

**HIGHLY CONJUGATED ARCHITECTURES AND LABILE REACTION INTERMEDIATES FROM COUPLING BETWEEN  $10\pi$  ELECTRON-DEFICIENT HETEROAROMATICS AND SYM-TRIHYDROXY- OR TRIAMINO-BENZENE DERIVATIVES**

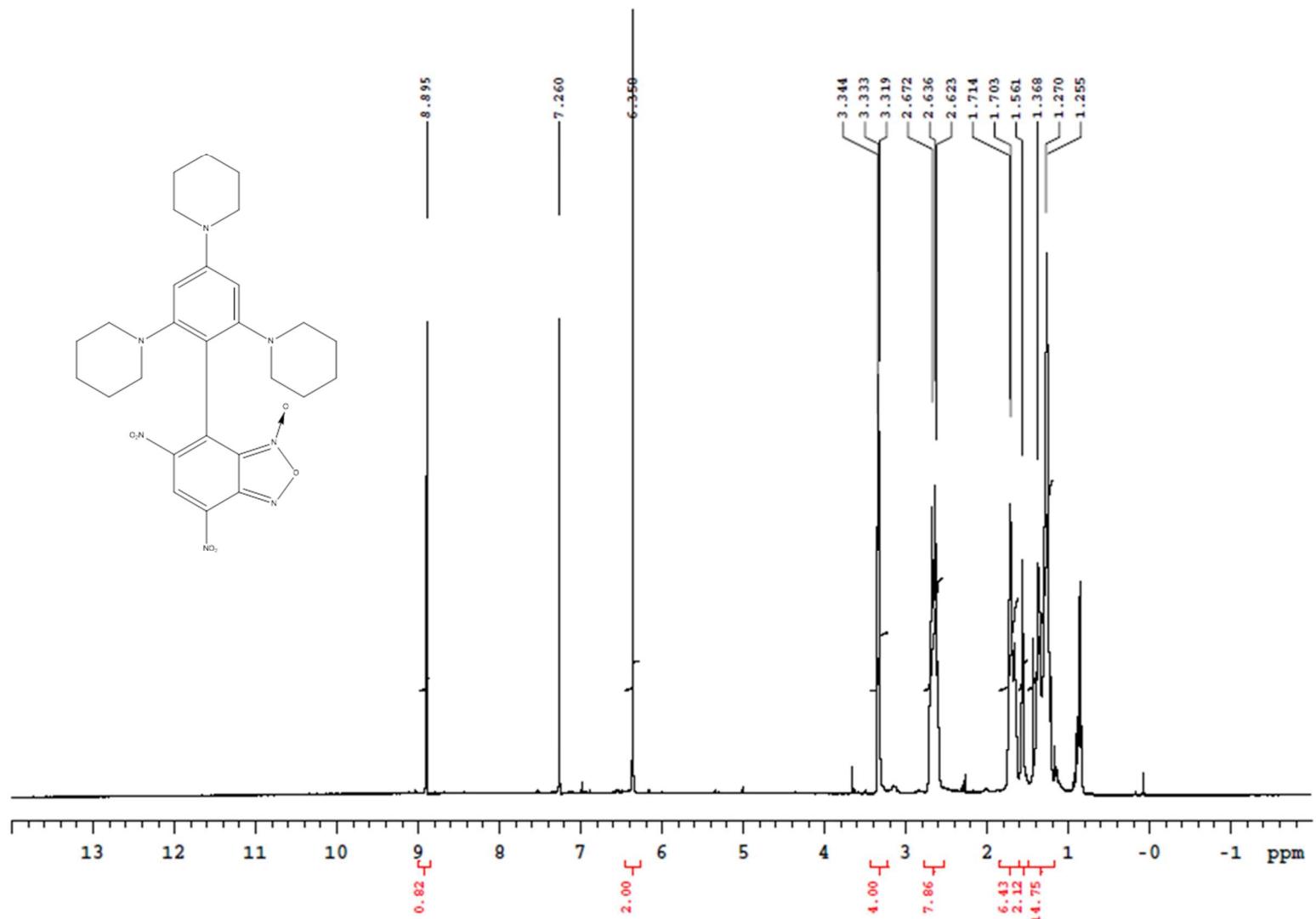
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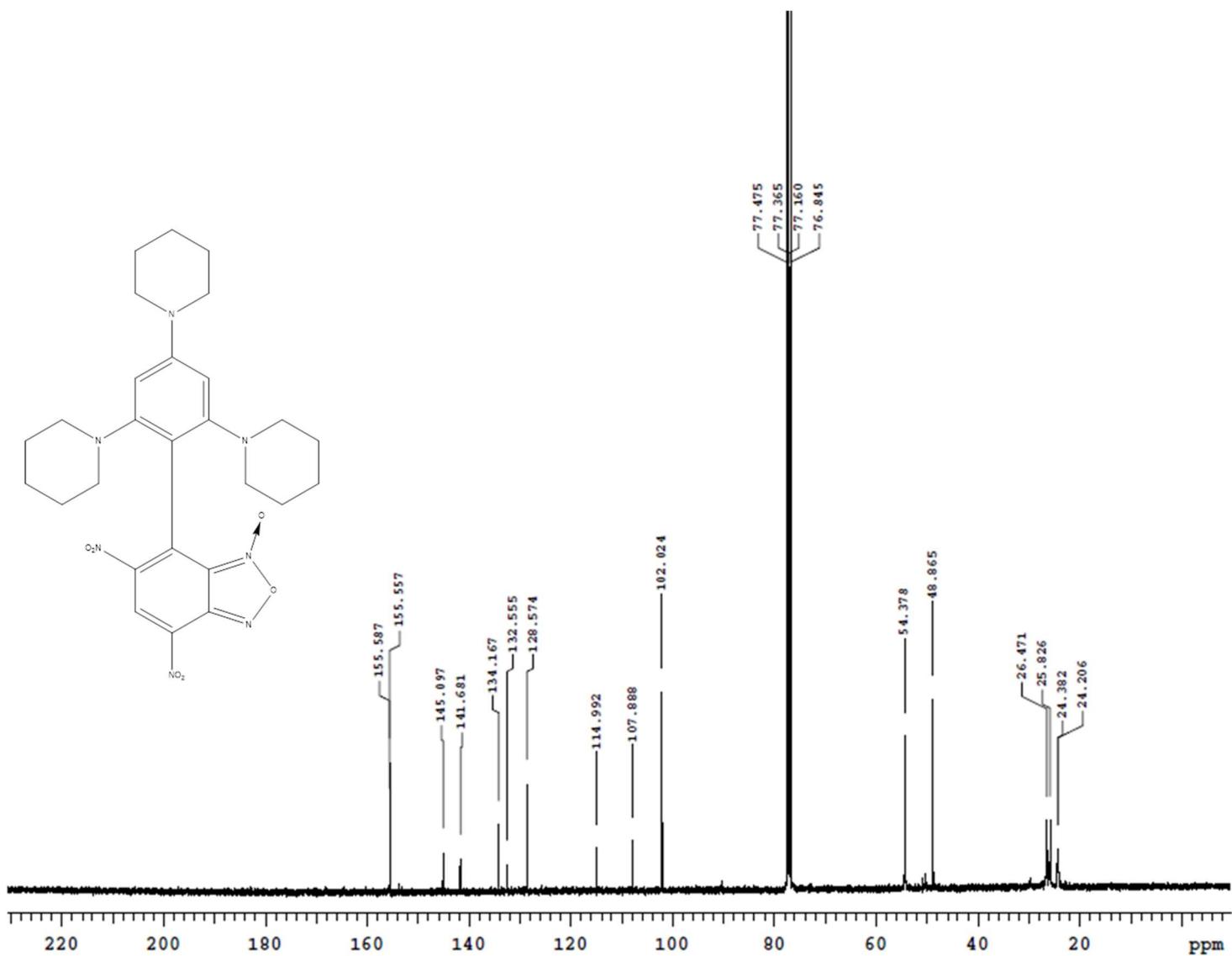
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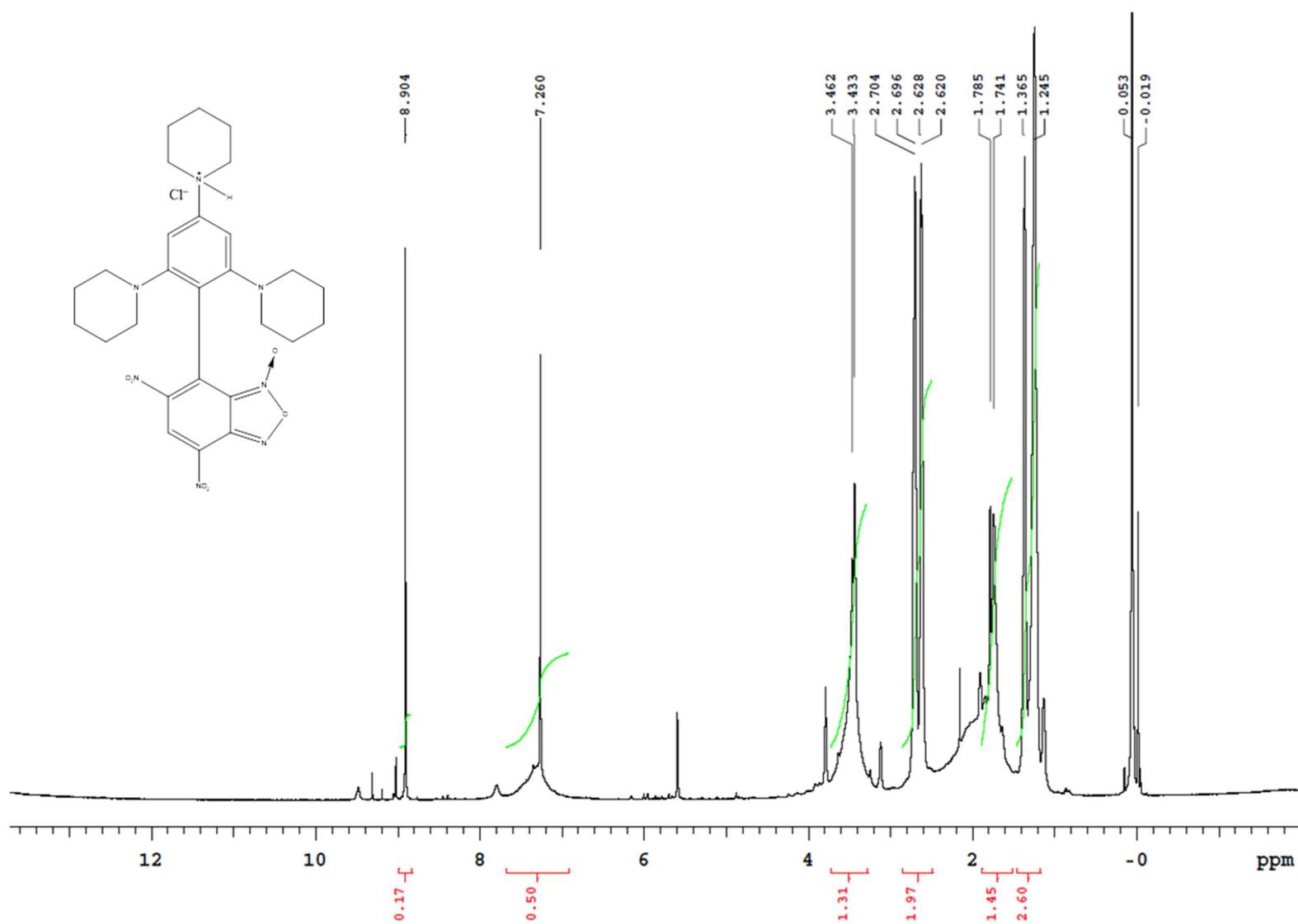
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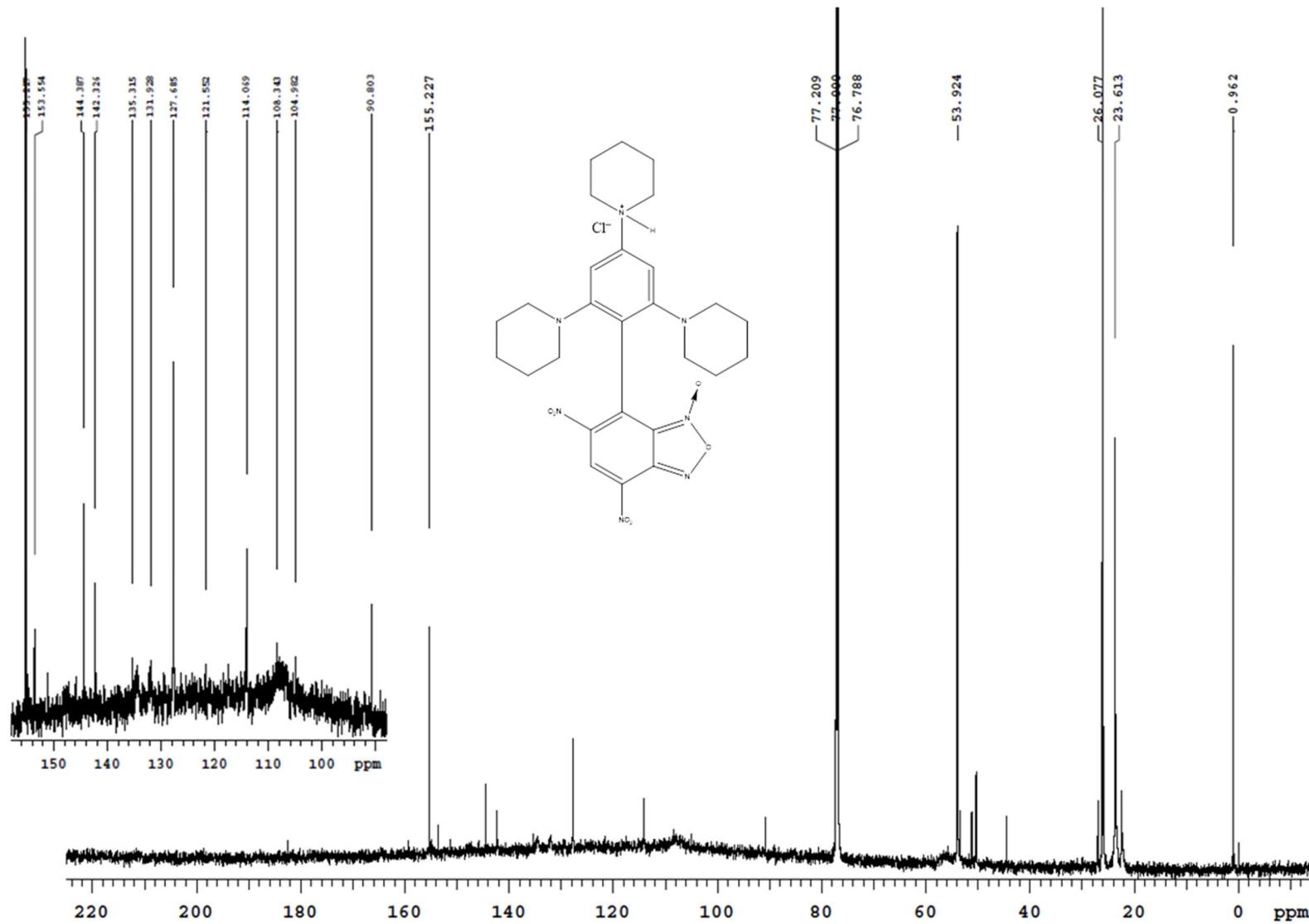
**Figure SI-1.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 25 °C) of compound 6.



