

## Supporting Online Material for

# Rapid and efficient synthesis of formamidines with catalyst-free and solvent-free

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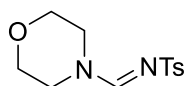
## 1. General Information

All melting points were determined on a Yanaco melting point apparatus and were uncorrected. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 5DX spectrometer. All spectra of  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) were recorded on a Bruker AVANCE NEO 400 MHz spectrometer in DMSO- $d_6$  or  $\text{CDCl}_3$  (otherwise as indicated) with TMS was used as an internal reference and  $J$  values are given in Hz. HRMS were obtained on a Bruker micrOTOF-Q II spectrometer. All amines were prepared by purchase, terminal ynones were prepared by purchase or literature methods<sup>1</sup> and sulfonyl azides prepared by literature methods.<sup>2</sup>

## References

- 1、 D. Chernyak, S. B. Gadamsetty, V. Gevorgyan. *Org Lett.* 2008, *10*, 2307–2310.
- 2、 D. Das and R. Samanta, *Adv. Synth. Catal.* 2018, *360*, 379–384.

## 2. Preparation and characterizations of compounds 4aa-4bl

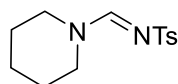


Chemical Formula: C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S

Molecular Weight: 268.33

**4-Methyl-N-(morpholinomethylene)benzenesulfonamide (4aa)**, To a solution of morpholine (1a, 88 mg, 1 mmol) and *p*-tosyl azide (2a, 354.9 mg, 1.8 mmol) was added, then slowly added but-3-yn-2-one (2a, 122.5 mg, 1.8 mmol), stirred at room temperature for corresponding time (detected by TLC or solidify). The residue was purified via flash chromatography (silica gel, 33% EtOAc in petroleum ether) to give of product **4aa** (254.9 mg, 95%) as a white solid, mp 173-175 °C (lit.<sup>1</sup> 179-180 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 3.74 (t, *J* = 4.8 Hz, 2H), 3.67 (s, 4H), 3.50 (t, *J* = 4.8 Hz, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.7, 142.7, 139.2, 129.4 (2C), 126.6 (2C), 66.8, 65.9, 50.3, 44.2, 21.5.

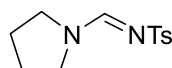
The products **4ab-4ax**, **4ba-4bl** were prepared by the similar procedure.



Chemical Formula: C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S

Molecular Weight: 266.36

**4-Methyl-N-(piperidin-1-ylmethylene)benzenesulfonamide (4ab)**. 218.4 mg (82%), yellow solid, mp 144-146 °C (lit.<sup>2</sup> 148-149 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.57 (t, *J* = 5.6 Hz, 2H), 3.38 (t, *J* = 4.8 Hz, 2H), 2.37 (s, 3H), 1.75-1.56 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.3, 142.4, 139.7, 129.3 (2C), 126.5 (2C), 51.9, 44.7, 26.5, 24.9, 24.0, 21.5.

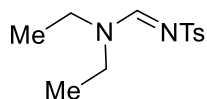


Chemical Formula: C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S

Molecular Weight: 252.33

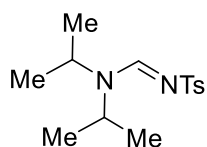
**4-Methyl-N-(pyrrolidin-1-ylmethylene)benzenesulfonamide (4ac)**. 189.2 mg (75%), white solid, mp 143-145 °C (lit.<sup>1</sup> 142-143 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ

8.30 (s, 1H), 7.76 (d,  $J = 8.4$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 3.56 (t,  $J = 6.6$  Hz, 2H), 3.44 (t,  $J = 7.0$  Hz, 2H), 2.37 (s, 3H), 1.95-1.91 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 142.4, 139.7, 129.3 (2C), 126.6 (2C), 50.0, 46.5, 25.1, 24.4, 21.5.



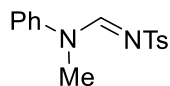
Chemical Formula:  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$   
Molecular Weight: 254.35

***N,N*-Diethyl-*N'*-tosylformimidamide (4ad).** 218.7 mg (86%), white solid, mp 73-75 °C (lit.<sup>1</sup> 76-77 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (s, 1H), 7.74 (d,  $J = 8.4$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 3.48-3.42 (m, 2H), 3.38-3.33 (m, 2H), 2.38 (s, 3H), 1.23 (t,  $J = 7.2$  Hz, 3H), 1.12 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 142.3, 139.8, 129.3 (2C), 126.4 (2C), 47.1, 41.0, 25.1, 14.5, 12.1.



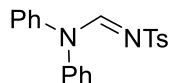
Chemical Formula:  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$   
Molecular Weight: 282.40

***N,N*-Diisopropyl-*N'*-tosylformimidamide (4ae).** 276.7 mg (98%), white solid, mp 102-104 °C (lit.<sup>3</sup> 98-100 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.18 (s, 1H), 7.63 (d,  $J = 8.4$  Hz, 2H), 7.33 (d,  $J = 8.4$  Hz, 2H), 4.26-4.15 (m, 1H), 3.91-3.81 (m, 1H), 2.35 (s, 3H), 1.23 (d,  $J = 6.8$  Hz, 6H), 1.17 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  156.7, 141.8, 140.3, 129.4 (2C), 125.7 (2C), 49.8, 47.3, 22.4 (2C), 20.9, 19.0 (2C).



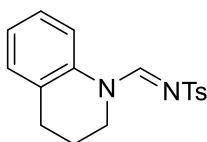
Chemical Formula:  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$   
Molecular Weight: 288.37

***N*-Methyl-*N*-phenyl-*N'*-tosylformimidamide (4af).** 173.0 mg (60%), white solid, mp 107-109 °C (lit.<sup>5</sup> 117-118 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (s, 1H), 7.81 (d,  $J = 8.4$  Hz, 2H), 7.42 (t,  $J = 7.8$  Hz, 2H), 7.33-7.27 (m, 3H), 7.19 (d,  $J = 7.6$  Hz, 2H), 3.43 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 143.3, 142.9, 138.9, 129.9 (2C), 129.5 (2C), 127.4, 126.8 (2C), 122.1 (2C), 36.1, 21.6.



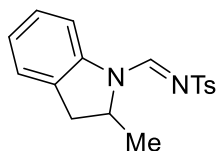
Chemical Formula: C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S  
Molecular Weight: 350.44

***N,N*-Diphenyl-*N'*-tosylformimidamide (4ag).** 89.0 mg (26%), white solid, mp 179-181 °C. IR (KBr)  $\nu$  3070, 2947, 1608, 1571, 1492, 1350, 1288, 1145 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.78 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.40-7.37 (m, 4H), 7.34 (d, *J* = 4.4 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.28 (d, *J* = 3.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.1, 143.5, 143.0, 139.9, 138.6, 129.9 (2C), 129.5 (2C), 129.4 (2C), 127.9, 127.6, 126.8 (2C), 126.7 (2C), 124.1 (2C), 21.6; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S, [M+H]<sup>+</sup> 351.1162; Found 351.1164.



Chemical Formula: C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S  
Molecular Weight: 314.40

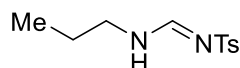
***N*-((3,4-Dihydroquinolin-1(2*H*)-yl)methylene)-4-methylbenzenesulfonamide (4ah).** 308.1 mg (98%), white solid, mp 158-160 °C. IR (KBr)  $\nu$  3070, 2912, 1652, 1500, 1346, 1303, 1149 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.86 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.19-7.12 (m, 3H), 3.87 (t, *J* = 6.2 Hz, 2H), 2.78 (t, *J* = 6.2 Hz, 2H), 2.40 (s, 3H), 1.99-1.93 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.1, 143.0, 138.9, 137.5, 129.9, 129.7, 129.5 (2C), 127.7, 126.8 (2C), 125.7, 117.3, 44.6, 26.9, 22.0, 21.6; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S, [M+H]<sup>+</sup> 315.1162; Found 315.1163.



Chemical Formula: C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S  
Molecular Weight: 314.40

**4-Methyl-*N*-(2-methylindolin-1-yl)methylenebenzenesulfonamide (4ai).** 304.9 mg (97%), white solid, mp 142-144 °C. IR (KBr)  $\nu$  3047, 2974, 1608, 1582, 1462, 1330,

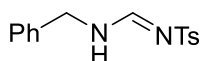
1292, 1145  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 1H), 7.81 (d,  $J = 8.4$  Hz, 2H), 7.28-7.22 (m, 4H), 7.18 (t,  $J = 6.4$  Hz, 1H), 7.12 (t,  $J = 7.2$  Hz, 1H), 4.79-4.73 (m, 1H), 3.47-3.36 (m, 1H), 2.73-2.69 (m, 1H), 2.39 (s, 3H), 1.32 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2, 142.8, 140.1, 139.0, 131.5, 129.5 (2C), 128.1, 126.7 (2C), 125.7, 118.9, 110.5, 56.2, 35.2, 21.6, 19.5; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$ ,  $[\text{M}+\text{H}]^+$  315.1162; Found 315.1162 .



Chemical Formula:  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$

Molecular Weight: 240.32

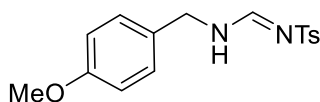
***N*-Propyl-*N'*-tosylformimidamide (4aj).** 156.2 mg (65%), yellow solid, mp 73-75  $^{\circ}\text{C}$ . IR (KBr)  $\nu$  3328, 3062, 2970, 1608, 1450, 1334, 1280, 1145  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 5.2$  Hz, 1H), 7.70 (t,  $J = 7.2$  Hz, 2H), 7.27-7.23 (m, 2H), 6.75 (s, 1H), 3.32-3.22 (m, 2H), 2.38 (s, 3H), 1.61-1.50 (m, 2H), 0.92-0.85 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0, 142.6, 139.3, 129.4 (2C), 126.4 (2C), 43.6, 21.8, 21.5, 11.3; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{11}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ ,  $[\text{M}+\text{H}]^+$  241.1005; Found 241.1006.



Chemical Formula:  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$

Molecular Weight: 288.37

***N*-Benzyl-*N'*-tosylformimidamide (4ak).** 271.9 mg (94%), white solid (lit.<sup>4</sup> colorless oil), mp 148-150  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.25 (s, 1H), 8.20 (d,  $J = 4.8$  Hz, 1H), 7.62 (t,  $J = 9.2$  Hz, 2H), 7.38-7.29 (m, 4H), 7.26 (t,  $J = 7.2$  Hz, 3H), 4.42 (d,  $J = 5.6$  Hz, 2H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  157.8, 142.0, 139.9, 136.9, 129.3 (2C), 128.4 (2C), 127.6 (2C), 127.3, 125.9 (2C), 44.4, 20.9.

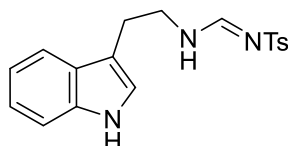


Chemical Formula:  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$

Molecular Weight: 318.39

***N*-(4-Methoxybenzyl)-*N'*-tosylformimidamide (4al).** 264.2 mg (83%), white solid, mp 135-137  $^{\circ}\text{C}$ . IR (KBr)  $\nu$  3340, 3178, 2947, 1658, 1612, 1512, 1438, 1338, 1292, 1246  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.17 (s, 1H), 8.15 (s, 1H), 7.61 (d,  $J =$

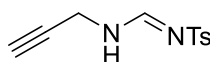
8.0 Hz, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 7.19 (t,  $J = 7.4$  Hz, 2H), 6.86 (d,  $J = 8.4$  Hz, 2H), 4.33 (s, 2H), 3.72 (d,  $J = 4.4$  Hz, 3H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  158.6, 157.4, 142.0, 139.9, 129.4 (2C), 129.1 (2C), 128.8, 125.9 (2C), 113.8 (2C), 55.1, 43.8, 20.9; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_3\text{S}$ ,  $[\text{M}+\text{H}]^+$  319.1111; Found 319.1113.



Chemical Formula:  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$

Molecular Weight: 341.43

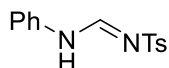
***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N'*-tosylformimidamide (4am).** 252.6 mg (74%), white solid, mp 169-171 °C. IR (KBr)  $\nu$  3445, 3047, 1666, 1438, 1338, 1276, 1145  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.84 (s, 1H), 8.86 (d,  $J = 4.8$  Hz, 1H), 8.09 (d,  $J = 4.8$  Hz, 1H), 7.63 (d,  $J = 8.0$  Hz, 2H), 7.45 (d,  $J = 8.0$  Hz, 1H), 7.38-7.28 (m, 3H), 7.13 (t,  $J = 9.0$  Hz, 1H), 7.06 (t,  $J = 7.6$  Hz, 1H), 6.99-6.93 (m, 1H), 3.52-3.47 (m, 2H), 2.88 (t,  $J = 7.2$  Hz, 2H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  157.7, 141.9, 140.1, 136.2, 129.4 (2C), 127.0, 125.8 (2C), 122.8, 121.0, 118.3, 118.2, 111.4, 110.9, 41.7, 23.7, 20.9; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_2\text{S}$ ,  $[\text{M}+\text{H}]^+$  342.1271; Found 342.1273.



Chemical Formula:  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$

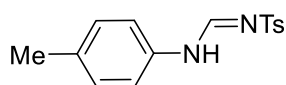
Molecular Weight: 236.29

***N*-(Prop-2-yn-1-yl)-*N'*-tosylformimidamide (4an).** 94.5 mg (40%), yellow solid, mp 168-170 °C. IR (KBr)  $\nu$  3310, 3059, 2924, 2121, 1616, 1419, 1330, 1284, 1149  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.20-9.15 (m, 1H), 8.12 (d,  $J = 4.4$  Hz, 1H), 7.65 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 4.02-4.0 (m, 2H), 3.23 (t,  $J = 2.4$  Hz, 1H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  157.6, 142.2, 139.6, 129.4 (2C), 126.0 (2C), 78.9, 74.5, 30.2, 20.9; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2\text{S}$ ,  $[\text{M}+\text{H}]^+$  237.0692; Found 237.0694.



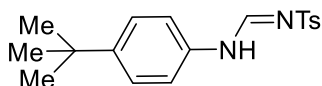
Chemical Formula: C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S  
Molecular Weight: 274.34

***N*-Phenyl-*N'*-tosylformimidamide (4ao).** 63.1 mg (23%), white solid, mp 198-200 °C (lit.<sup>6</sup> 197 °C). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.20 (s, 1H), 8.24 (s, 1H), 7.75-7.70 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.19-7.14 (m, 1H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 157.1, 142.7, 139.0, 137.6, 129.7 (2C), 129.1 (2C), 126.3 (2C), 125.3, 120.8 (2C), 21.0; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>S, [M+H]<sup>+</sup> 272.0849; Found 275.0851.



Chemical Formula: C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S  
Molecular Weight: 288.37

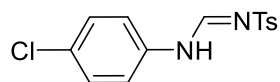
***N*-*p*-Tolyl-*N'*-tosylformimidamide (4ap).** 167.2 mg (58%), white solid, mp 183-185 °C. IR (KBr) ν 3439, 3182, 3039, 1650, 1593, 1462, 1338, 1300, 1149 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.70 (s, 1H), 8.21 (s, 1H), 7.75-7.70 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 3H), 2.36 (d, *J* = 2.8 Hz, 3H) 2.26 (d, *J* = 4.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 154.4, 142.5, 139.1, 134.9, 134.5, 129.6 (2C), 129.4 (2C), 126.2 (2C), 120.6, 117.9, 20.9, 20.5; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S, [M+H]<sup>+</sup> 289.1005; Found 289.1007.



Chemical Formula: C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S  
Molecular Weight: 330.45

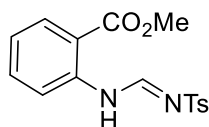
***N*-(4-(*tert*-Butyl)phenyl)-*N'*-tosylformimidamide (4aq).** 304.0 mg (92%), yellow solid, mp 157-159 °C. IR (KBr) ν 3300, 3136, 2962, 1600, 1462, 1408, 1369, 1284, 1145 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.18 (s, 1H), 8.70 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 1.30 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 149.5, 143.3, 138.3, 134.5, 129.7 (2C), 126.8 (2C), 125.9, 120.7, 118.5 (2C), 34.6, 31.3 (3C), 21.6; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>S, [M+H]<sup>+</sup> 331.1475; Found 331.1475.





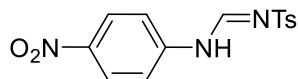
Chemical Formula: C<sub>14</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>2</sub>S  
Molecular Weight: 308.78

**N-(4-Chlorophenyl)-N'-tosylformimidamide (4ar).** 182.1 mg (59%), white solid, mp 190-192 °C. IR (KBr)  $\nu$  3170, 3066, 2927, 1650, 1585, 1496, 1458, 1342, 1296, 1149 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.05 (s, 1H), 8.28 (s, 1H), 7.73 (t, *J* = 9.2 Hz, 2H), 7.67 (d, *J* = 4.8 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.37-7.32 (m, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  154.7, 142.7, 138.8, 136.4, 129.6 (2C), 129.5, 129.0 (2C), 126.3 (2C), 122.3 (2C), 20.9; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S, [M+H]<sup>+</sup> 309.0459; Found 309.0461.



Chemical Formula: C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S  
Molecular Weight: 332.37

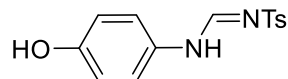
**Methyl-2-(N'-tosylformimidamido)benzoate (4as).** 130.0 mg (60%), yellow solid, mp 141-143 °C. IR (KBr)  $\nu$  3247, 3062, 2954, 1698, 1625, 1446, 1338, 1145 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.33 (s, 1H), 8.78 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.59-7.54 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 6.4 Hz, 2H), 7.21-7.14 (m, 1H), 3.92 (d, *J* = 10.4 Hz, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.6, 154.3, 143.5, 140.2, 137.9, 134.9, 132.0, 129.6 (2C), 127.1 (2C), 124.3, 116.5, 115.4, 52.8, 21.6; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>S, [M+H]<sup>+</sup> 333.0904; Found 333.0903.



Chemical Formula: C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>S  
Molecular Weight: 319.34

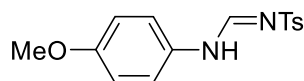
**N-(4-Nitrophenyl)-N'-tosylformimidamide (4at).** 104.0 mg (33%), yellow solid, mp 212-214 °C. IR (KBr)  $\nu$  3236, 3086, 1650, 1600, 1516, 1342, 1308, 1153 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.26 (s, 1H), 8.38 (s, 1H), 8.28-8.23 (m, 2H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.77 (t, *J* = 6.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz,

2H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  157.3, 144.2, 143.5, 142.9, 138.3, 129.5 (2C), 126.6 (2C), 125.4 (2C), 117.7 (2C), 21.0; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_4\text{S}$ ,  $[\text{M}+\text{H}]^+$  320.0700; Found 320.0702.



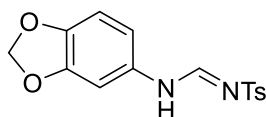
Chemical Formula:  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$   
Molecular Weight: 290.34

***N*-(4-Hydroxyphenyl)-*N'*-tosylformimidamide (4au).** 203.2 mg (70%), white solid, mp 239-241 °C. IR (KBr)  $\nu$  3456, 3178, 3043, 2889, 1658, 1600, 1516, 1415, 1342, 1280  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.58 (d,  $J = 4.8$  Hz, 1H), 9.50 (s, 1H), 8.14 (d,  $J = 5.2$  Hz, 1H), 7.72-7.67 (m, 2H), 7.42 (d,  $J = 8.8$  Hz, 1H), 7.35 (d,  $J = 8.0$  Hz, 2H), 7.09 (d,  $J = 8.8$  Hz, 1H), 6.76-6.73 (m, 2H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  156.9, 154.8, 142.3, 139.4, 129.5 (2C), 129.1, 126.1 (2C), 122.3 (2C), 115.3 (2C), 20.9; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_3\text{S}$ ,  $[\text{M}+\text{H}]^+$  291.0798; Found 291.0801.



Chemical Formula:  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$   
Molecular Weight: 304.36

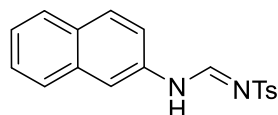
***N*-(4-Methoxyphenyl)-*N'*-tosylformimidamide (4av).** 273.9 mg (90%), white solid, mp 155-157 °C. IR (KBr)  $\nu$  3456, 3136, 2873, 1639, 1597, 1516, 1462, 1296, 1249, 1150  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.20 (s, 1H), 8.58 (s, 1H), 7.72 (d,  $J = 8.0$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 7.12 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 3.80 (s, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 155.1, 143.3, 138.4, 130.2, 129.7 (2C), 126.7 (2C), 120.8 (2C), 115.1 (2C), 55.7, 21.6; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ ,  $[\text{M}+\text{H}]^+$  305.0955; Found 305.0957.



Chemical Formula:  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$   
Molecular Weight: 318.35

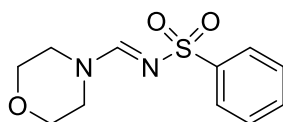
***N*-(Benzo[*d*][1,3]dioxol-5-yl)-*N'*-tosylformimidamide (4aw).** 238.7 mg (75%), white solid, mp 148-150 °C. IR (KBr)  $\nu$  3294, 3039, 2954, 1584, 1496, 1462, 1346,

1300, 1145, 1087, 921  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.94 (s, 1H), 8.56 (s, 1H), 7.78-7.72 (m, 2H), 7.27 (s, 1H), 7.25 (d,  $J = 3.6$  Hz, 1H), 6.78 (d,  $J = 4.0$  Hz, 1H), 6.72-6.68 (m, 1H), 6.63 (d,  $J = 2.0$  Hz, 1H), 5.99 (s, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 148.9, 146.3, 143.4, 138.2, 131.4, 129.7 (2C), 126.8 (2C), 112.6, 108.9, 102.0, 101.2, 21.6; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_4\text{S}$ ,  $[\text{M}+\text{H}]^+$  319.0747; Found 319.0749.



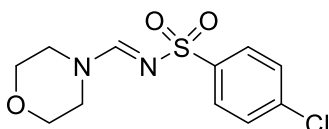
Chemical Formula:  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$   
Molecular Weight: 324.40

***N*-(Naphthalen-2-yl)-*N*'-tosylformimidamide (4ax).** 256.6 mg (60%), yellow solid, mp 132-134  $^{\circ}\text{C}$ . IR (KBr)  $\nu$  3271, 3059, 2920, 1616, 1396, 1280, 1145, 1087  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (s, 1H), 8.73 (s, 1H), 7.91-7.88 (m, 2H), 7.84-7.76 (m, 3H), 7.57-7.54 (m, 2H), 7.49-7.47 (m, 1H), 7.45-7.41 (m, 1H), 7.32 (d,  $J = 7.2$  Hz, 1H), 7.24 (s, 1H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 143.4, 138.1, 134.3, 133.0, 129.7 (2C), 128.7, 127.8, 127.4, 127.1, 126.9 (2C), 126.3, 125.6, 120.9, 118.5, 21.6; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$ ,  $[\text{M}+\text{H}]^+$  325.1005; Found 325.1007.



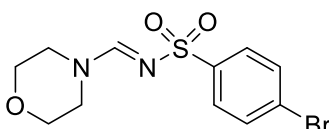
Chemical Formula:  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$   
Molecular Weight: 254.30

***N*-(Morpholinomethylene)benzenesulfonamide (4ba).** 244.1 mg (96%), white solid, mp 129-131  $^{\circ}\text{C}$  (lit.<sup>5</sup> 137-138  $^{\circ}\text{C}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (s, 1H), 7.87 (d,  $J = 7.2$  Hz, 2H), 7.53-7.43 (m, 3H), 3.73 (t,  $J = 4.8$  Hz, 2H), 3.66 (s, 4H), 3.49 (t,  $J = 4.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8, 142.1, 132.1, 128.8 (2C), 126.5 (2C), 66.8, 65.9, 50.4, 44.3.



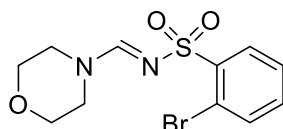
Chemical Formula: C<sub>11</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>3</sub>S  
Molecular Weight: 288.75

**4-Chloro-*N*-(morpholinomethylene)benzenesulfonamide (4bb).** 268.5 mg (93%), white solid, mp 152-154 °C (lit.<sup>1</sup> 159-160 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 3.74 (t, *J* = 5.0 Hz, 2H), 3.67 (s, 4H), 3.50 (t, *J* = 4.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.8, 140.6, 138.5, 129.1 (2C), 128.1 (2C), 66.8, 65.9, 50.5, 44.4.



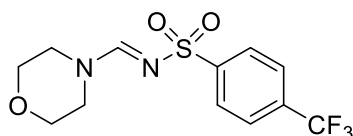
Chemical Formula: C<sub>11</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>3</sub>S  
Molecular Weight: 333.20

**4-Bromo-*N*-(morpholinomethylene)benzenesulfonamide (4bc).** 299.8 mg (90%), white solid, mp 158-160 °C (lit.<sup>1</sup> 166-167 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 3.74 (t, *J* = 4.8 Hz, 2H), 3.67 (s, 4H), 3.50 (t, *J* = 5.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.8, 141.2, 132.1 (2C), 128.3 (2C), 126.9, 66.8, 65.9, 50.5, 44.4.



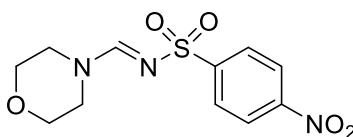
Chemical Formula: C<sub>11</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>3</sub>S  
Molecular Weight: 333.20

**2-Bromo-*N*-(morpholinomethylene)benzenesulfonamide (4bd).** 293.2 mg (88%), white solid, mp 138-140 °C. IR (KBr) ν 3086, 2974, 2931, 2850, 1616, 1446, 1346, 1296 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.76 (t, *J* = 5.0 Hz, 2H), 3.69 (s, 4H), 3.56 (t, *J* = 4.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.7, 140.4, 135.0, 133.3, 130.7, 127.8, 120.2, 67.0, 66.0, 50.6, 44.6; HRMS (ESI-TOF) (*m/z*). Calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S, [M+H]<sup>+</sup> 332.9903; Found 332.9905.



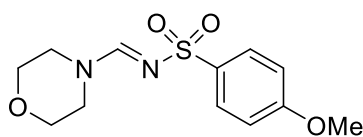
Chemical Formula: C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S  
Molecular Weight: 322.30

***N*-(Morpholinomethylene)-4-(trifluoromethyl)benzenesulfonamide (4be).** 293.2 mg (91%), white solid, mp 156-158 °C (lit.<sup>7</sup> 154-157 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (s, 1H), 8.0 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 3.75 (t, *J* = 4.8 Hz, 2H), 3.68 (s, 4H), 3.52 (t, *J* = 5.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.0, 145.6 (q, *J* = 1.1, 2C), 133.8 (q, *J* = 32.7, 1C), 127.2, 126.0 (q, *J* = 3.7, 2C), 123.4 (q, *J* = 271.2, 1C), 66.8, 65.9, 50.6, 44.5.



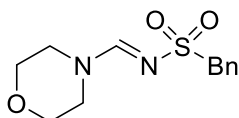
Chemical Formula: C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>S  
Molecular Weight: 299.30

***N*-(Morpholinomethylene)-4-nitrobenzenesulfonamide (4bf).** 269.3 mg (90%), white solid, mp 161-163 °C (lit.<sup>1</sup> 167-168 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.21 (s, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 3.77 (t, *J* = 5.0 Hz, 2H), 3.69 (s, 4H), 3.54 (t, *J* = 4.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.0, 149.7, 147.8, 127.9 (2C), 124.2 (2C), 66.8, 65.9, 50.7, 44.6.



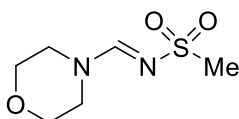
Chemical Formula: C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S  
Molecular Weight: 284.33

**4-Methoxy-*N*-(morpholinomethylene)benzenesulfonamide (4bg).** 261.5 mg (92%), white solid, mp 141-143 °C (lit.<sup>1</sup> 143-144 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.72 (t, *J* = 4.8 Hz, 2H), 3.65 (s, 4H), 3.47 (t, *J* = 4.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.5, 157.5, 133.9, 128.6 (2C), 114.0 (2C), 66.9, 65.9, 55.6, 50.3, 44.2.



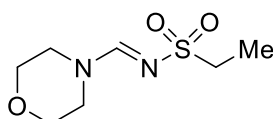
Chemical Formula:  $C_{12}H_{16}N_2O_3S$   
Molecular Weight: 268.33

***N*-(Morpholinomethylene)-1-phenylmethanesulfonamide (4bh)**. 254.9 mg (95%), white solid, mp 154-156 °C (lit.<sup>7</sup> 154-163 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (s, 1H), 7.33 (s, 5H), 4.24 (s, 2H), 3.63 (s, 4H), 3.57 (t, *J* = 4.8 Hz, 2H), 3.23 (t, *J* = 4.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.9, 131.0 (2C), 130.3, 128.5 (2C), 128.4, 66.9, 66.0, 59.7, 50.2, 44.2.



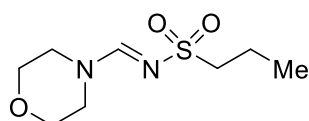
Chemical Formula:  $C_6H_{12}N_2O_3S$   
Molecular Weight: 192.23

***N*-(Morpholinomethylene)ethanesulfonamide (4bi)**. 180.6 mg (94%), white solid, mp 140-142 °C (lit.<sup>7</sup> 140-142 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (s, 1H), 3.75 (t, *J* = 4.8 Hz, 2H), 3.72-3.66 (m, 4H), 3.48 (t, *J* = 4.8 Hz, 2H), 2.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.8, 66.9, 65.9, 50.3, 44.2, 42.0.



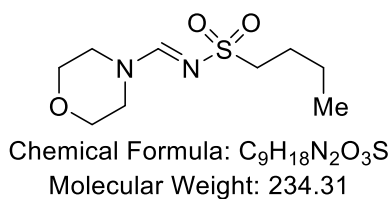
Chemical Formula:  $C_7H_{14}N_2O_3S$   
Molecular Weight: 206.26

***N*-(Morpholinomethylene)ethanesulfonamide (4bj)**. 198.0 mg (96%), yellow liquid (lit.<sup>1</sup> colorless liquid). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 1H), 3.73 (t, *J* = 4.8 Hz, 2H), 3.68 (s, 4H), 3.48 (t, *J* = 4.8 Hz, 2H), 3.03-2.97 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.2, 66.9, 65.9, 50.2, 48.1, 44.1, 8.3.



Chemical Formula:  $C_8H_{16}N_2O_3S$   
Molecular Weight: 220.29

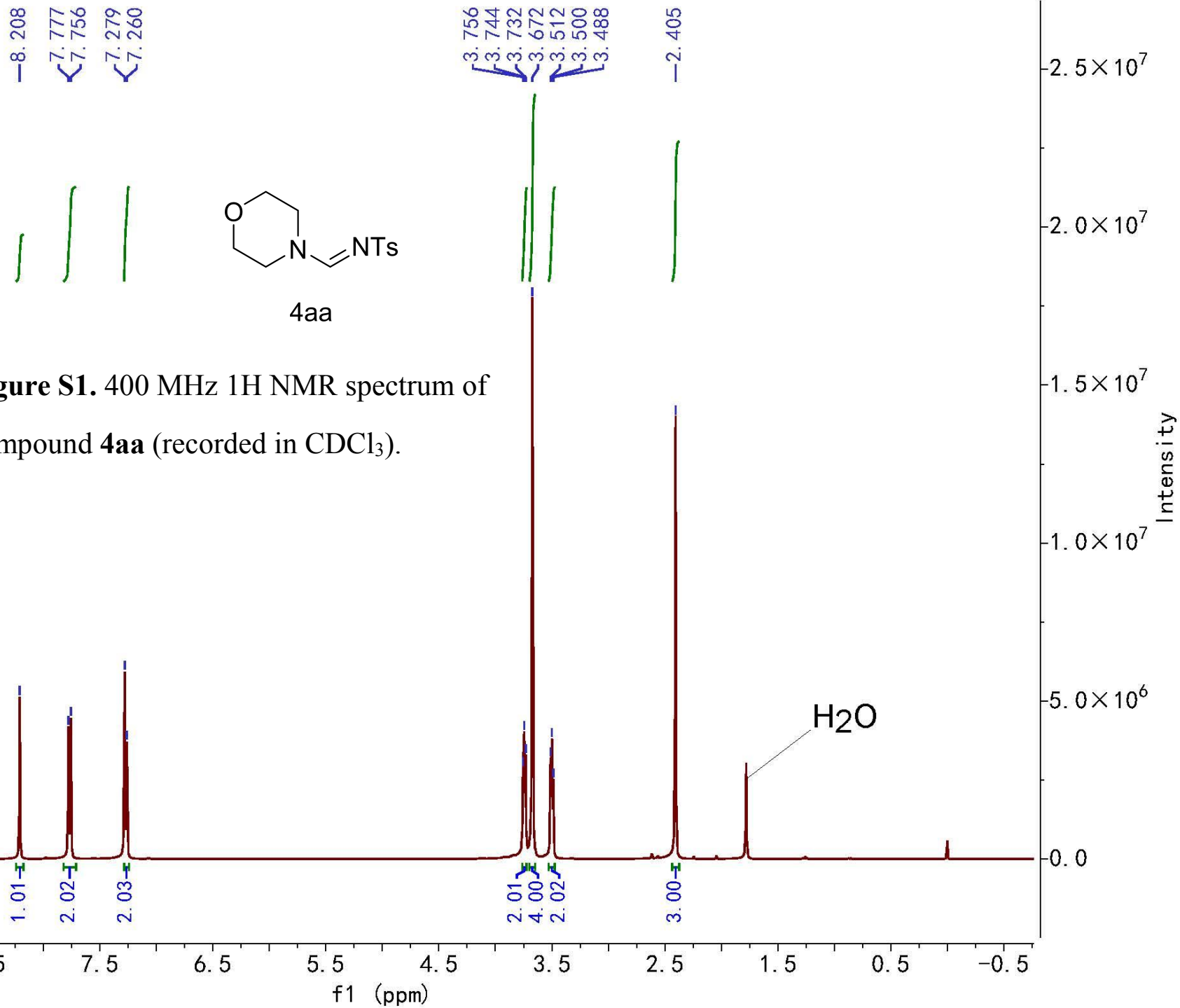
***N*-(Morpholinomethylene)propane-1-sulfonamide (4bk).** 202.6 mg (92%), white solid, mp 85-87 °C. IR (KBr)  $\nu$  3074, 2978, 2935, 2870, 1643, 1450, 1346, 1273  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 3.74 (t,  $J = 4.8$  Hz, 2H), 3.68 (s, 4H), 3.48 (t,  $J = 5.0$  Hz, 2H), 2.96 (t,  $J = 7.8$  Hz, 2H), 1.83-1.74 (m, 2H), 1.01 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 66.9, 66.0, 55.6, 50.3, 44.2, 17.4, 13.1; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_8\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ ,  $[\text{M}+\text{H}]^+$  221.0955; Found 221.0956.



***N*-(Morpholinomethylene)butane-1-sulfonamide (4bl).** 215.5 mg (92%), white solid, mp 105-107 °C. IR (KBr)  $\nu$  3078, 2966, 2935, 2866, 1616, 1450, 1346, 1269, 1130  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 3.73 (t,  $J = 4.8$  Hz, 2H), 3.68 (s, 4H), 3.48 (t,  $J = 4.8$  Hz, 2H), 2.98 (t,  $J = 8.0$  Hz, 2H), 1.77-1.71 (m, 2H), 1.46-1.37 (m, 2H), 0.91 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 66.9, 66.0, 53.6, 50.3, 44.1, 25.6, 21.6, 13.6; HRMS (ESI-TOF) ( $m/z$ ). Calcd for  $\text{C}_9\text{H}_{19}\text{N}_2\text{O}_3\text{S}$ ,  $[\text{M}+\text{H}]^+$  235.1111; Found 235.1112.

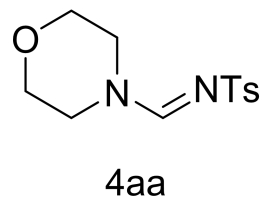
## References

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- 6、 A. Contini, E. Erba, P. Trimarco. *ARKIVOC*, **2008**, *12*, 136.
- 7、 Q. Gou, Z. Liu, T. Cao, X. Tan, W. Shi, M. Ran, F. Cheng, J. Qin. *J. Org. Chem.*, **2020**, *85*, 2092–2102.



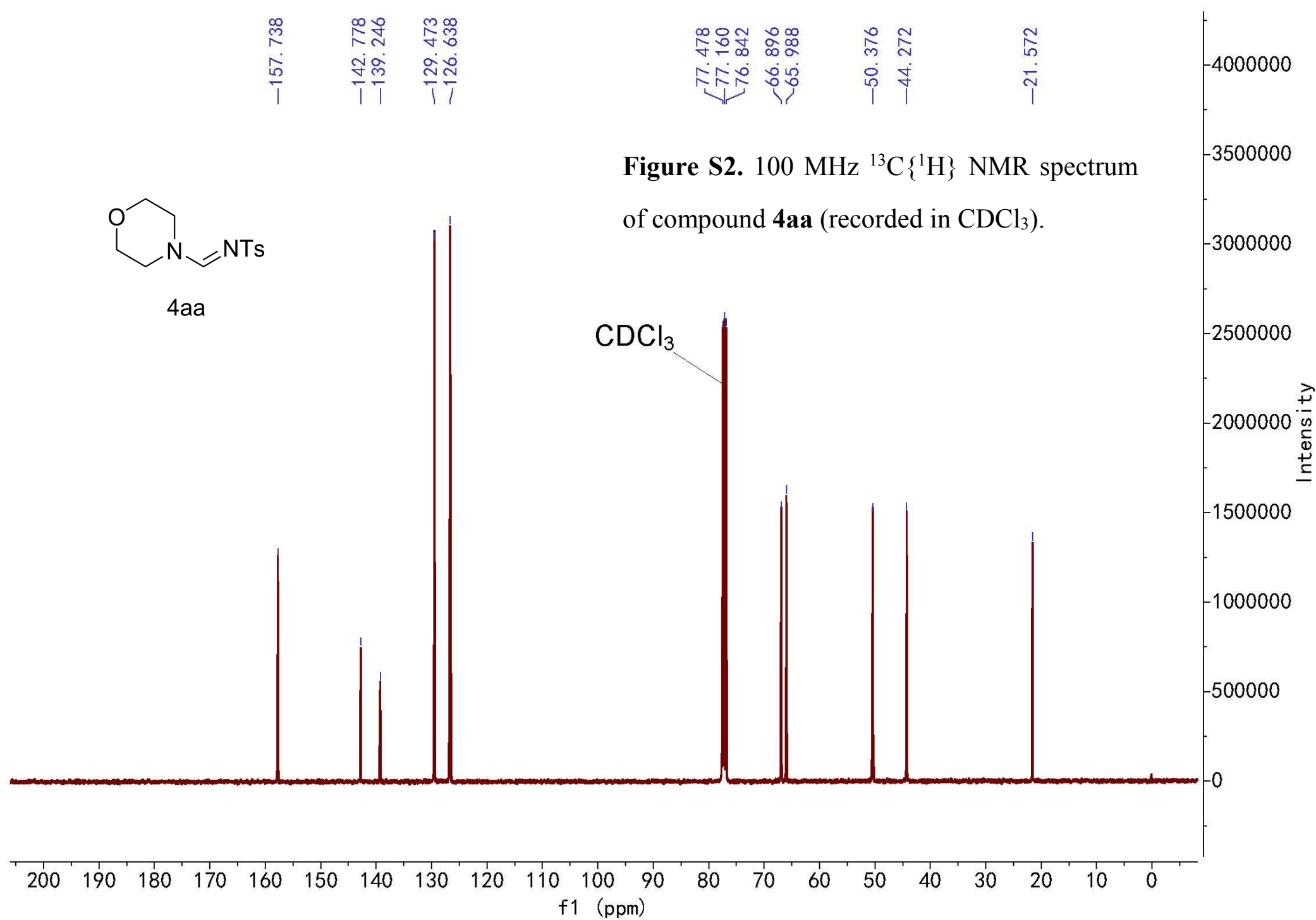
**Figure S1.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4aa** (recorded in  $\text{CDCl}_3$ ).

