.1126.



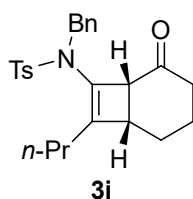
To an oven-dried tube was added ynamide **1g**<sup>7</sup> (95.5 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3g** (80.4 mg, 0.22 mmol) in 74% yield.

**3g**:  $R_f = 0.32$  [5:1 petroleum ether/EtOAc]; white solid; mp = 61–62 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.65 (d, 2H,  $J = 8.3$  Hz), 7.27 (d, 2H,  $J = 8.6$  Hz), 3.48-3.33 (m, 2H), 3.31 (br, 1H), 2.90 (br, 1H), 2.42 (s, 3H), 2.12-2.06 (m, 1H), 1.98-1.89 (m, 2H), 1.75-1.74 (m, 3H), 1.64-1.60 (m, 2H), 1.52-1.44 (m, 2H), 1.37-1.25 (m, 3H), 0.91 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.4, 143.7, 143.5, 137.1, 129.7, 127.5, 127.0, 53.8, 47.6, 40.5, 38.6, 31.5, 24.0, 21.8, 19.6, 17.4, 13.9, 12.6; IR (neat) ( $\text{cm}^{-1}$ ) 2957s, 2727m, 1693s, 1458m, 1031m, 815s, 572m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{28}\text{NO}_3\text{S}$   $[\text{M} + \text{H}]^+$  362.1784, found 362.1784.



To an oven-dried tube was added ynamide **2h**<sup>6</sup> (102.73 mg, 0.36 mmol), cyclohexenone **1a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3h** (81.0 mg, 0.21 mmol) in 71% yield.

**3h**: *R<sub>f</sub>* = 0.38 [5:1 petroleum ether/EtOAc]; white solid; mp = 152–153 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ 7.58 (d, 2H, *J* = 8.3 Hz), 7.32–7.29 (m, 3H), 7.25–7.22 (m, 4H), 3.39 (br, 1H), 2.89 (br, 1H), 2.46–2.38 (m, 4H), 2.12–2.01 (m, 1H), 1.94–1.82 (m, 2H), 1.70–1.59 (m, 5H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 210.9, 144.0, 142.9, 138.4, 136.8, 129.7, 129.5, 129.4, 129.0, 128.4, 128.1, 55.5, 40.1, 39.3, 24.1, 21.8, 17.7, 12.2; IR (neat) (cm<sup>-1</sup>) 2966m, 2861w, 1685s, 1492m, 1226w, 1089s, 542m; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>3</sub>S [M + H]<sup>+</sup> 382.1471, found 382.1471.

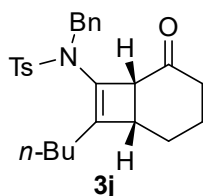


To an oven-dried tube was added ynamide **2i**<sup>8</sup> (117.9 mg, 0.36 mmol), cyclohexenone **1a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3i** (110.2 mg, 0.26 mmol) in 87% yield.

**3i**: *R<sub>f</sub>* = 0.28 [5:1 petroleum ether/EtOAc]; white solid; mp = 55–56 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ 7.74 (d, 2H, *J* = 8.2 Hz), 7.34–7.25 (m, 7H), 4.69, 4.51 (ABq, 2H, *J<sub>AB</sub>* = 14.9 Hz), 3.18 (br, 1H), 2.82 (br, 1H), 2.45 (s, 3H), 2.30–2.22 (m, 1H), 1.95–1.78 (m, 4H), 1.46–1.25 (m, 5H), 0.80 (t, 3H, *J* = 7.4 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 210.7, 148.4, 144.0, 136.8, 136.4, 129.8, 128.6, 128.1, 127.8, 127.7, 126.3, 53.6, 51.5, 40.6, 37.0, 29.1, 24.3, 21.8, 19.8, 17.3, 14.4; IR (neat) (cm<sup>-1</sup>) 2925m, 2867w, 1595w, 1351m, 1070w, 856m, 556s; HRMS (ESI): *m/z* calcd for C<sub>25</sub>H<sub>30</sub>NO<sub>3</sub>S [M + H]<sup>+</sup>

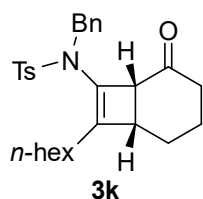


424.1941, found 424.1941.



To an oven-dried tube was added ynamide **1j**<sup>8</sup> (122.9 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3j** (121.6 mg, 0.28 mmol) in 93% yield.

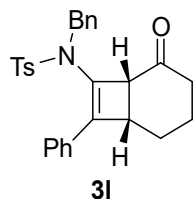
**3j**: *R<sub>f</sub>* = 0.27 [5:1 petroleum ether/EtOAc]; white solid; mp = 57–58 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ 7.73 (d, 2H, *J* = 8.3 Hz), 7.36-7.26 (m, 7H), 4.70, 4.49 (ABq, 2H, *J<sub>AB</sub>* = 14.8 Hz), 3.19 (br, 1H), 2.81 (br, 1H), 2.45 (s, 3H), 2.31-2.24 (m, 1H), 1.93-1.78 (m, 4H), 1.47-1.16 (m, 7H), 0.85 (t, 3H, *J* = 7.0 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 210.6, 148.6, 144.0, 136.7, 136.4, 129.8, 128.6, 128.1, 127.8, 127.7, 126.1, 53.6, 51.5, 40.6, 37.0, 28.5, 26.8, 24.3, 22.9, 21.8, 17.3, 14.1; IR (neat) (cm<sup>-1</sup>) 2925m, 2869w, 1598w, 1348m, 1090w, 832m, 557s; HRMS (ESI): *m/z* calcd for C<sub>26</sub>H<sub>32</sub>NO<sub>3</sub>S [M + H]<sup>+</sup> 438.2097, found 438.2090.



To an oven-dried tube was added ynamide **1k**<sup>1</sup> (133.0 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3k** (118 mg, 0.25 mmol) in 85% yield.

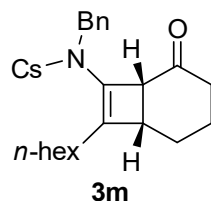
**3k**: *R<sub>f</sub>* = 0.29 [5:1 petroleum ether/EtOAc]; white solid; mp = 62–63 °C; <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>),  $\delta$  7.73 (d, 2H,  $J = 8.3$  Hz), 7.33-7.23 (m, 7H), 4.70, 4.49 (ABq, 2H,  $J_{AB} = 14.9$  Hz), 3.19 (br, 1H), 2.81 (br, 1H), 2.45 (s, 3H), 2.29-2.23 (m, 1H), 1.93-1.77 (m, 4H), 1.46-1.33 (m, 4H), 1.31-1.13 (m, 7H), 0.89 (t, 3H,  $J = 7.0$  Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  210.7, 148.6, 144.0, 136.8, 136.4, 129.8, 128.6, 128.1, 127.8, 127.7, 126.1, 53.6, 51.5, 40.6, 37.0, 31.8, 29.6, 27.1, 26.4, 24.3, 22.8, 21.8, 17.3, 14.3; IR (neat) (cm<sup>-1</sup>) 2925s, 2853m, 1594w, 1347s, 1070w, 863m, 557s; HRMS (ESI):  $m/z$  calcd for C<sub>28</sub>H<sub>36</sub>NO<sub>3</sub>S [M + H]<sup>+</sup> 466.2410, found 466.2410.



To an oven-dried tube was added ynamide **1l**<sup>1</sup> (130.1 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3l** (123.9 mg, 0.27 mmol) in 90% yield.

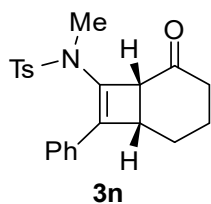
**3l**:  $R_f = 0.20$  [5:1 petroleum ether/EtOAc]; white solid; mp = 151–152 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, 2H,  $J = 8.3$  Hz), 7.37-7.34 (m, 7H), 7.18-7.17 (m, 3H), 7.02-7.00 (m, 2H), 4.55, 4.42 (ABq, 2H,  $J_{AB} = 14.4$  Hz), 3.29 (s, 2H), 2.46 (s, 3H), 2.18-1.93 (m, 3H), 1.61-1.48 (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  210.8, 144.7, 144.3, 136.3, 135.5, 132.1, 130.0, 128.9, 128.6, 128.52, 128.48, 128.1, 128.0, 127.4, 126.8, 55.5, 51.2, 40.6, 37.4, 24.9, 21.8, 17.5; IR (neat) (cm<sup>-1</sup>) 2924m, 2869w, 1693s, 1368s, 1143m, 662s, 654s; HRMS (ESI):  $m/z$  calcd for C<sub>28</sub>H<sub>28</sub>NO<sub>3</sub>S [M + H]<sup>+</sup> 458.1784, found 458.1784.



To an oven-dried tube was added ynamide **1m**<sup>9</sup> (140.1 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M),

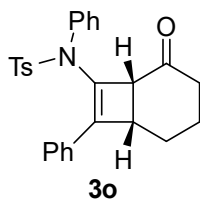
and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3m** (121.3 mg, 0.25mmol) in 83% yield.

**3m**:  $R_f = 0.25$  [6:1 petroleum ether/EtOAc]; yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.79 (d, 2H,  $J = 8.6$  Hz), 7.50 (d, 2H,  $J = 8.6$  Hz), 7.30-7.25 (m, 5H), 4.69, 4.50 (ABq, 2H,  $J_{AB} = 14.7$  Hz), 3.20 (br, 1H), 2.82 (br, 1H), 2.26-2.19 (m, 1H), 1.94-1.77 (m, 3H), 1.50-1.42 (m, 2H), 1.34-1.26 (m, 4H), 1.25-1.12 (m, 6H), 0.89 (t, 3H,  $J = 7.0$  Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  210.3, 149.3, 139.7, 138.2, 136.0, 129.5, 129.1, 128.7, 128.1, 127.9, 125.7, 53.3, 51.7, 40.8, 37.0, 31.8, 29.5, 27.1, 26.3, 24.3, 22.7, 17.4, 14.3; IR (neat) (cm<sup>-1</sup>) 2924s, 2185m, 1690s, 1476w, 1330m, 847m, 623s; HRMS (ESI):  $m/z$  calcd for C<sub>27</sub>H<sub>33</sub>ClNO<sub>3</sub>S [M + H]<sup>+</sup> 486.1864, found 486.1864.



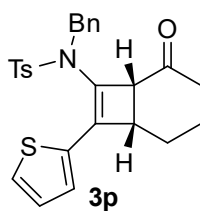
To an oven-dried tube was added ynamide **1n**<sup>1</sup> (102.7 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3n** (104.6 mg, 0.27 mmol) in 91% yield.

**3n**:  $R_f = 0.23$  [5:1 petroleum ether/EtOAc]; white solid; mp = 91–92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.77 (d, 2H,  $J = 8.3$  Hz), 7.43-7.40 (m, 2H), 7.37-7.30 (m, 5H), 3.54 (d, 1H,  $J = 4.3$  Hz), 3.48 (br, 1H), 2.97 (s, 3H), 2.71-2.64 (m, 1H), 2.43 (s, 3H), 2.25-2.16 (m, 2H), 2.07-1.95 (m, 1H), 1.77-1.67 (m, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  210.9, 144.1, 141.8, 135.5, 131.7, 129.9, 128.8, 128.6, 127.9, 127.3, 55.0, 40.2, 37.4, 35.7, 24.8, 21.7, 17.8, one carbon missing due to overlap, overlapped signal at 128.8 ppm; IR (neat) (cm<sup>-1</sup>) 2937m, 2875w, 1692s, 1494m, 1229w, 1157m, 676s; HRMS (ESI):  $m/z$  calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>3</sub>S [M + H]<sup>+</sup> 382.1471, found 382.1470.



To an oven-dried tube was added ynamide **1o**<sup>10</sup> (125.08 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3o** (109.3 mg, 0.25 mmol) in 82% yield.

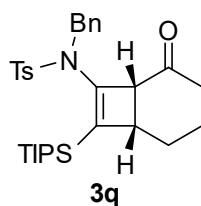
**3o**:  $R_f$  = 0.39 [5:1 petroleum ether/EtOAc]; white solid; mp = 140–141 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.62–7.58 (m, 2H), 7.55 (d, 2H,  $J$  = 8.3 Hz), 7.37–7.27 (m, 5H), 7.24–7.19 (m, 5H), 3.64 (d, 1H,  $J$  = 4.1 Hz), 3.49–3.44 (m, 1H), 2.72–2.66 (m, 1H), 2.39 (s, 3H), 2.25–2.07 (m, 3H), 1.80–1.71 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  211.2, 145.0, 144.2, 138.5, 136.1, 131.2, 129.5, 129.4, 129.1, 128.7, 128.5, 128.2, 127.7, 127.3, 56.1, 40.5, 37.2, 24.9, 21.8, 17.8, one carbon missing due to overlap, overlapped signal at 128.7 ppm; IR (neat) (cm<sup>-1</sup>) 2924m, 2858w, 1688s, 1447m, 1236w, 1054m, 583s; HRMS (ESI):  $m/z$  calcd for C<sub>27</sub>H<sub>26</sub>NO<sub>3</sub>S [M + H]<sup>+</sup> 444.1628, found 444.1628.



To an oven-dried tube was added ynamide **1p**<sup>11</sup> (132.5 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3p** (59.5 mg, 0.13 mmol) in 43% yield.

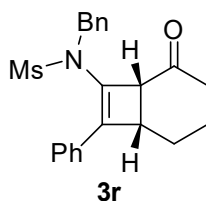
**3p**:  $R_f$  = 0.22 [5:1 petroleum ether/EtOAc]; white solid; mp = 153–154 °C; <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>),  $\delta$  7.84 (d, 2H,  $J = 8.3$  Hz), 7.36-7.34 (m, 3H), 7.21-7.18 (m, 3H), 7.13-7.11 (m, 2H), 7.03-7.01 (m, 2H), 4.57, 4.52 (ABq, 2H,  $J_{AB} = 14.4$  Hz), 3.41 (d, 1H,  $J = 4.2$  Hz), 3.27-3.24 (m, 1H), 2.46 (s, 3H), 2.17-2.13 (m, 1H), 2.01-1.85 (m, 2H), 1.65-1.56 (m, 1H), 1.47-1.36 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  209.9, 144.3, 138.2, 136.3, 135.5, 134.2, 130.1, 128.6, 128.5, 128.04, 128.02, 127.5, 127.3, 127.2, 124.4, 55.4, 50.9, 40.7, 38.3, 24.9, 21.8, 17.2; IR (neat) (cm<sup>-1</sup>) 2922m, 2850w, 1690s, 1453m, 1353s, 930m, 557s; HRMS (ESI):  $m/z$  calcd for C<sub>26</sub>H<sub>26</sub>NO<sub>3</sub>S<sub>2</sub> [M + H]<sup>+</sup> 464.1349, found 464.1349.



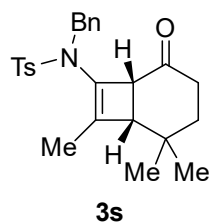
To an oven-dried tube was added ynamide **1q**<sup>1</sup> (159.0 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3q** (82.1 mg, 0.15 mmol) in 51% yield.

**3q**:  $R_f = 0.21$  [5:1 petroleum ether/EtOAc]; white solid; mp = 139–140 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  7.73 (d, 2H,  $J = 8.3$  Hz), 7.32-7.21 (m, 4H), 7.25-7.23 (m, 3H), 4.78, 4.59 (ABq, 2H,  $J_{AB} = 14.6$  Hz), 3.67 (d, 1H,  $J = 4.3$  Hz), 2.97-2.94 (m, 1H), 2.45 (s, 3H), 2.02-1.82 (m, 4H), 1.71-1.60 (m, 2H), 1.33-1.25 (m, 3H), 1.07 (d, 9H,  $J = 7.5$  Hz), 1.00 (d, 9H,  $J = 7.5$  Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  210.5, 150.9, 144.8, 144.0, 137.0, 136.0, 129.7, 129.3, 128.5, 128.1, 128.0, 56.3, 52.4, 41.1, 39.1, 27.4, 21.8, 19.5, 19.4, 18.1, 12.2; IR (neat) (cm<sup>-1</sup>) 3032w, 2926m, 1697s, 1495m, 1347s, 1029w, 552m; HRMS (ESI):  $m/z$  calcd for C<sub>31</sub>H<sub>44</sub>NO<sub>3</sub>SSi [M + H]<sup>+</sup> 538.2806, found 538.2806.



To an oven-dried tube was added ynamide **1r**<sup>12</sup> (102.6 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3r** (67.4 mg, 0.22 mmol) in 74% yield.

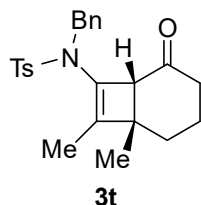
**3r**: *R<sub>f</sub>* = 0.16 [5:1 petroleum ether/EtOAc]; yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ 7.47-7.45 (m, 2H), 7.39-7.31 (m, 4H), 7.24-7.20 (m, 4H), 4.66, 4.61 (ABq, 2H, *J*<sub>AB</sub> = 14.6 Hz), 3.52 (d, 1H, *J* = 4.2 Hz), 3.38 (br, 1H), 3.02 (s, 3H), 2.54-2.49 (m, 1H), 2.20-2.11 (m, 2H), 1.81-1.60 (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 211.6, 144.2, 135.5, 131.7, 129.1, 128.8, 128.7, 128.3, 127.3, 127.0, 54.9, 52.3, 41.8, 41.1, 37.1, 25.0, 17.5, one carbon missing due to overlap, overlapped signal at 128.8 ppm; IR (neat) (cm<sup>-1</sup>) 3430w, 2928m, 1696s, 1350s, 1120w, 1085w, 696m; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>3</sub>S [M + H]<sup>+</sup> 382.1471, found 382.1471.



To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), 4,4-dimethyl-cyclohexenone **2b** (38.4 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and Tf<sub>2</sub>NH (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3s** (104.4 mg, 0.25 mmol) in 82% yield.

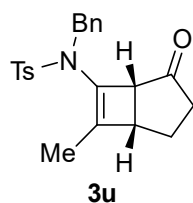
**3s**: *R<sub>f</sub>* = 0.31 [5:1 petroleum ether/EtOAc]; white solid; mp = 114–115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ 7.73 (d, 2H, *J* = 8.3 Hz), 7.34-7.27 (m, 7H), 4.63, 4.51 (ABq, 2H, *J*<sub>AB</sub> = 15.0 Hz), 3.17 (br, 1H), 2.45 (s, 3H), 2.34 (br, 1H), 2.02-1.92 (m, 1H), 1.79-1.78 (m, 3H), 1.56-1.48 (m, 2H), 1.19-1.13 (m, 1H), 1.00 (s, 3H), 0.77 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 CDCl<sub>3</sub>) δ 211.7, 145.4, 144.1, 136.8, 136.4, 129.9, 128.7, 128.3, 127.9, 127.8, 127.6, 54.1, 51.5, 51.1, 35.8, 32.6, 30.9, 28.1, 25.2, 21.8, 15.5; IR (neat)

( $\text{cm}^{-1}$ ) 3450w, 2954m, 1693s, 1496m, 1165s, 1044w, 544m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{30}\text{NO}_3\text{S}$   $[\text{M} + \text{H}]^+$  424.1941, found 424.1941.



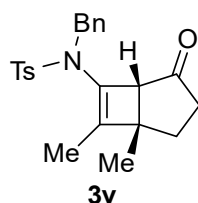
To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), 3-methyl-cyclohexenone **2c** (33.0 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3t** (51.0 mg, 0.12 mmol) in 42% yield.

**3t**:  $R_f$  = 0.38 [5:1 petroleum ether/EtOAc]; white solid; mp = 112–113 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.74 (d, 2H,  $J$  = 8.3 Hz), 7.34-7.27 (m, 7H), 4.66, 4.51 (ABq, 2H,  $J_{AB}$  = 14.8 Hz), 2.74 (q, 1H,  $J$  = 2.2 Hz), 2.45 (s, 3H), 1.78-1.65 (m, 3H), 1.55 (d, 3H,  $J$  = 2.3 Hz), 1.46-1.42 (m, 1H), 1.30-1.23 (m, 2H), 0.94 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.8, 148.1, 144.2, 136.8, 136.5, 130.0, 128.7, 128.2, 128.0, 127.8, 126.0, 62.1, 51.6, 43.3, 39.9, 31.1, 23.8, 22.0, 18.5, 10.2; IR (neat) ( $\text{cm}^{-1}$ ) 3442w, 2923s, 1696m, 1352s, 1164m, 1018w, 545m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{28}\text{NO}_3\text{S}$   $[\text{M} + \text{H}]^+$  410.1784, found 410.1783.



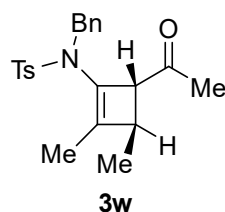
To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), cyclopentenone **2d** (24.6 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3u** (110.4 mg, 0.29 mmol) in 96% yield.

**3u**:  $R_f = 0.17$  [5:1 petroleum ether/EtOAc]; white solid; mp = 100–101 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.72 (d, 2H,  $J = 8.3$  Hz), 7.35–7.24 (m, 7H), 4.51, 4.44 (ABq, 2H,  $J_{AB} = 15.0$  Hz), 2.94 (br, 1H), 2.90 (br, 1H), 2.45 (s, 3H), 1.94–1.78 (m, 2H), 1.74–1.73 (m, 3H), 1.70–1.64 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  216.0, 144.3, 144.2, 136.5, 136.2, 130.0, 129.2, 128.6, 127.9, 127.8, 127.5, 54.3, 51.3, 40.2, 34.1, 21.8, 19.9, 13.1. Spectral data are in agreement with literature values<sup>15</sup>.



To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), 3-methyl-2-cyclopentenone **2e** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3v** (52.5 mg, 0.13 mmol) in 44% yield.

**3v**:  $R_f = 0.43$  [5:1 petroleum ether/EtOAc]; yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.73 (d, 2H,  $J = 8.3$  Hz), 7.35–7.24 (m, 7H), 4.48 (s, 2H), 2.53 (br, 1H), 2.46 (s, 3H), 1.94–1.78 (m, 2H), 1.63 (d, 3H,  $J = 1.9$  Hz), 1.44–1.35 (m, 2H), 1.14 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  216.3, 147.7, 144.1, 136.4, 136.1, 129.9, 128.6, 128.4, 128.0, 127.8, 127.6, 61.1, 51.4, 46.2, 36.0, 26.9, 21.8, 21.3, 10.4; IR (neat) ( $\text{cm}^{-1}$ ) 3031w, 2924s, 1729s, 1351m, 1121w, 1027m, 658m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{26}\text{NO}_3\text{S}$   $[\text{M} + \text{H}]^+$  396.1628, found 396.1628.

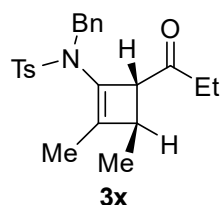


To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), (*E*)-3-penten-2-one **2f** (26.6 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the



reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3w** (83.2 mg, 0.22 mmol) in 72% yield.

**3w**:  $R_f = 0.52$  [5:1 petroleum ether/EtOAc]; colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.72 (d, 2H,  $J = 8.3$  Hz), 7.33-7.27 (m, 7H), 4.66, 4.42 (ABq, 2H,  $J_{AB} = 15.0$  Hz), 3.25 (br, 1H), 2.44 (s, 3H), 2.38-2.32 (m, 1H), 1.95 (s, 3H), 1.33-1.32 (m, 3H), 1.02 (d, 3H,  $J = 6.8$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  208.1, 143.9, 140.4, 136.5, 129.8, 128.8, 128.6, 128.1, 127.9, 127.4, 63.0, 52.1, 38.1, 28.6, 21.8, 16.9, 12.1, one carbon missing due to overlap; overlapped signal at 127.9 ppm; IR (neat) ( $\text{cm}^{-1}$ ) 3450w, 2960m, 1694s, 1455m, 1166s, 1025w, 609m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{26}\text{NO}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  384.1628, found 384.1628.

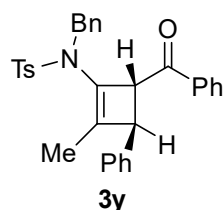


To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), (*E*)-4-hexen-3-one **2g** (29.4 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3x** (98.8 mg, 0.25 mmol) in 83% yield.

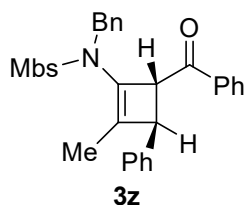
**3x**:  $R_f = 0.54$  [5:1 petroleum ether/EtOAc]; white solid; mp = 69–70 °C; 7.72 (d, 2H,  $J = 8.3$  Hz), 7.32-7.28 (m, 7H), 4.63, 4.44 (ABq, 2H,  $J_{AB} = 14.9$  Hz), 3.31-3.29 (m, 1H), 2.44 (s, 3H), 2.37-2.32 (m, 1H), 2.32-2.26 (m, 2H), 1.26-1.25 (m, 3H), 1.02 (d, 3H,  $J = 6.9$  Hz), 0.92 (t, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.1, 143.8, 140.4, 136.6, 136.5, 129.8, 128.7, 128.6, 128.2, 127.8, 127.4, 61.9, 52.2, 38.2, 35.1, 21.7, 16.9, 12.0, 7.6; IR (neat) ( $\text{cm}^{-1}$ ) 3450w, 2922m, 1708s, 1598m, 1354s, 1117w, 598m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{28}\text{NO}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  398.1784, found 398.1784.

To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), (*E*)-chalcone **2h** (62.5 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at

rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3y** (126.2 mg, 0.25 mmol) in 81% yield.



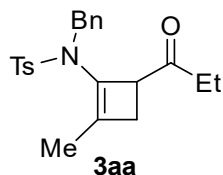
**3y**:  $R_f = 0.38$  [5:1 petroleum ether/EtOAc]; white solid; mp = 69–70 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), 7.77 (d, 2H,  $J = 8.4$  Hz), 7.67–7.65 (m, 2H), 7.53–7.49 (m, 1H), 7.45–7.43 (m, 2H), 7.37–7.27 (m, 8H), 7.22 (d, 2H,  $J = 8.1$  Hz), 7.06–7.03 (m, 2H), 4.67 (s, 2H), 4.38–4.36 (m, 1H), 3.46 (br, 1H), 2.37 (s, 3H), 1.20–1.19 (m, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.7, 143.8, 140.0, 139.7, 137.0, 136.8, 136.4, 133.3, 130.9, 129.8, 128.9, 128.7, 128.6, 128.5, 127.8, 127.7, 127.5, 127.4, 60.1, 52.7, 49.5, 21.7, 12.4, one carbon missing due to overlap, overlapped signal at 128.9 ppm; IR (neat) ( $\text{cm}^{-1}$ ) 3029w, 2921s, 1728m, 1350m, 1120w, 812m, 546s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{32}\text{H}_{30}\text{NO}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  508.1941, found 508.1942.



To an oven-dried tube was added ynamide **1b**<sup>2</sup> (113.5 mg, 0.36 mmol), (*E*)-chalcone **2h** (62.5 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3z** (118.7 mg, 0.23 mmol) in 76% yield.

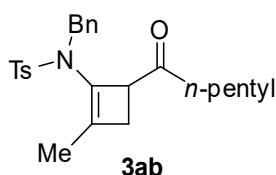
**3z**:  $R_f = 0.14$  [5:1 petroleum ether/EtOAc]; white solid; mp = 120–121 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.82 (d, 2H,  $J = 8.9$  Hz), 7.68 (d, 2H,  $J = 6.9$  Hz), 7.53–7.49 (m, 1H), 7.45–7.43 (m, 2H), 7.37–7.27 (m, 8H), 7.05–7.03 (m, 2H), 6.89–6.87 (m, 2H), 4.69, 4.65 (ABq, 2H,  $J_{AB} = 14.9$  Hz), 4.39–4.37 (m, 1H), 3.81 (s, 3H), 3.46 (br, 1H),

1.22 (t, 3H,  $J = 1.6$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8, 163.1, 139.8, 139.4, 136.9, 136.5, 133.2, 131.6, 131.1, 129.8, 128.9, 128.67, 128.64, 128.57, 128.53, 127.8, 127.5, 127.4, 114.3, 60.0, 55.7, 52.5, 49.5, 12.4; IR (neat) ( $\text{cm}^{-1}$ ) 3431s, 2922m, 1701m, 1455s, 1126m, 833m, 555m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{32}\text{H}_{30}\text{NO}_4\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  524.1890, found 524.1893. Spectral data are in agreement with literature values<sup>2</sup>.



To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), 1-penten-3-one **2i** (25.2 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3aa** (79.0 mg, 0.21 mmol) in 69% yield.

**3aa**:  $R_f = 0.50$  [5:1 petroleum ether/EtOAc]; colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.71 (d, 2H,  $J = 8.2$  Hz), 7.32-7.27 (m, 7H), 4.61-4.43 (m, 2H), 3.78-3.75 (m, 1H), 2.44 (s, 3H), 2.33-2.14 (m, 4H), 1.34-1.32 (m, 3H), 0.90 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.3, 143.9, 137.5, 136.63, 136.58, 129.9, 129.9, 128.6, 128.3, 127.9, 127.4, 53.6, 52.3, 34.7, 30.9, 21.8, 14.5, 7.6; IR (neat) ( $\text{cm}^{-1}$ ) 3451m, 2923m, 1708s, 1597w, 1350s, 1164s, 814m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{26}\text{NO}_3\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  384.1628, found 384.1627.

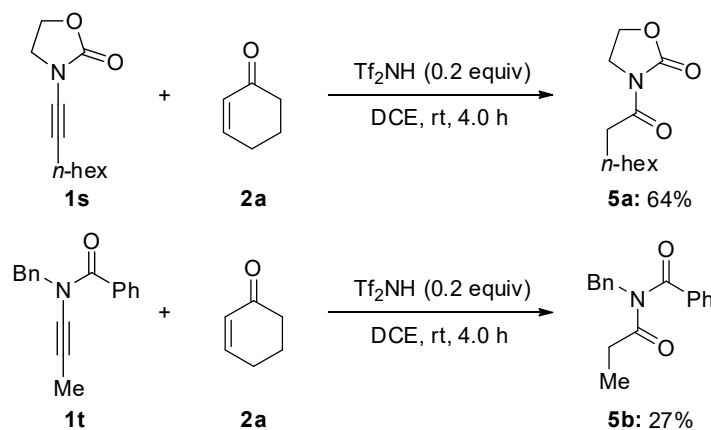


To an oven-dried tube was added ynamide **1a**<sup>1</sup> (107.8 mg, 0.36 mmol), 1-octen-3-one **2j** (37.9 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 10.0 min. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [isocratic eluent: 10:1 petroleum ether /EtOAc] to afford cyclobutenamide **3ab** (104.4 mg, 0.25 mmol)

in 82% yield.

**3ab**:  $R_f = 0.61$  [5:1 petroleum ether/EtOAc]; colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.71 (d, 2H,  $J = 8.2$  Hz), 7.32-7.28 (m, 7H), 4.60-4.43 (m, 2H), 3.77-3.74 (m, 1H), 2.44 (s, 3H), 2.31-2.09 (m, 4H), 1.44-1.13 (m, 9H), 0.88 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.1, 143.8, 137.2, 136.75, 136.66, 129.9, 128.6, 128.3, 127.9, 127.4, 53.6, 52.2, 41.5, 31.5, 30.9, 23.2, 22.7, 21.8, 14.5, 14.2, one carbon missing due to overlap, overlapped signal at 127.9 ppm; IR (neat) ( $\text{cm}^{-1}$ ) 3446s, 2955m, 1706m, 1352s, 1164s, 1048w, 665m; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{32}\text{NO}_3\text{S}$   $[\text{M} + \text{H}]^+$  426.2097, found 426.2097.

### 1.3 [2 + 2] Cycloaddition of *N*-acyl ynamides.

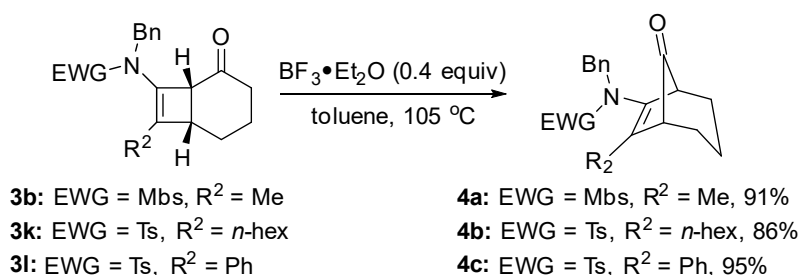


To an oven-dried tube was added ynamide **1s**<sup>1</sup> (70.3 mg, 0.36 mmol), cyclohexenone **2a** (28.8 mg, 0.30 mmol), DCE (1.5 mL, ynamide *concn* = 0.24 M), and  $\text{Tf}_2\text{NH}$  (16.9 mg, 0.06 mmol) at rt. Then the reaction vessel was capped and stirred at rt for 4.0 h. After the reaction was judged to be complete by TLC, the reaction mixture was purified by flash silica gel column chromatography [gradient eluent: 10:1~6:1 petroleum ether/EtOAc] to afford amide **5a** (44.8 mg, 0.23 mmol) in 64% yield. **5a**:  $R_f = 0.30$  [6:1 petroleum ether/EtOAc]; white solid; mp = 39–40 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.41 (t, 2H,  $J = 8.1$  Hz), 4.02 (t, 2H,  $J = 8.0$  Hz), 2.92 (t, 2H,  $J = 7.5$  Hz), 1.70-1.64 (m, 2H), 1.36-1.35 (m, 8H), 0.88 (t, 3H,  $J = 6.5$  Hz); Spectral data are in agreement with literature values.<sup>13</sup>

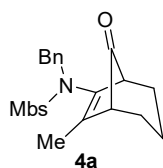
Amide **5b** (40.9 mg, 0.19 mmol) was prepared from ynamide **1t**<sup>15</sup> (89.8 mg, 0.36 mmol), and cyclohexenone **2a** (28.8 mg, 0.30 mmol) in 27% yield after stirring at rt

for 4.0 h. **5b**:  $R_f = 0.45$  [10:1 petroleum ether/EtOAc]; colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.51 (m, 3H), 7.44-7.38 (m, 2H), 7.30-7.21 (m, 5H), 5.00 (s, 2H), 2.41 (q, 2H,  $J = 7.3$  Hz), 1.05 (t, 3H,  $J = 7.3$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 174.4, 137.6, 136.1, 132.5, 128.9, 128.7, 128.5, 127.9, 127.6, 49.6, 32.1, 9.8; IR (neat) ( $\text{cm}^{-1}$ ) 3334w, 2929w, 1656s, 1346m, 1191m, 1022s, 692s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{NO}_2$   $[\text{M} + \text{H}]^+$  268.1332, found 268.1335.

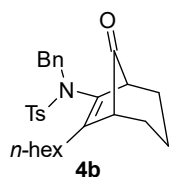
### 1.4 Chemical Transformations of Cyclobutenamides **3**.



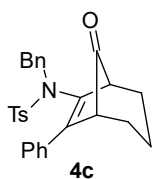
To an oven-dried tube were added cyclobutenamide **3b** (41.2 mg, 0.10 mmol), toluene (1.5 mL, cyclobutenamide concn = 0.067 M) and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (4.9  $\mu\text{L}$ , 0.04 mmol) at rt. The reaction vessel was then capped it and directly heated to 105 °C. After stirring at 105 °C for 1.0 h, the reaction mixture was cooled to rt slowly. The crude mixture was purified by flash silica gel column chromatography [gradient eluent: 7:1~5:1 petroleum ether/EtOAc] to afford bicyclic ketone **4a** (37.4 mg, 0.091 mmol) in 91% yield.



**4a**:  $R_f = 0.28$  [5:1 petroleum ether/EtOAc]; white solid; mp = 114–115 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d, 2H,  $J = 8.9$  Hz), 7.33-7.23 (m, 5H), 7.01 (d, 2H,  $J = 8.9$  Hz), 4.68 (d, 1H,  $J = 14.4$  Hz), 4.26 (d, 1H,  $J = 14.5$  Hz), 3.89 (s, 3H), 2.57 (br, 1H), 2.29 (br, 1H), 1.71-1.68 (m, 1H), 1.68 (s, 3H), 1.58-1.50 (m, 2H), 1.46-1.37 (m, 1H), 1.22-1.08 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.4, 163.3, 139.9, 136.2, 131.5, 129.5, 128.7, 128.3, 128.1, 114.6, 55.8, 55.3, 52.9, 50.8, 29.2, 27.6, 17.2, 13.6, one carbon missing due to overlap, overlapped signal at 128.7 ppm; Spectral data are in agreement with literature values<sup>14</sup>.

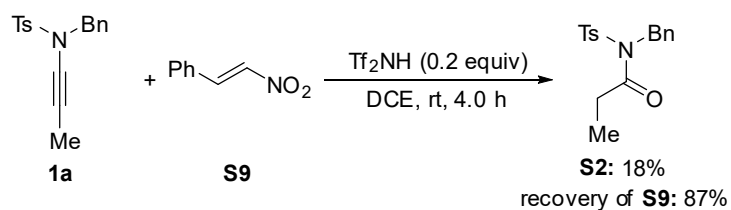
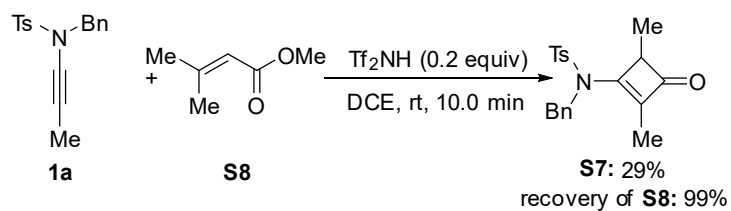
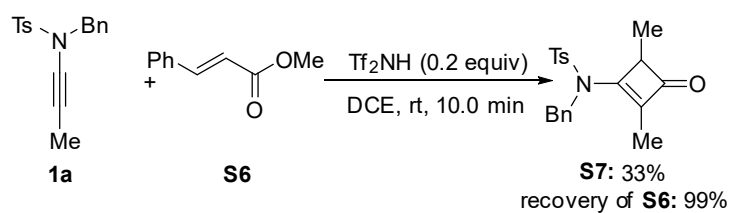
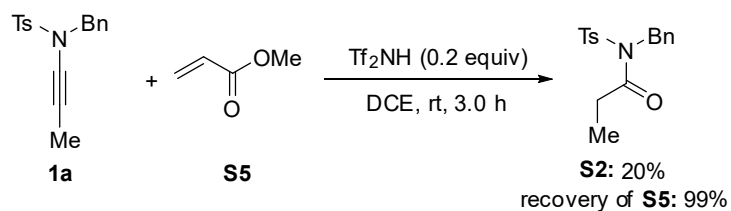
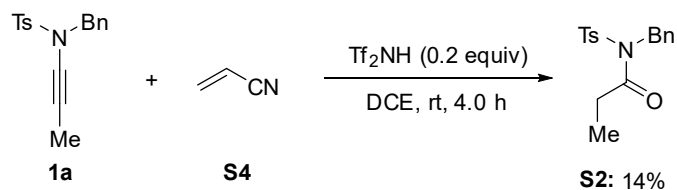
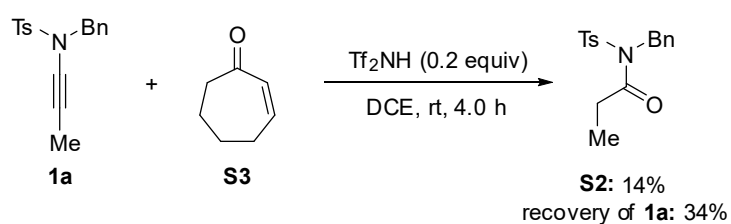
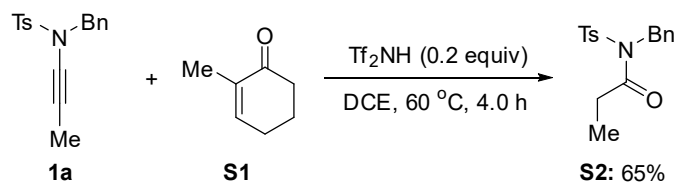
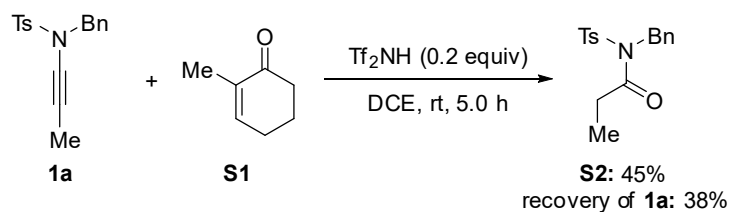


Bicyclic ketone **4b** (39.9 mg, 0.086 mmol) was prepared from cyclobutenamide **3k** (46.5 mg, 0.10 mmol) in 86% yield after stirring at 105 °C for 30.0 min. **4b**:  $R_f = 0.35$  [10:1 petroleum ether/EtOAc]; white solid; mp = 109–110 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d, 2H,  $J = 8.0$  Hz), 7.35–7.26 (m, 7H), 4.66 (d, 1H,  $J = 14.3$  Hz), 4.29 (d, 1H,  $J = 14.3$  Hz), 2.68 (br, 1H), 2.46 (s, 3H), 2.29 (br, 1H), 2.23–2.18 (m, 1H), 2.04–1.97 (m, 1H), 1.71–1.52 (m, 6H), 1.46–1.38 (m, 2H), 1.20–1.04 (m, 6H), 0.88 (d, 3H,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.2, 144.6, 144.0, 137.2, 136.1, 130.1, 128.7, 128.6, 128.2, 127.8, 127.5, 53.2, 53.1, 50.8, 31.8, 30.0, 29.2, 28.8, 28.6, 27.2, 22.8, 21.8, 17.5, 14.3; IR (neat) ( $\text{cm}^{-1}$ ) 2929br, 2858w, 1761m, 1495m, 1344s, 1156s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{28}\text{H}_{36}\text{NO}_3\text{S}$   $[\text{M} + \text{H}]^+$  466.2410, found 466.2408.



Bicyclic ketone **4c** (43.5 mg, 0.095 mmol) was prepared from cyclobutenamide **3l** (45.8 mg, 0.10 mmol) in 95% yield after stirring at 105 °C for 30.0 min. **4c**:  $R_f = 0.27$  [6:1 petroleum ether/EtOAc]; white solid; mp = 135–136 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d, 2H,  $J = 8.1$  Hz), 7.36 (d, 2H,  $J = 8.1$  Hz), 7.28–7.15 (m, 6H), 6.97–6.89 (m, 4H), 4.45 (d, 1H,  $J = 14.4$  Hz), 4.18 (d, 1H,  $J = 14.4$  Hz), 3.06–3.04 (m, 1H), 2.87–2.85 (m, 1H), 2.49 (s, 3H), 2.17–2.12 (m, 1H), 1.89–1.82 (m, 1H), 1.74–1.63 (m, 2H), 1.44–1.39 (m, 1H), 1.29–1.23 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.1, 144.3, 136.7, 136.3, 135.7, 133.8, 130.4, 130.2, 128.574, 128.566, 128.55, 128.52, 128.2, 127.7, 127.5, 55.4, 54.6, 52.6, 30.0, 29.1, 21.8, 17.5; IR (neat) ( $\text{cm}^{-1}$ ) 2921m, 2859w, 1764s, 1455m, 1348s, 1269w, 1165s; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{28}\text{H}_{28}\text{NO}_3\text{S}$   $[\text{M} + \text{H}]^+$  458.1784, found 458.1793.

## 1.5 Failed [2 + 2] Cycloadditions.



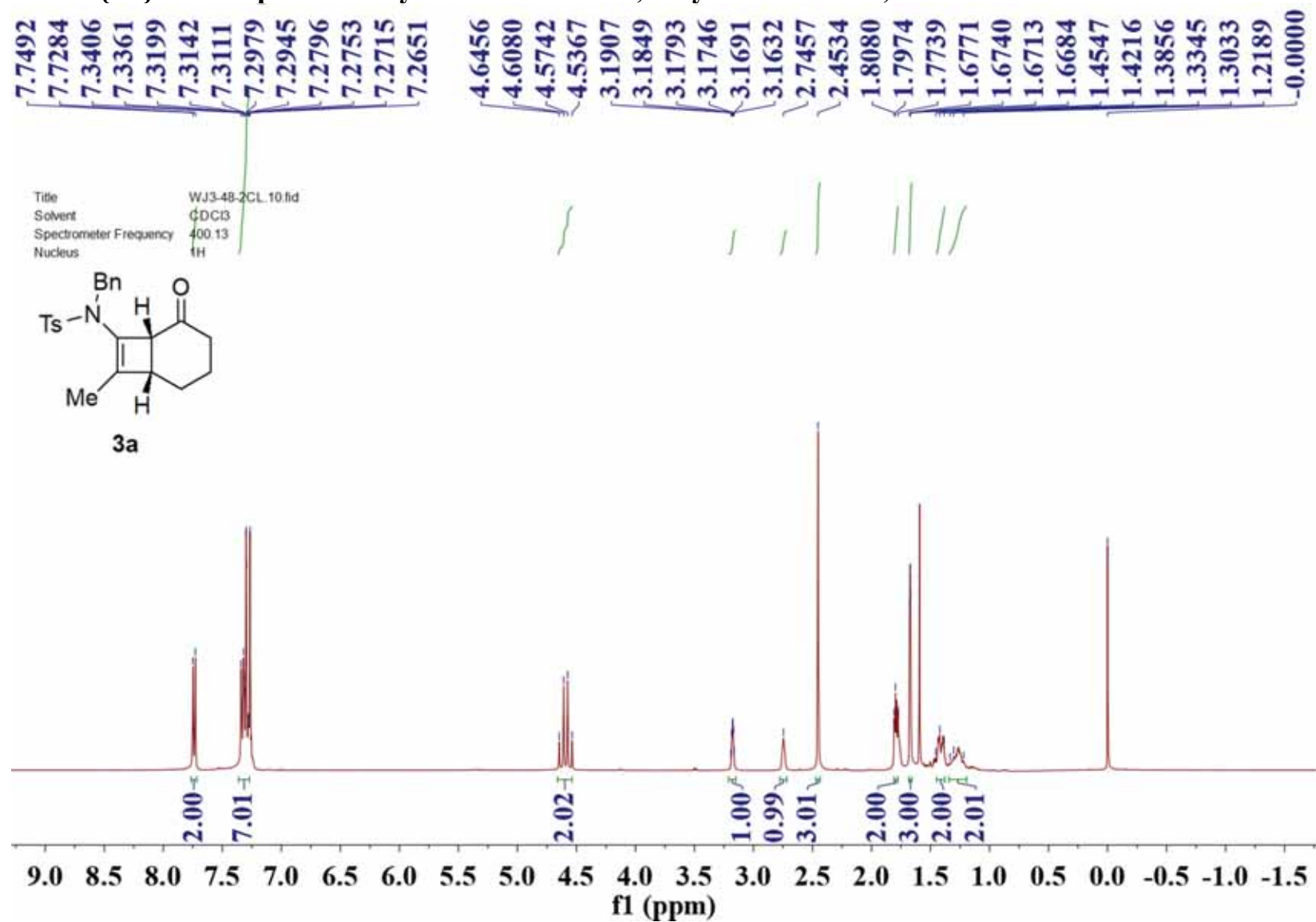
## References

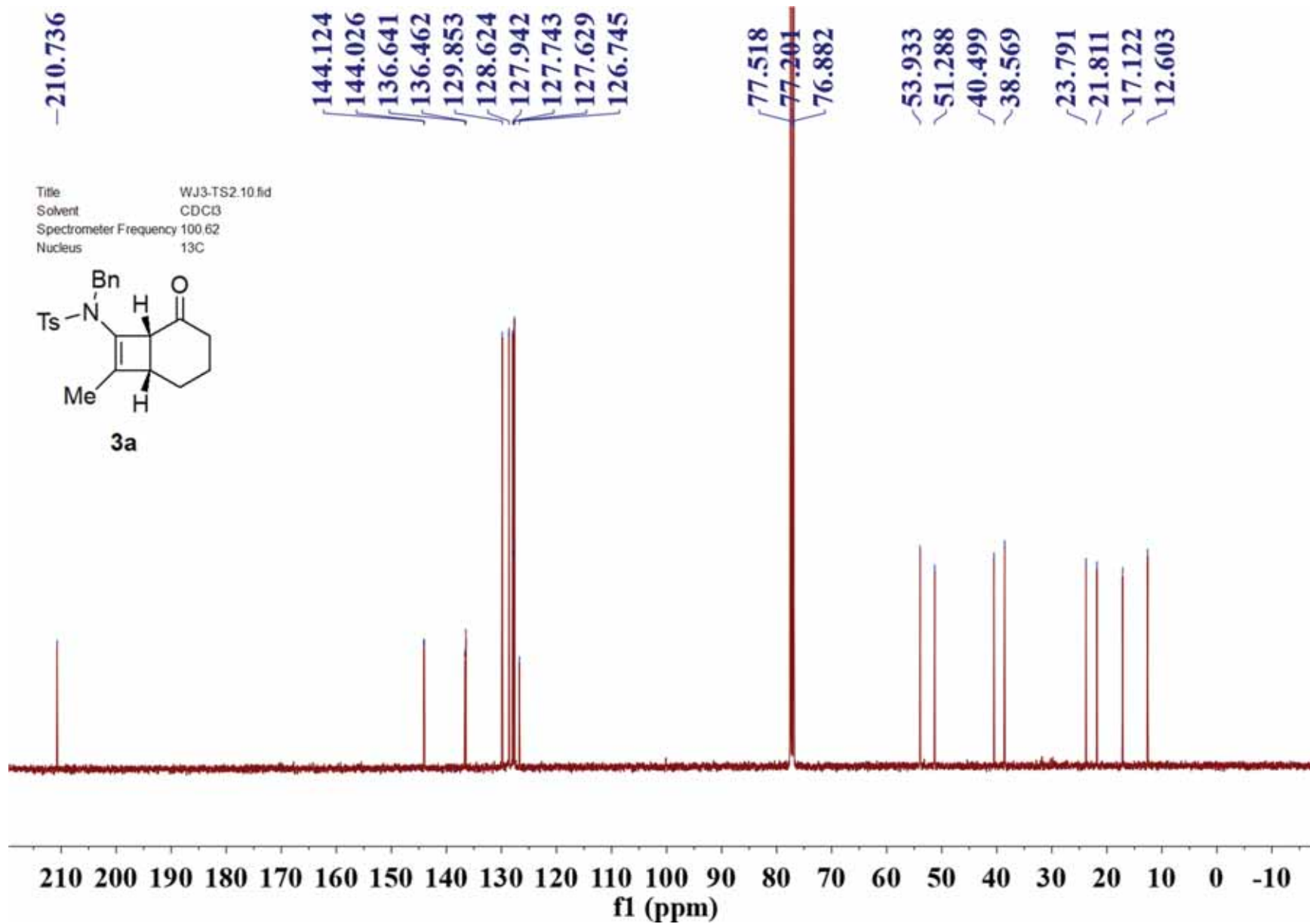
- (1) Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz and E. L. Vera, *Org. Lett.*, 2004, **6**, 1151-1154.
- (2) H. Li, R. P. Hsung, K. A. DeKorver and Y. Wei, *Org. Lett.*, 2010, **12**, 3780-3783.
- (3) Y. Yang, H. Liu, C. Peng, J. Wu, J. Zhang, Y. Qiao, X.-N. Wang and J. Chang, *Org. Lett.*, 2016, **18**, 5022-5025.
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- (14) X.-N. Wang, E. H. Krenske, R. C. Johnston, K. N. Houk and R. P. Hsung, *J. Am. Chem. Soc.*, 2015, **137**, 5596-5601.
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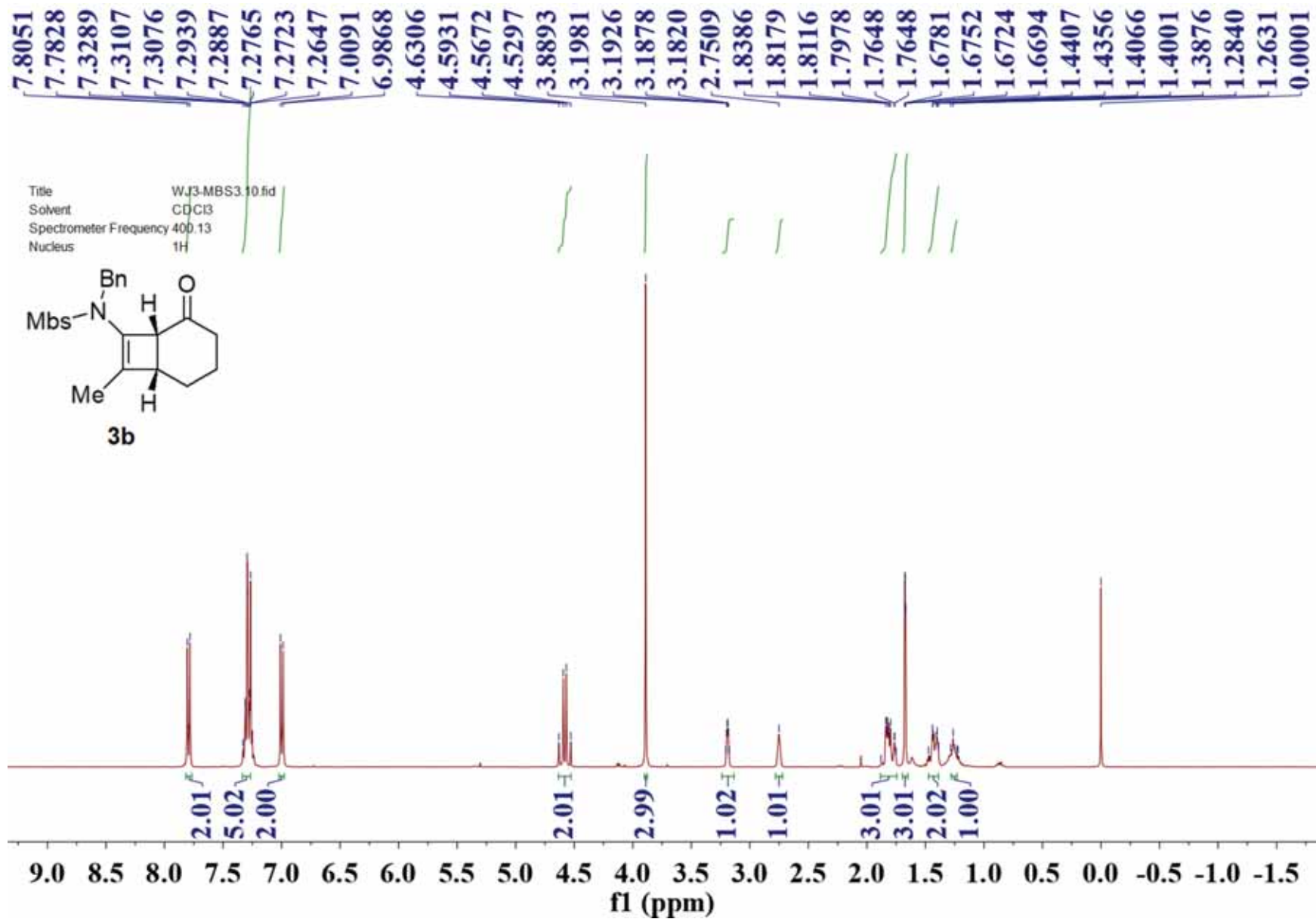


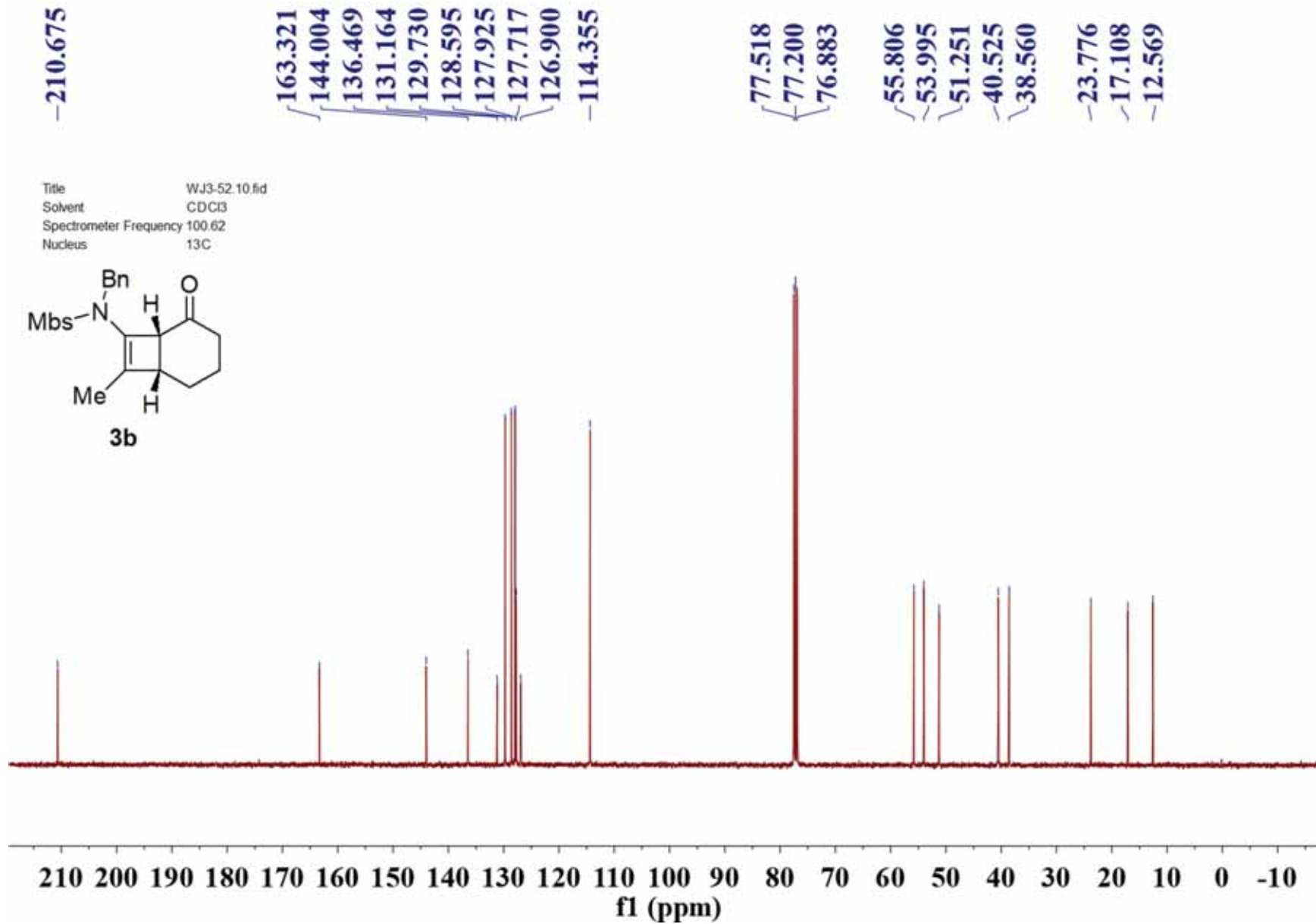
## Part II Copies of $^1\text{H}$ NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and NOESY Spectra.