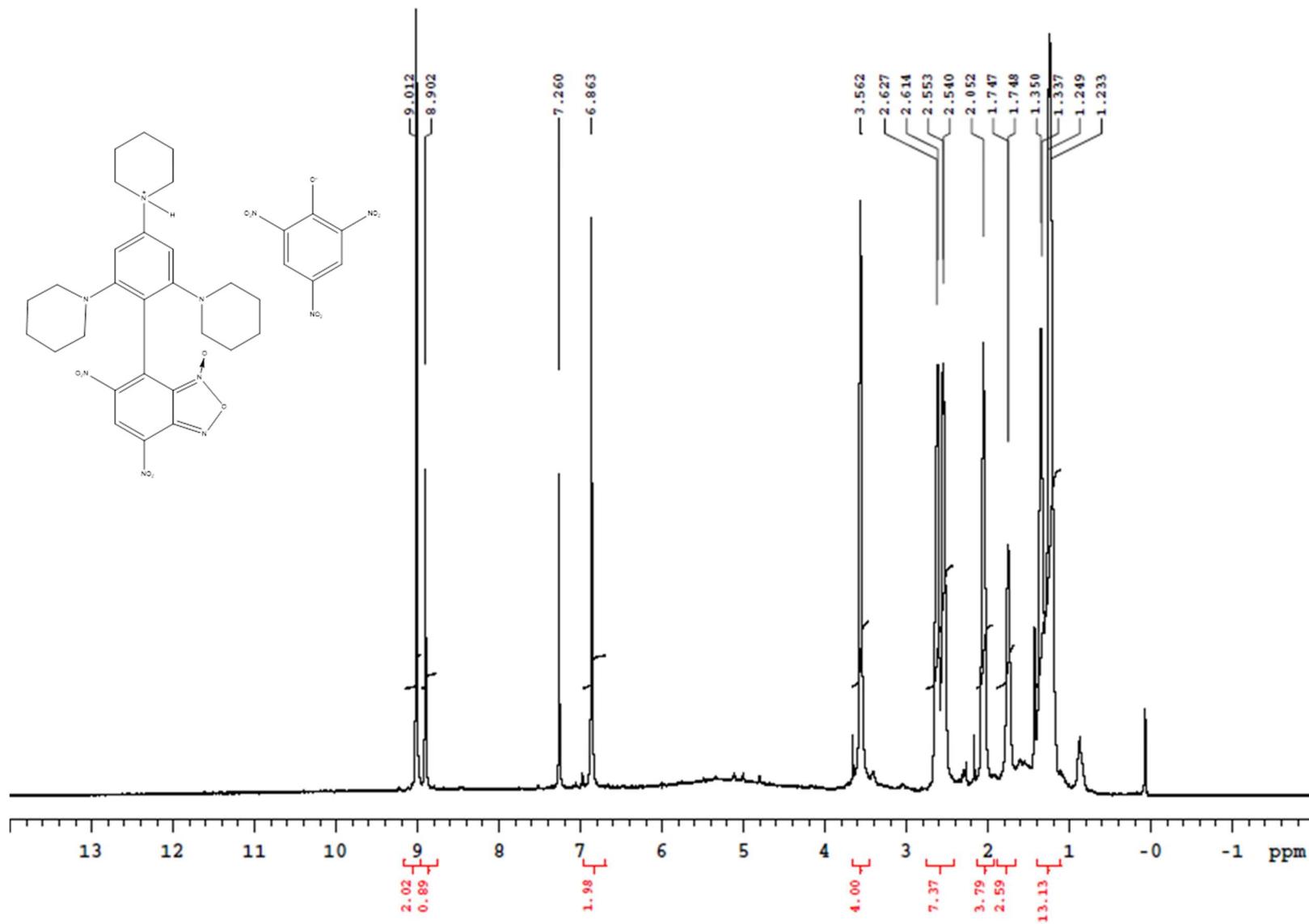
**Figure SI-2.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100.56 MHz, 25 °C) of compound **6**.



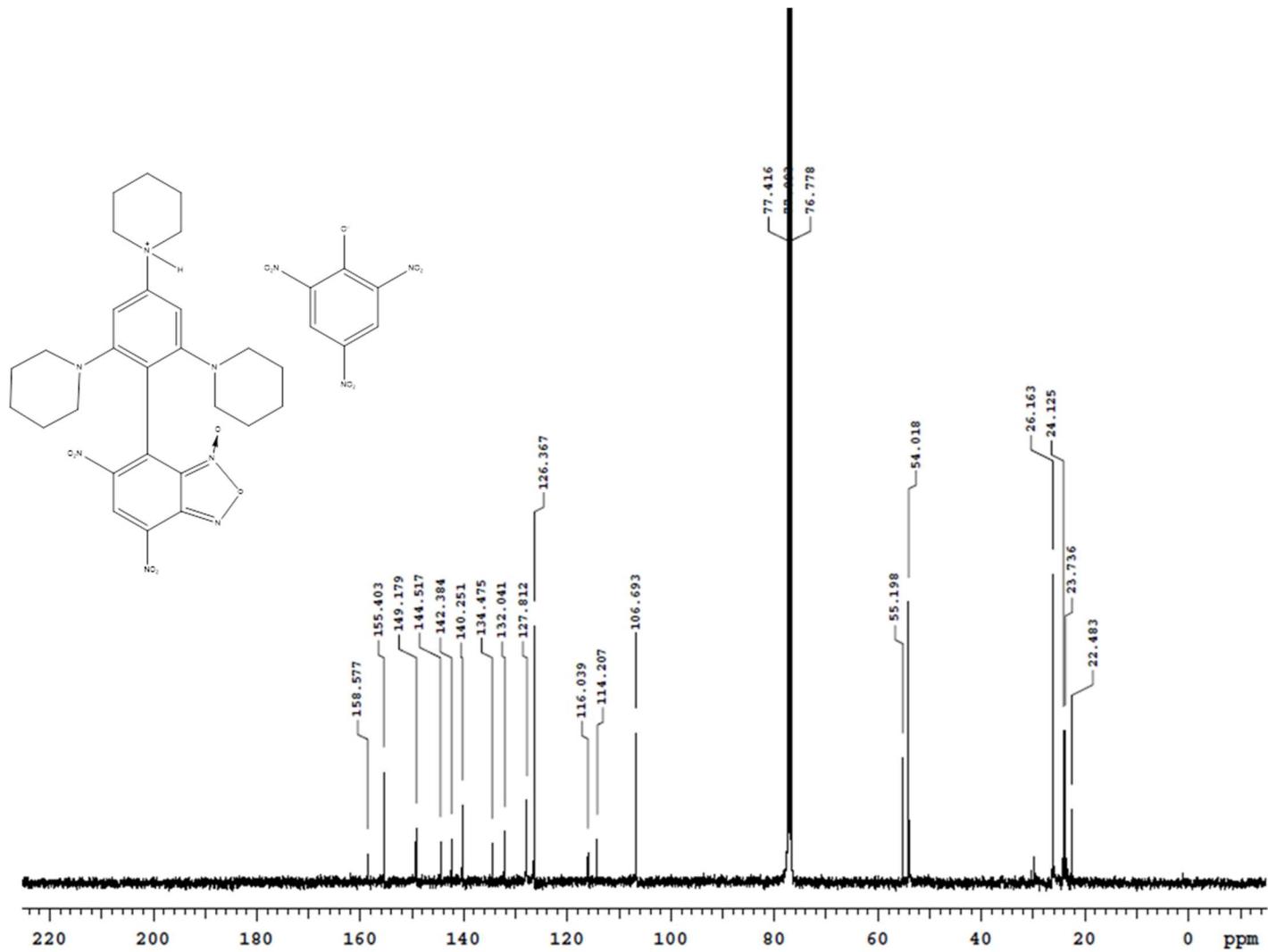
**Figure SI-3.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 600 MHz, 25 °C) of compound  $6\text{H}^+\text{Cl}^-$ .