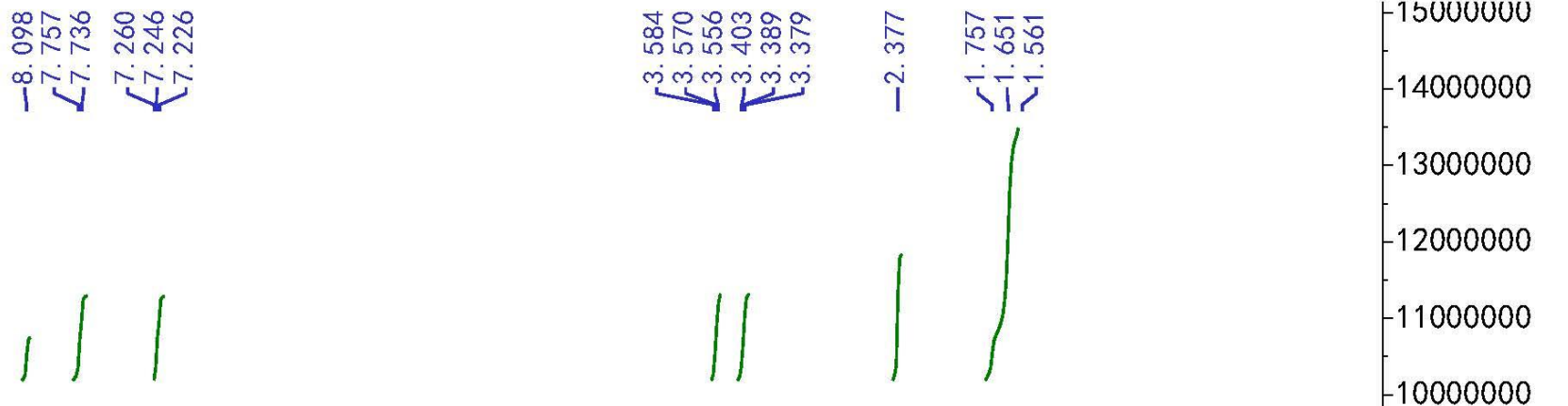




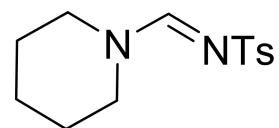
—157.738  
—142.778  
—139.246  
—129.473  
—126.638  
  
77.478  
77.160  
76.842  
66.896  
65.988  
—50.376  
—44.272  
—21.572

**Figure S2.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4aa** (recorded in  $\text{CDCl}_3$ ).

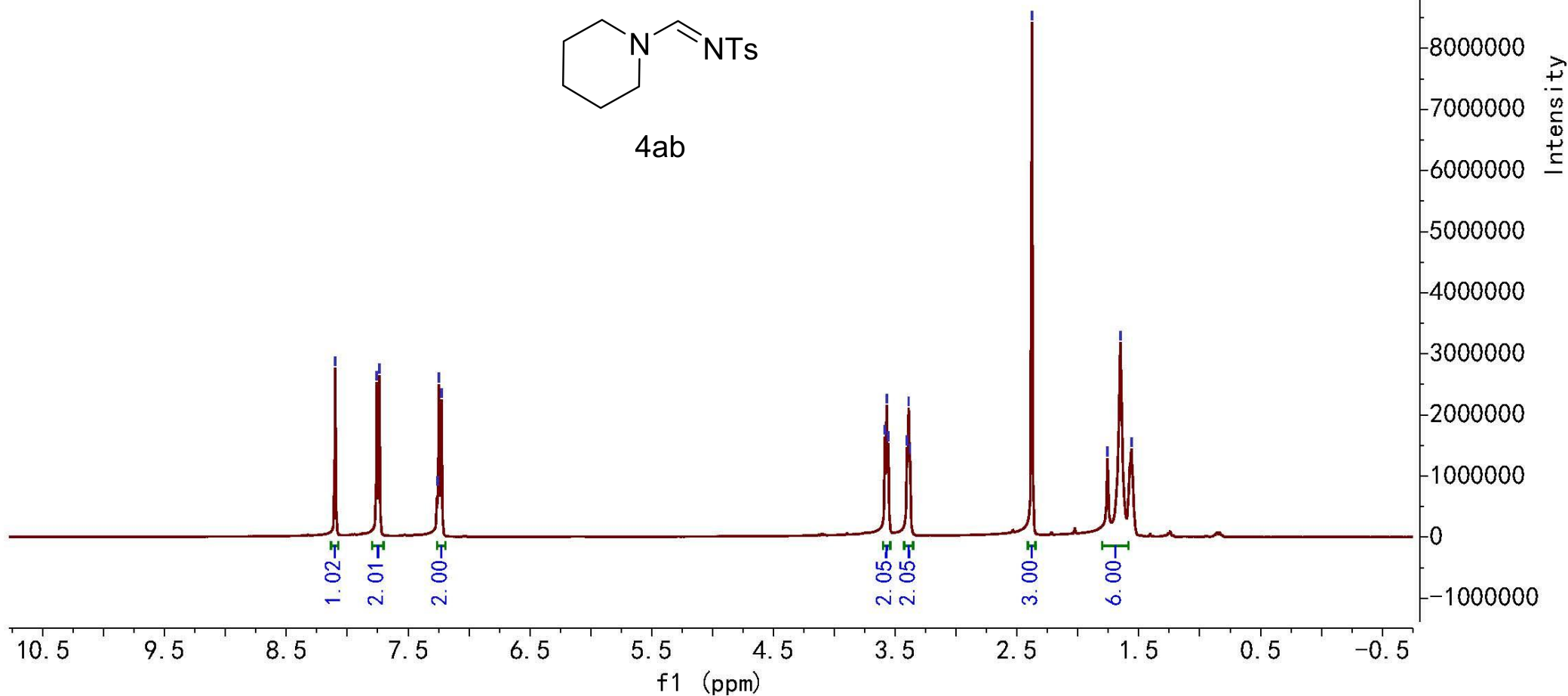




**Figure S3.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4ab** (recorded in  $\text{CDCl}_3$ ).

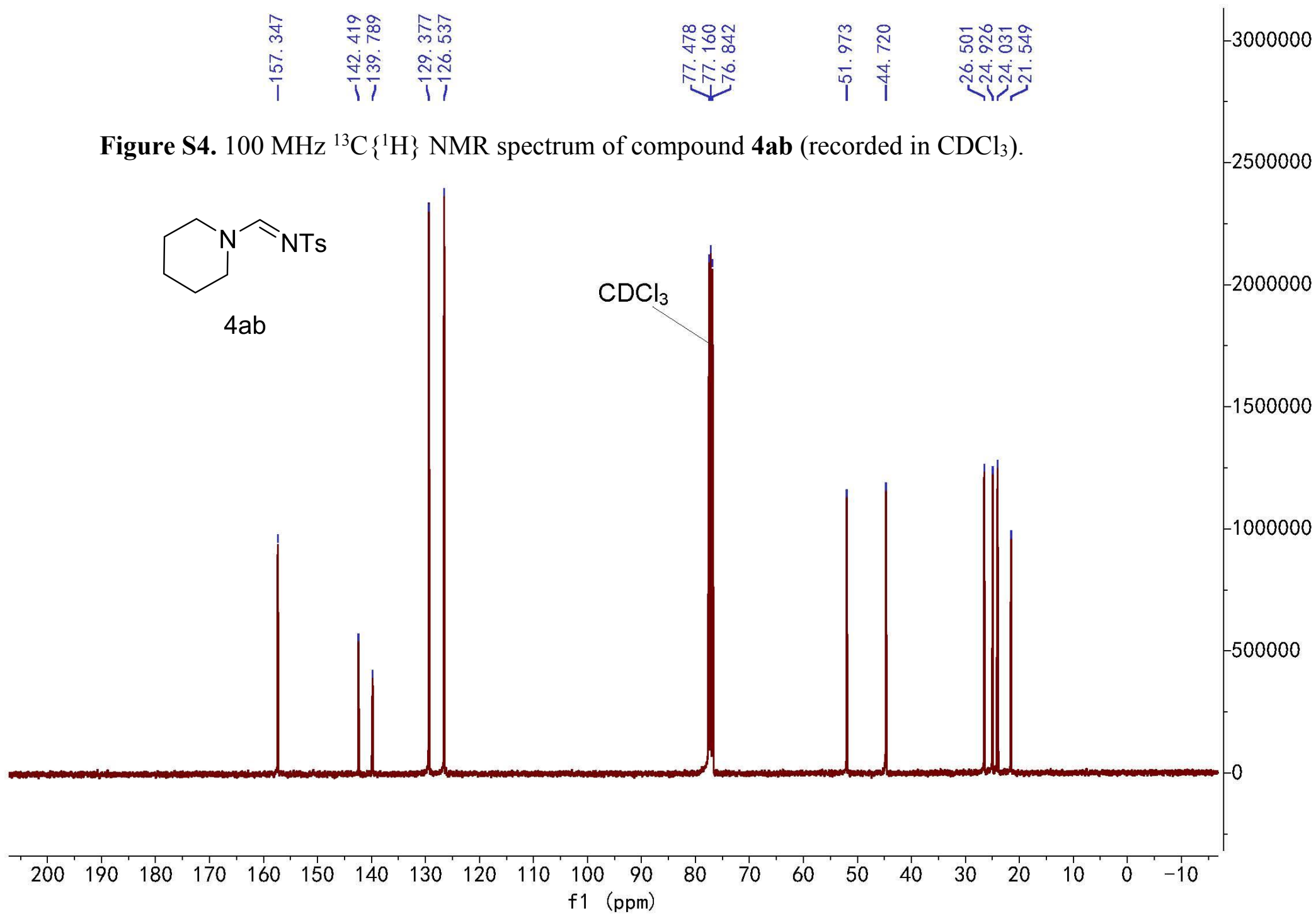
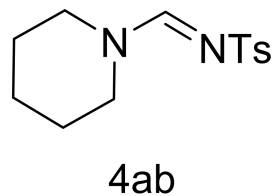


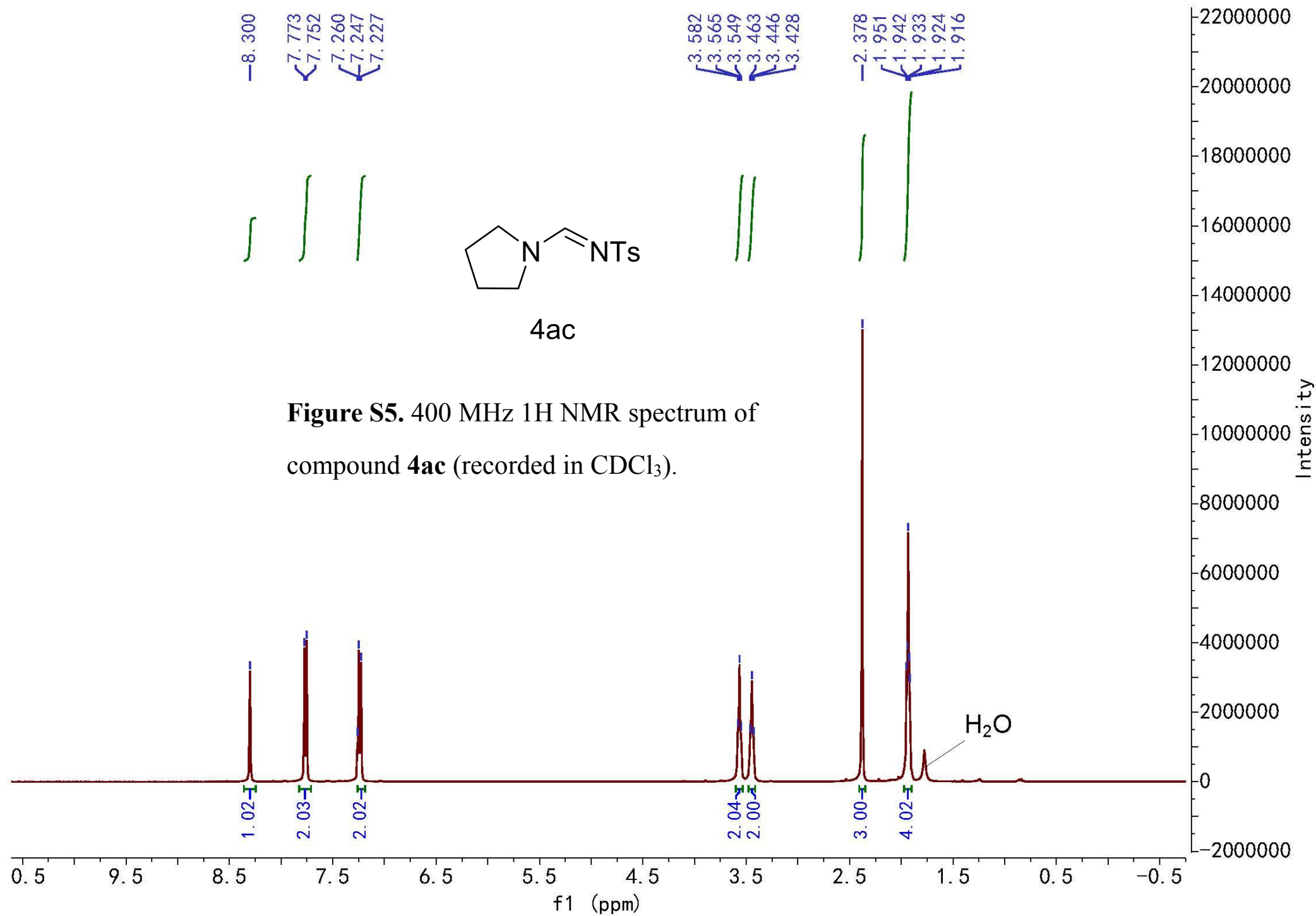
**4ab**

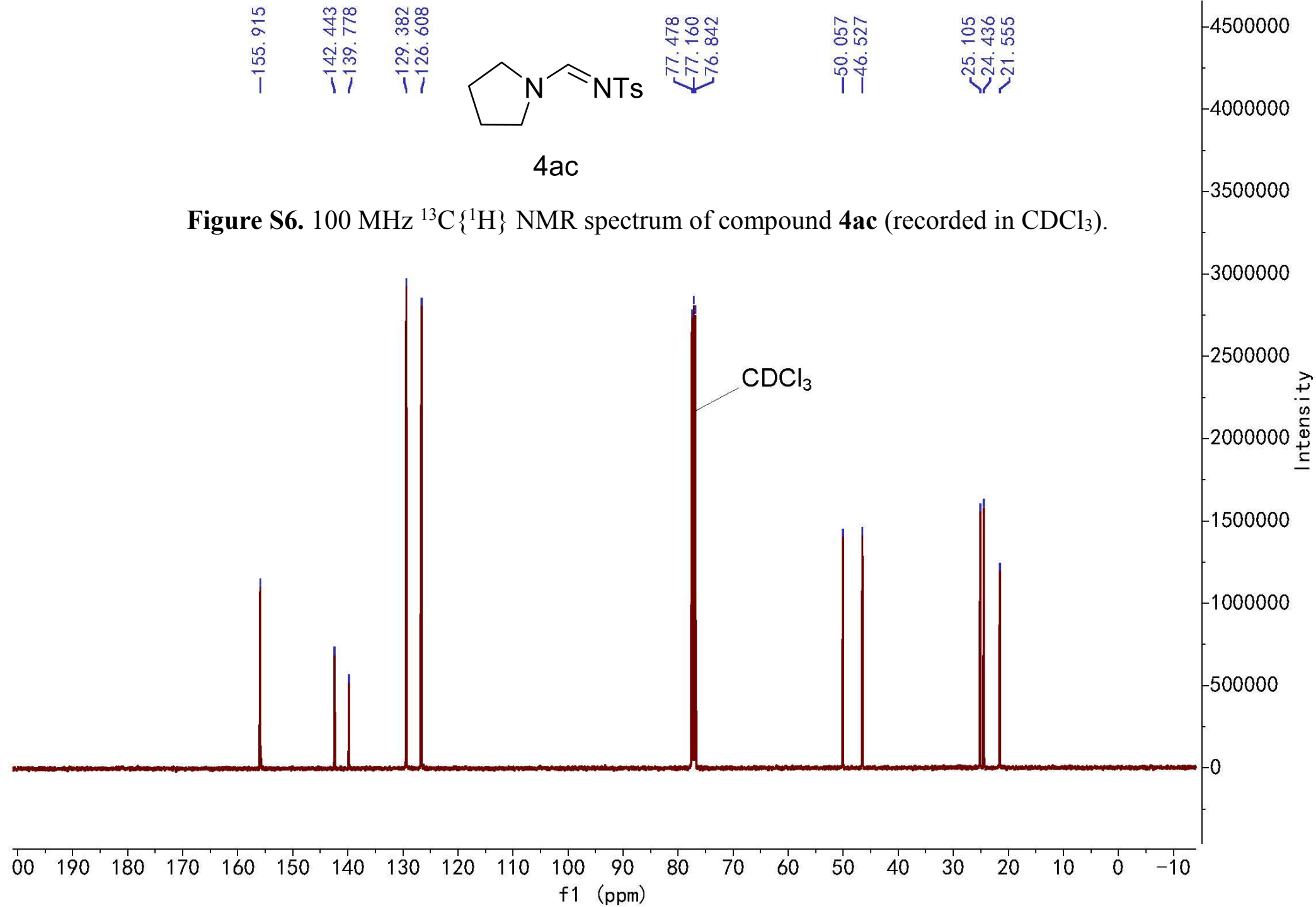


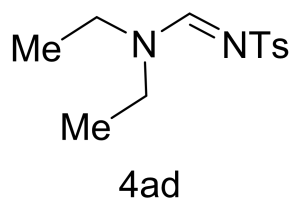
—157.347      —142.419      —139.789      —129.377      —126.537  
                  —77.478      —77.160      —76.842      —51.973      —44.720      —26.501  
                  —24.926      —24.031      —21.549

**Figure S4.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ab** (recorded in  $\text{CDCl}_3$ ).

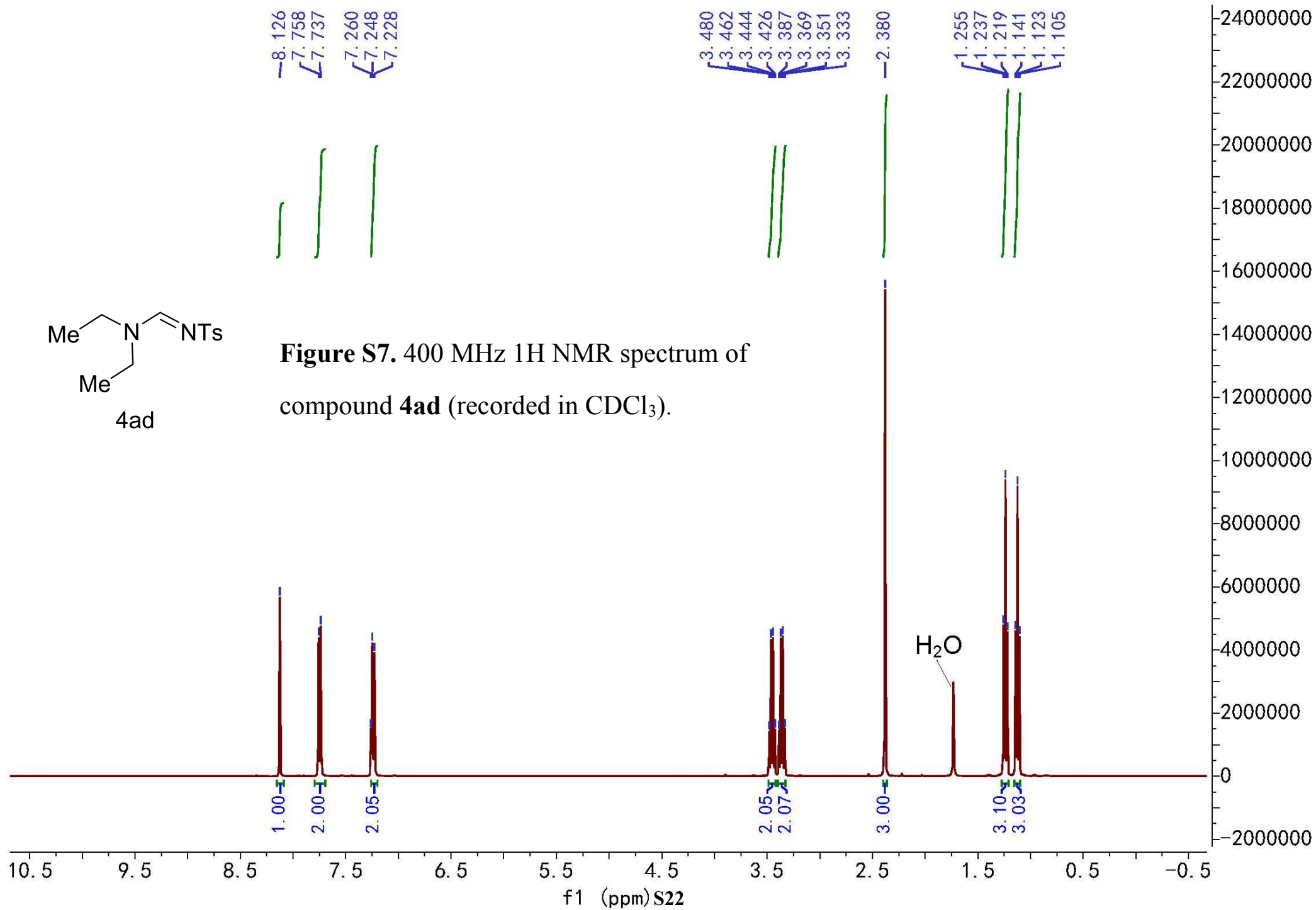






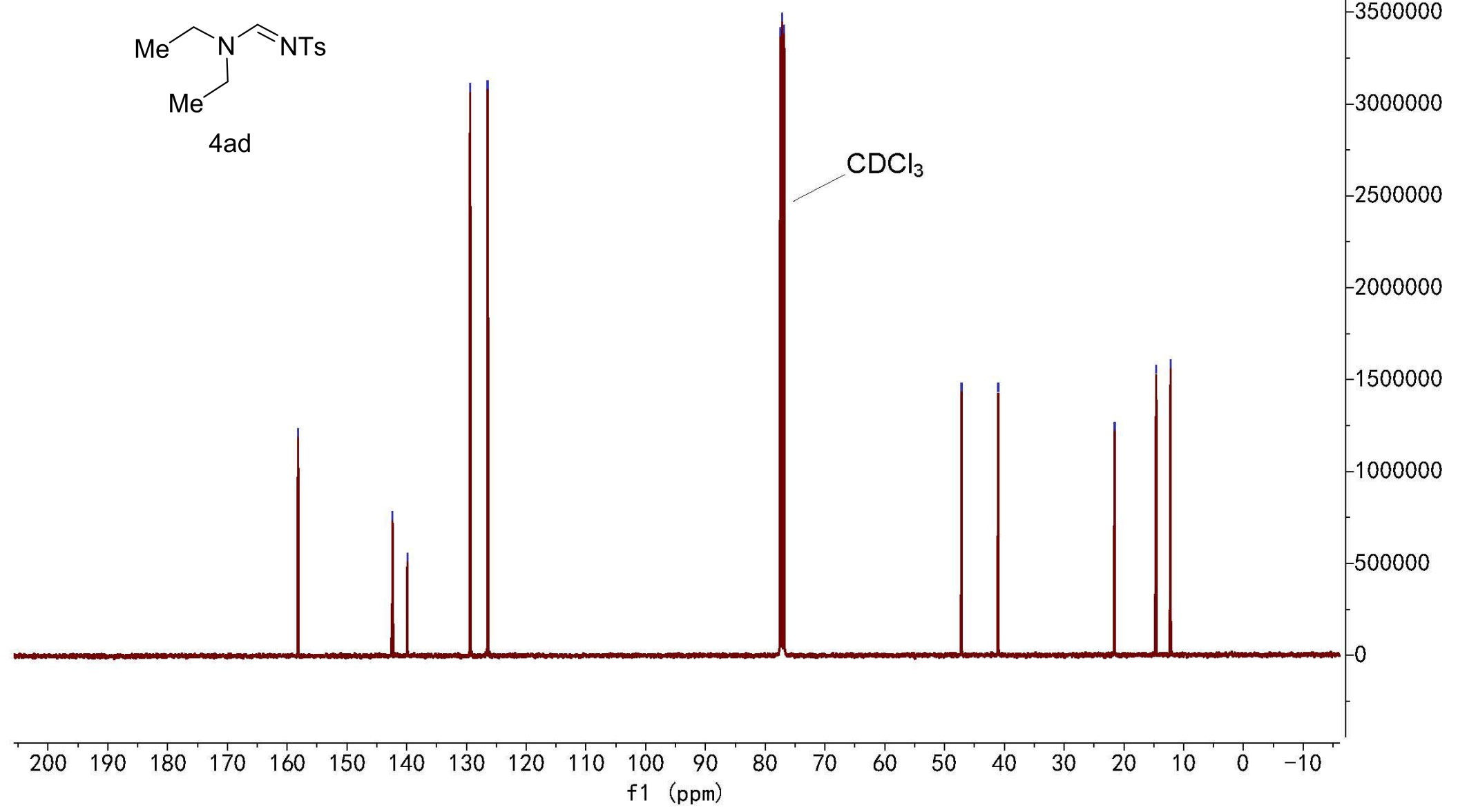
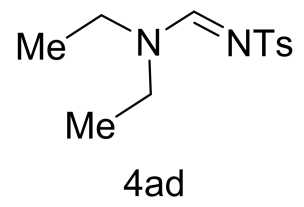


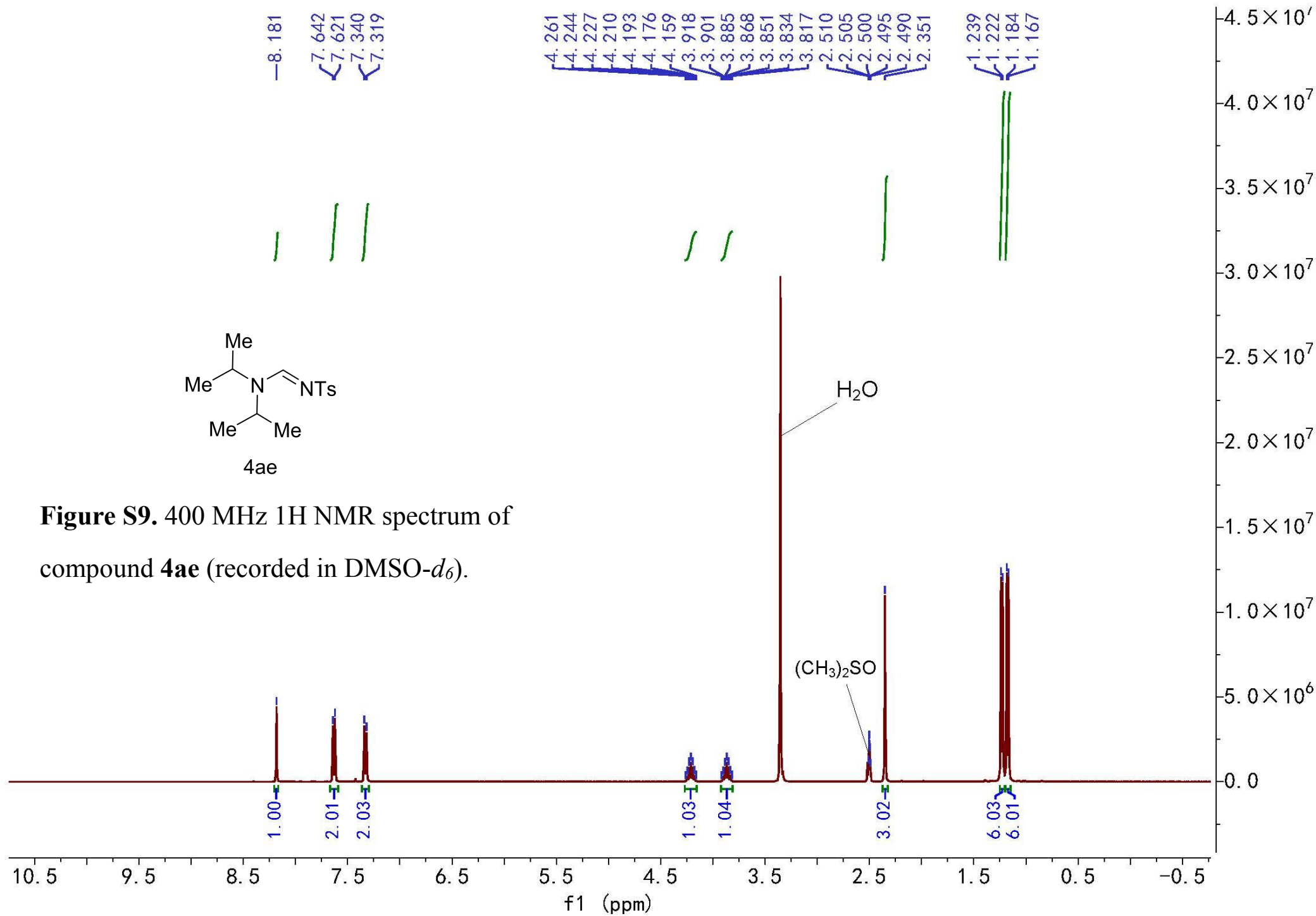
**Figure S7.** 400 MHz <sup>1</sup>H NMR spectrum of compound **4ad** (recorded in CDCl<sub>3</sub>).



158.162  
142.376  
139.864  
129.377  
126.453  
77.478  
77.160  
76.842  
47.147  
41.005  
21.559  
14.597  
12.177

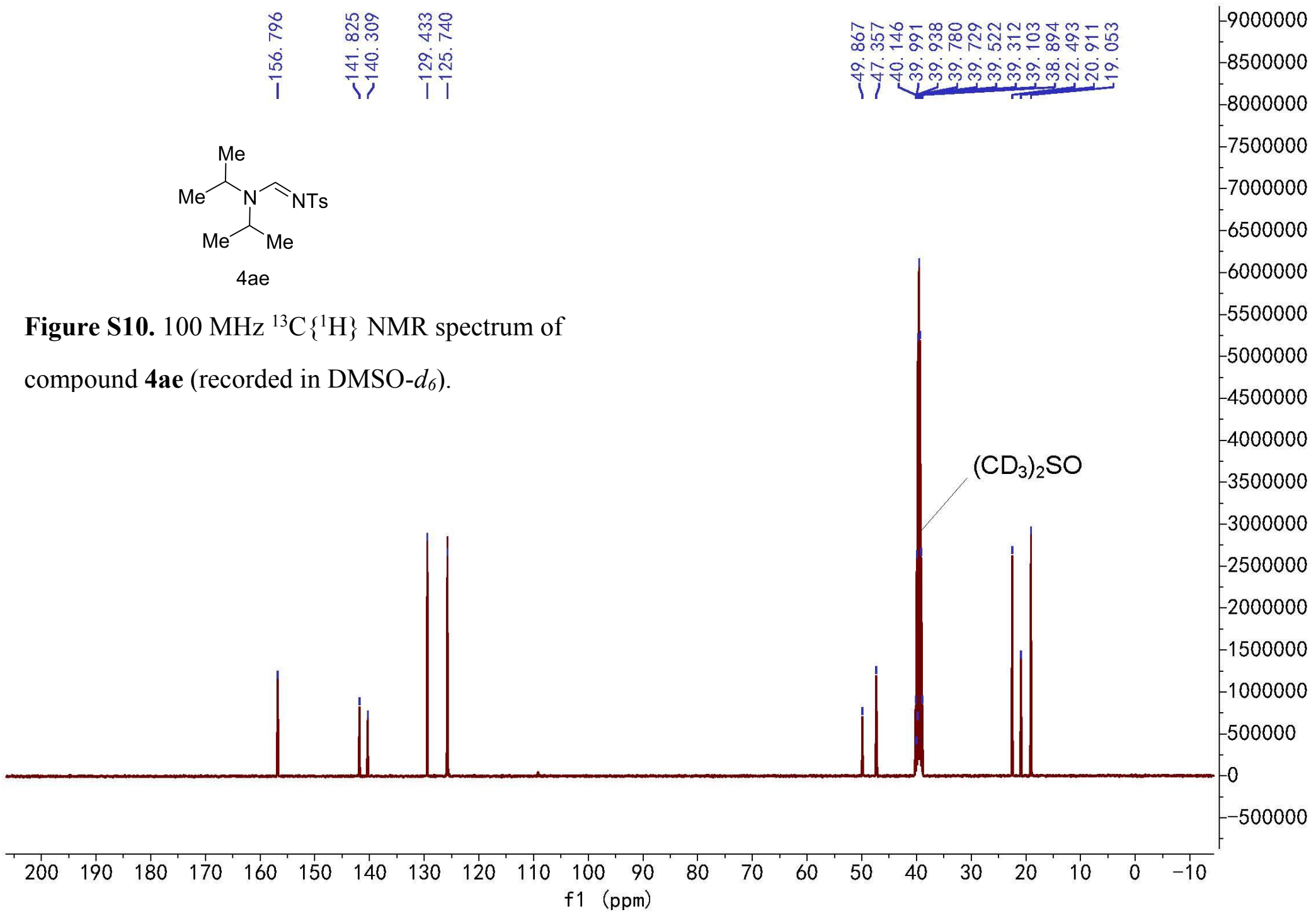
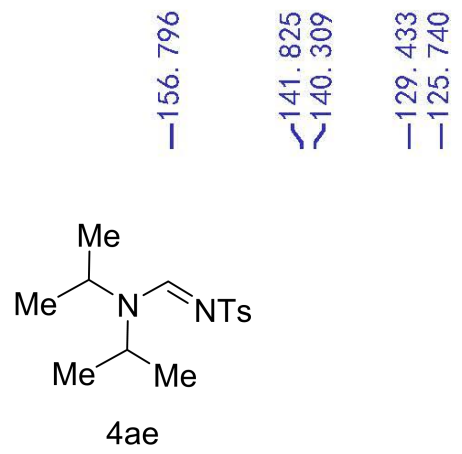
Figure S8. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ad** (recorded in  $\text{CDCl}_3$ ).



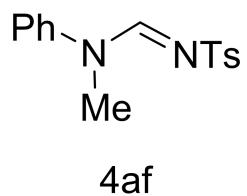


**Figure S9.** 400 MHz <sup>1</sup>H NMR spectrum of compound **4ae** (recorded in DMSO-*d*<sub>6</sub>).

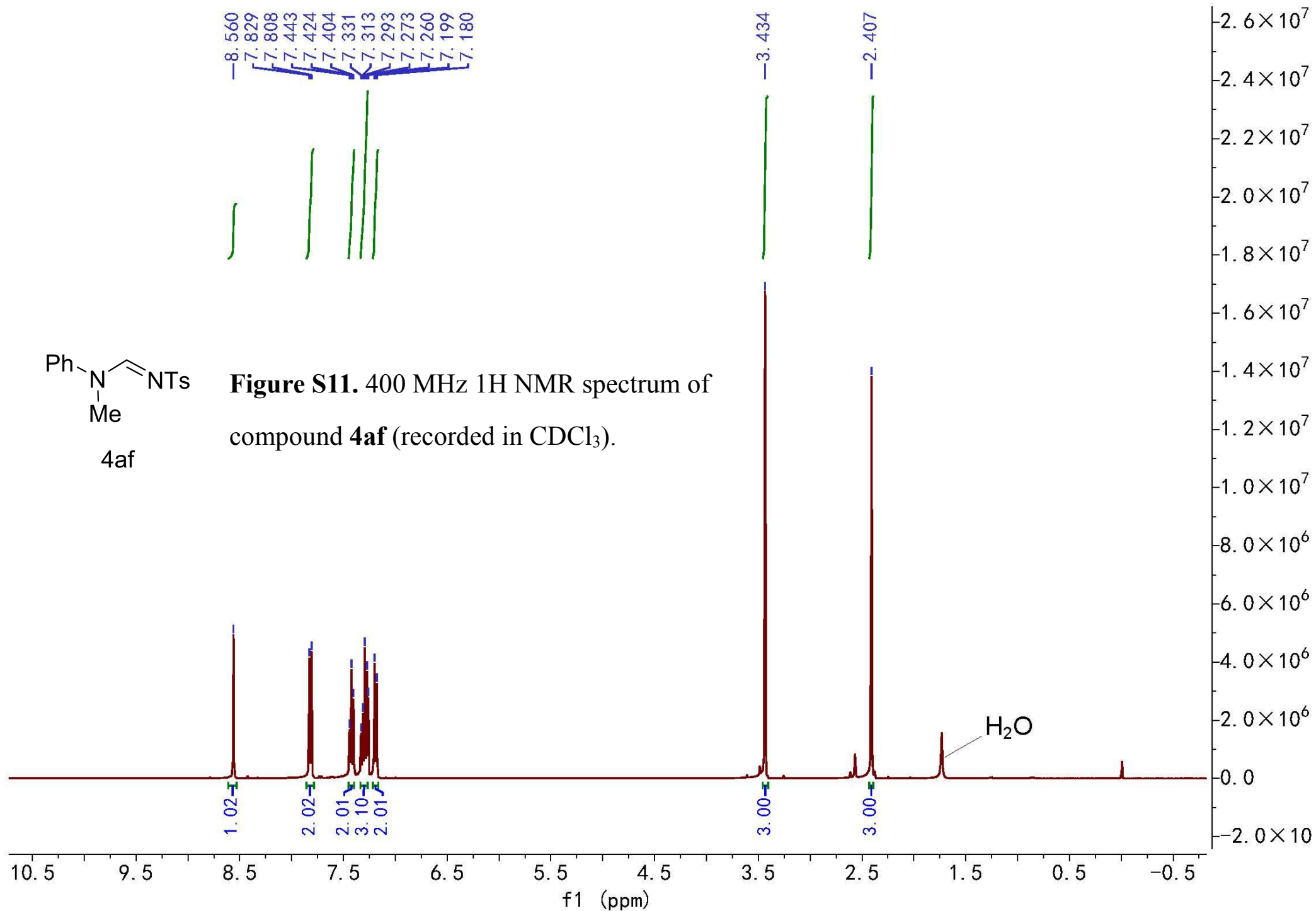




**Figure S10.** 100 MHz <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound **4ae** (recorded in DMSO-*d*<sub>6</sub>).