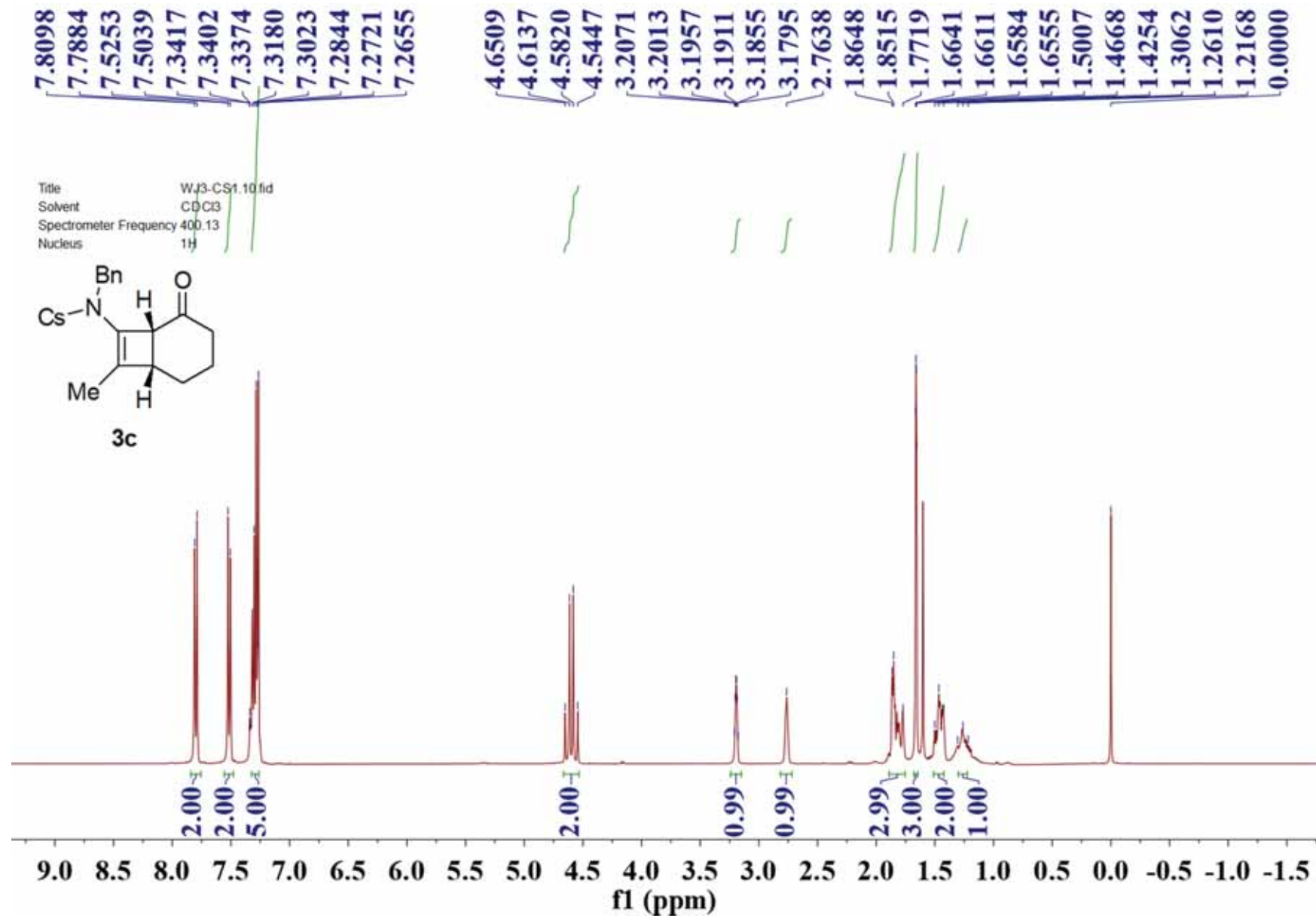
### $^1\text{H}$ NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of Cyclobutenamides 3, Bicyclic Ketones 4, and Amide 5b.

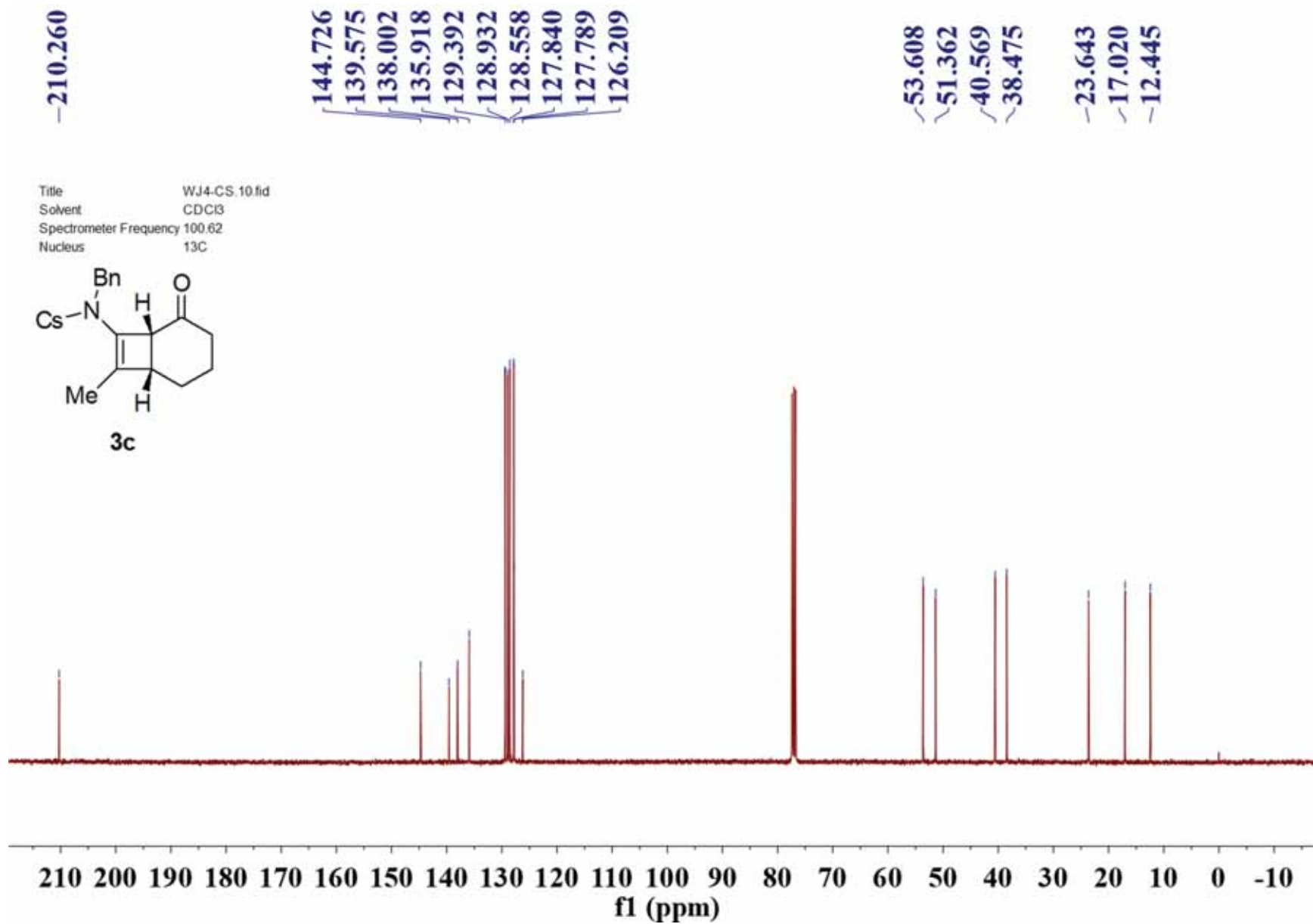


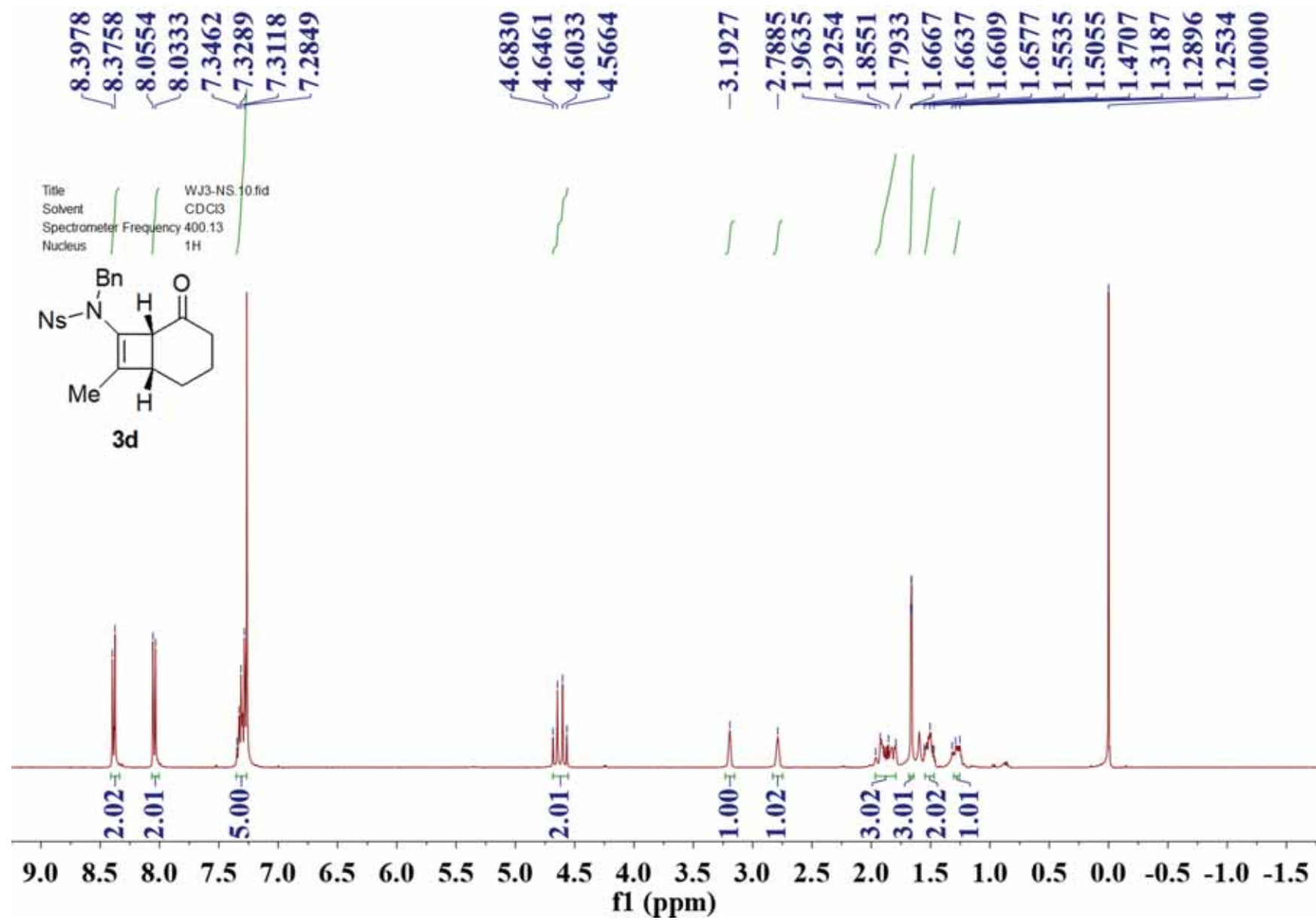


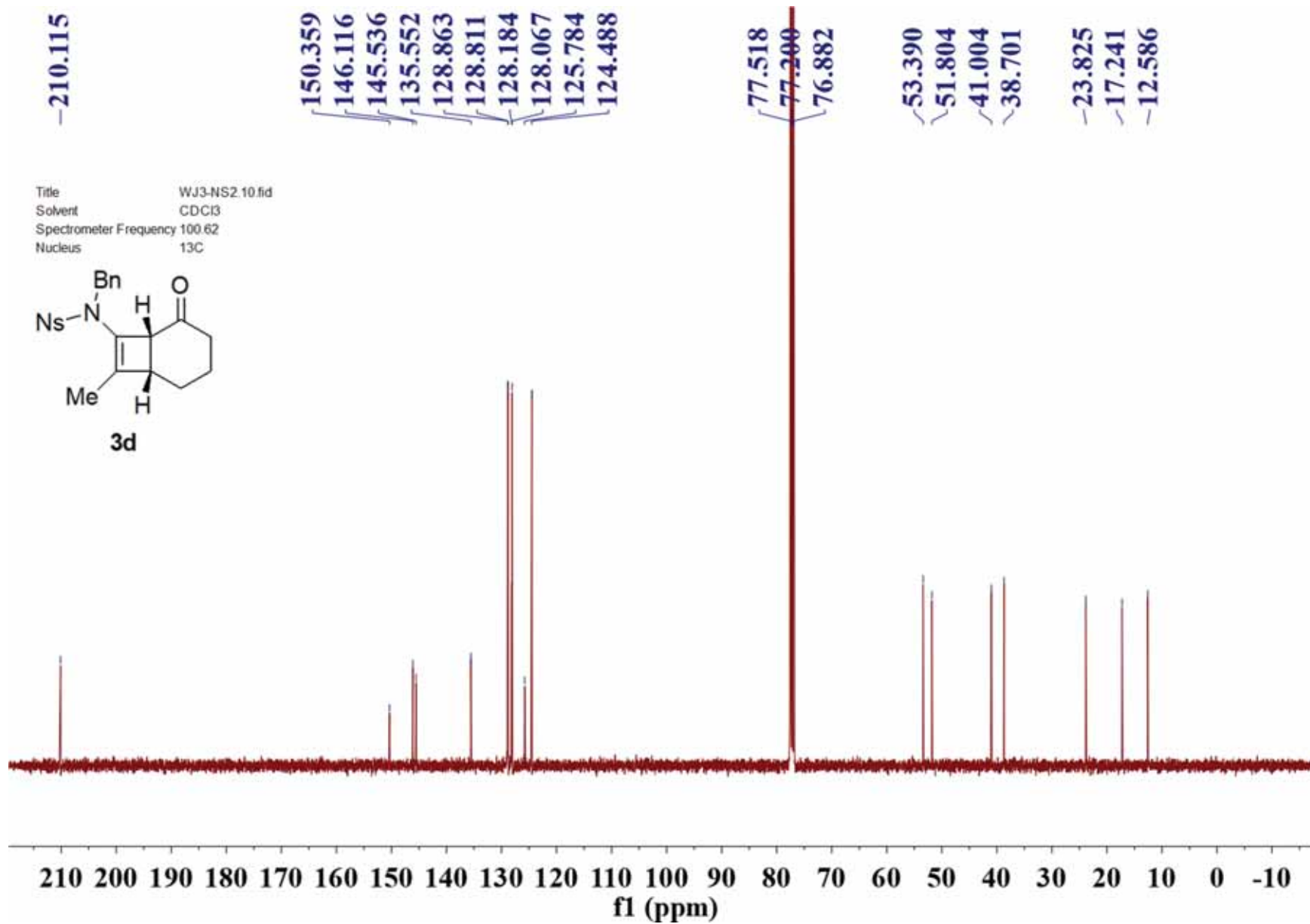




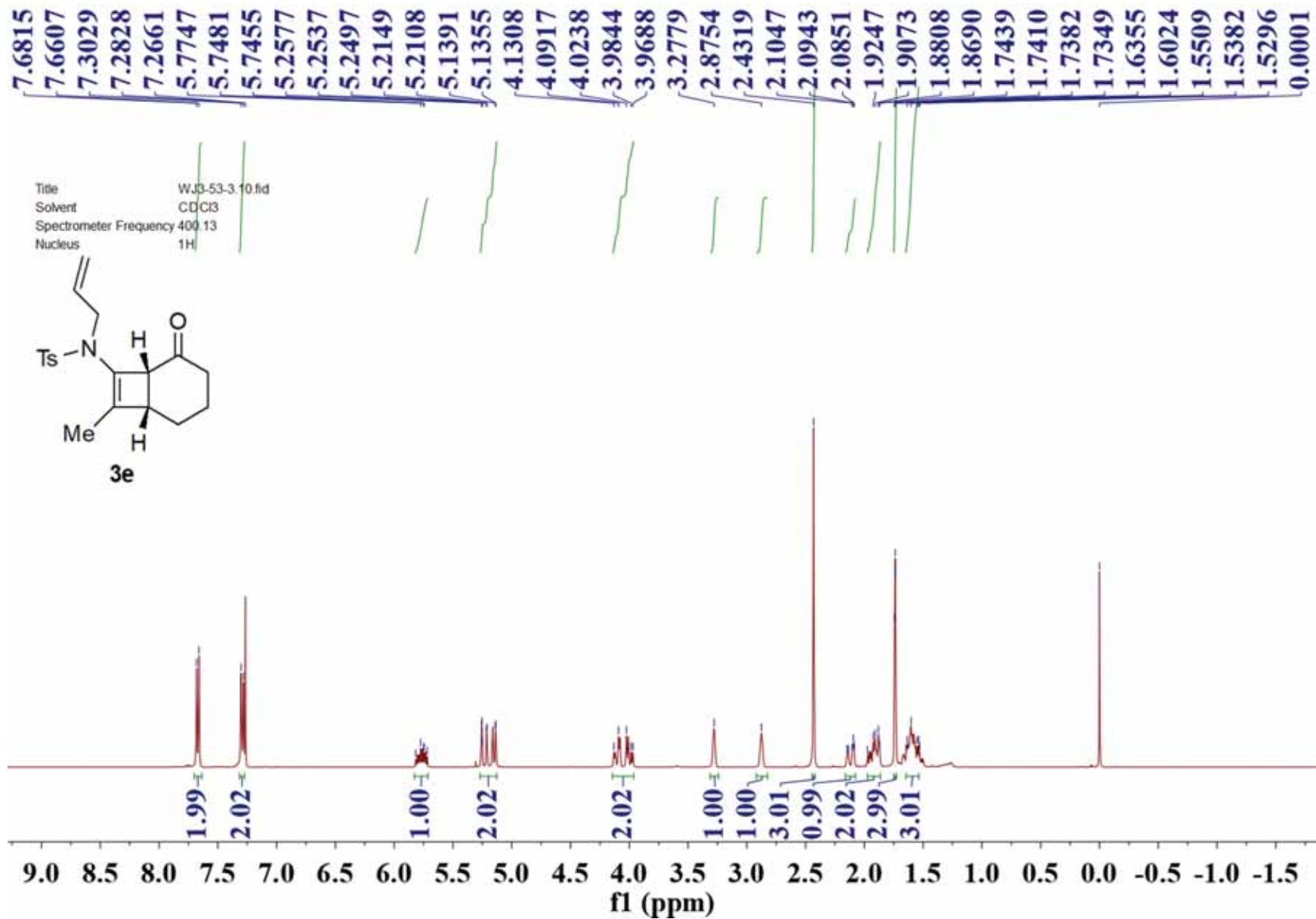












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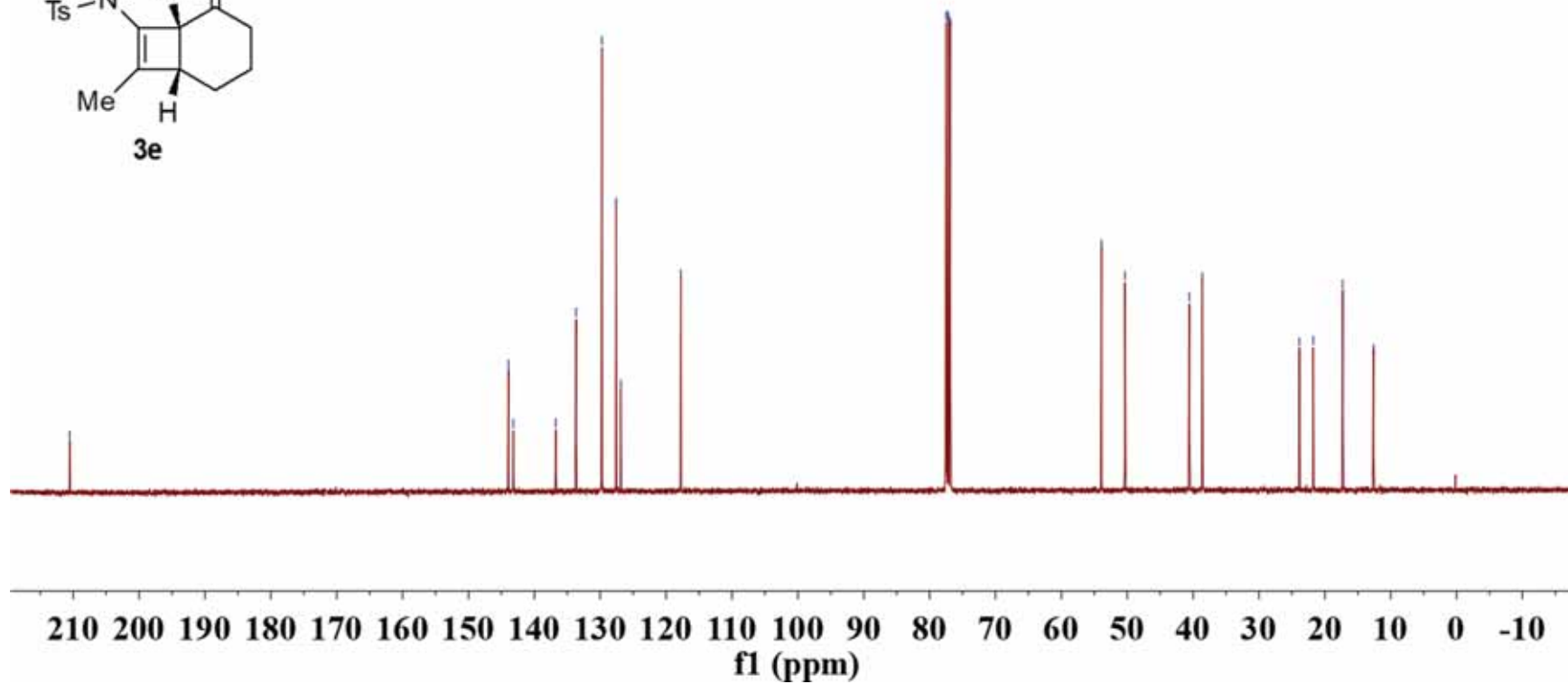
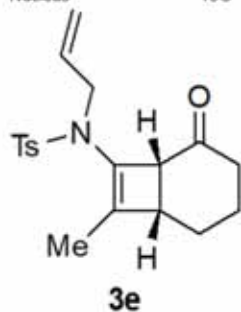
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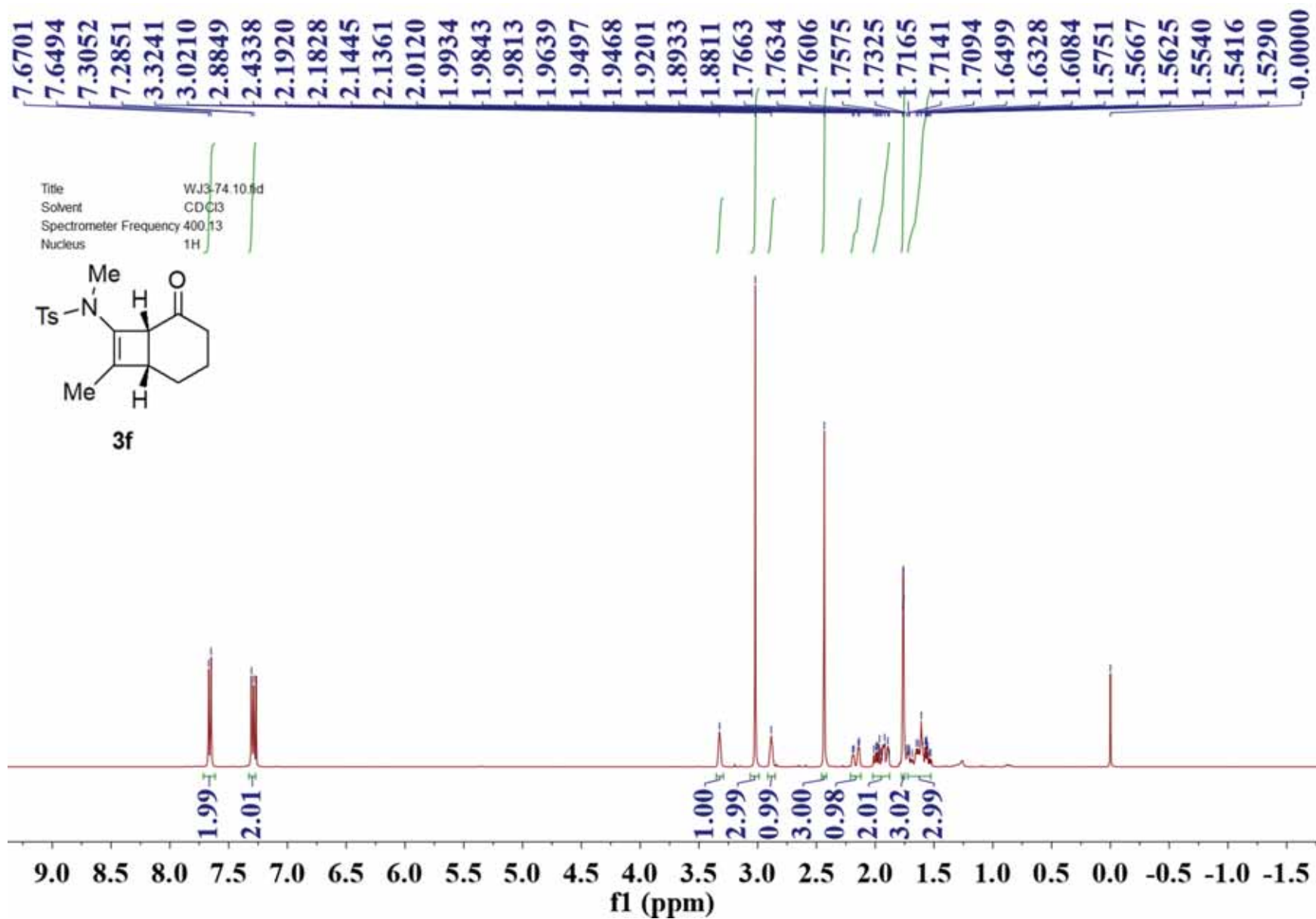
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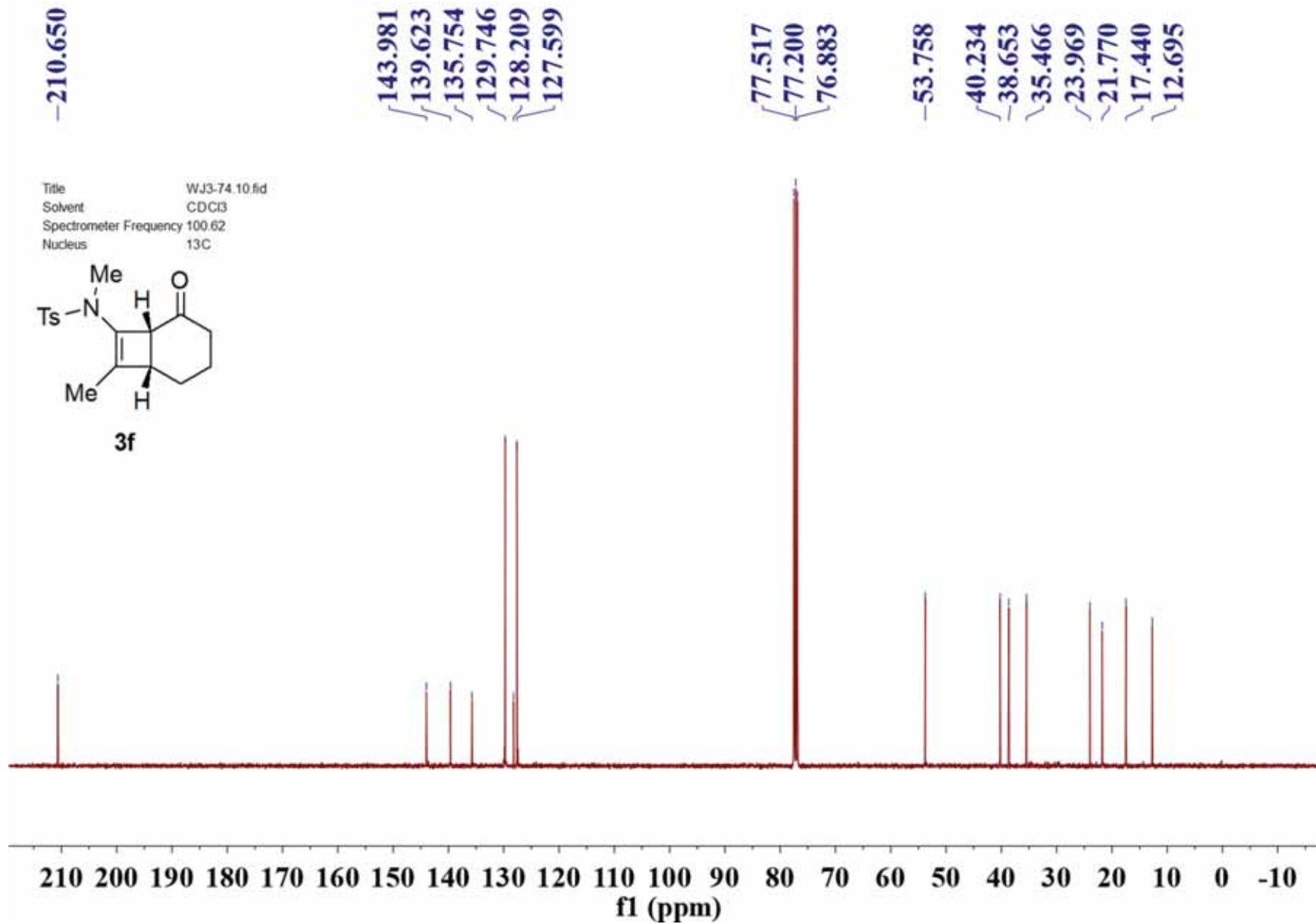
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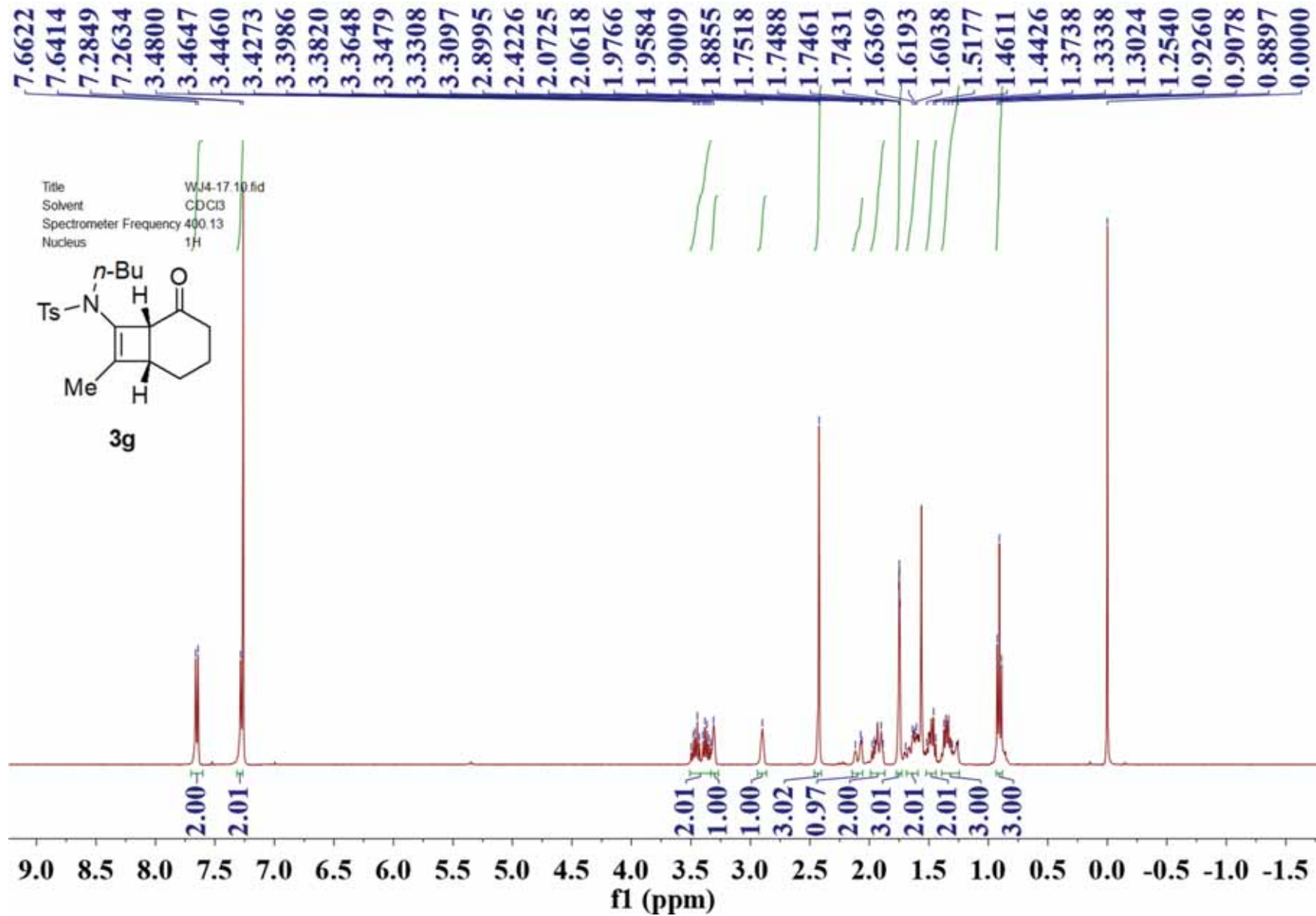
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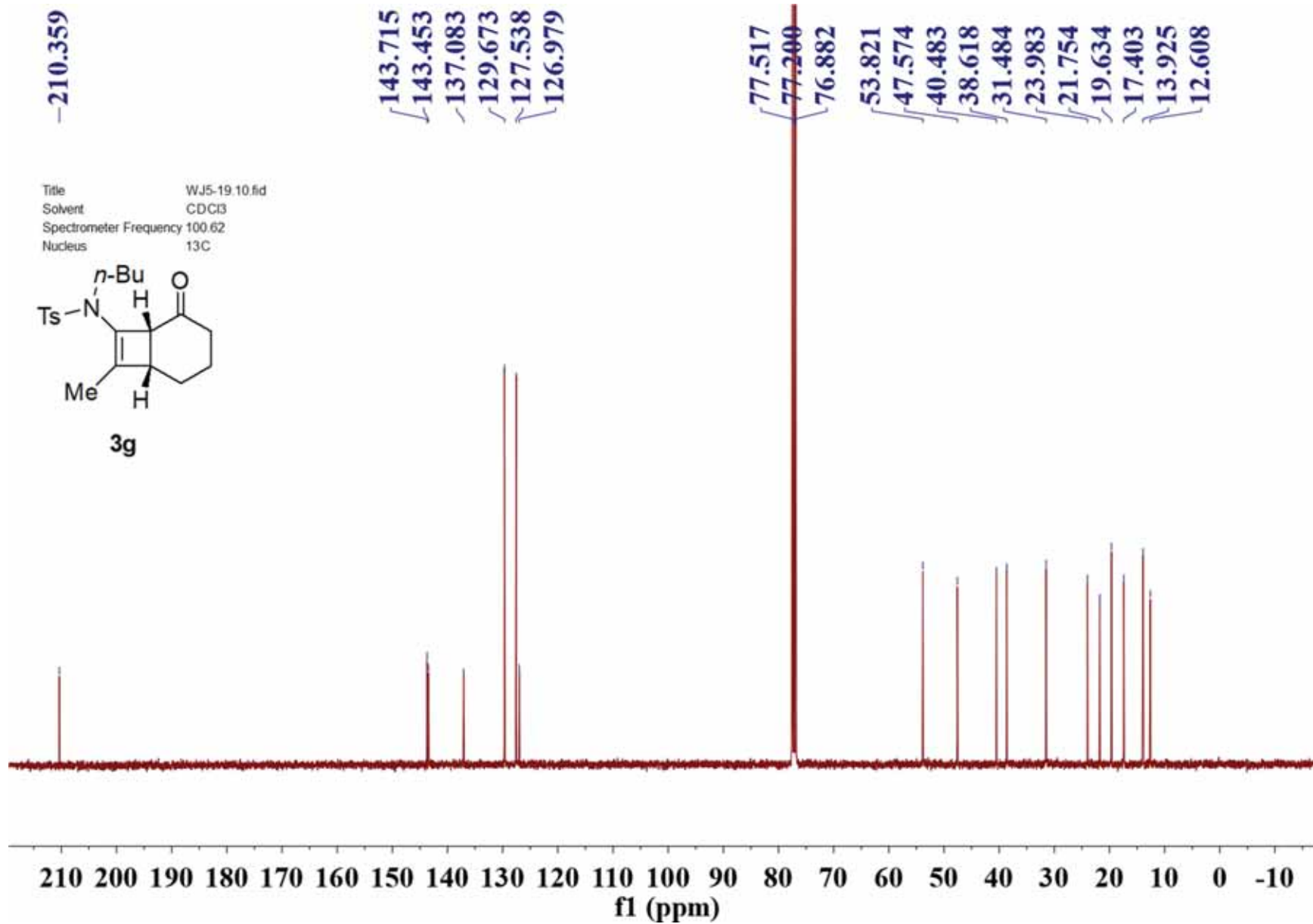
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Nucleus 13C

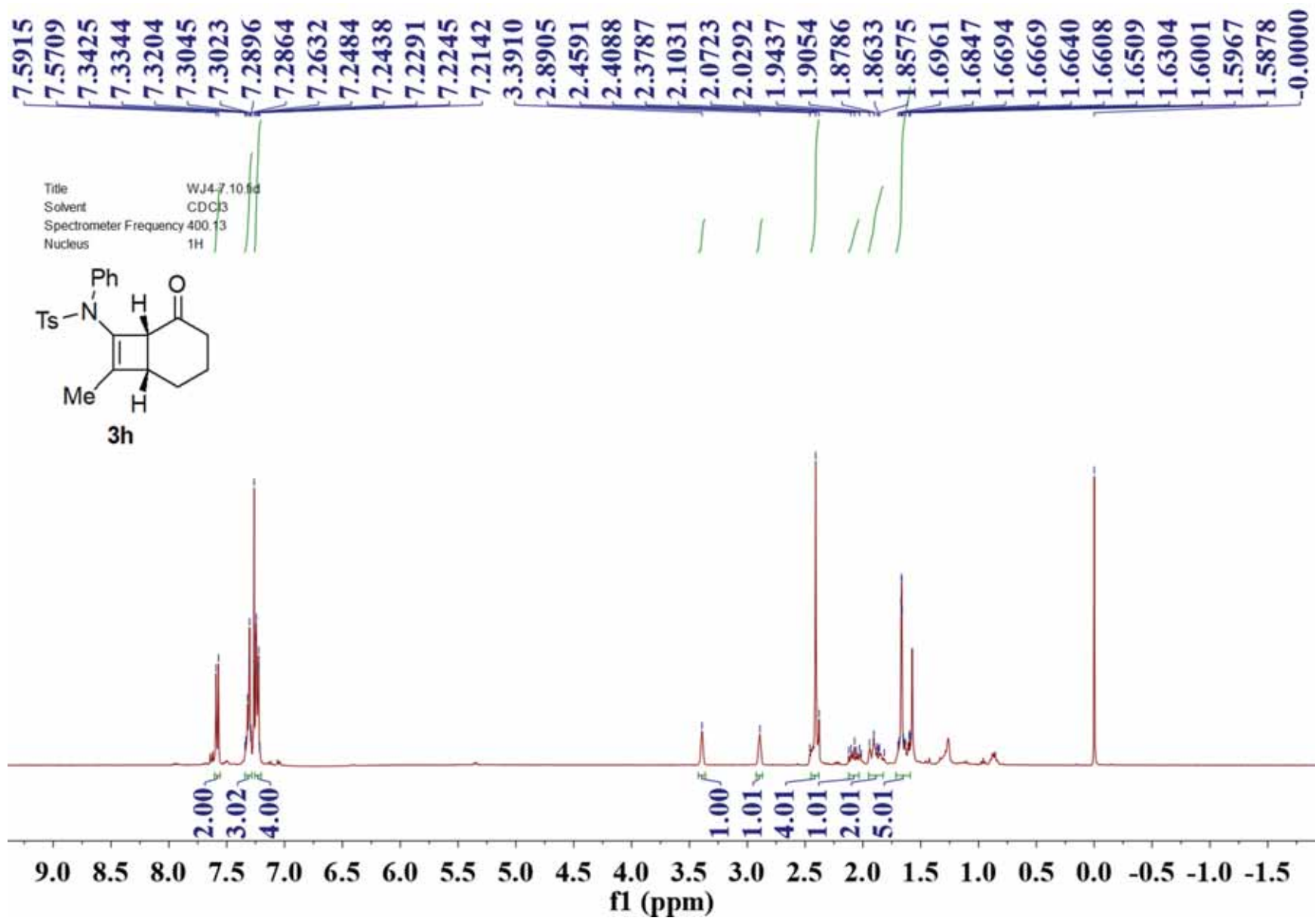












-210.939

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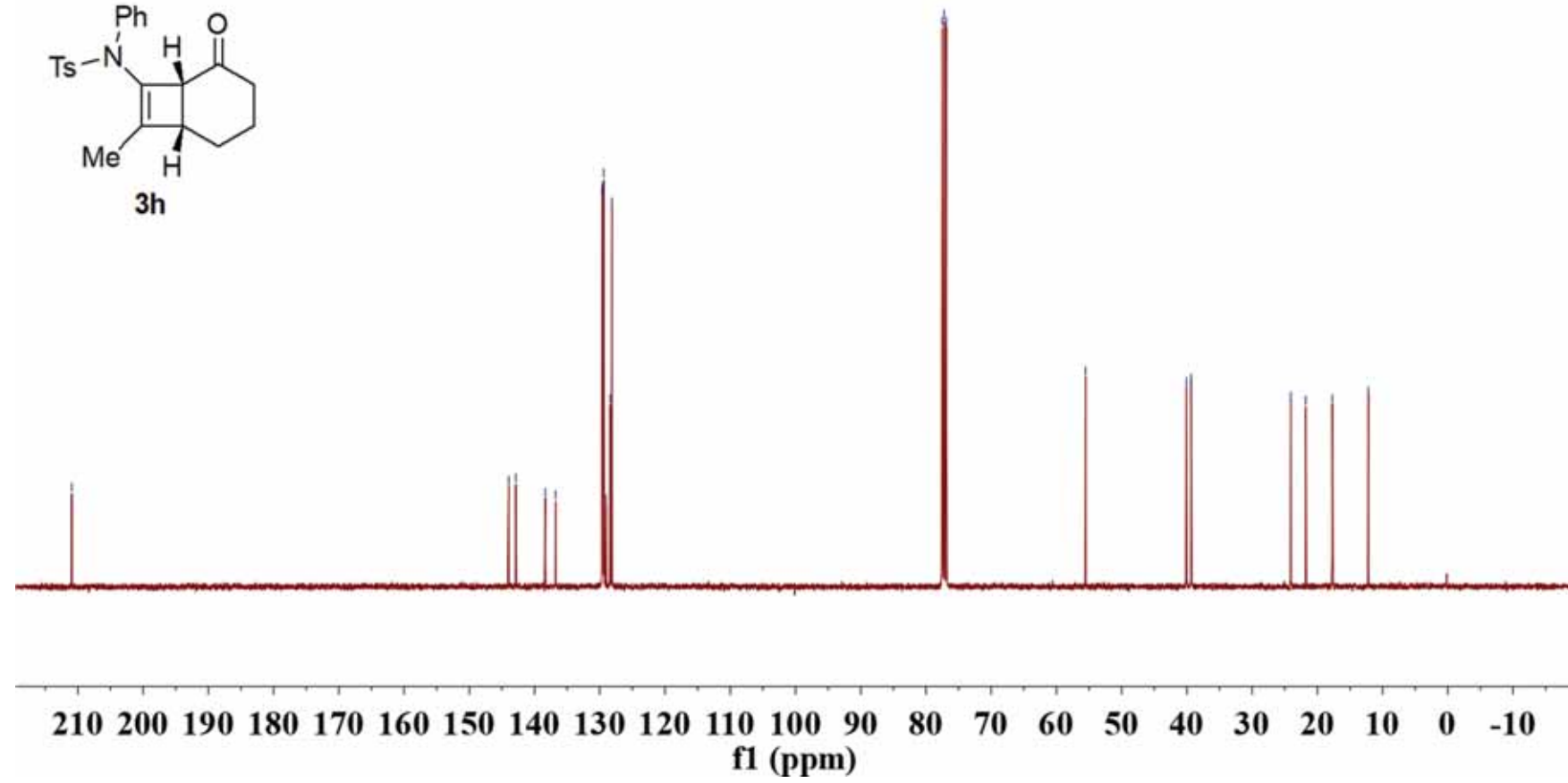
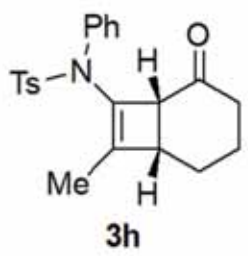
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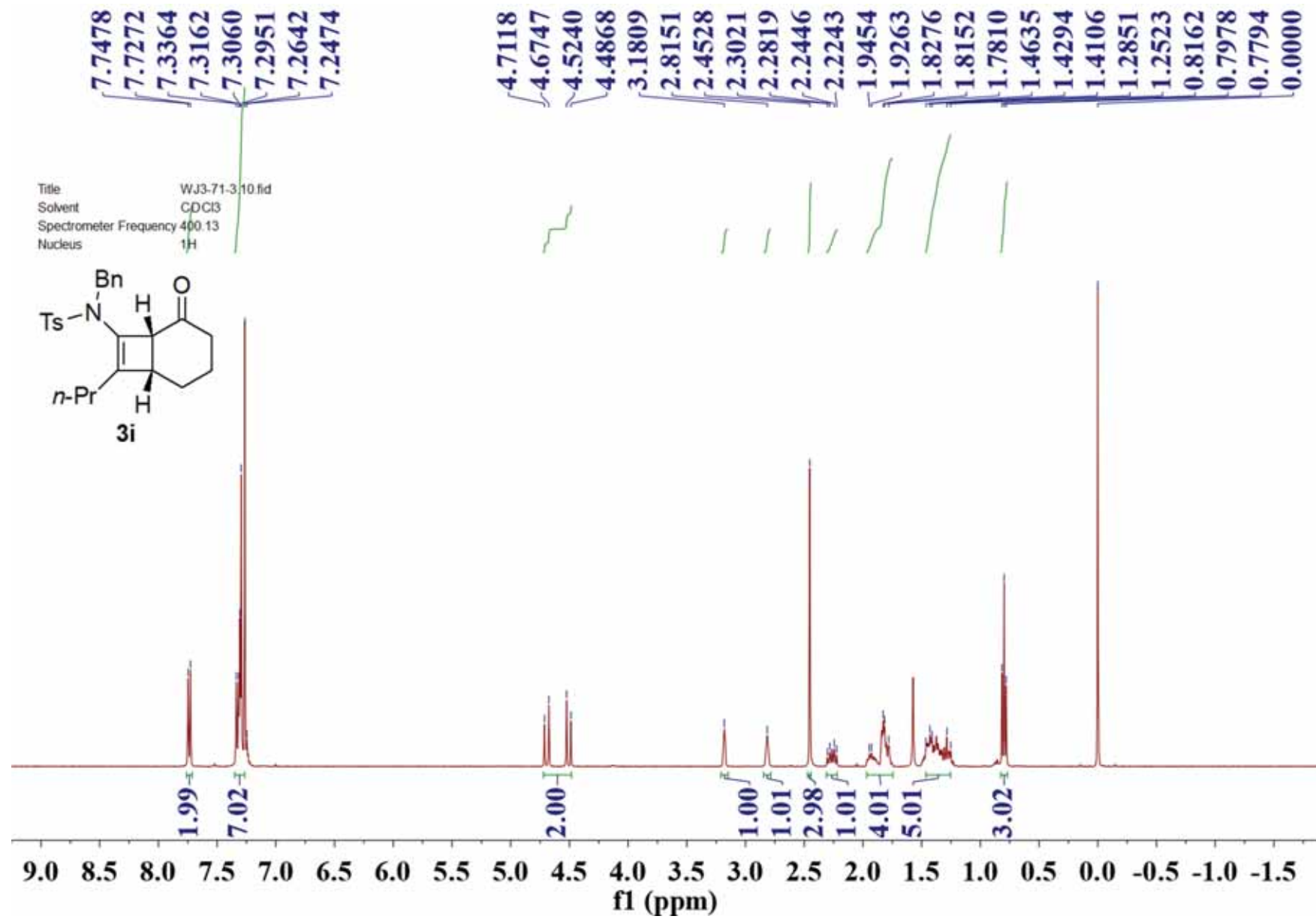
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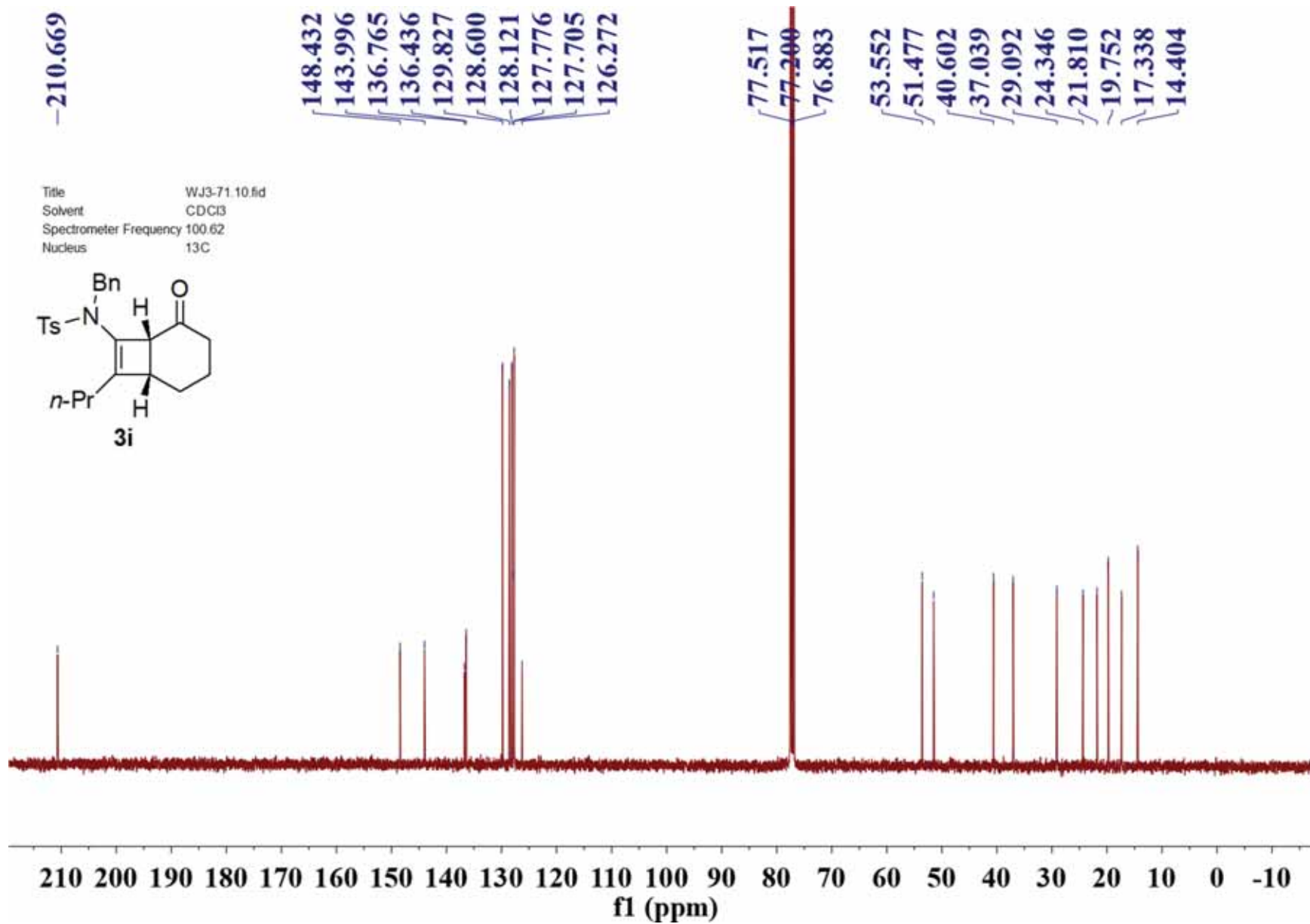
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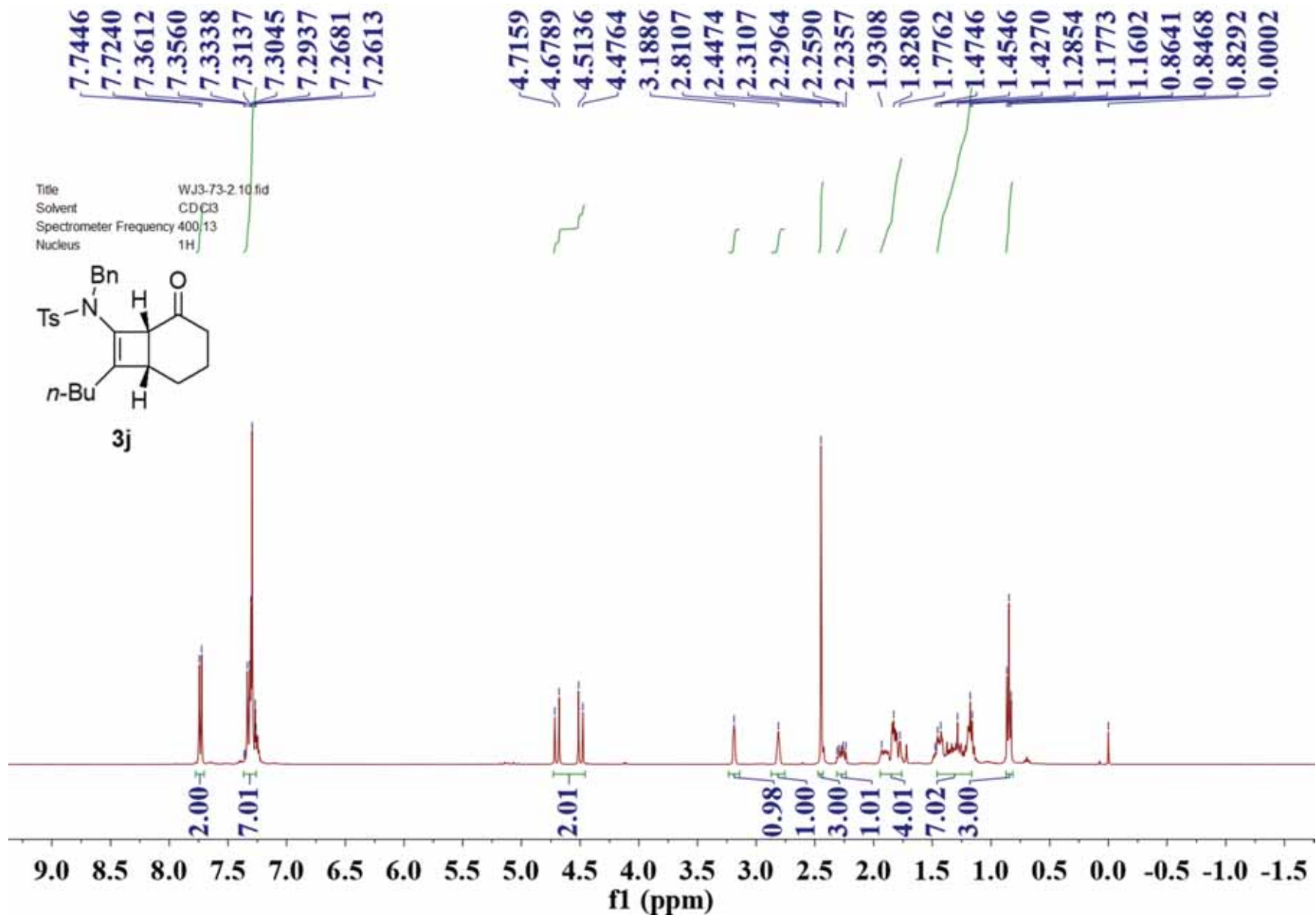
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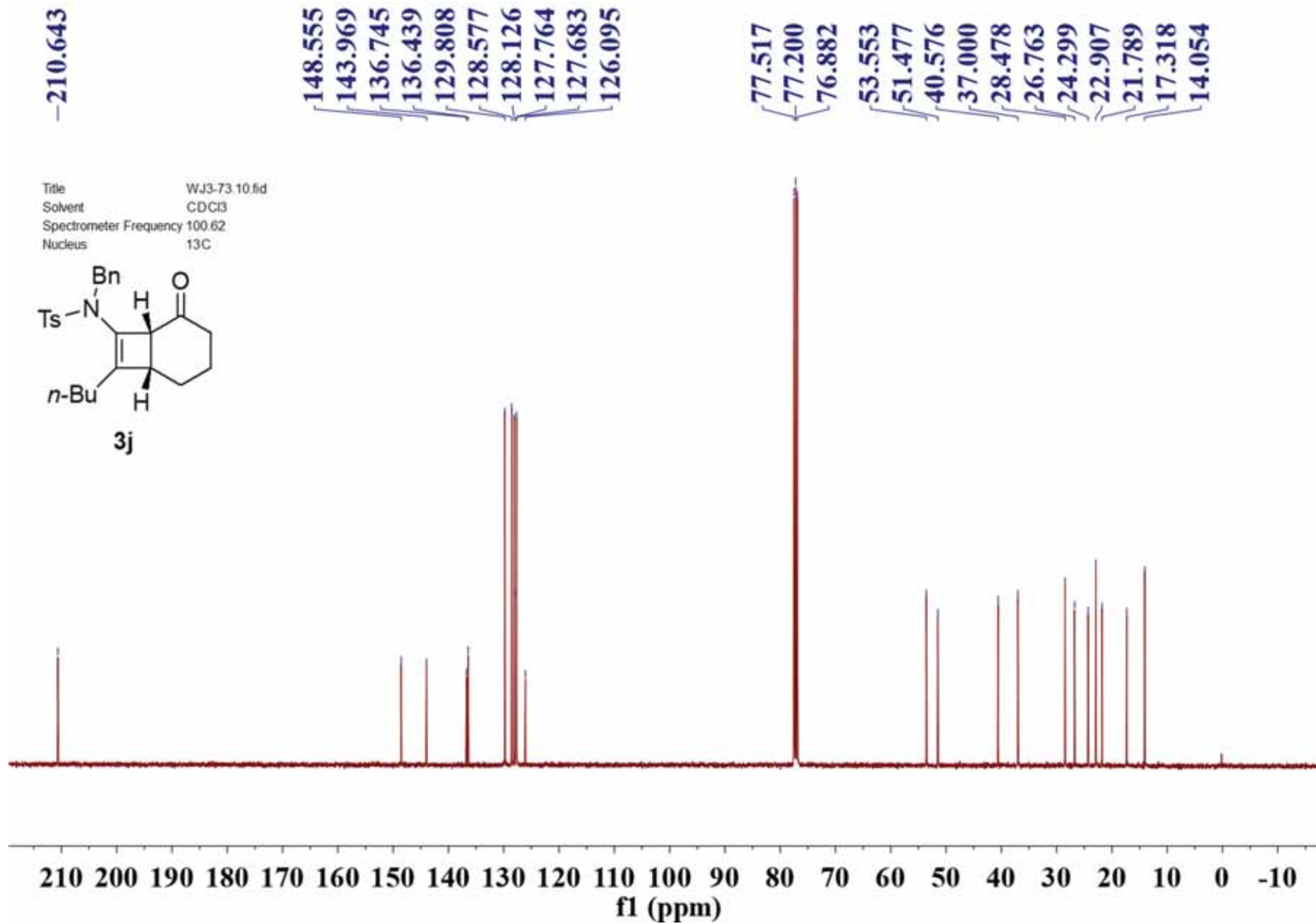