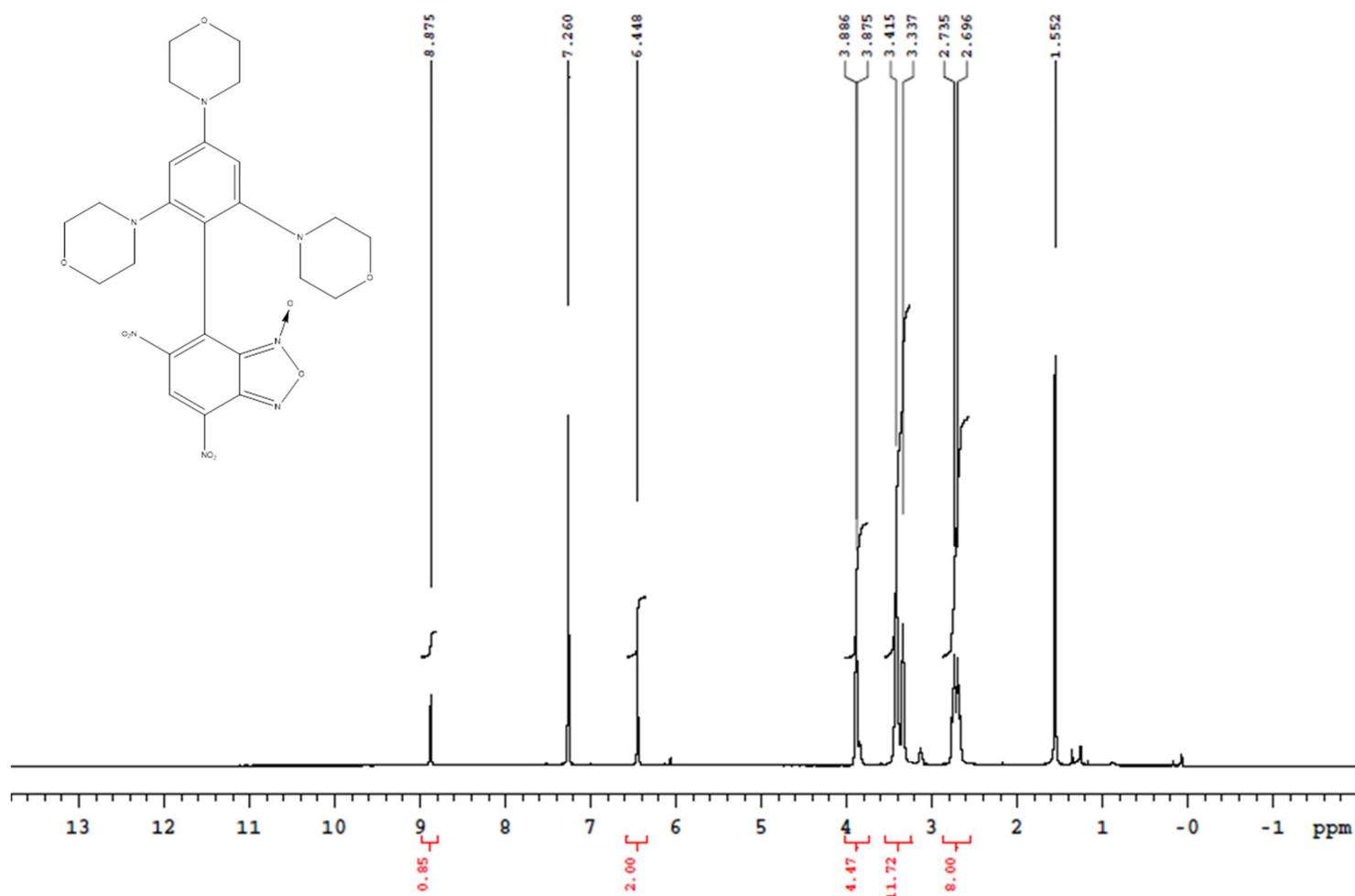
**Figure SI-4.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 150.56 MHz, 25 °C) of compound  $\mathbf{6H}^+\text{Cl}^-$ .



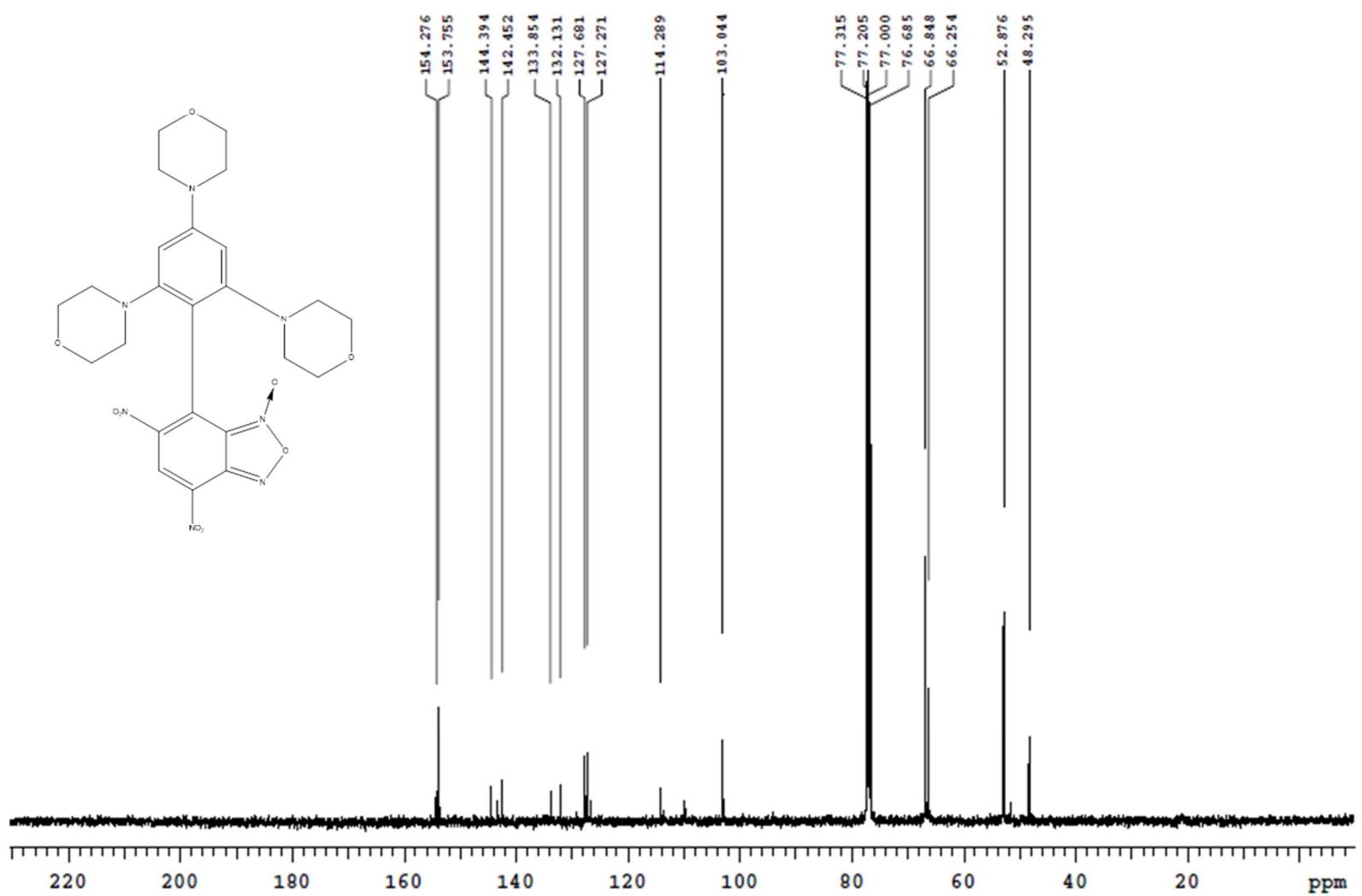
**Figure SI-5.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 25 °C) of compound **6H<sup>+</sup>picrate**.



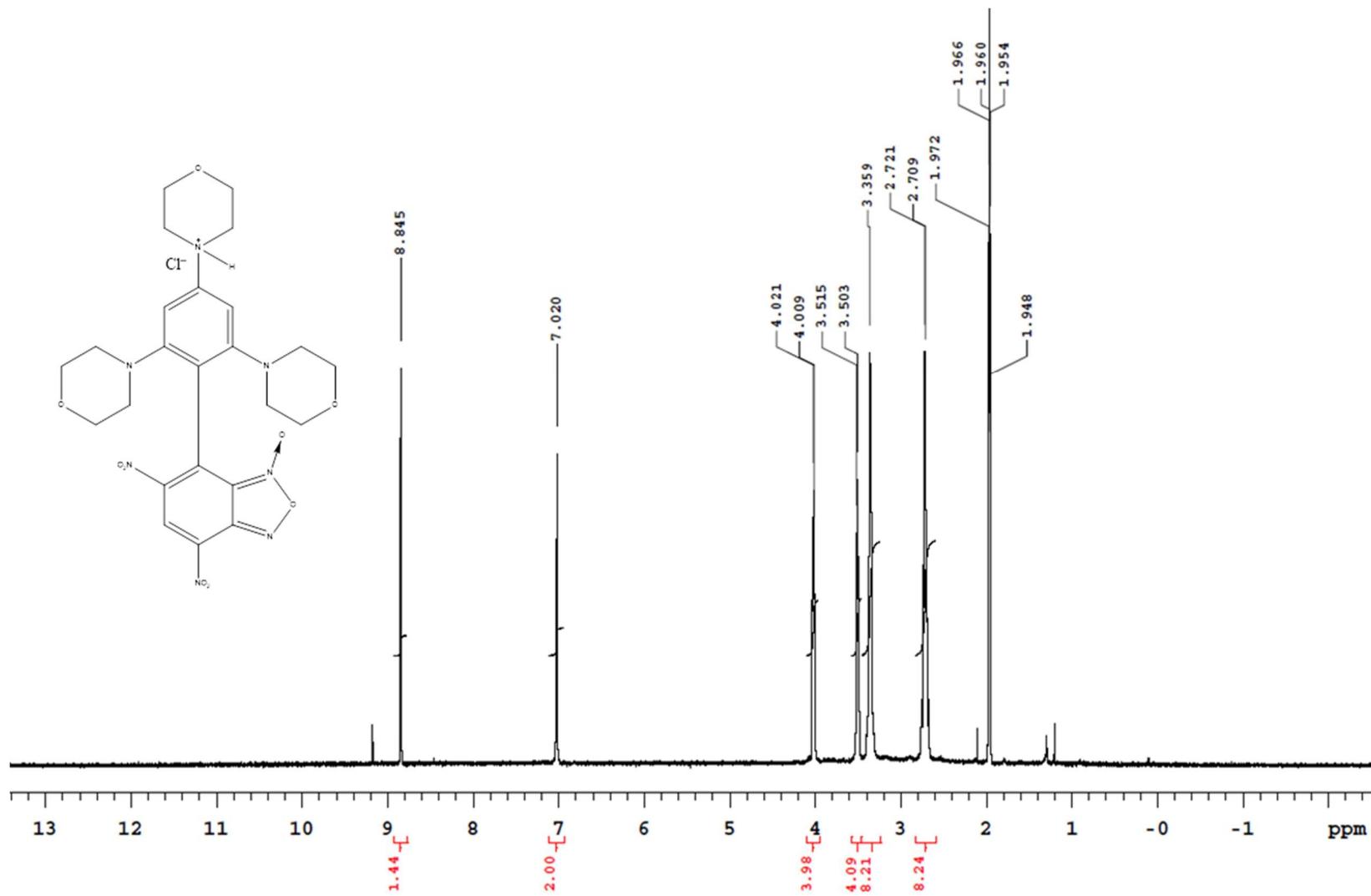
**Figure SI-6.** <sup>13</sup>C NMR spectrum ( $\text{CDCl}_3$ , 100.56 MHz, 25 °C) of compound **6H<sup>+</sup>picrate**.