**Figure S11.** 400 MHz <sup>1</sup>H NMR spectrum of compound **4af** (recorded in CDCl<sub>3</sub>).



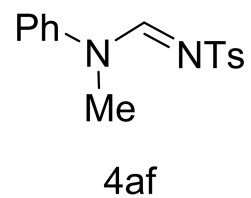
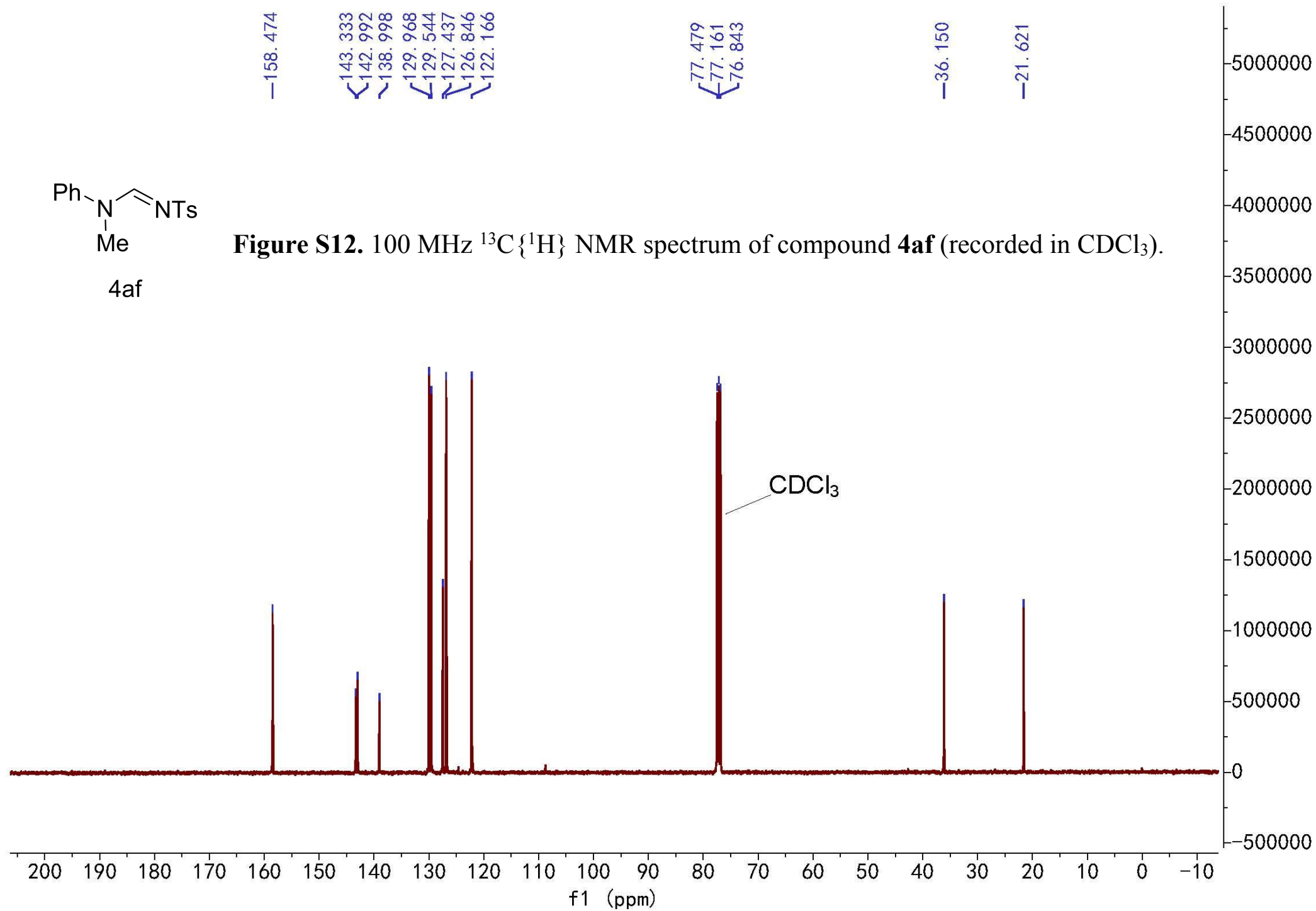
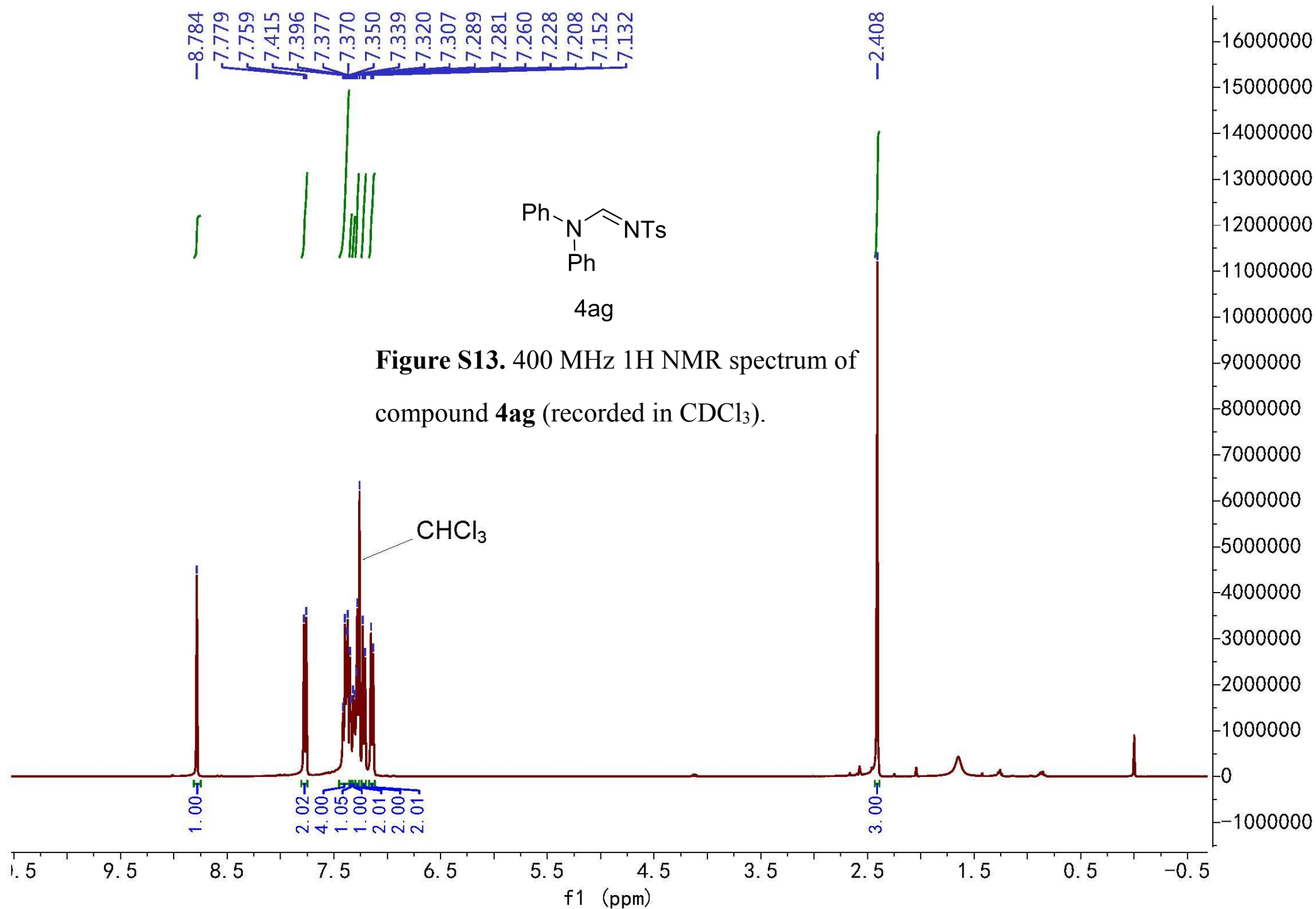


Figure S12. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4af** (recorded in  $\text{CDCl}_3$ ).





158.106  
143.526  
143.068  
139.948  
138.634  
129.943  
129.557  
129.423  
127.945  
127.641  
126.867  
126.726  
124.156

77.478  
77.161  
76.843

21.658

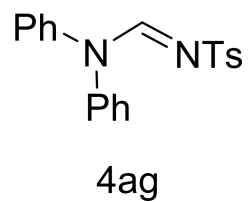
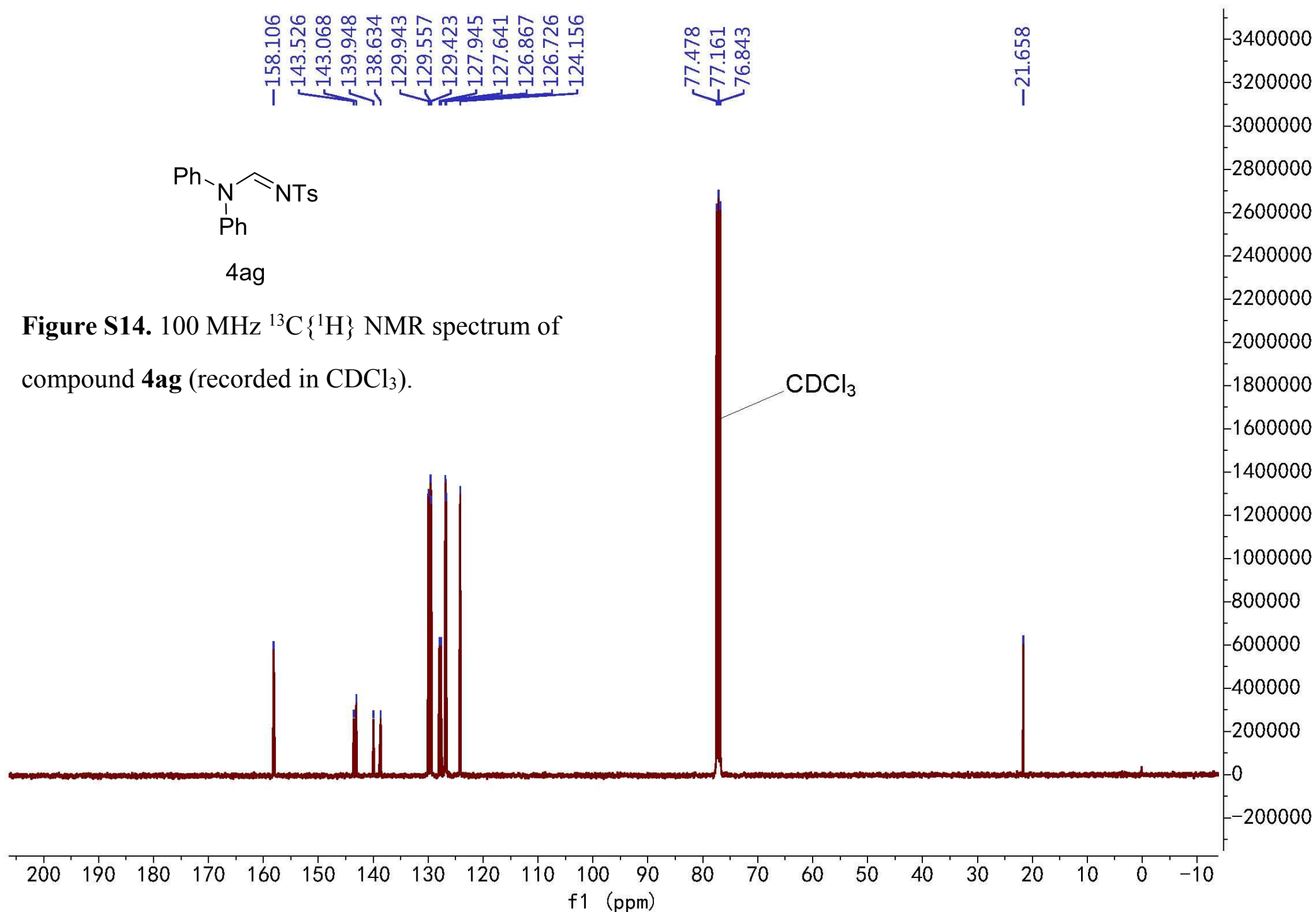
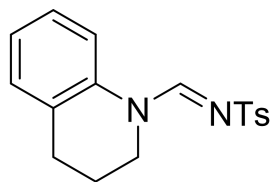


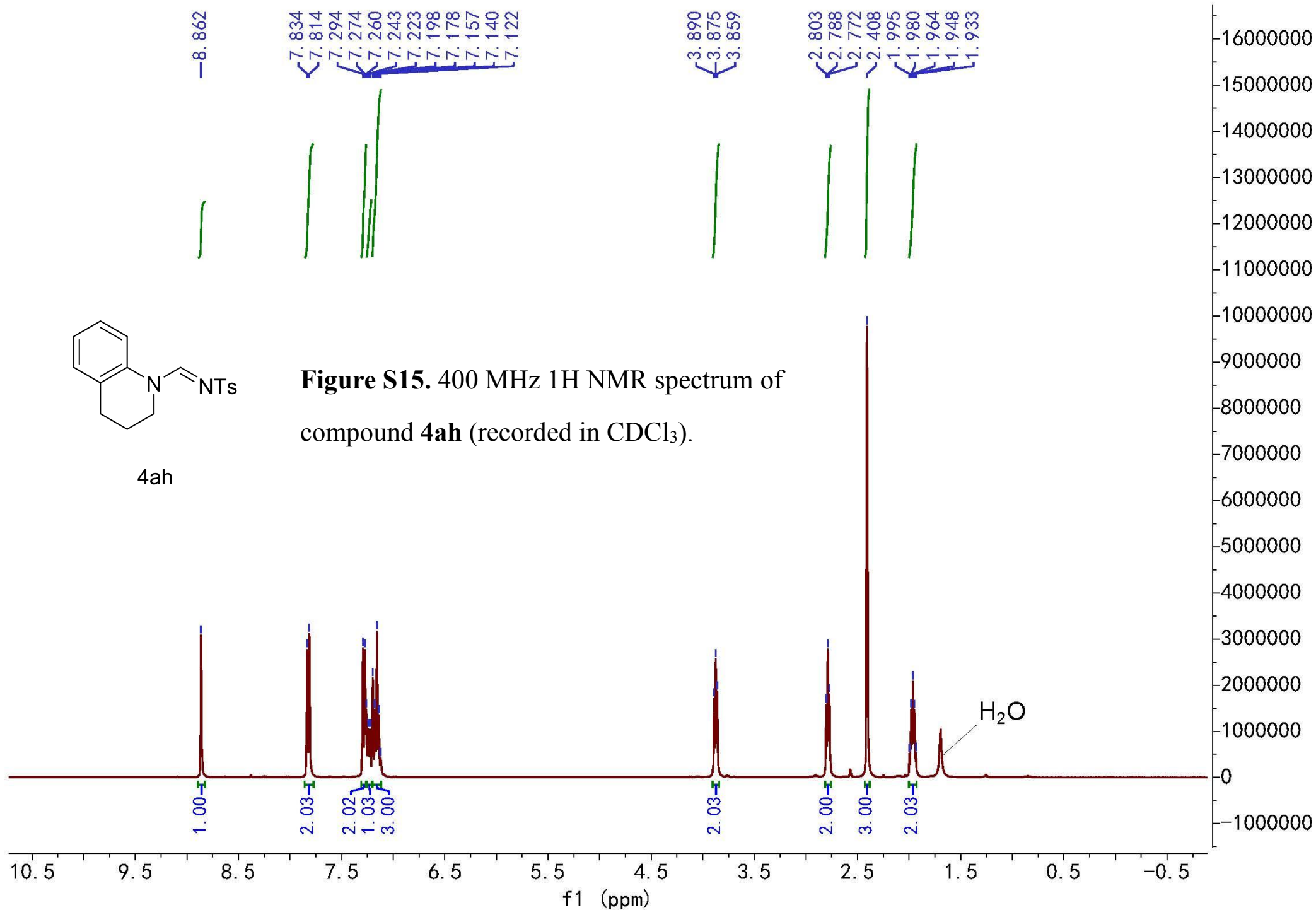
Figure S14. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ag** (recorded in  $\text{CDCl}_3$ ).





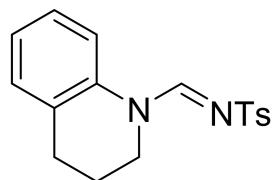
4ah

**Figure S15.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4ah** (recorded in  $\text{CDCl}_3$ ).

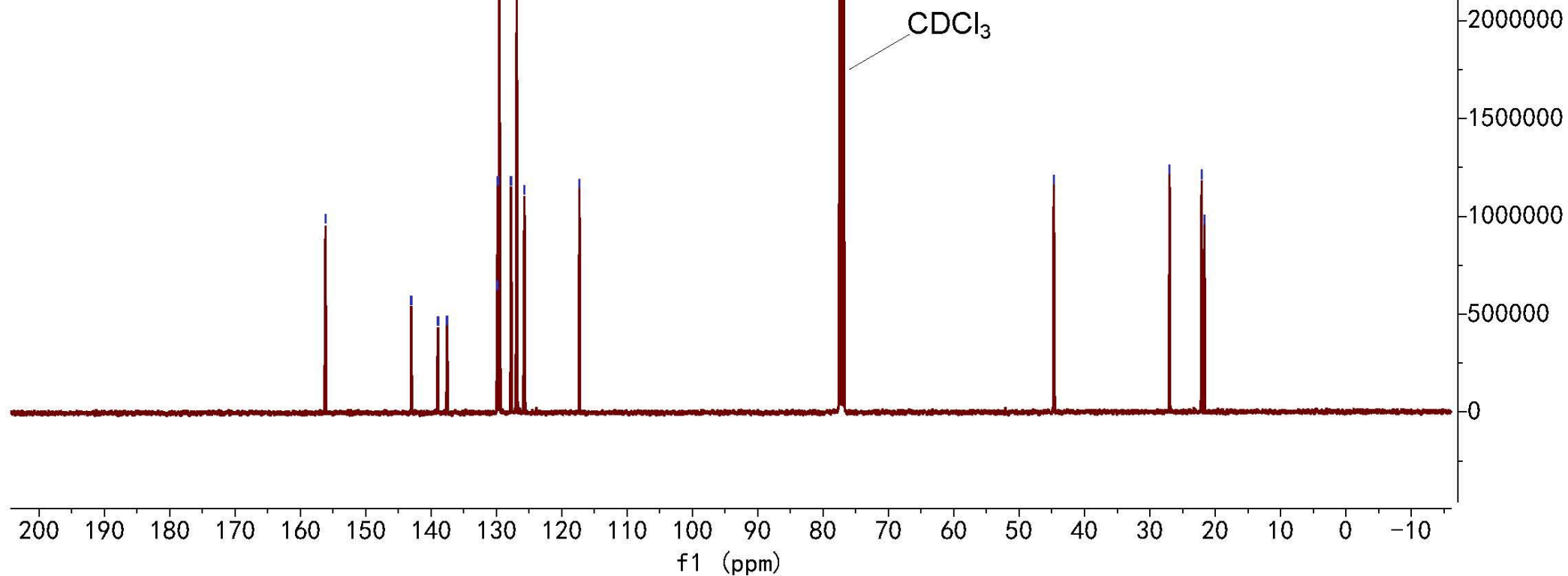




**Figure S16.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ah** (recorded in  $\text{CDCl}_3$ ).



**4ah**



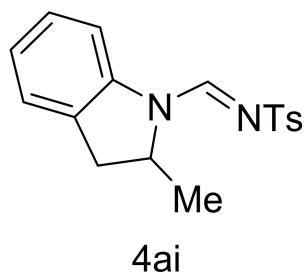
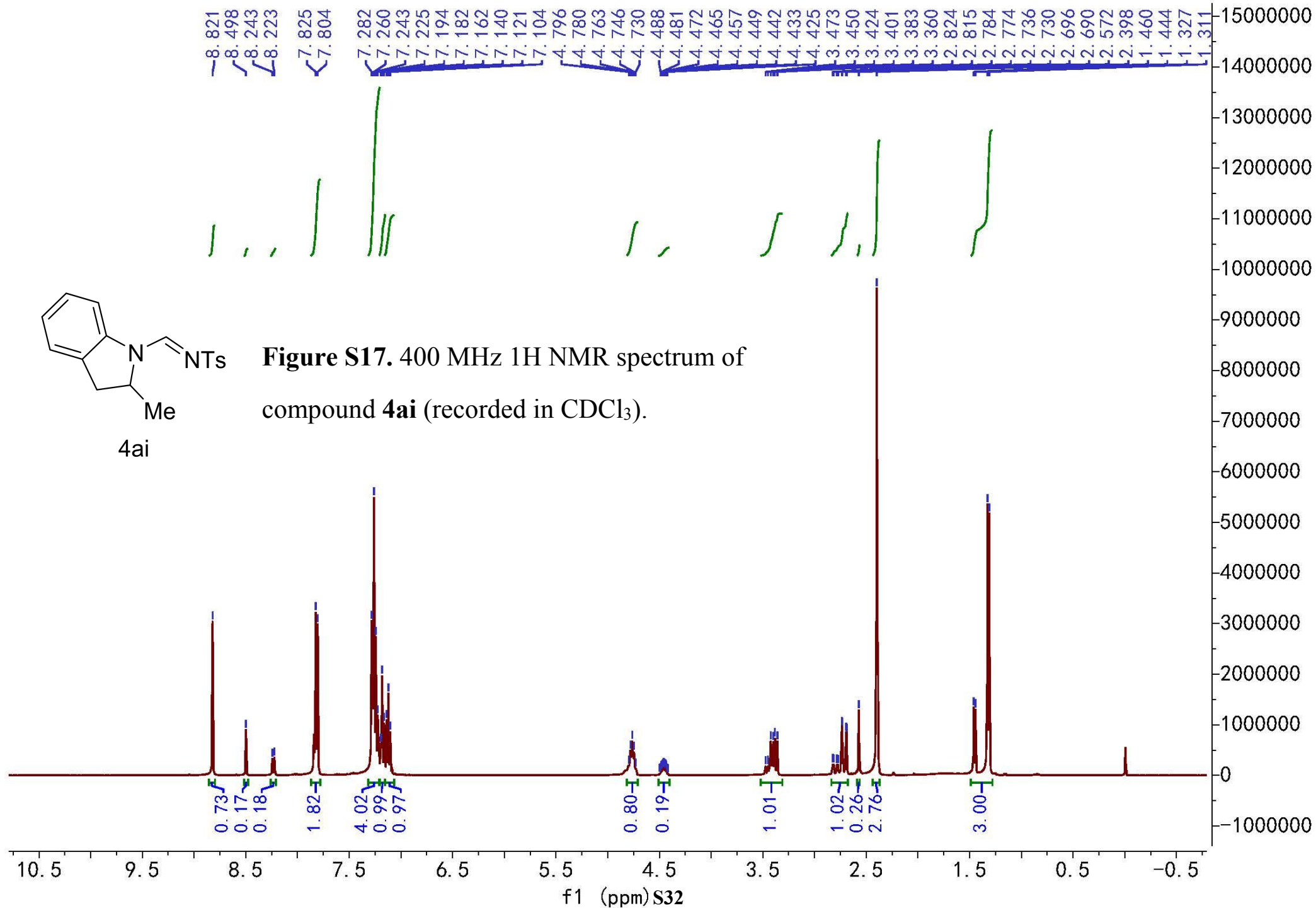


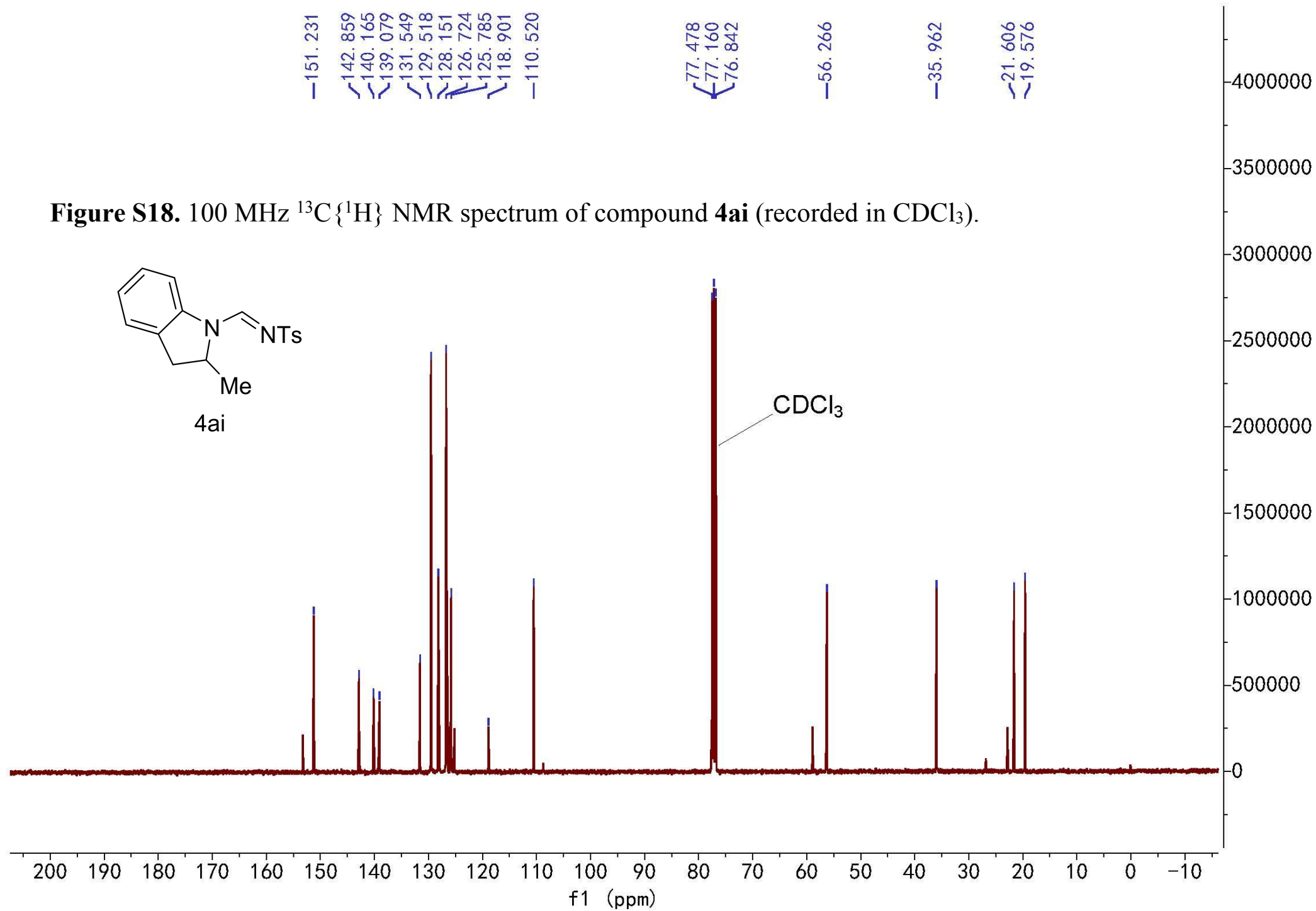
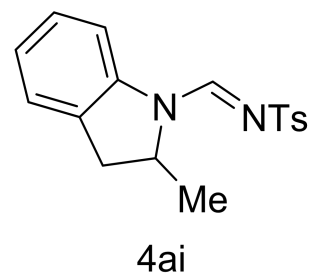
Figure S17. 400 MHz <sup>1</sup>H NMR spectrum of compound 4ai (recorded in CDCl<sub>3</sub>).

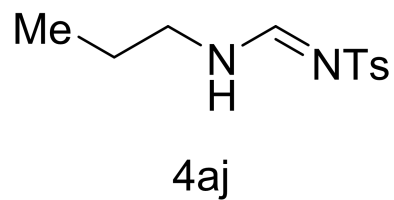




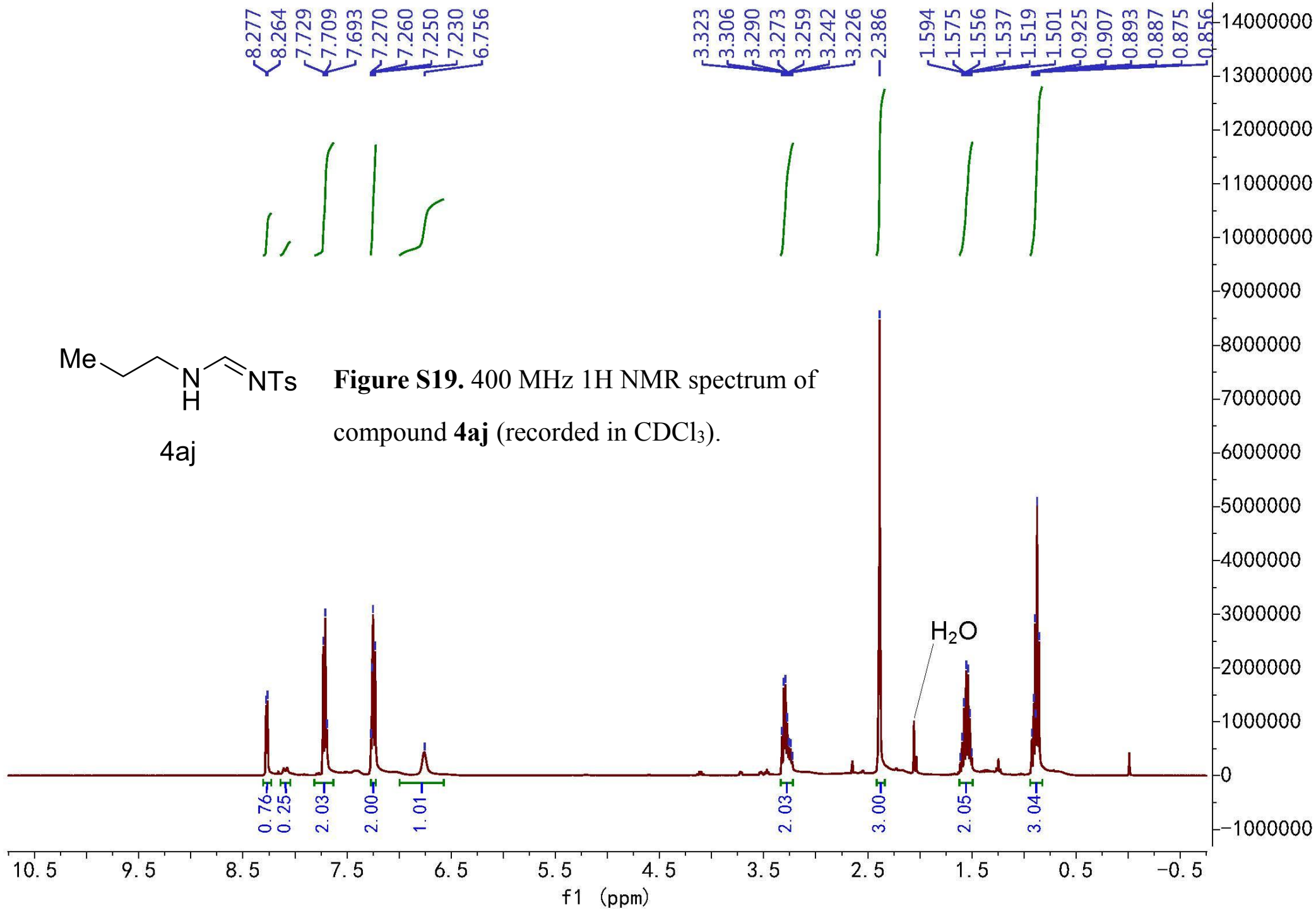
— 151.231  
 / 142.859  
 / 140.165  
 / 139.079  
 / 131.549  
 / 129.518  
 / 128.151  
 / 126.724  
 / 125.785  
 / 118.901  
 — 110.520  
  
 { 77.478  
 { 77.160  
 { 76.842  
  
 — 56.266  
  
 — 35.962  
  
 / 21.606  
 / 19.576

**Figure S18.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ai** (recorded in  $\text{CDCl}_3$ ).



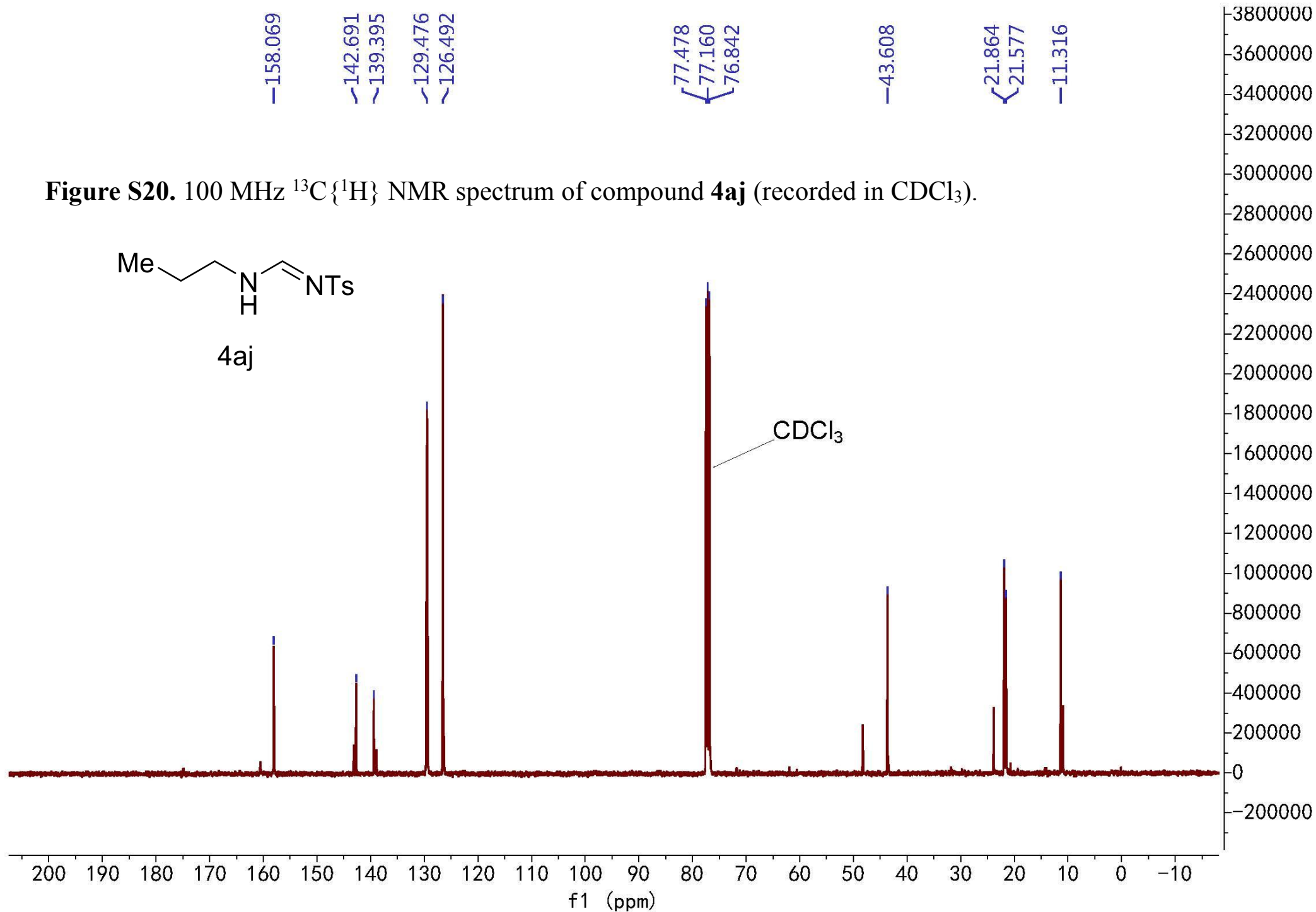
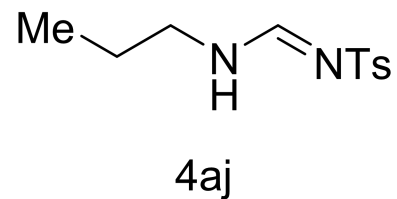


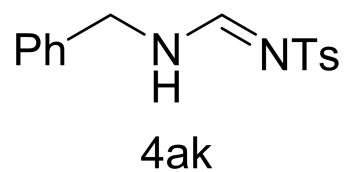
**Figure S19.** 400 MHz <sup>1</sup>H NMR spectrum of compound **4aj** (recorded in CDCl<sub>3</sub>).



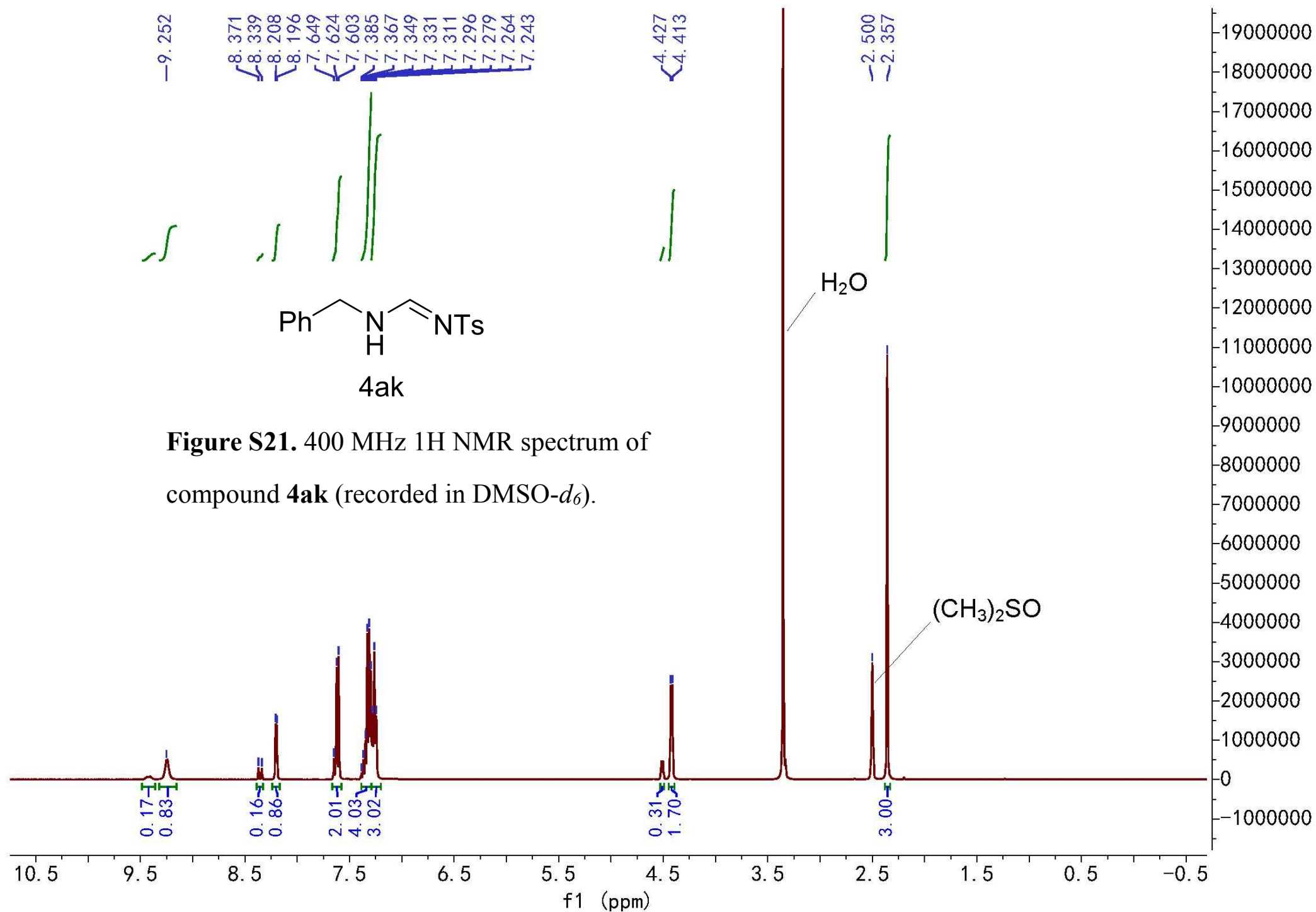
158.069 142.691 139.395 129.476 126.492 77.478 77.160 76.842 43.608 21.864 21.577 11.316

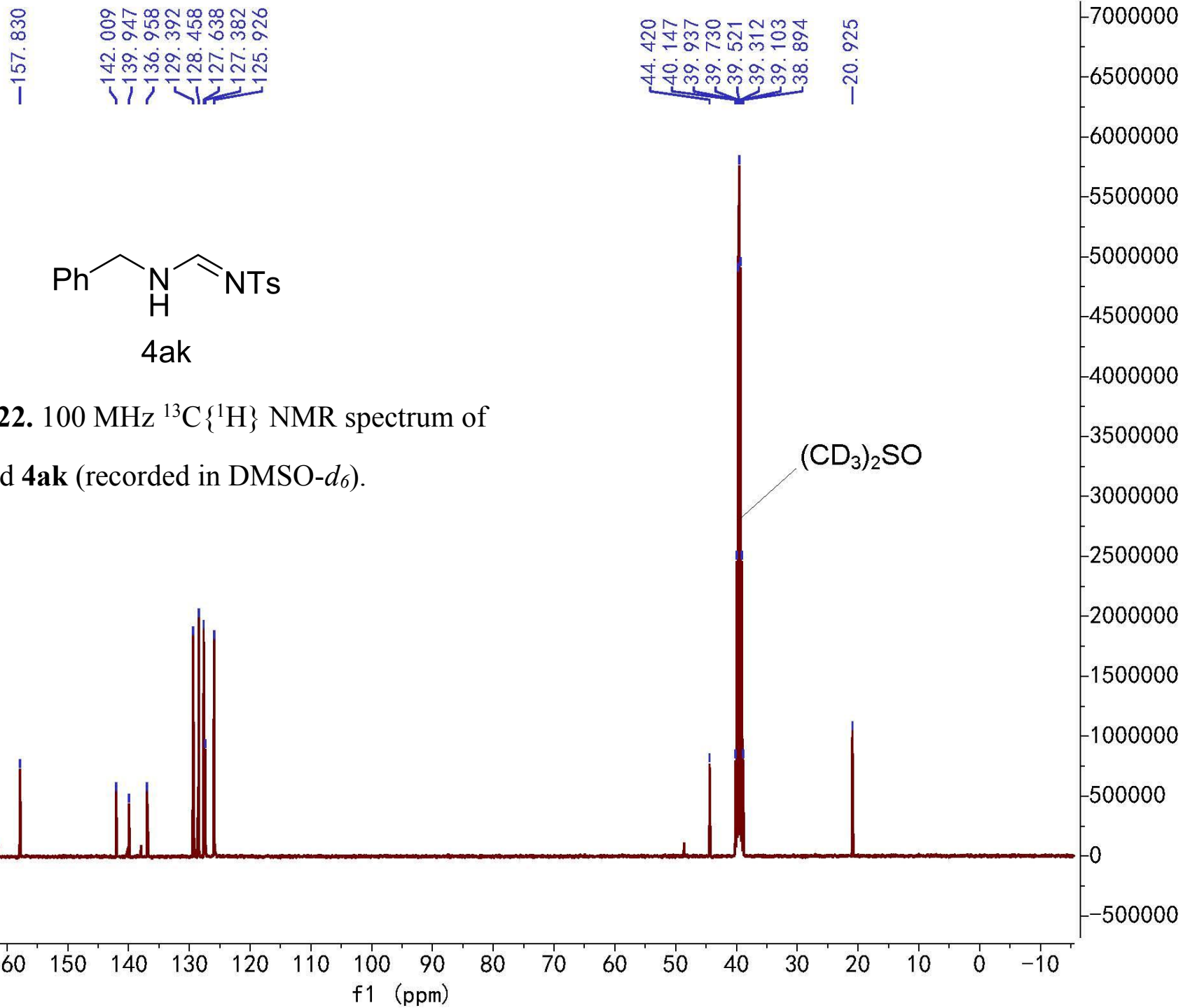
Figure S20. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4aj** (recorded in  $\text{CDCl}_3$ ).