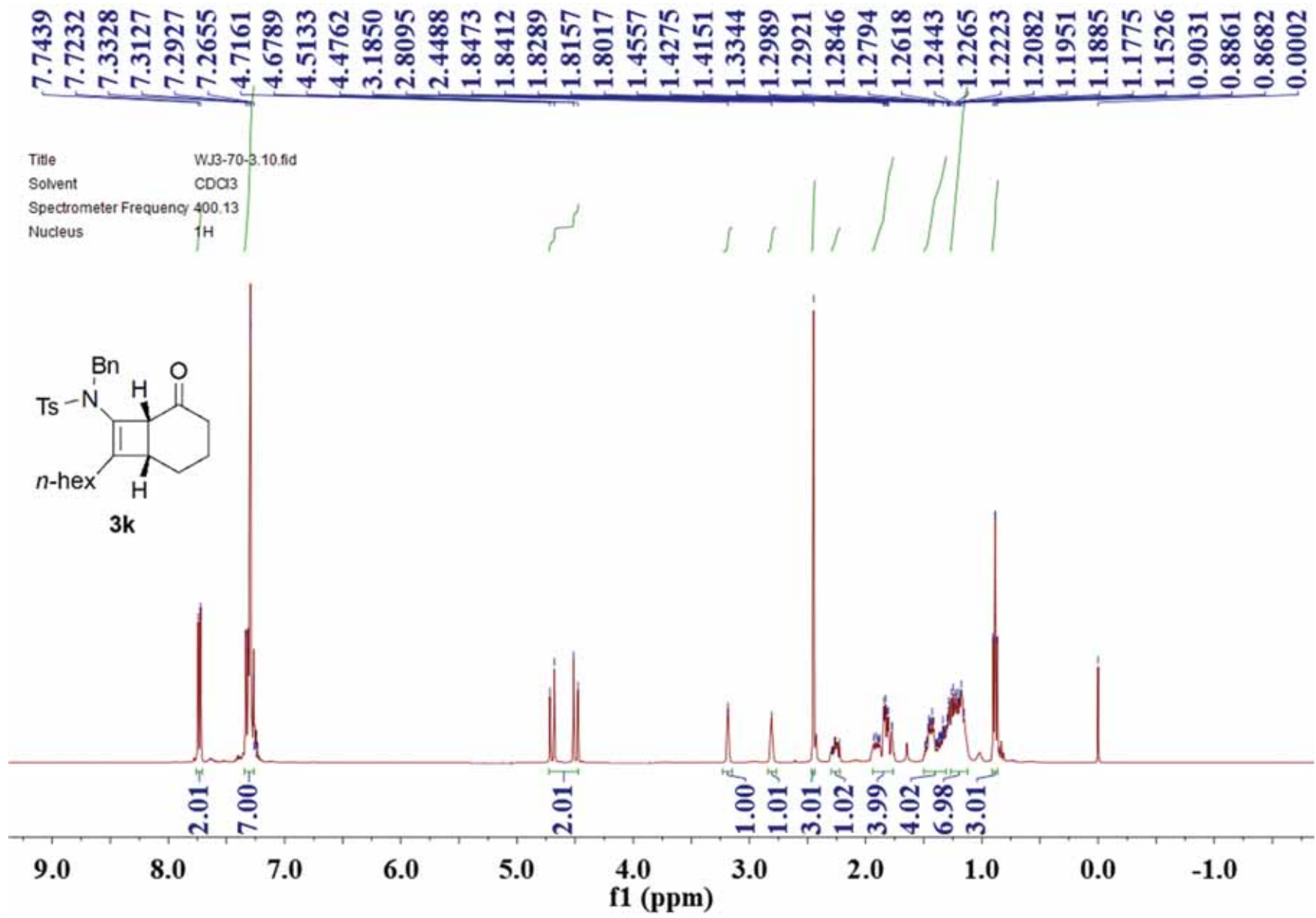


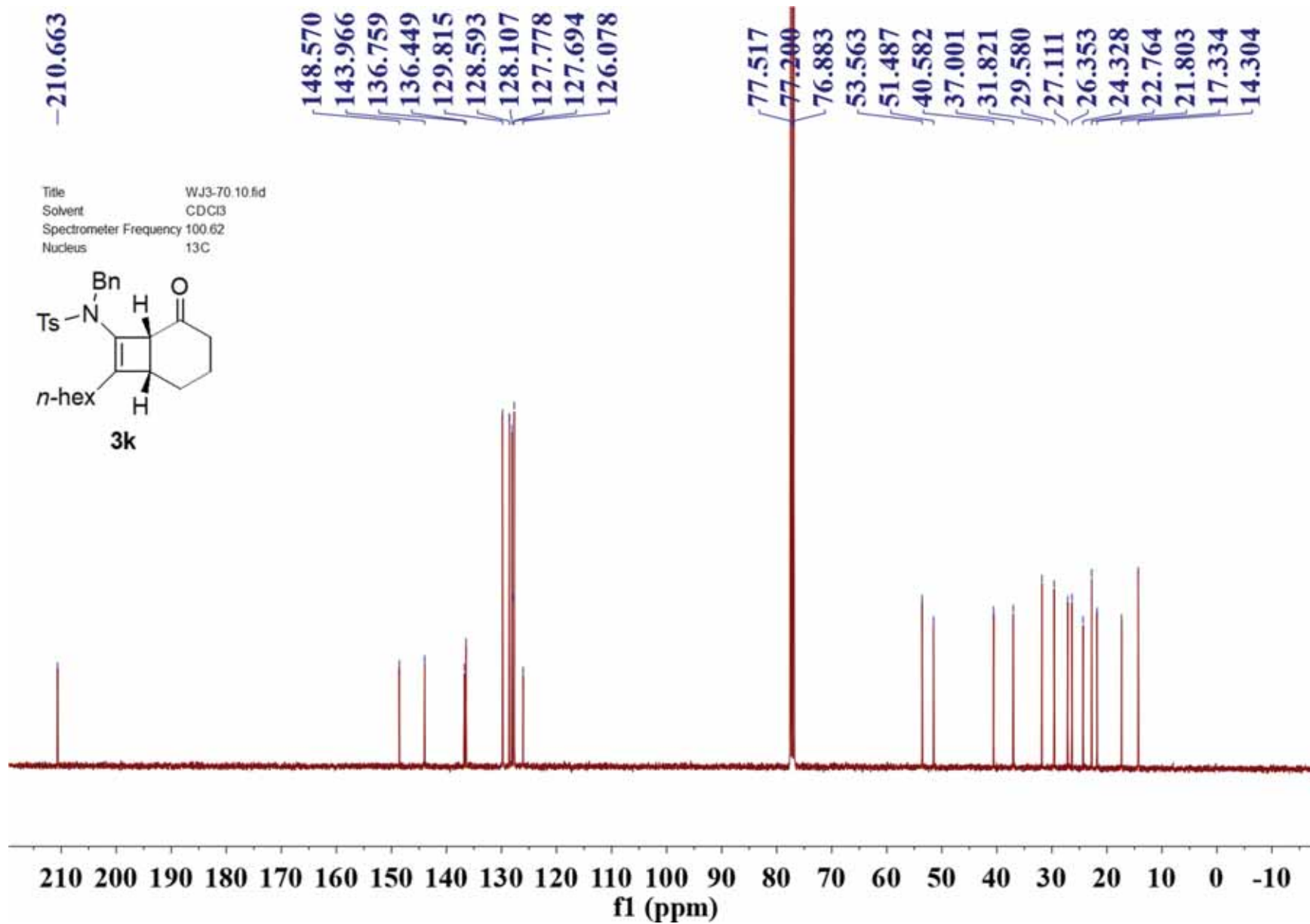


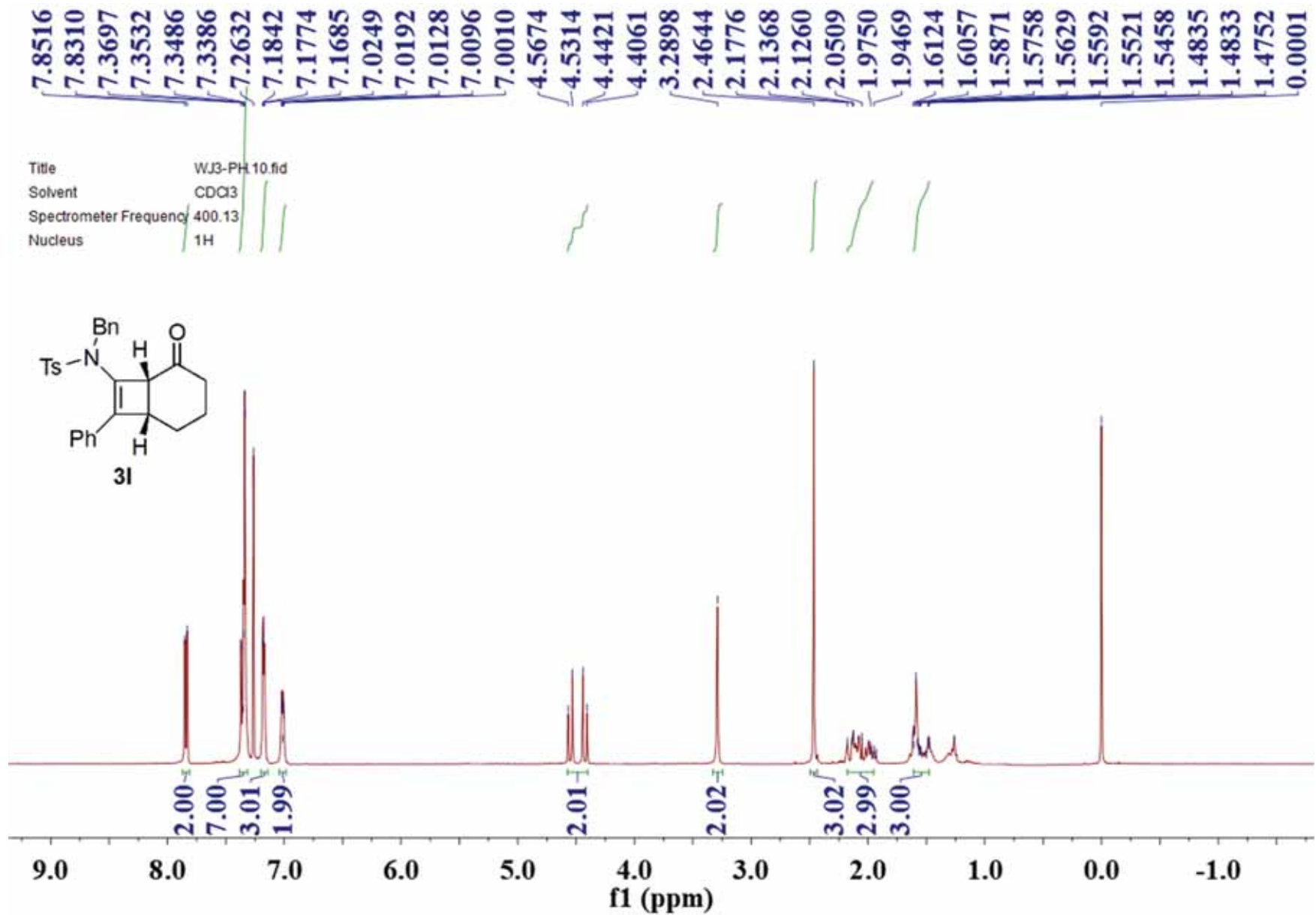


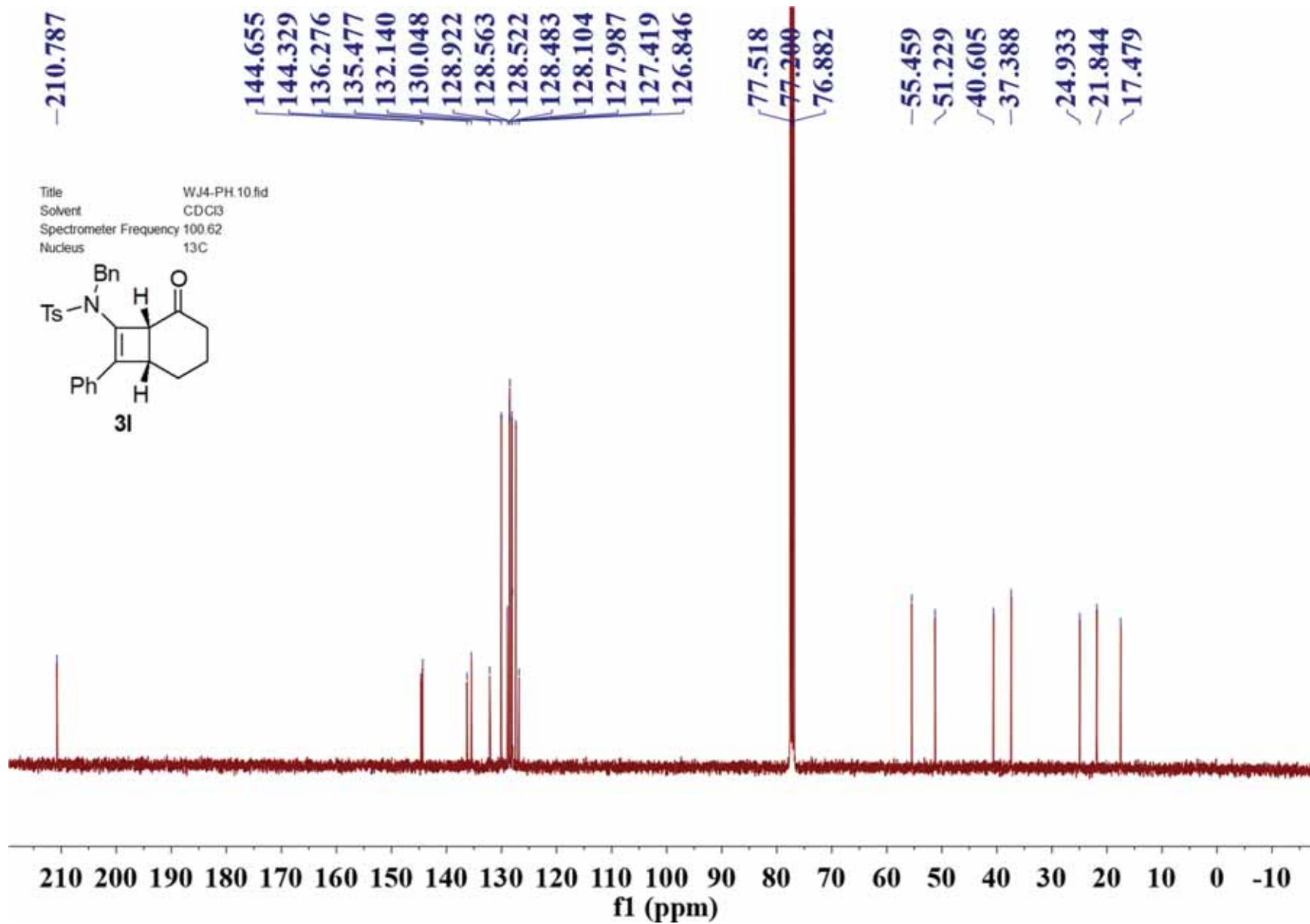




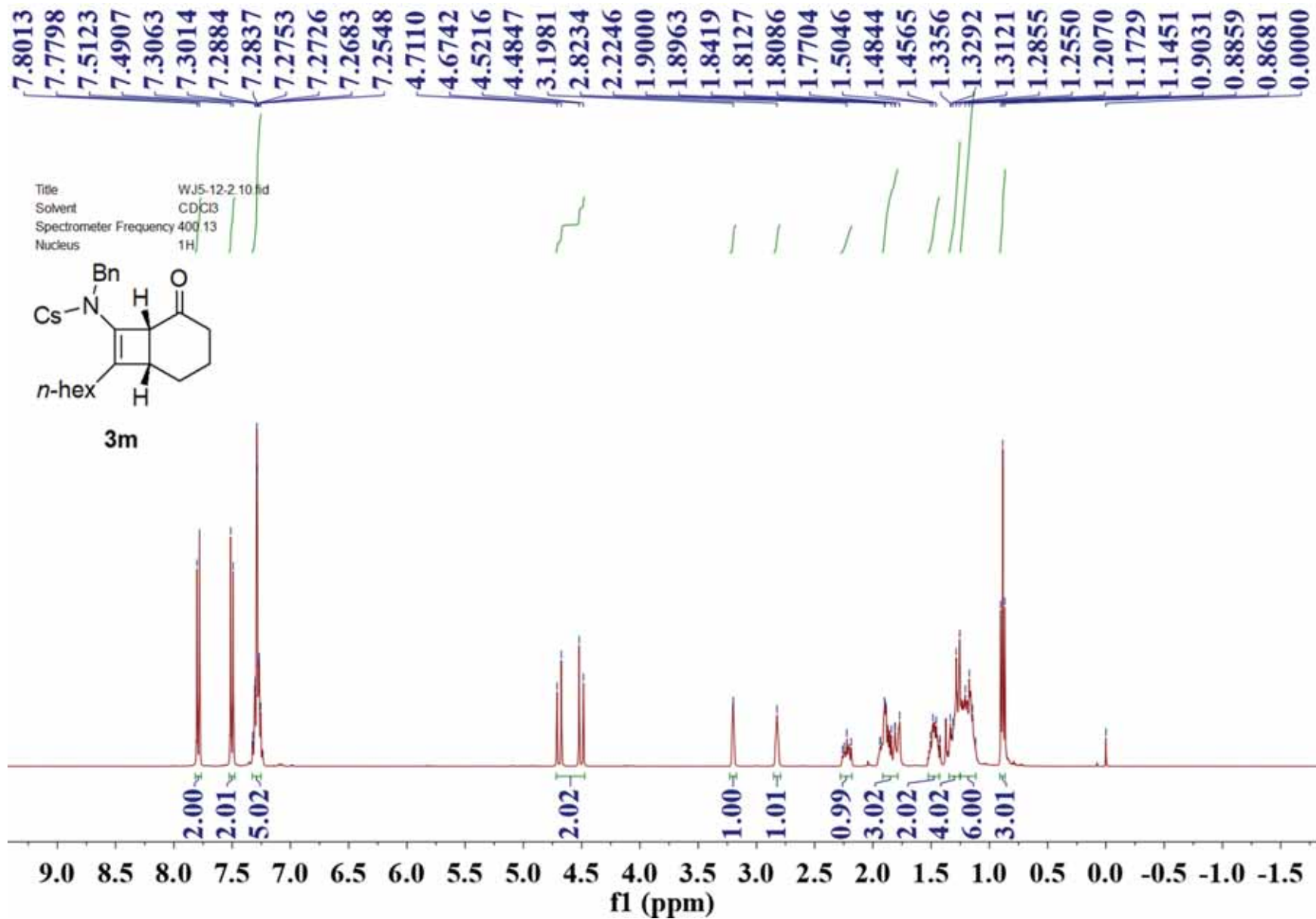










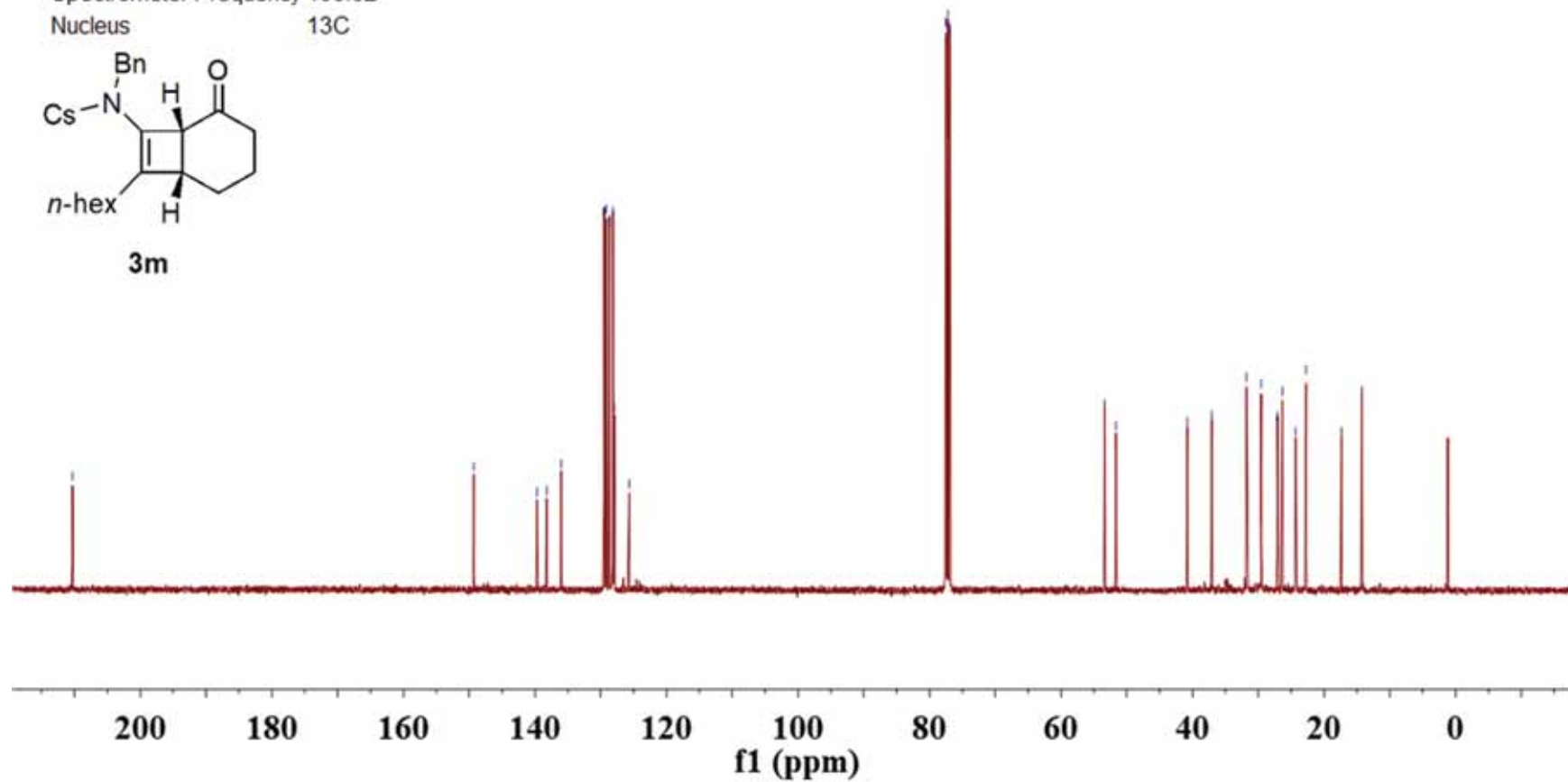
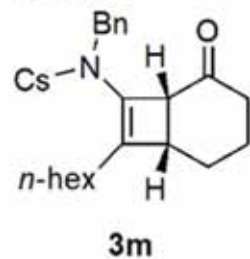


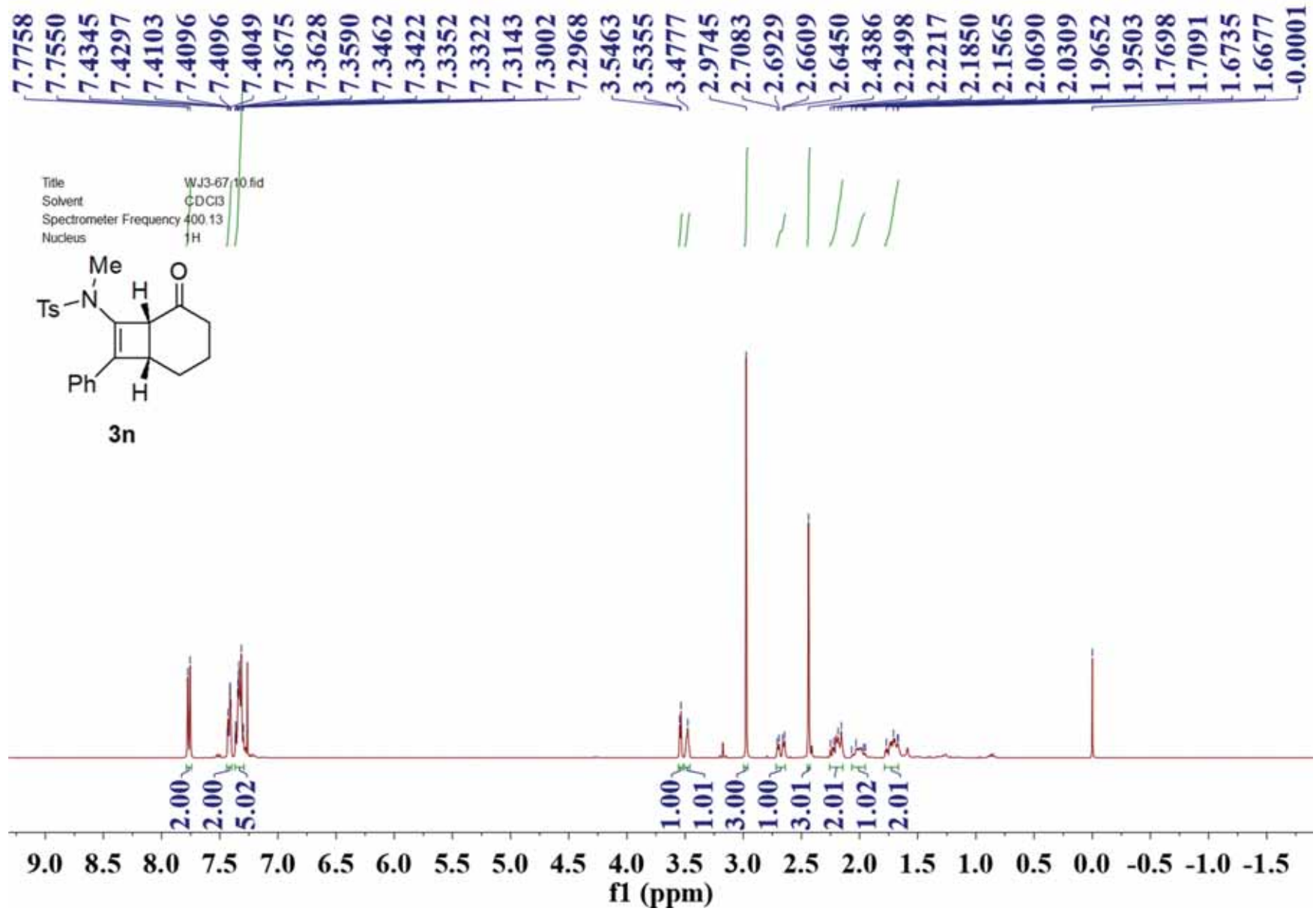
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Nucleus 13C





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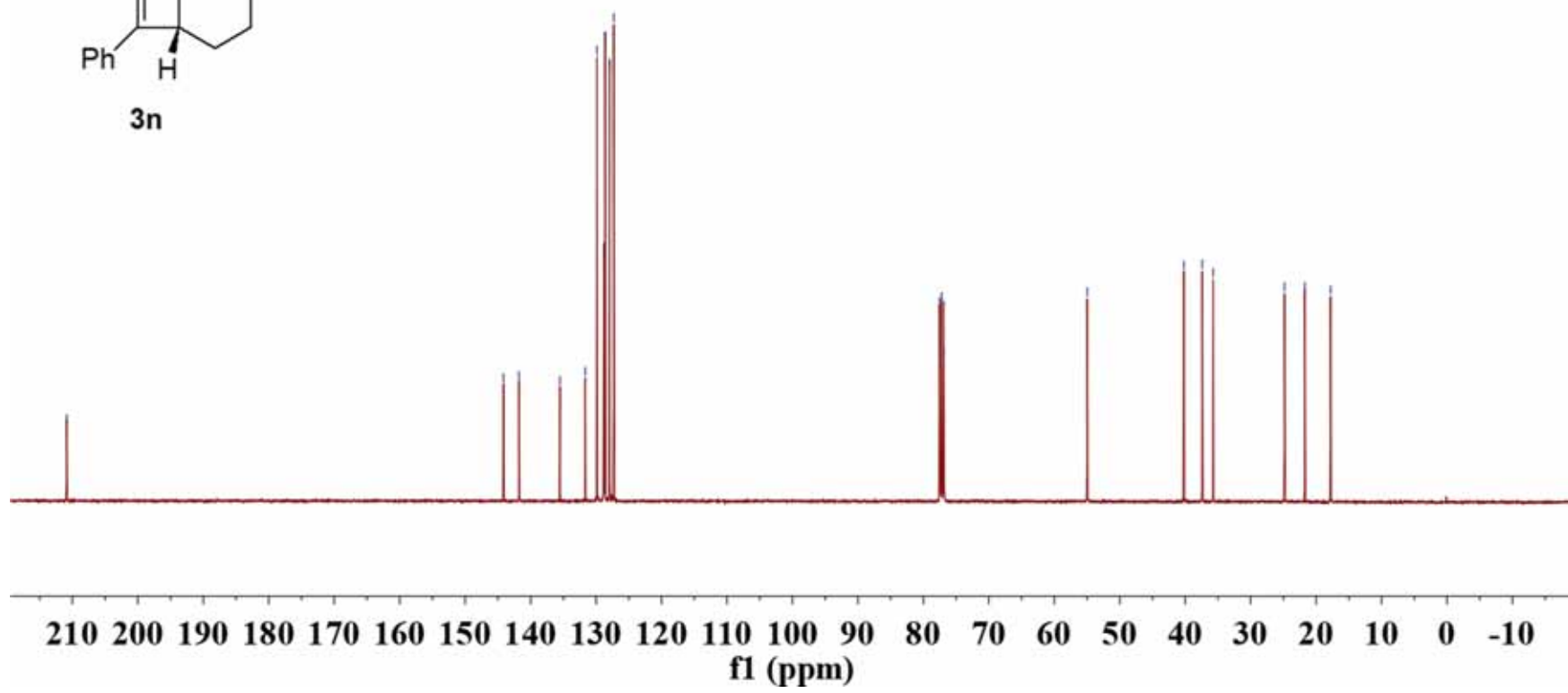
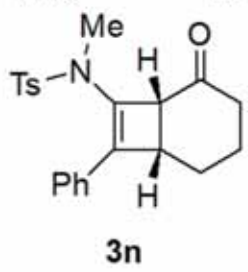
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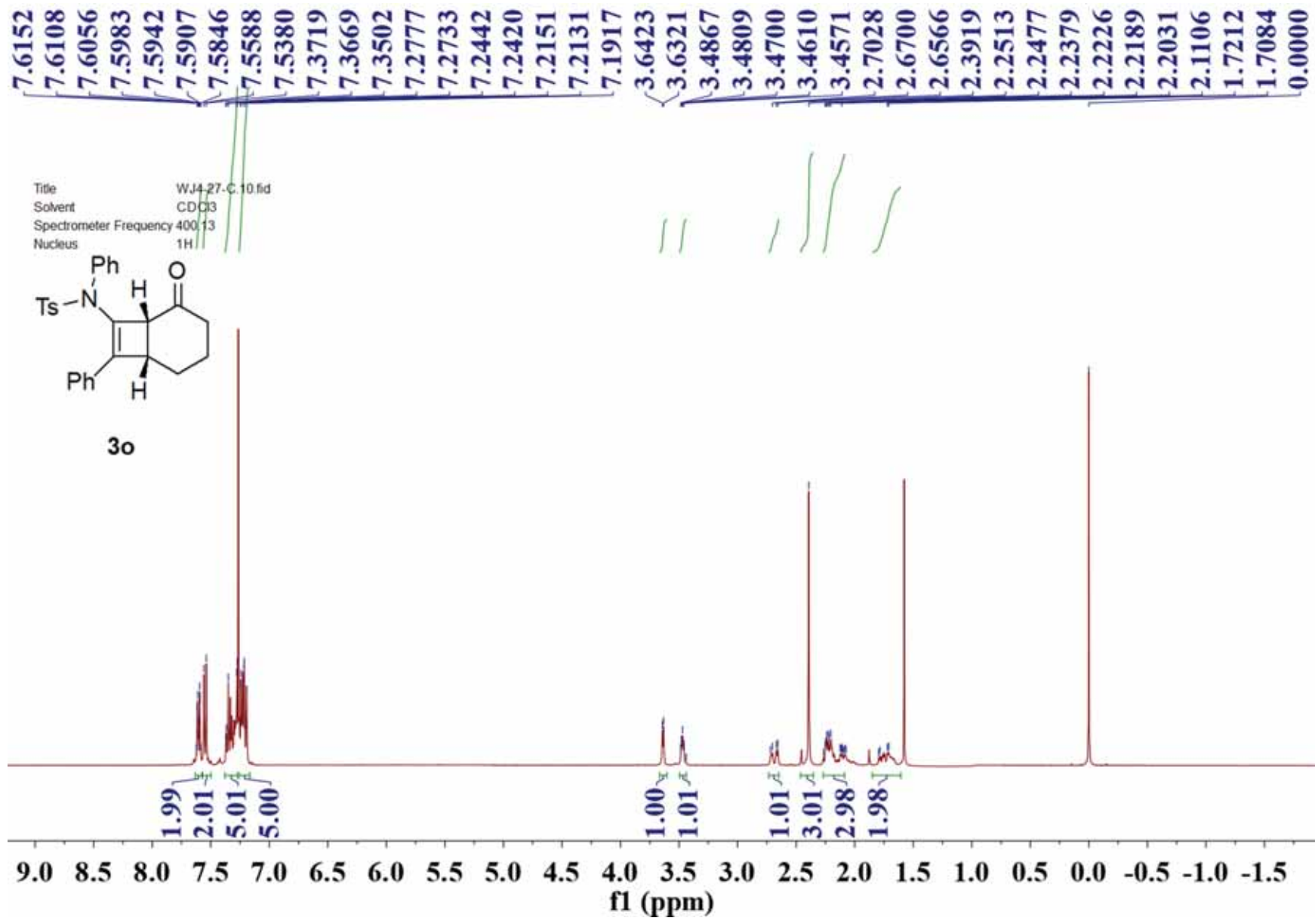
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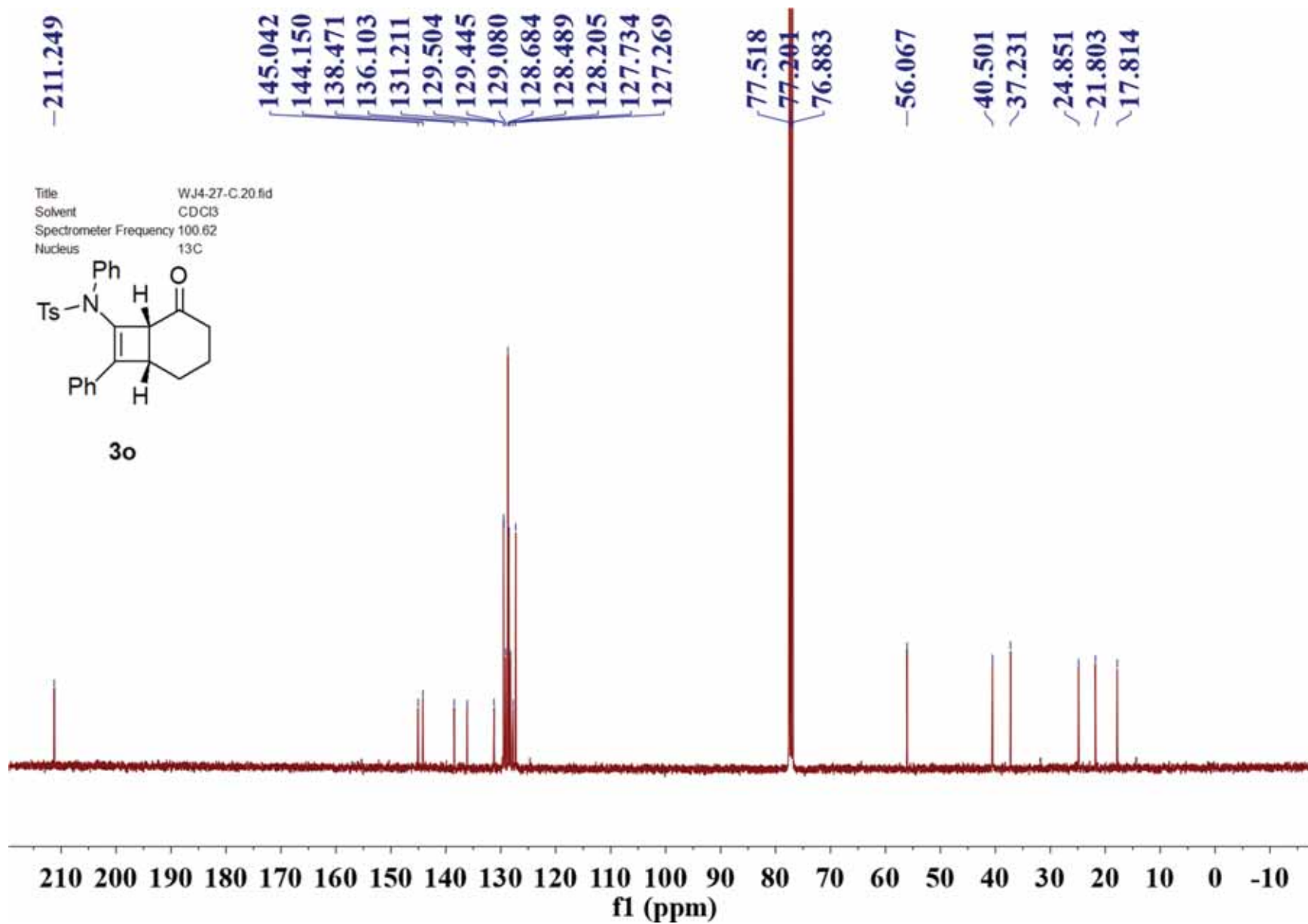
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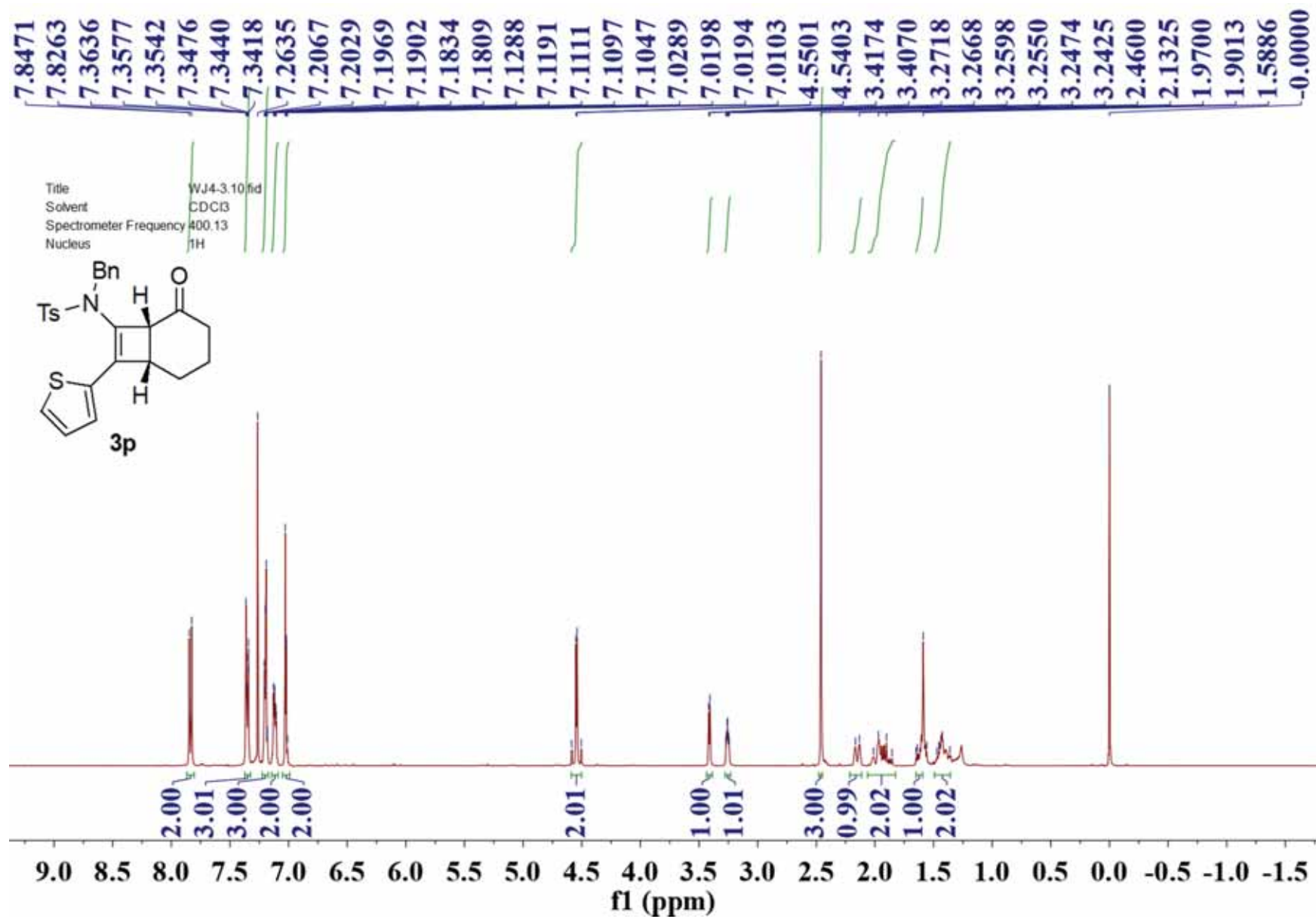
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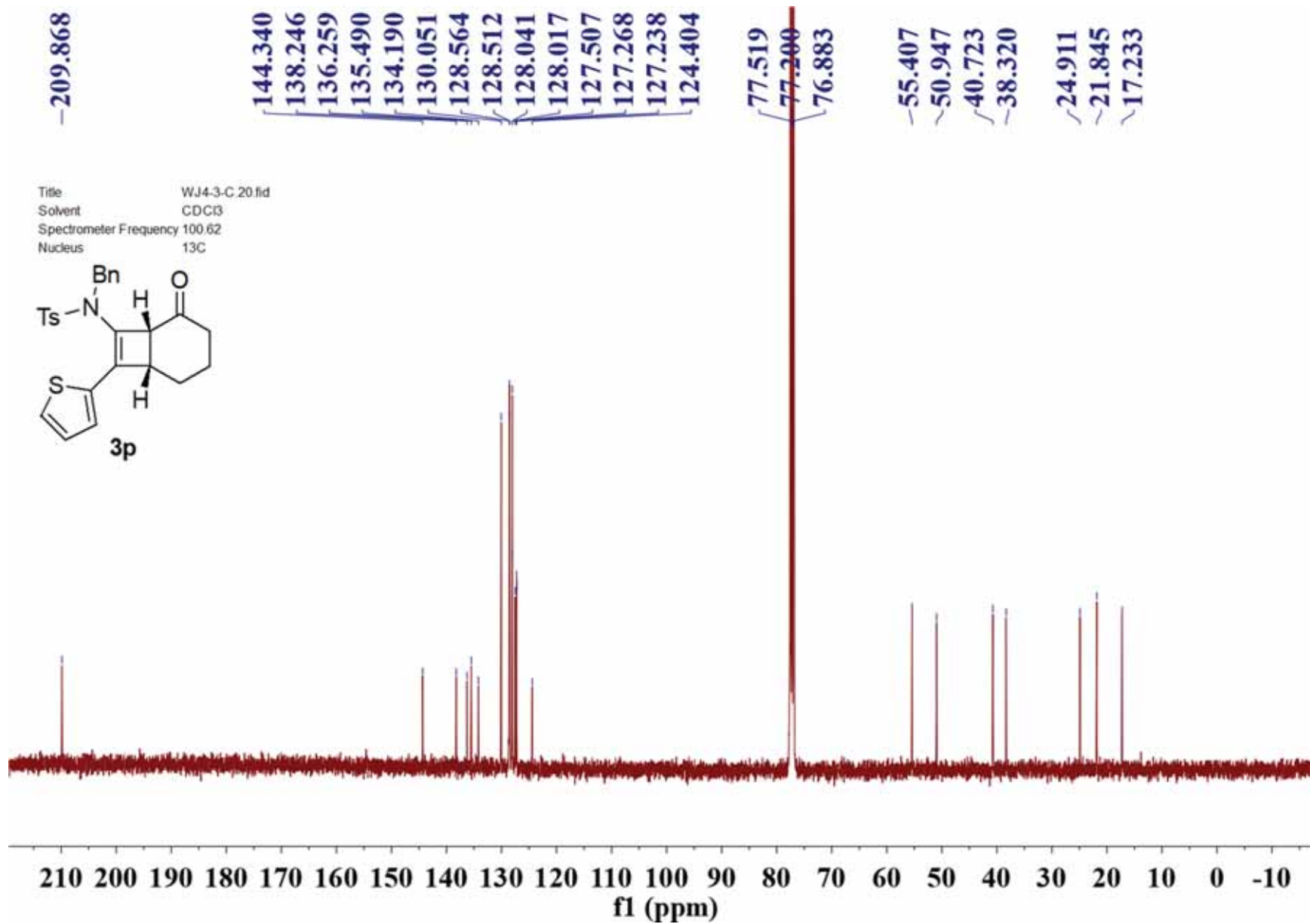
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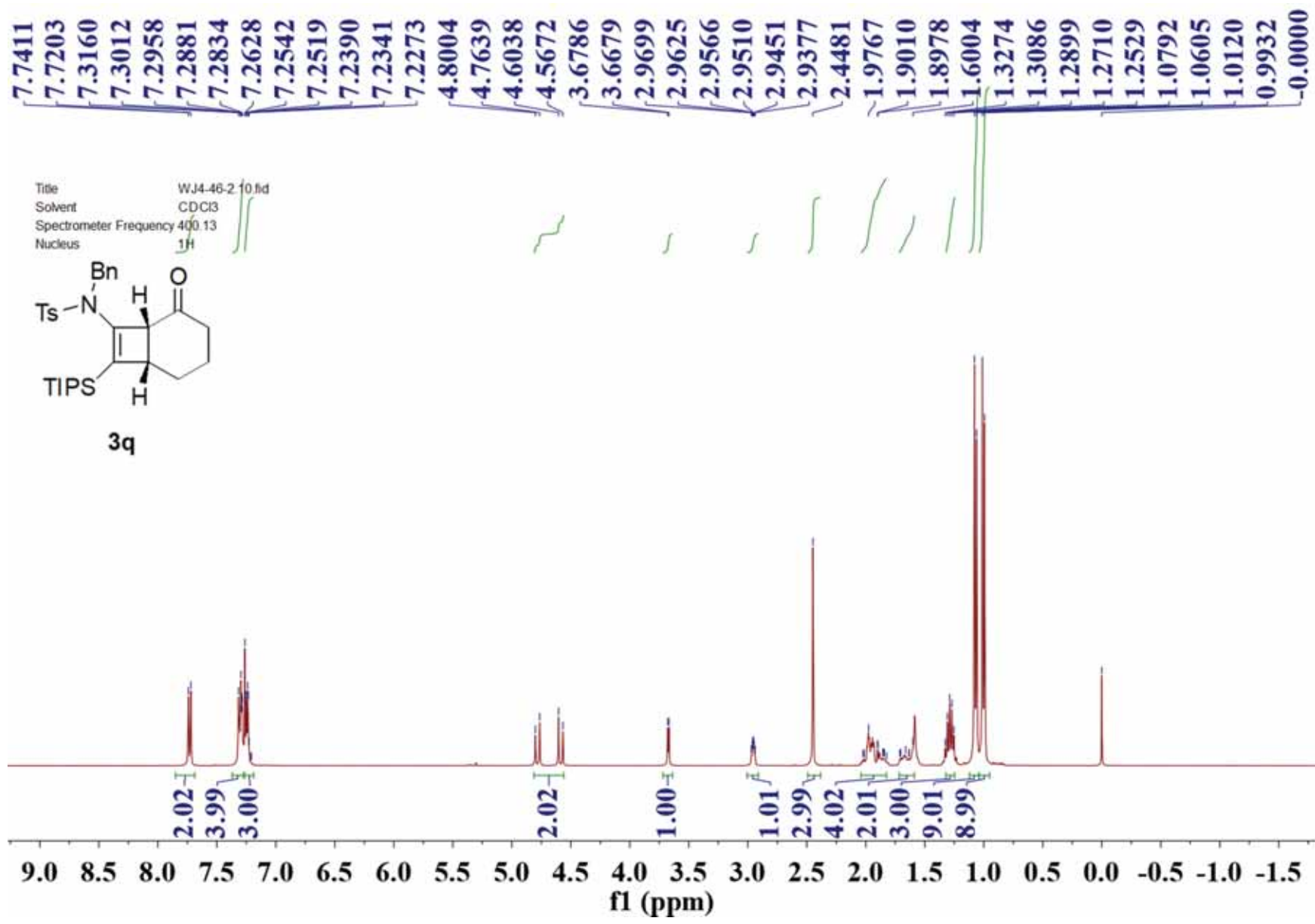