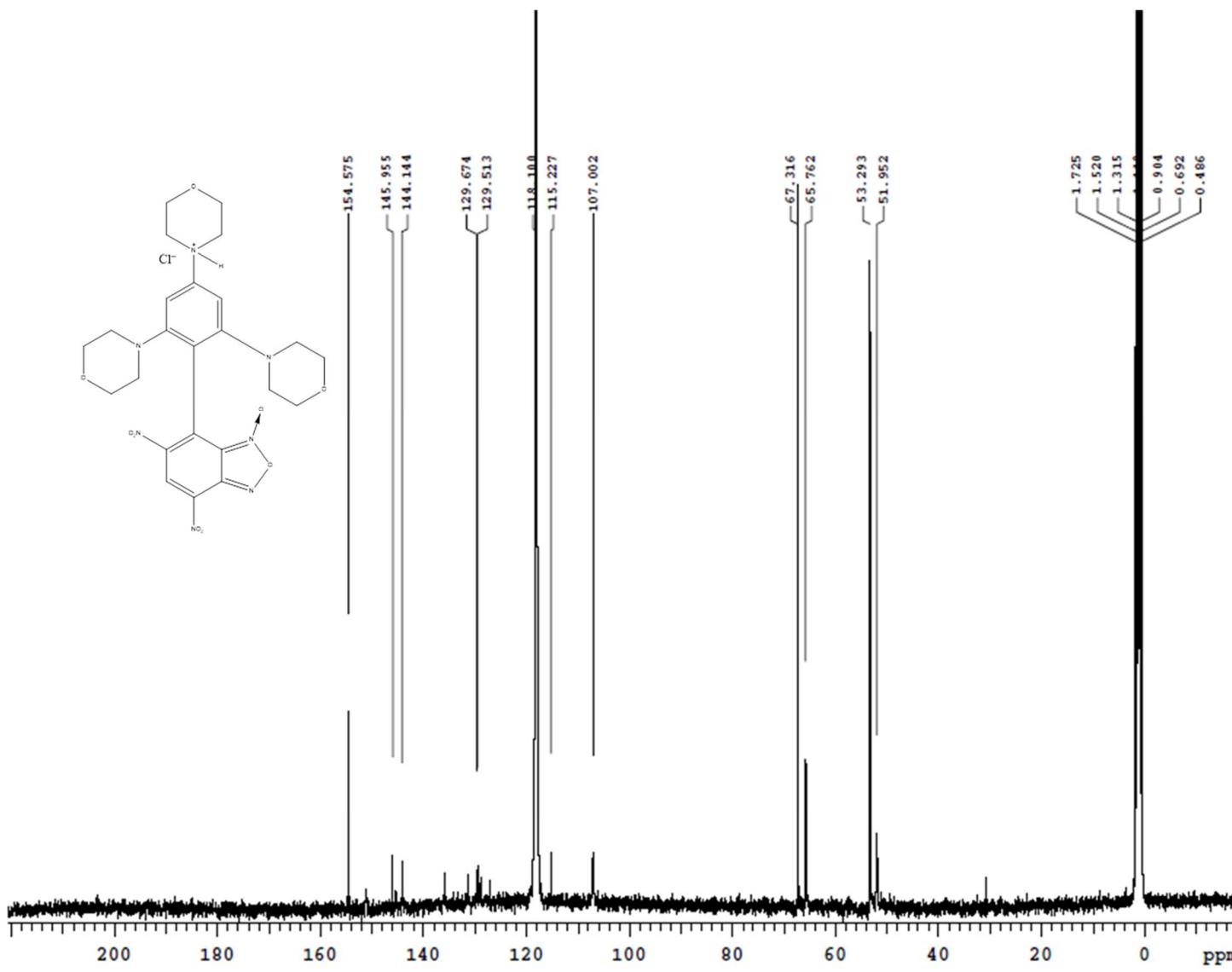
**Figure SI-7.** <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 25 °C) of compound 7.



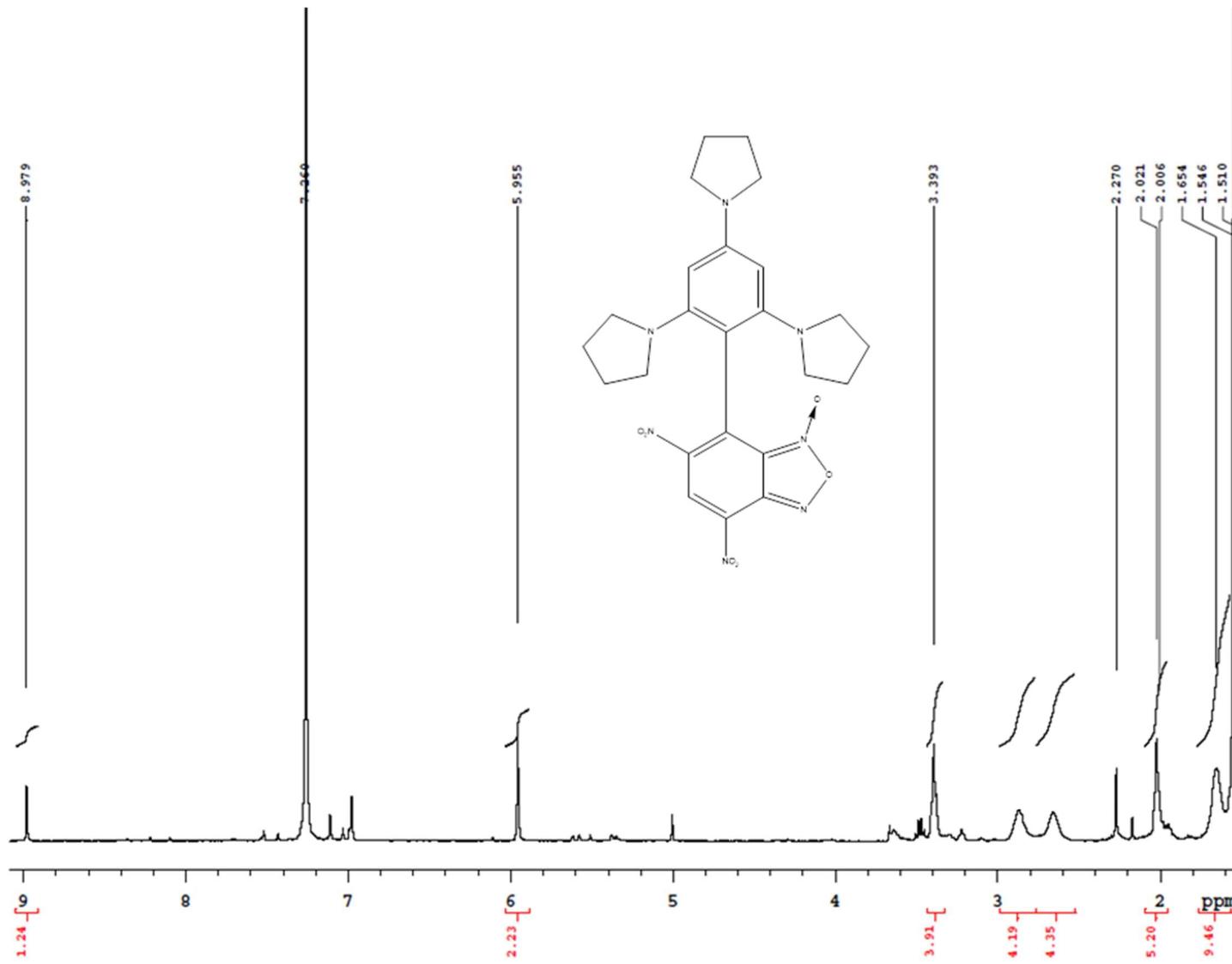
**Figure SI-8.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100.56 MHz, 25 °C) of compound 7.



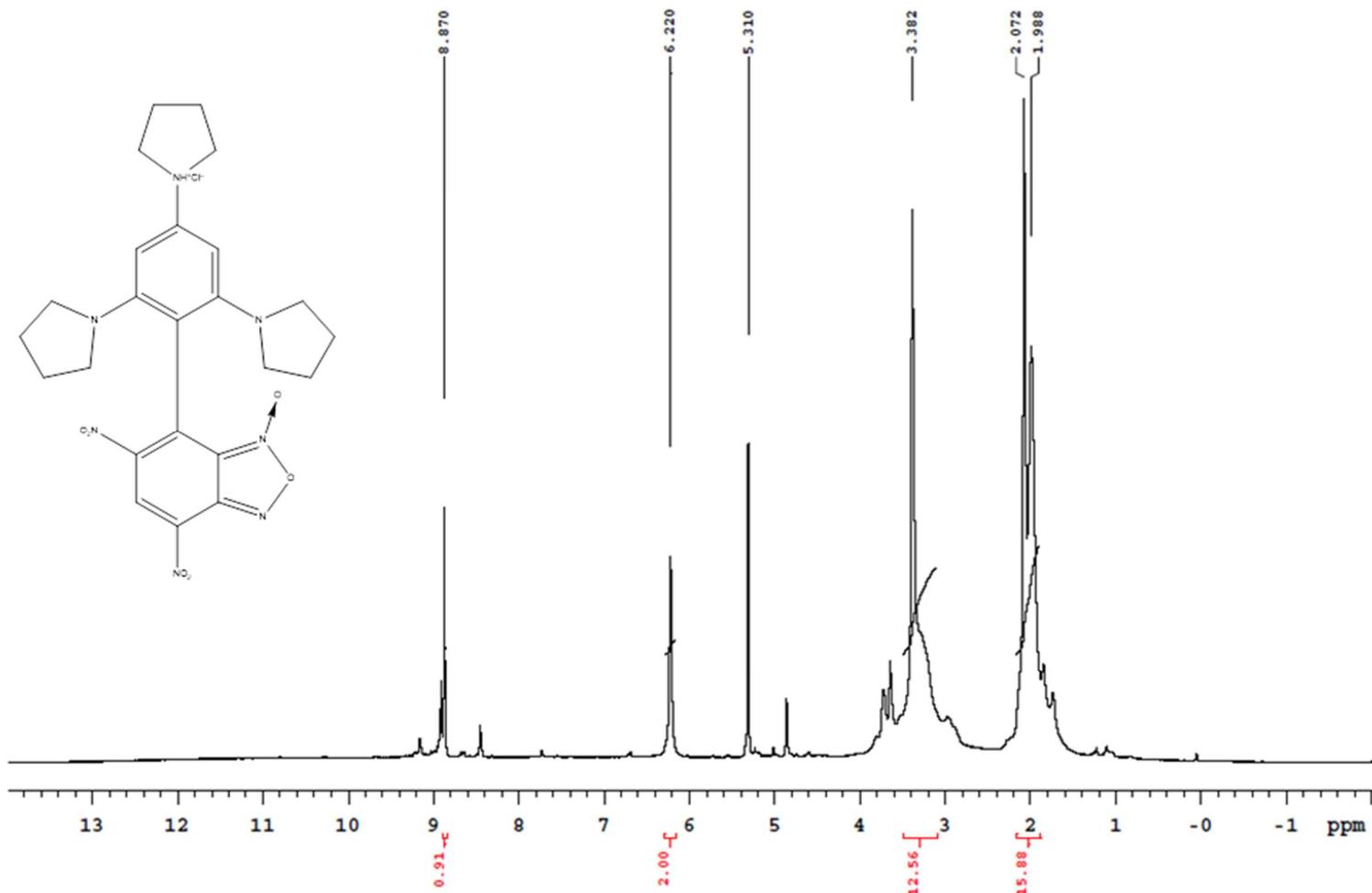
**Figure SI-9.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 25 °C) of compound  $7\text{H}^+\text{Cl}^-$ .