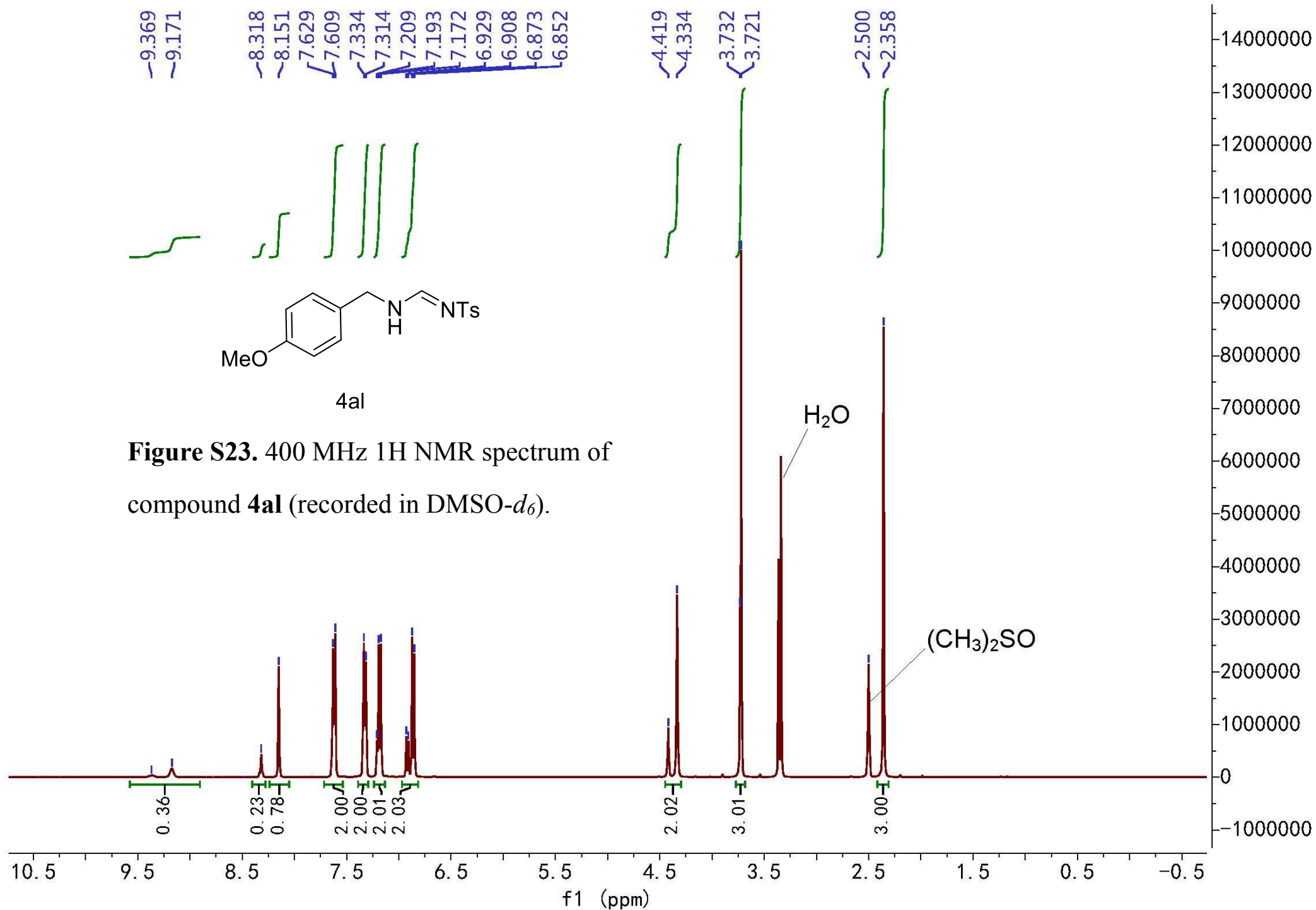


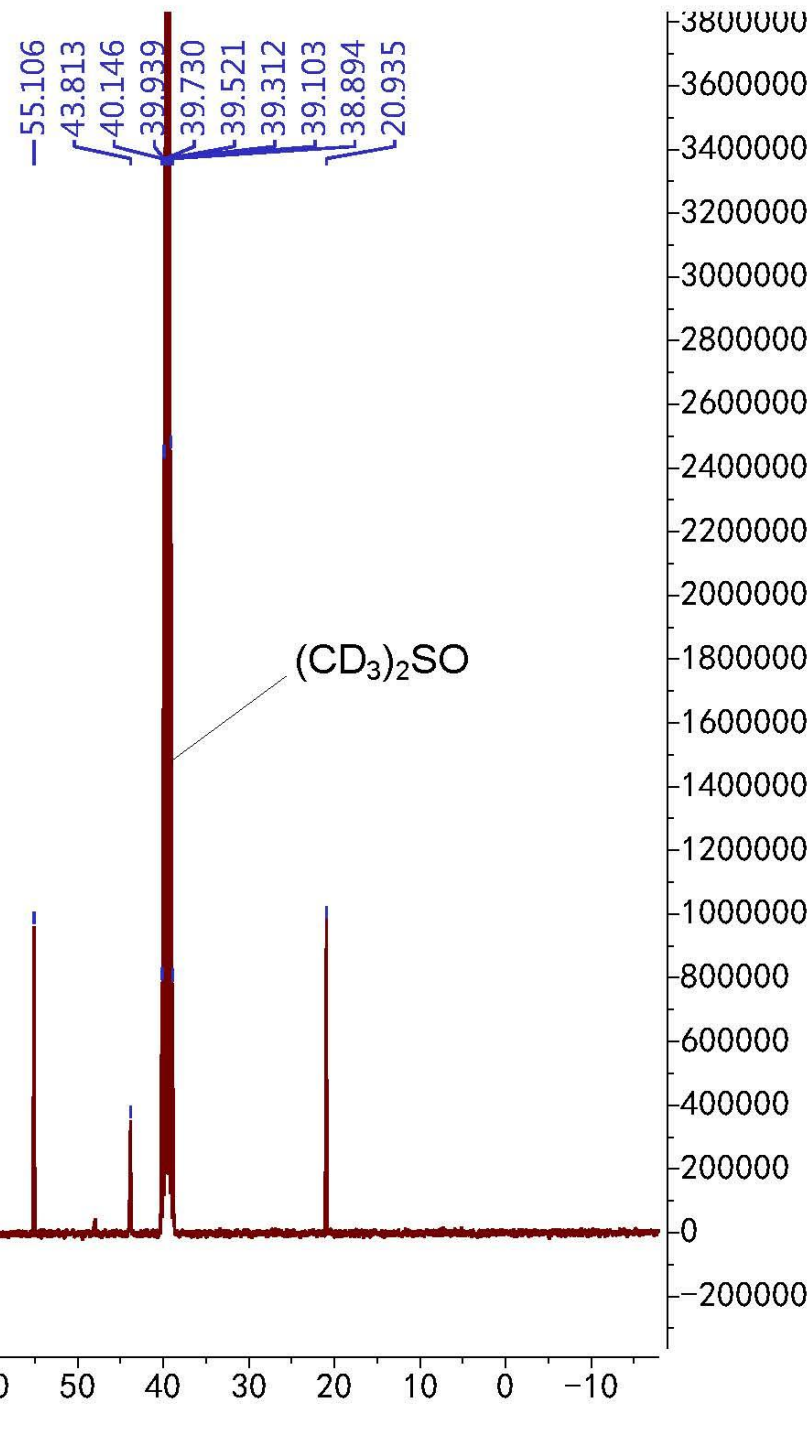
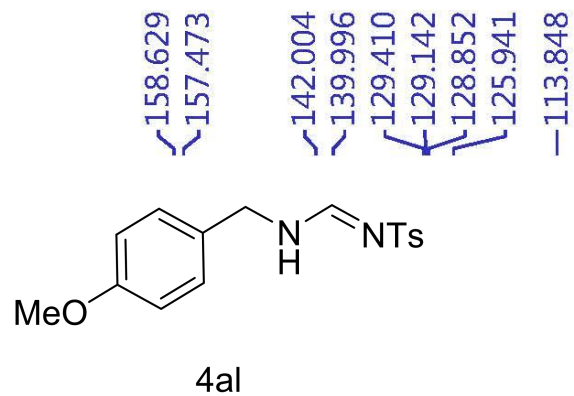
**Figure S21.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4ak** (recorded in  $\text{DMSO-}d_6$ ).



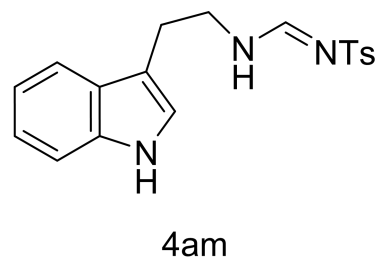


**Figure S22.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ak** (recorded in  $\text{DMSO-}d_6$ ).

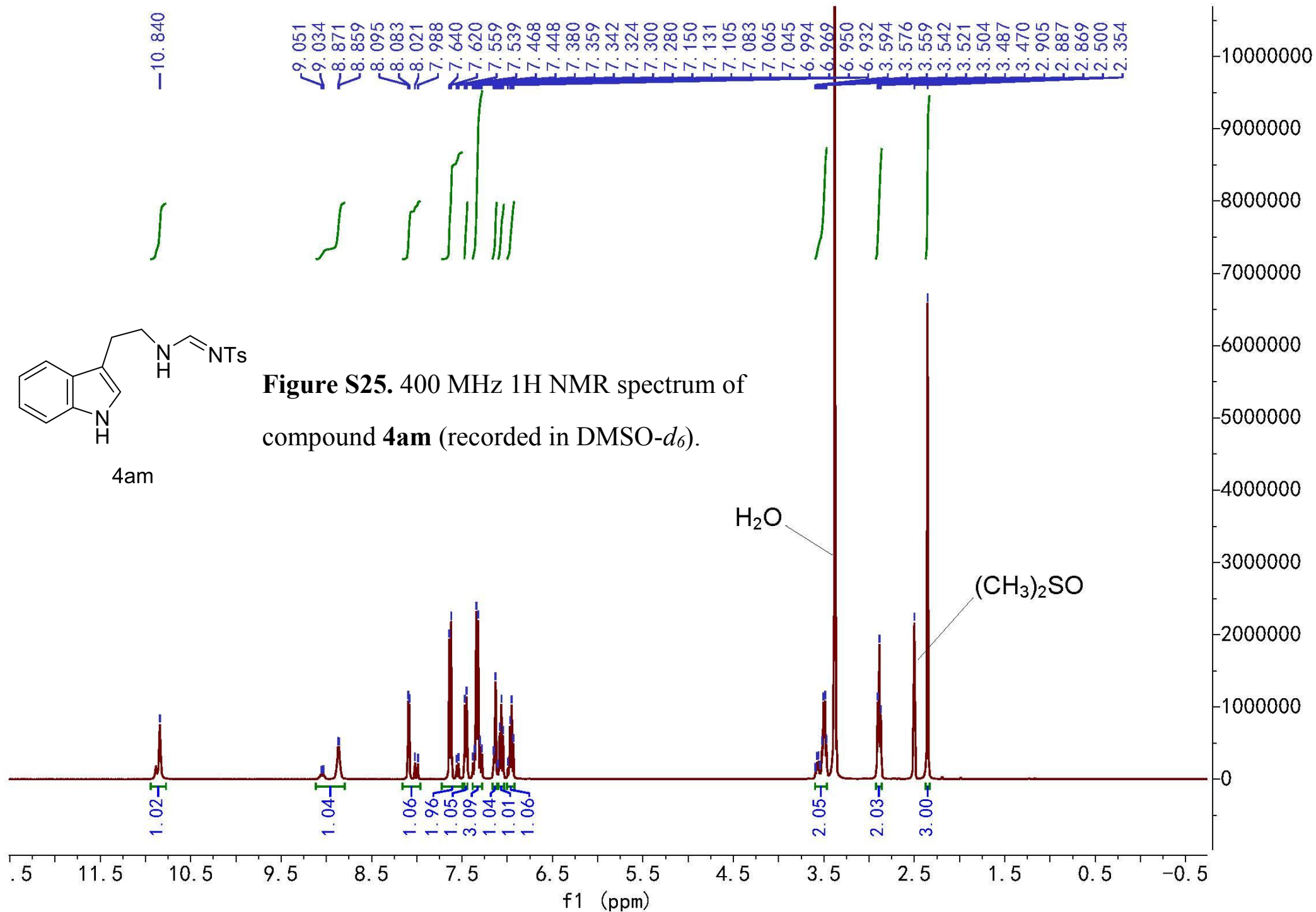




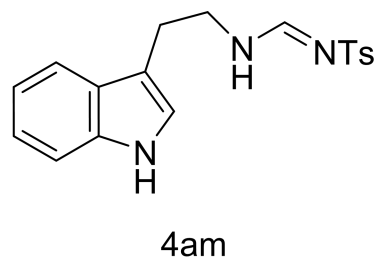
**Figure S24.** 100 MHz <sup>13</sup>C {<sup>1</sup>H} NMR spectrum of compound **4al** (recorded in DMSO-*d*<sub>6</sub>).



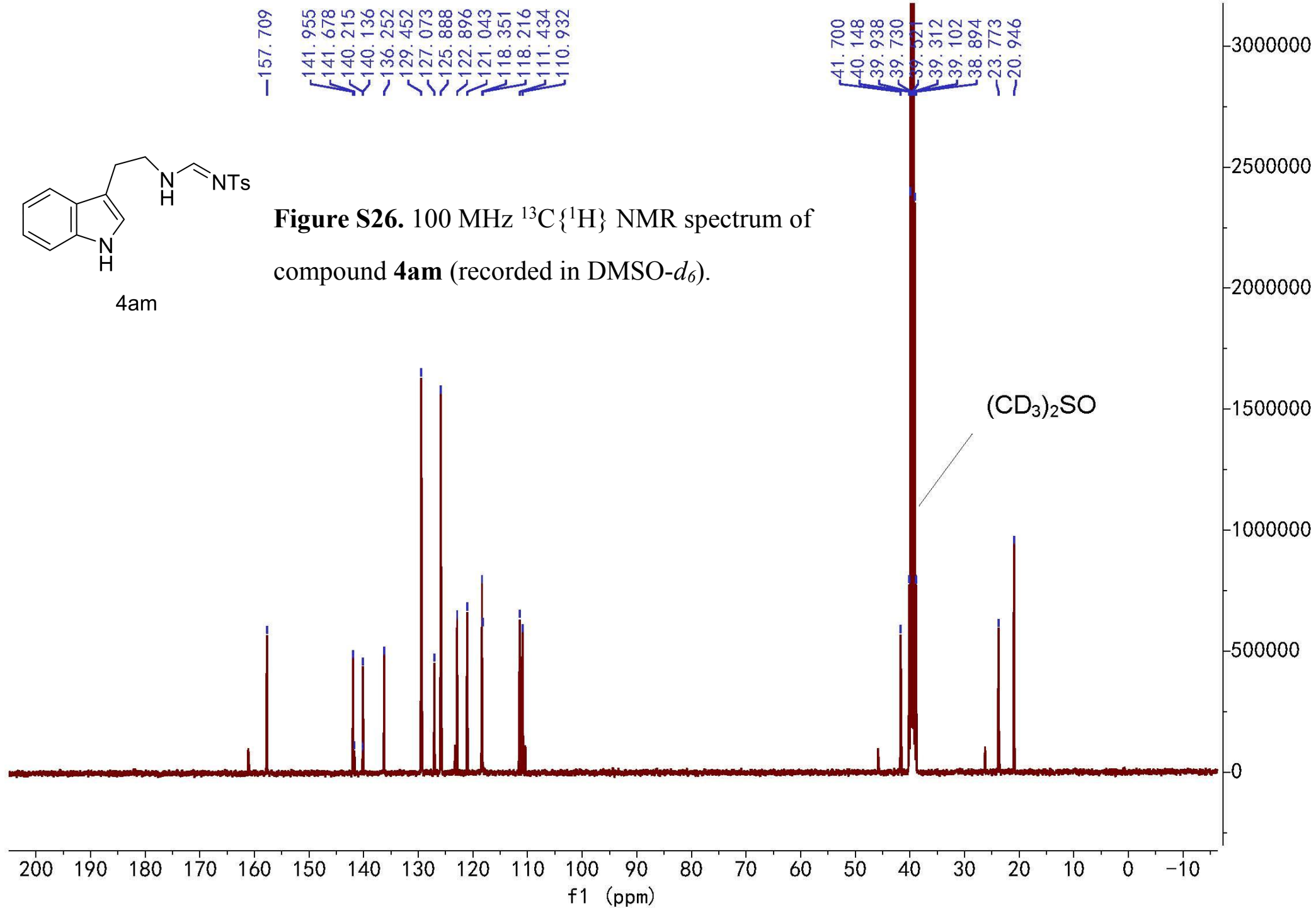
**Figure S25.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4am** (recorded in  $\text{DMSO-}d_6$ ).

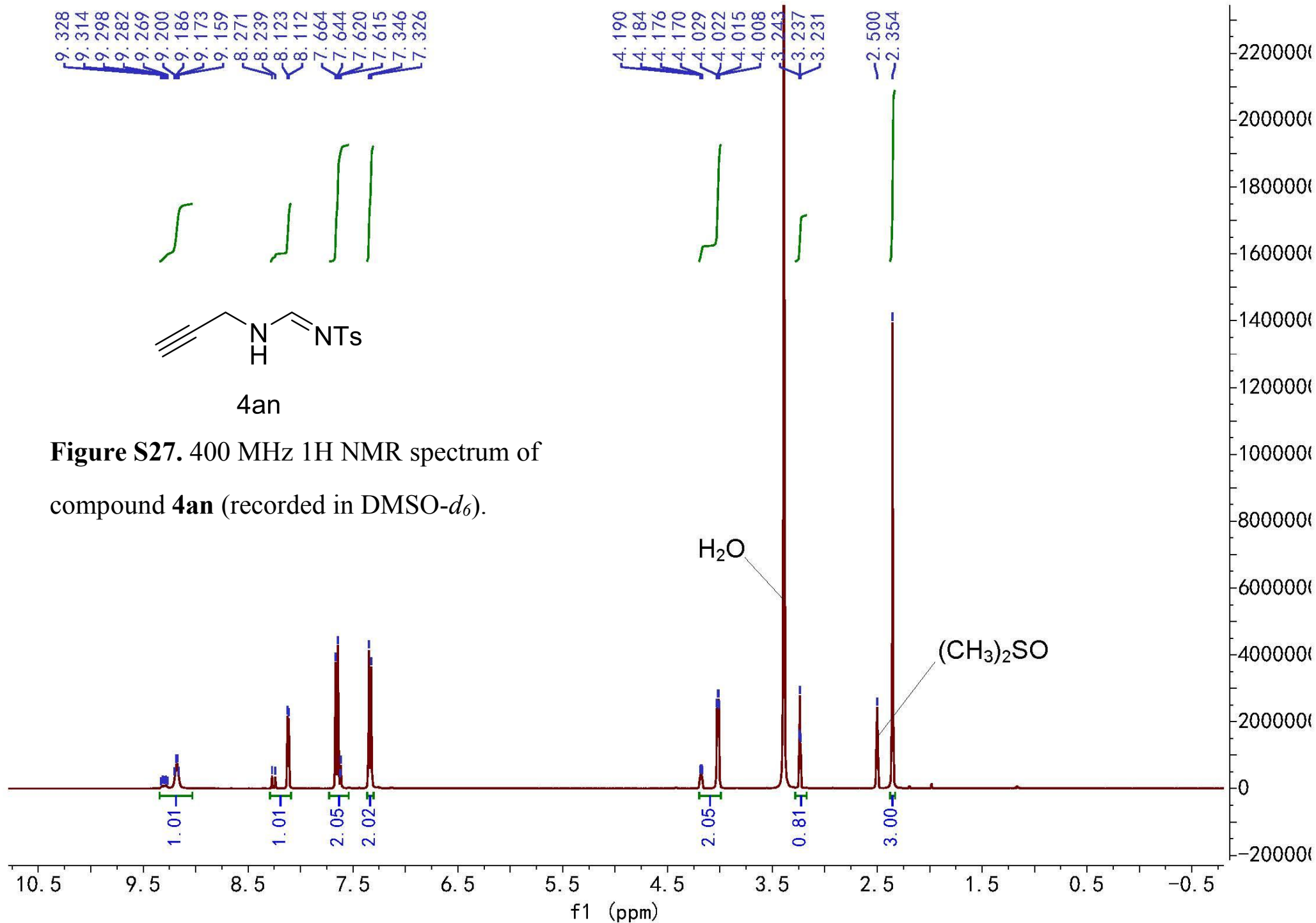






**Figure S26.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4am** (recorded in  $\text{DMSO-}d_6$ ).



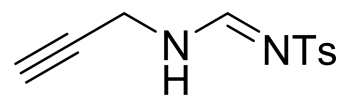


—157.657  
—142.264  
—139.645  
—129.495  
—126.084

—78.964  
—74.511

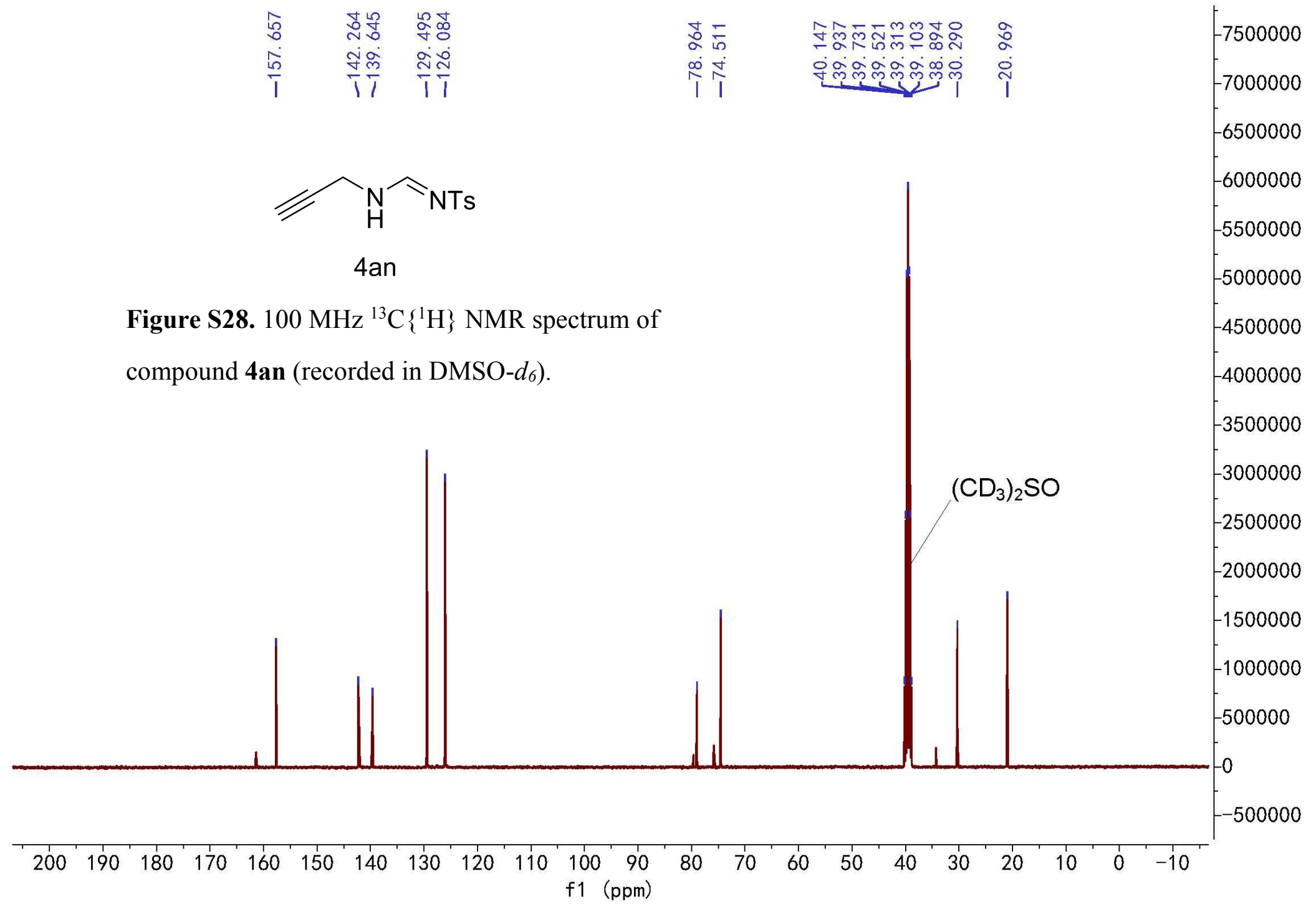
—40.147  
—39.937  
—39.731  
—39.521  
—39.313  
—39.103  
—38.894  
—30.290

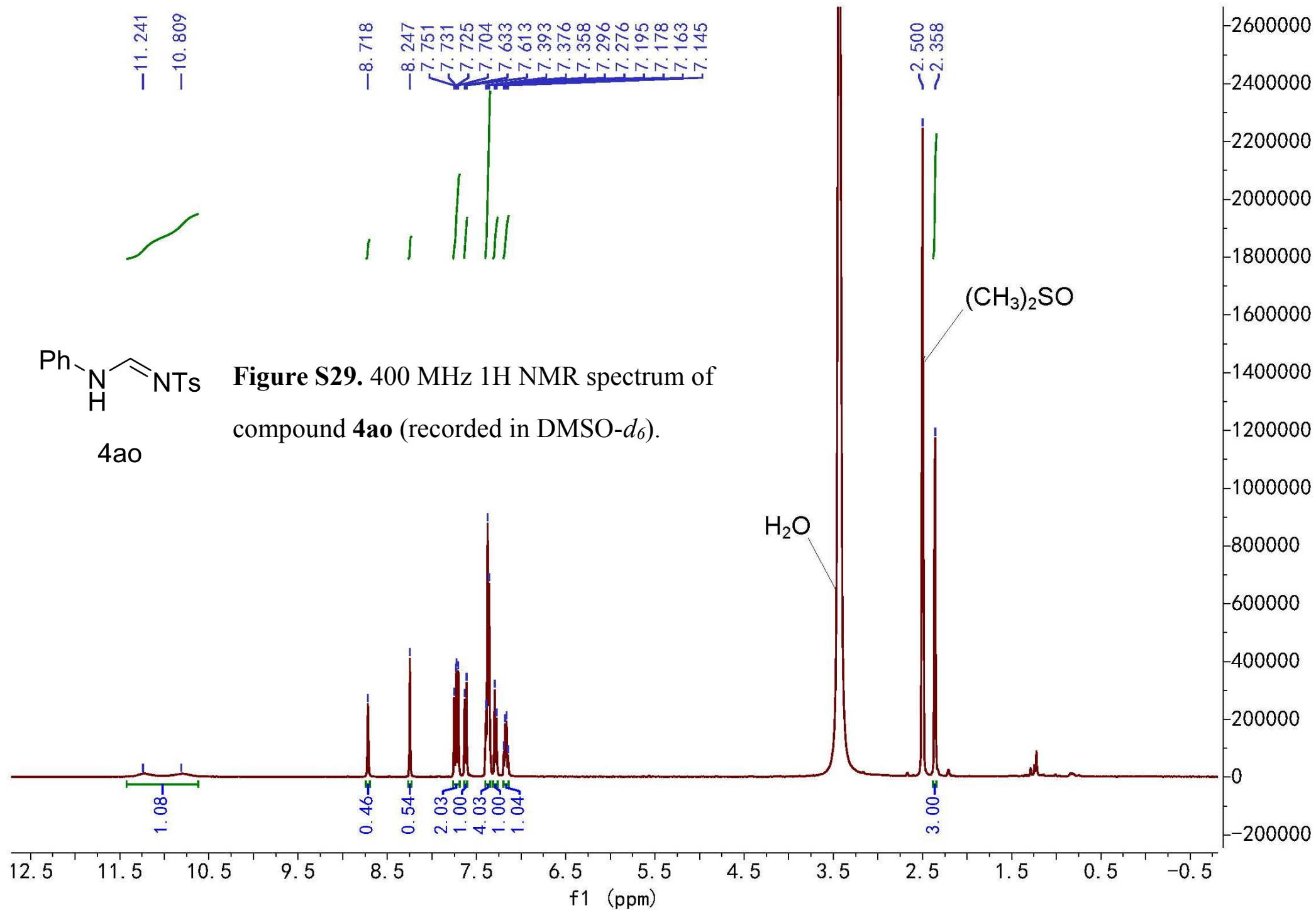
—20.969

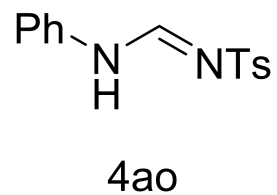


4an

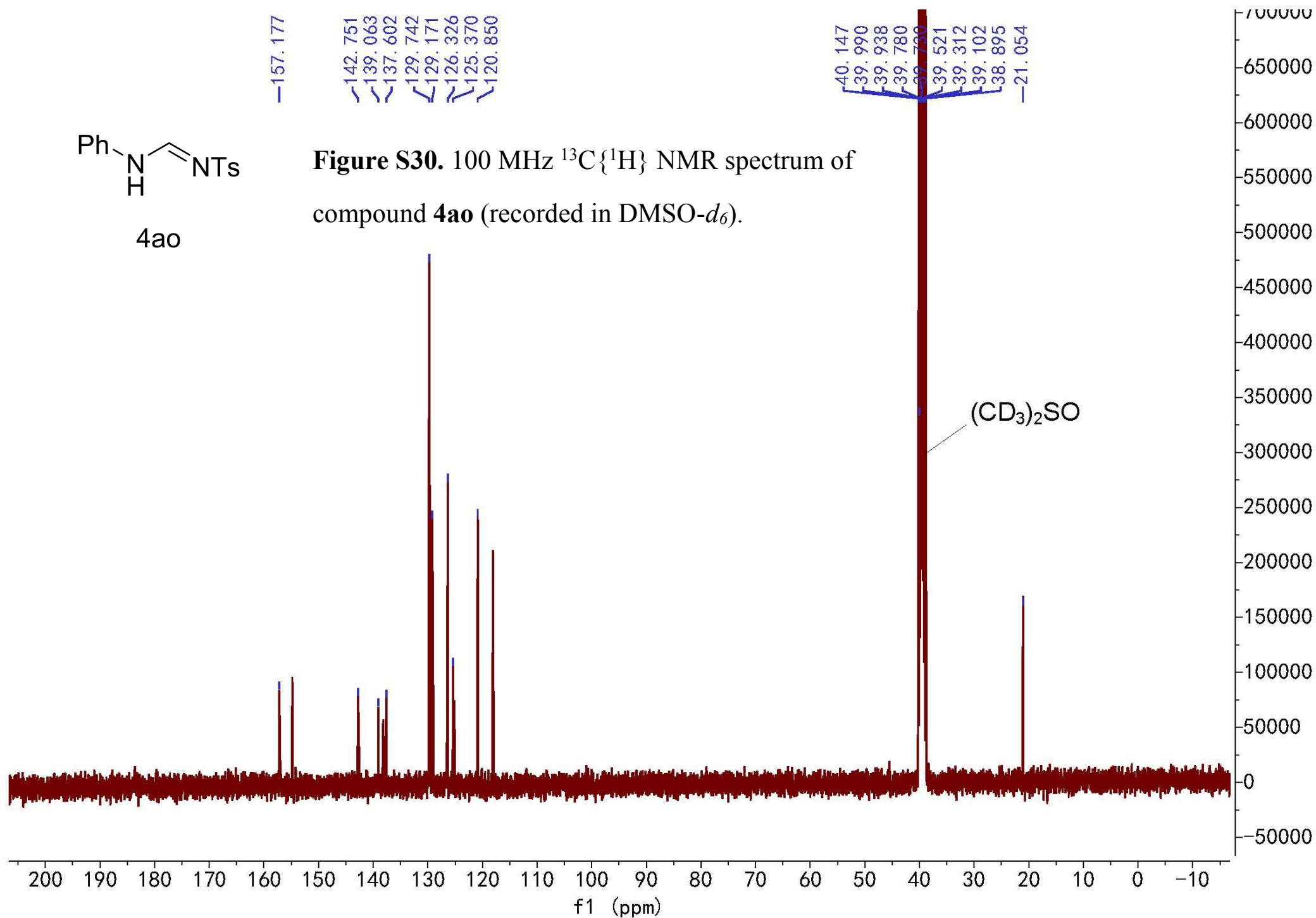
**Figure S28.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4an** (recorded in DMSO- $d_6$ ).

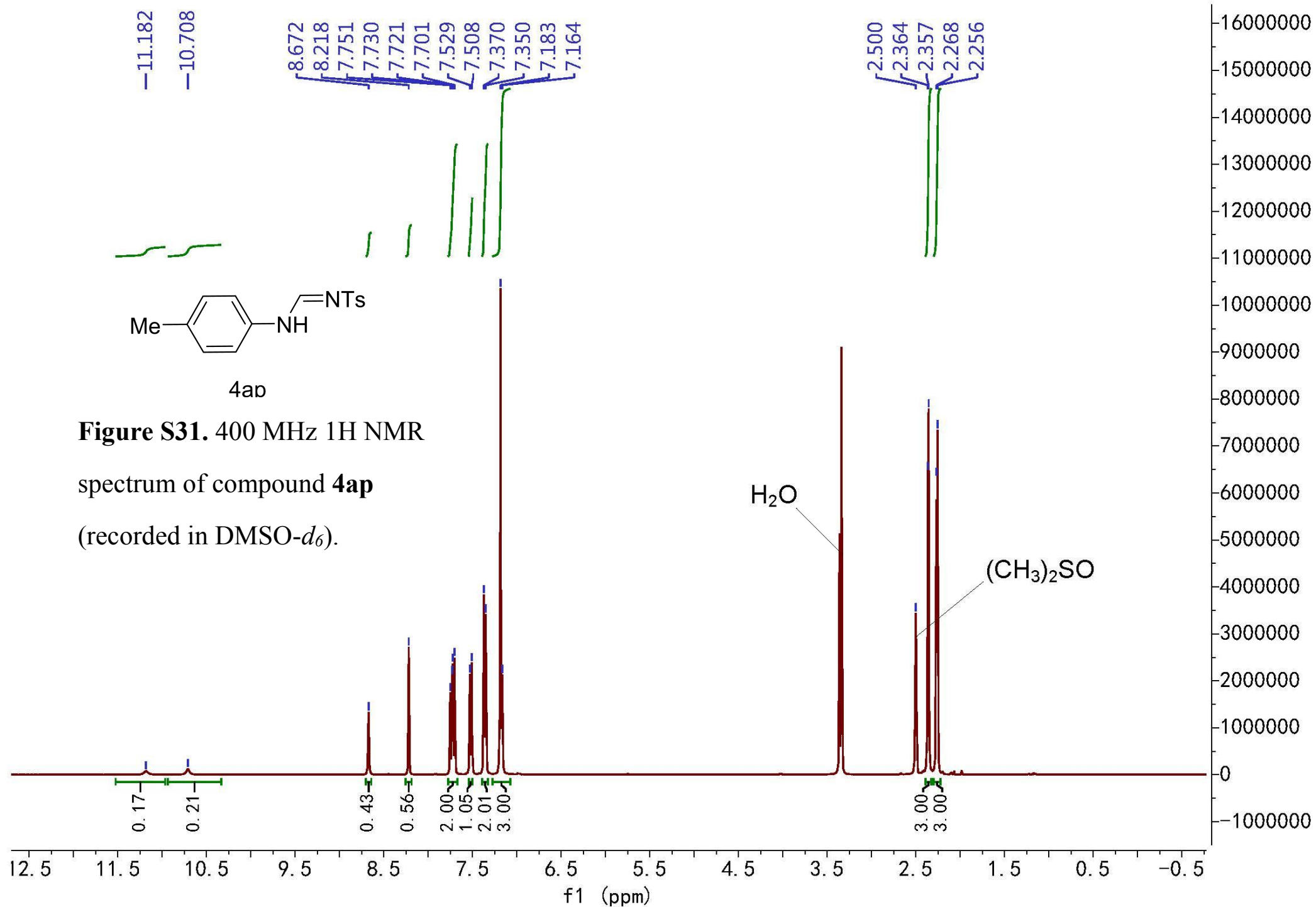


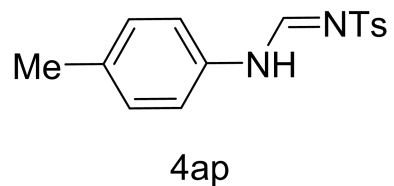




**Figure S30.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ao** (recorded in  $\text{DMSO-}d_6$ ).



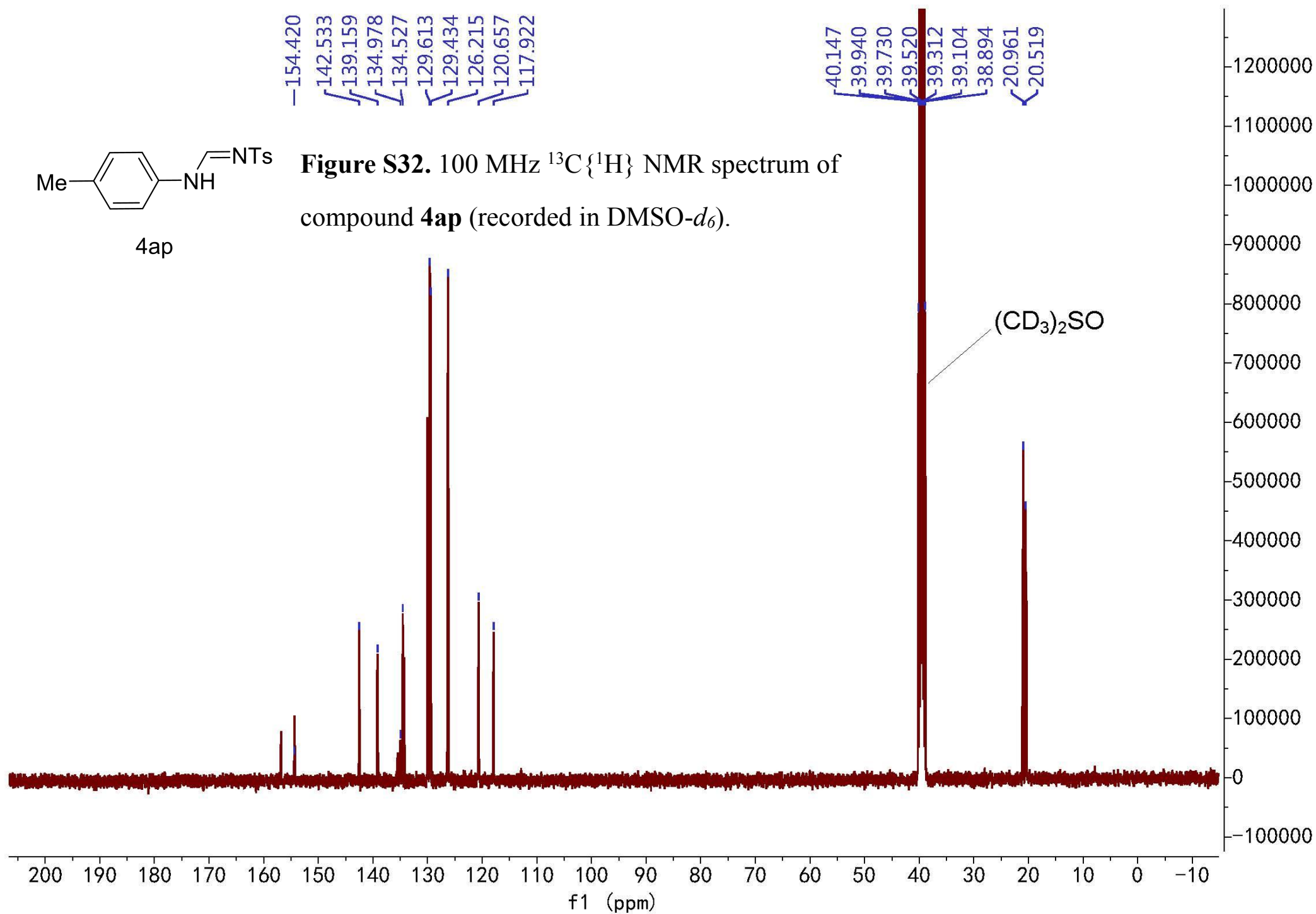


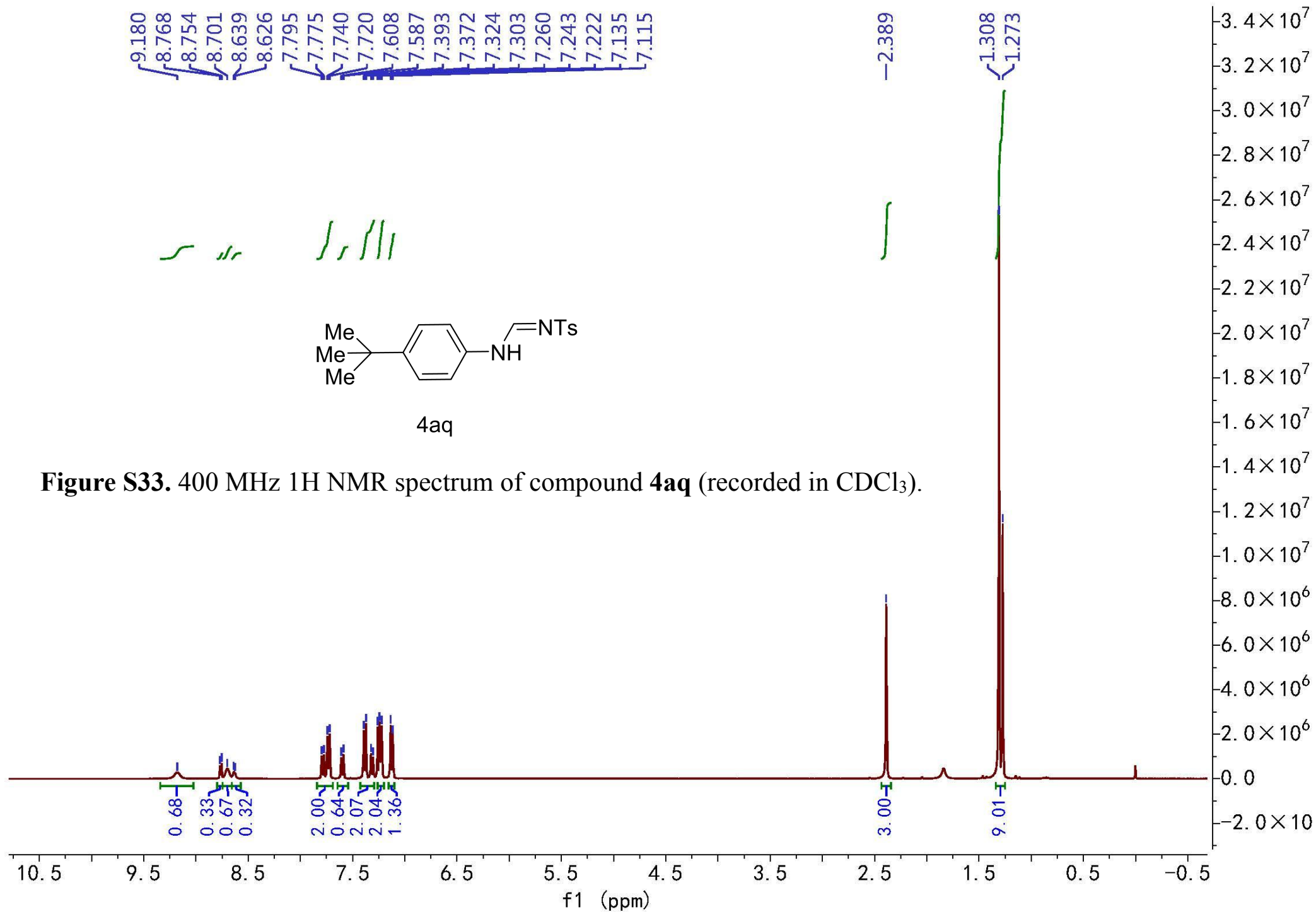


154.420  
142.533  
139.159  
134.978  
134.527  
129.613  
129.434  
126.215  
120.657  
117.922