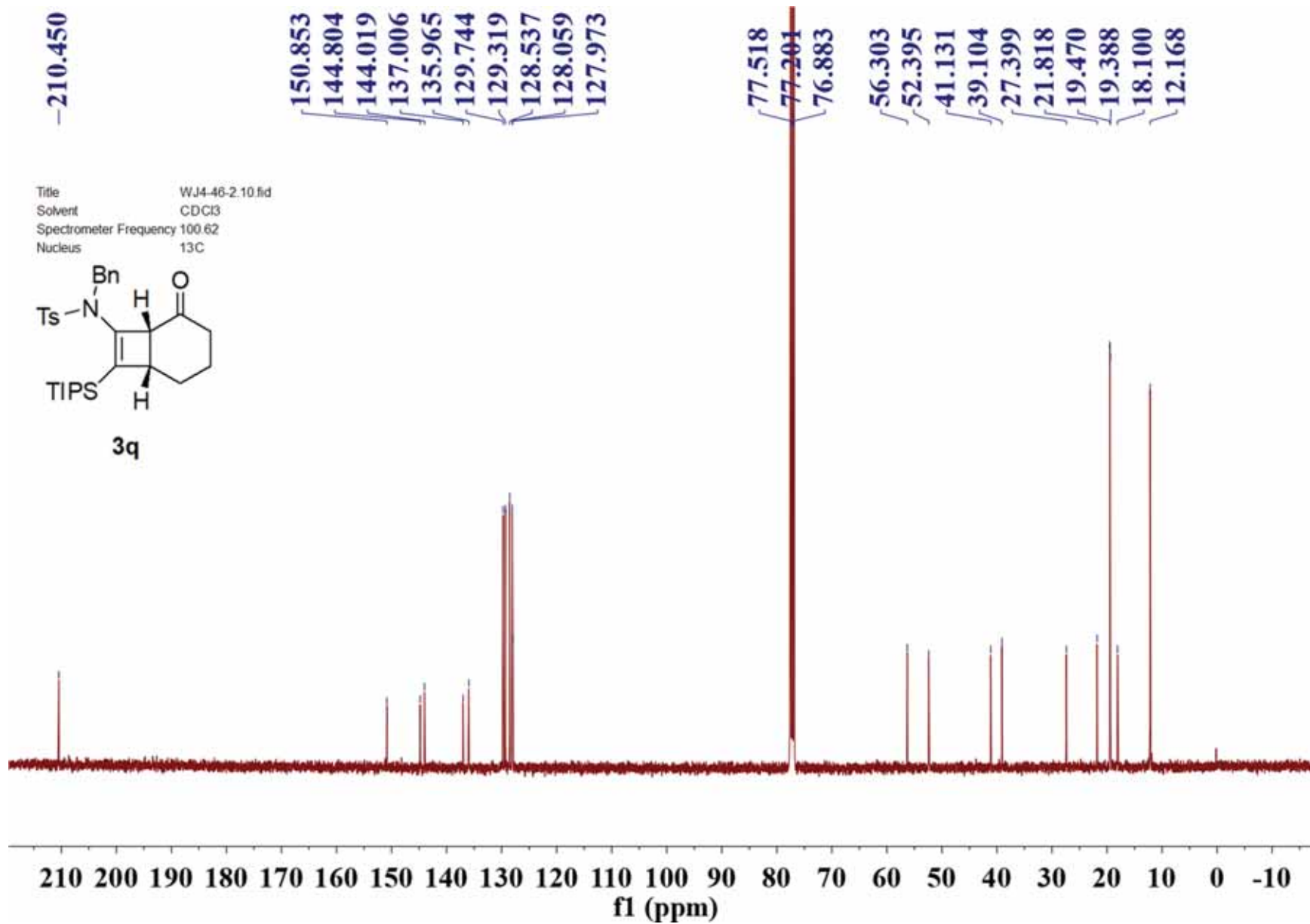


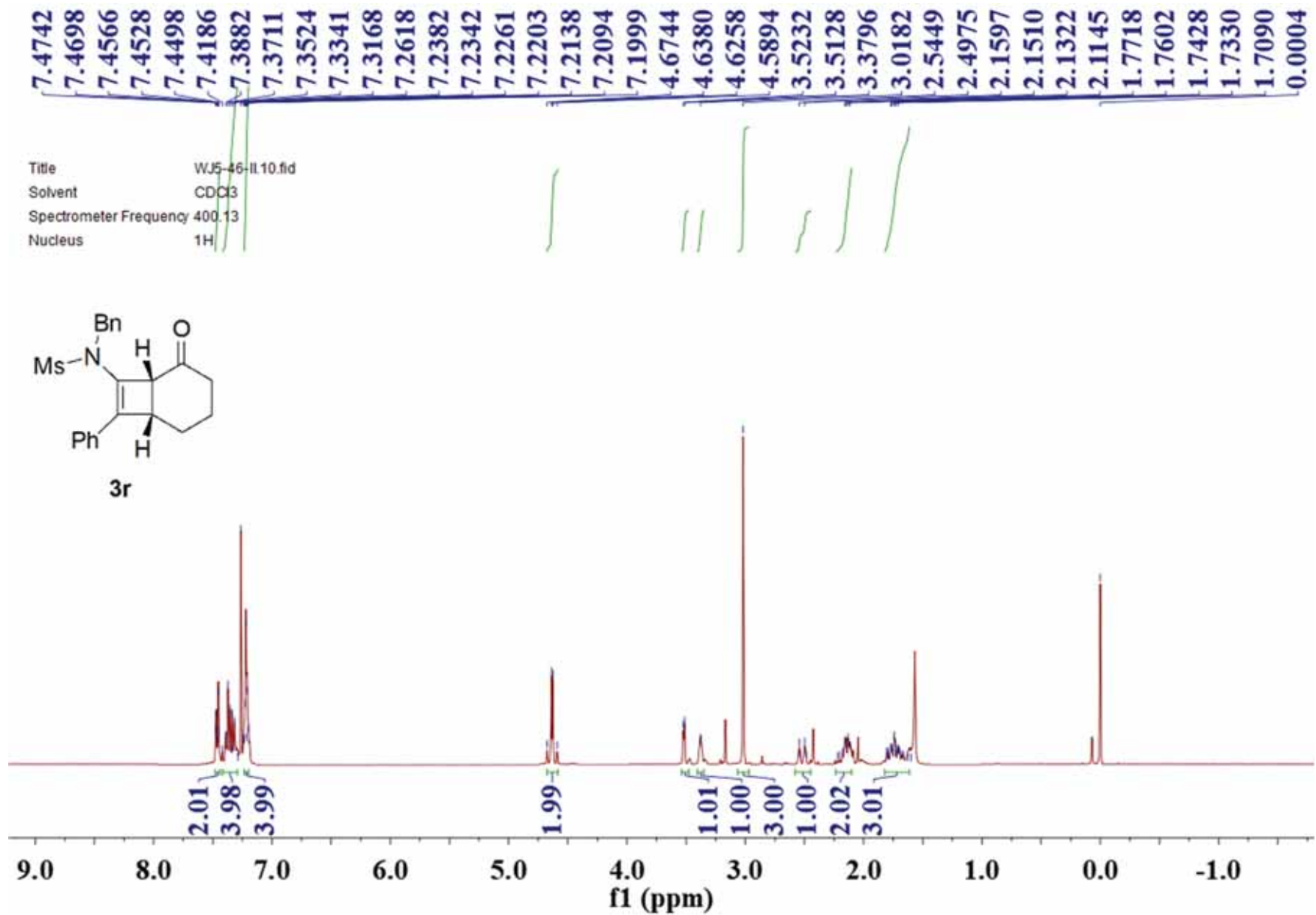


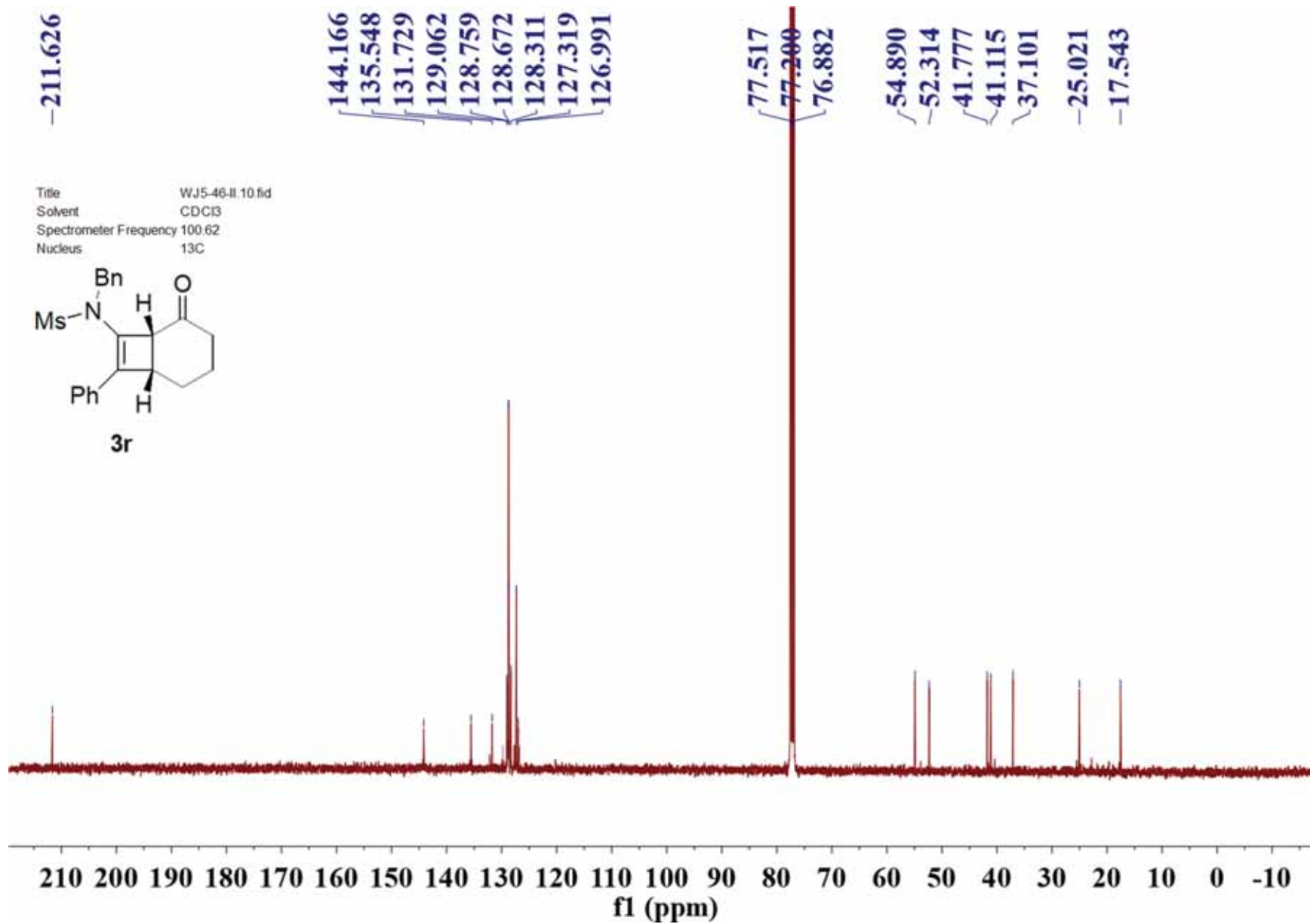


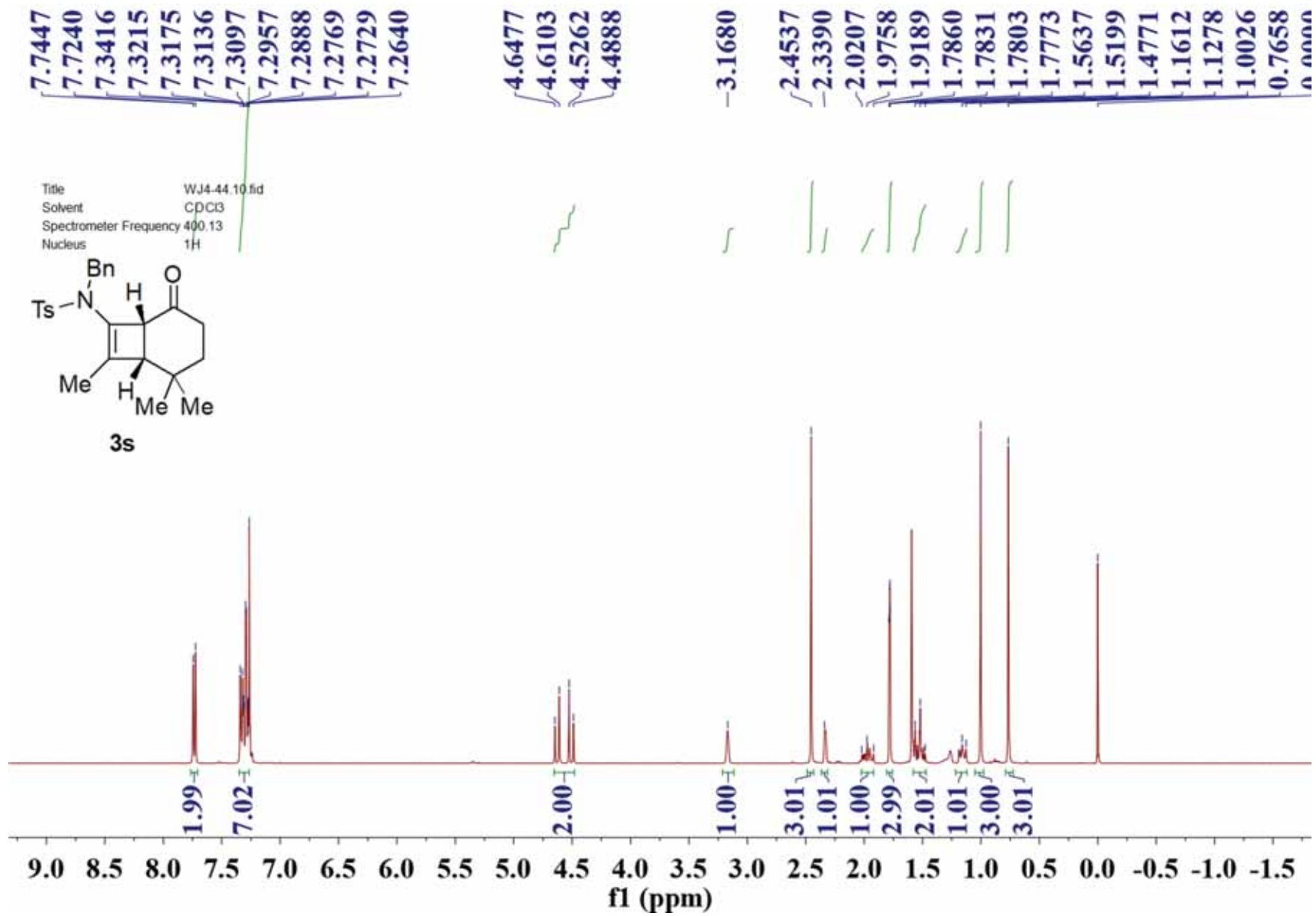


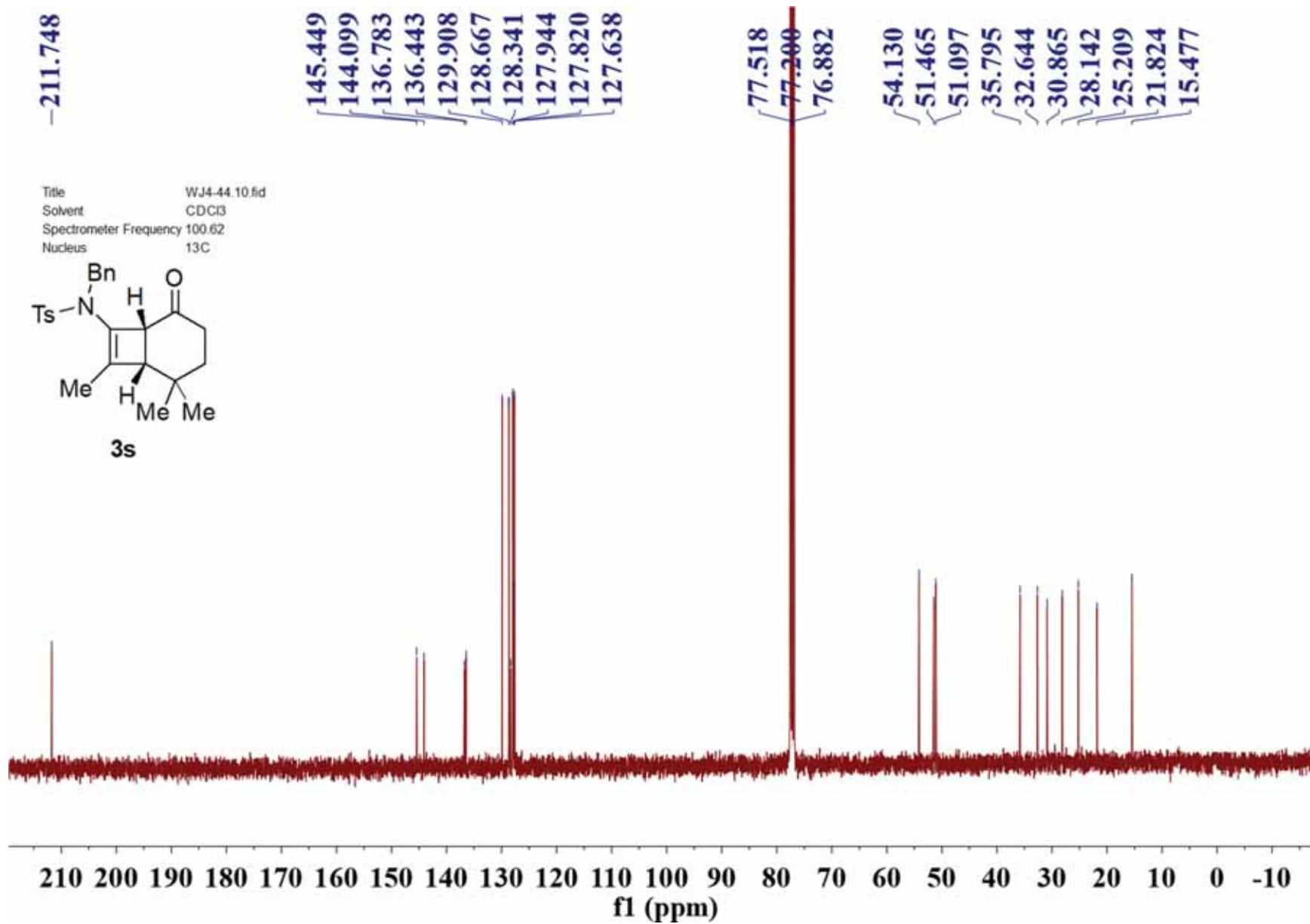


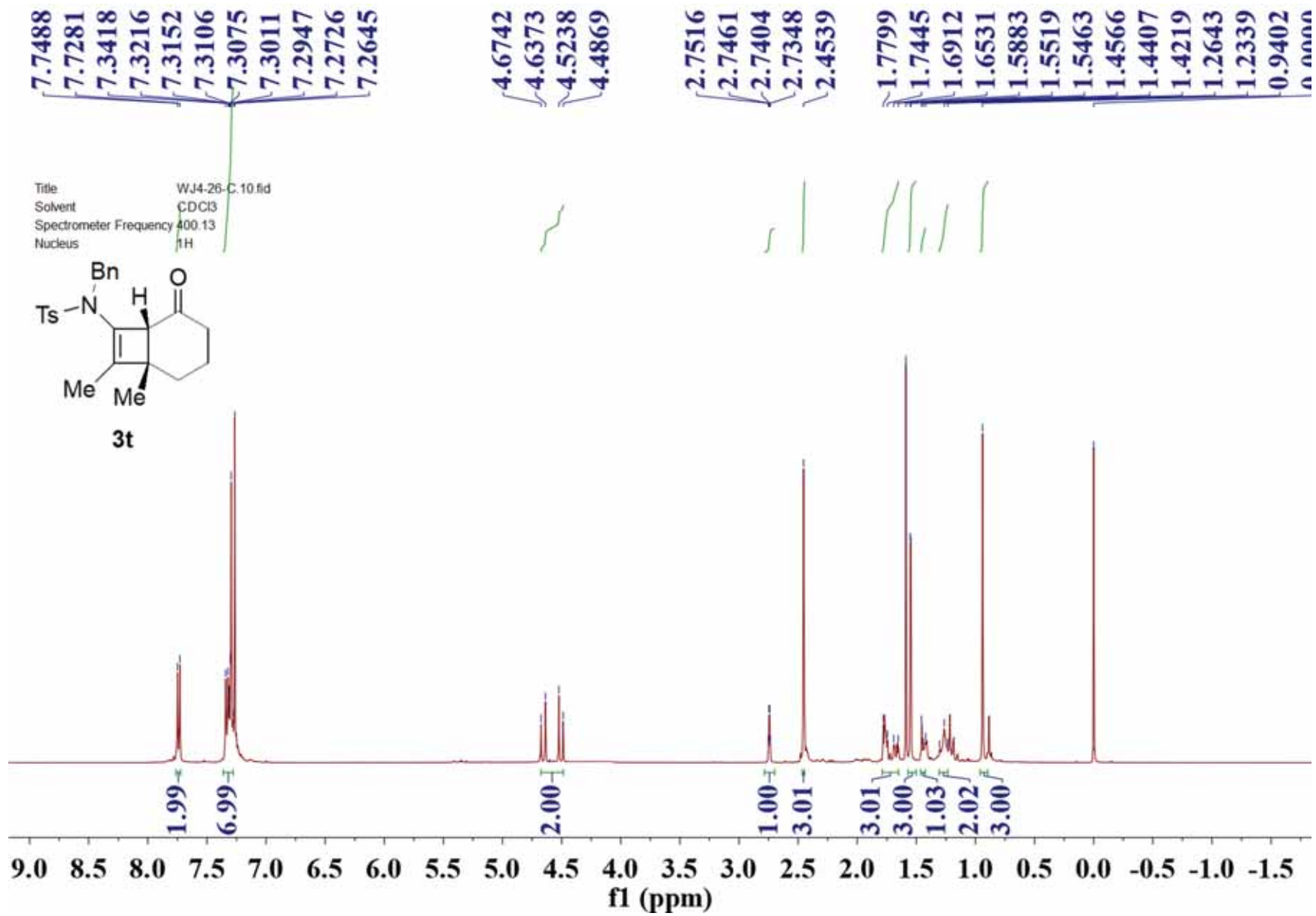


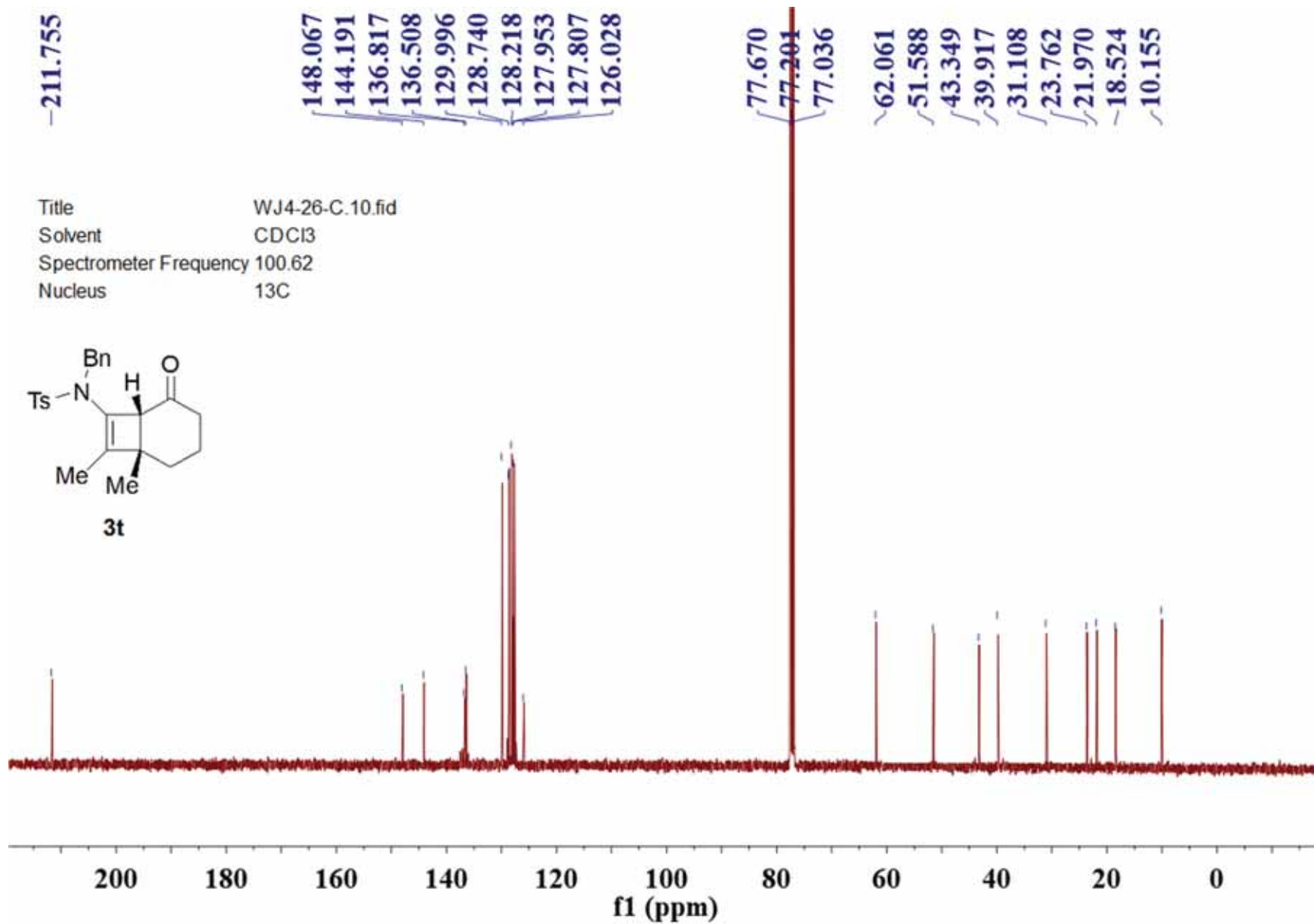




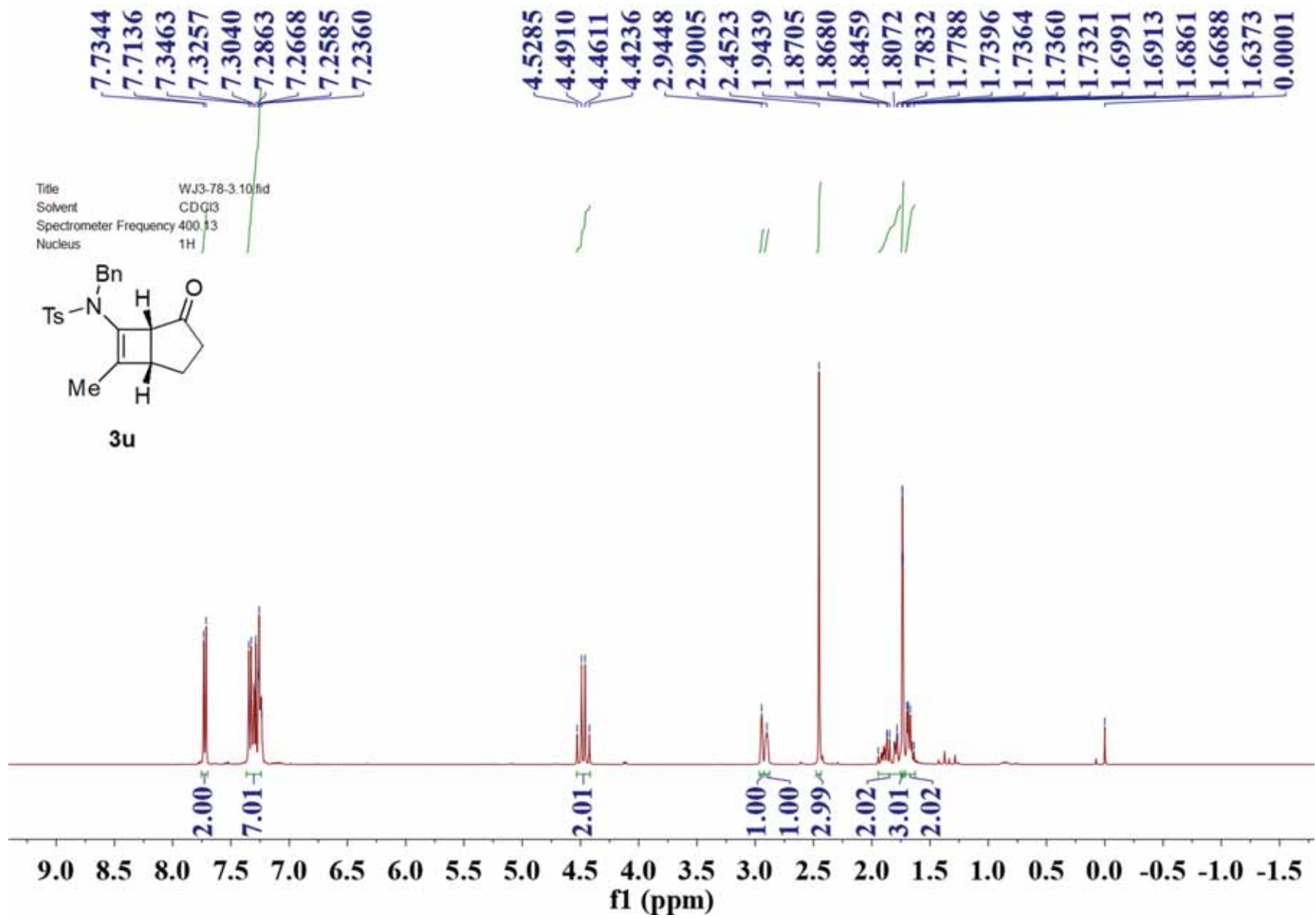












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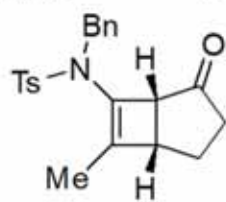
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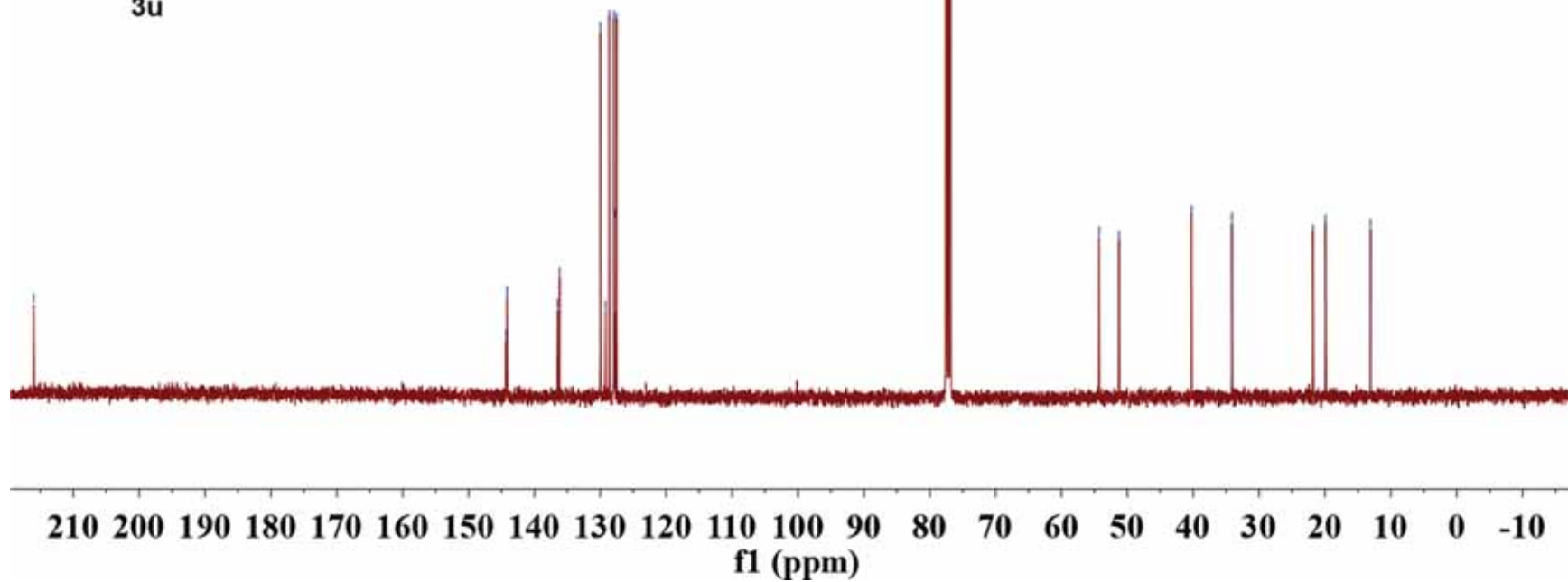
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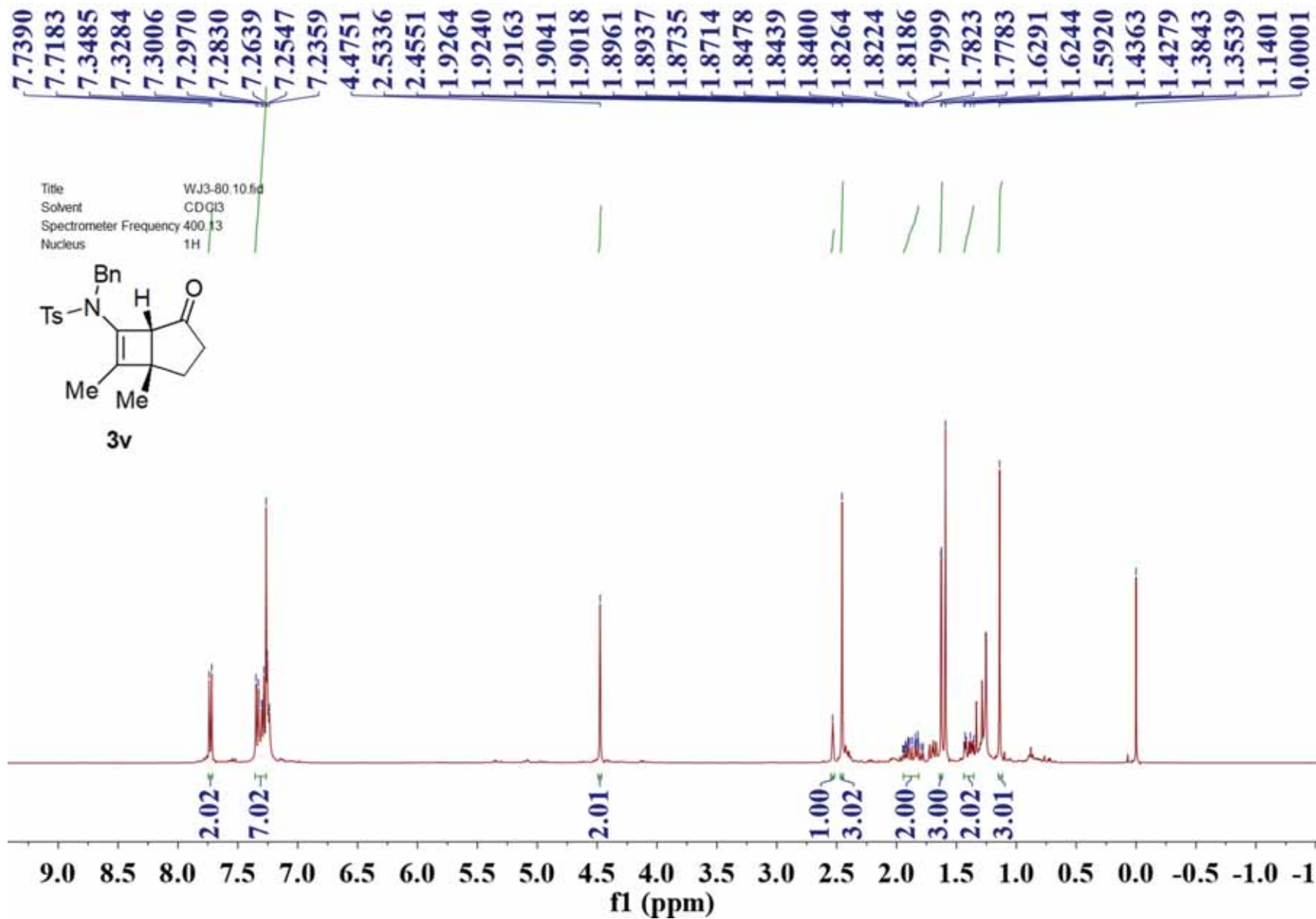
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Nucleus 13C



3u





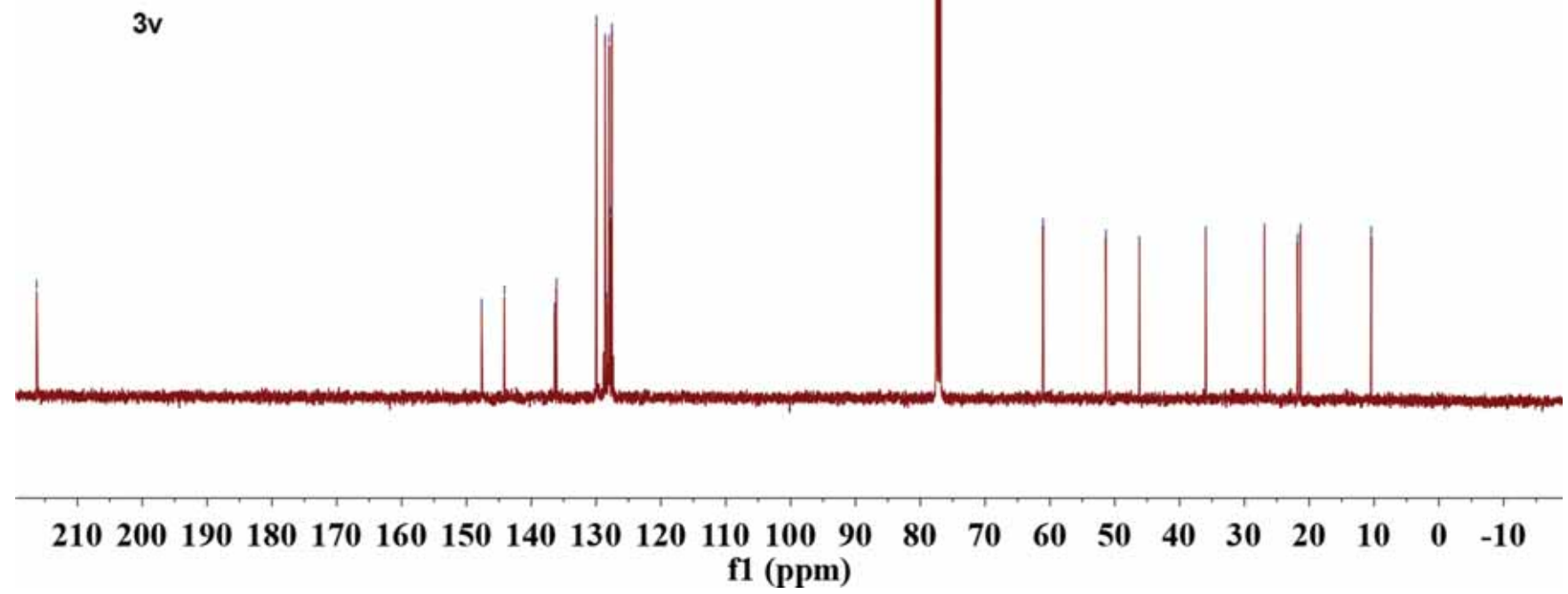
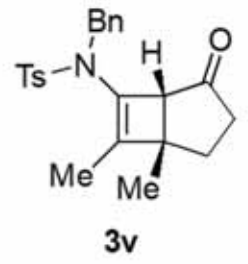
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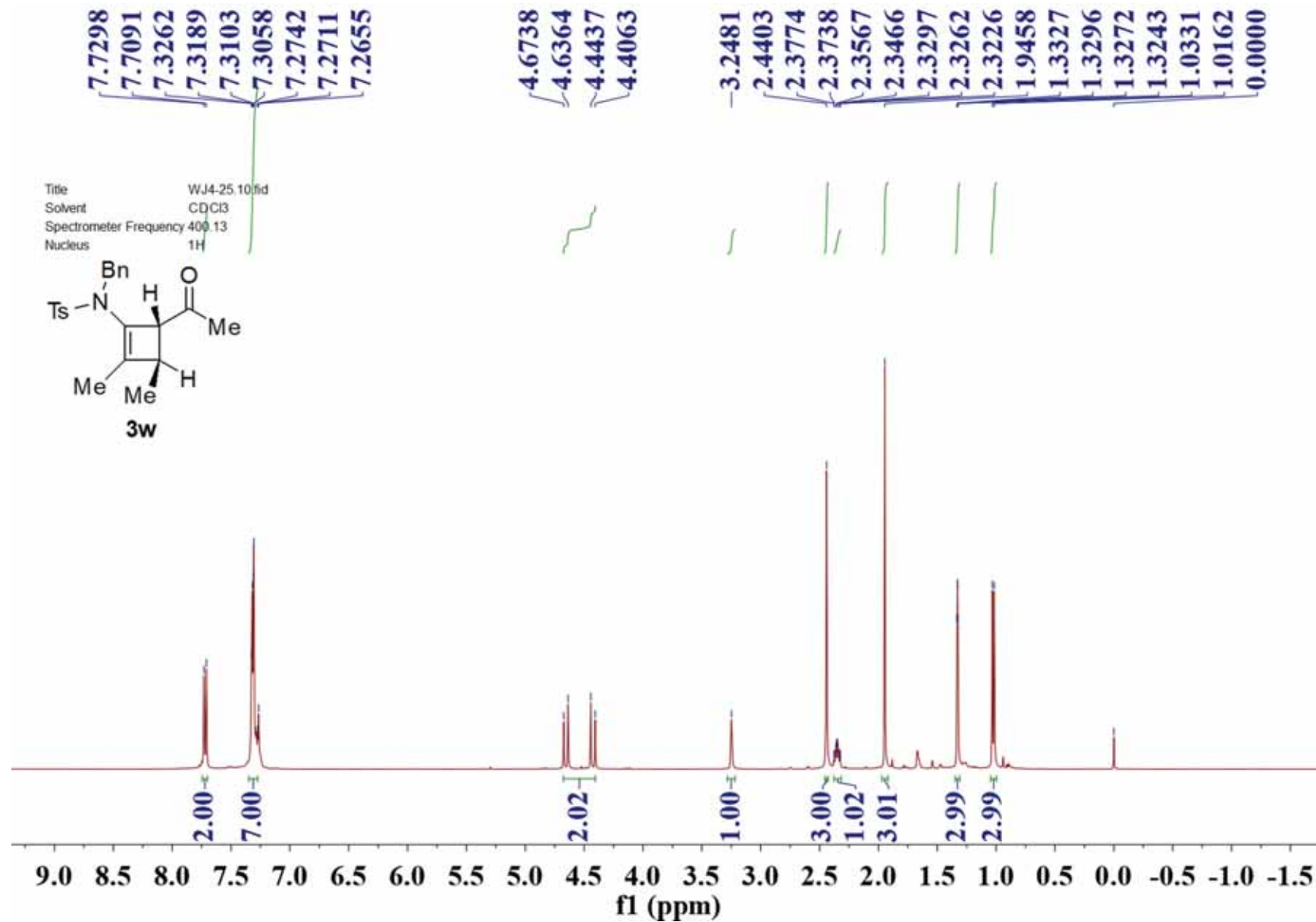
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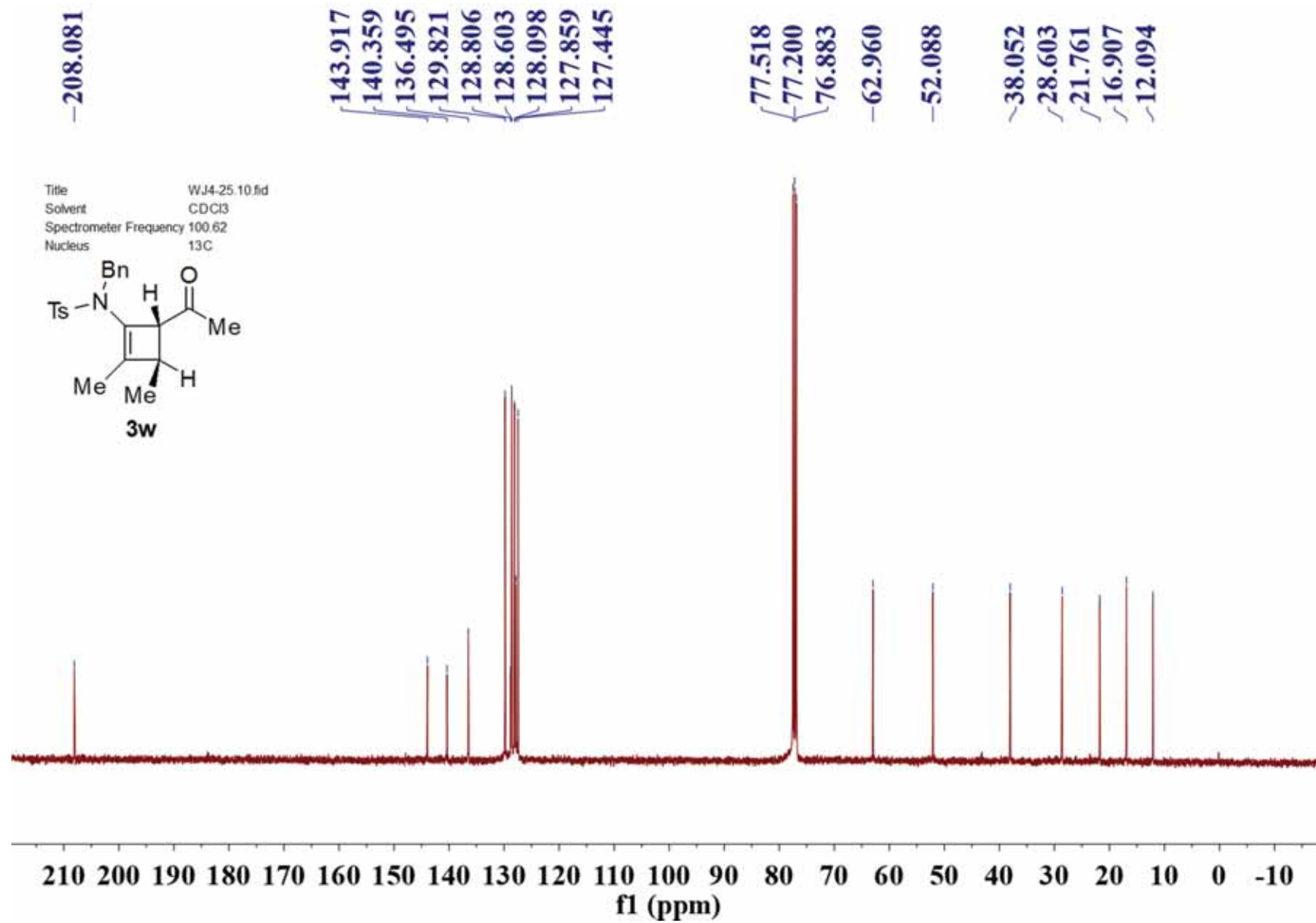
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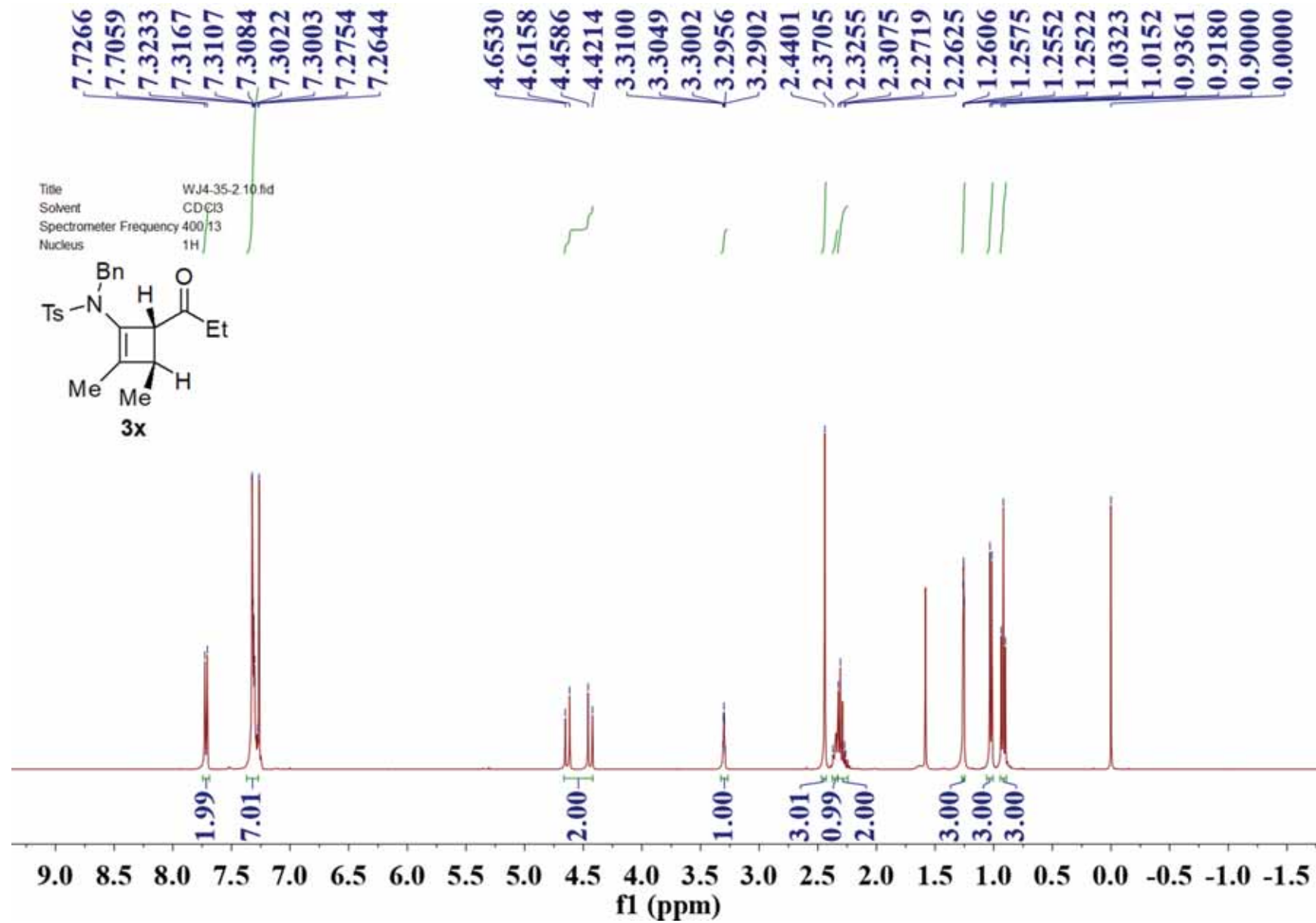
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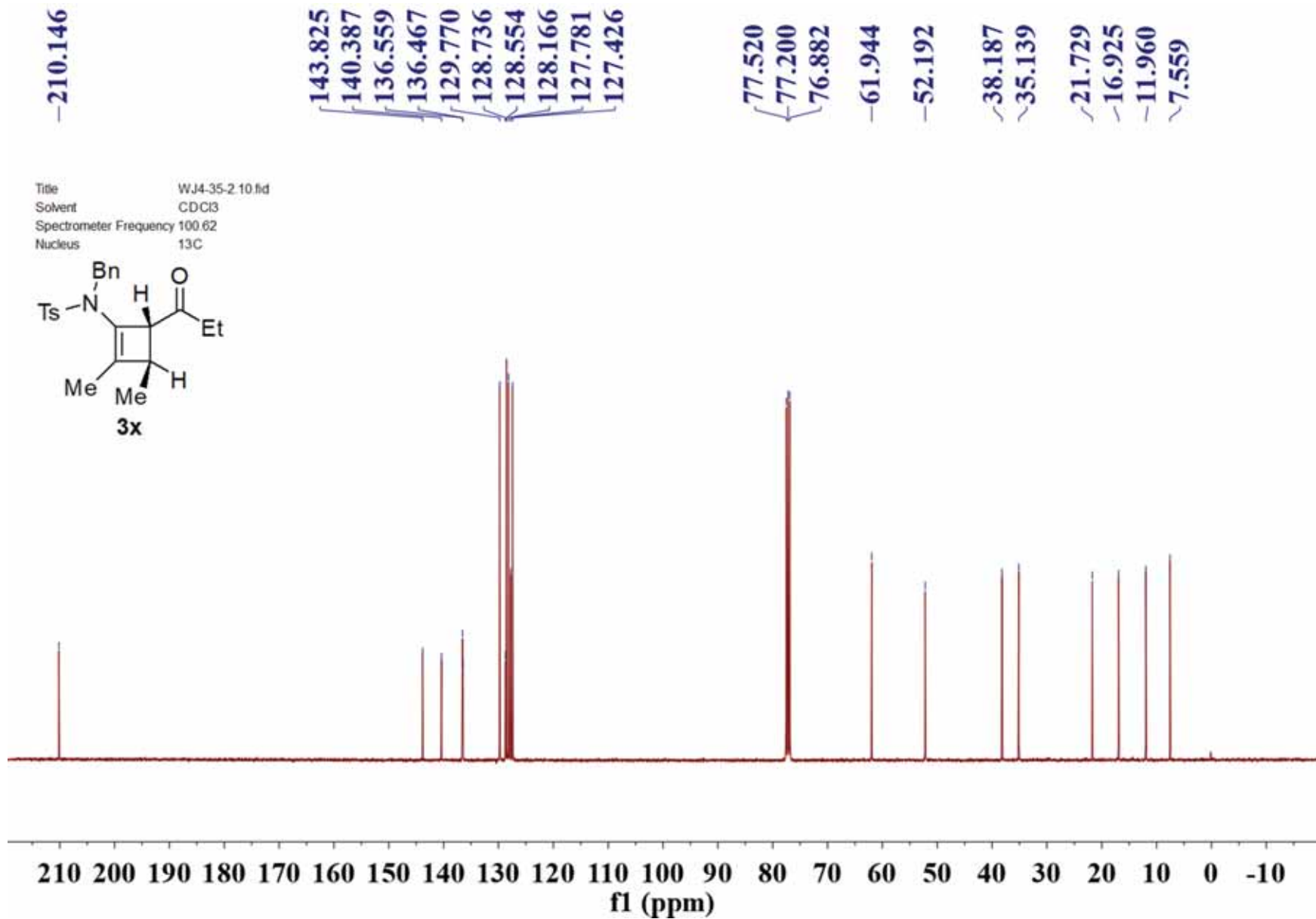
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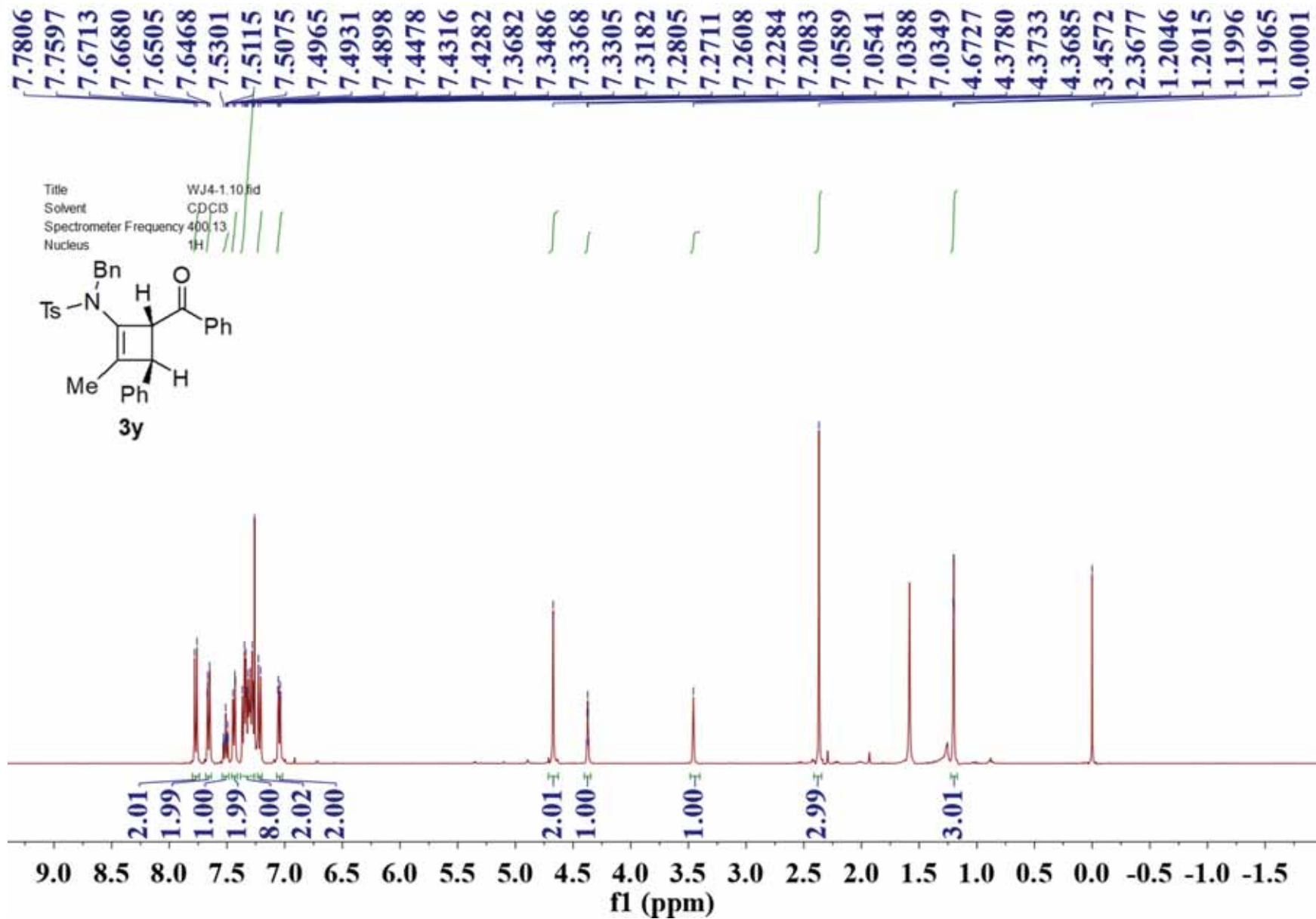