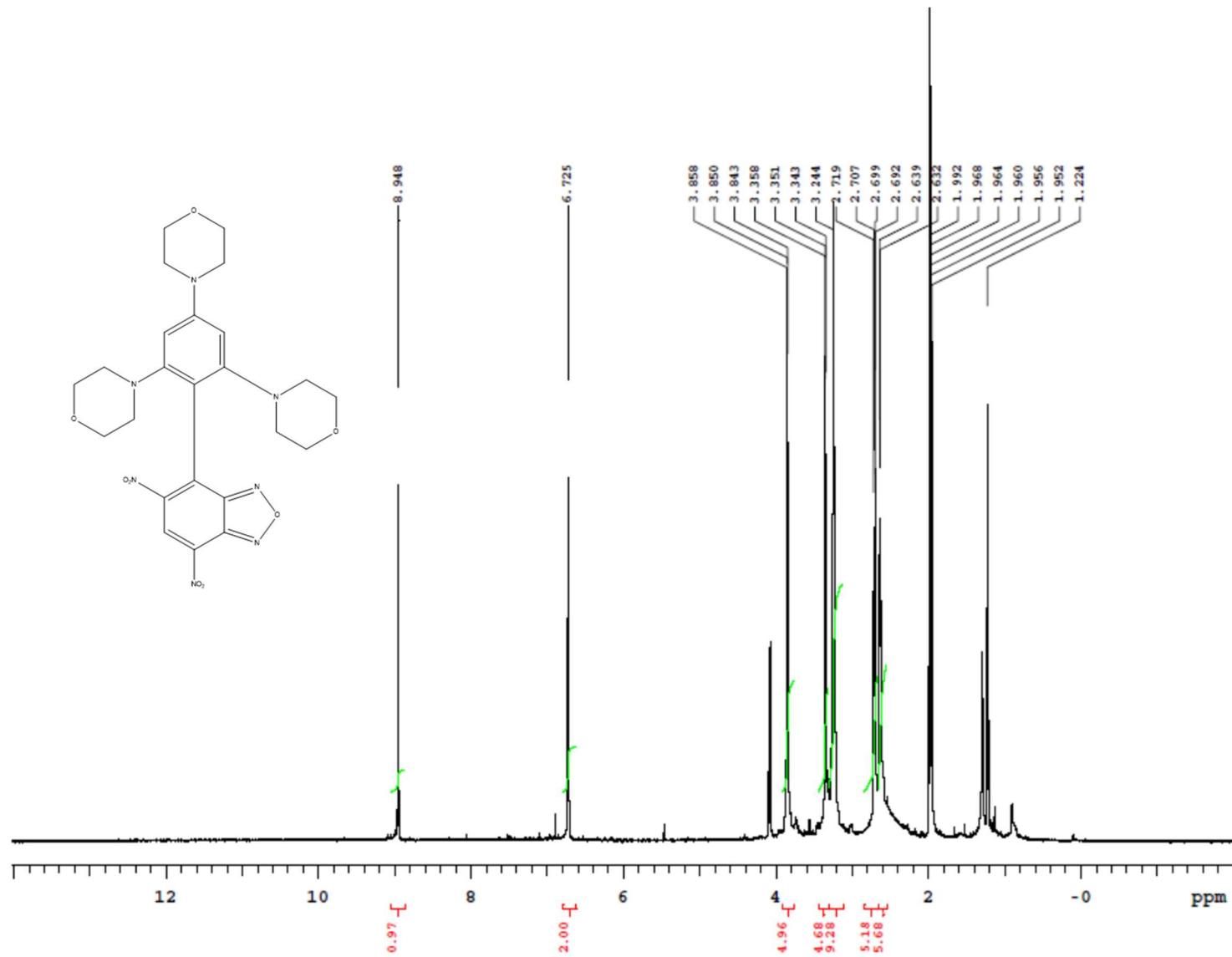
**Figure SI-10.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100.56 MHz, 25 °C) of compound  $7\text{H}^+\text{Cl}^-$ .



**Figure SI-11.** <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, 25 °C) of compound 8.



**Figure SI-12.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 600 MHz, 0 °C) of compound  $\mathbf{8H}^+\text{Cl}^-$ .



**Figure SI-13.** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 600 MHz, 25 °C) of compound **10**.

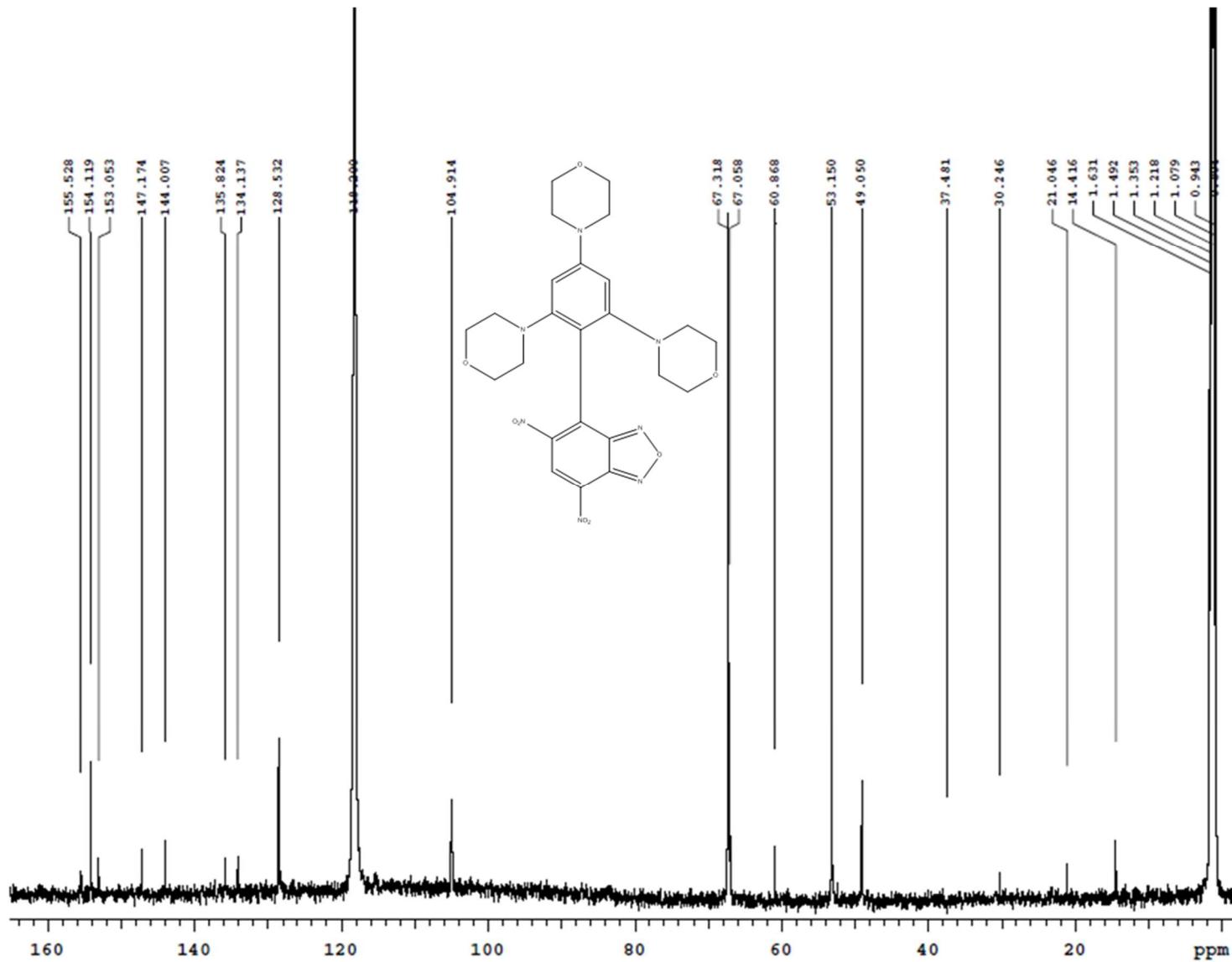
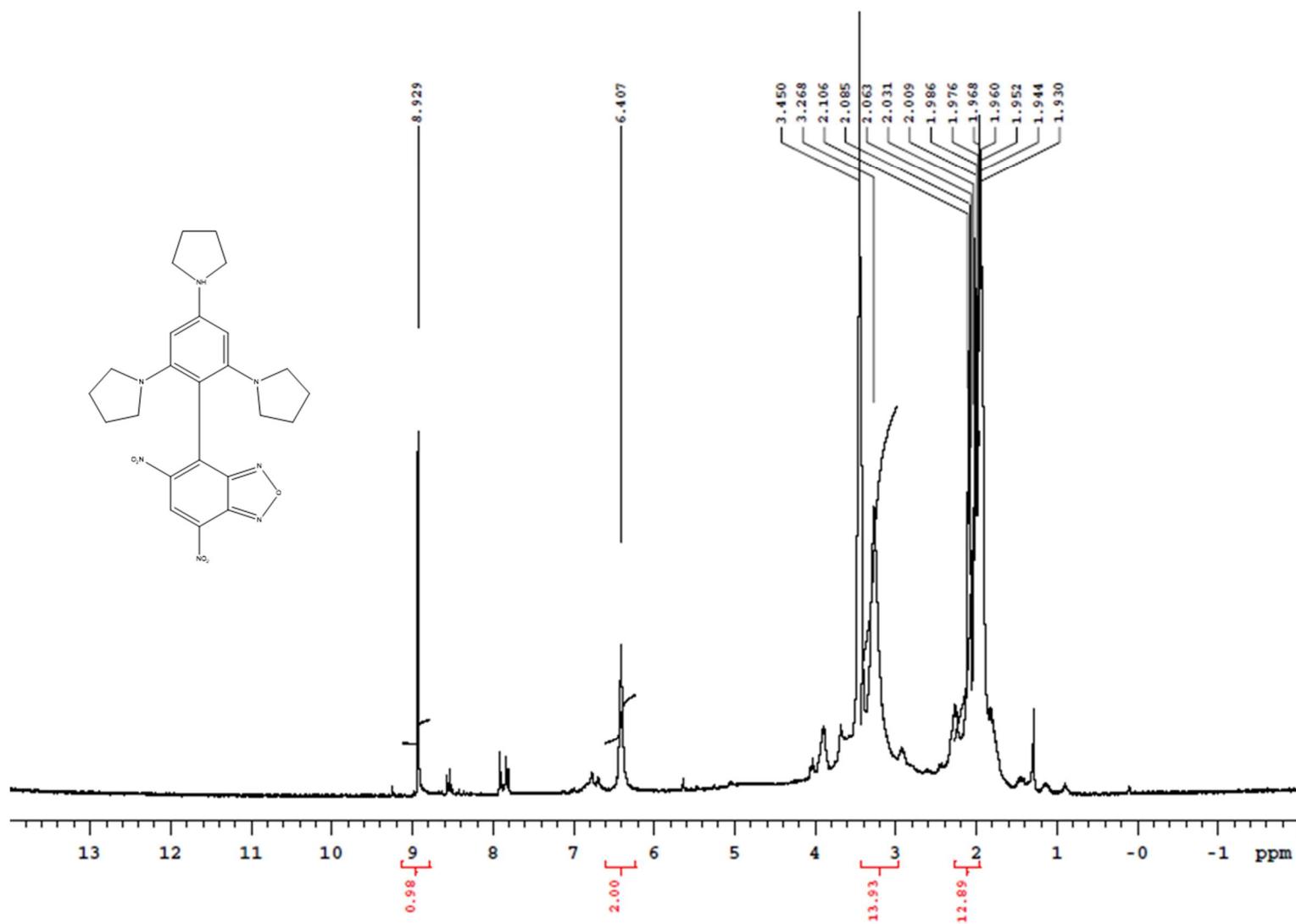
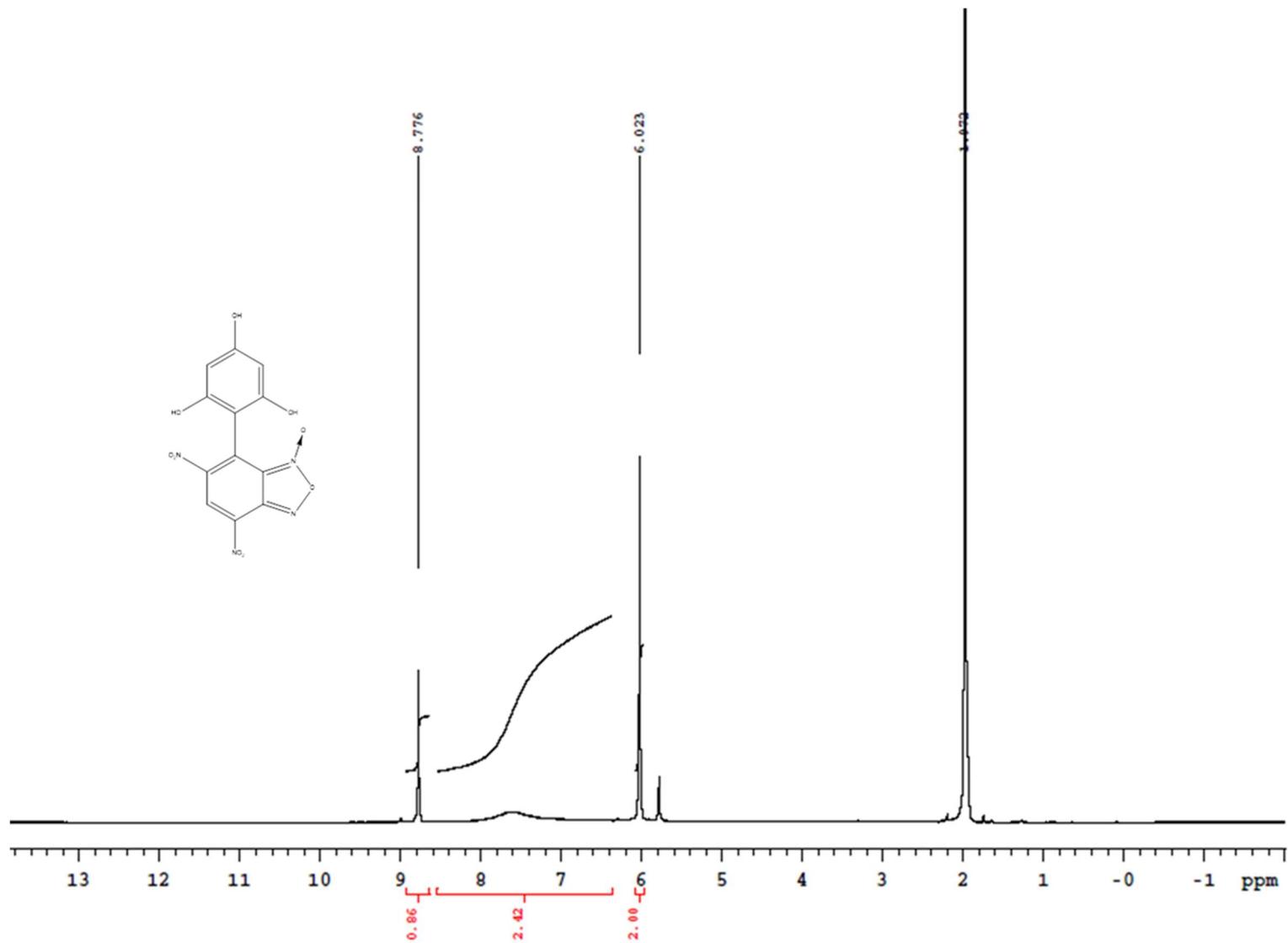