40.147  
39.940  
39.730  
39.520  
39.312  
39.104  
38.894  
20.961  
20.519

**Figure S32.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ap** (recorded in  $\text{DMSO-}d_6$ ).





**Figure S33.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4aq** (recorded in  $\text{CDCl}_3$ ).

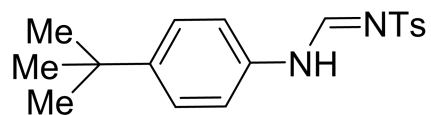


155.486  
149.580  
143.383  
138.323  
134.570  
129.722  
126.859  
125.960  
120.730  
118.547

77.478  
77.160  
76.842

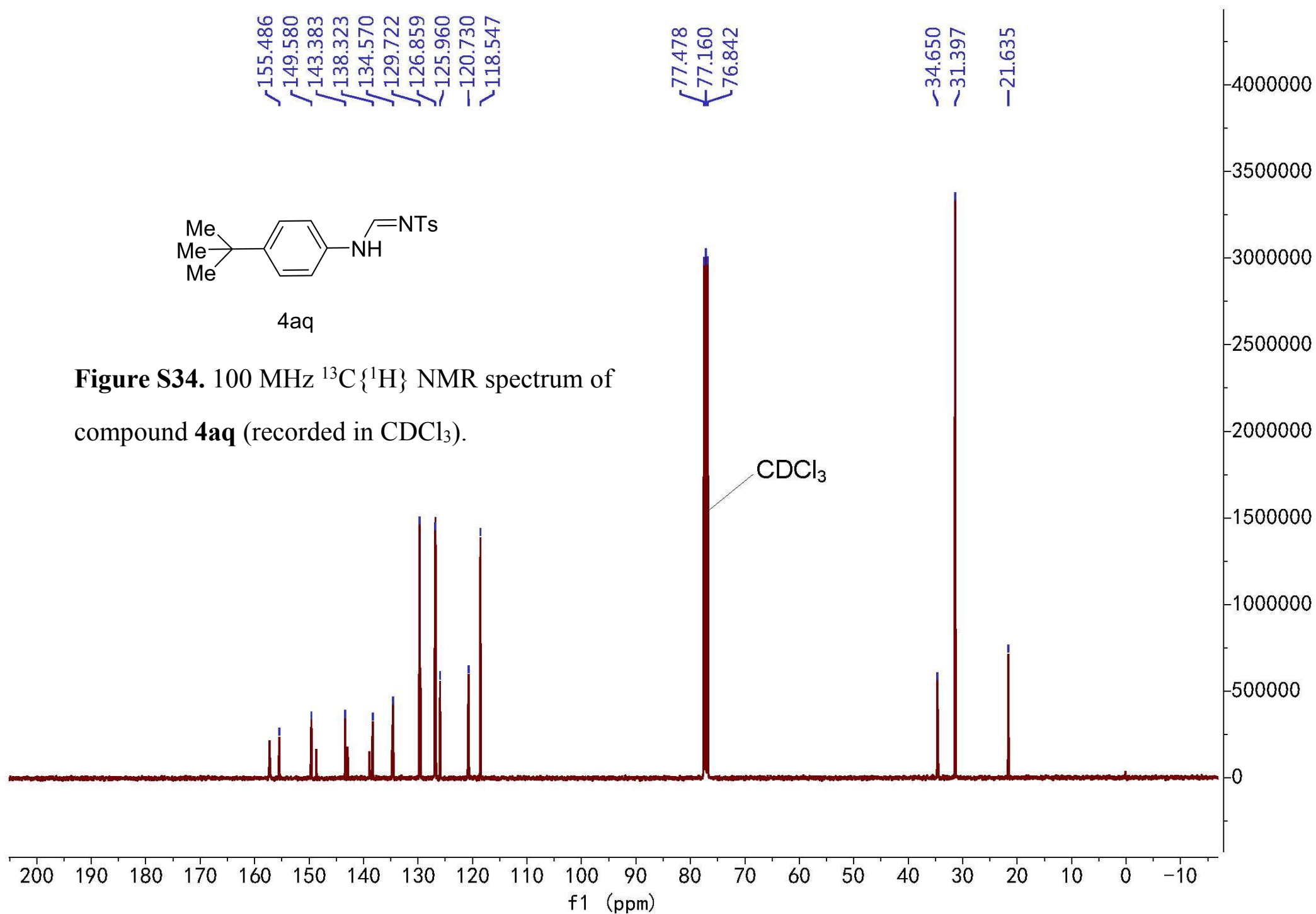
34.650  
31.397

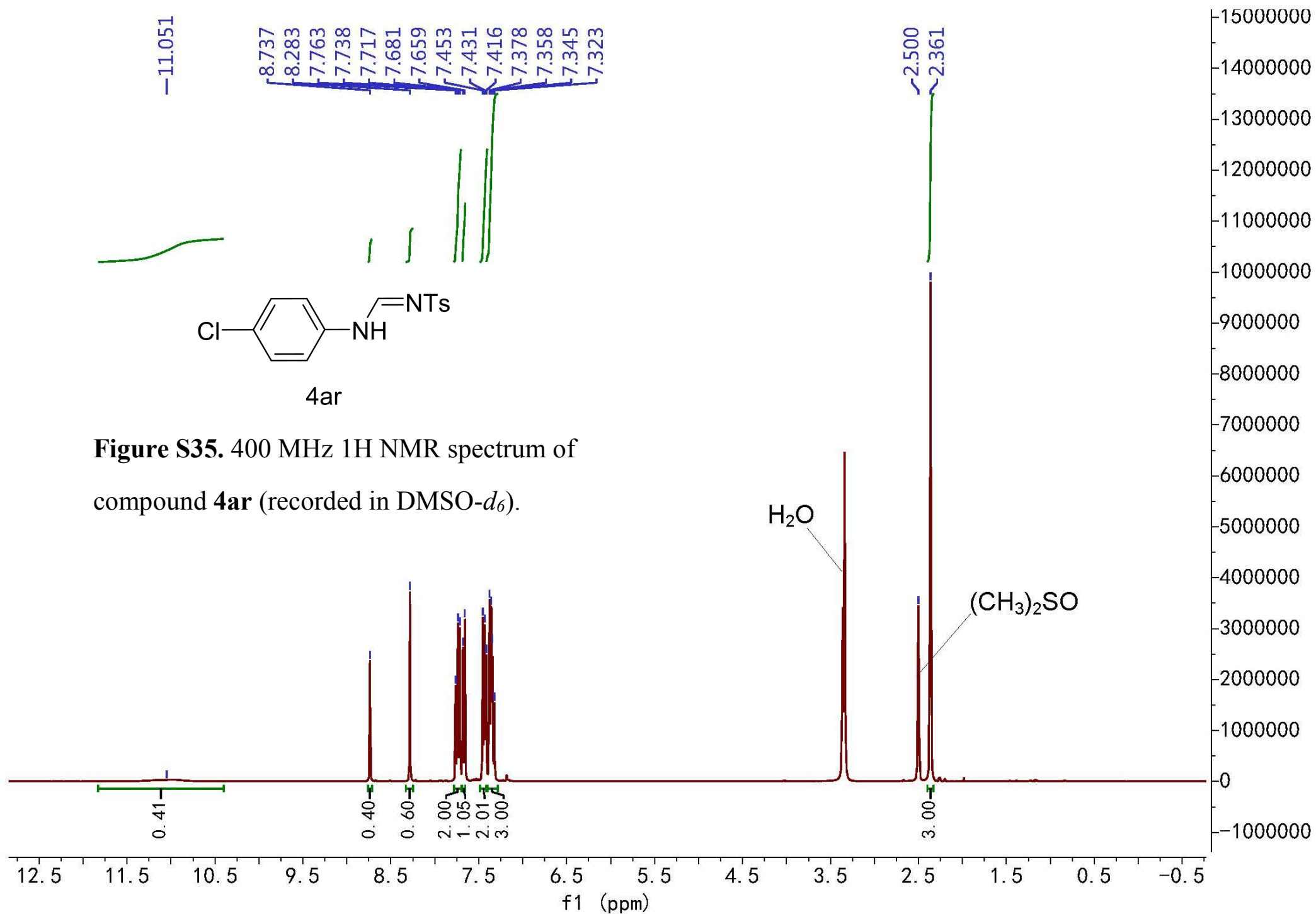
21.635



4aq

**Figure S34.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4aq** (recorded in  $\text{CDCl}_3$ ).

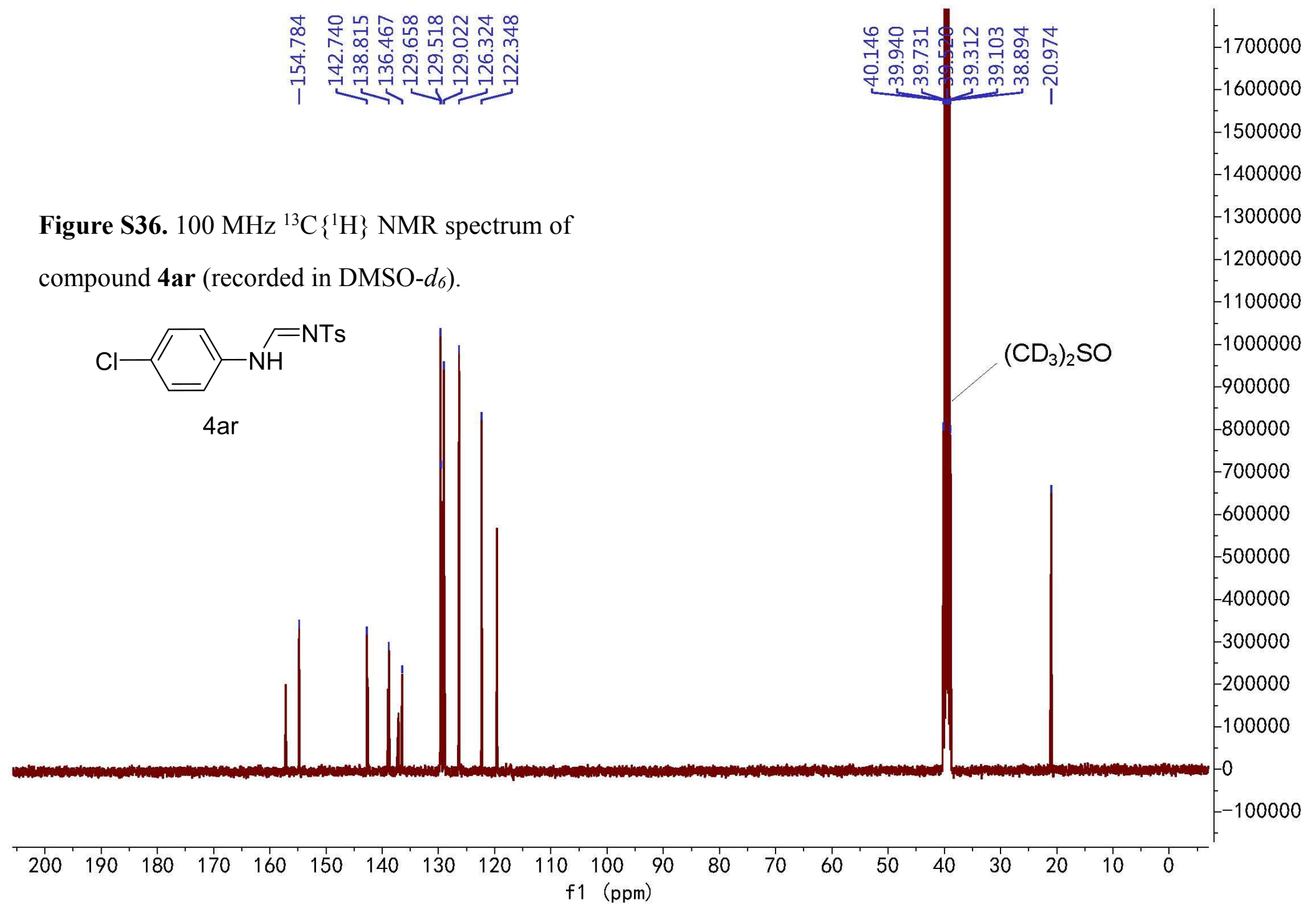
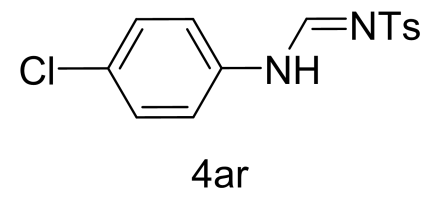


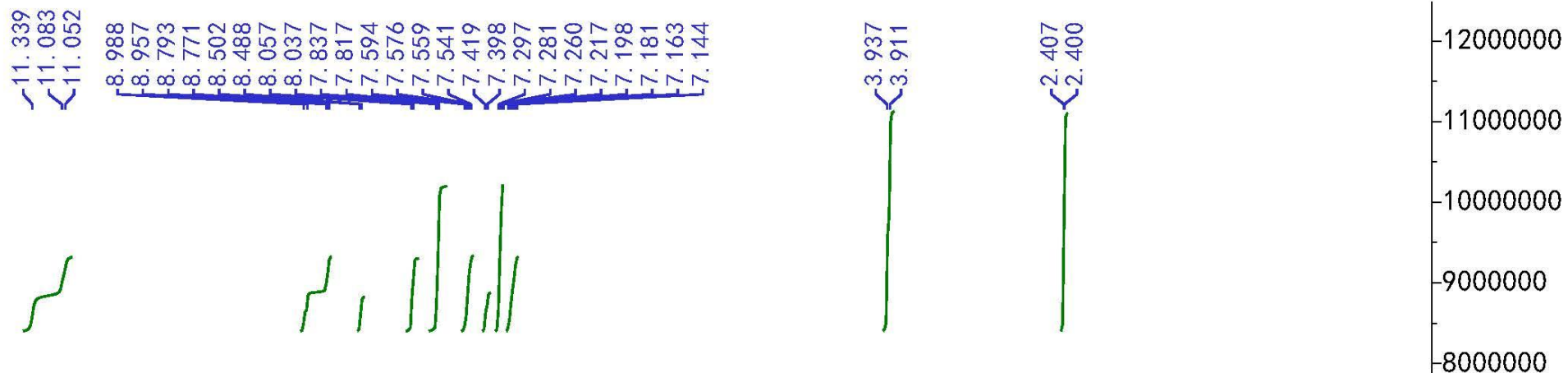


154.784  
142.740  
138.815  
136.467  
129.658  
129.518  
129.022  
126.324  
122.348

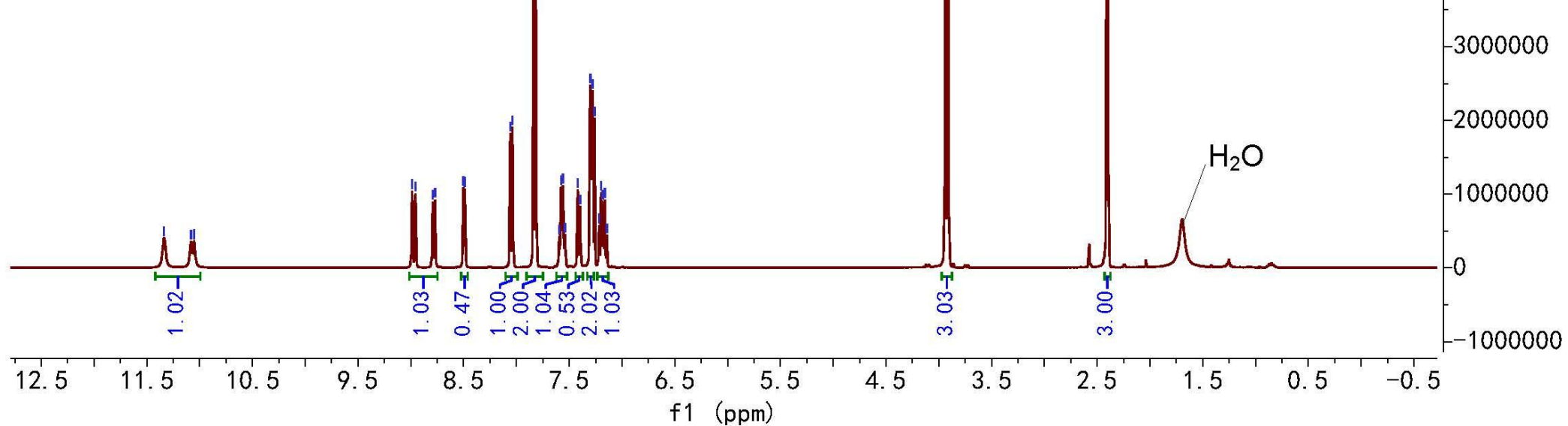
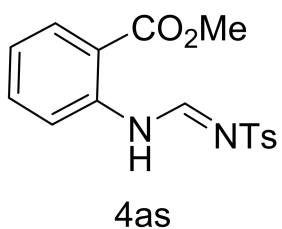
40.146  
39.940  
39.731  
39.520  
39.312  
39.103  
38.894  
20.974

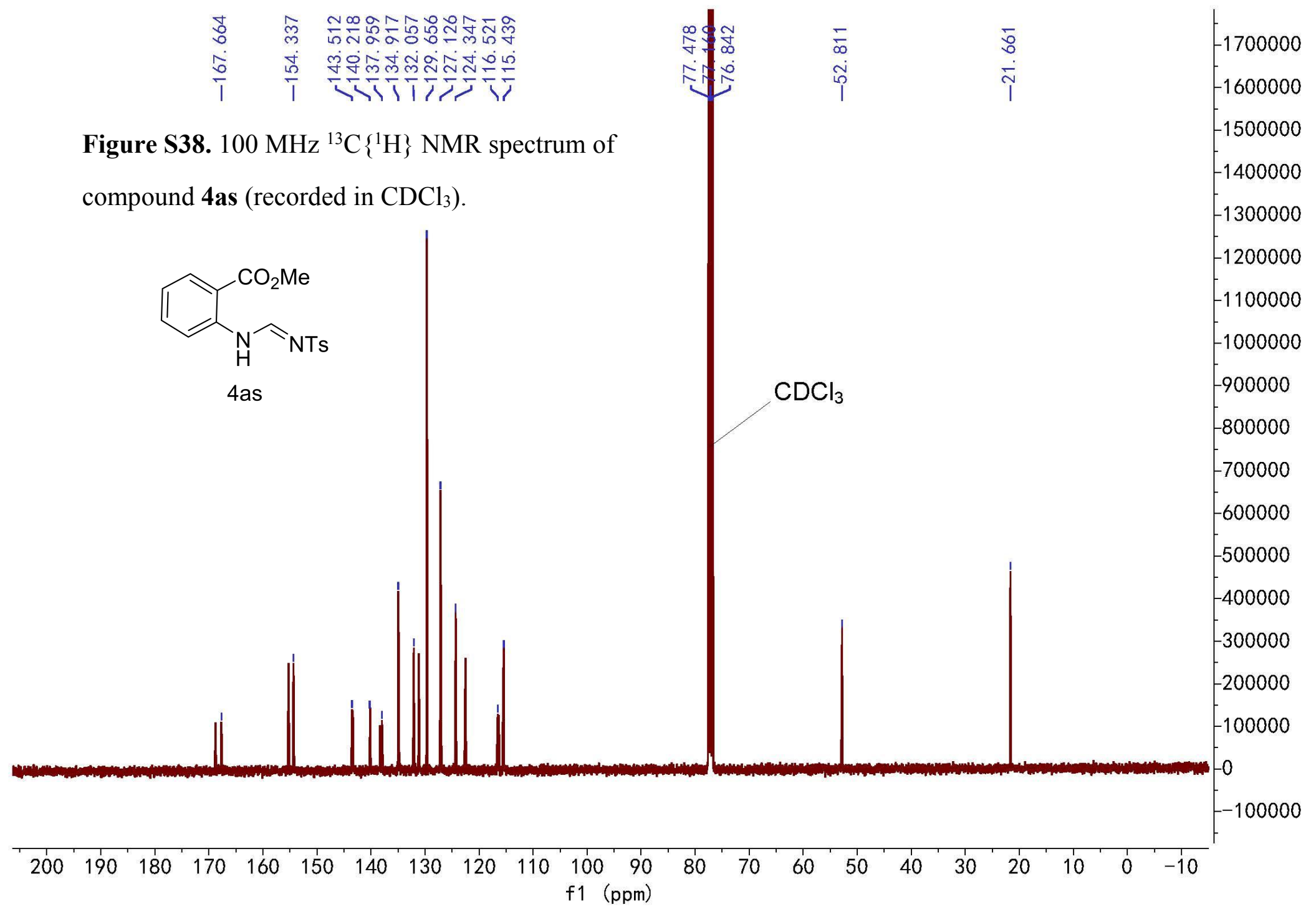
**Figure S36.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ar** (recorded in  $\text{DMSO-}d_6$ ).



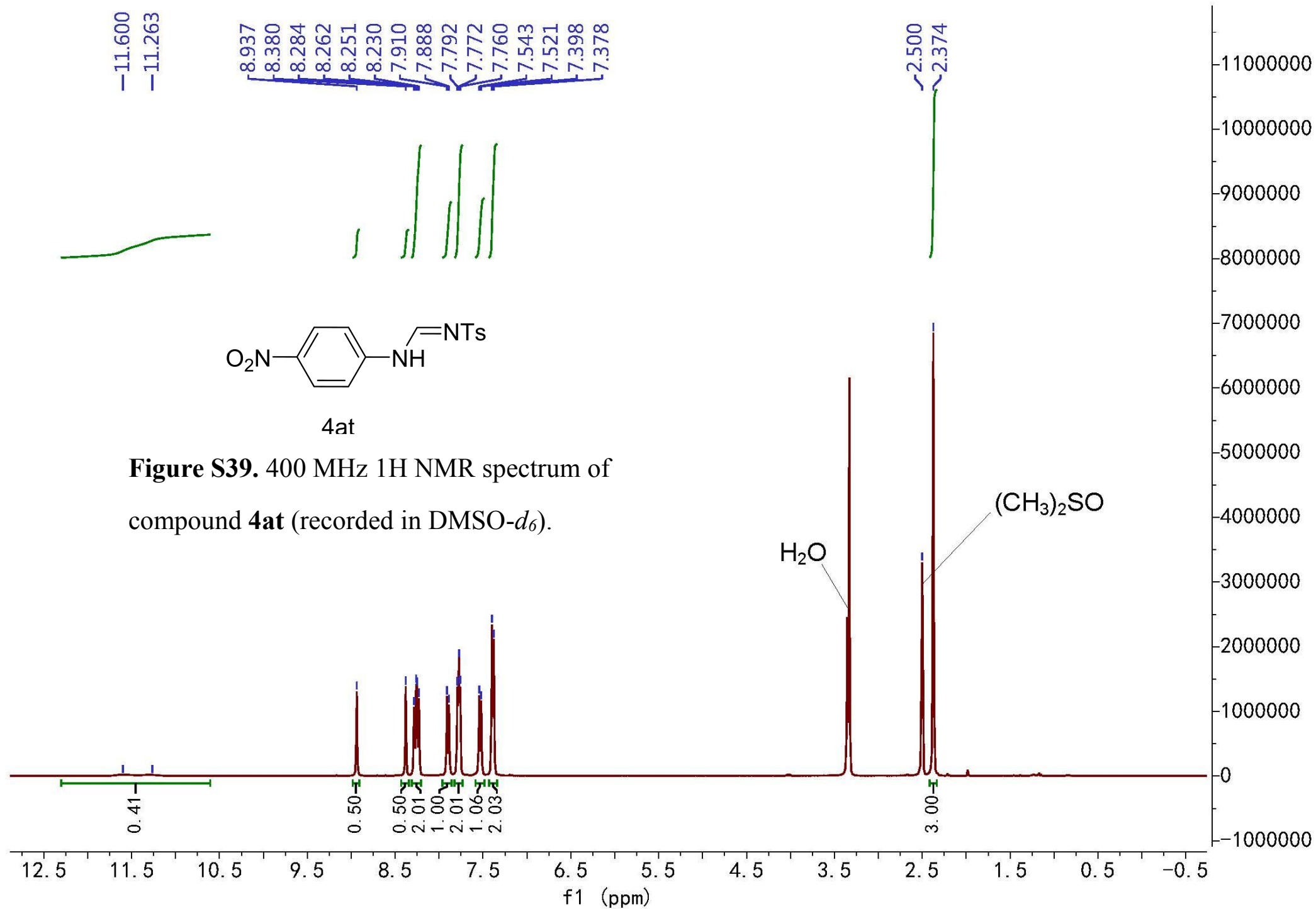


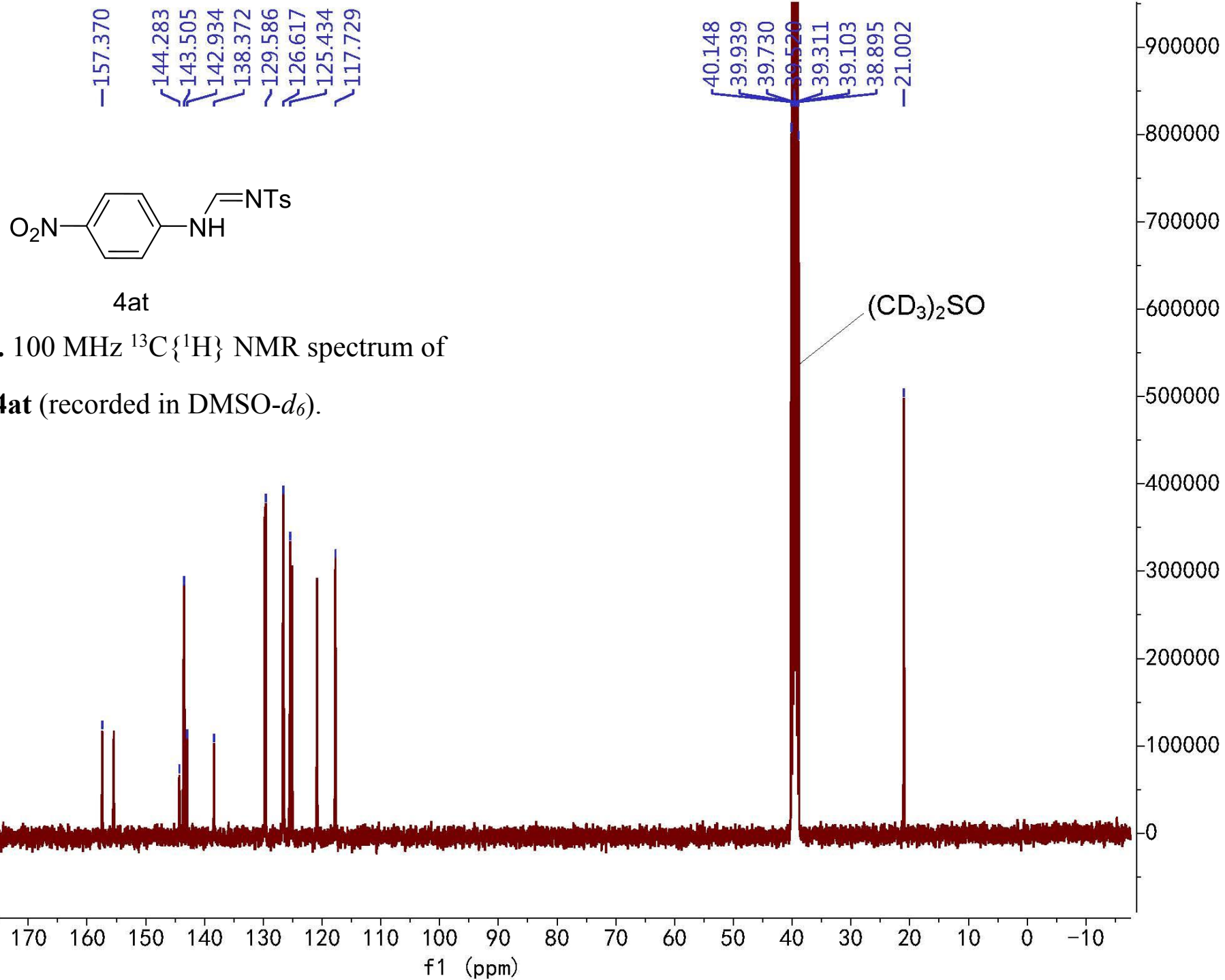
**Figure S37.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4as** (recorded in  $\text{CDCl}_3$ ).