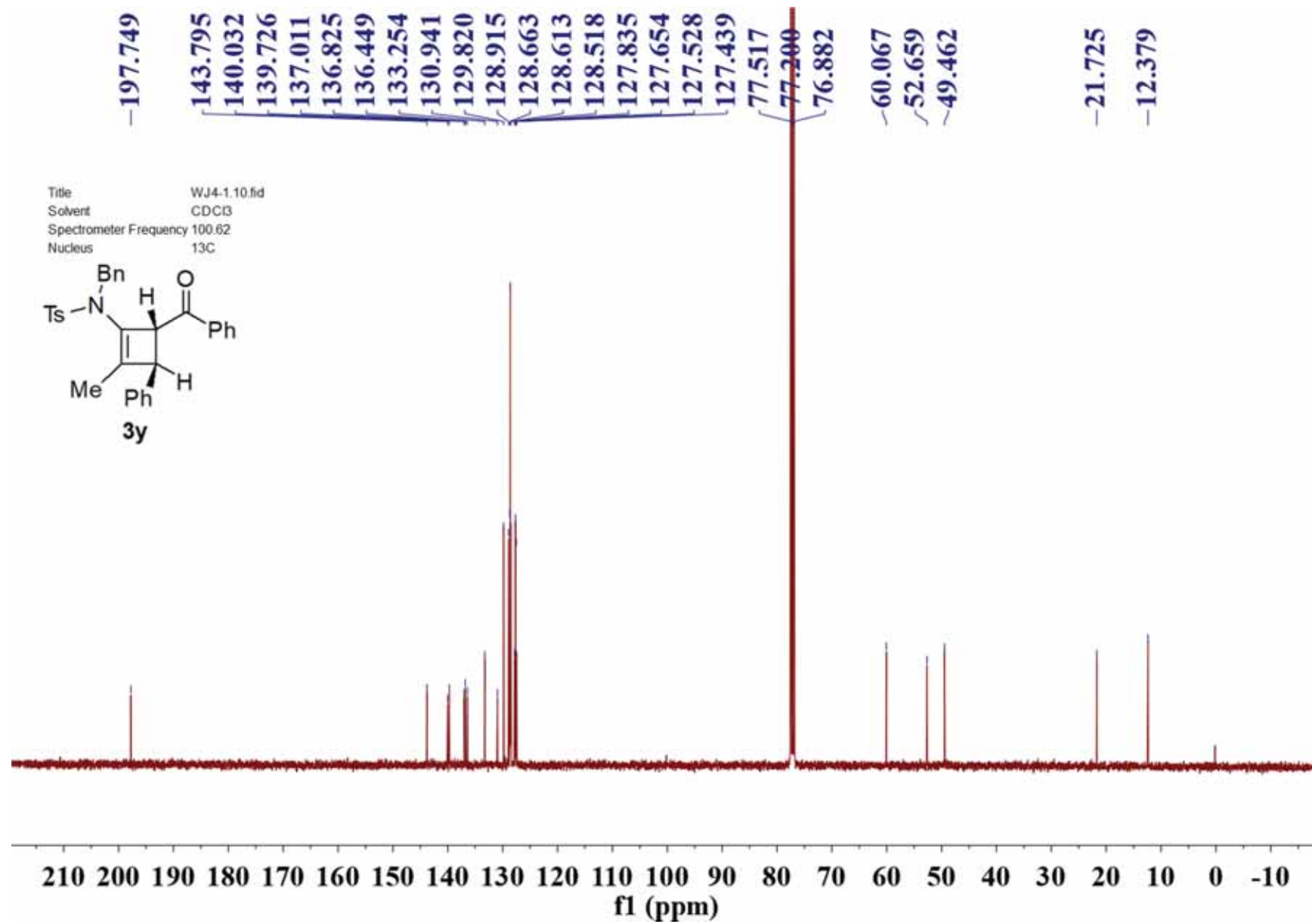


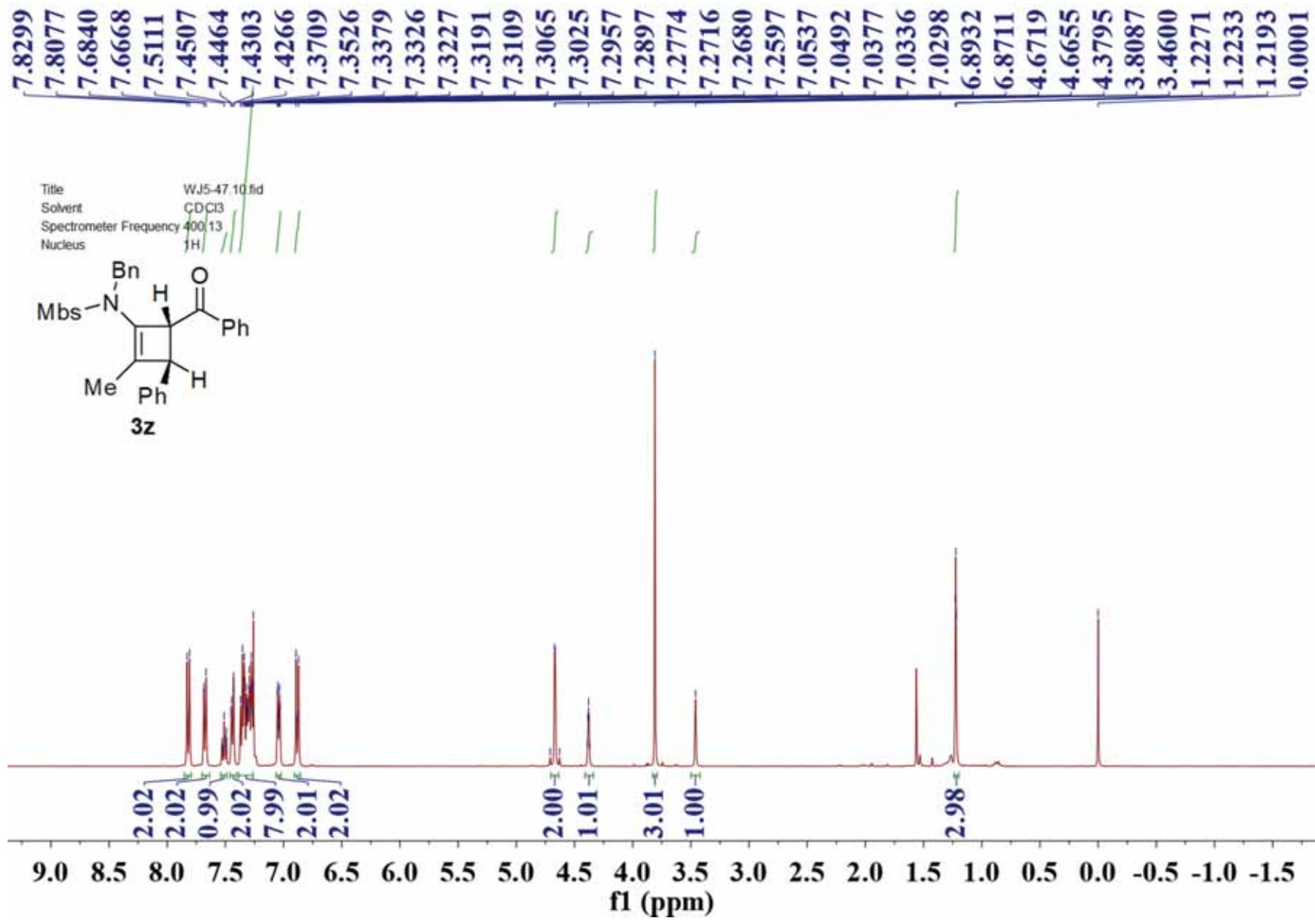


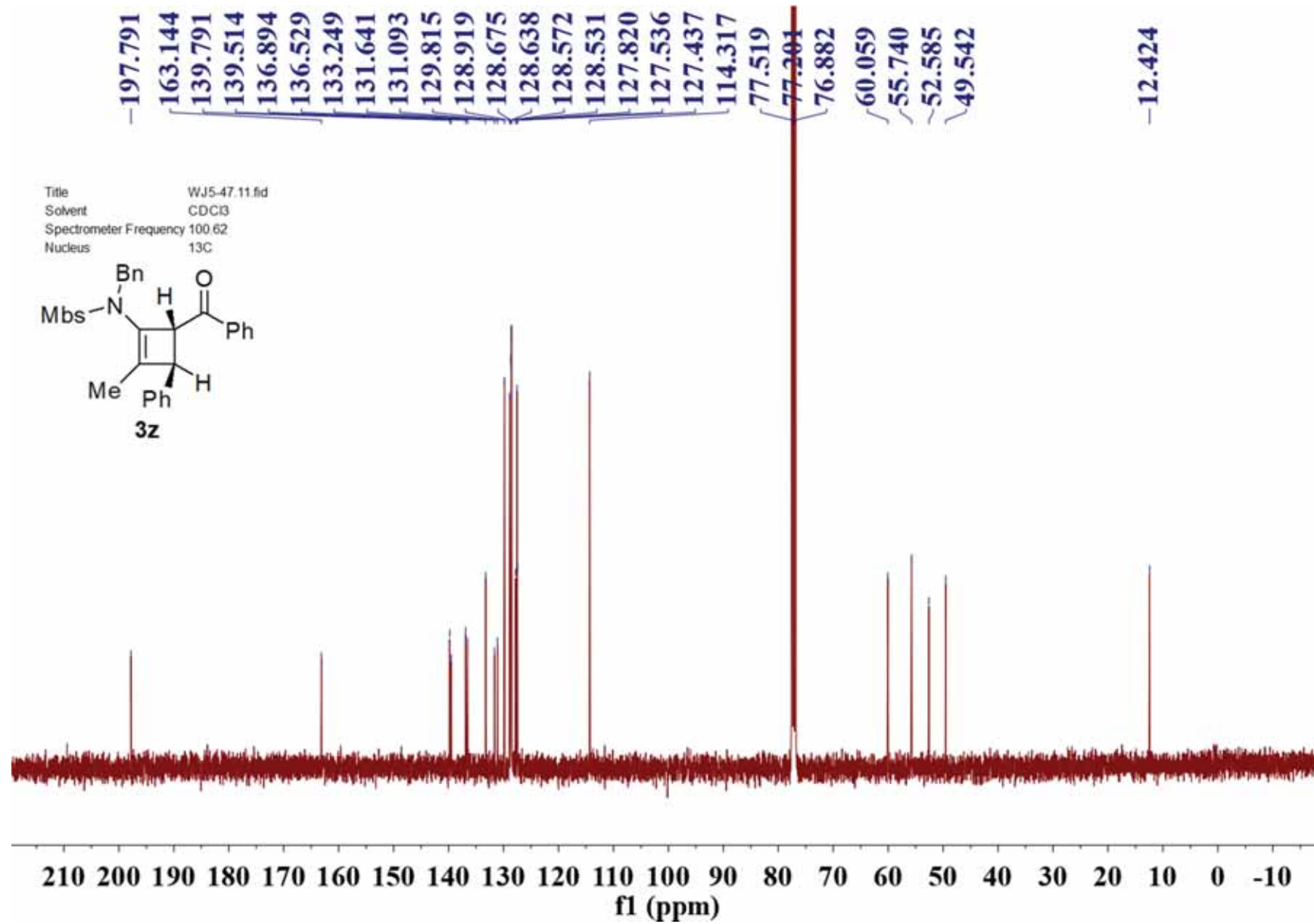


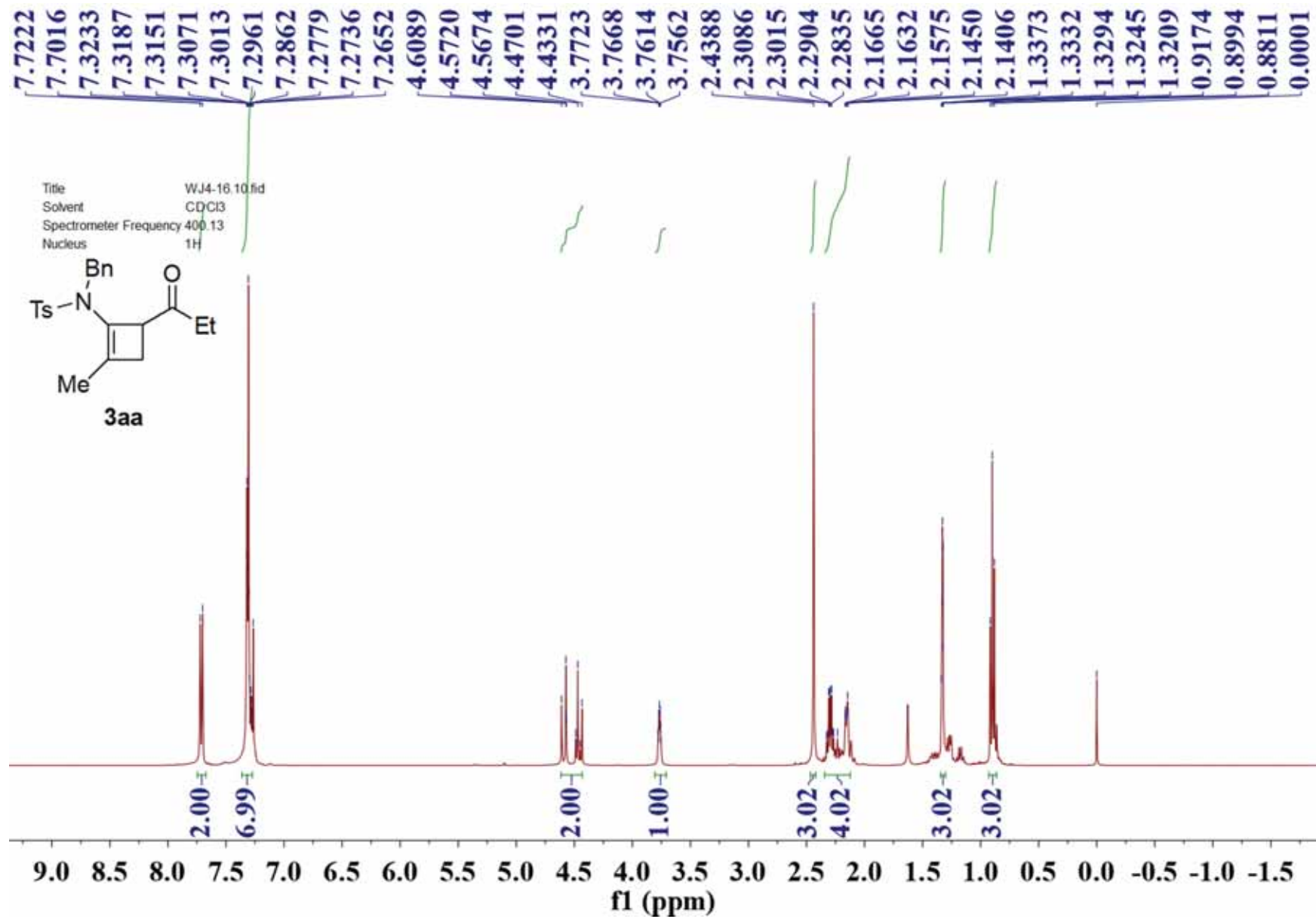


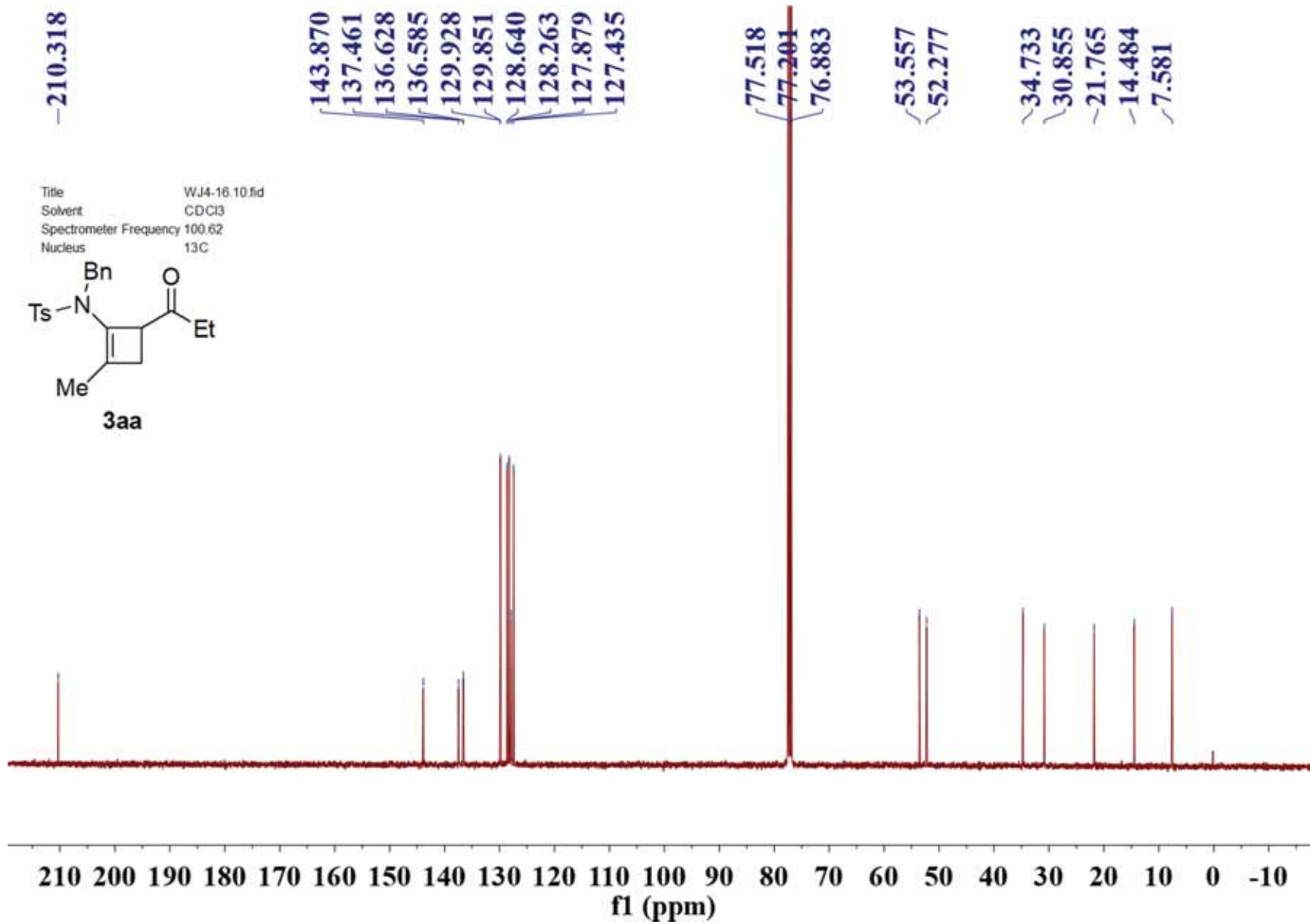


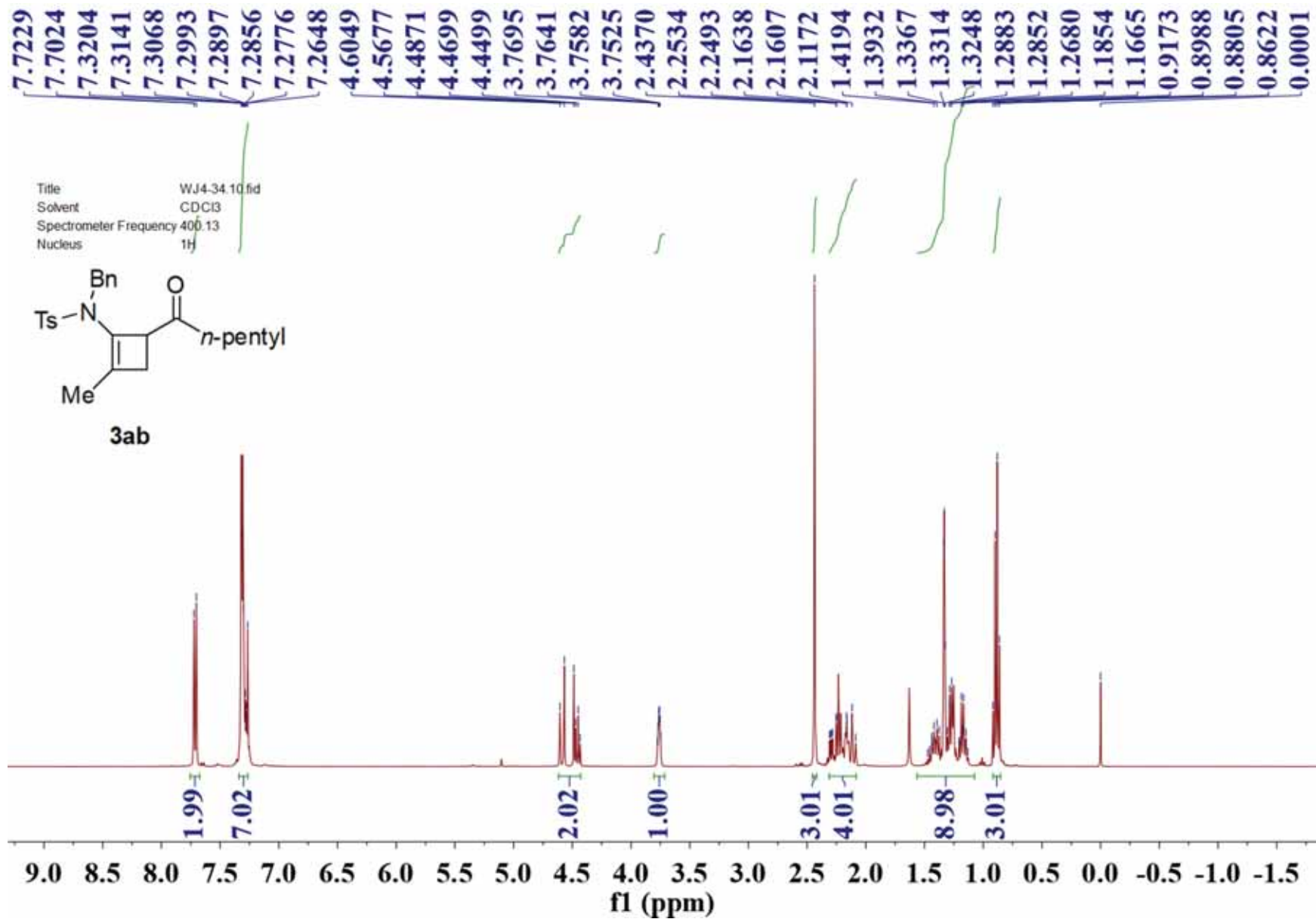


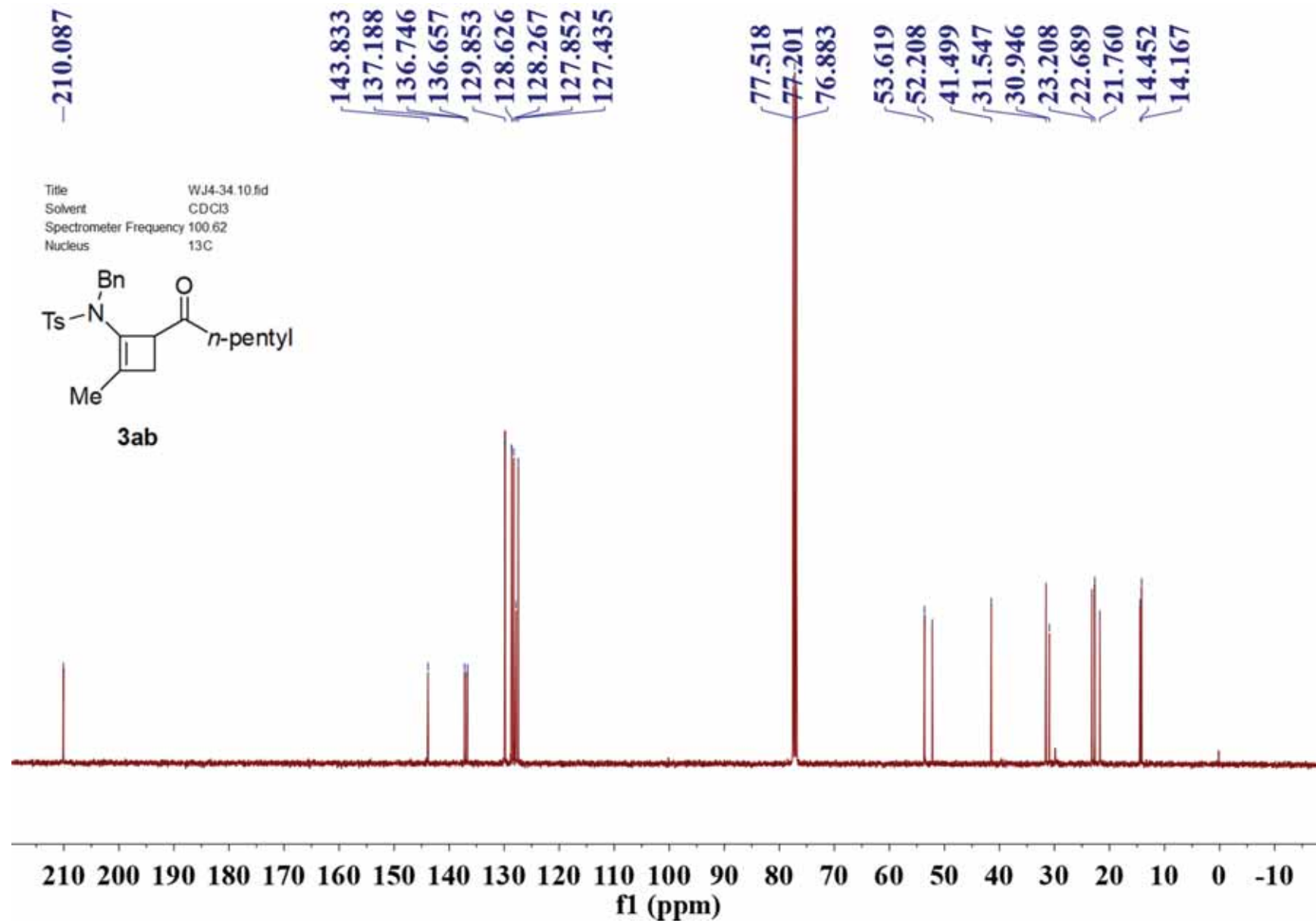




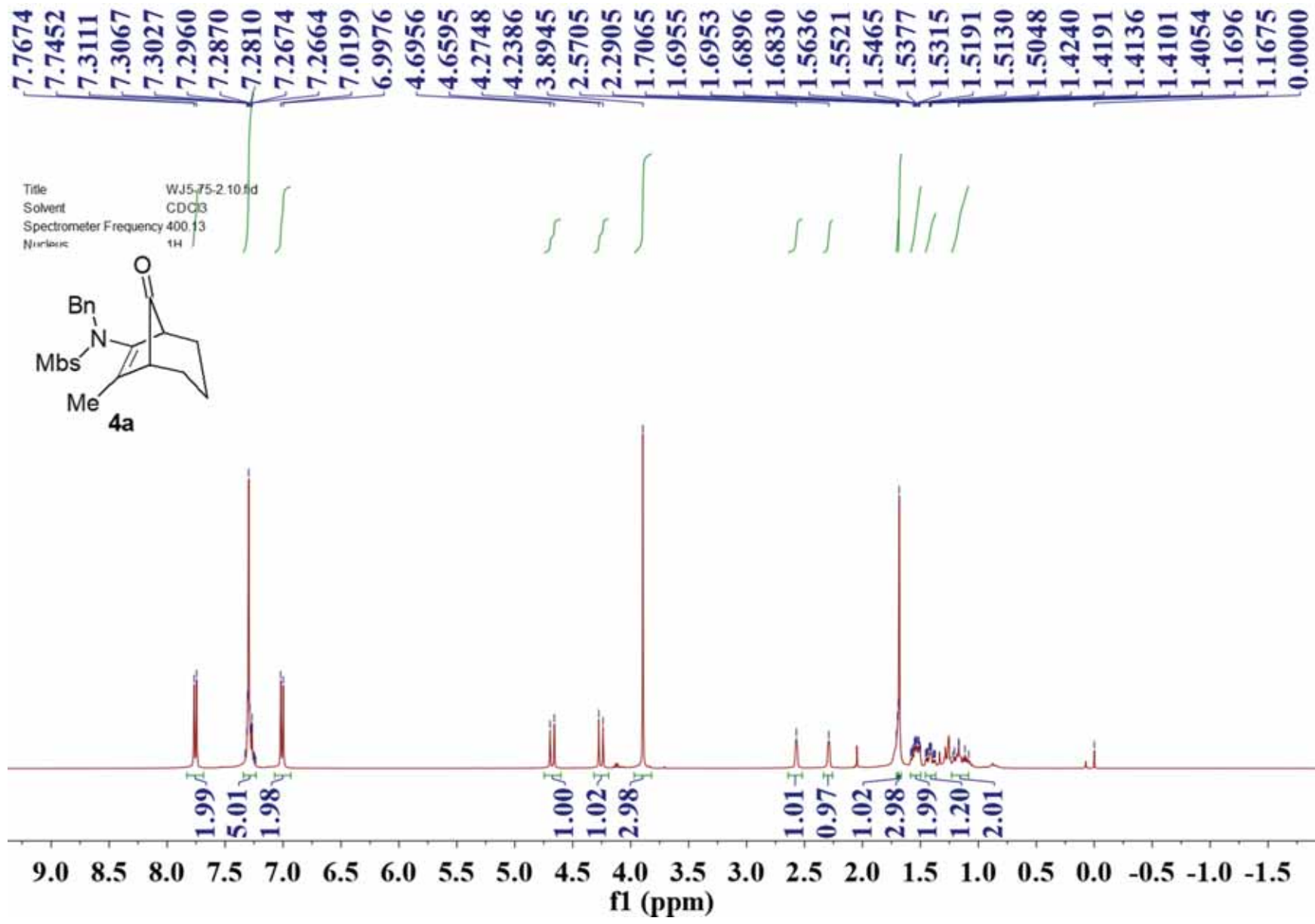


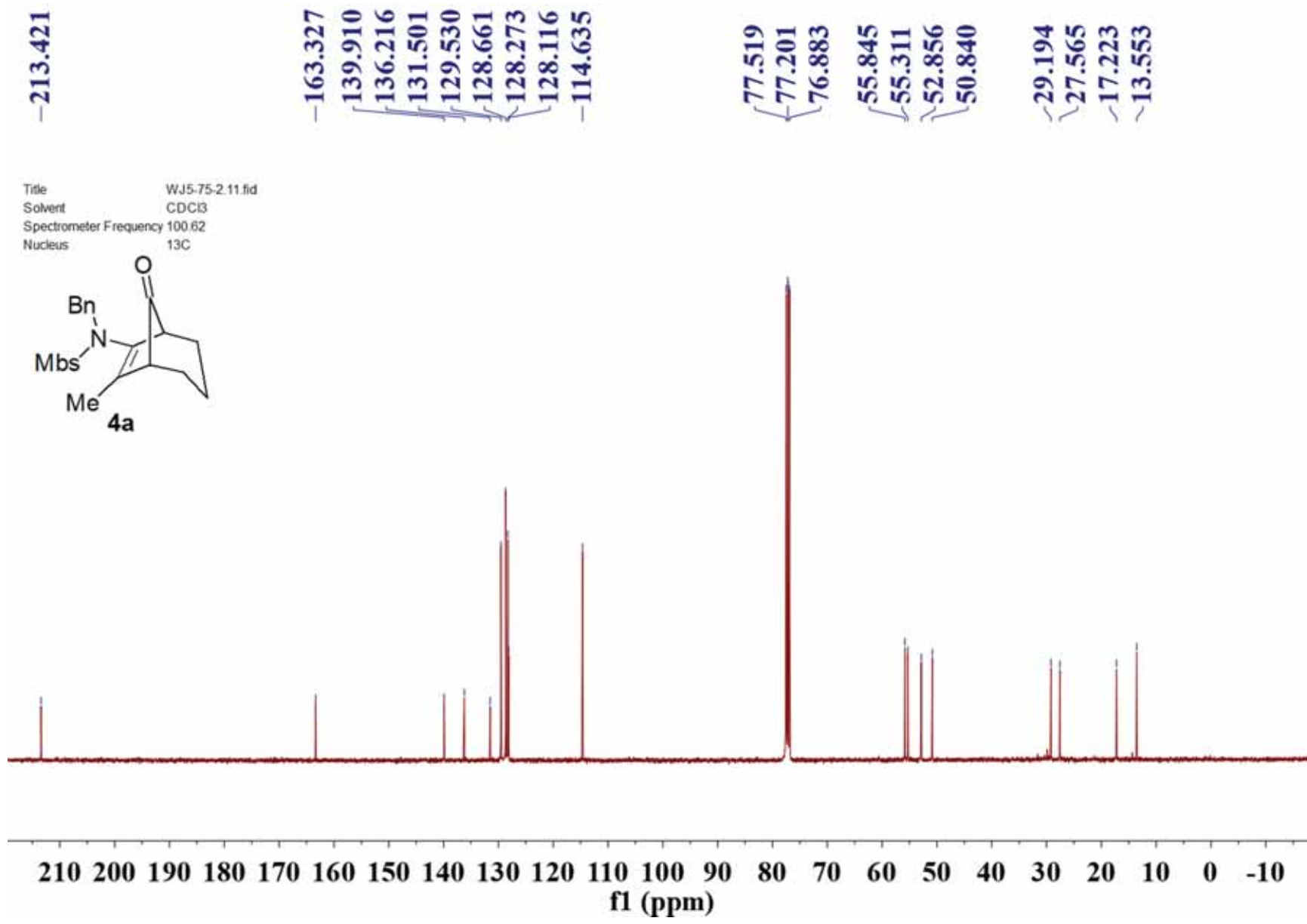


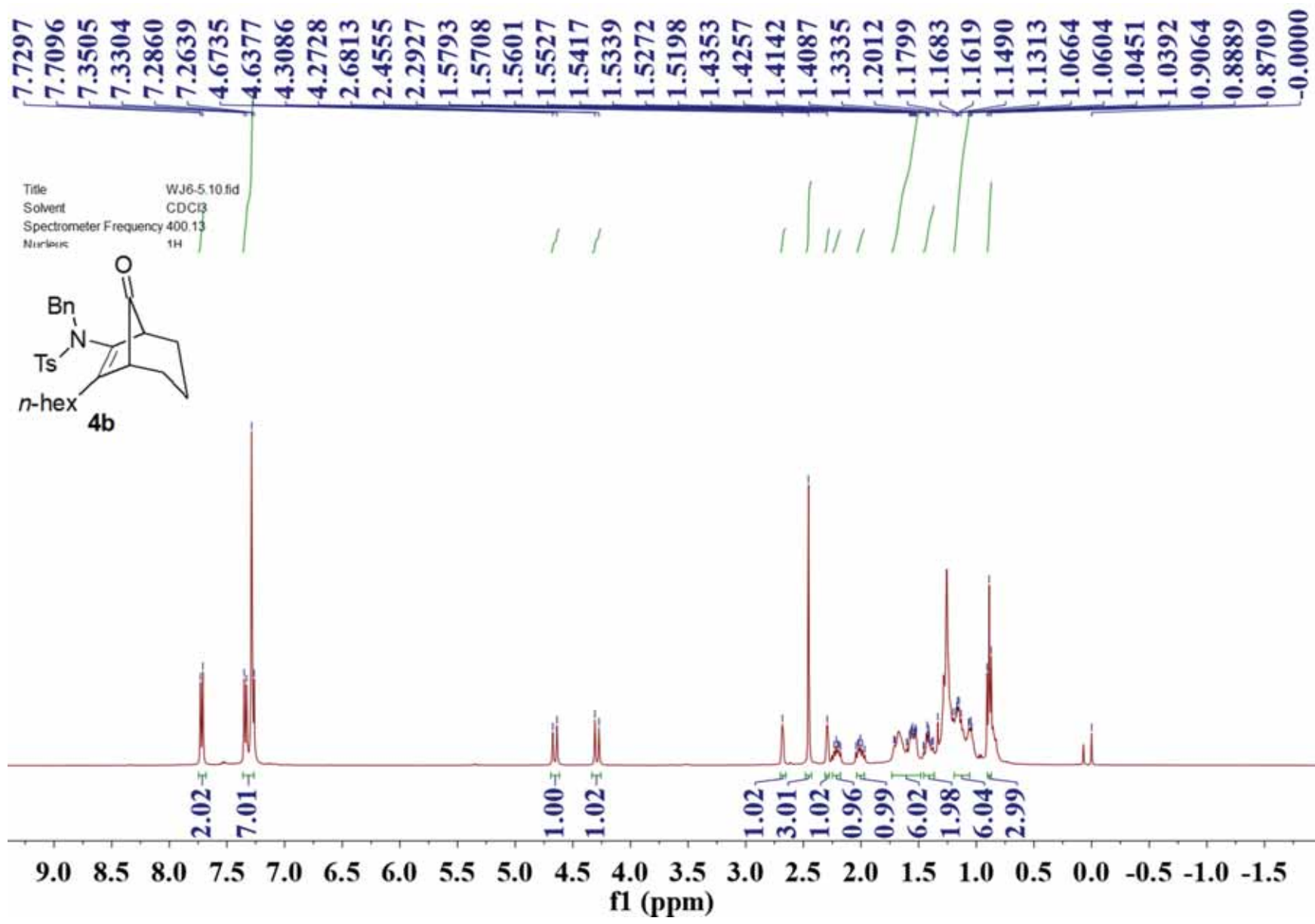


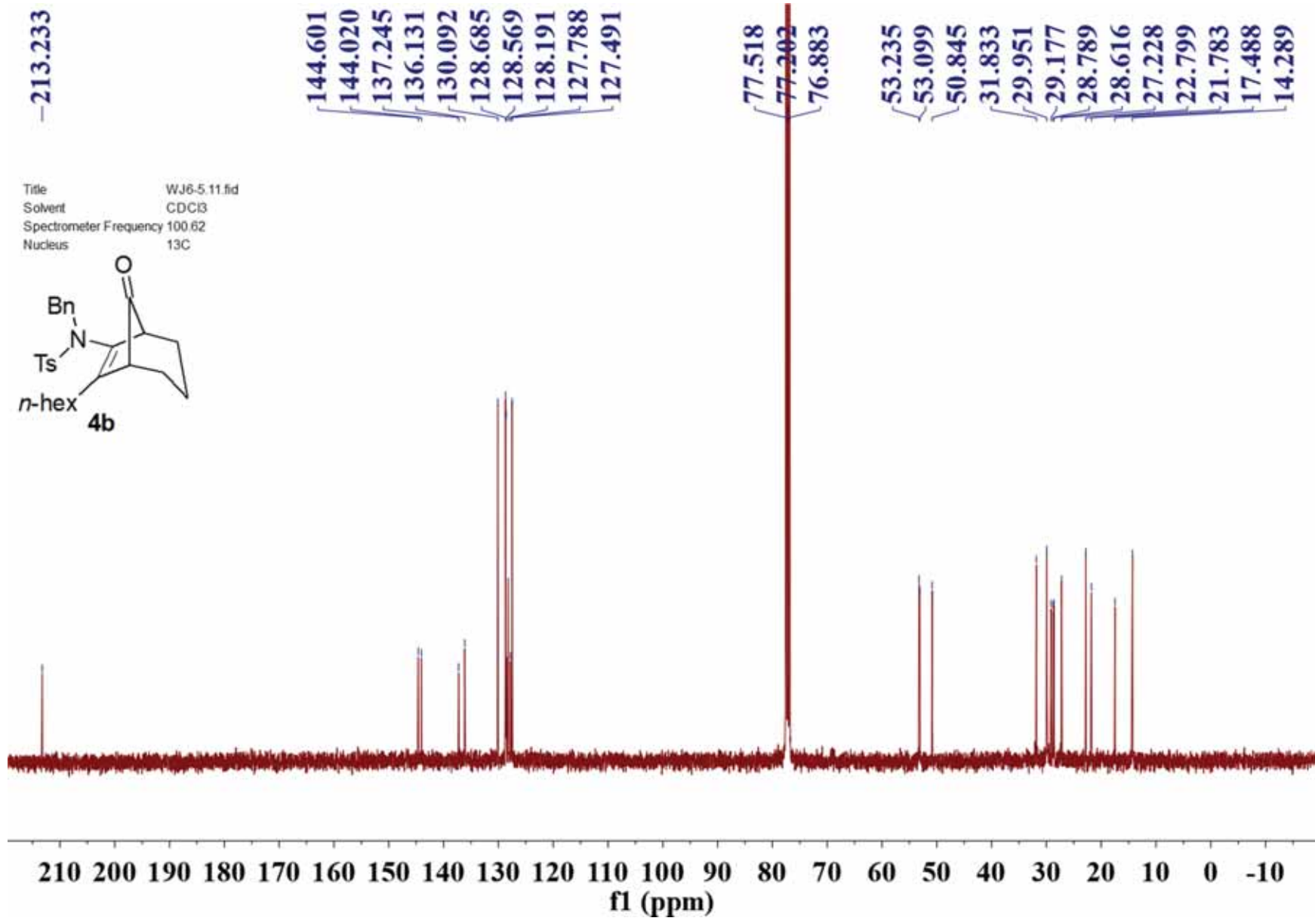


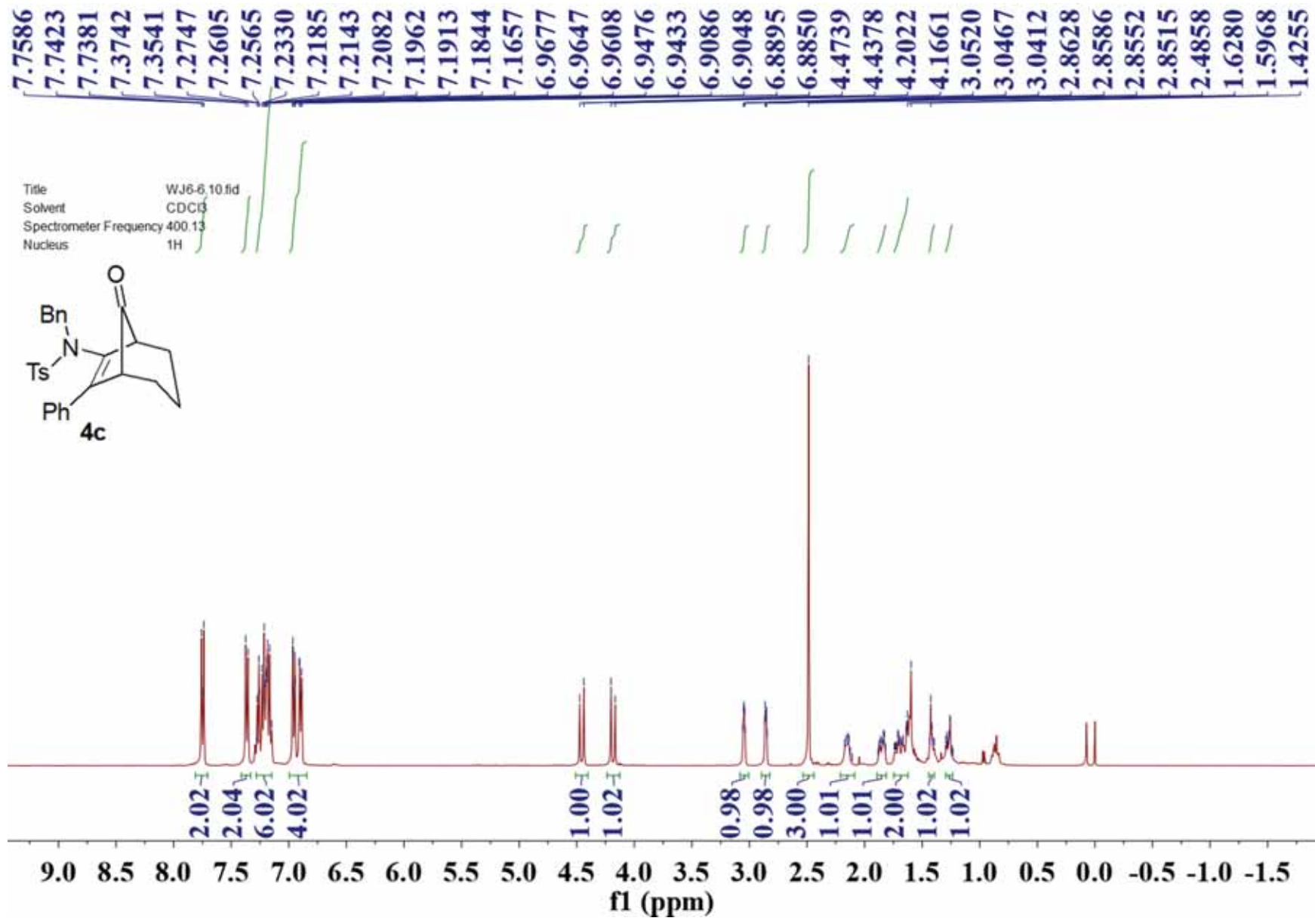


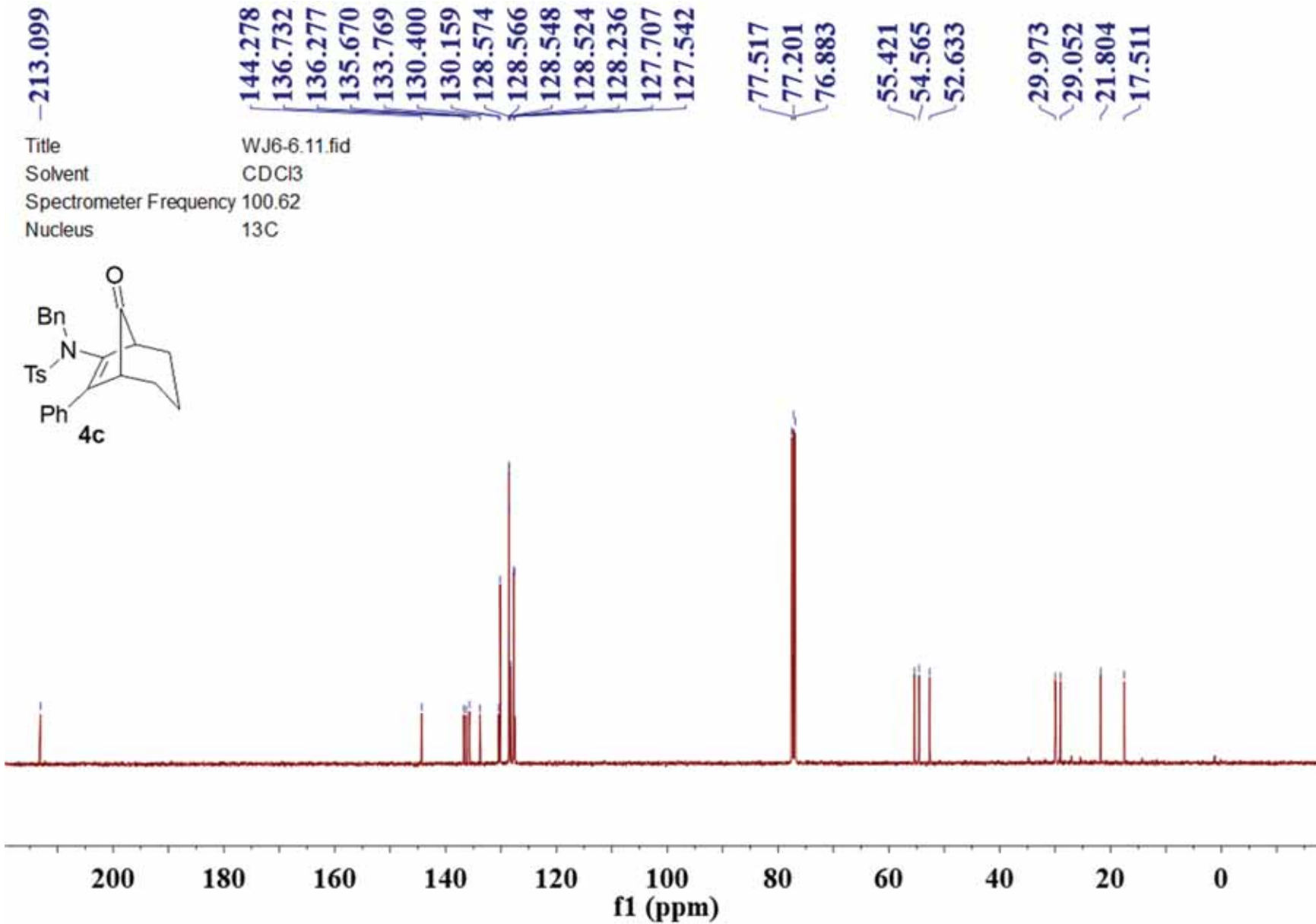


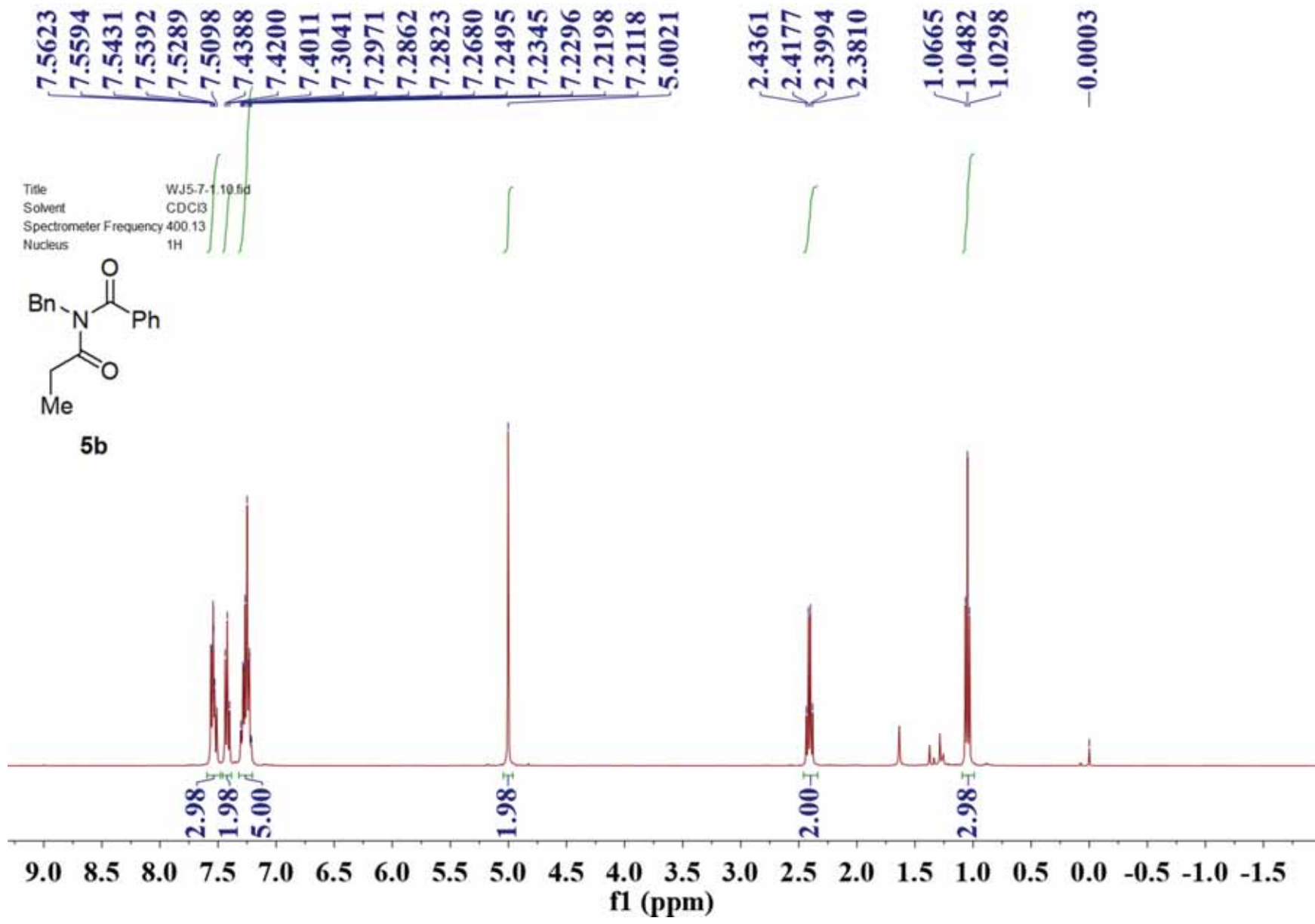


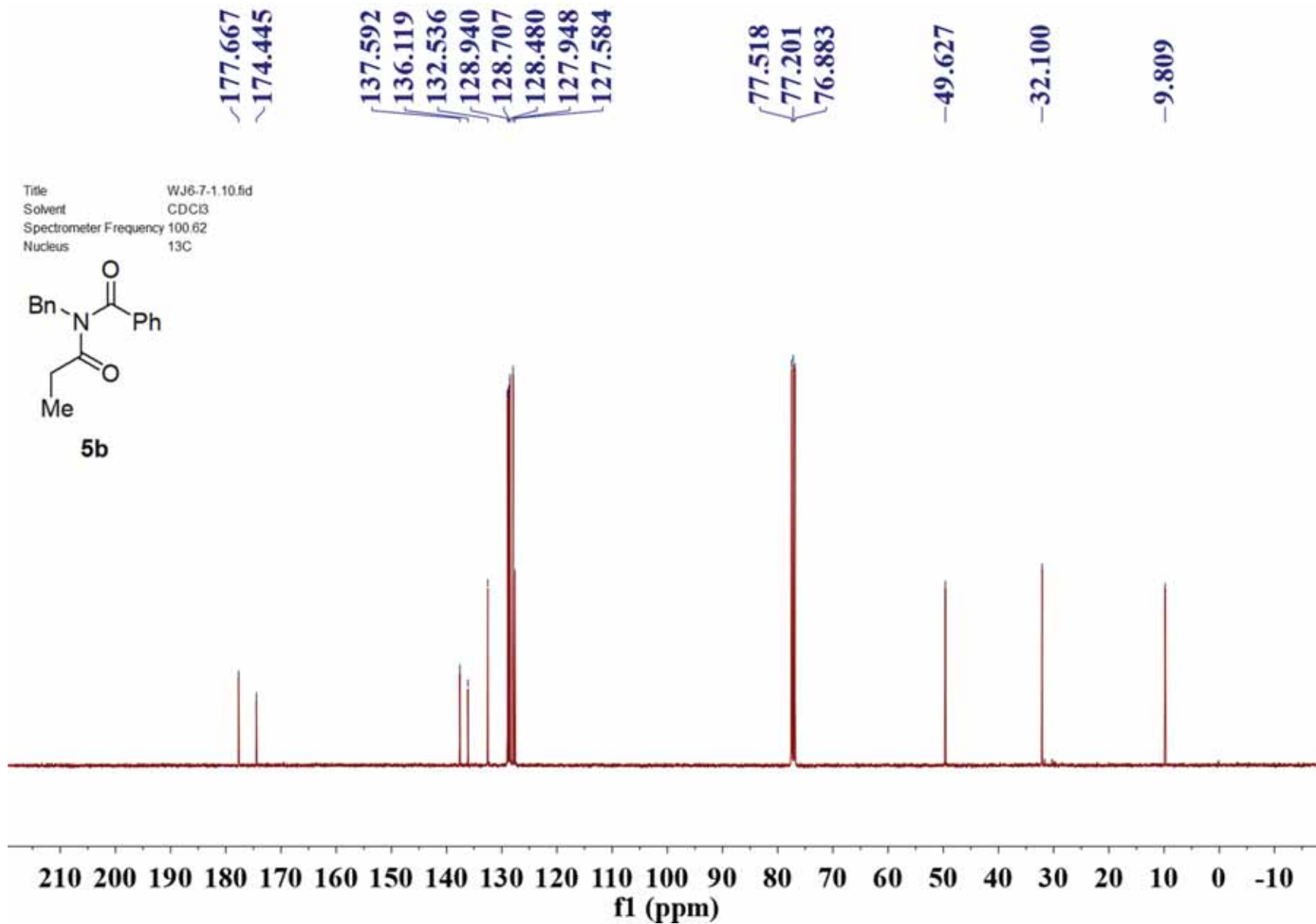






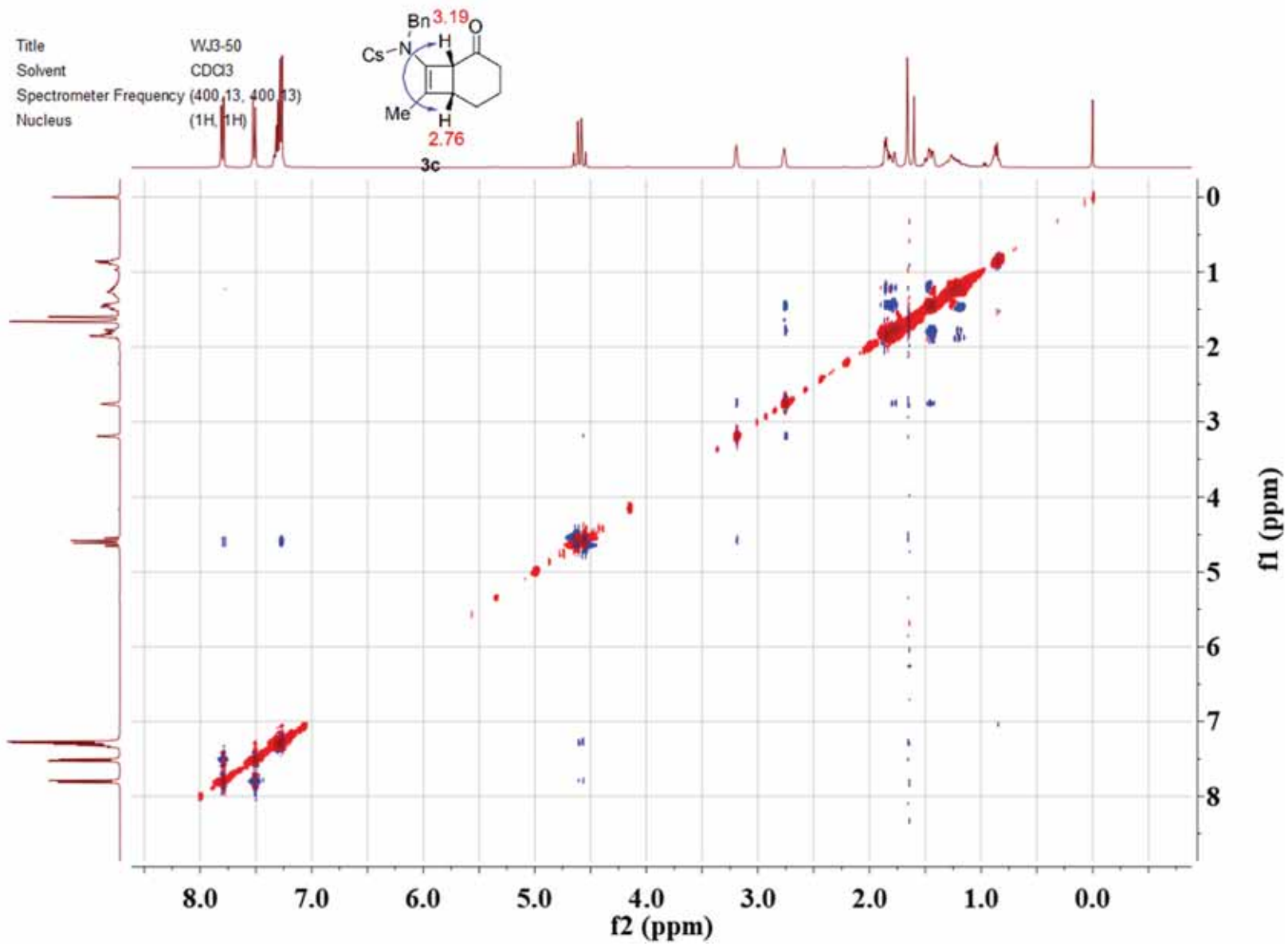


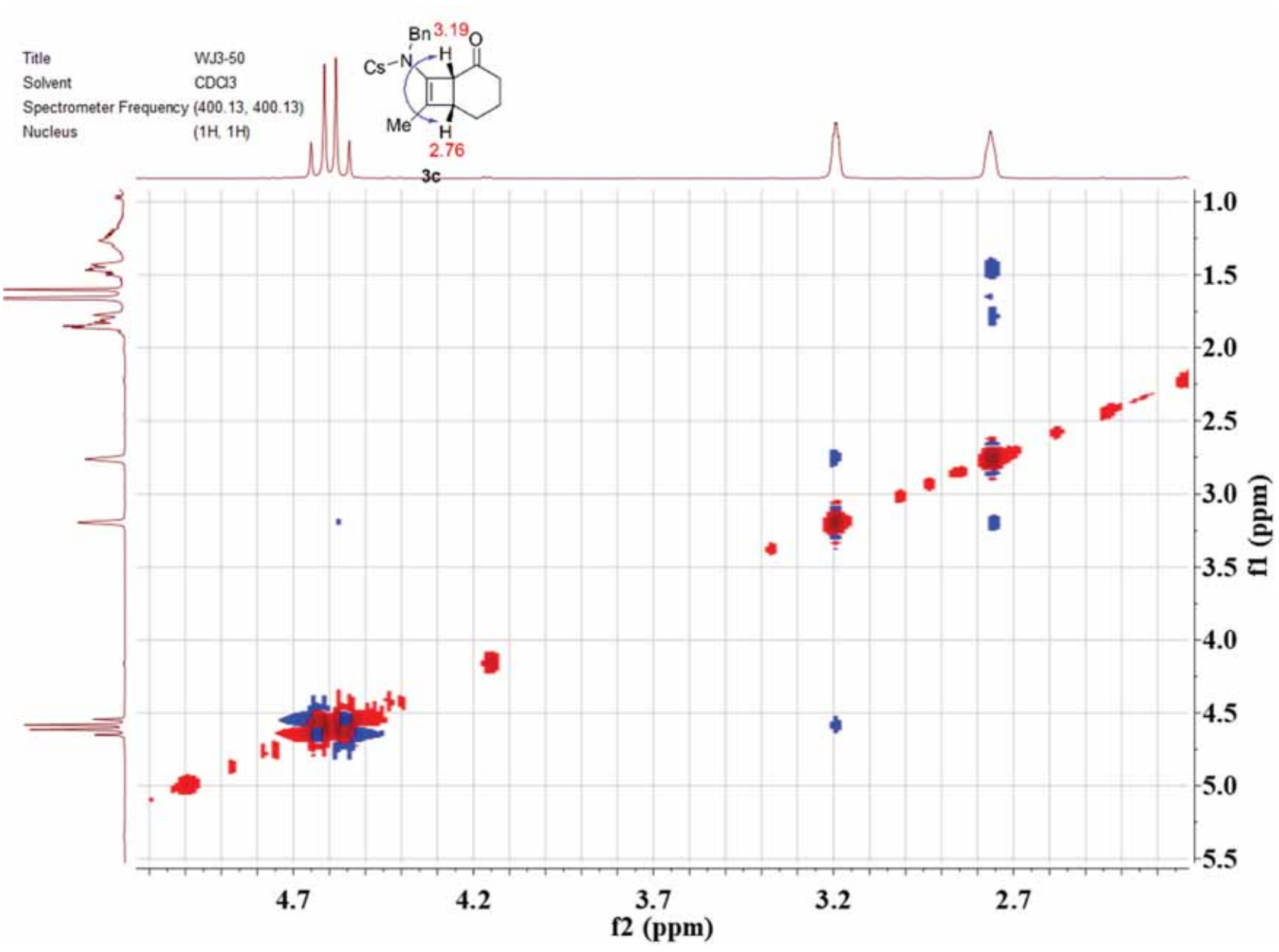




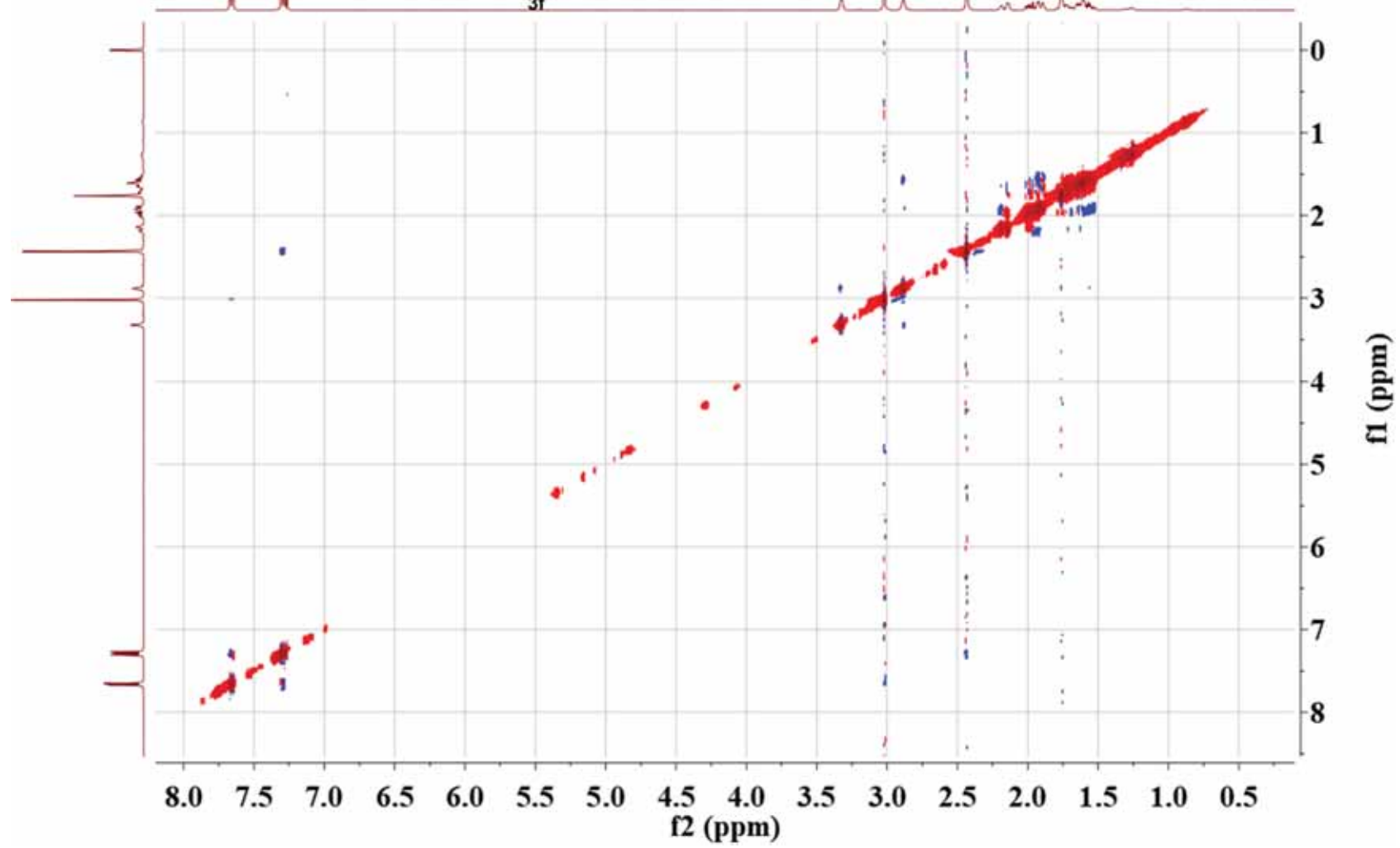


### NOESY Spectra of Cyclobutenamides 3.

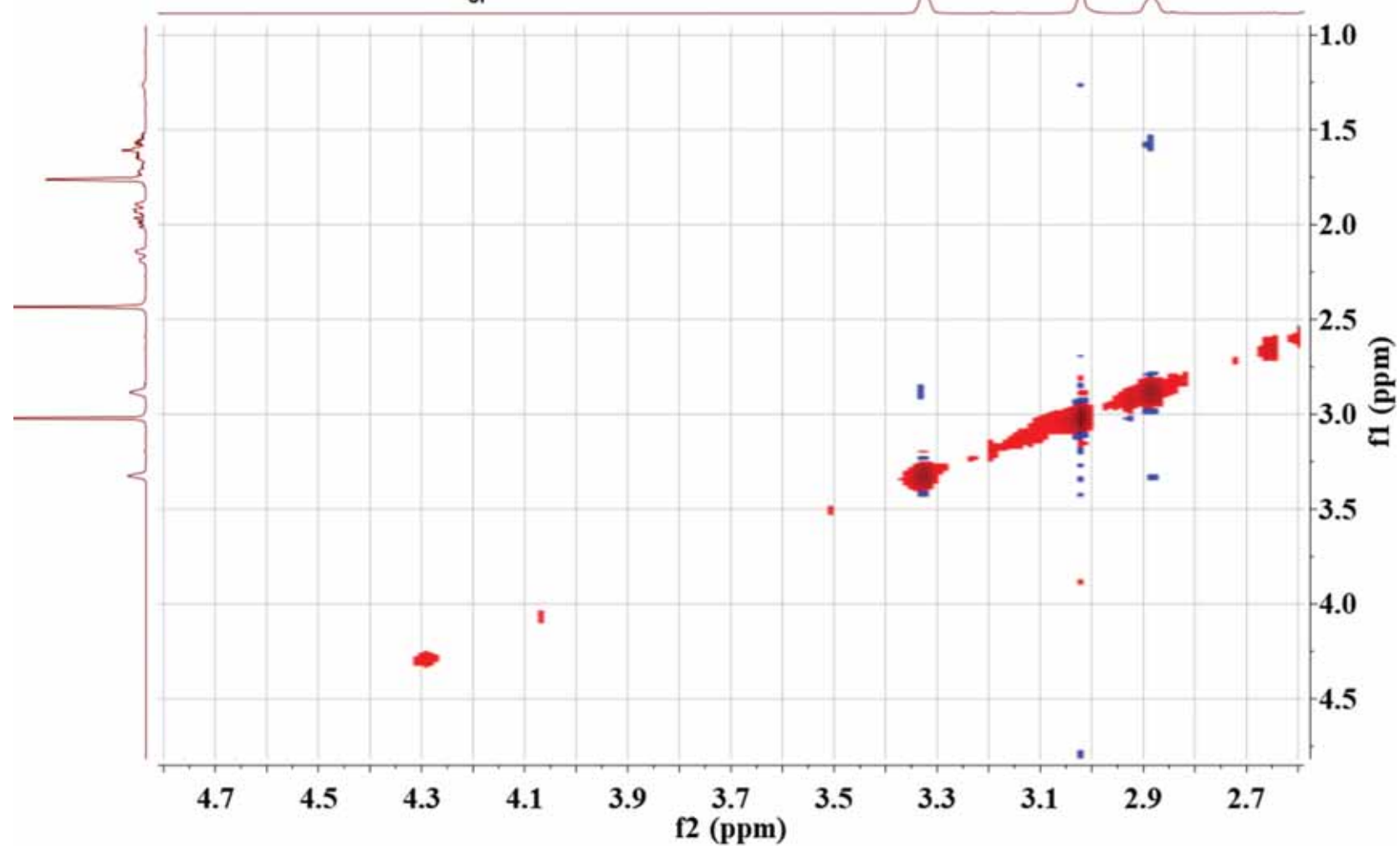




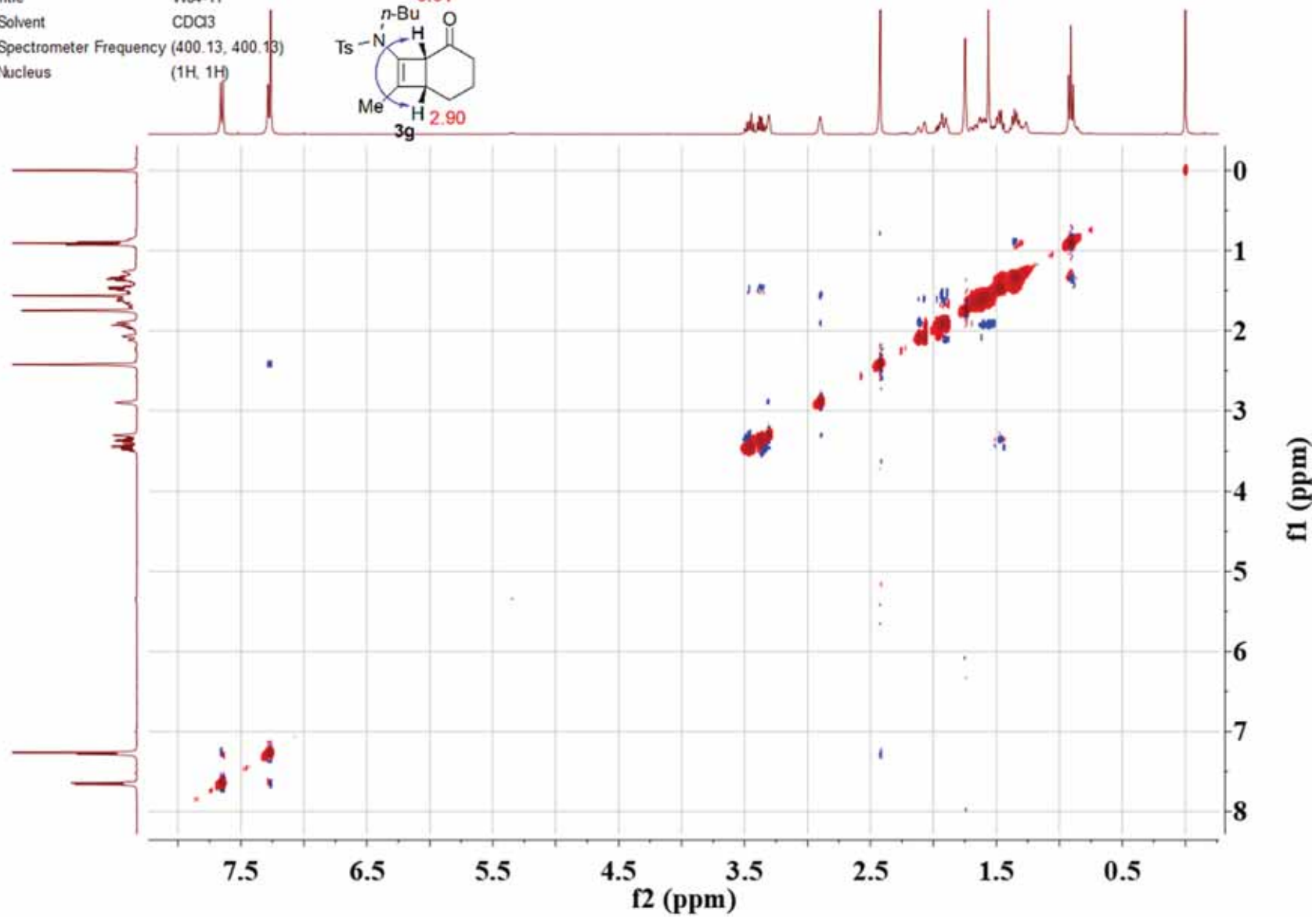
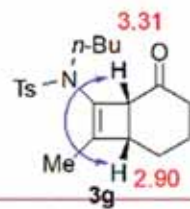
Title WJ3-74  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



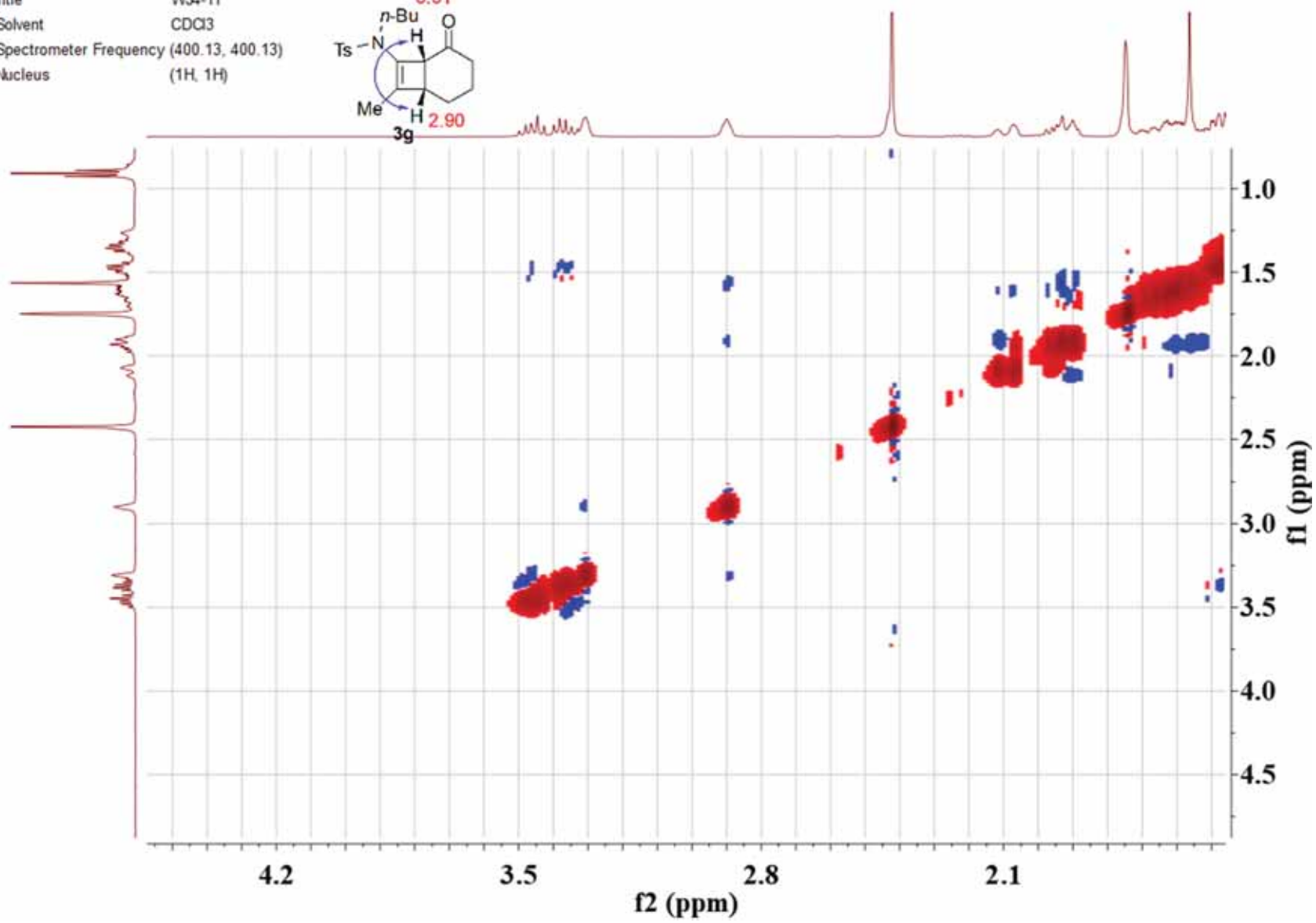