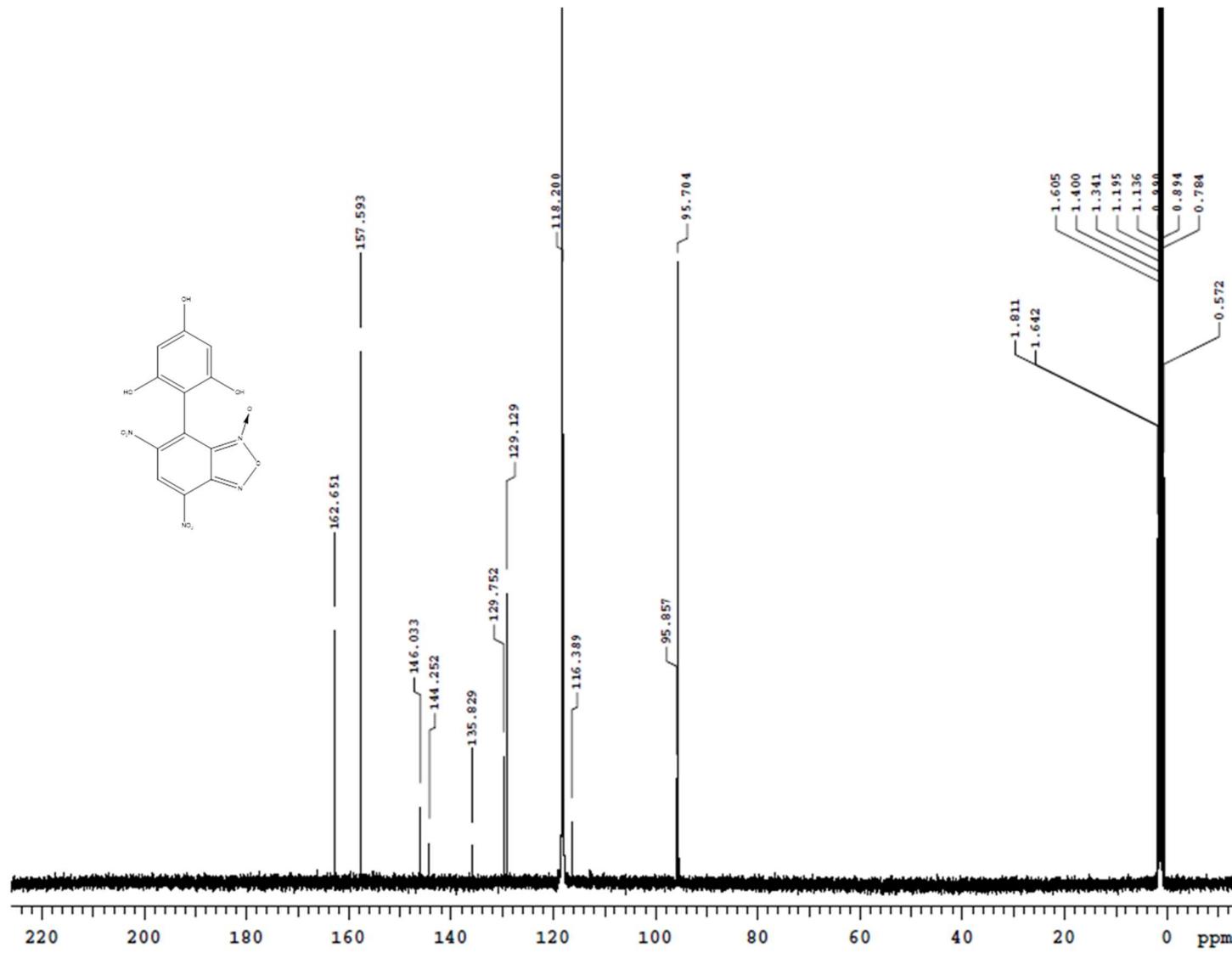
Figure SI-14.  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 100.6 MHz, 25 °C) of compound 10.



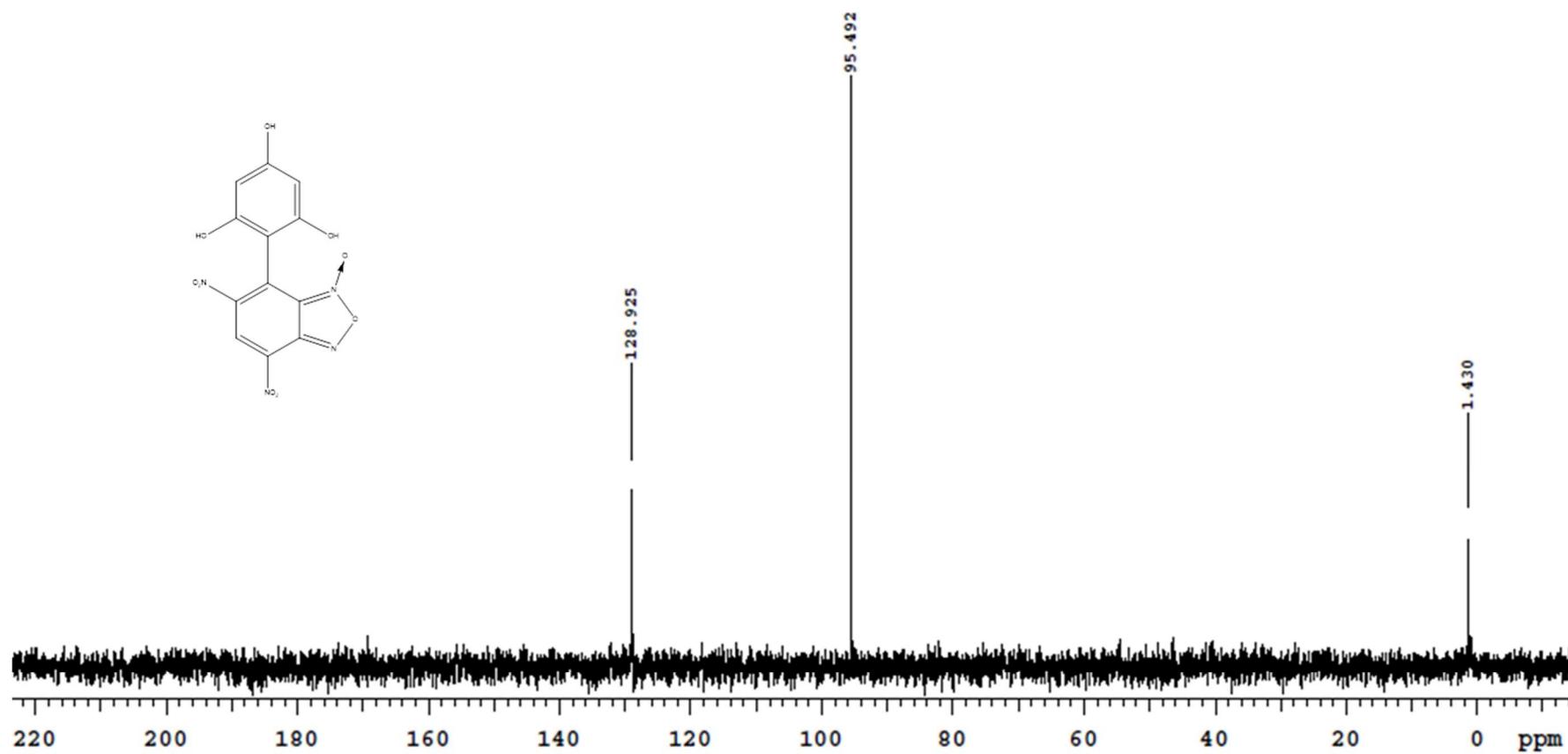
**Figure SI-15.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 300 MHz, 25 °C) of compound 11.