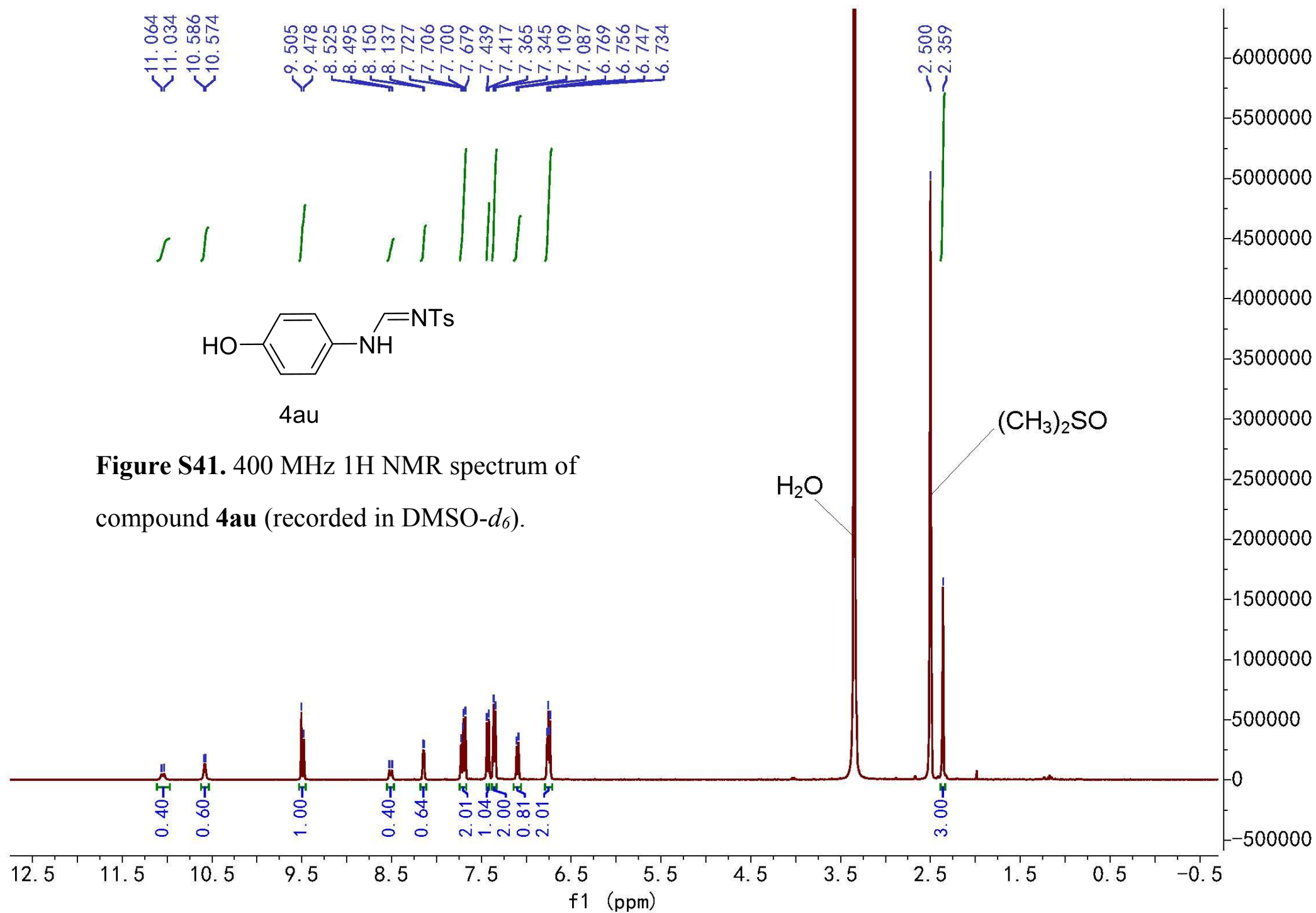


**Figure S38.** 100 MHz <sup>13</sup>C {<sup>1</sup>H} NMR spectrum of compound **4as** (recorded in CDCl<sub>3</sub>).

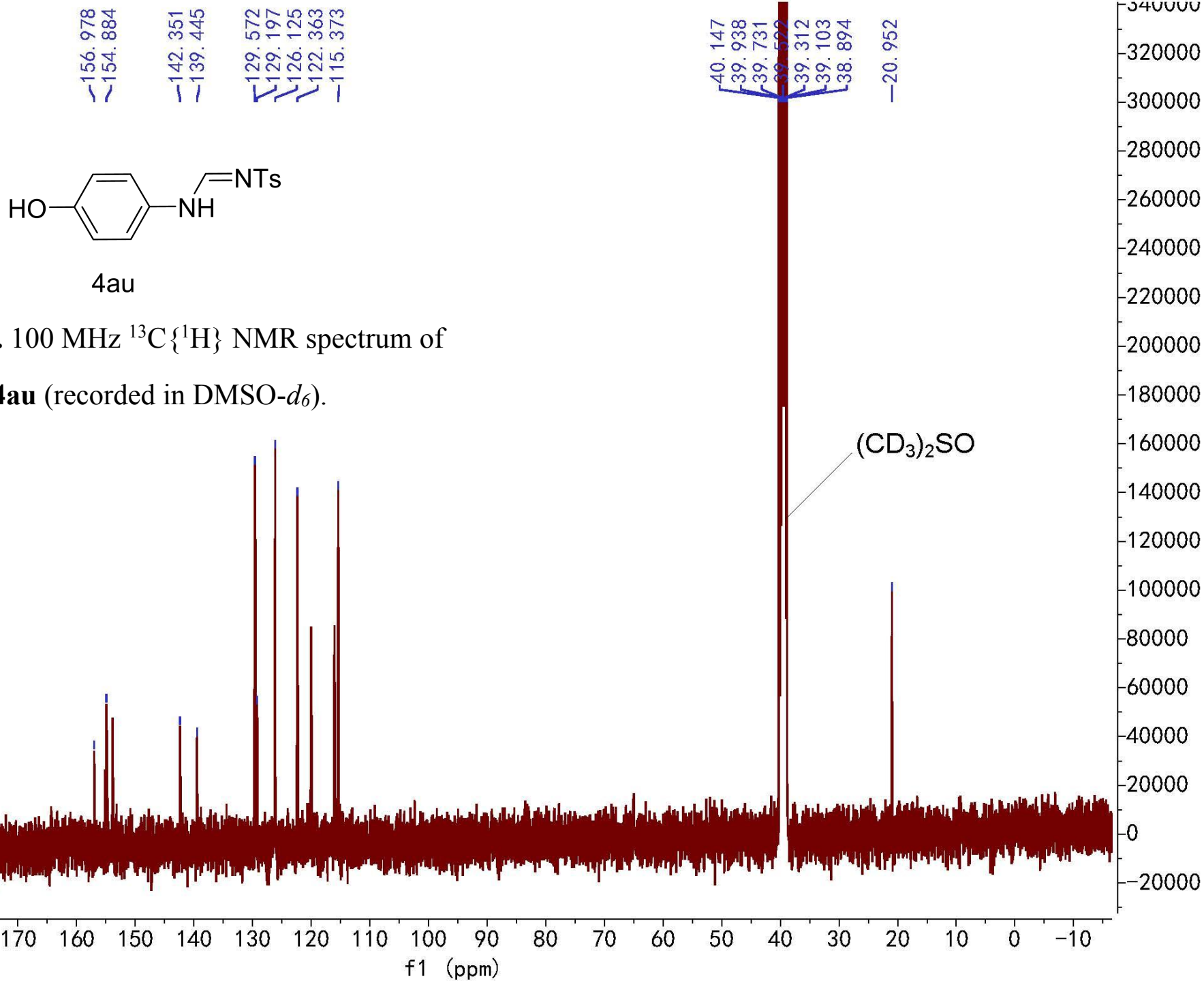


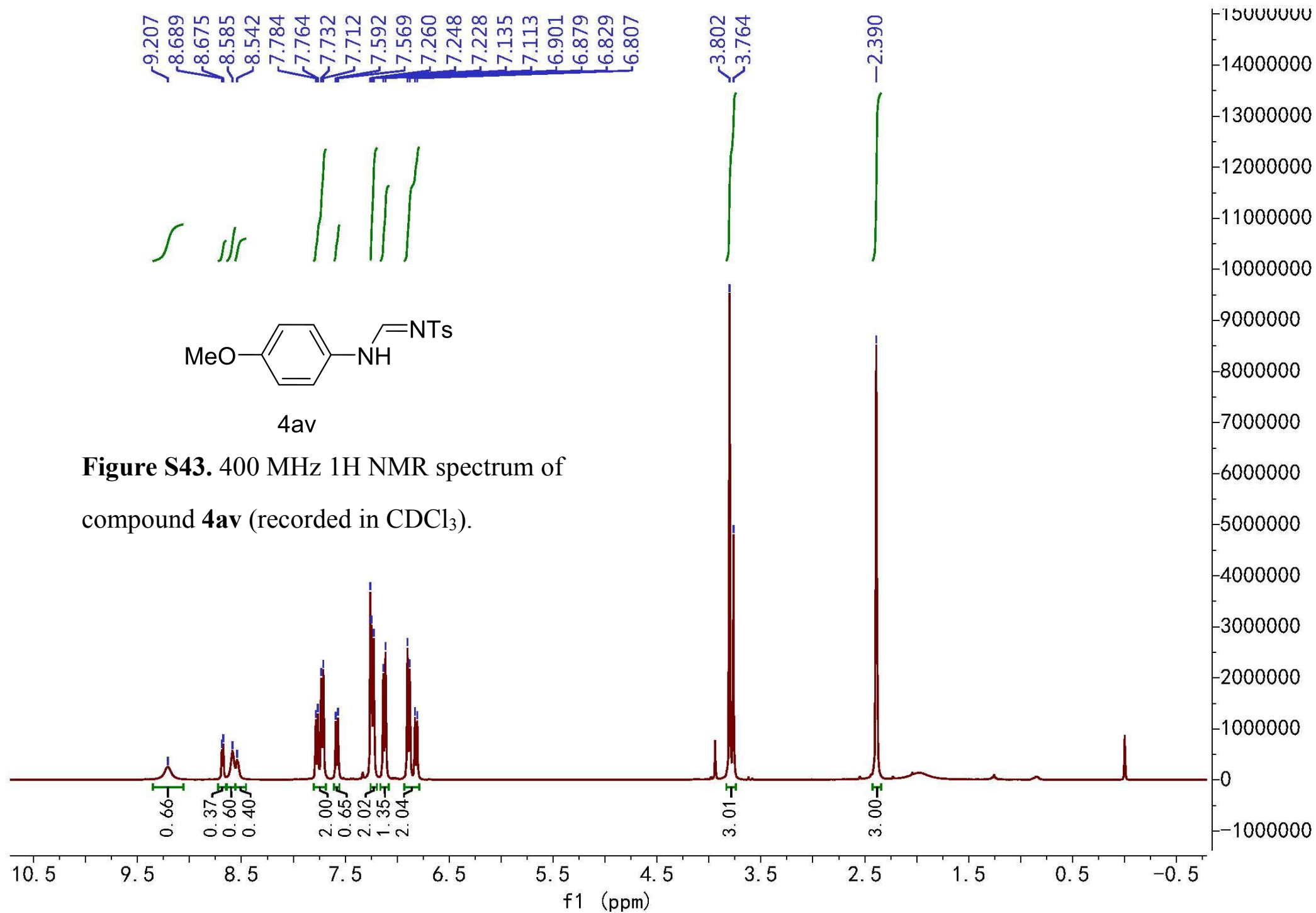


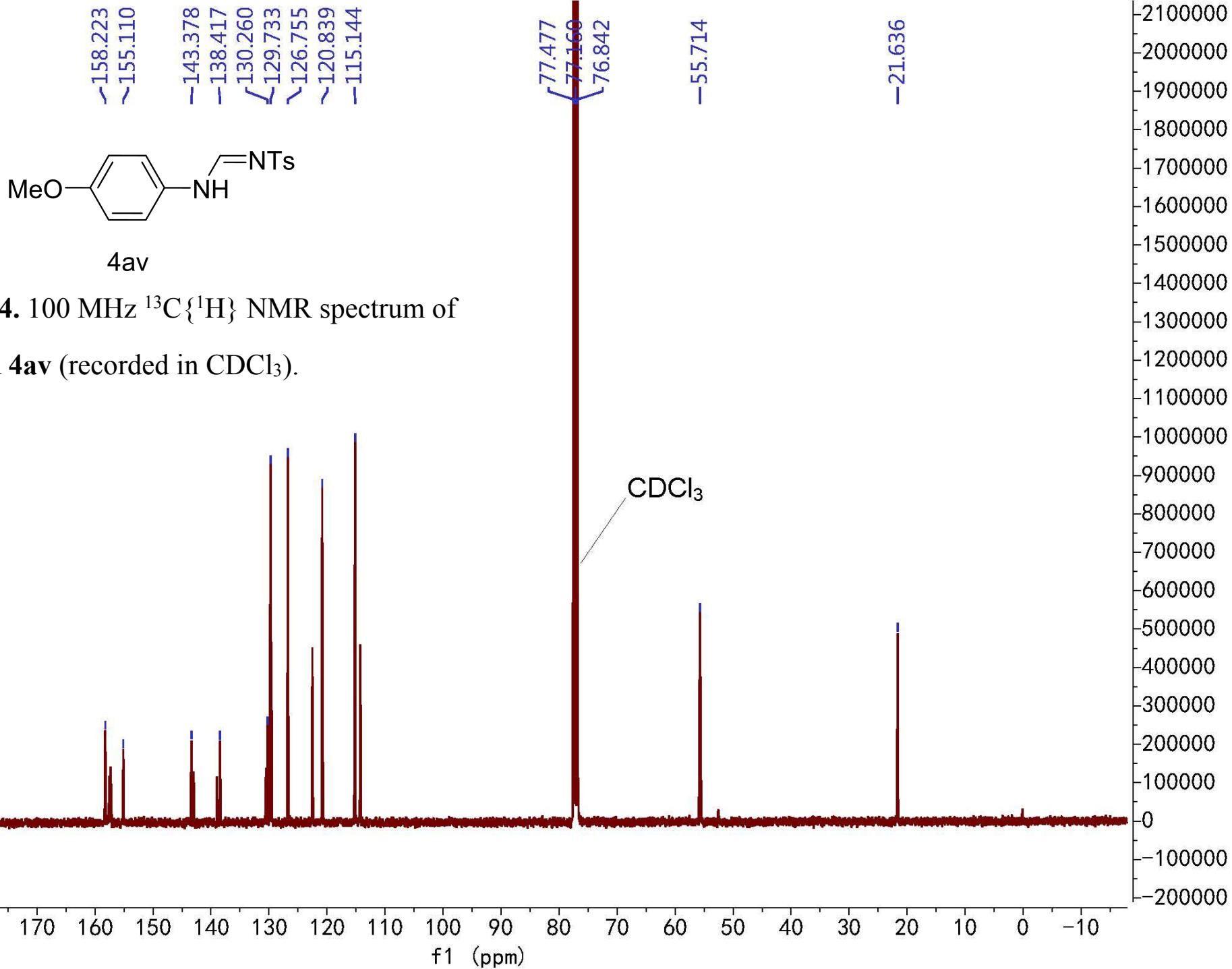
**Figure S40.** 100 MHz  $^{13}C\{^1H\}$  NMR spectrum of compound **4at** (recorded in DMSO- $d_6$ ).







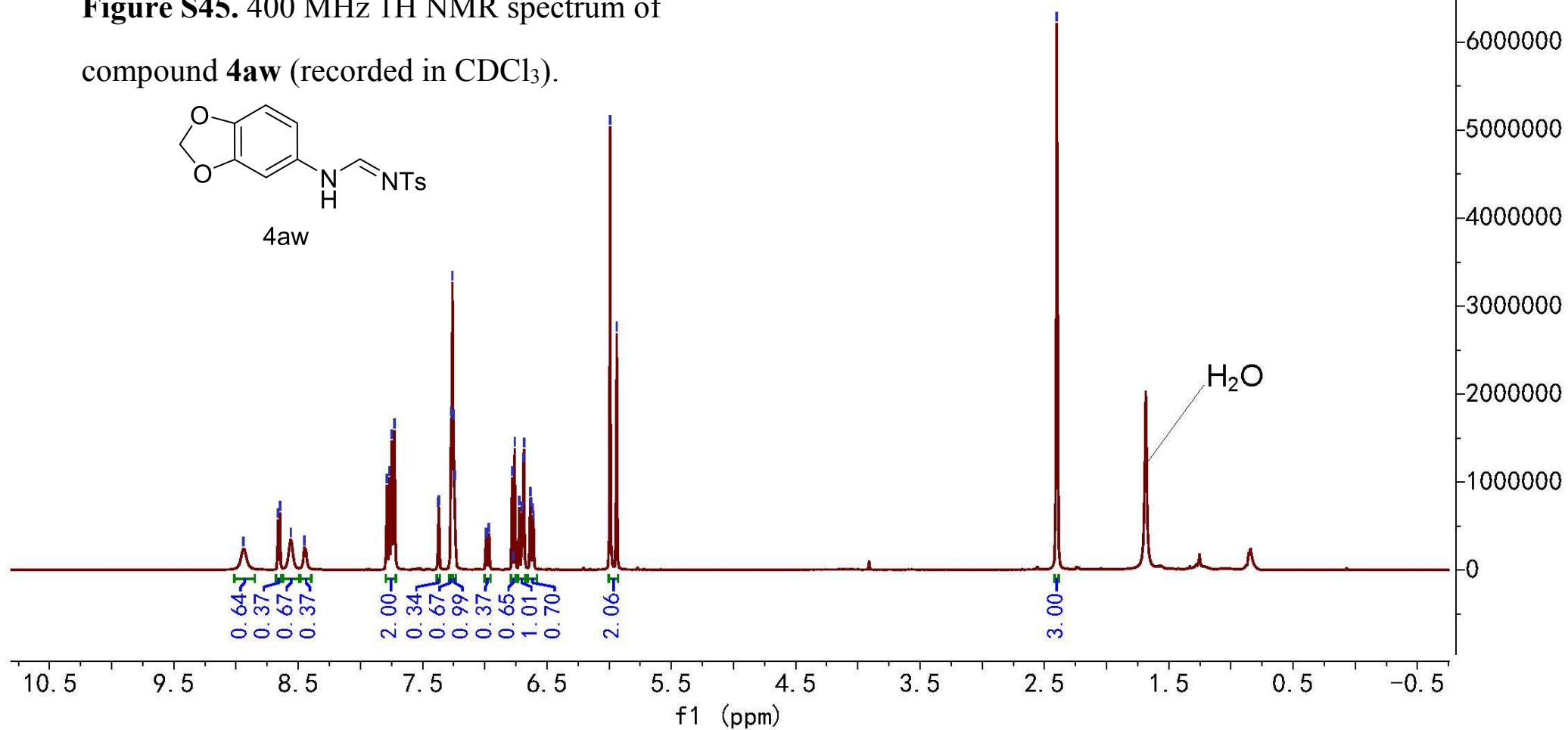
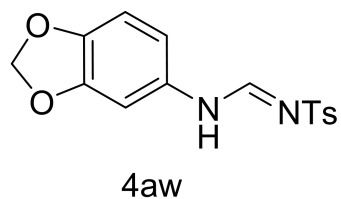




**Figure S44.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4av** (recorded in  $\text{CDCl}_3$ ).



**Figure S45.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4aw** (recorded in  $\text{CDCl}_3$ ).



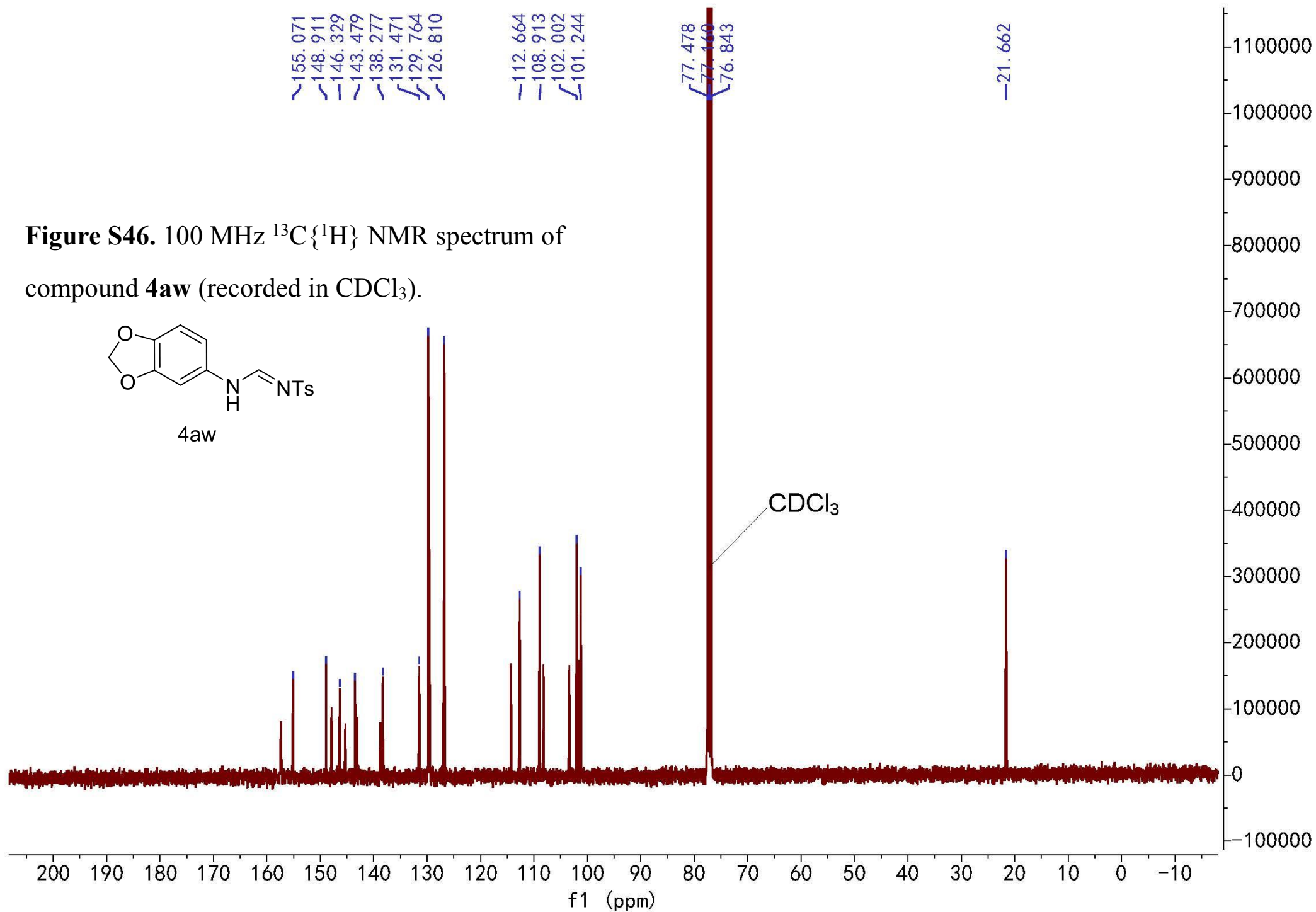
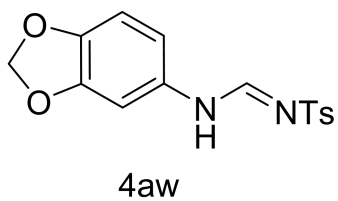
155.071  
148.911  
146.329  
143.479  
138.277  
131.471  
129.764  
126.810

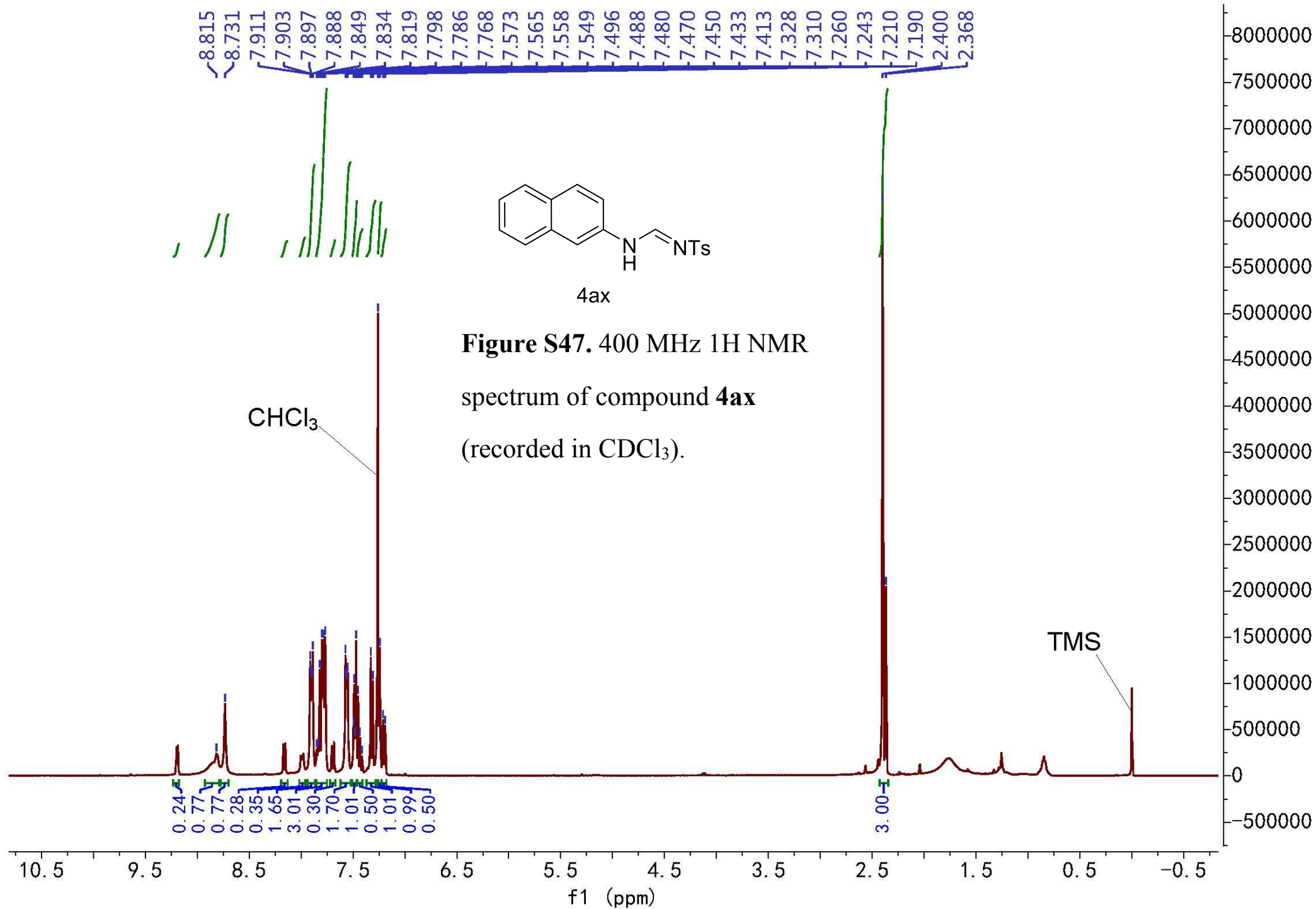
112.664  
108.913  
102.002  
101.244

77.478  
77.160  
76.843

-21.662

**Figure S46.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4aw** (recorded in  $\text{CDCl}_3$ ).



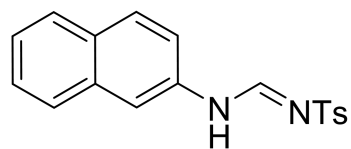


158.910  
143.481  
138.147  
134.305  
133.048  
129.734  
128.798  
127.823  
127.493  
127.194  
126.953  
126.349  
125.616  
120.979  
118.542

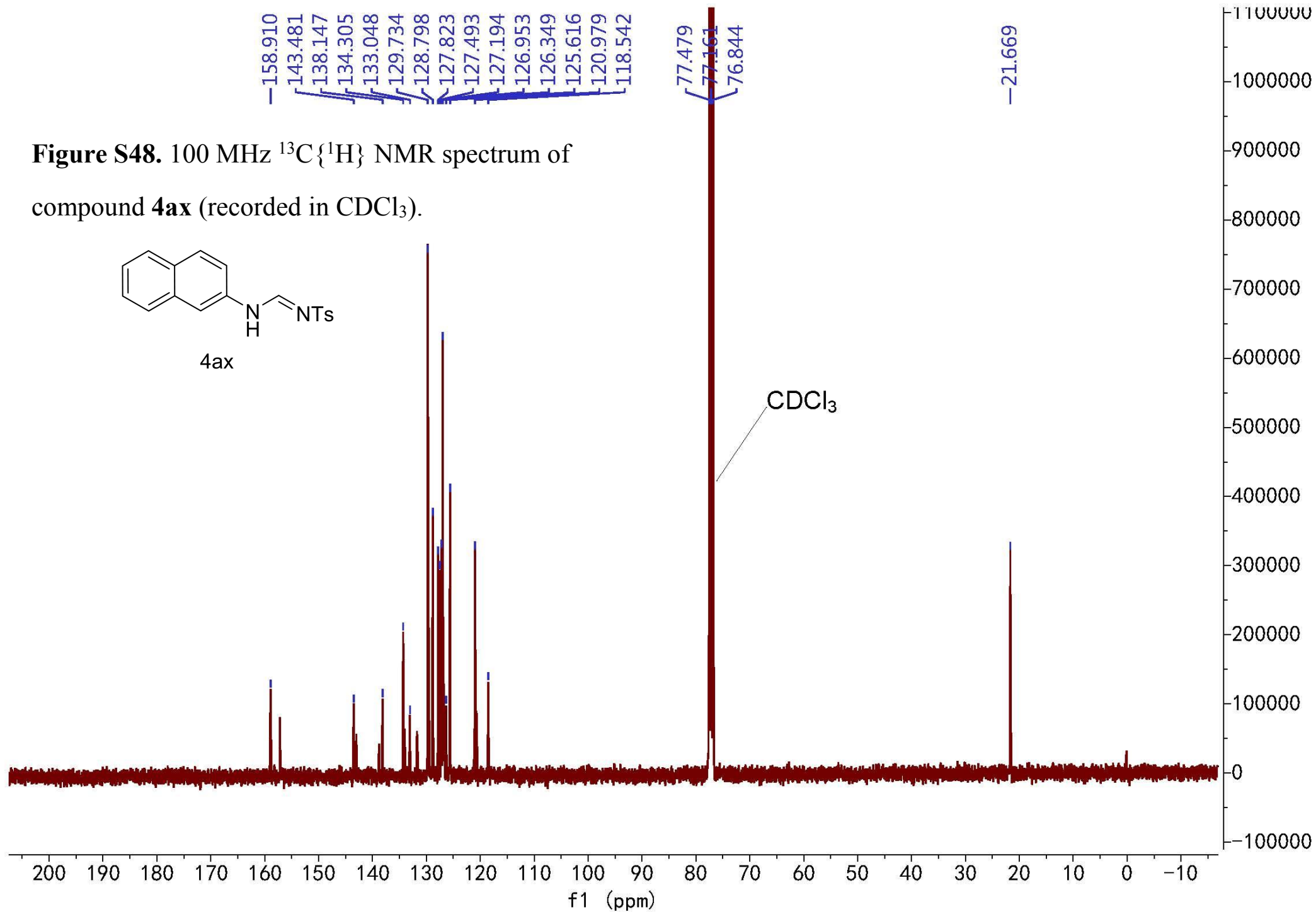
77.479  
77.161  
76.844

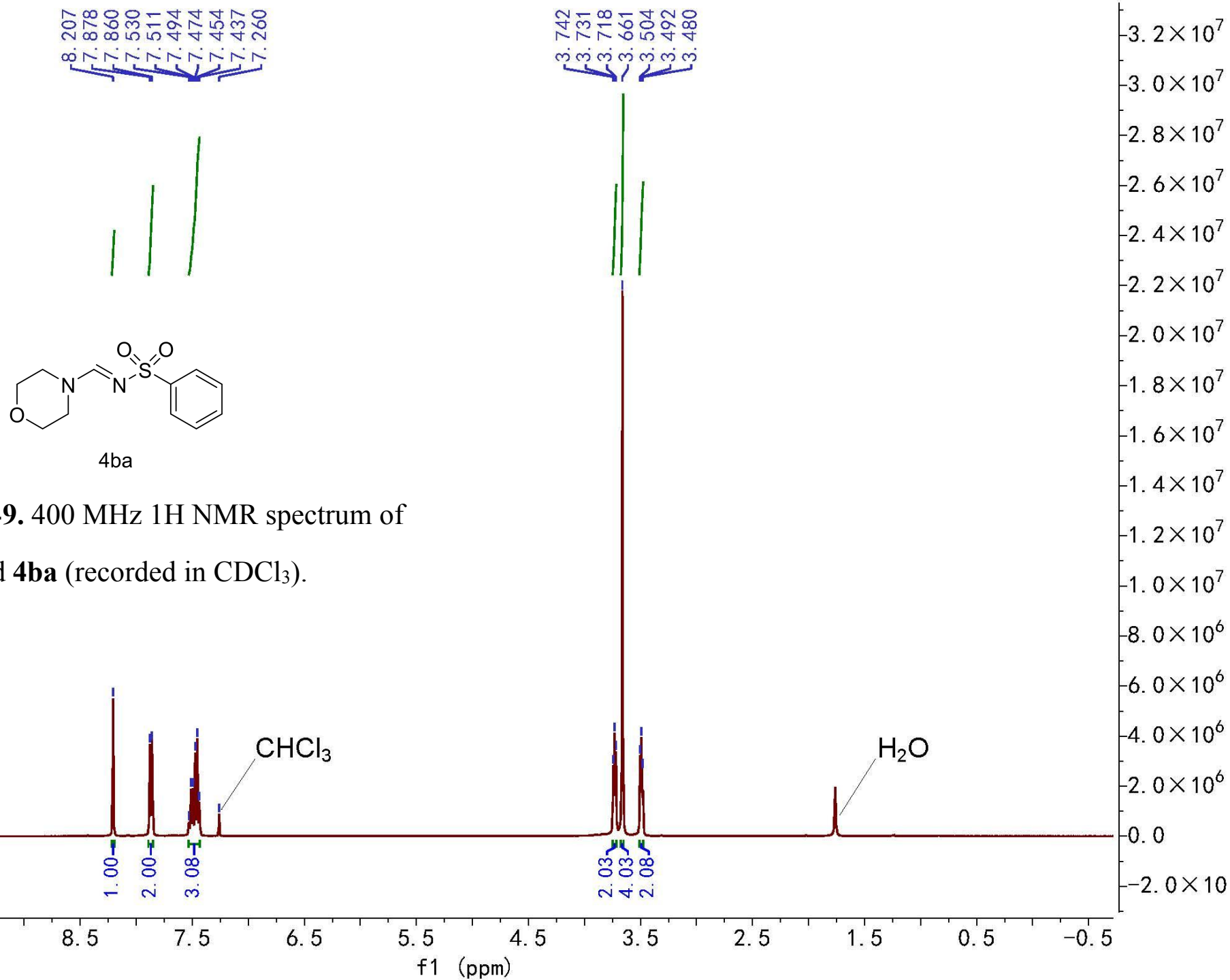
21.669

**Figure S48.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4ax** (recorded in  $\text{CDCl}_3$ ).

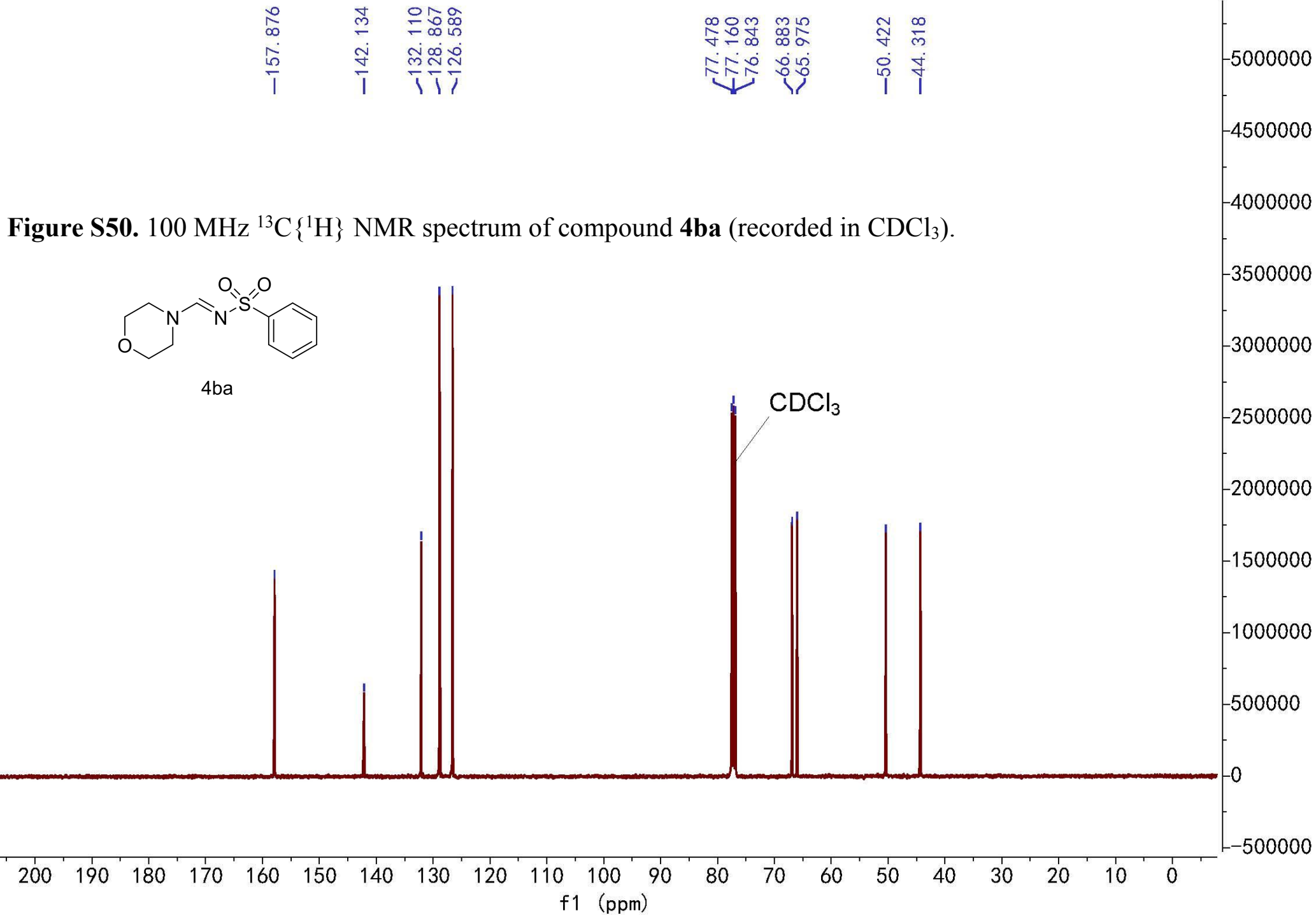


**4ax**



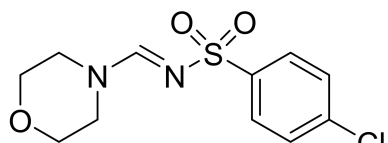






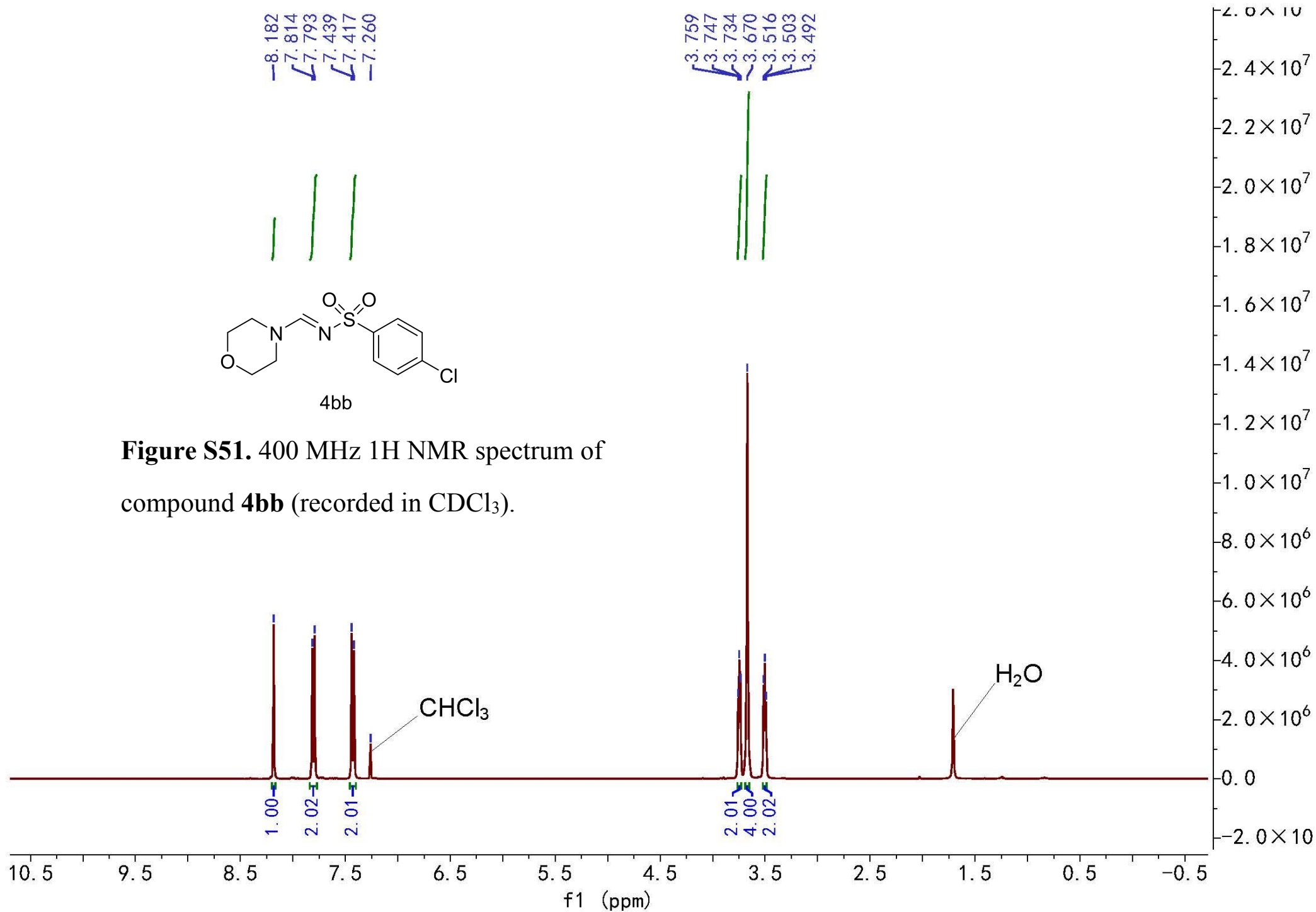
8.182  
7.814  
7.793  
7.439  
7.417  
7.260

3.759  
3.747  
3.734  
3.670  
3.516  
3.503  
3.492



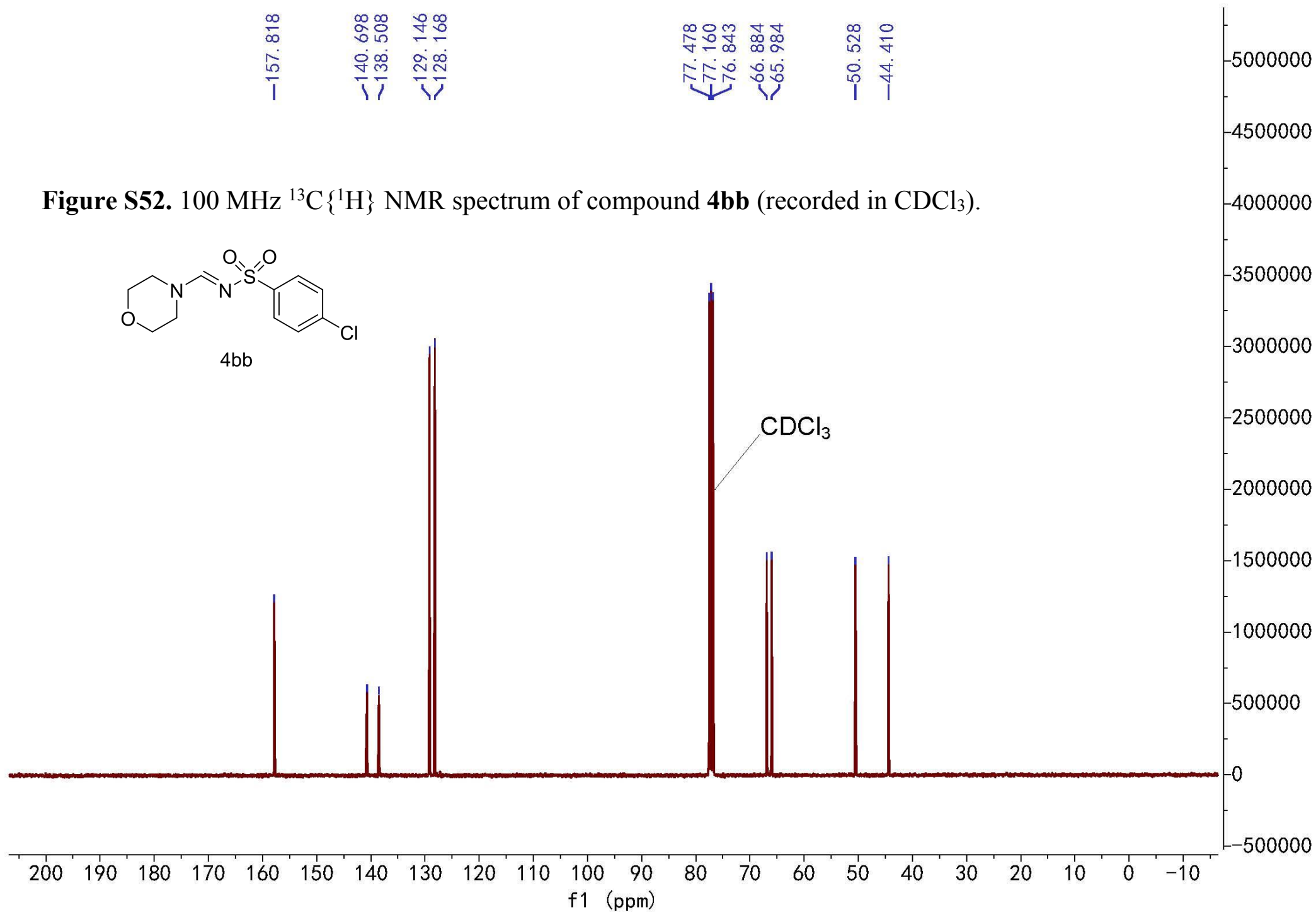
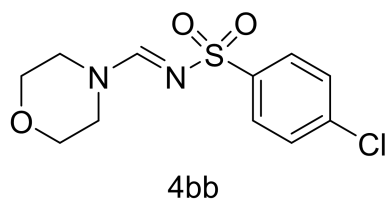
4bb

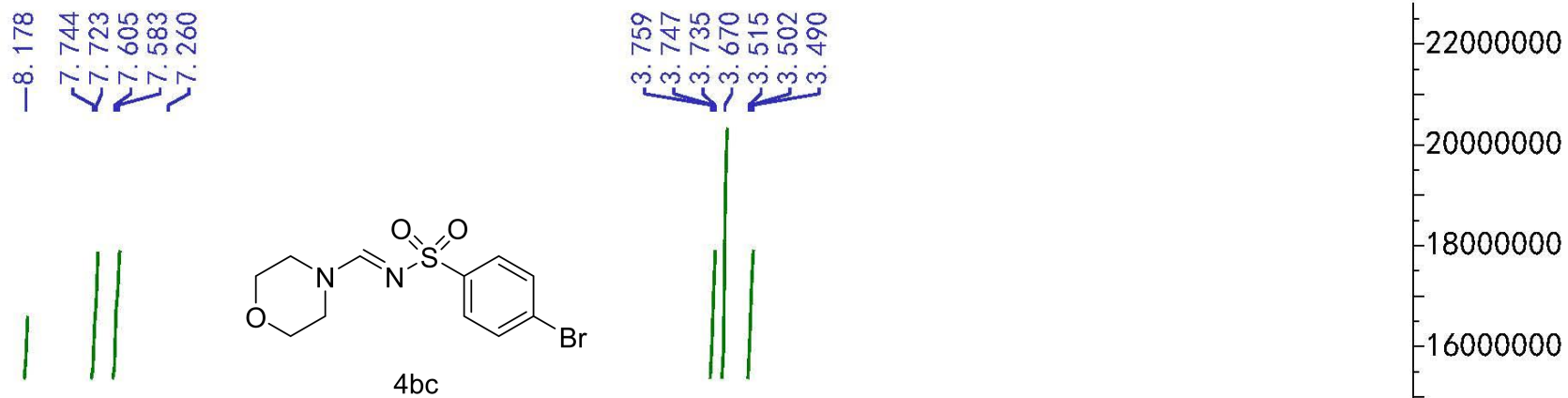
**Figure S51.** 400 MHz <sup>1</sup>H NMR spectrum of compound **4bb** (recorded in CDCl<sub>3</sub>).