Title WJ3-74  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



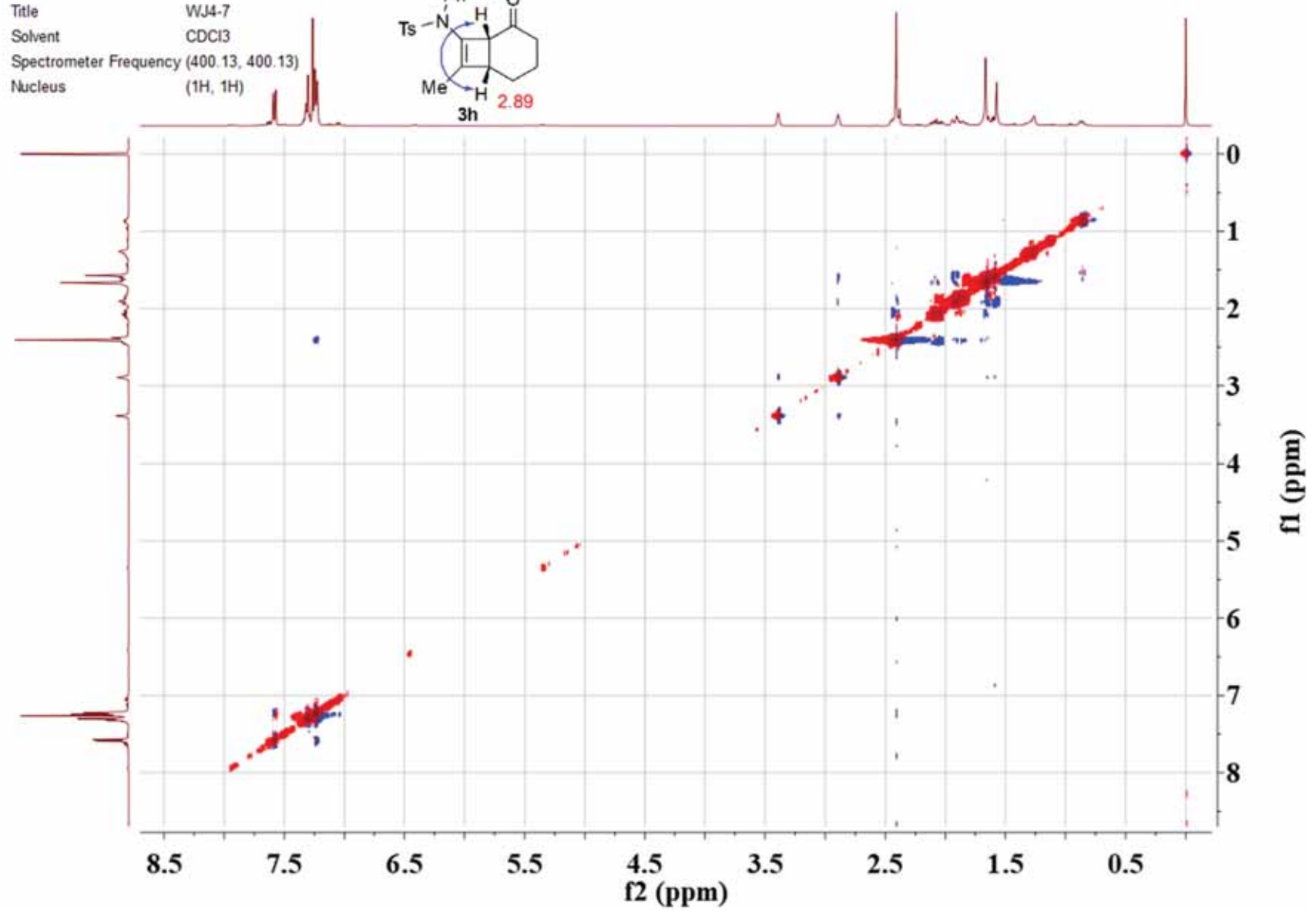
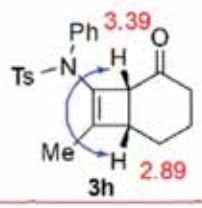
Title WJ4-11  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



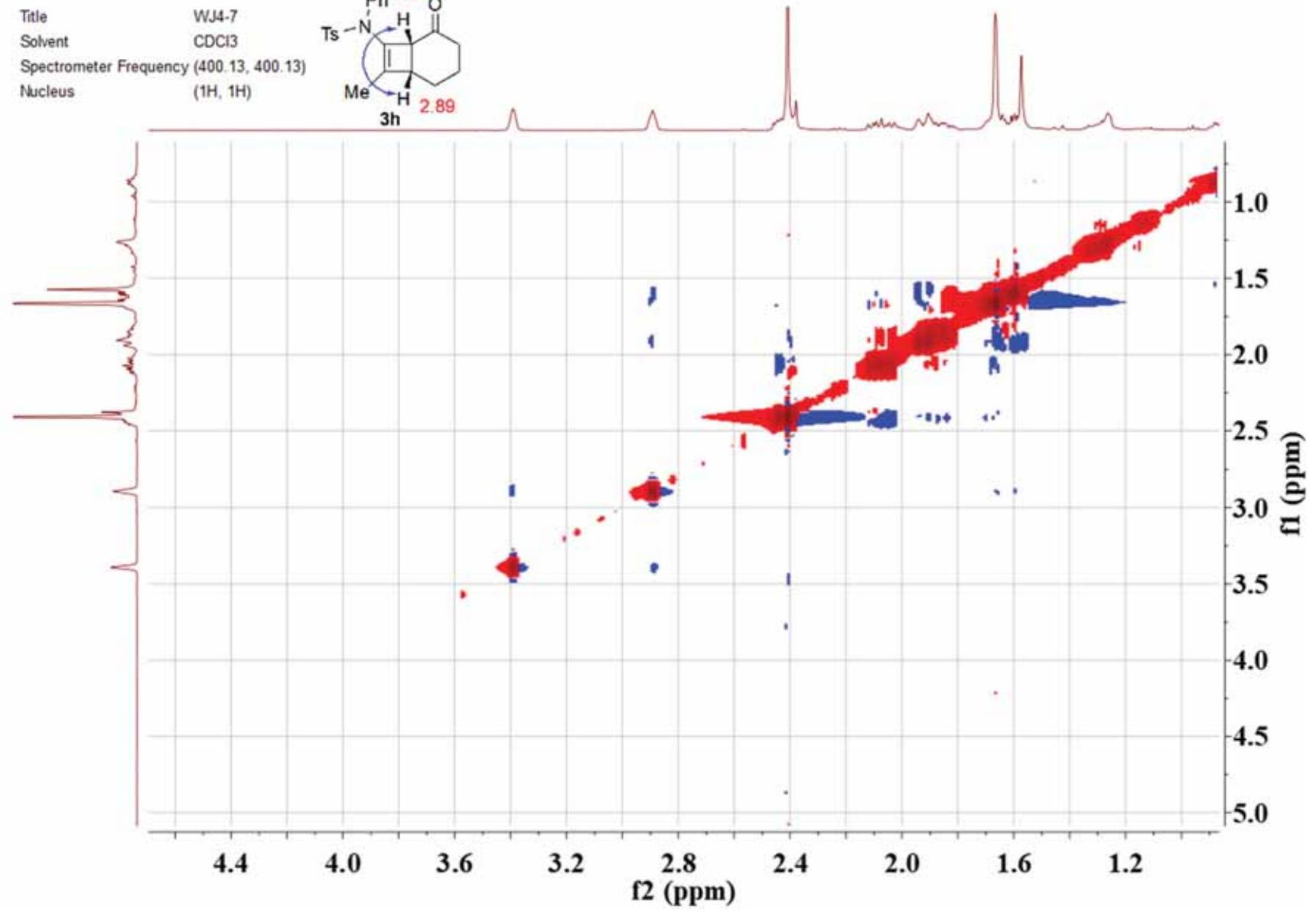
Title WJ4-11  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



Title WJ4-7  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

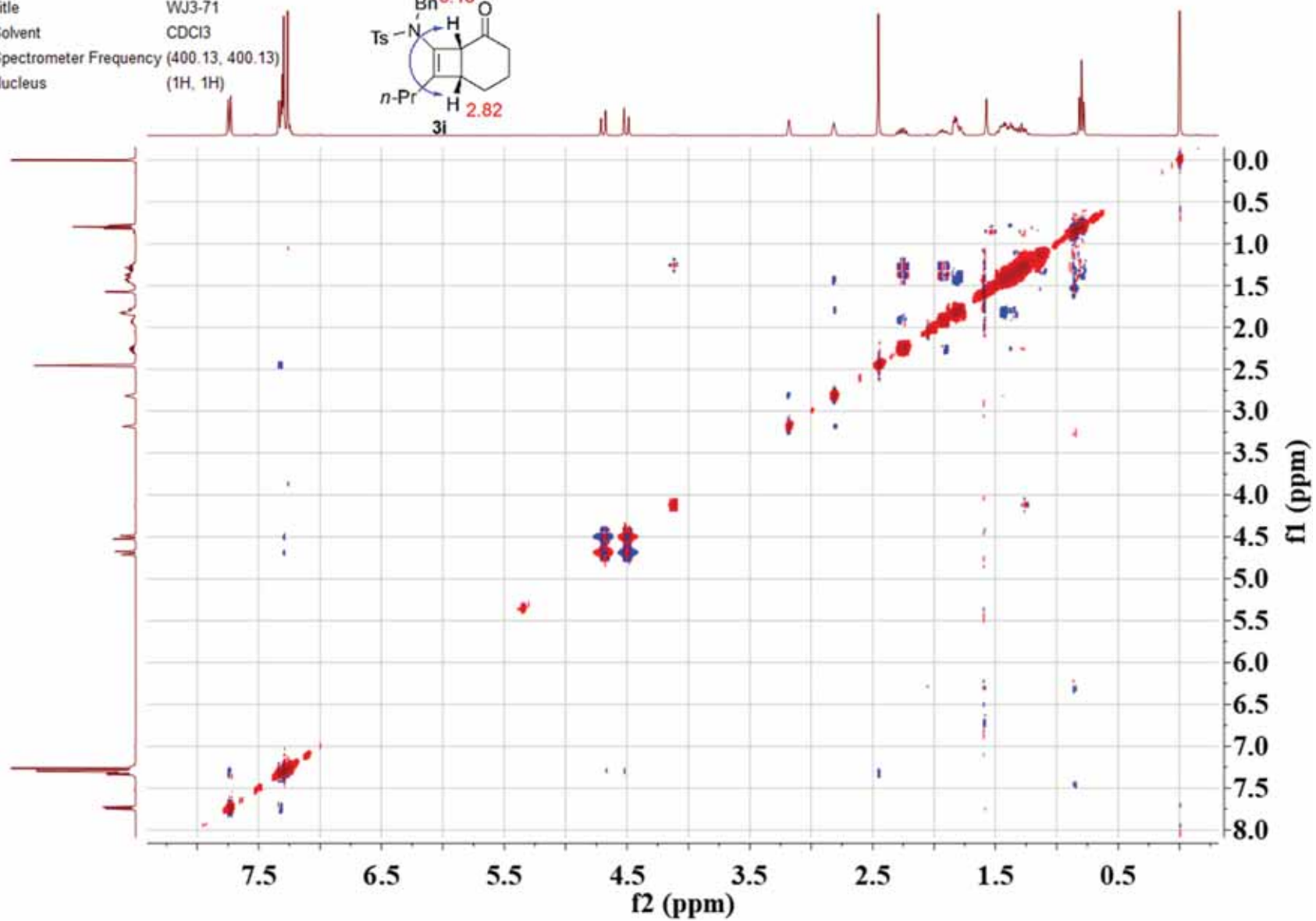


Title WJ4-7  
Solvent CDCl<sub>3</sub>  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

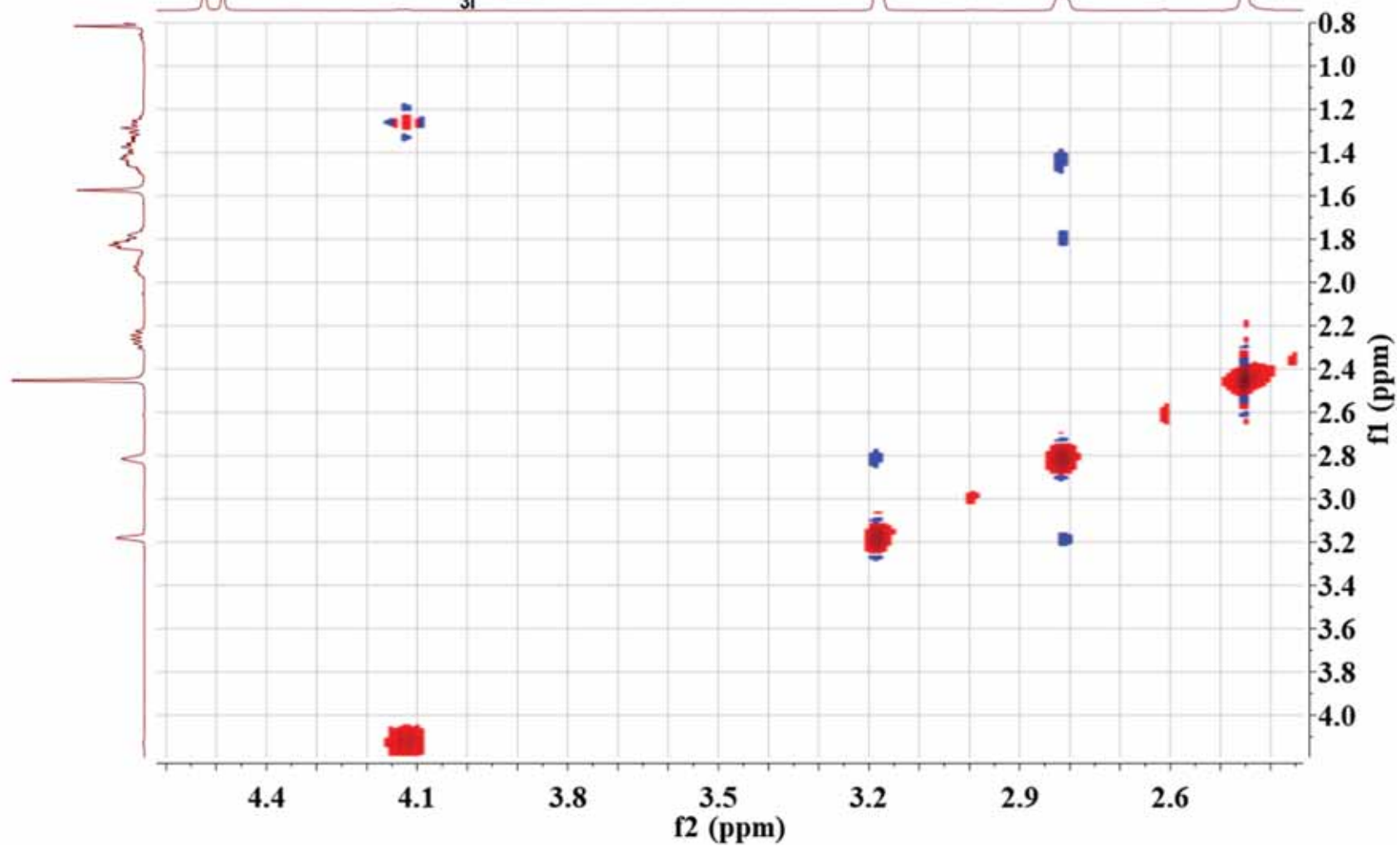
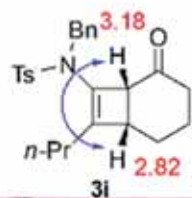




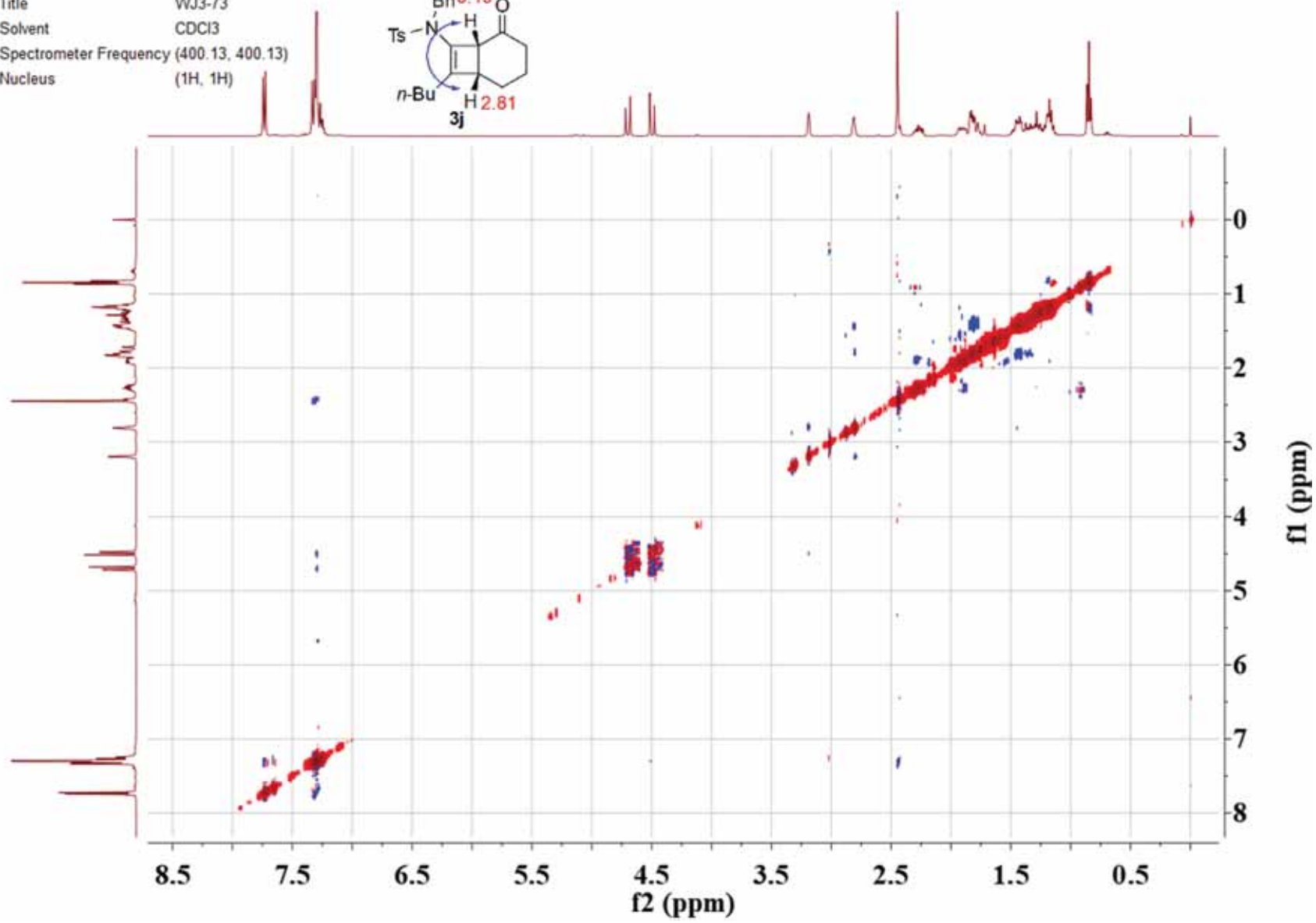
Title WJ3-71  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



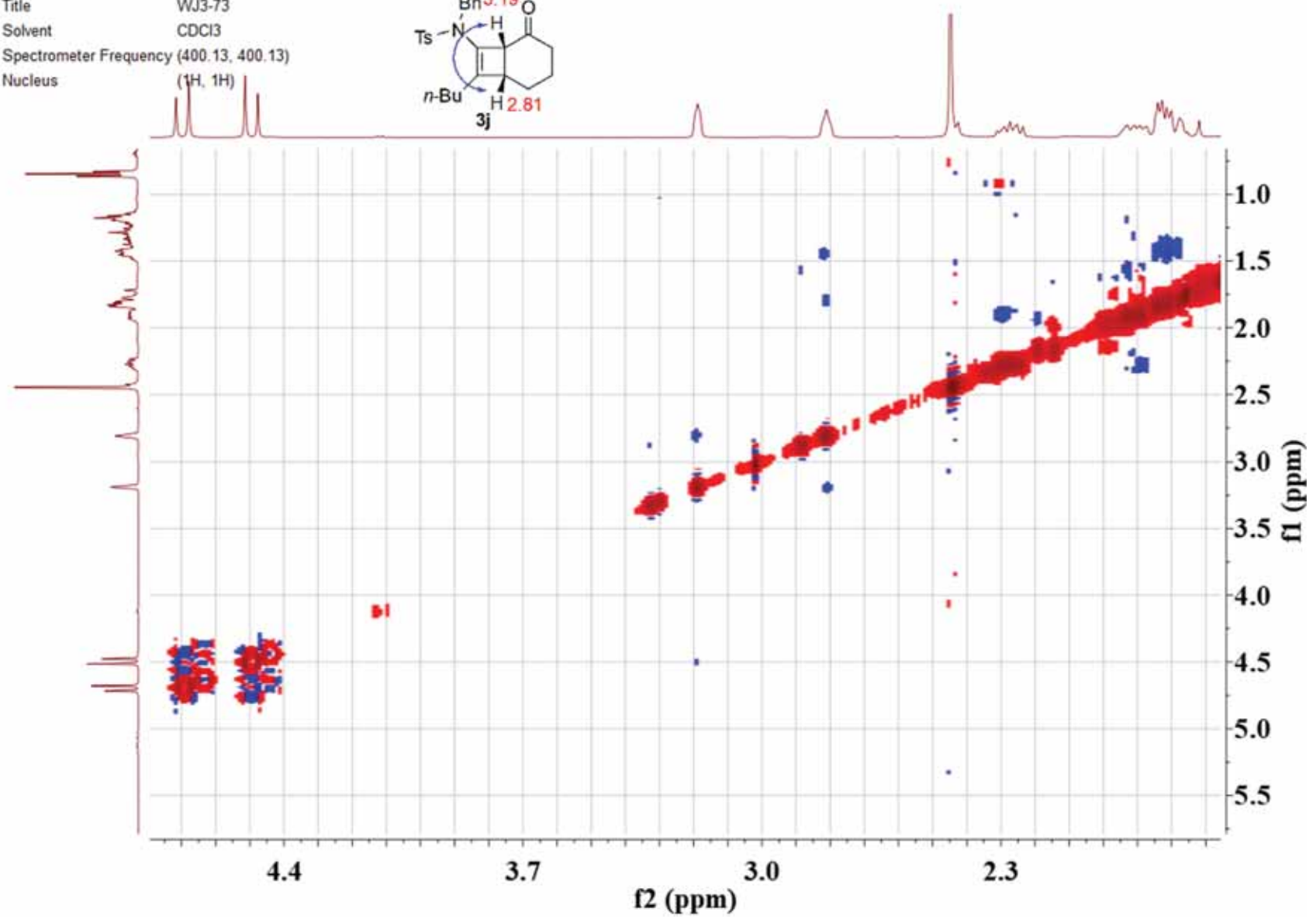
Title WJ3-71  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



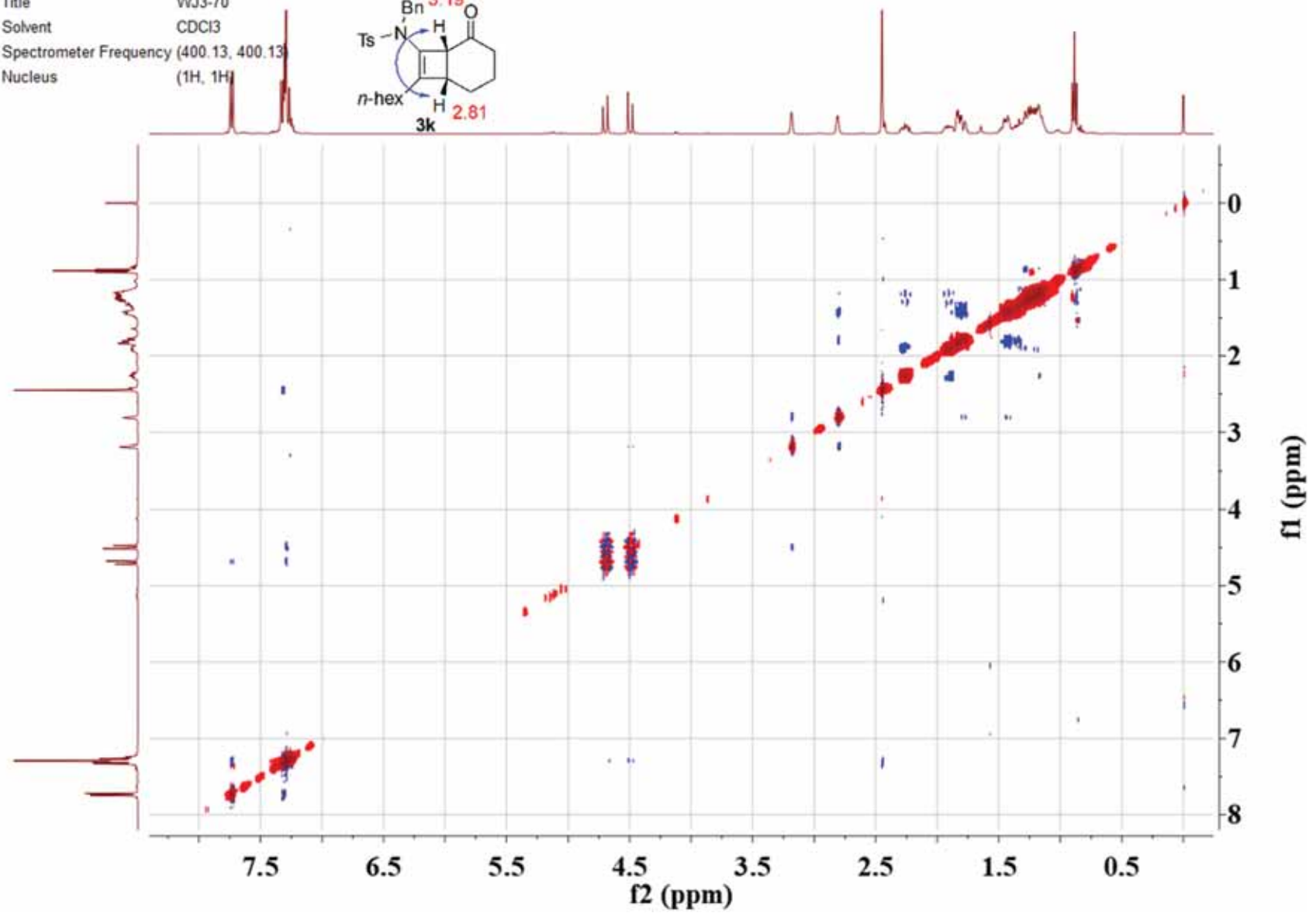
Title WJ3-73  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



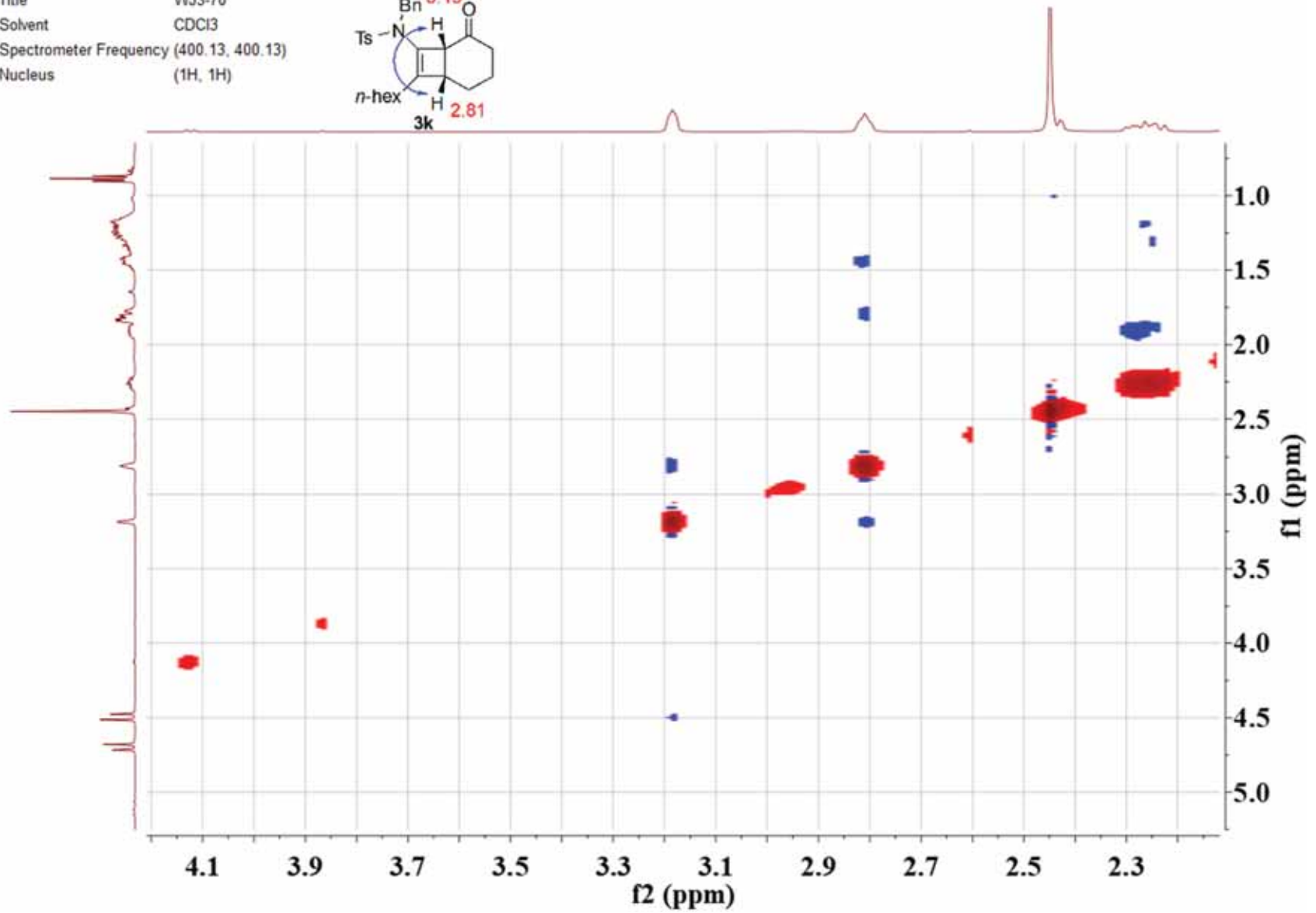
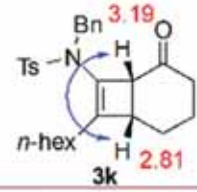
Title WJ3-73  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