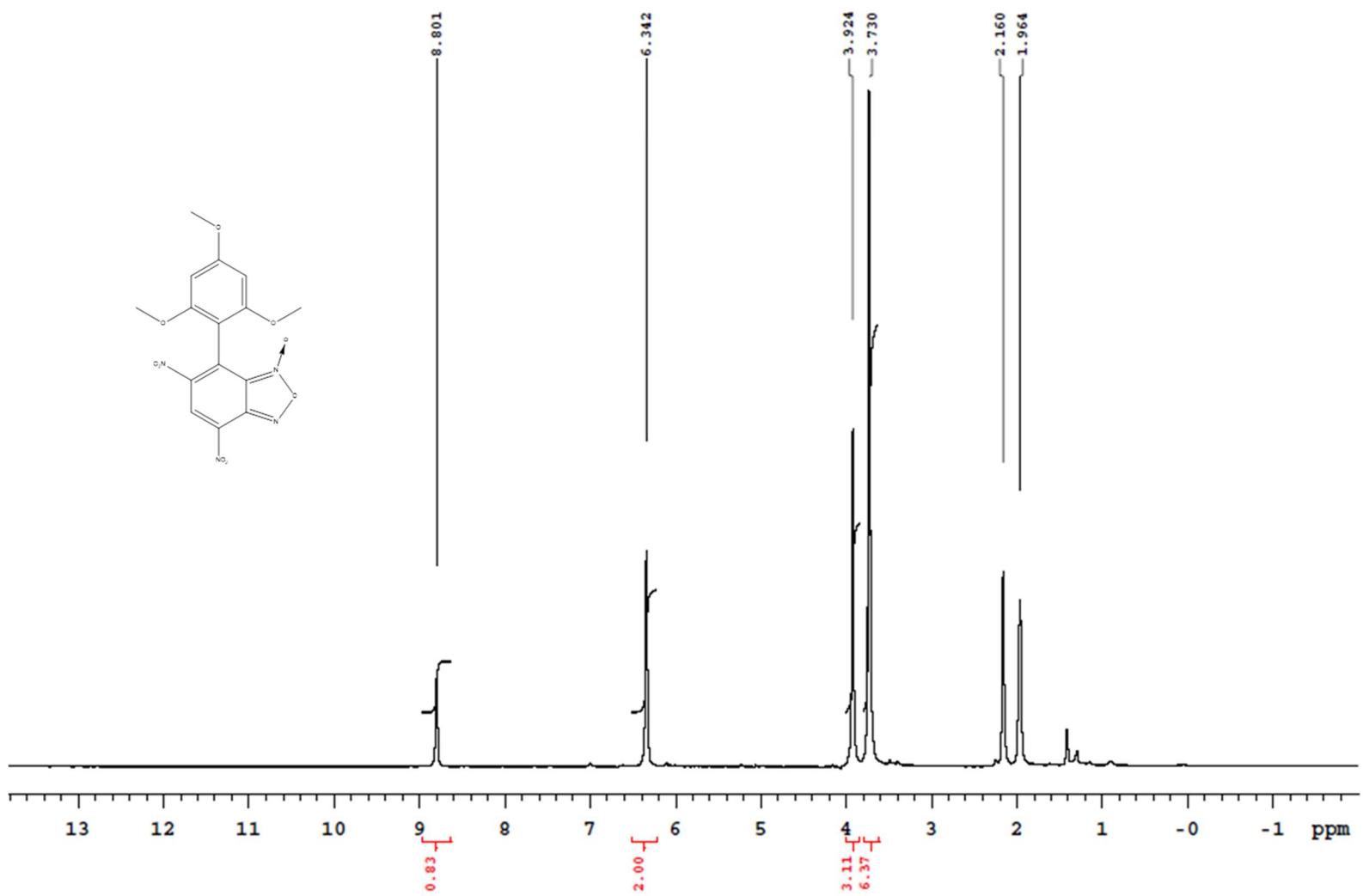
**Figure SI-16.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 300 MHz, 25 °C) of compound 14.



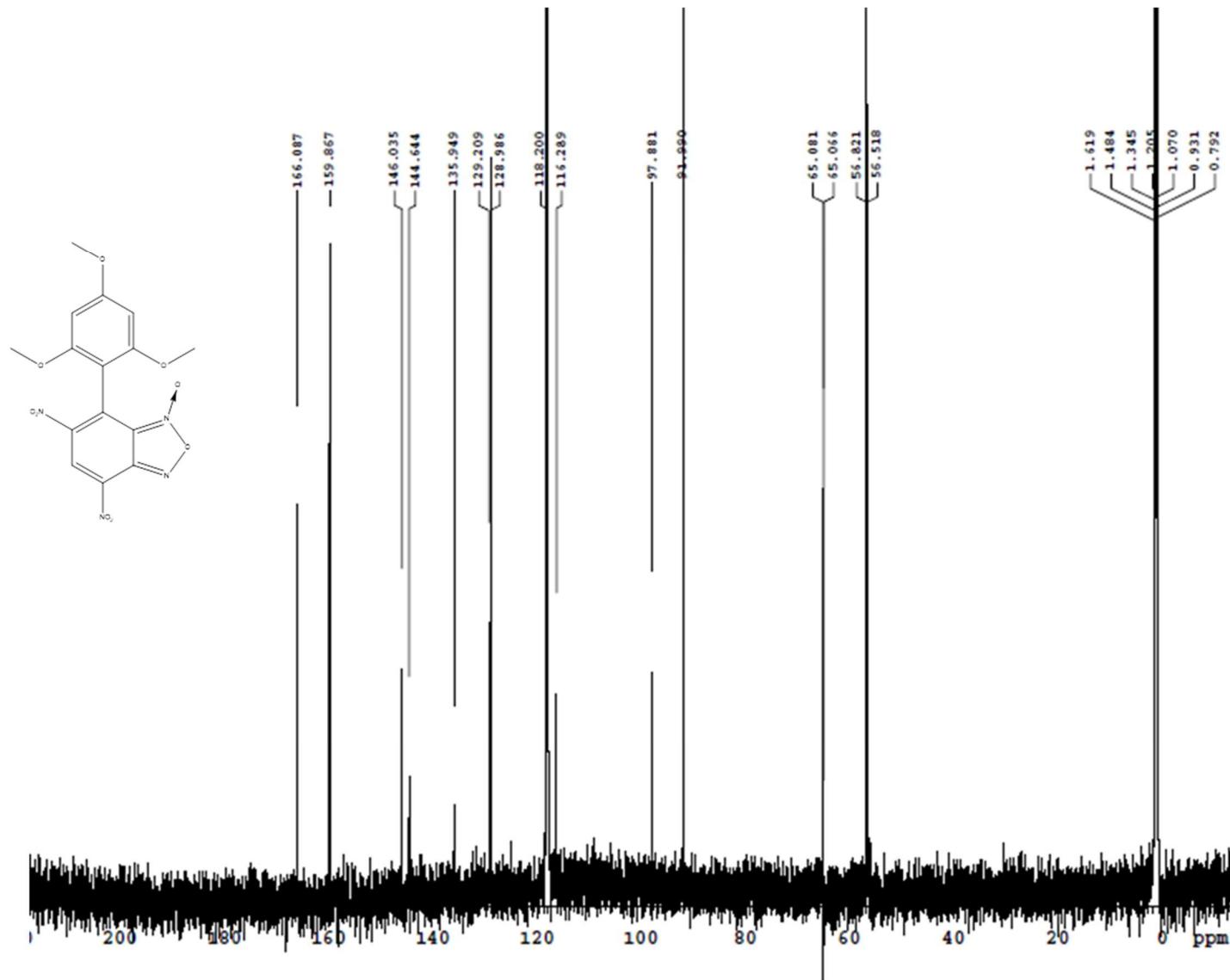
**Figure SI-17.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ,  $100.56 \text{ MHz}$ ,  $25^\circ\text{C}$ ) of compound 14.



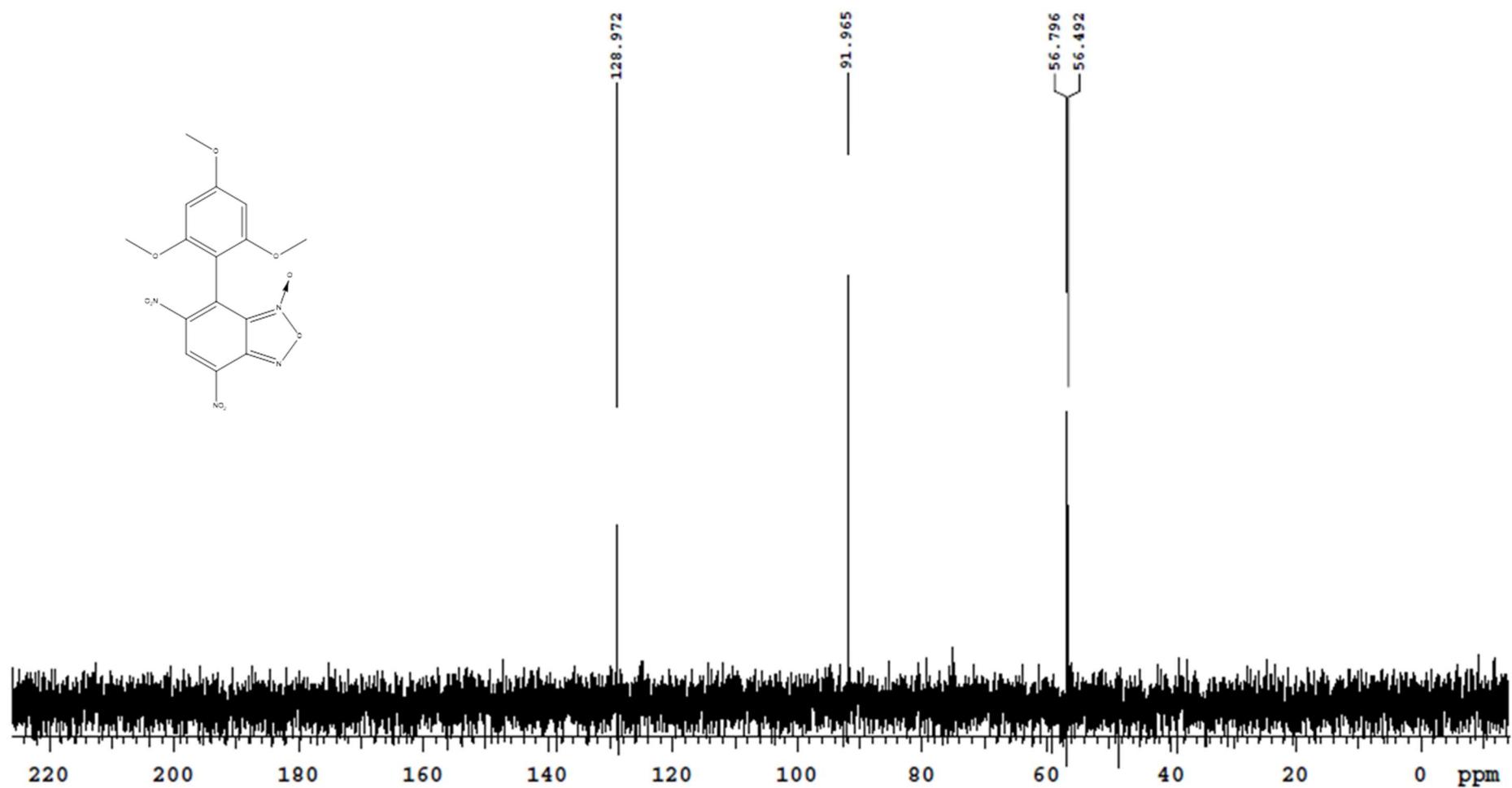
**Figure SI-18.** DEPT 135 spectrum ( $\text{CD}_3\text{CN}$ , 100.56 MHz, 25 °C) of compound **14**.