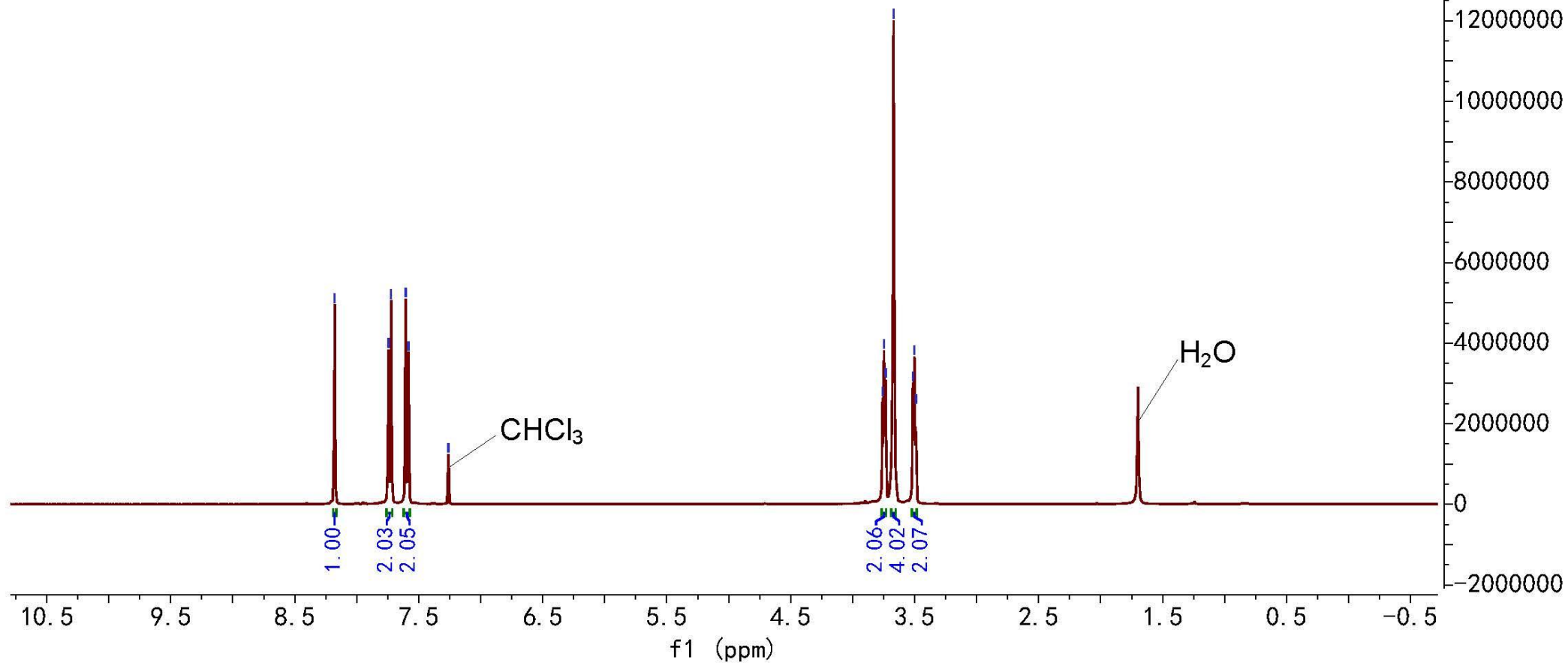
157.818  
140.698  
138.508  
129.146  
128.168  
77.478  
77.160  
76.843  
66.884  
65.984  
50.528  
44.410

**Figure S52.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bb** (recorded in  $\text{CDCl}_3$ ).

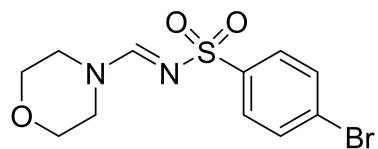




**Figure S53.** 400 MHz <sup>1</sup>H NMR spectrum of compound **4bc** (recorded in CDCl<sub>3</sub>).

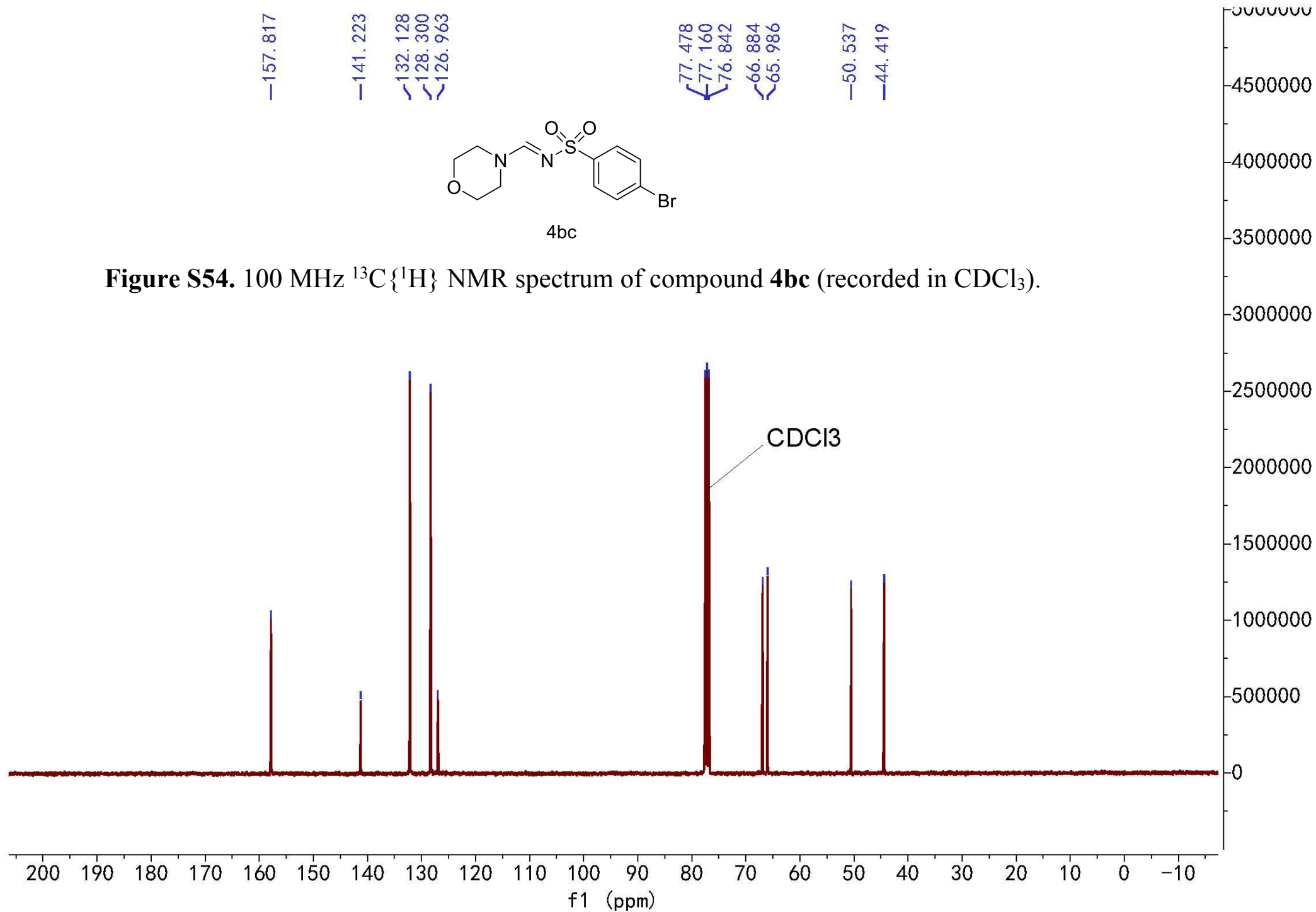


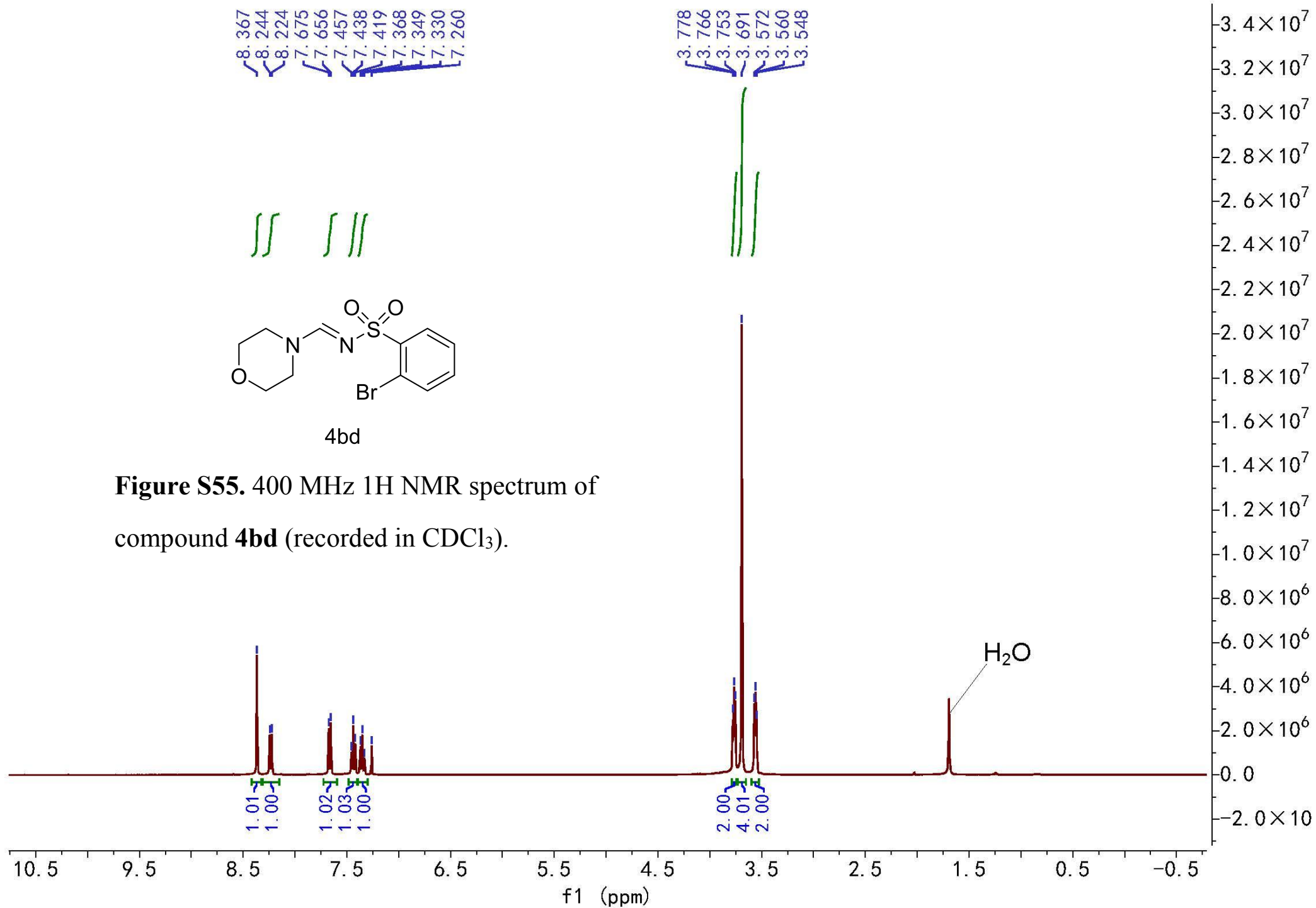
—157.817  
—141.223  
—132.128  
—128.300  
—126.963  
  
—77.478  
—77.160  
—76.842  
—66.884  
—65.986  
  
—50.537  
—44.419

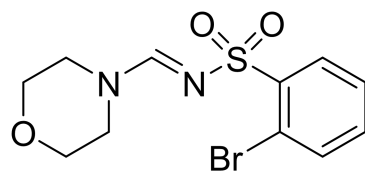


4bc

**Figure S54.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bc** (recorded in  $\text{CDCl}_3$ ).

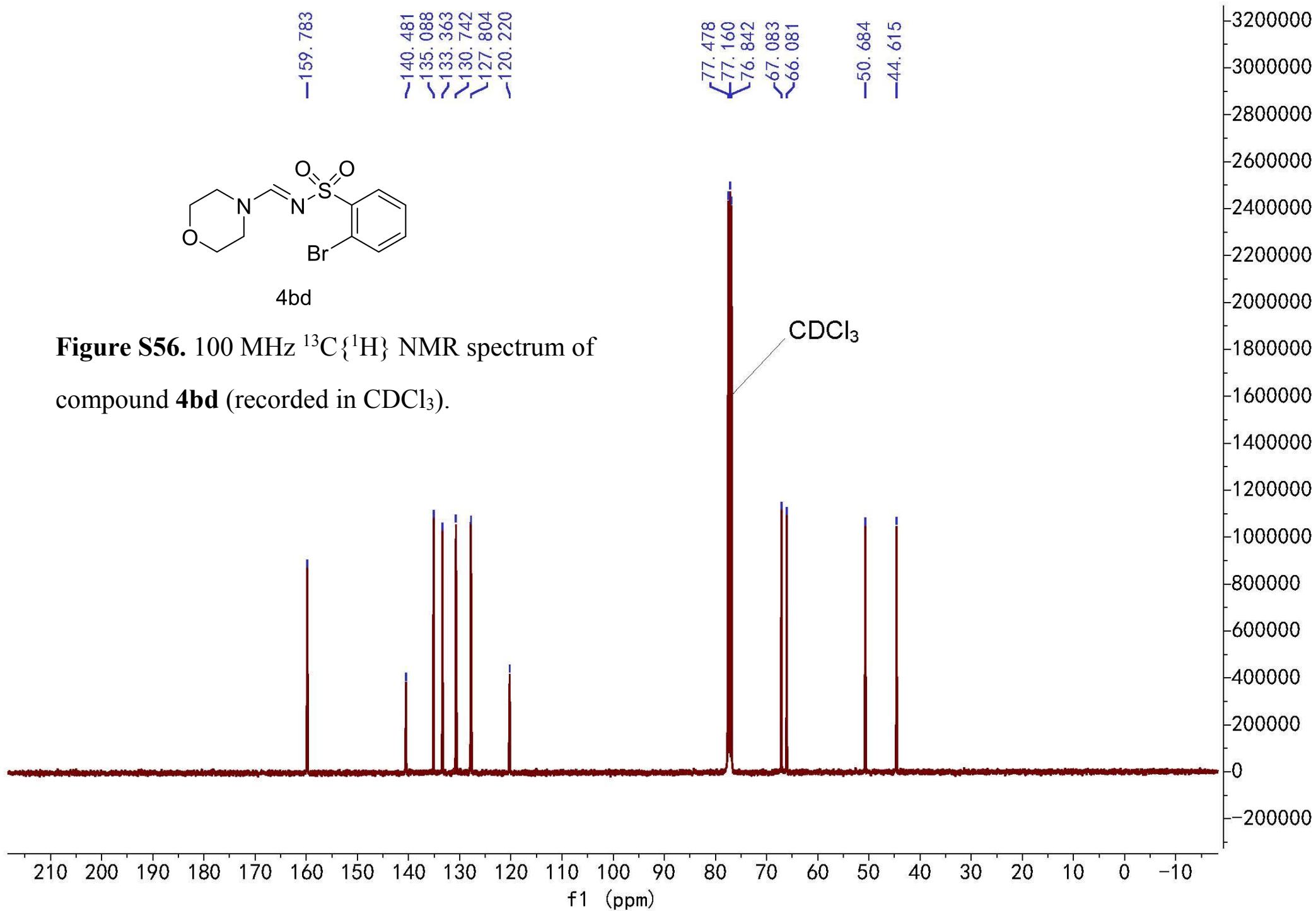


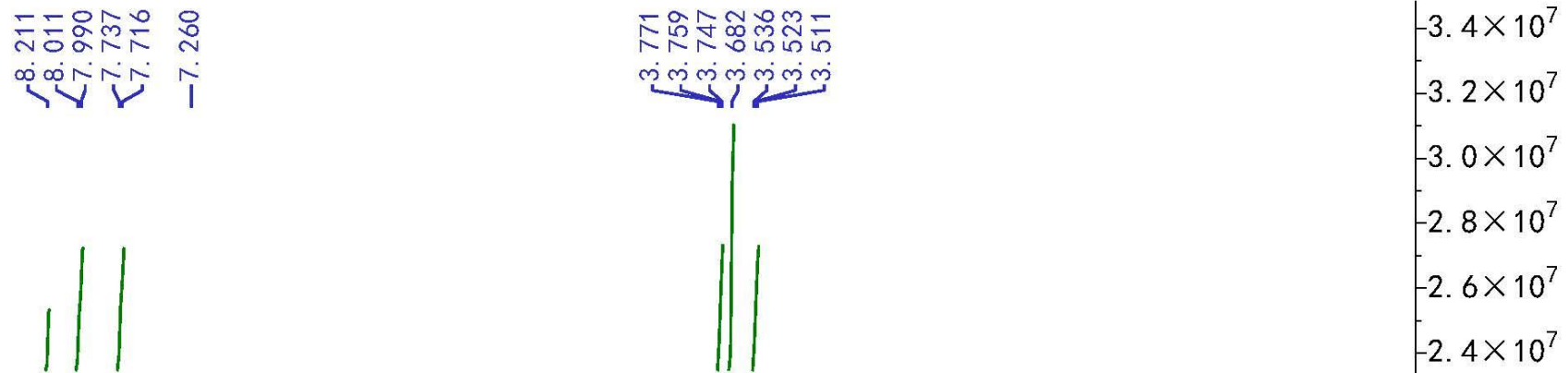




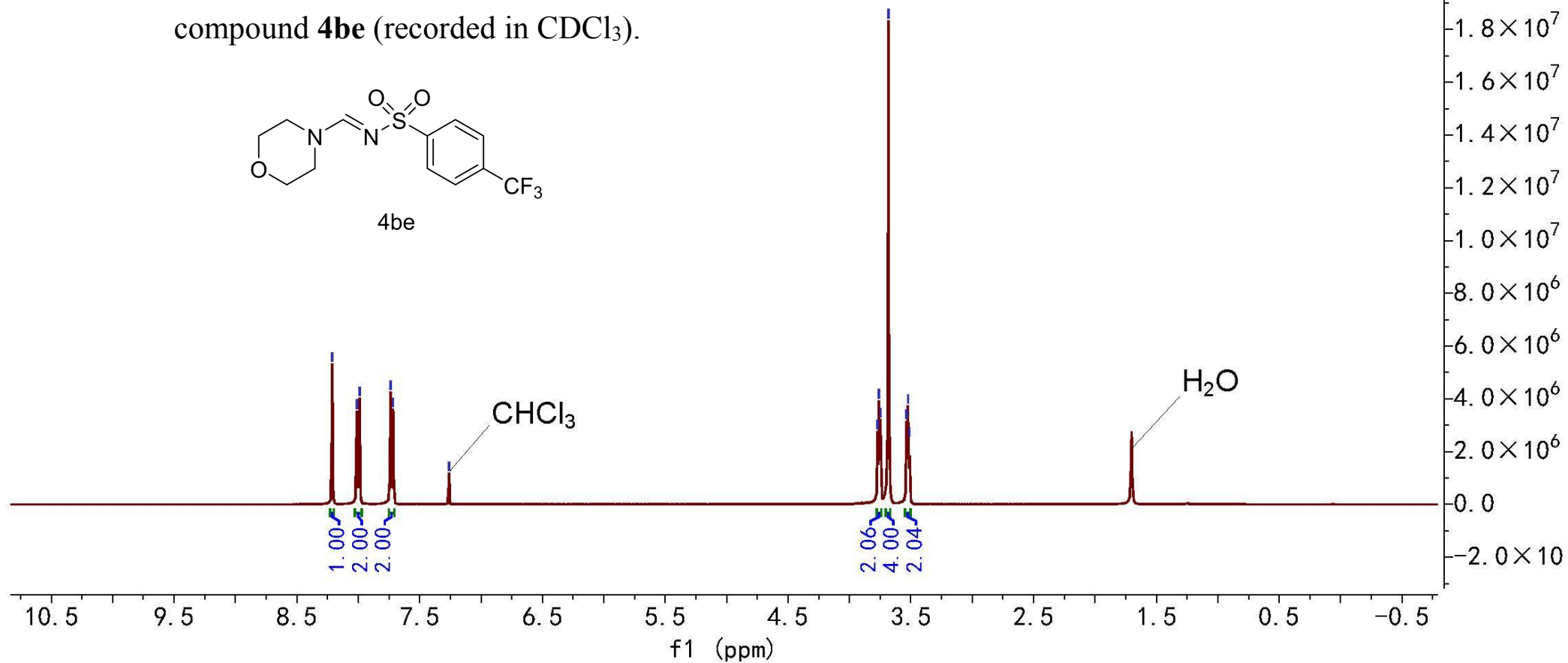
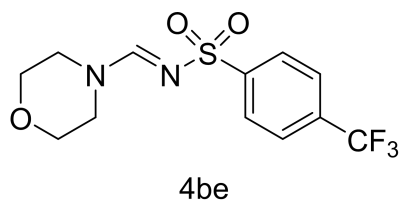
4bd

**Figure S56.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bd** (recorded in  $\text{CDCl}_3$ ).

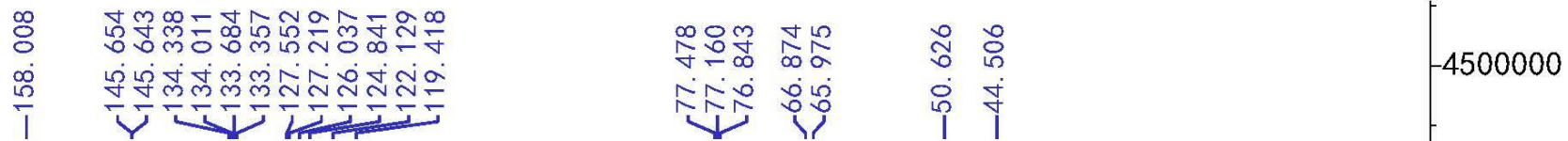




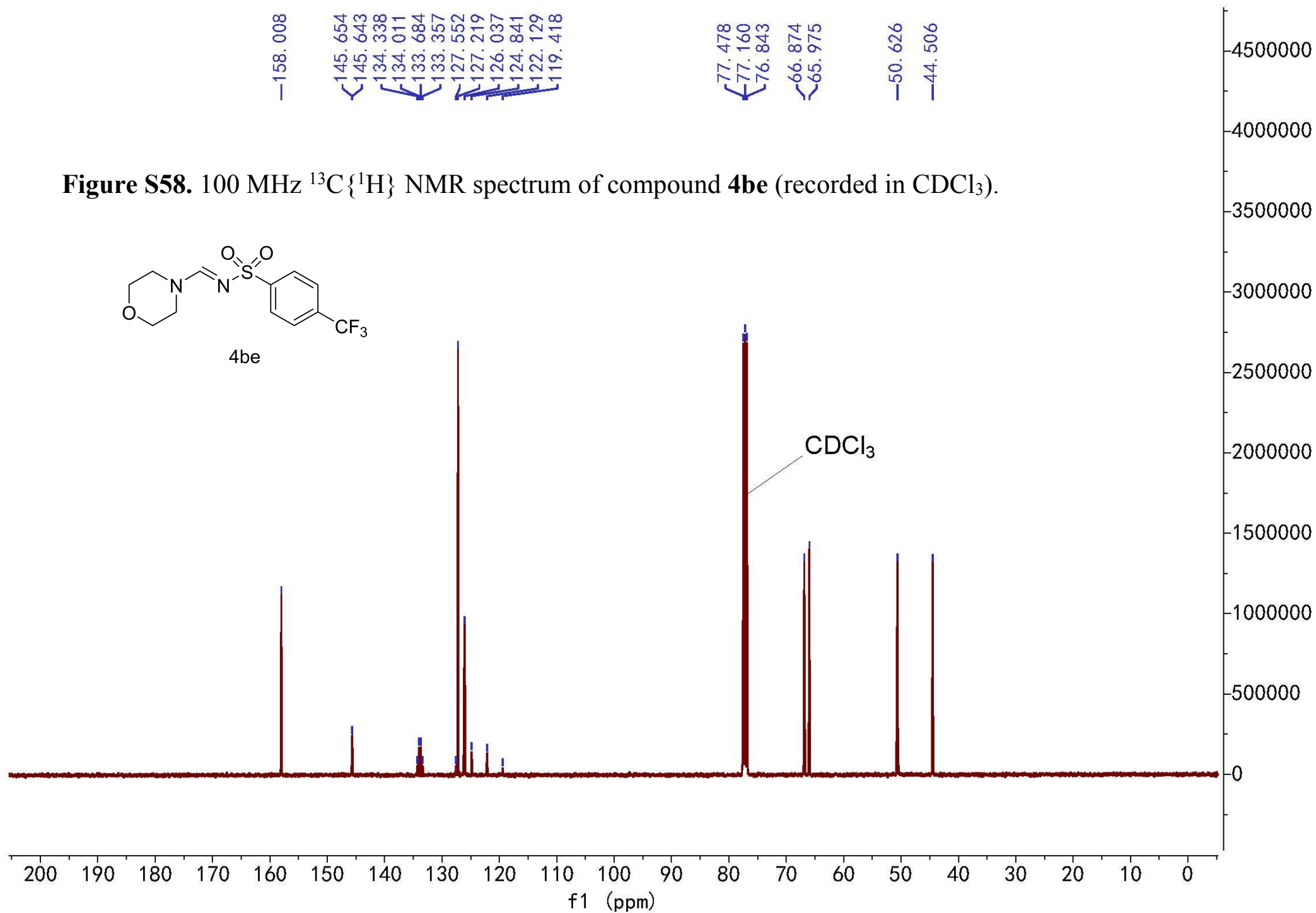
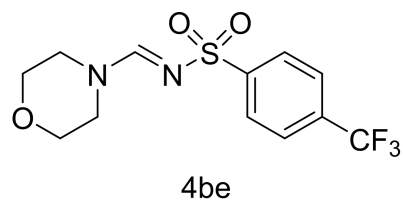
**Figure S57.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4be** (recorded in  $\text{CDCl}_3$ ).

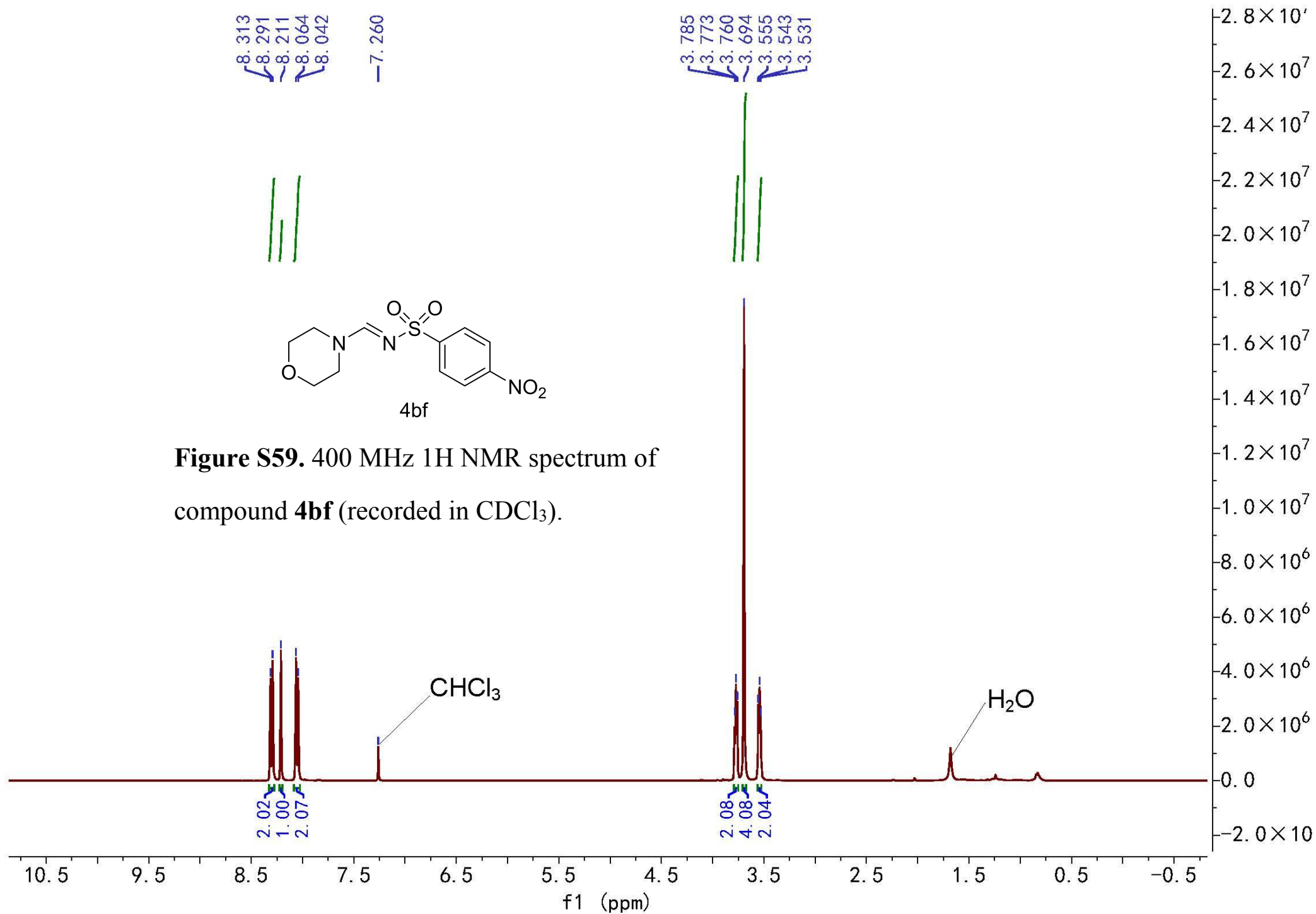






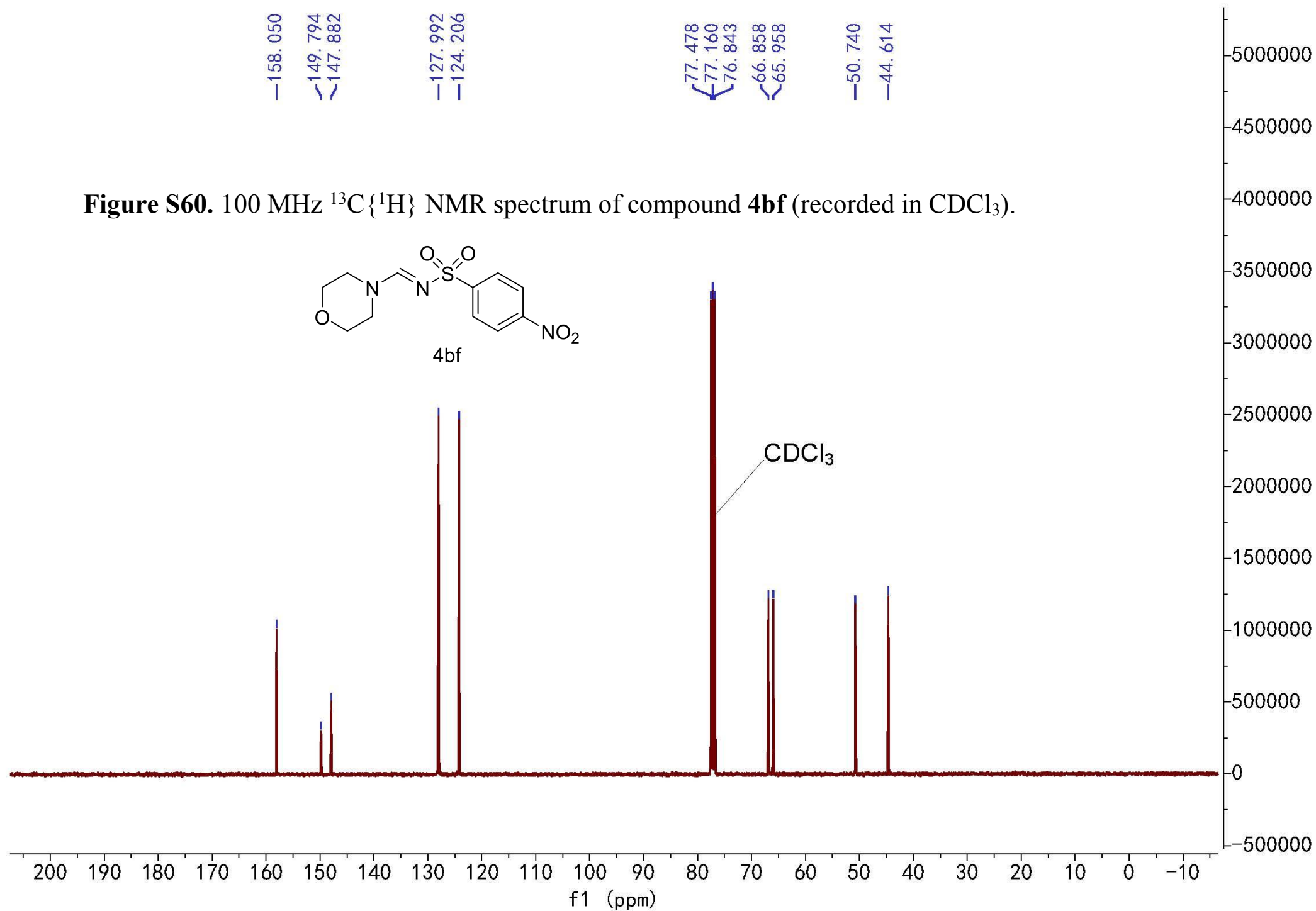
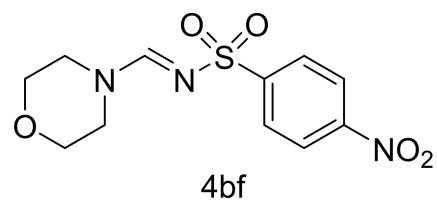
**Figure S58.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4be** (recorded in  $\text{CDCl}_3$ ).

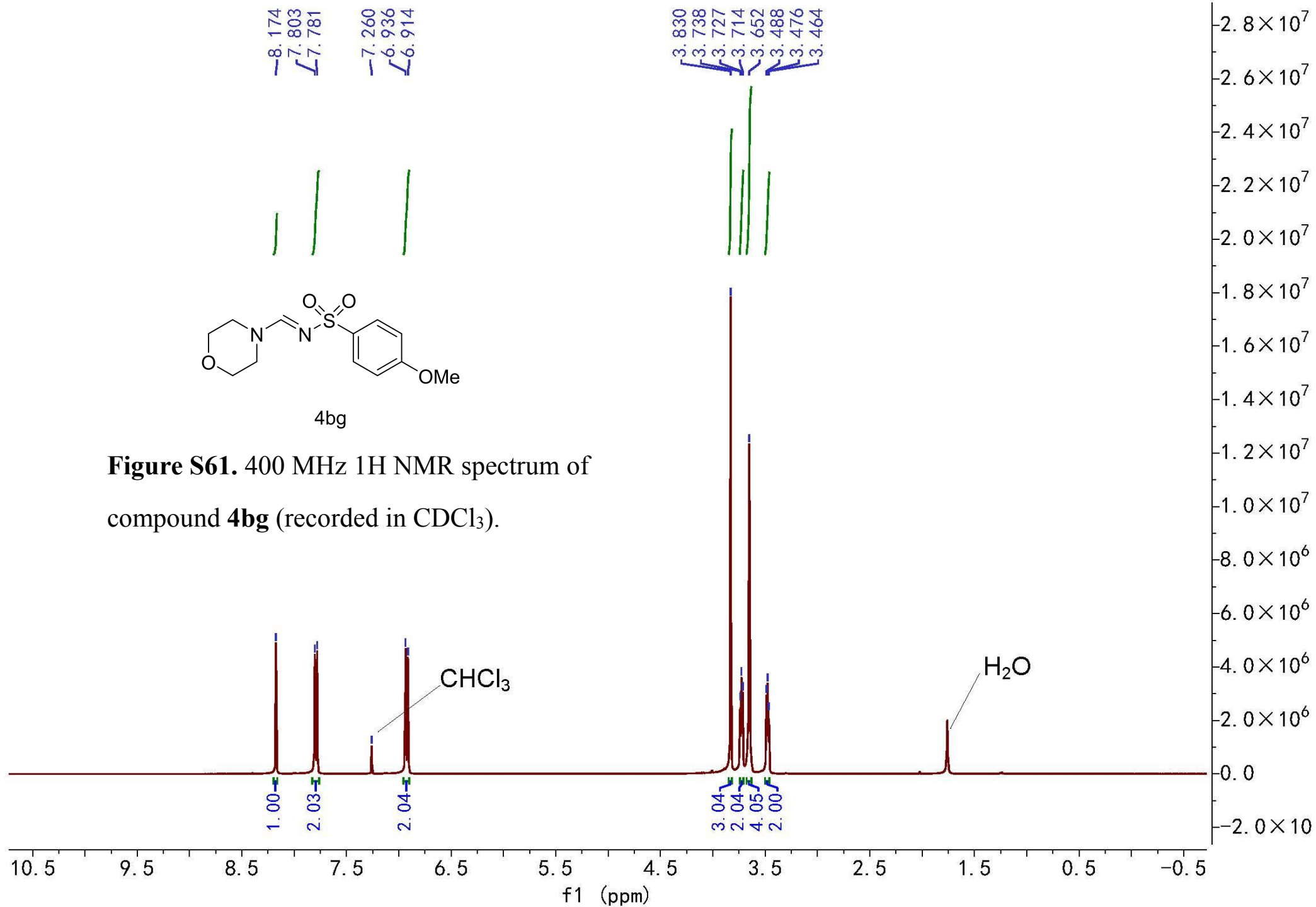


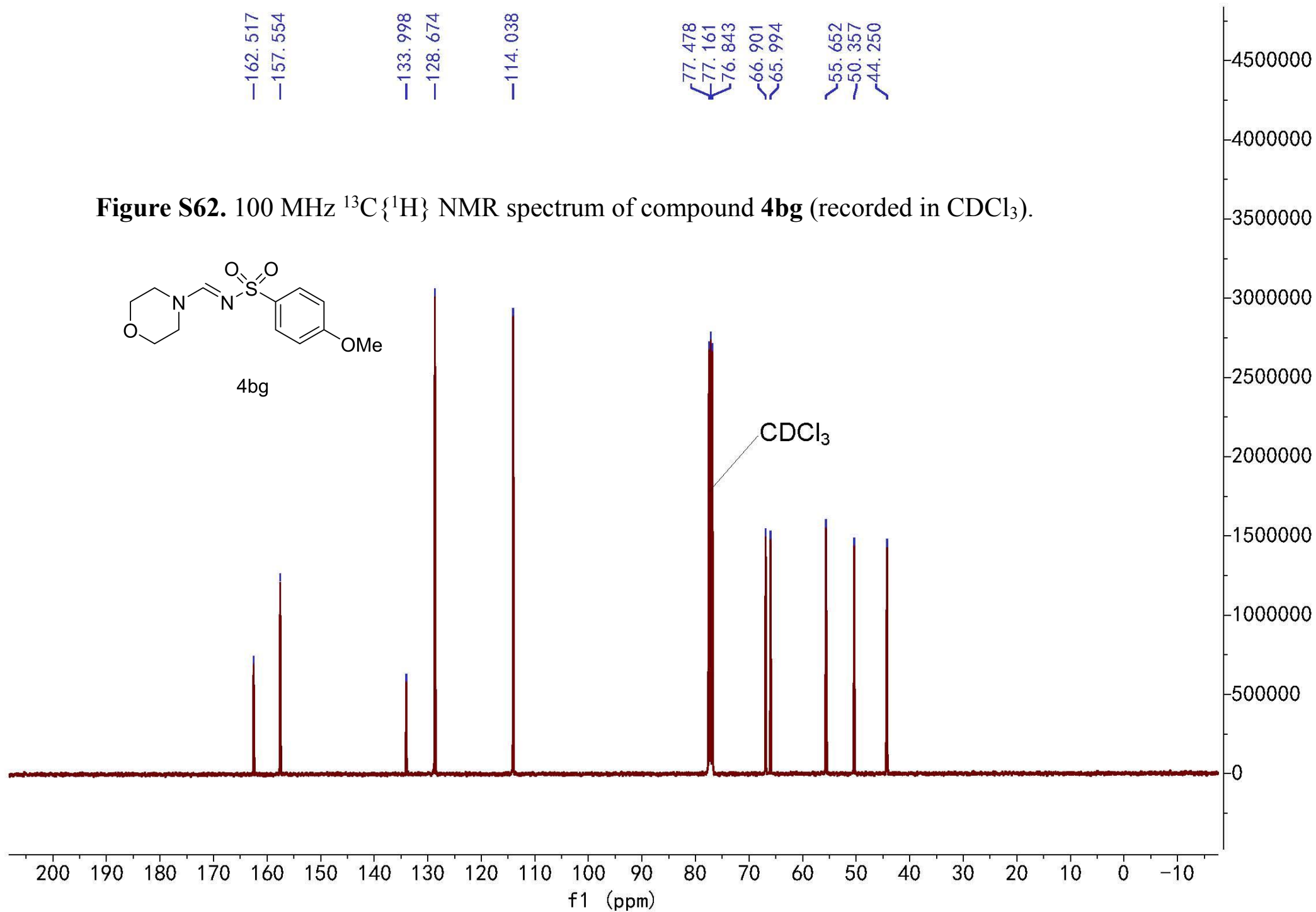


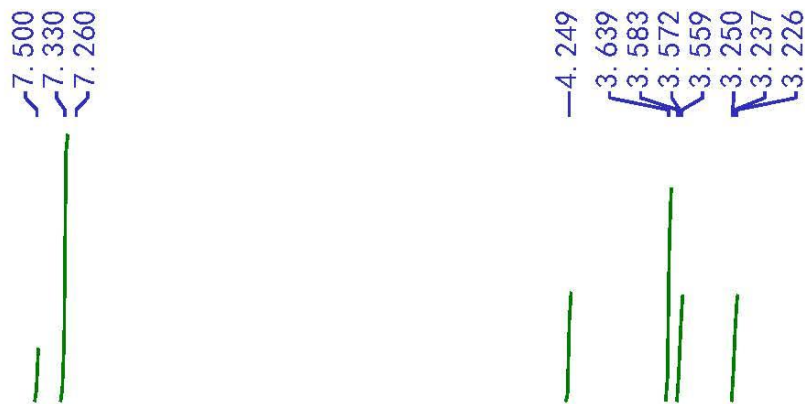
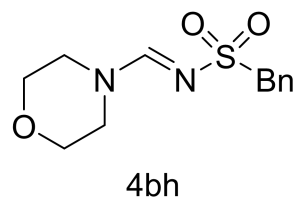
158.050  
149.794  
147.882  
127.992  
124.206  
77.478  
77.160  
76.843  
66.858  
65.958  
50.740  
44.614

Figure S60. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bf** (recorded in  $\text{CDCl}_3$ ).