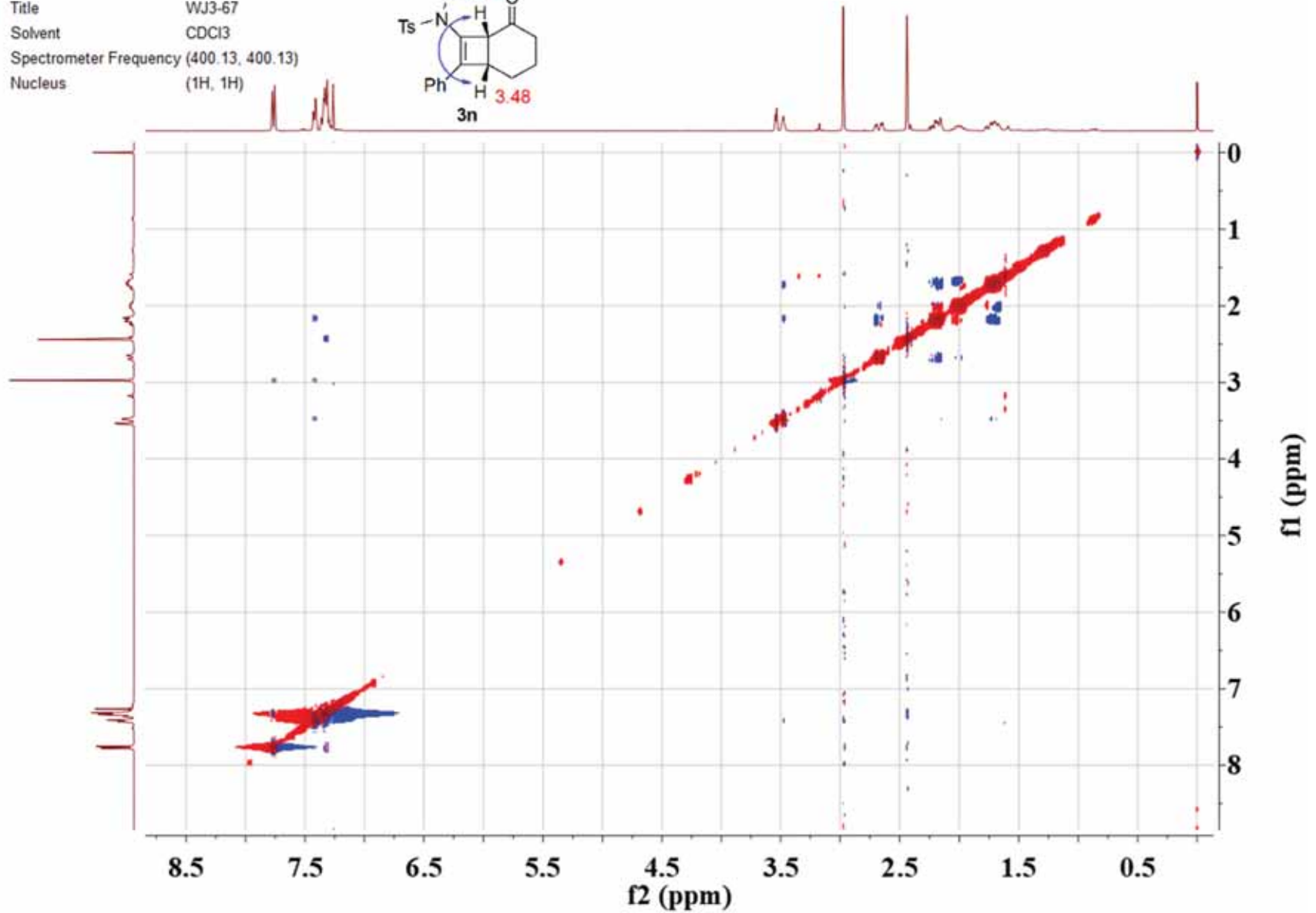
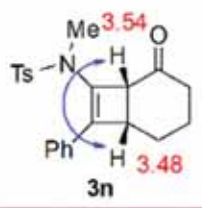
Title WJ3-70  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



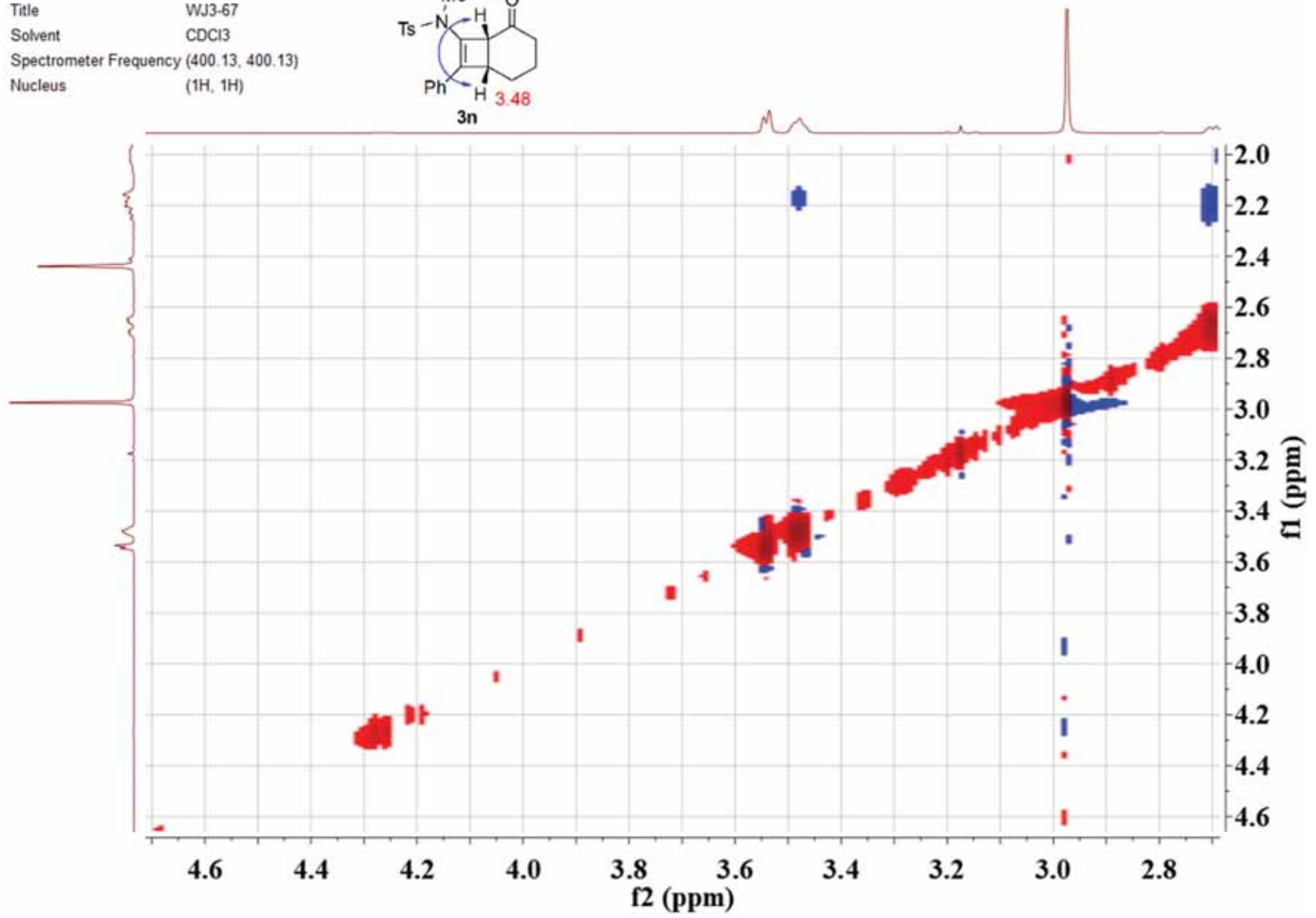
Title WJ3-70  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



Title WJ3-67  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

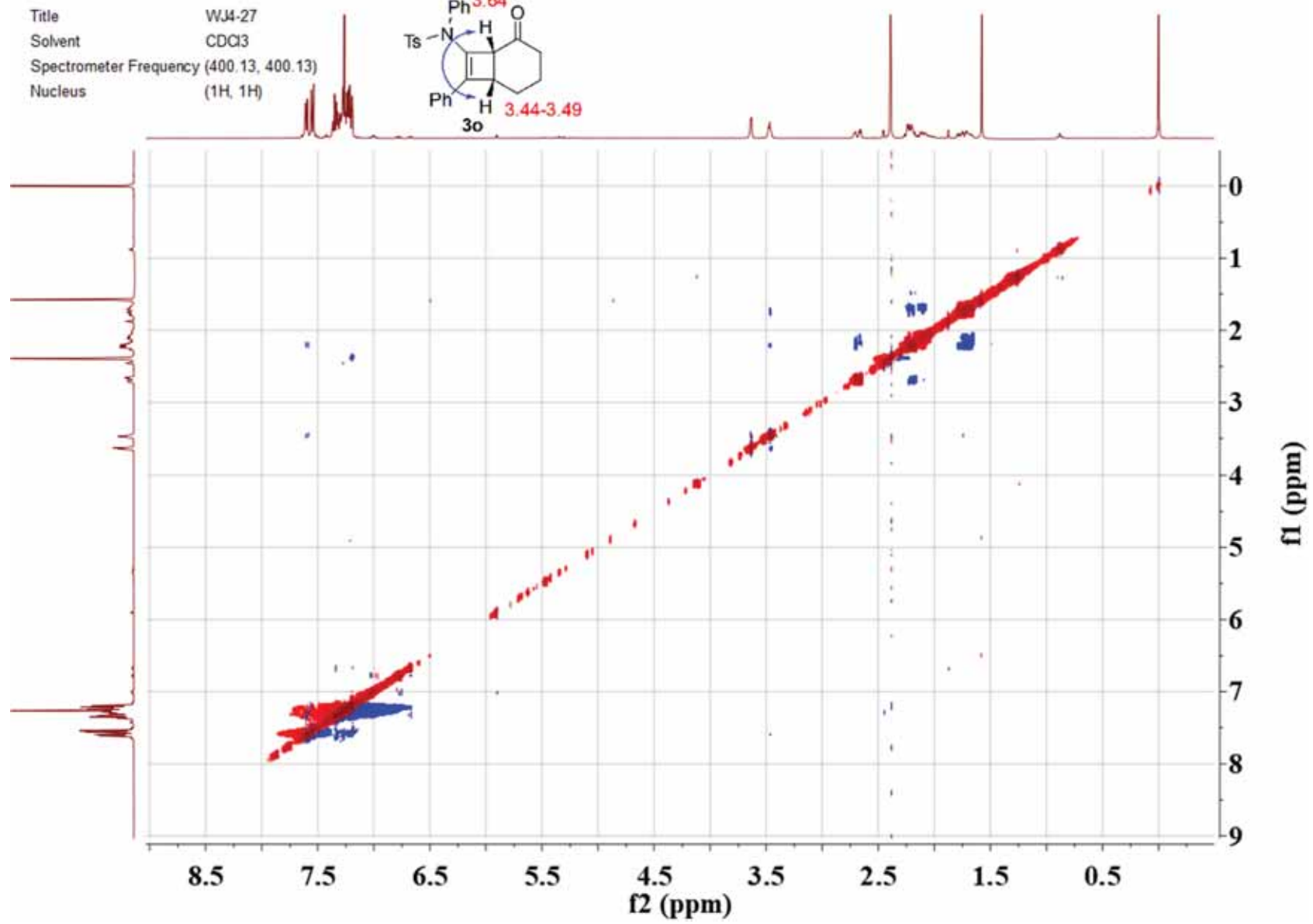


Title WJ3-67  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

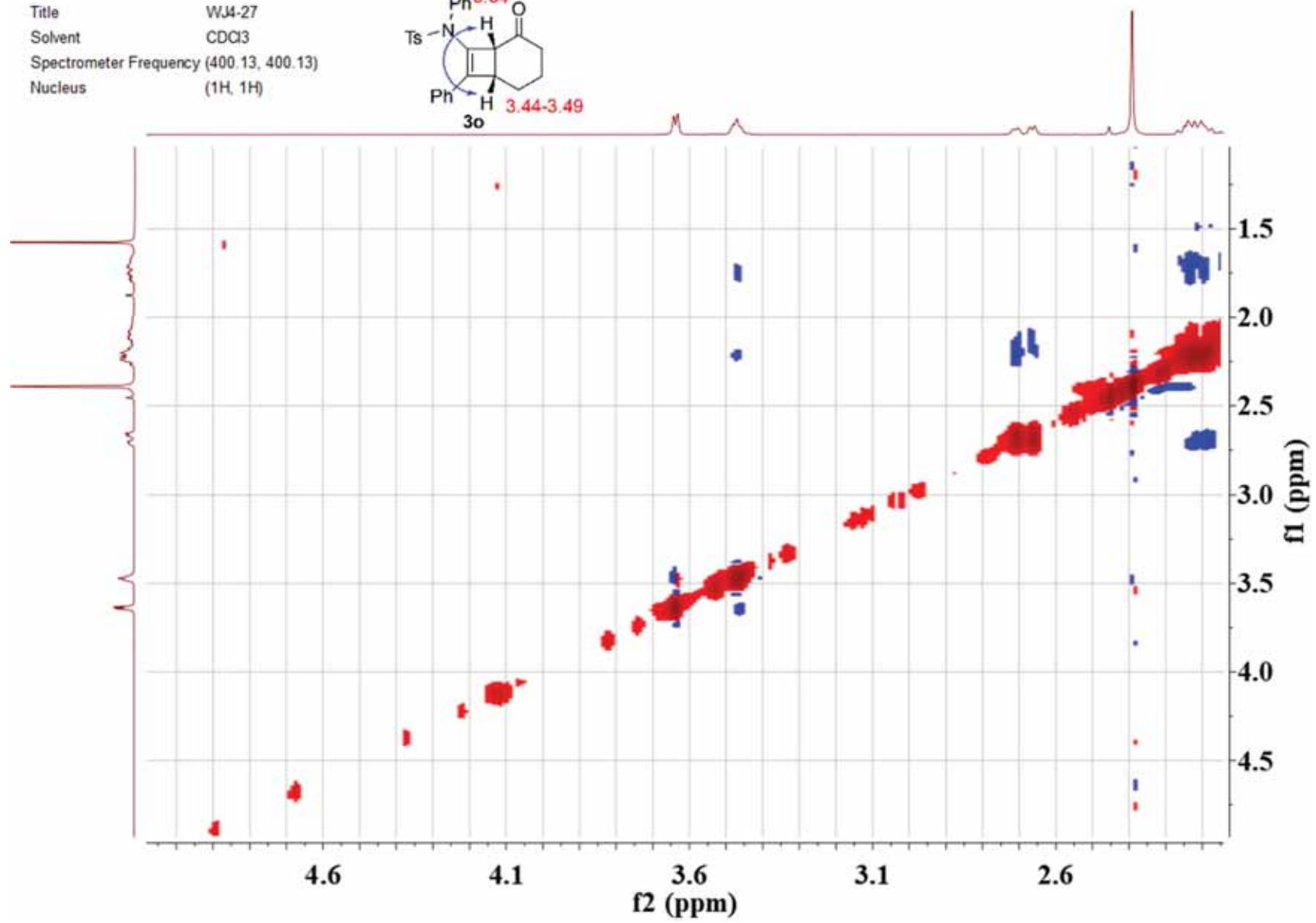




Title WJ4-27  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

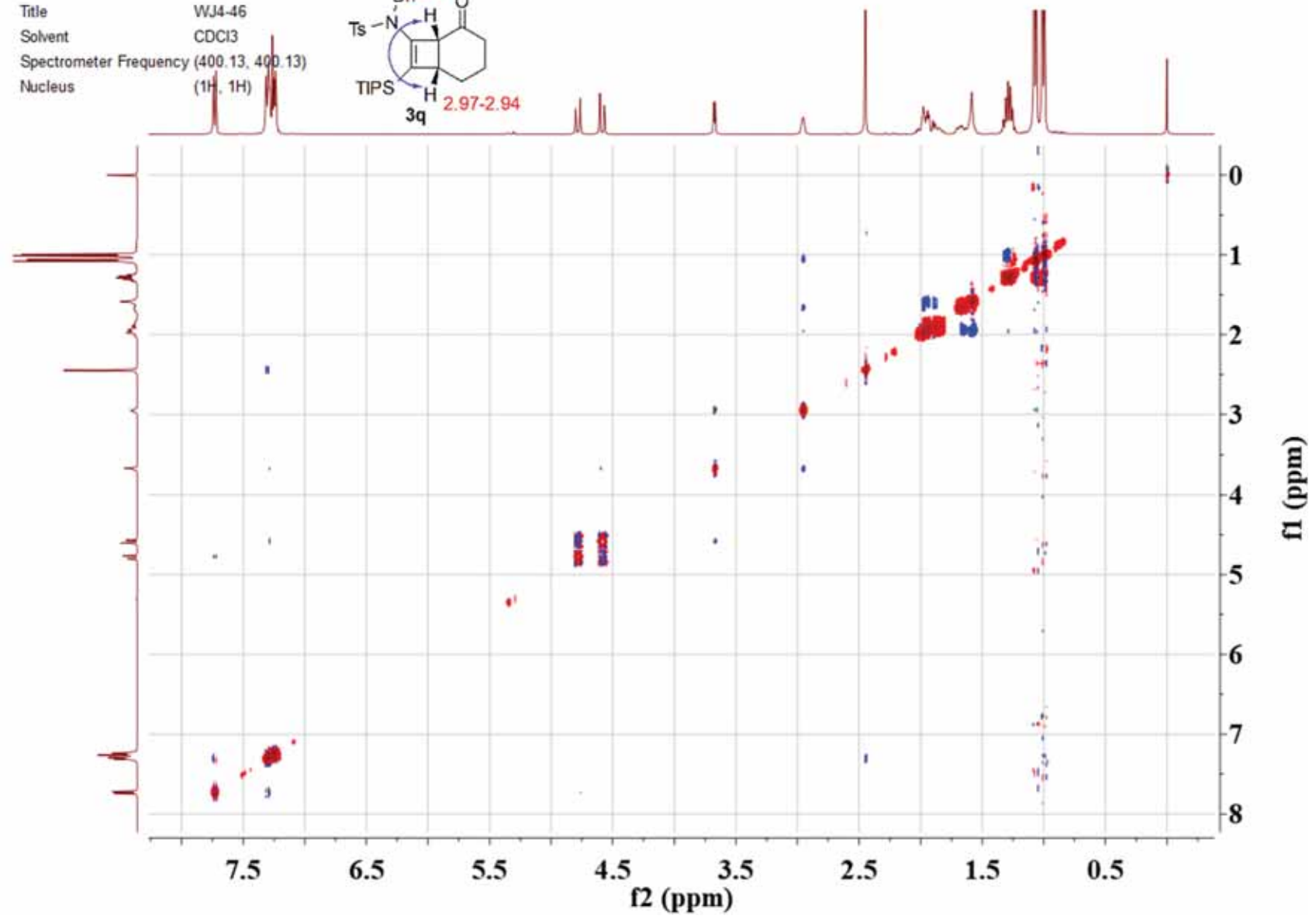
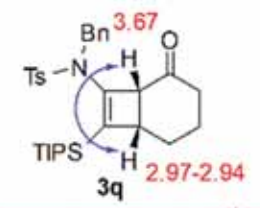


Title WJ4-27  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

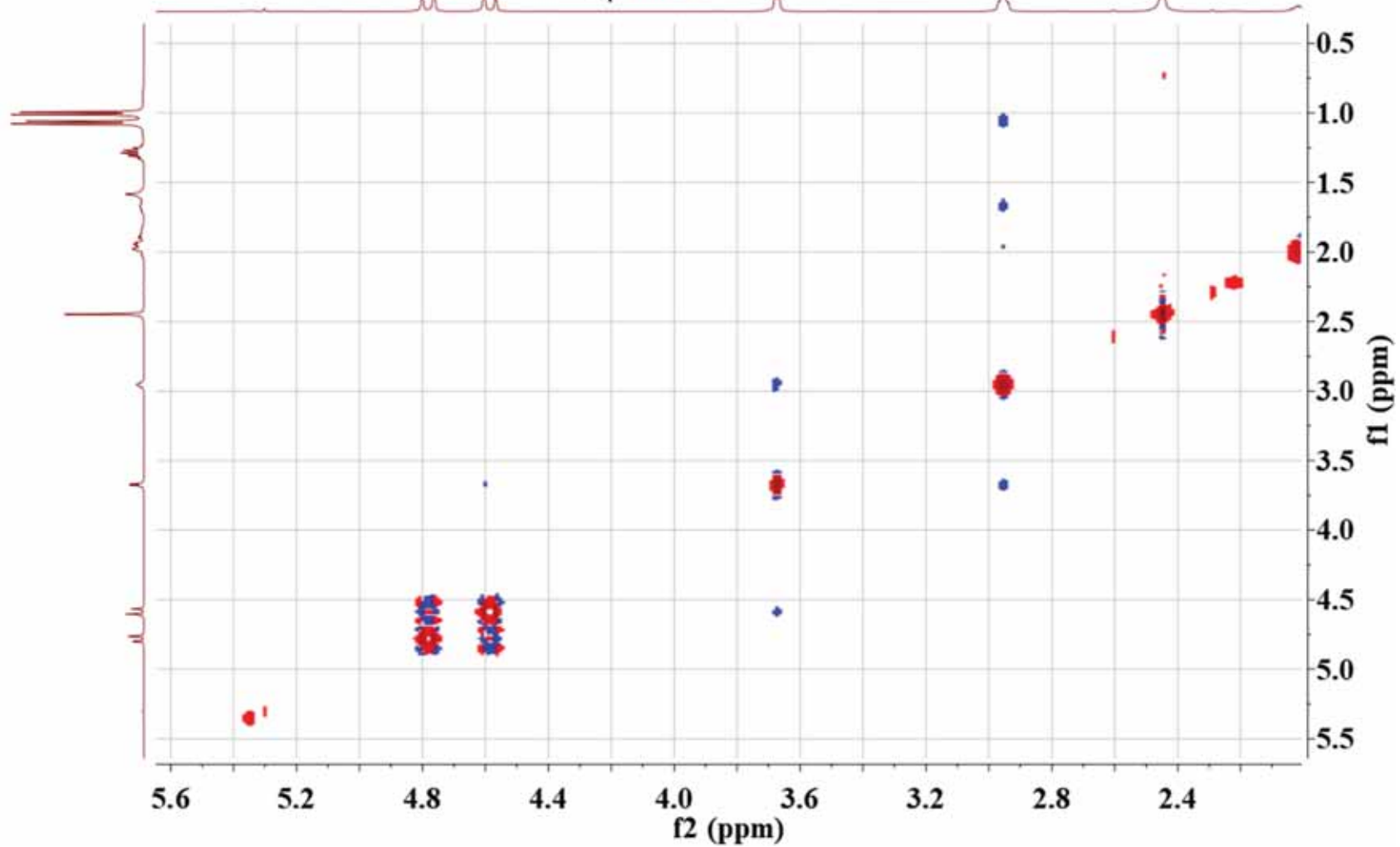
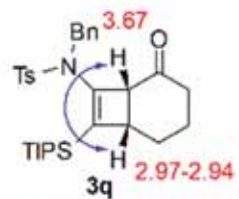


S106

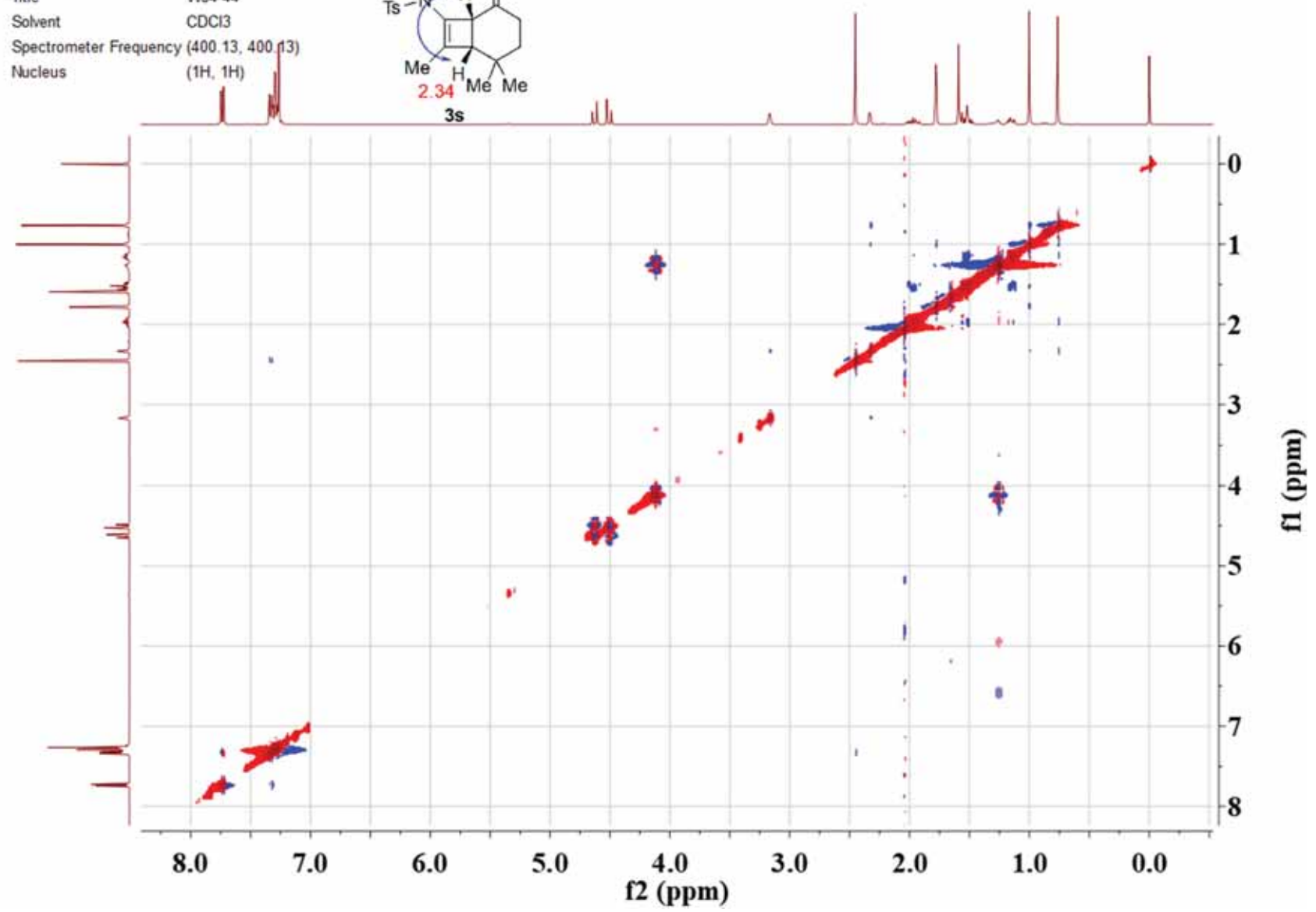
Title WJ4-46  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



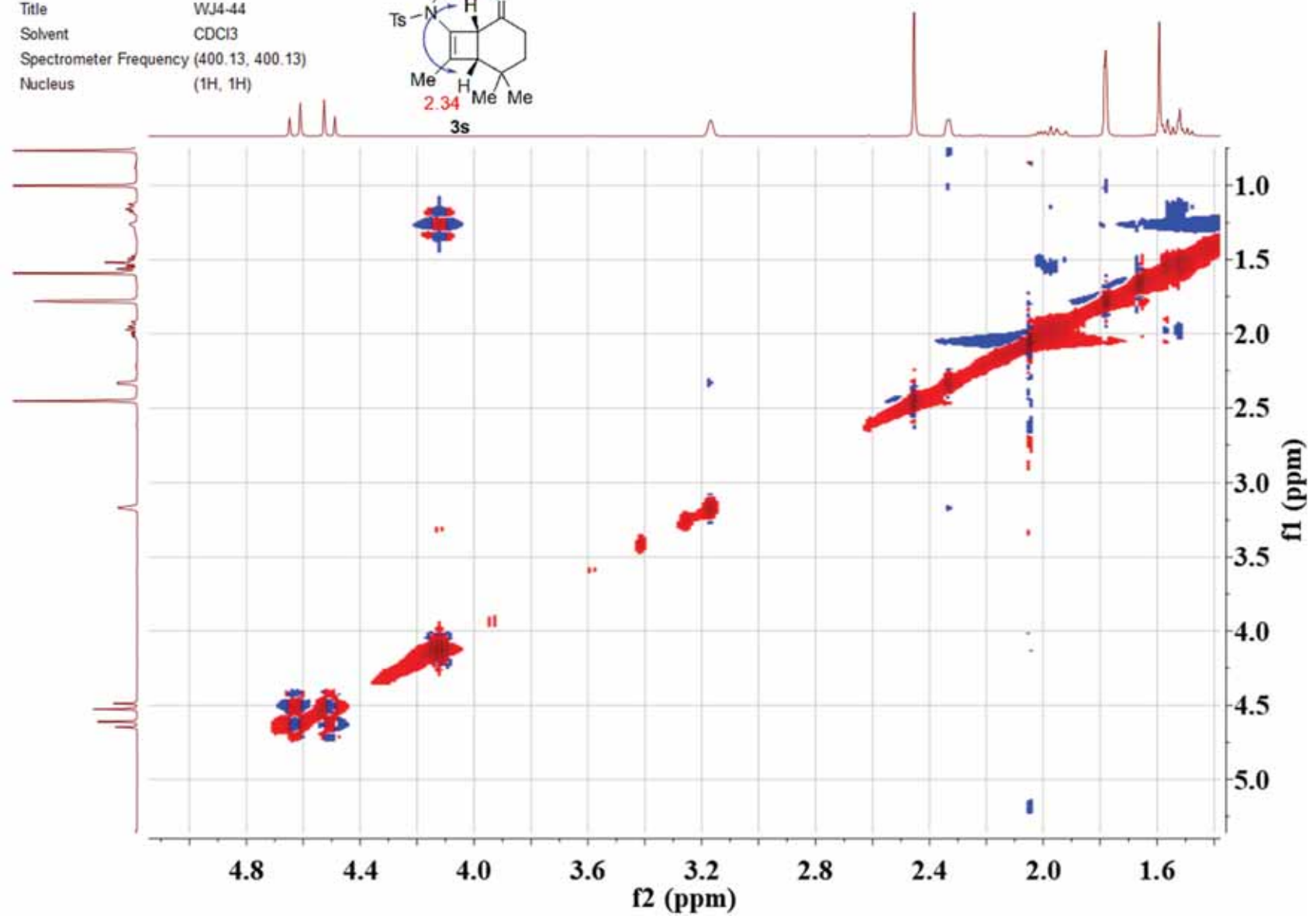
Title WJ4-46  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



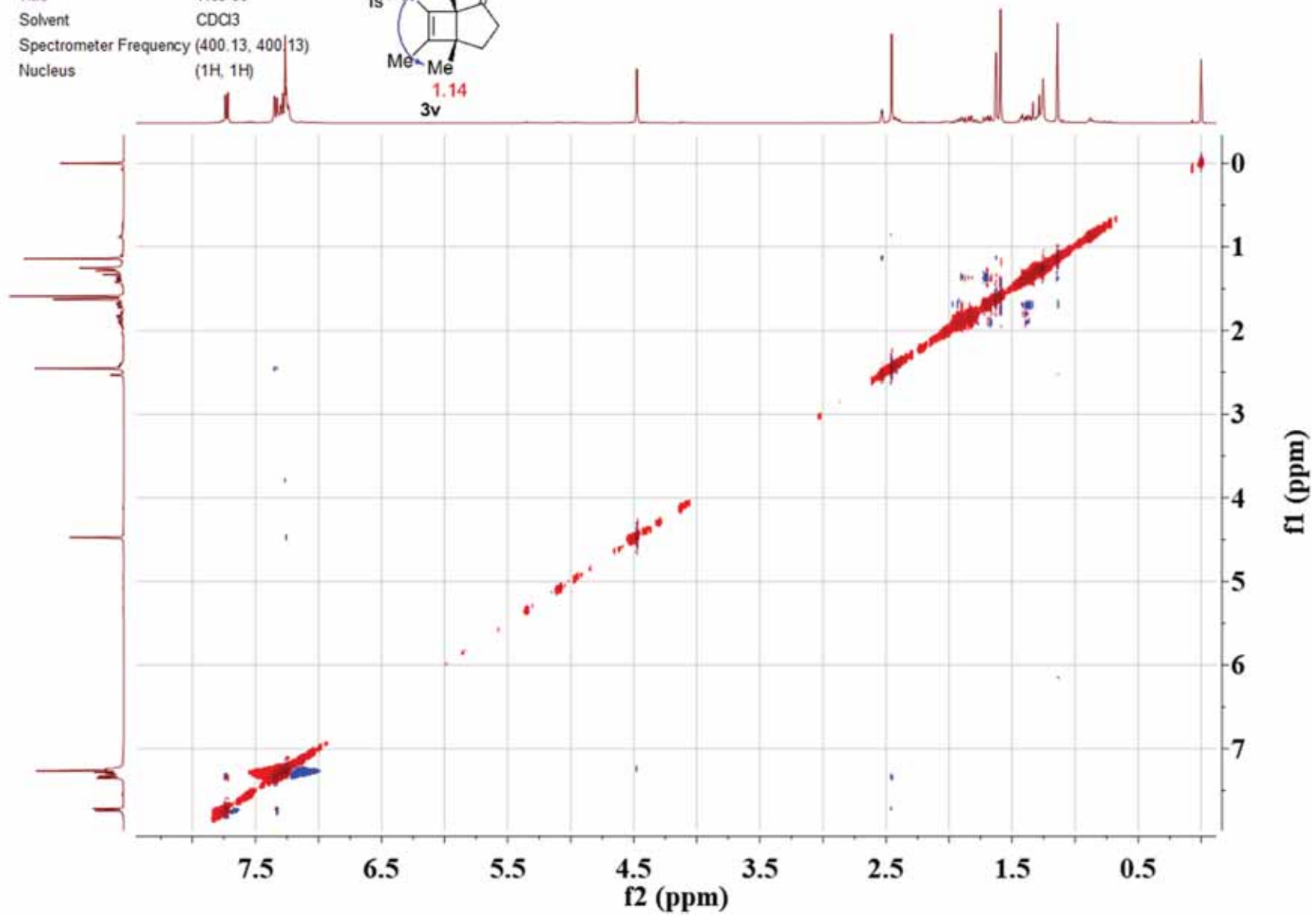
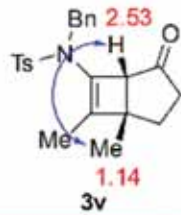
Title WJ4-44  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



Title WJ4-44  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

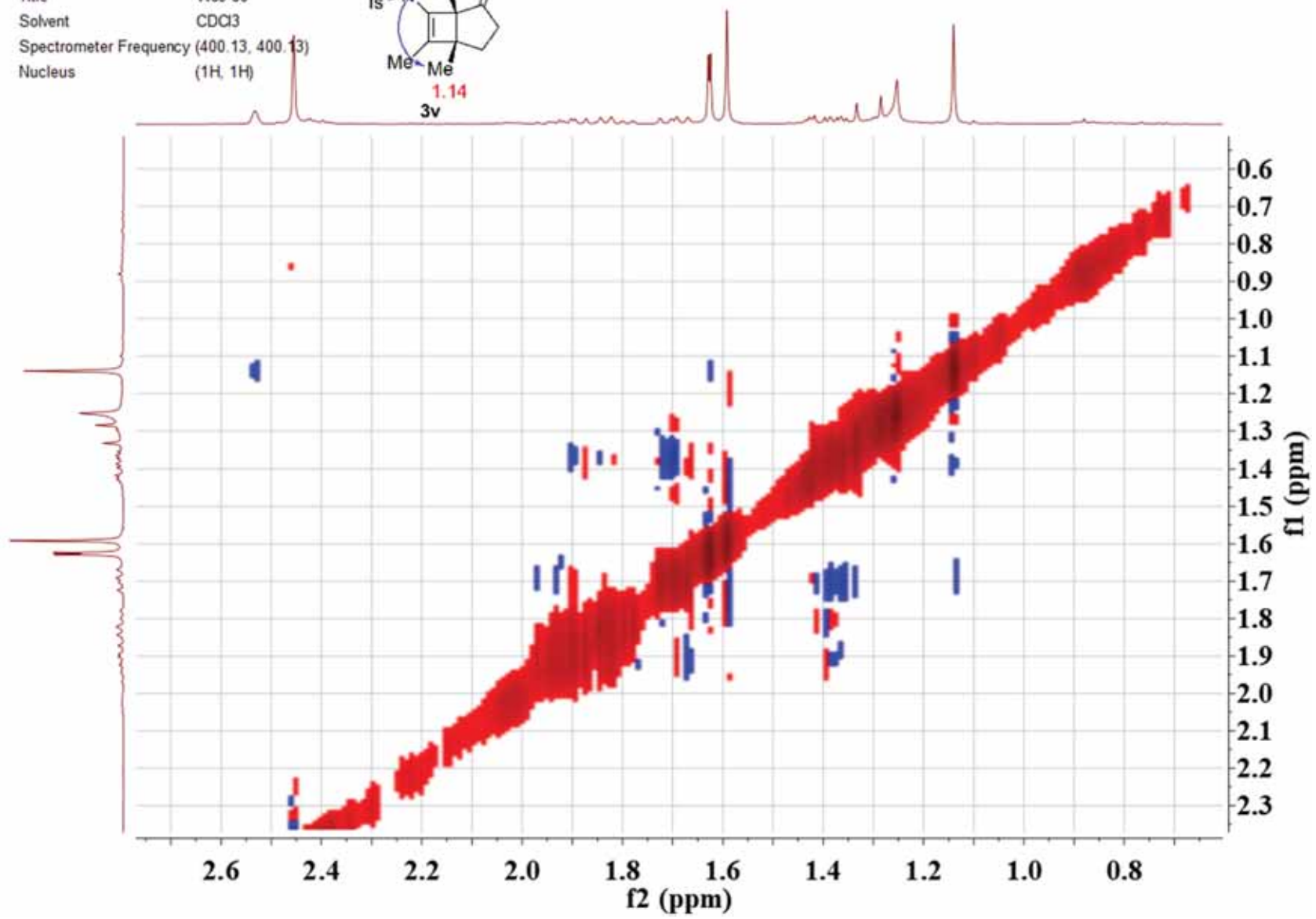


Title WJ3-80  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



S111

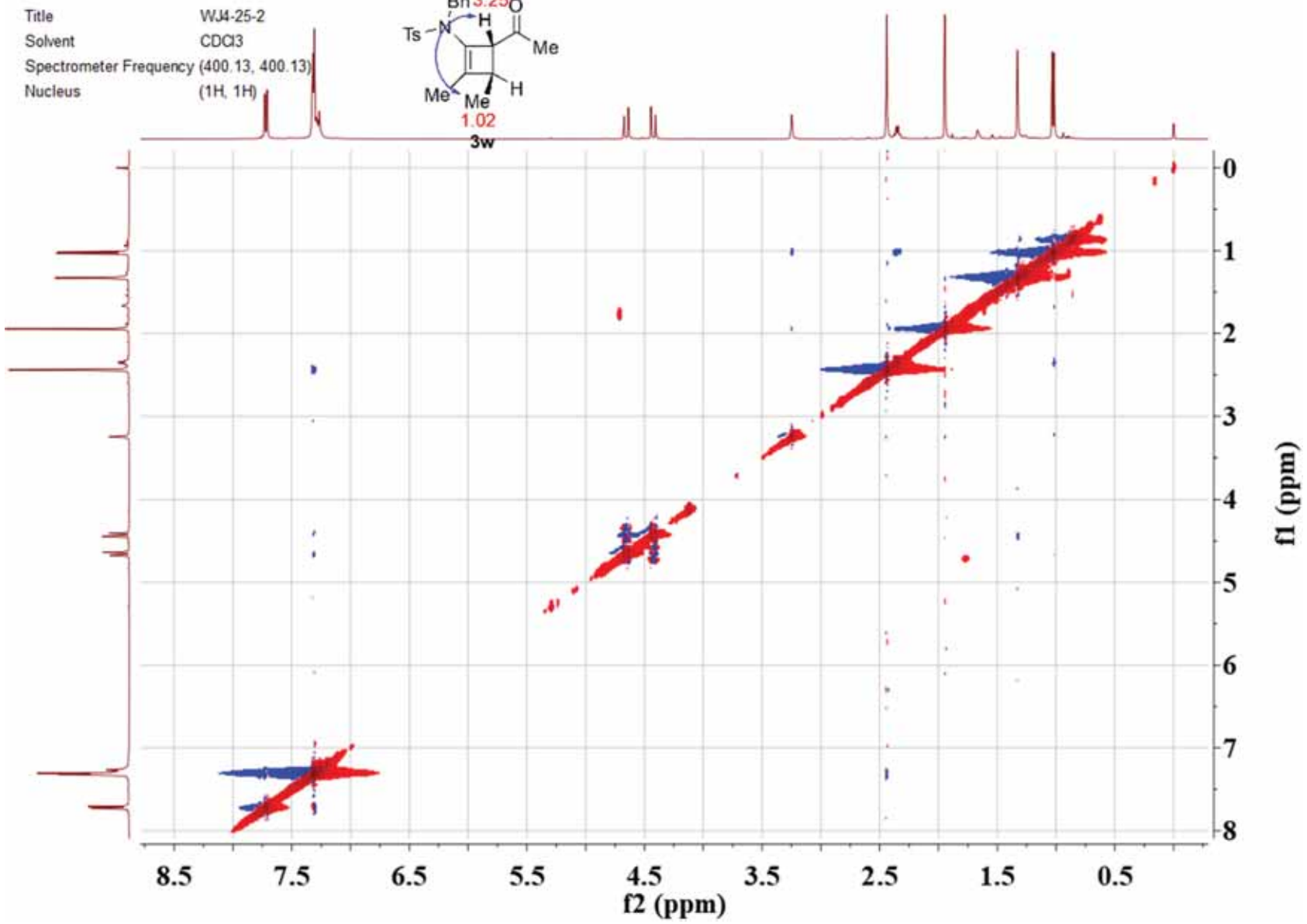
Title WJ3-80  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



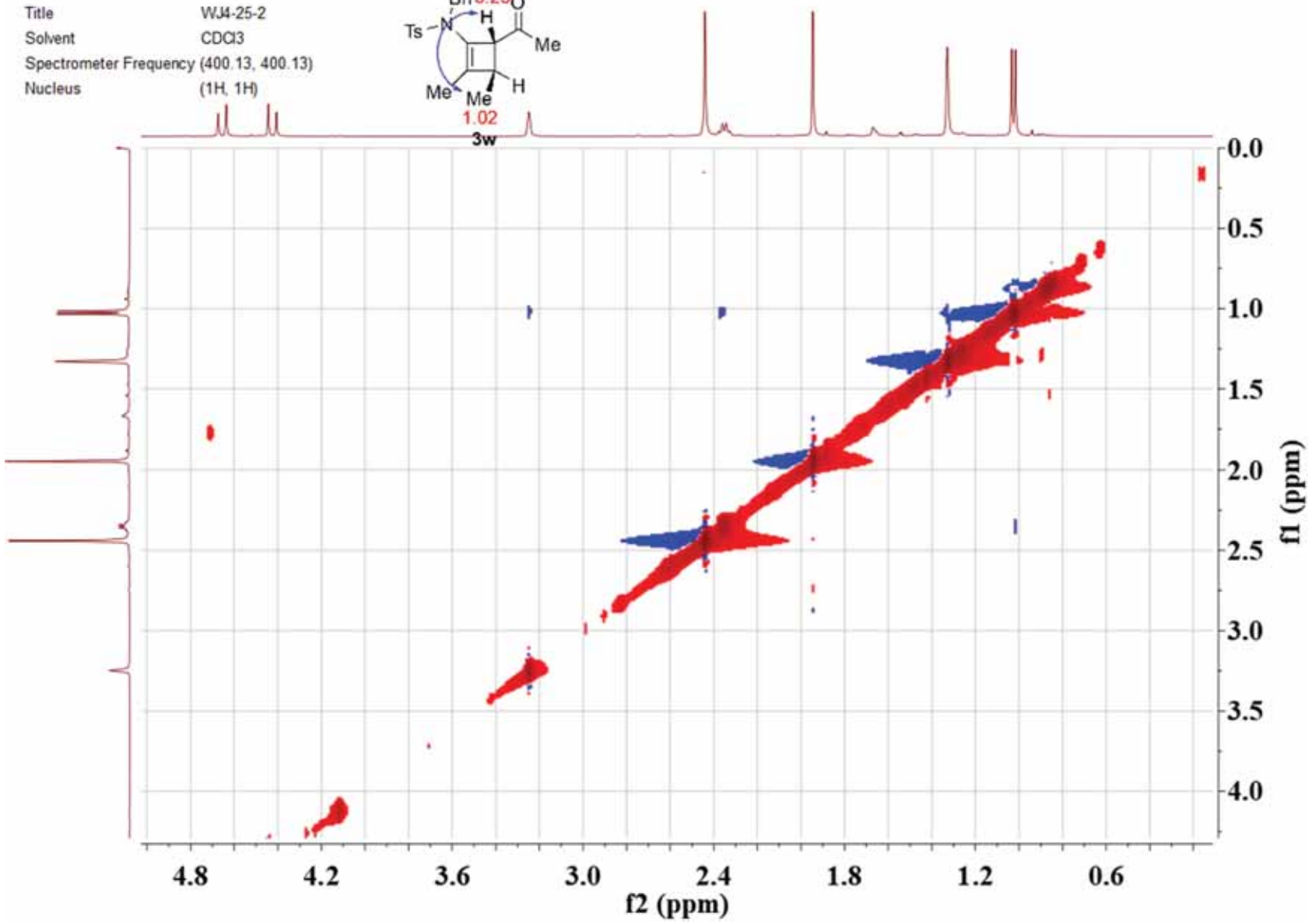
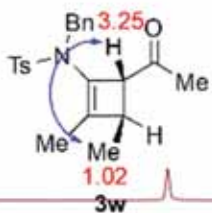
S112

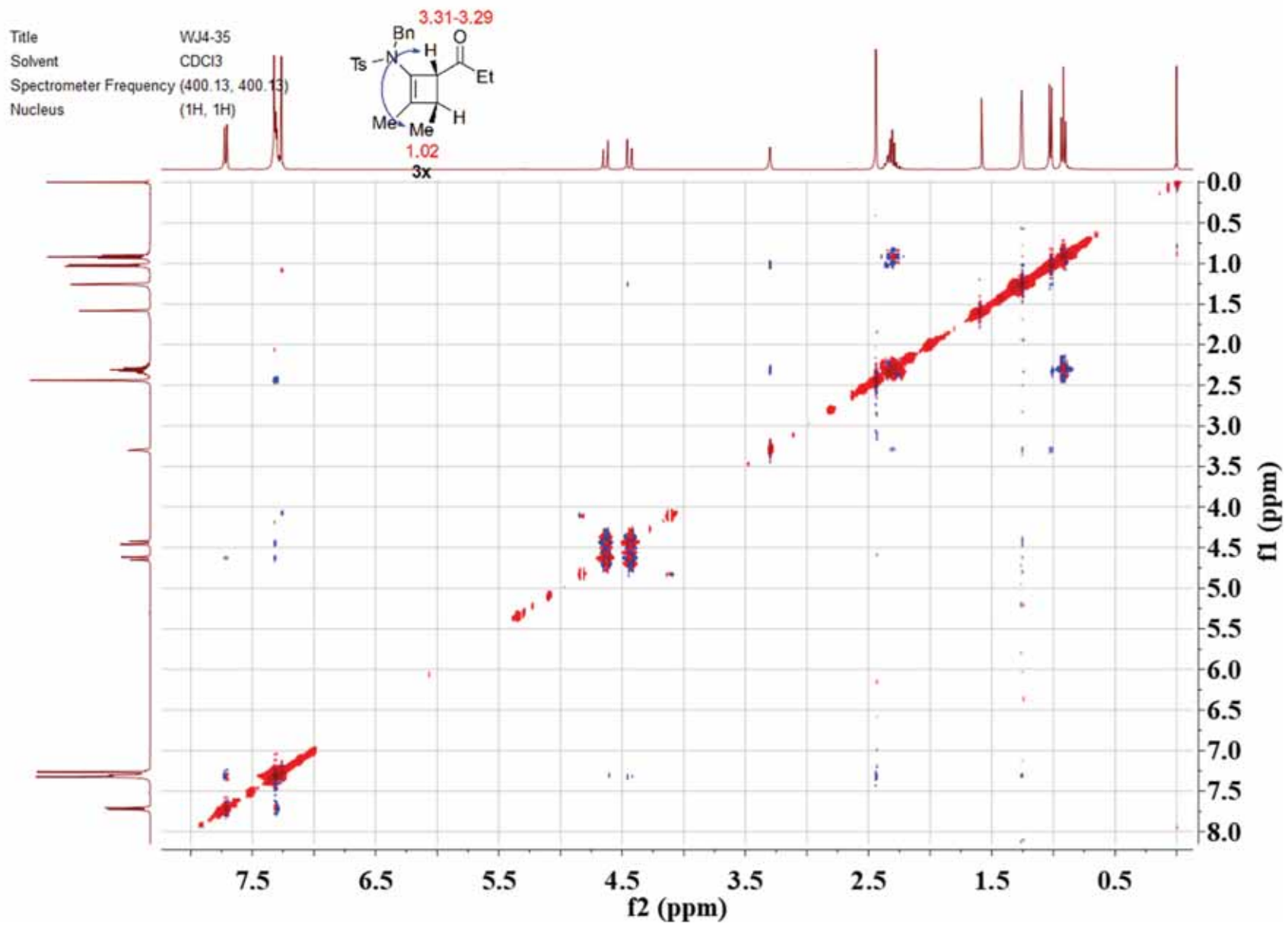


Title WJ4-25-2  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



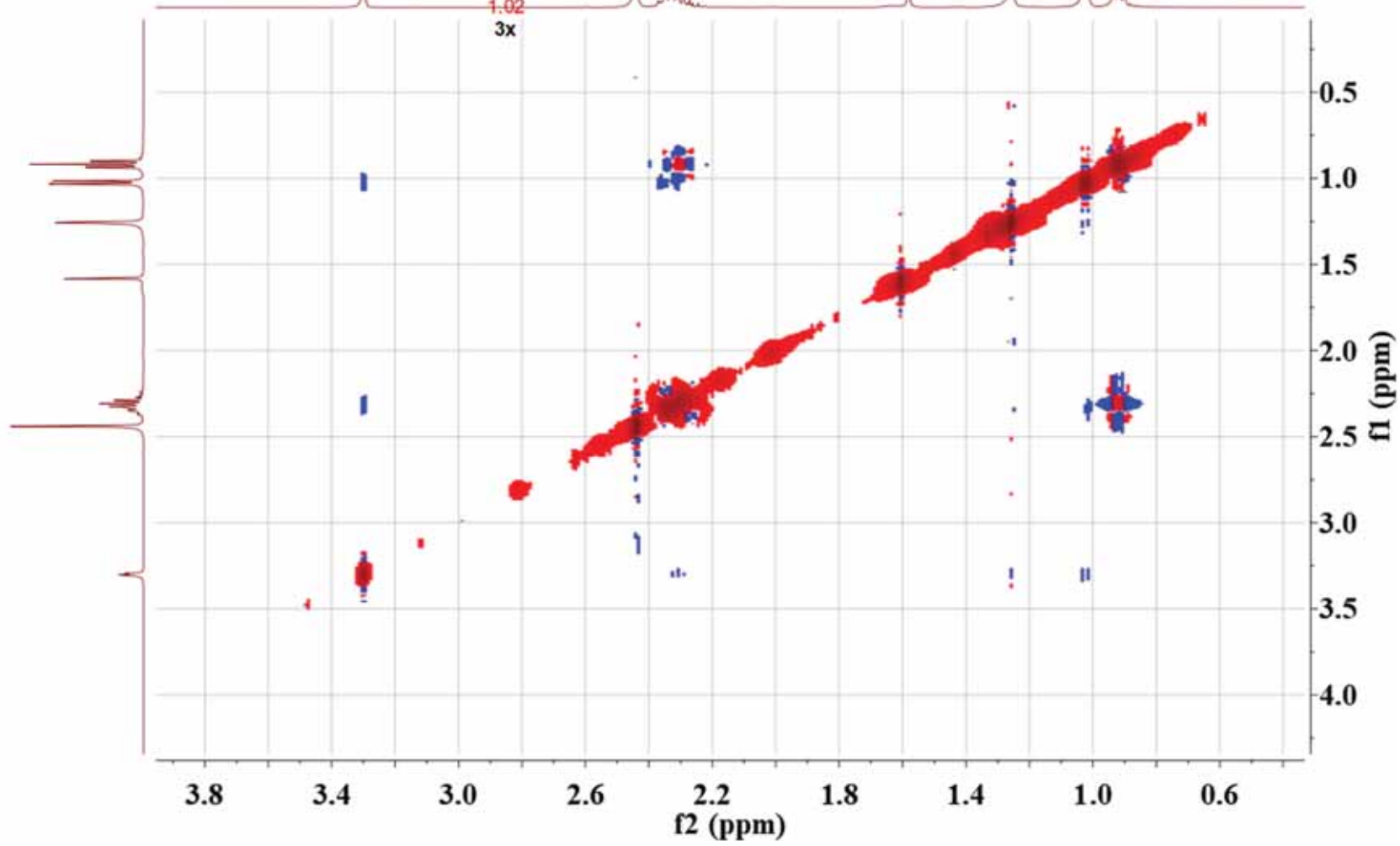
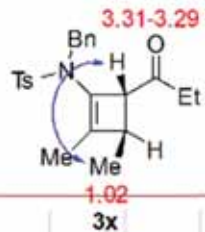
Title WJ4-25-2  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



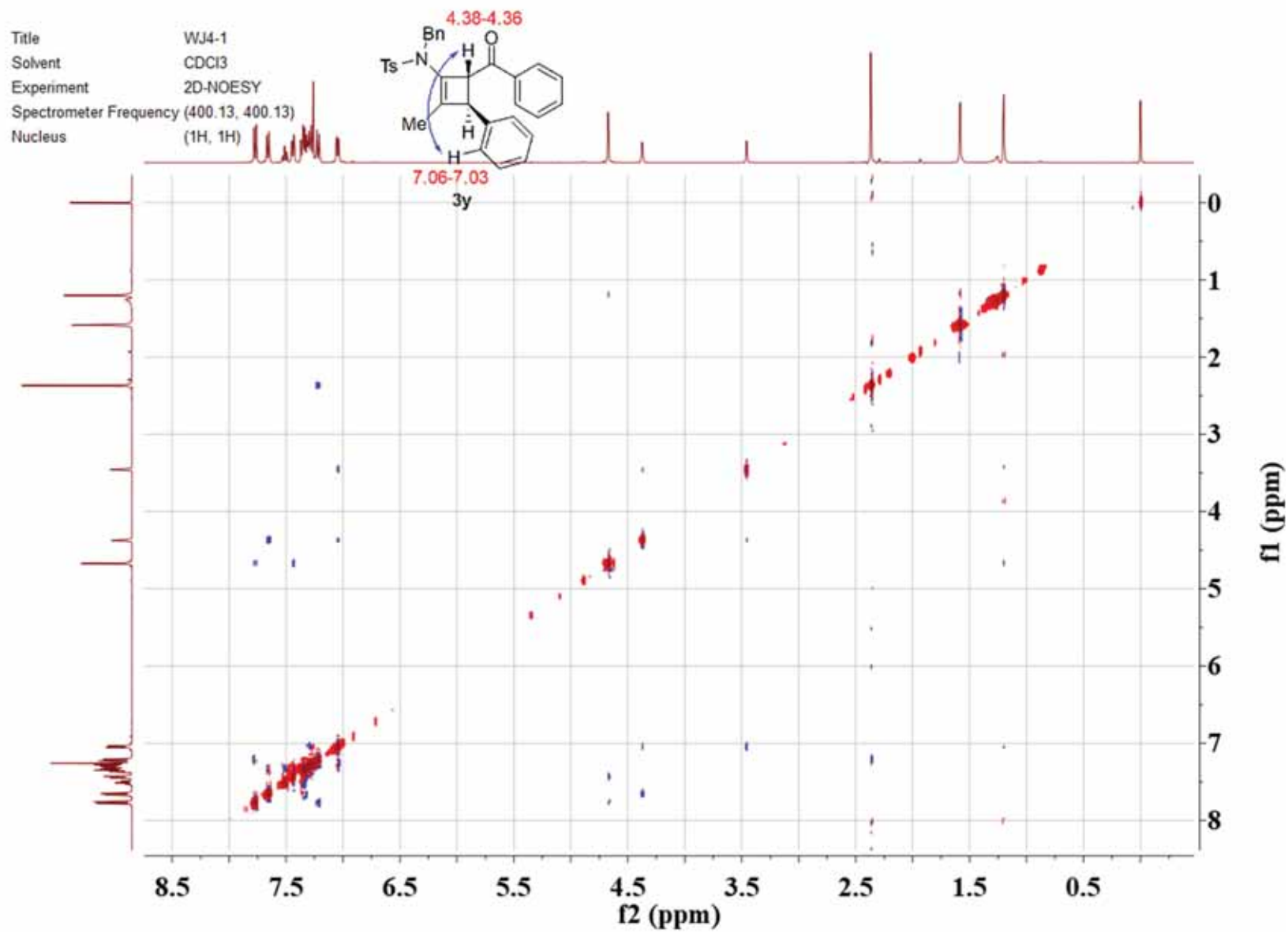


S115

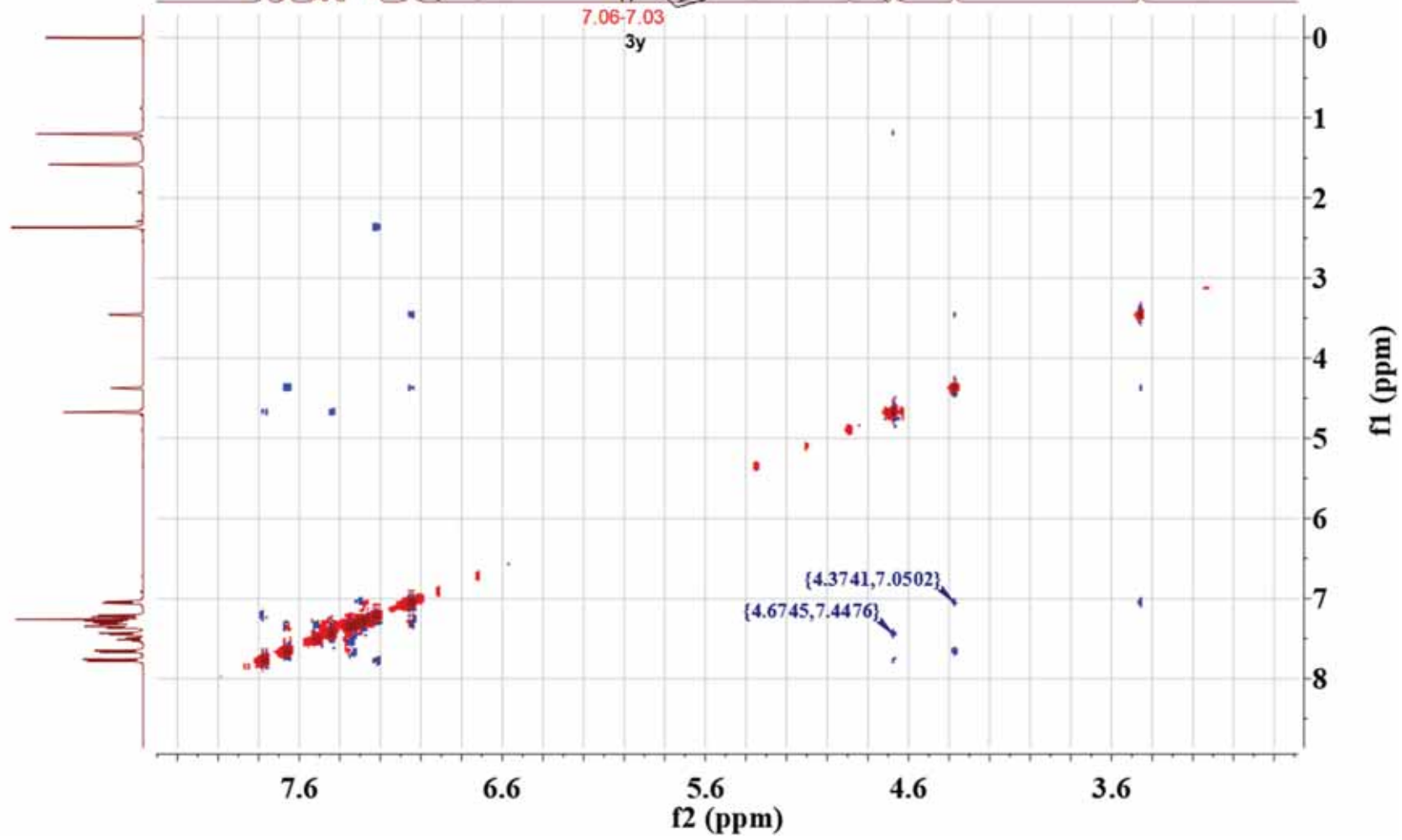
Title WJ4-35  
Solvent CDCl3  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



# NOESY, COSY, HSQC, and HMBC Spectra of Cyclobutenamides 3y and 3z.

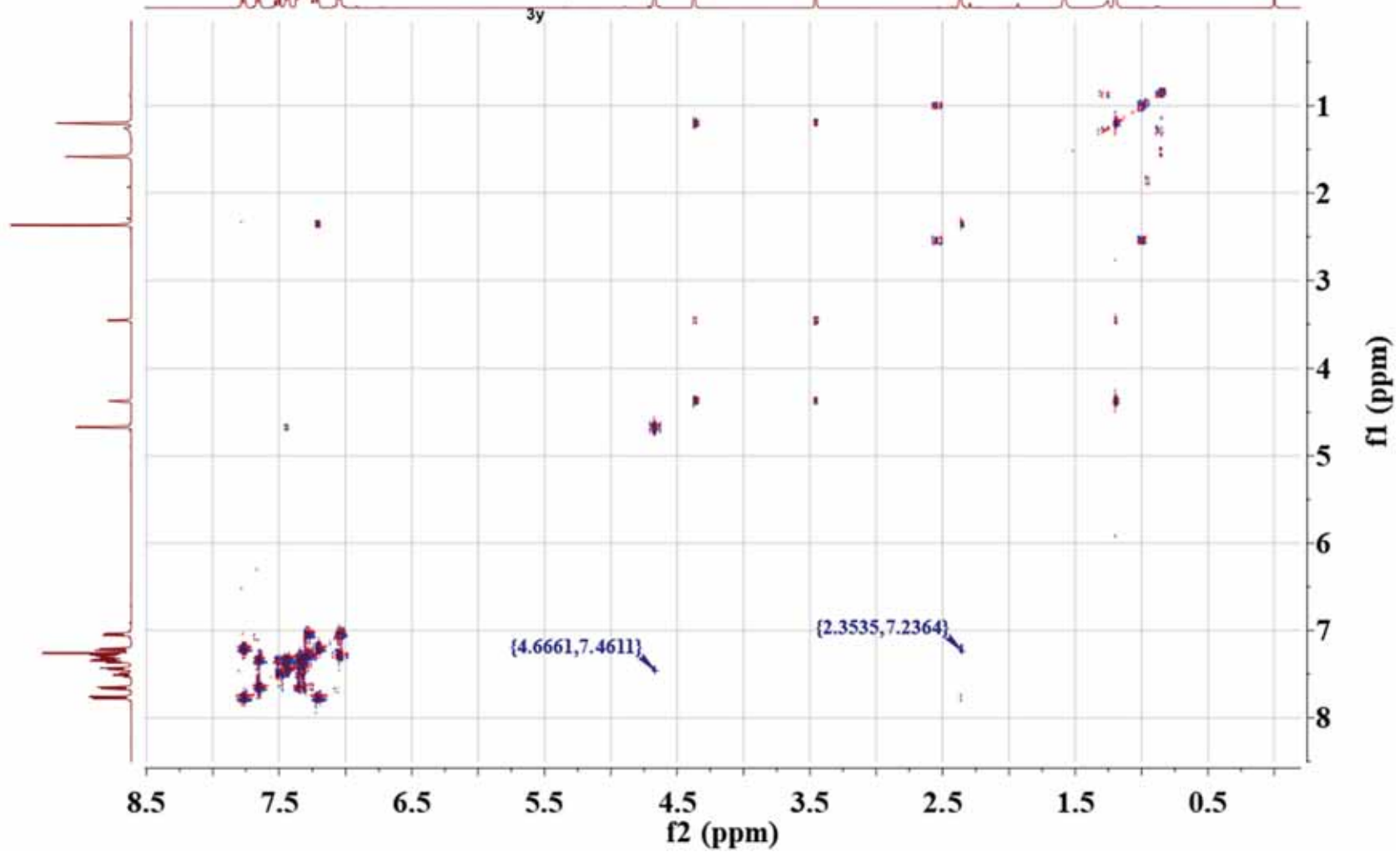
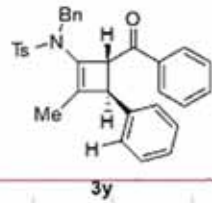


Title WJ4-1  
Solvent CDCl3  
Experiment 2D-NOESY  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

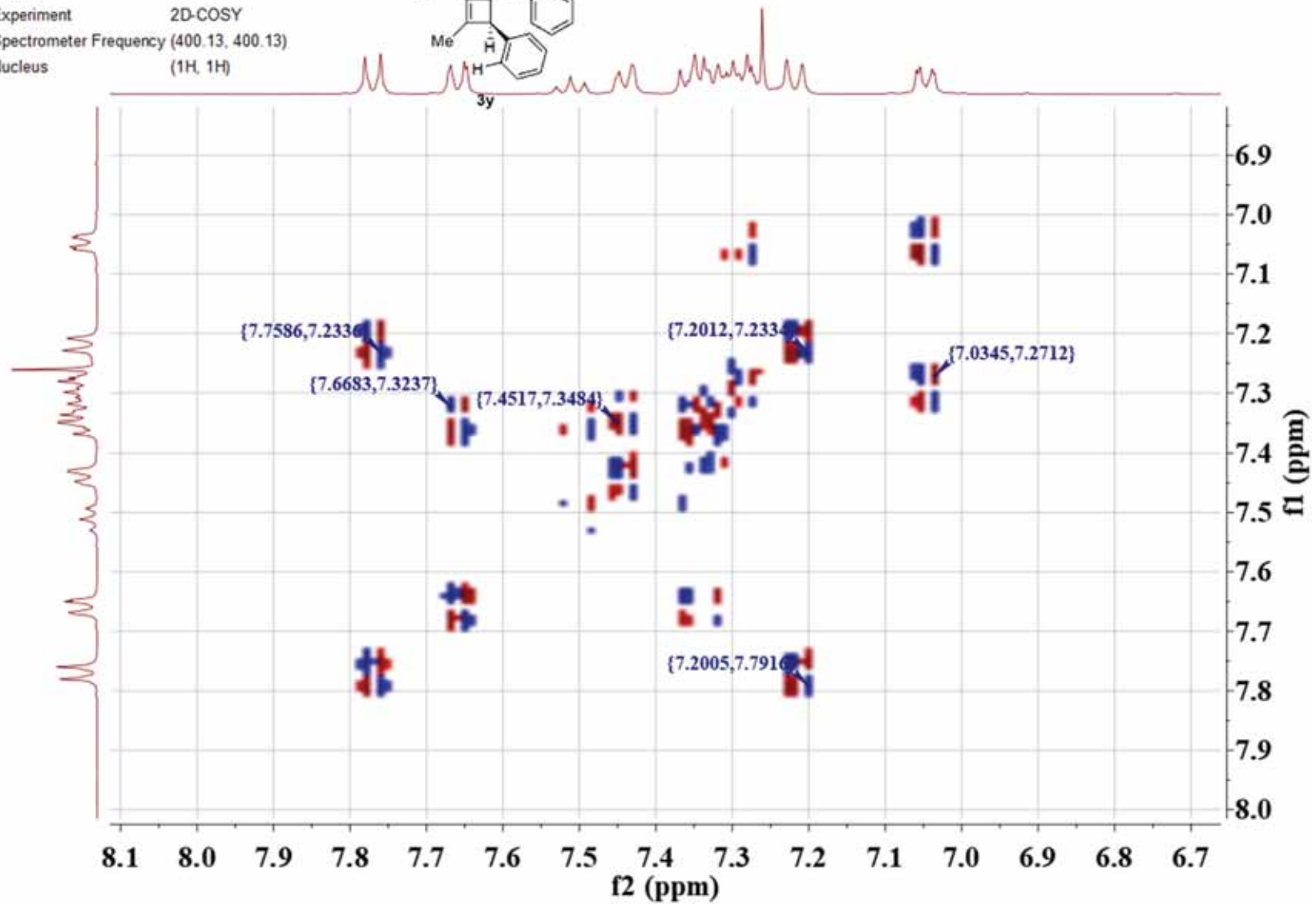
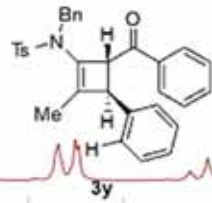


S118

Title WJ4-1  
Solvent CDCl3  
Experiment 2D-COSY  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

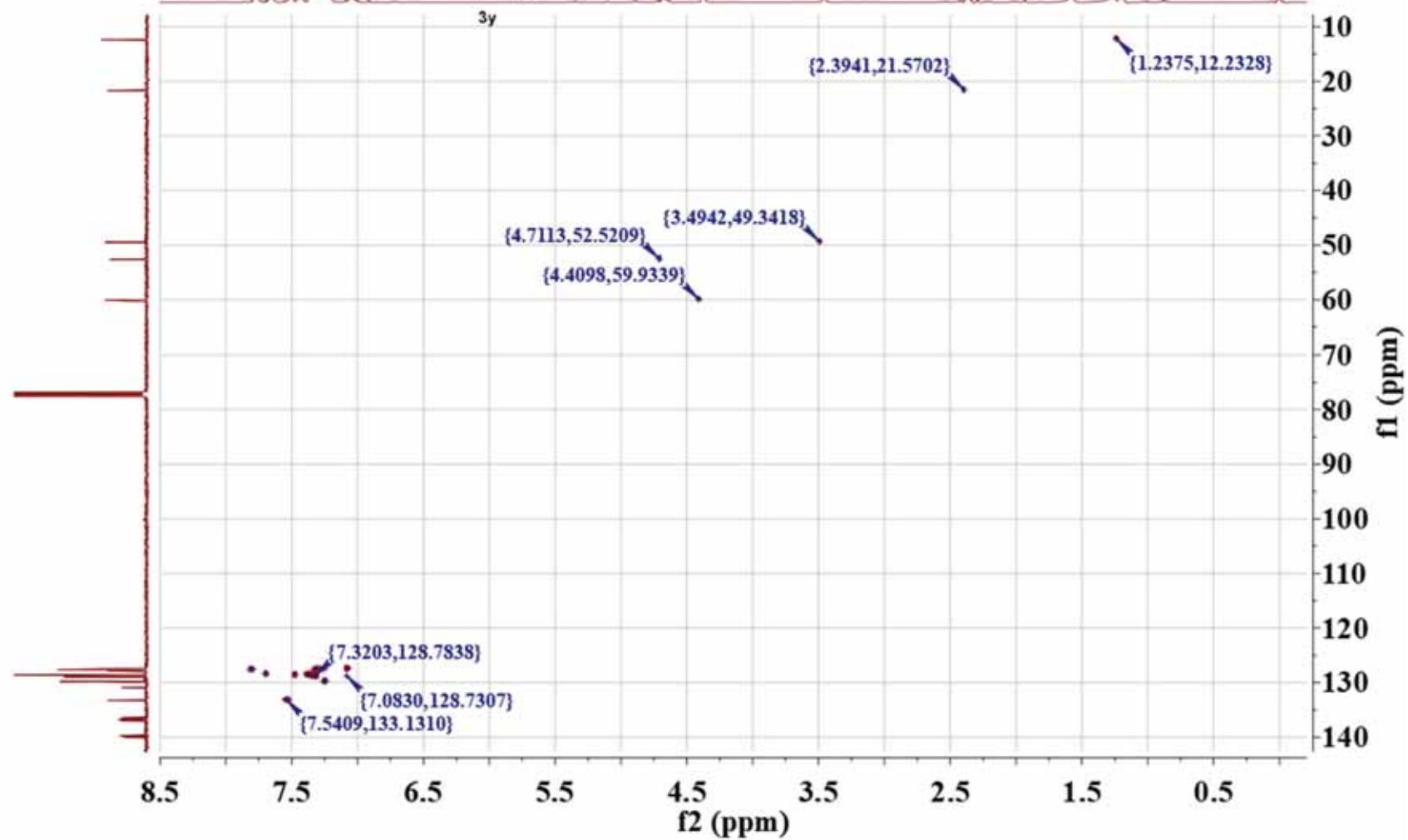
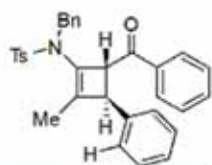


Title WJ4-1  
Solvent CDCl3  
Experiment 2D-COSY  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

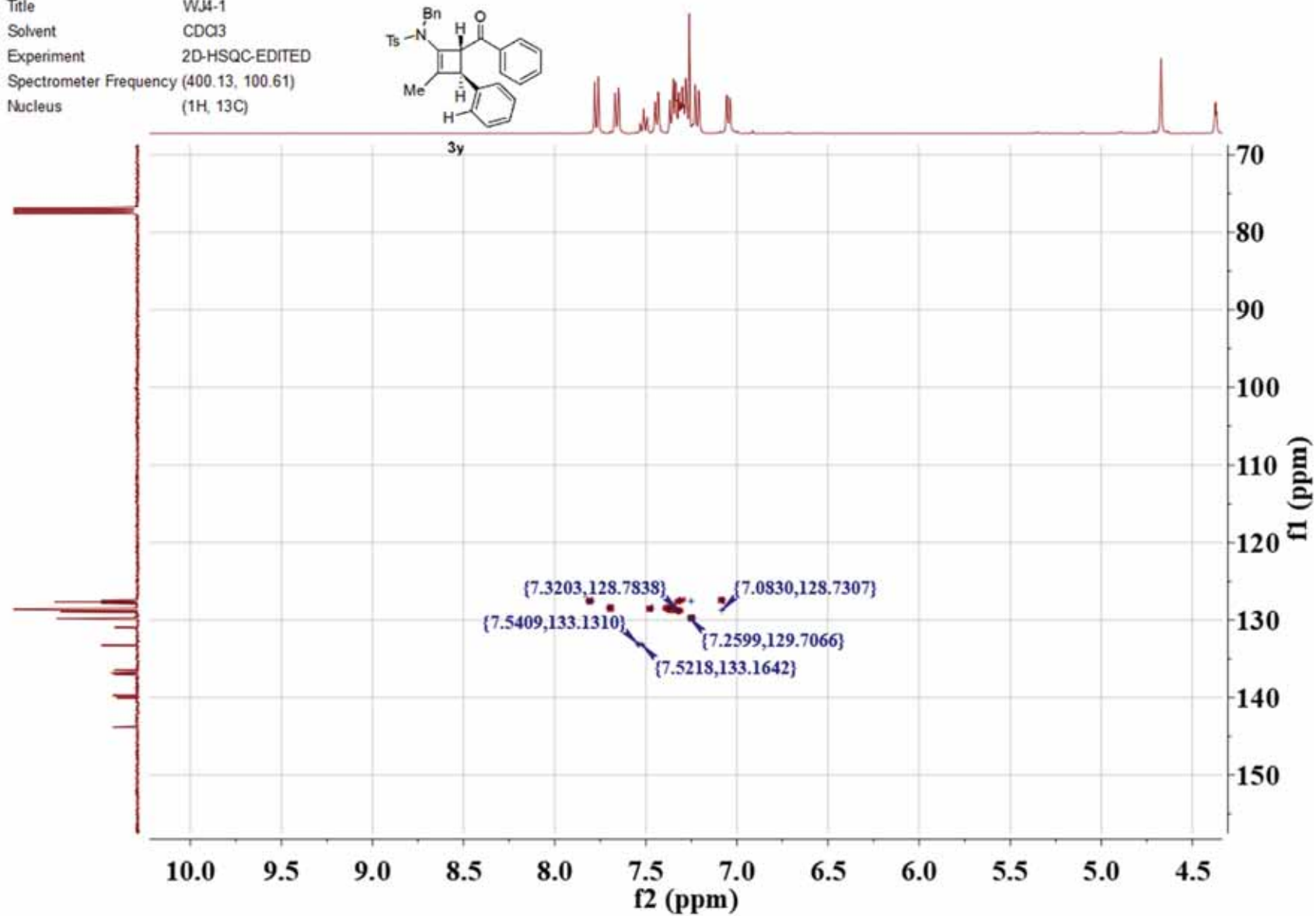
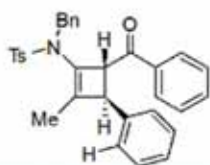




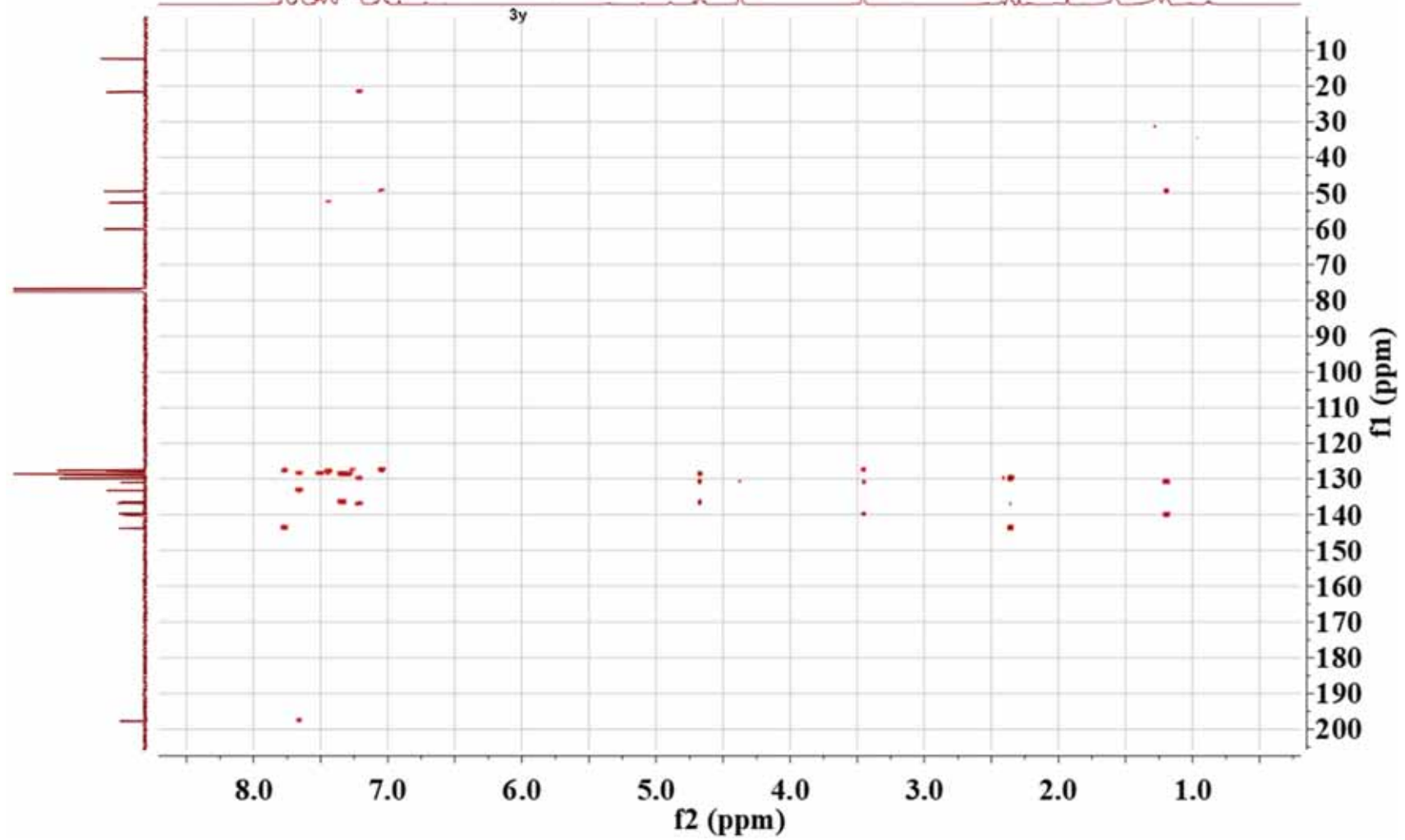
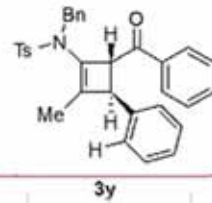
Title WJ4-1  
Solvent CDCl3  
Experiment 2D-HSQC-EDITED  
Spectrometer Frequency (400.13, 100.61)  
Nucleus (1H, 13C)



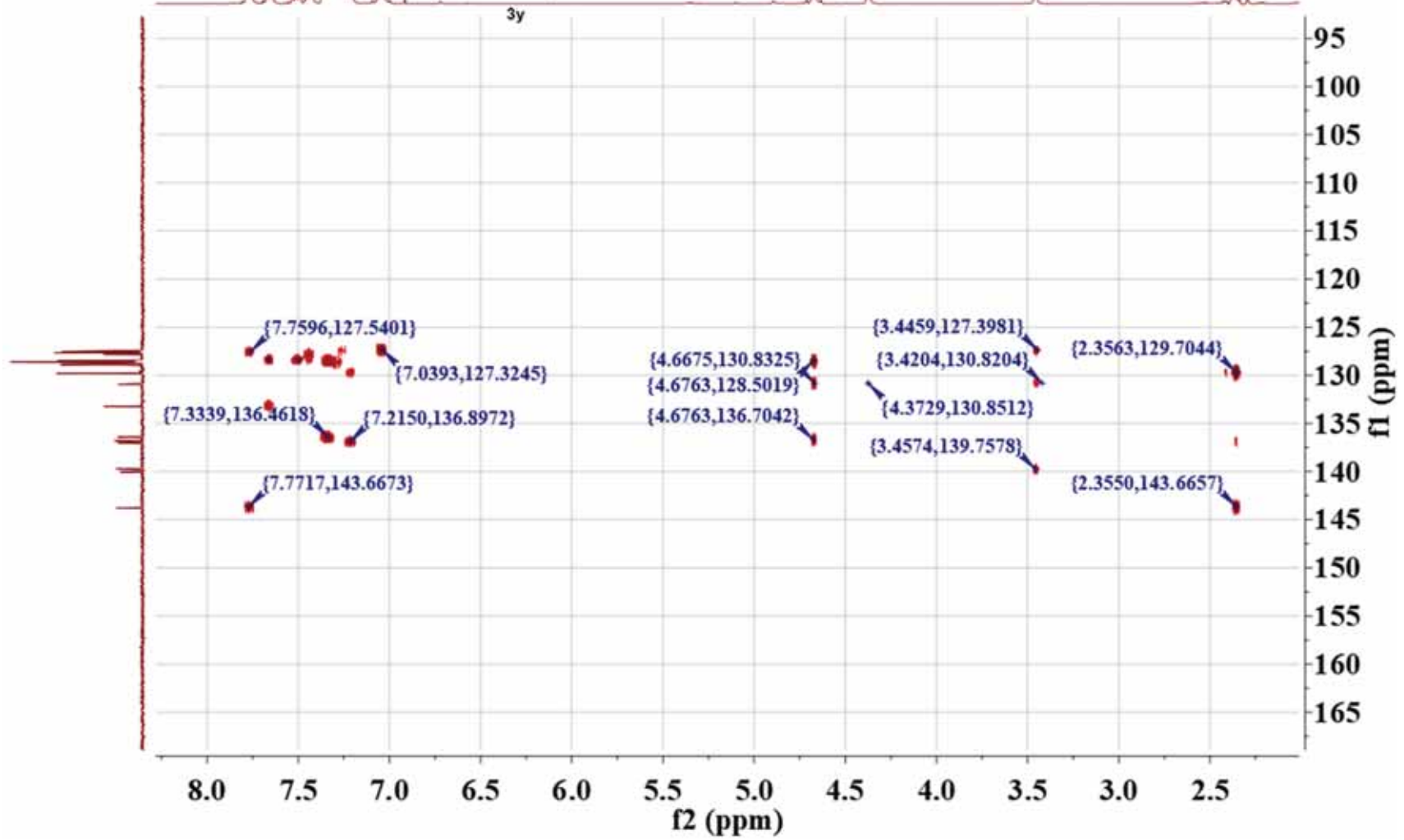
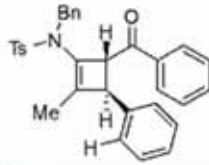
Title WJ4-1  
Solvent CDCl3  
Experiment 2D-HSQC-EDITED  
Spectrometer Frequency (400.13, 100.61)  
Nucleus (1H, 13C)



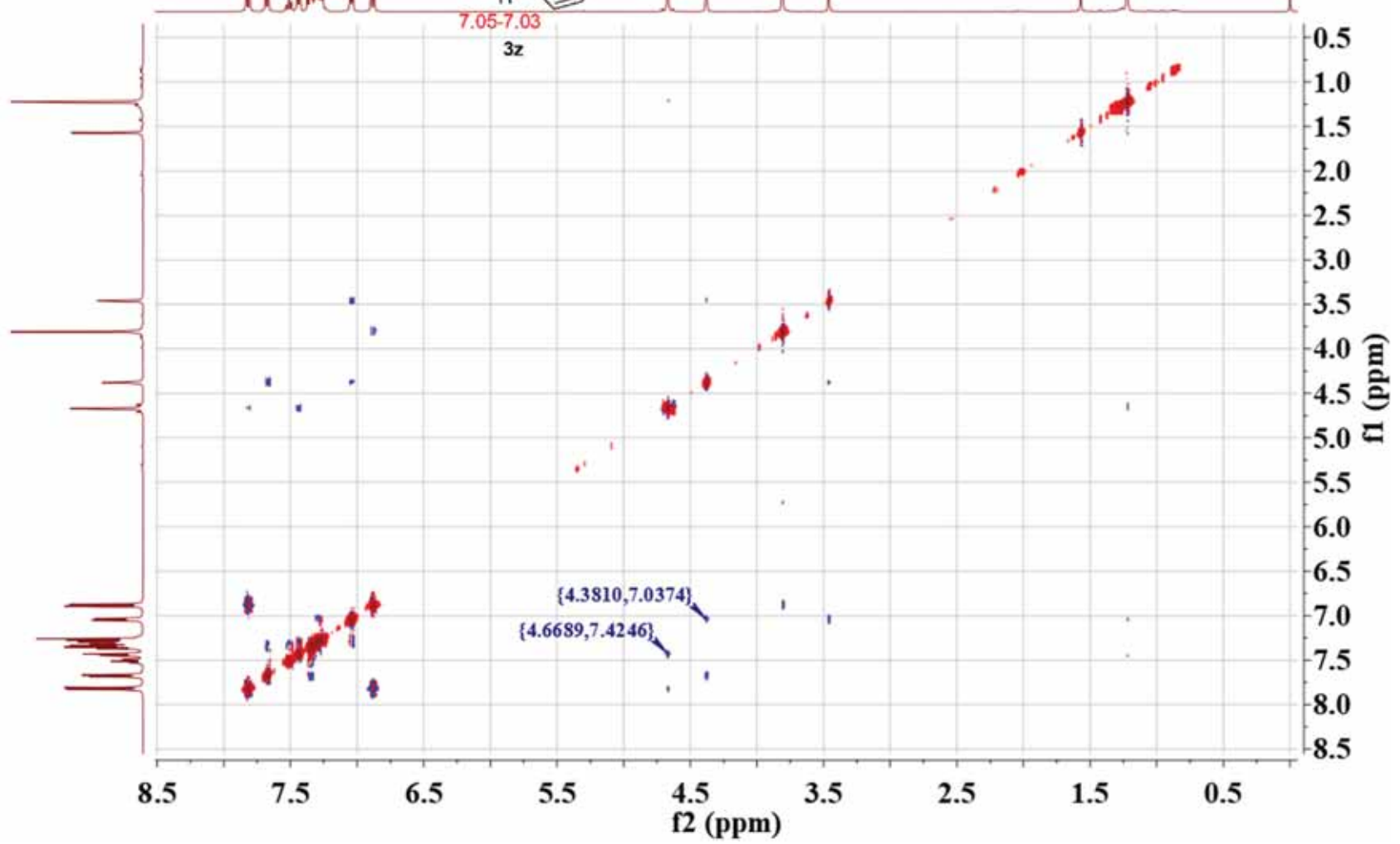
Title WJ4-1  
Solvent CDCl3  
Experiment 2D-HMBC  
Spectrometer Frequency (400.13, 100.61)  
Nucleus (1H, 13C)



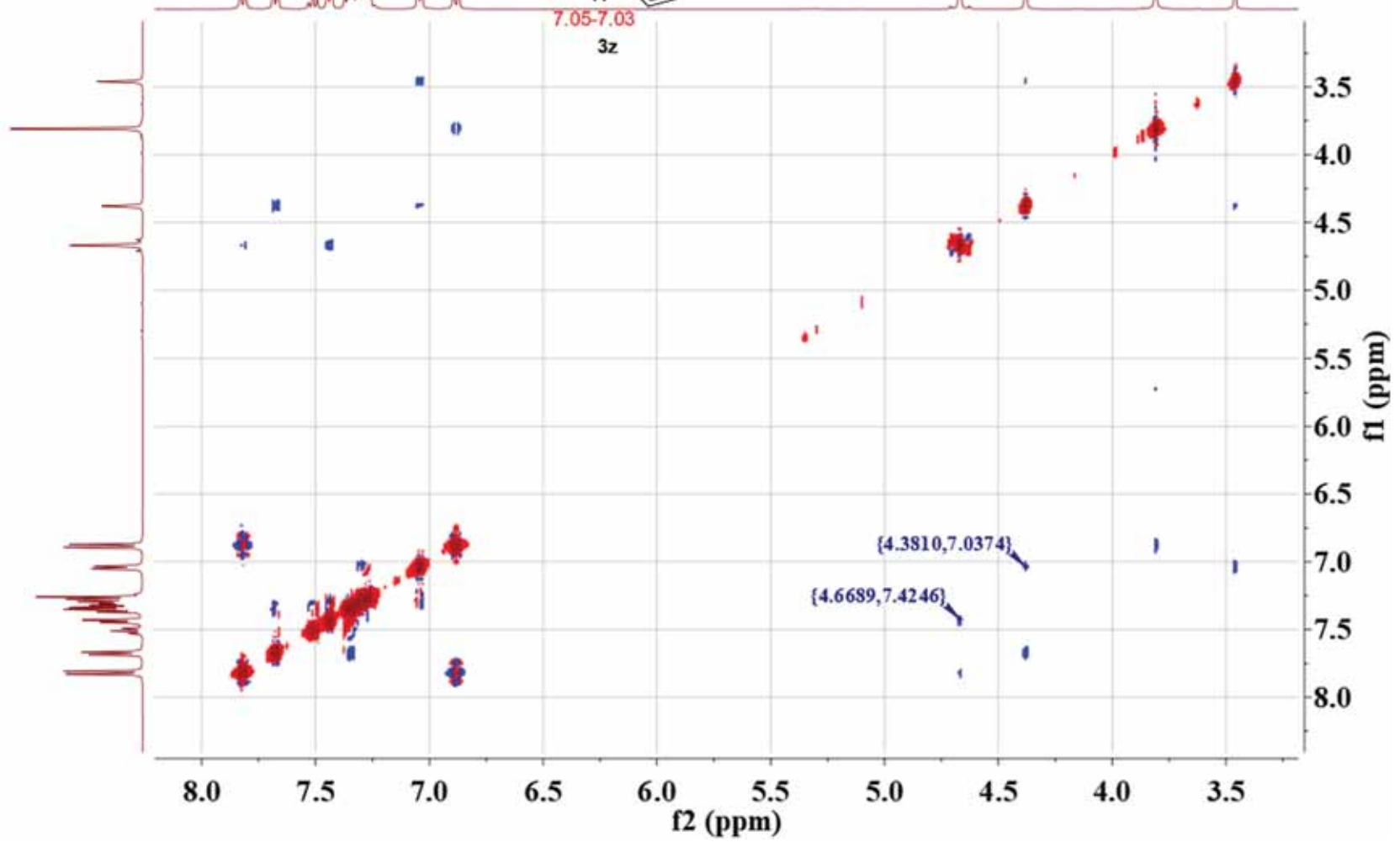
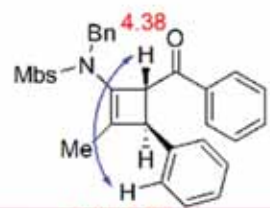
Title WJ4-1  
Solvent CDCl3  
Experiment 2D-HMBC  
Spectrometer Frequency (400 13 100.61  
Nucleus (1H, 13C)



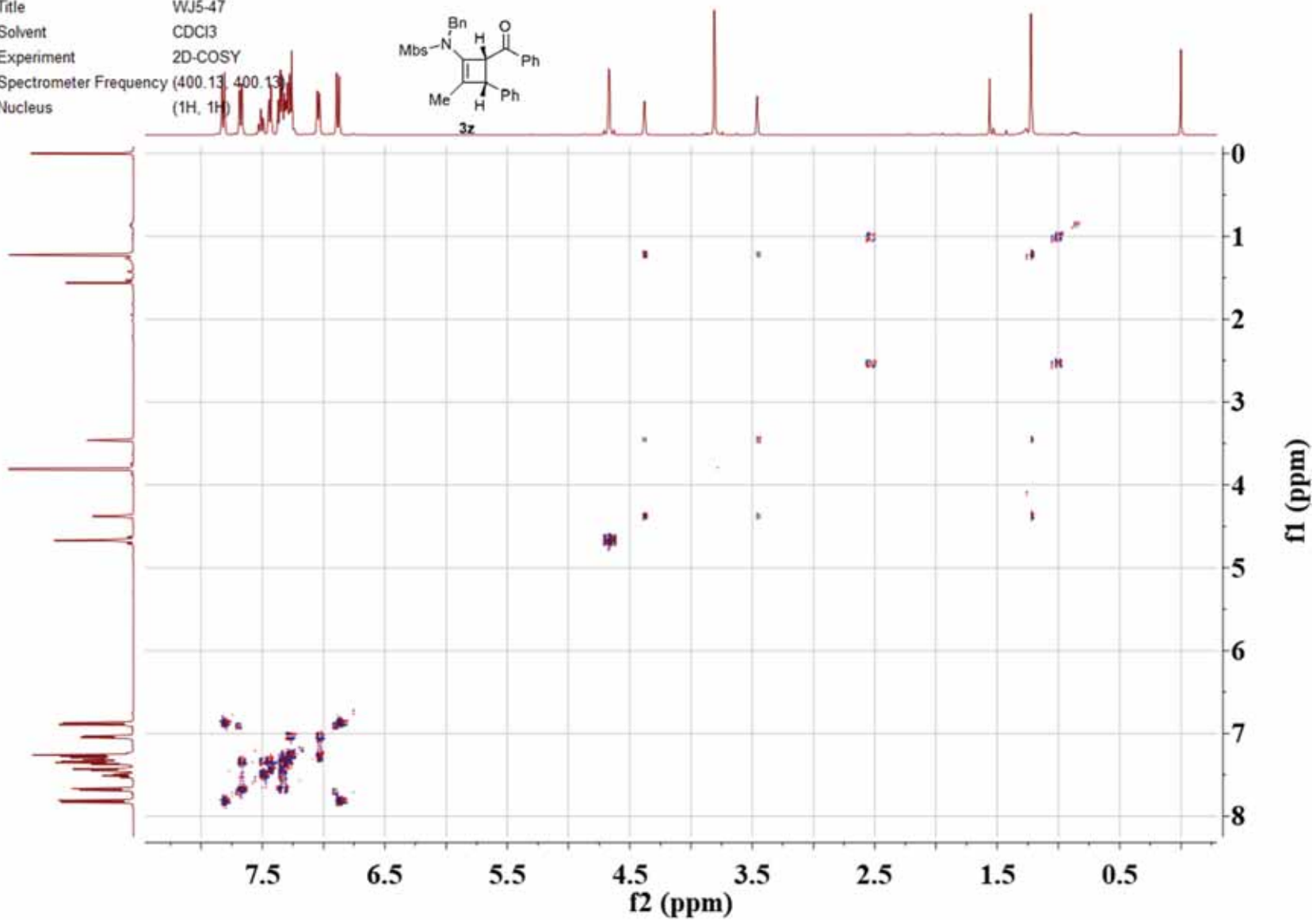
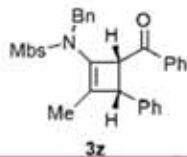
Title WJ5-47  
Solvent CDCl3  
Experiment 2D-NOESY  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



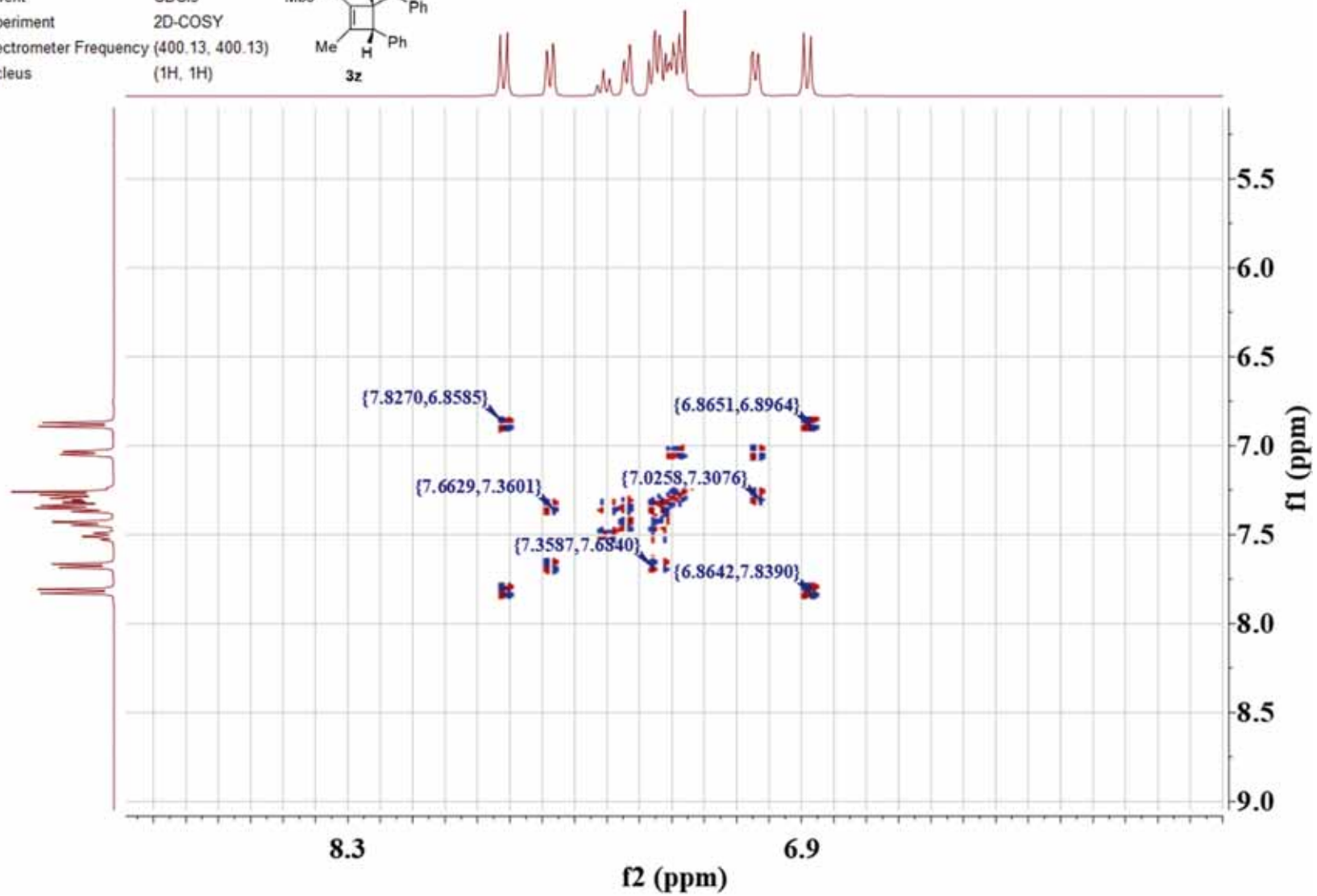
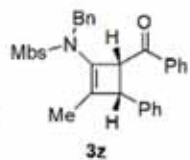
Title WJ5-47  
Solvent CDCl3  
Experiment 2D-NOESY  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)



Title WJ5-47  
Solvent CDCl3  
Experiment 2D-COSY  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

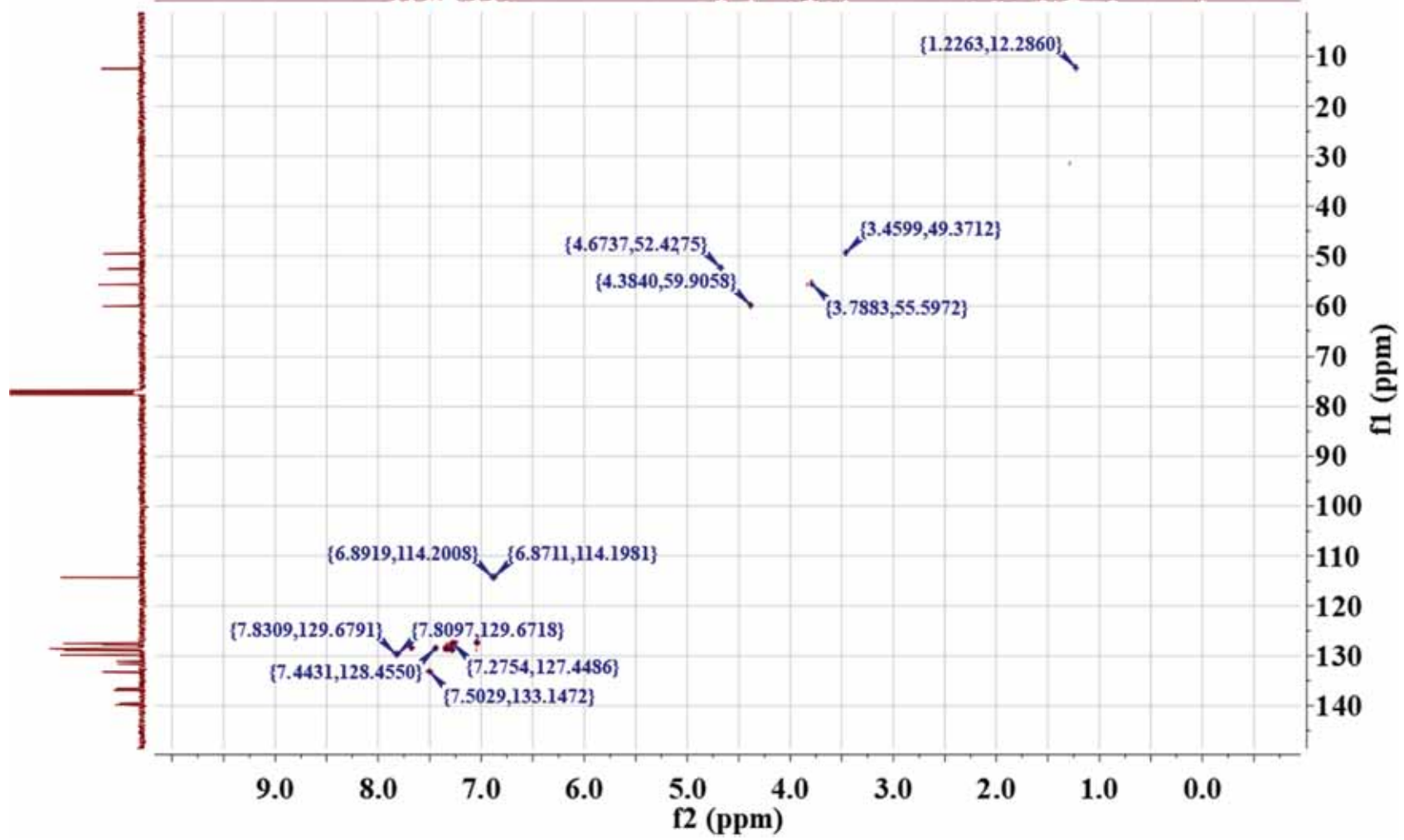
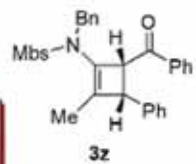


Title WJ5-47  
Solvent CDCl3  
Experiment 2D-COSY  
Spectrometer Frequency (400.13, 400.13)  
Nucleus (1H, 1H)

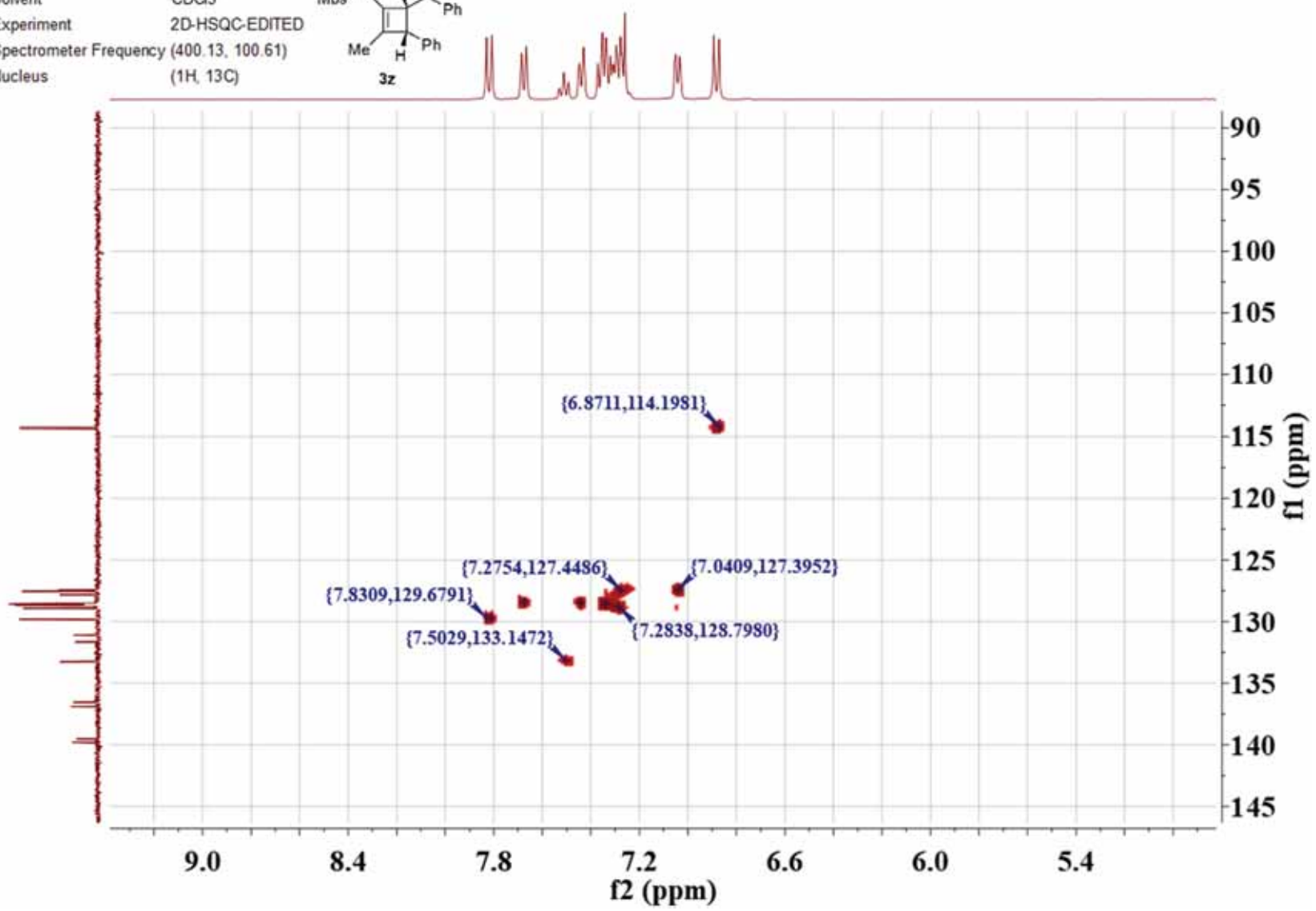
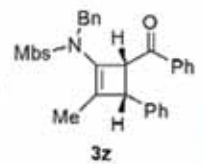




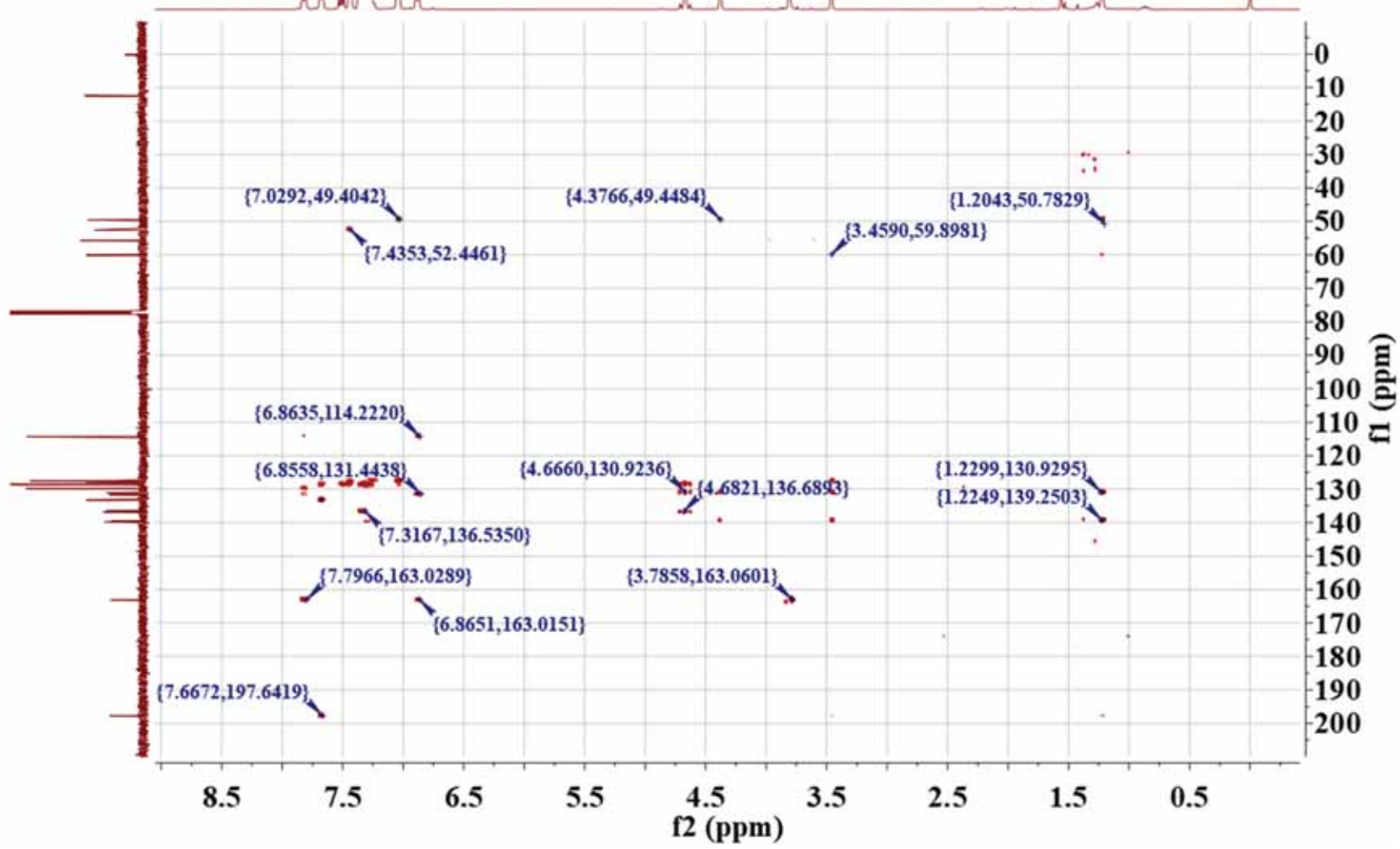
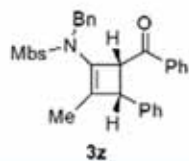
Title WJ5-47  
 Solvent CDCl3  
 Experiment 2D-HSQC-EDITED  
 Spectrometer Frequency (400.13, 100.61)  
 Nucleus (1H, 13C)



Title WJ5-47  
Solvent CDCl3  
Experiment 2D-HSQC-EDITED  
Spectrometer Frequency (400.13, 100.61)  
Nucleus (1H, 13C)



Title WJ5-47  
Solvent CDCl3  
Experiment 2D-HMBC  
Spectrometer Frequency (400.13, 100.61)  
Nucleus (1H, 13C)



Title WJ5-47  
Solvent CDCl3  
Experiment 2D-HMBC  
Spectrometer Frequency (400.13, 100.61)  
Nucleus (1H, 13C)