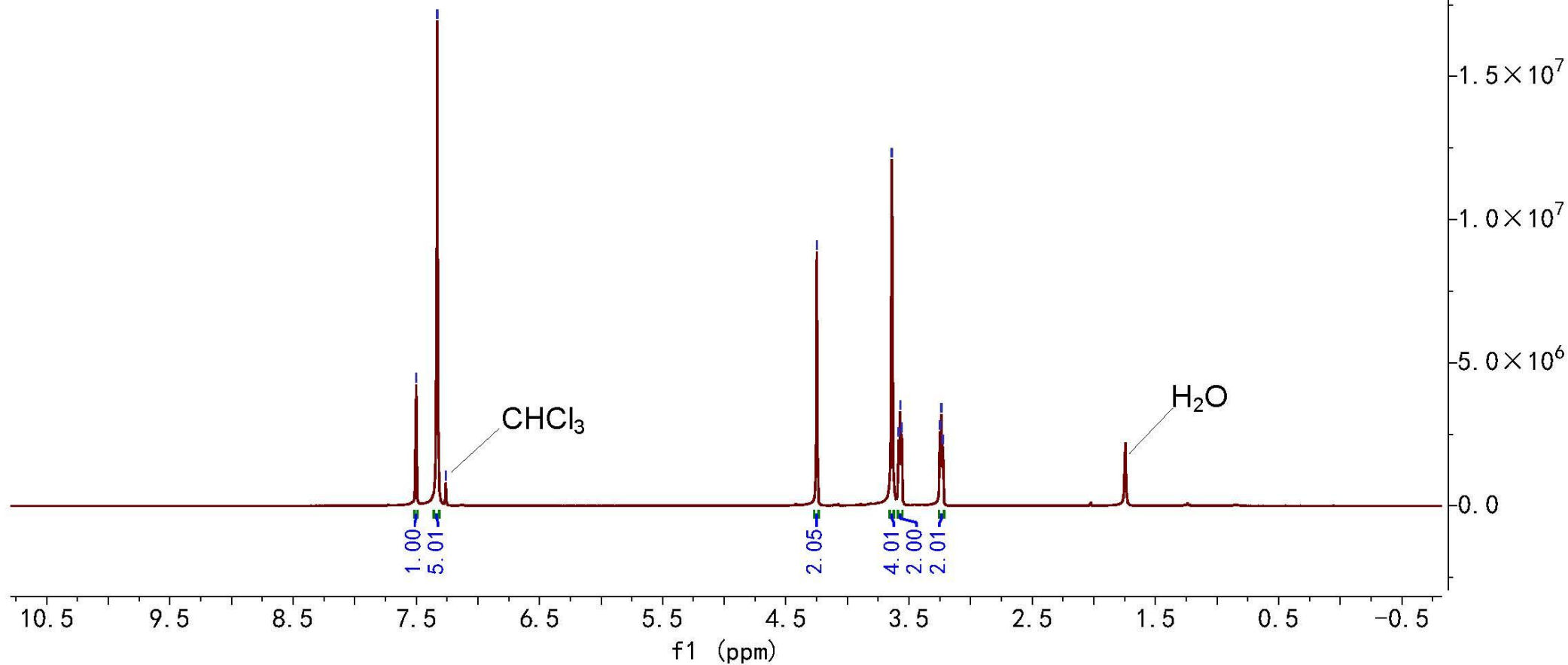








**Figure S63.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4bh** (recorded in  $\text{CDCl}_3$ ).



-158.995

131.069

130.377

128.548

128.461

77.478

77.160

76.842

66.972

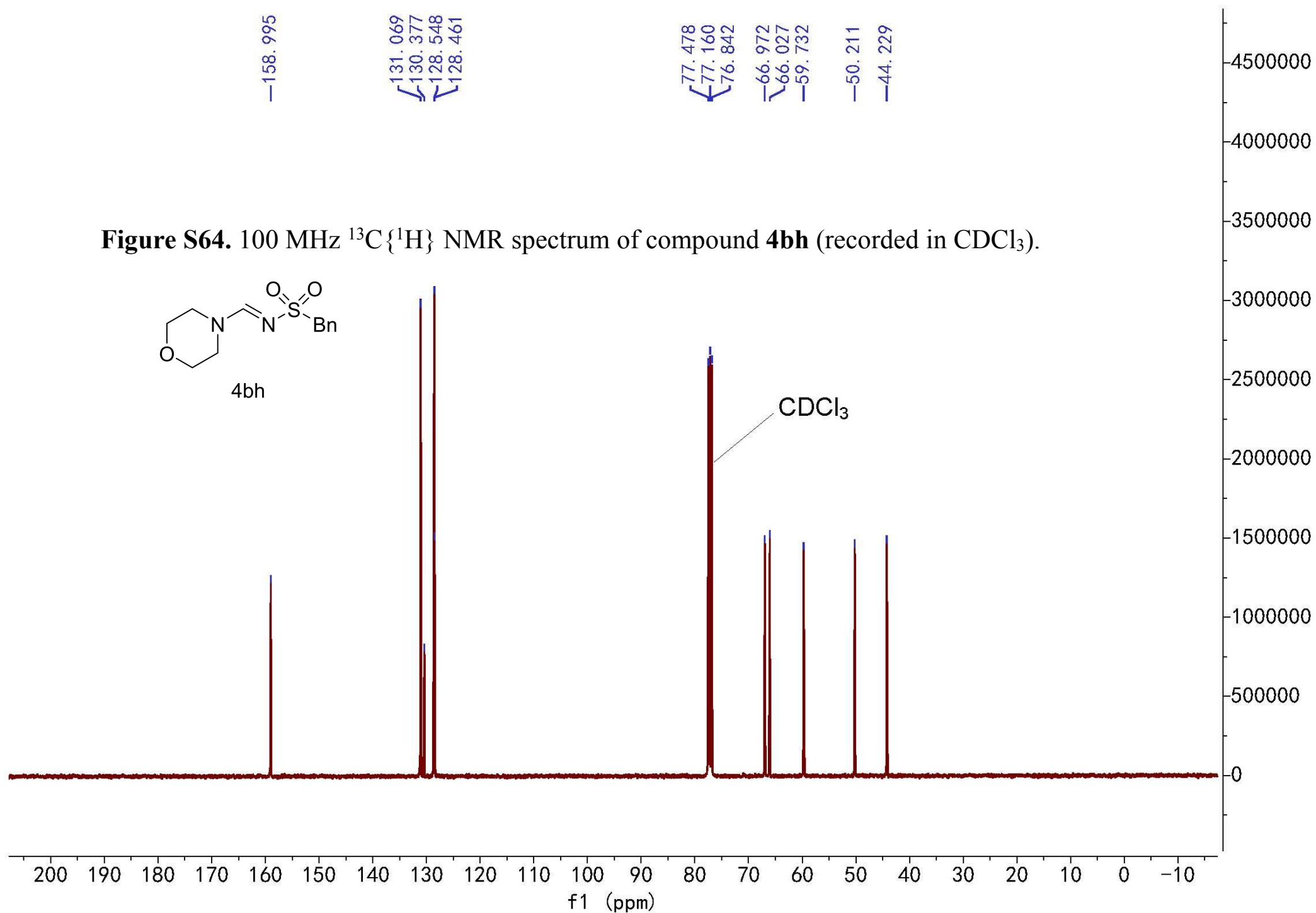
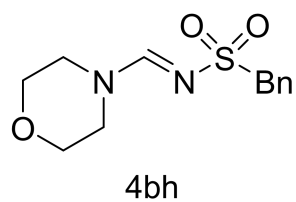
66.027

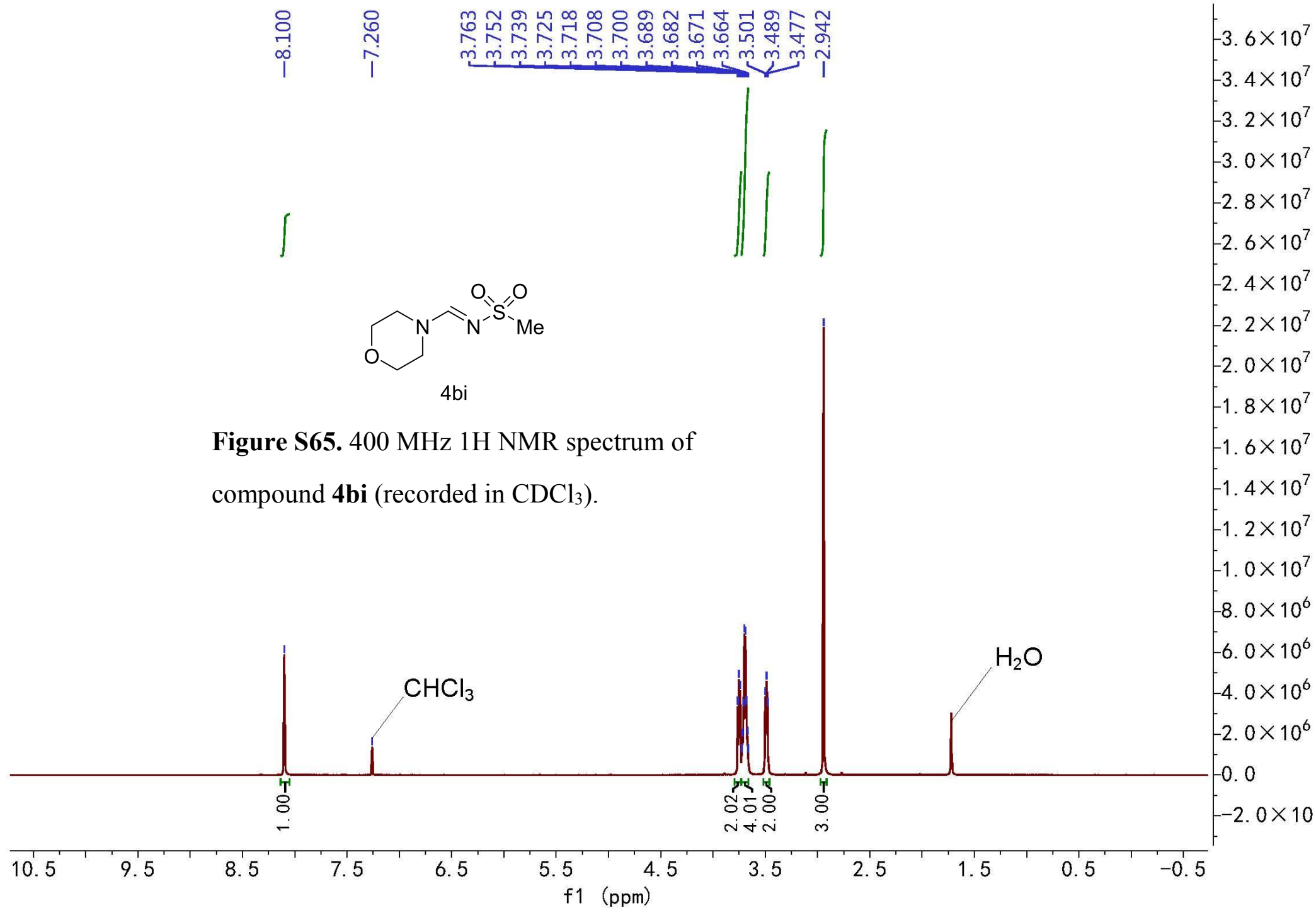
59.732

50.211

44.229

**Figure S64.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bh** (recorded in  $\text{CDCl}_3$ ).





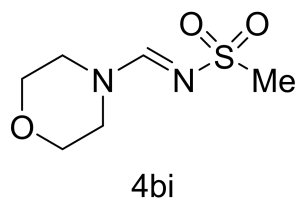


-157.891

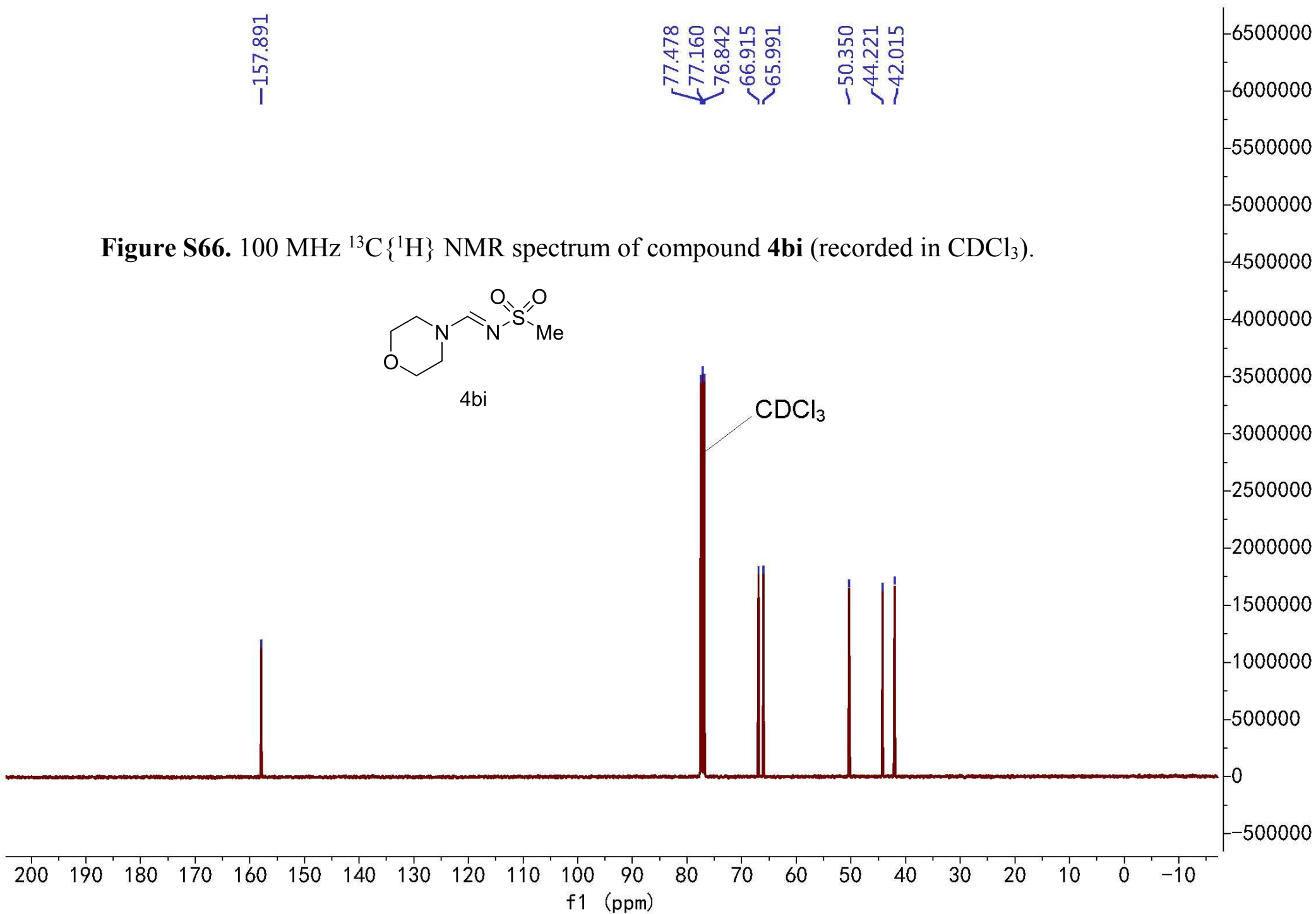
77.478  
77.160  
76.842  
66.915  
65.991

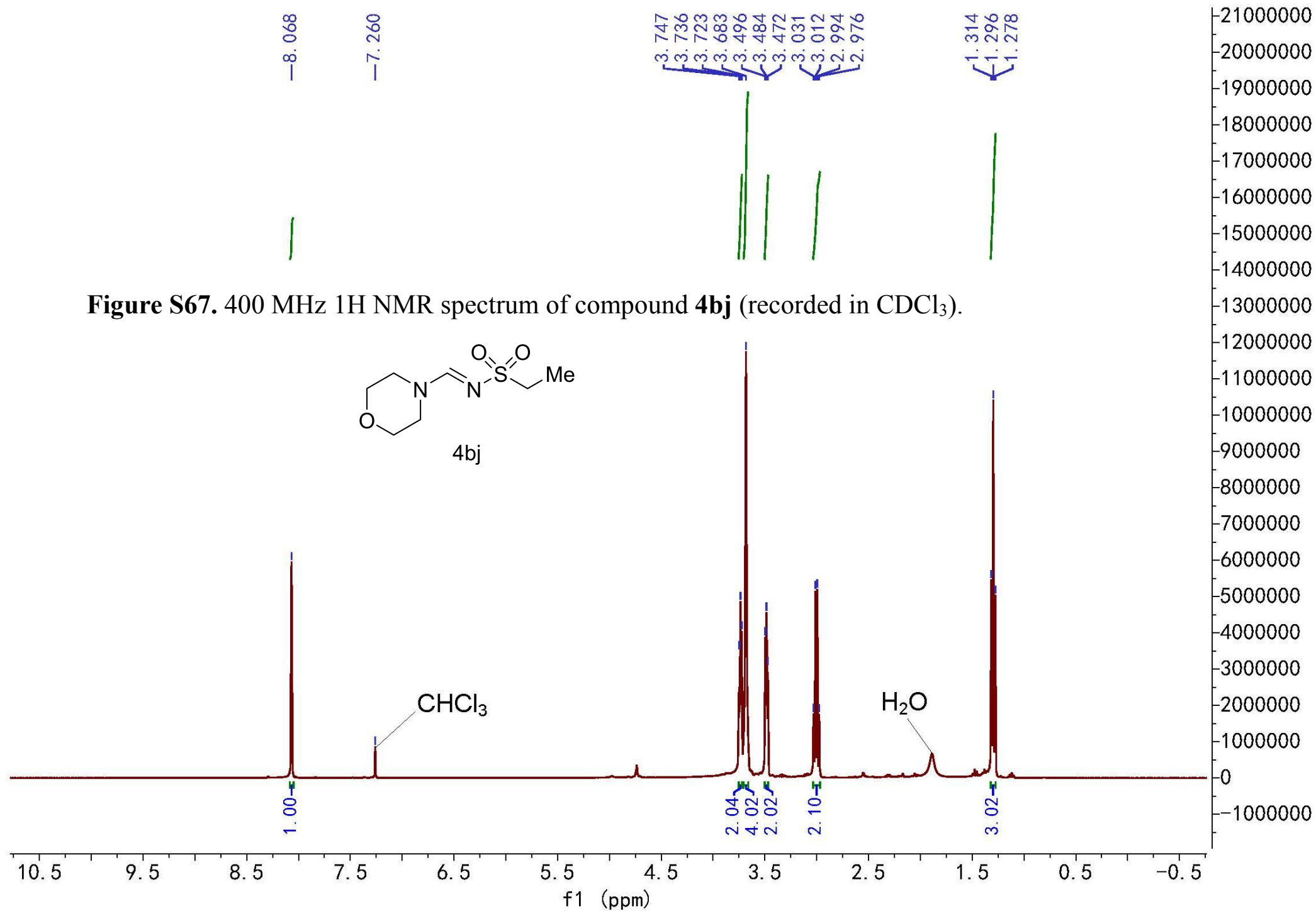
50.350  
44.221  
42.015

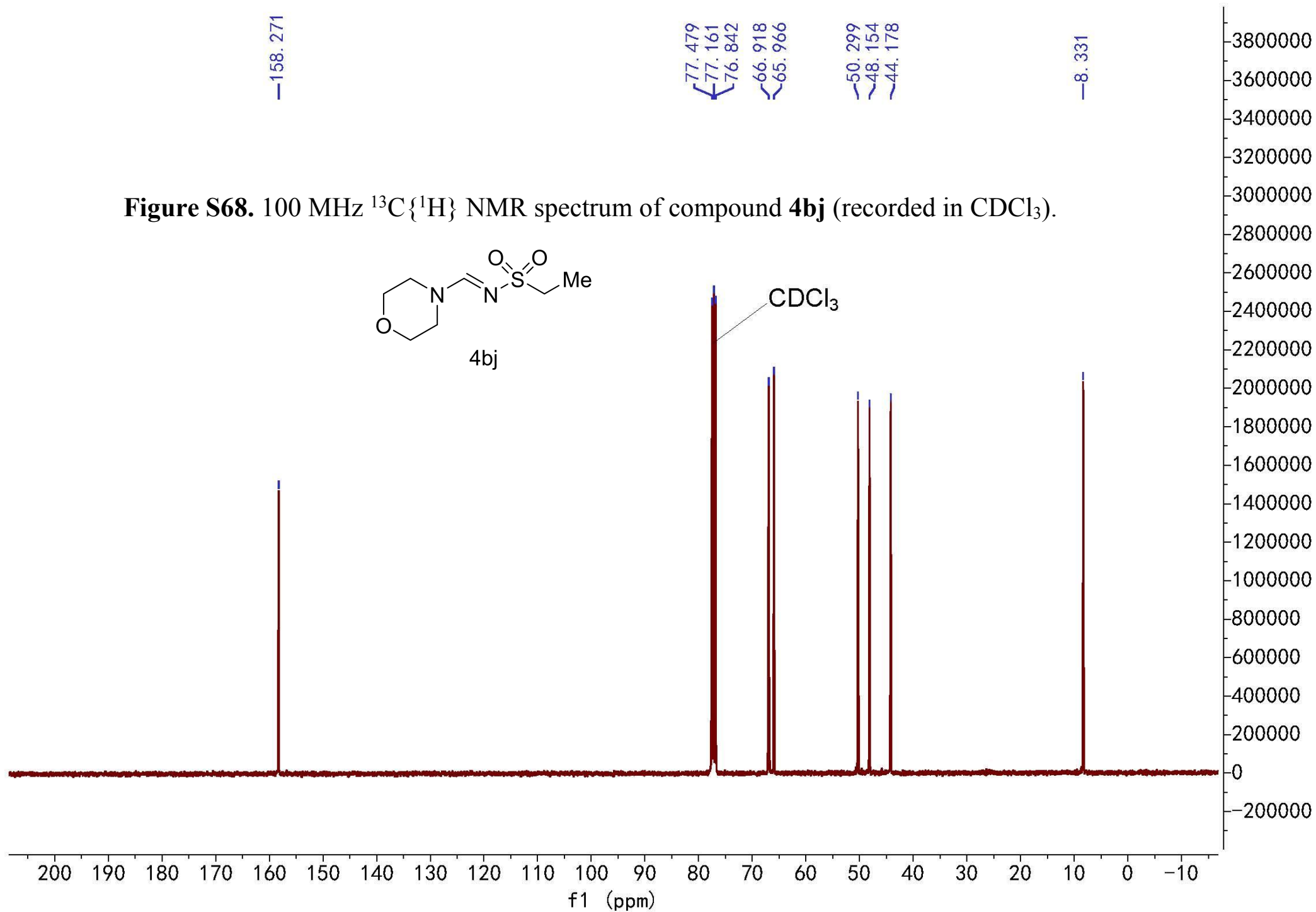
**Figure S66.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bi** (recorded in  $\text{CDCl}_3$ ).

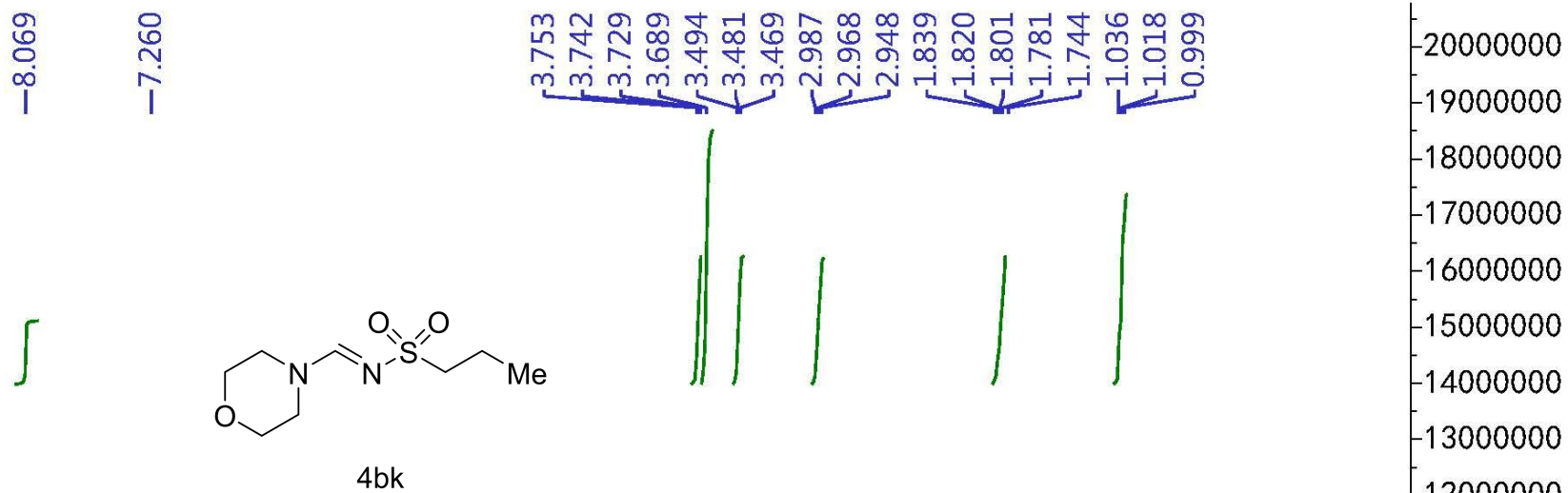


$\text{CDCl}_3$

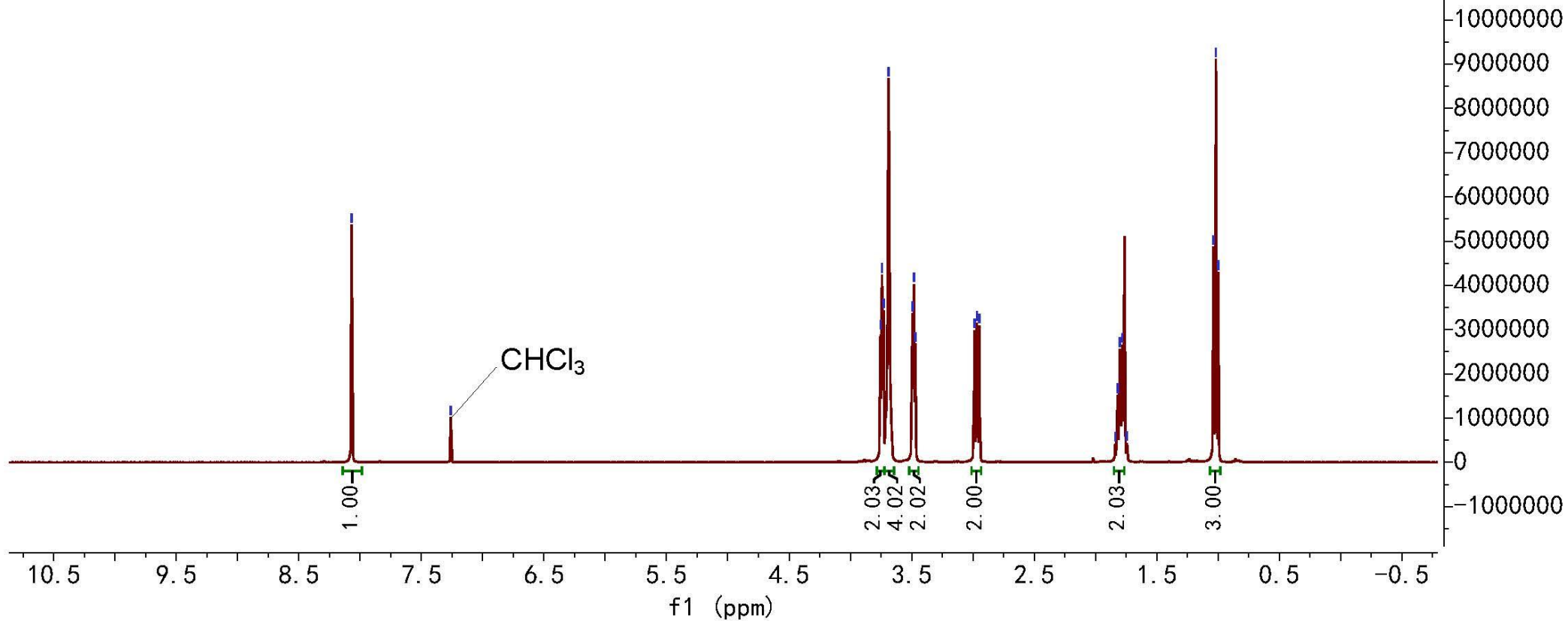








**Figure S69.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4bk** (recorded in  $\text{CDCl}_3$ ).



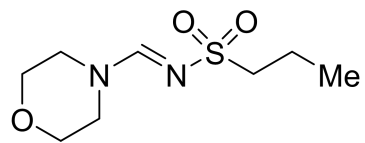
158.135

77.478  
77.160  
76.843

66.947  
66.012

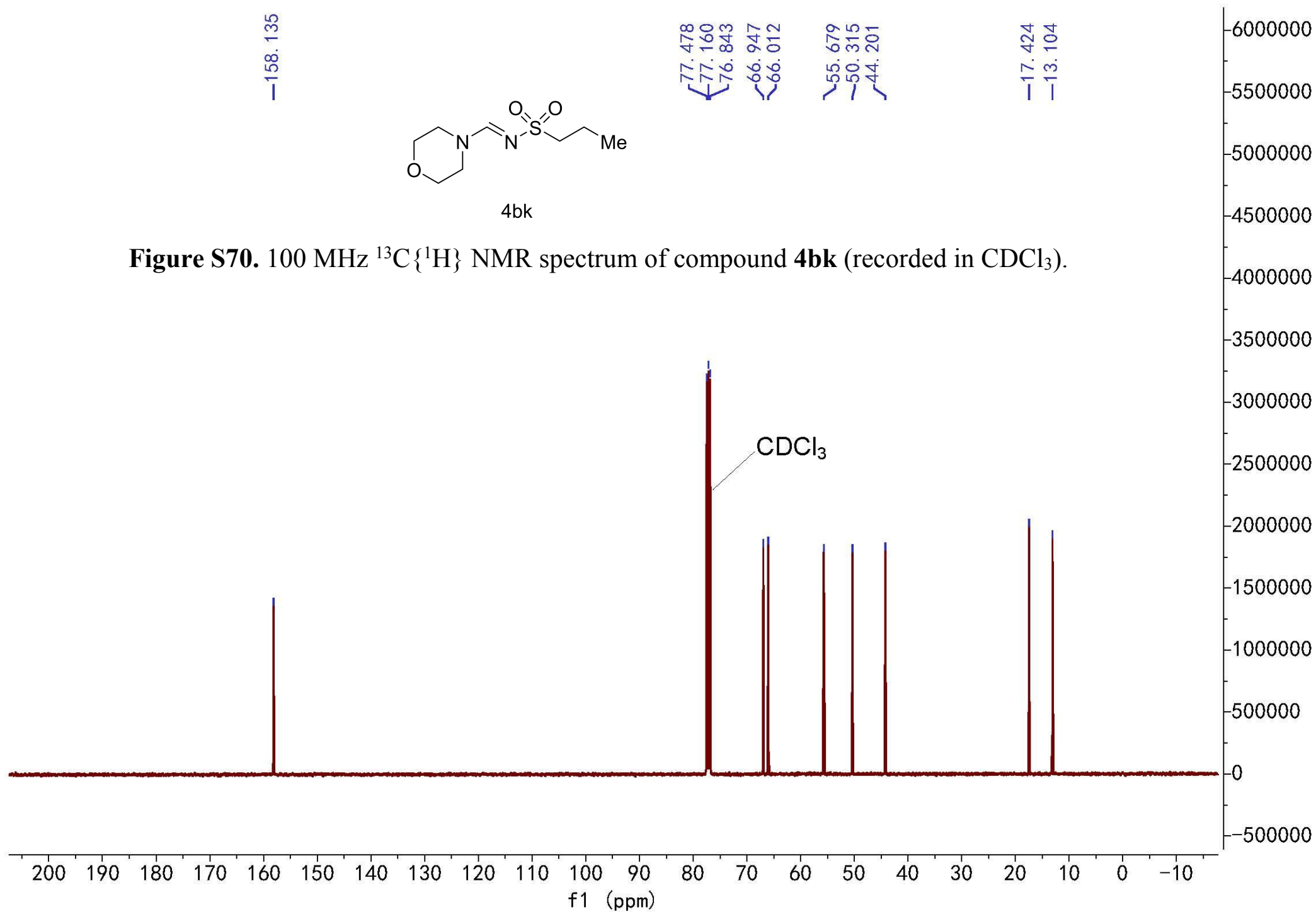
55.679  
50.315  
44.201

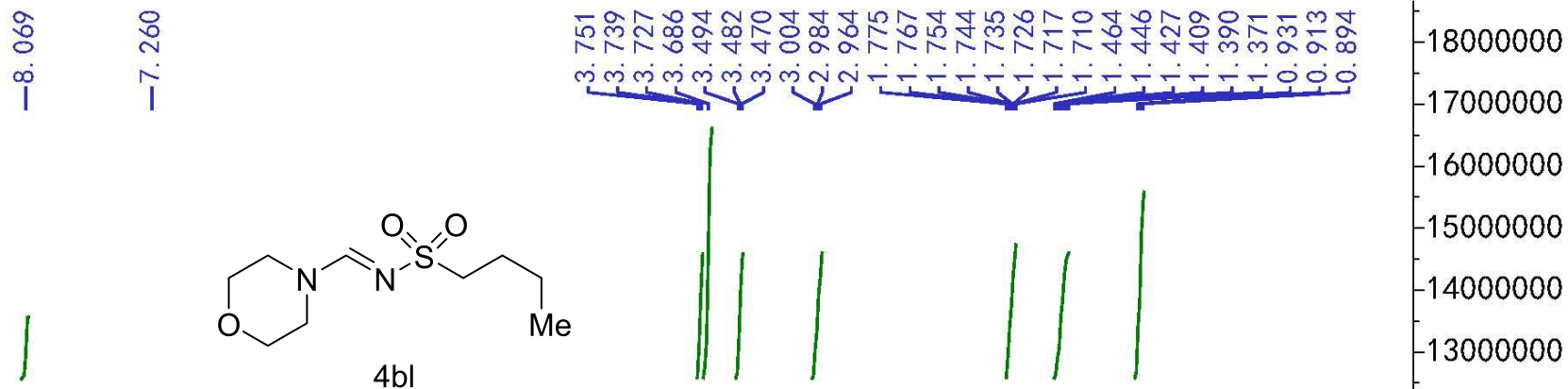
17.424  
13.104



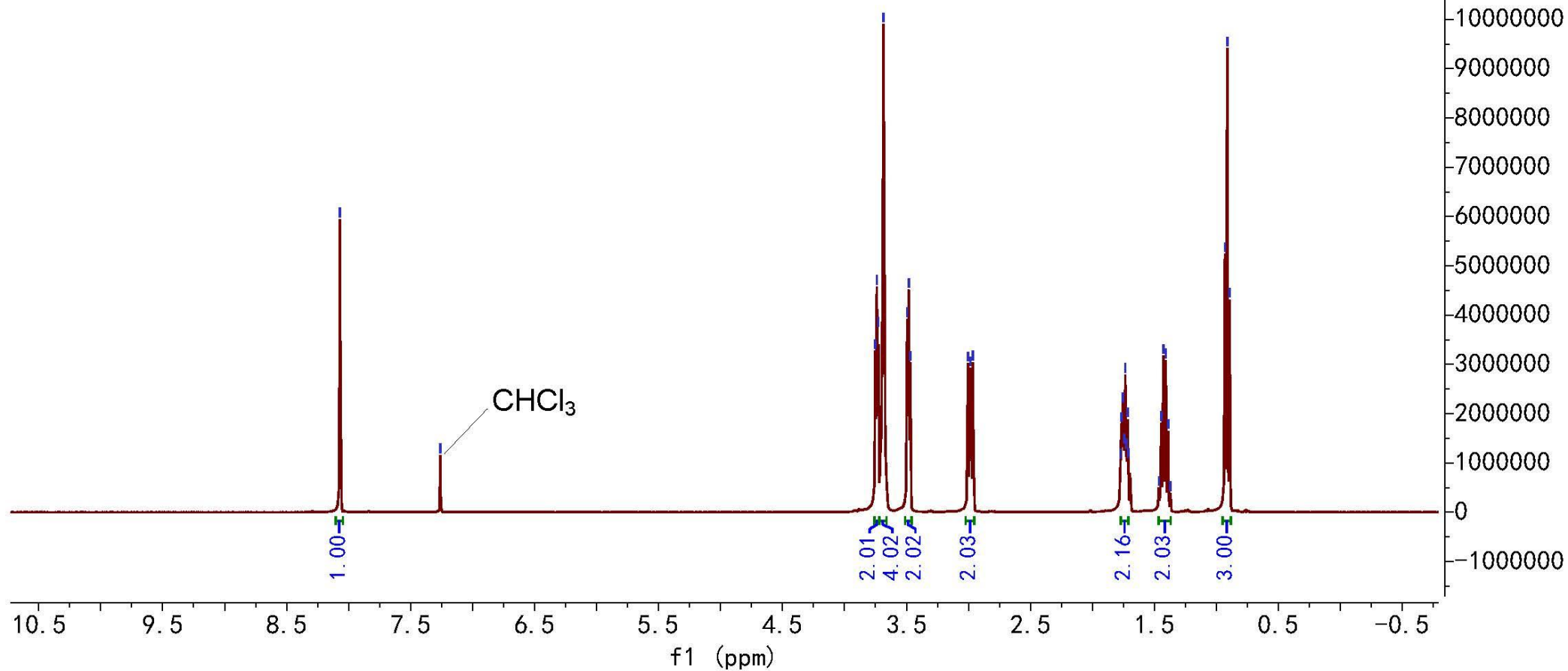
4bk

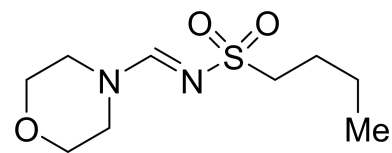
Figure S70. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bk** (recorded in  $\text{CDCl}_3$ ).





**Figure S71.** 400 MHz  $^1\text{H}$  NMR spectrum of compound **4bl** (recorded in  $\text{CDCl}_3$ ).





4bl

—158.121

77.480

77.161

76.843

66.944

66.002

53.682

50.302

44.189

—25.648

—21.636

—13.681

**Figure S72.** 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4bl** (recorded in  $\text{CDCl}_3$ ).