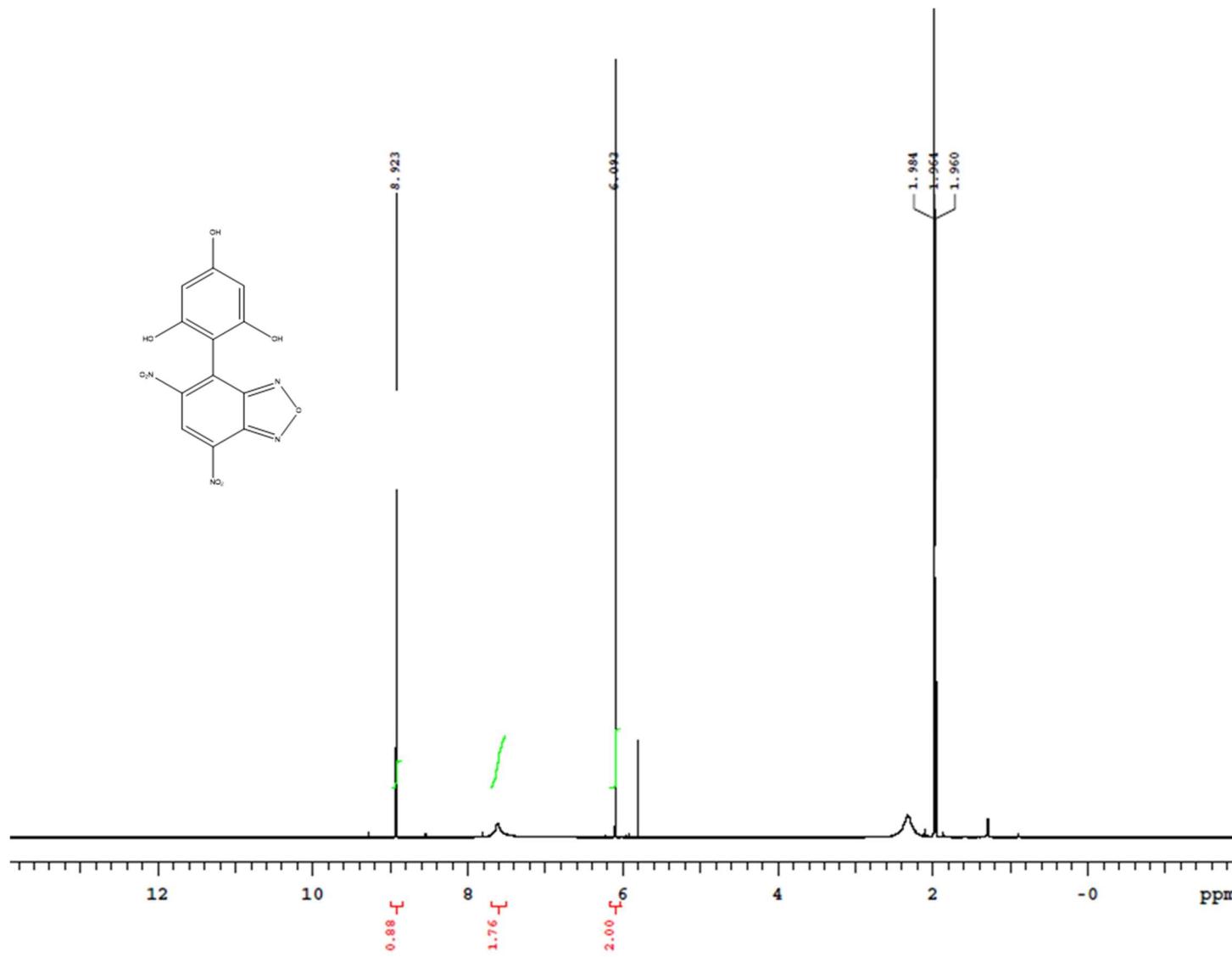
**Figure SI-19.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 300 MHz, 25 °C) of compound 15.



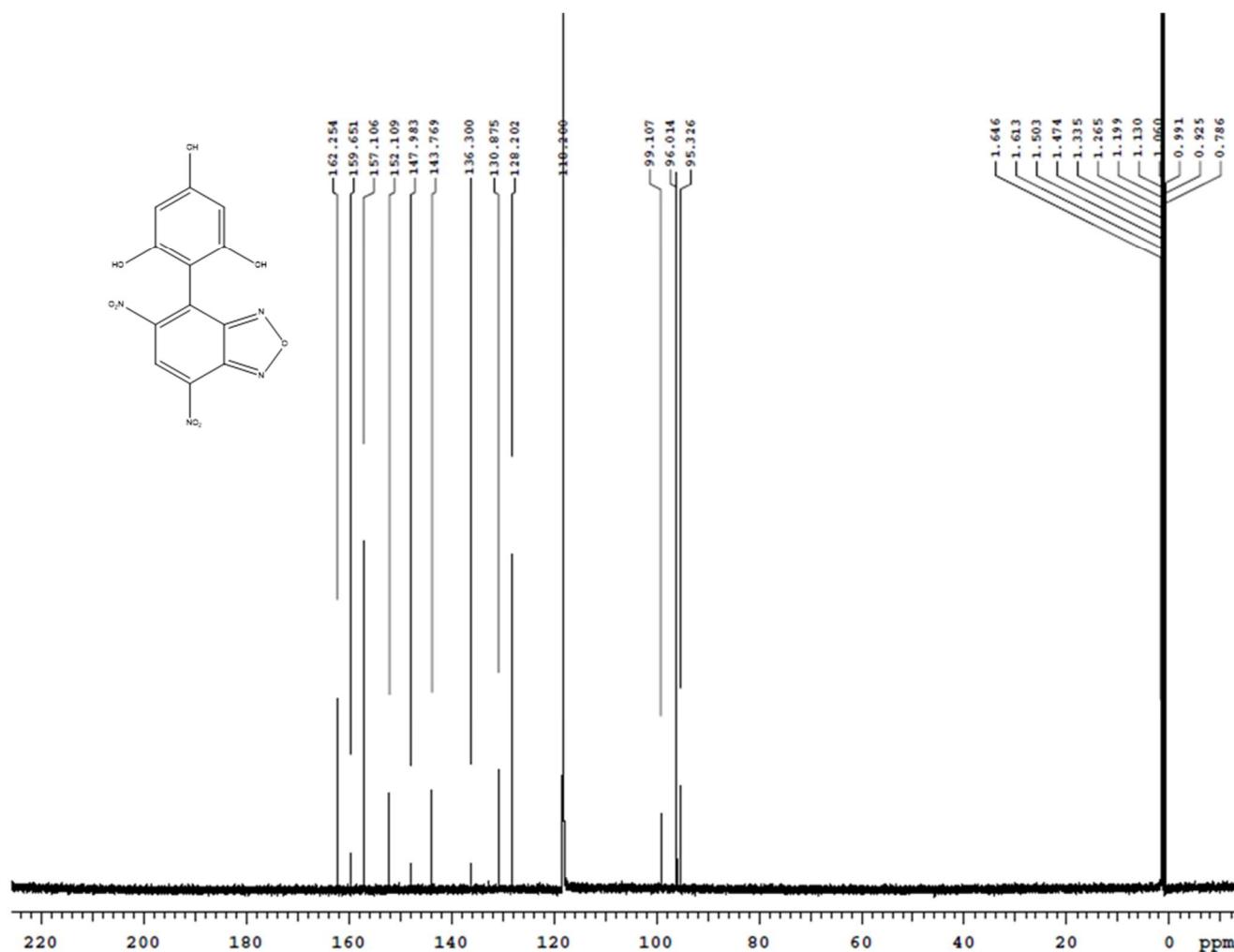
**Figure SI-20.**  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 150.80 MHz, 25 °C) of compound 15; signals at 65 ppm are electric spikes as can be seen in DEPT in Fig. SI-17).



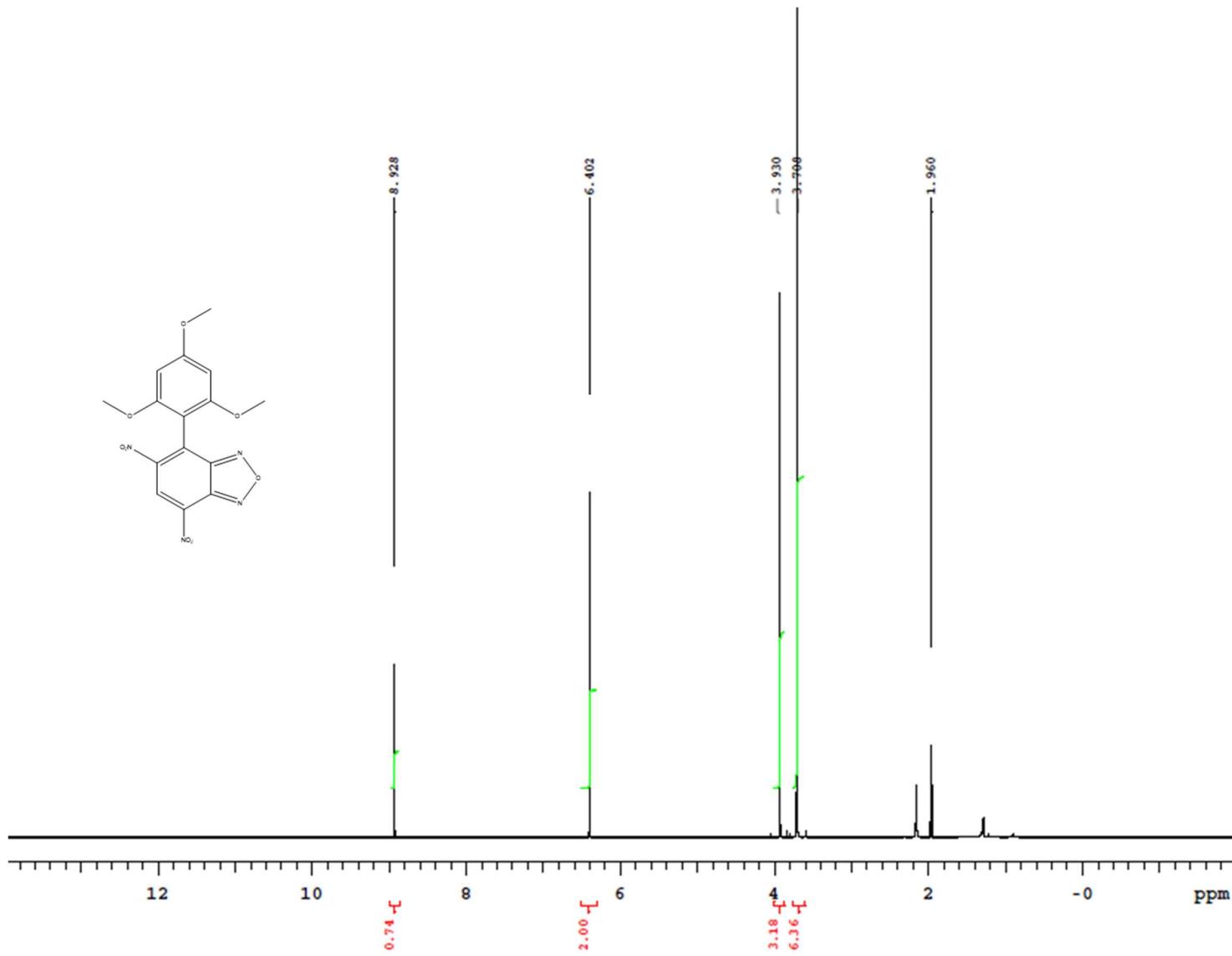
**Figure SI-21.** DEPT 135 spectrum ( $\text{CD}_3\text{CN}$ , 150.80 MHz, 25 °C) of compound 15.



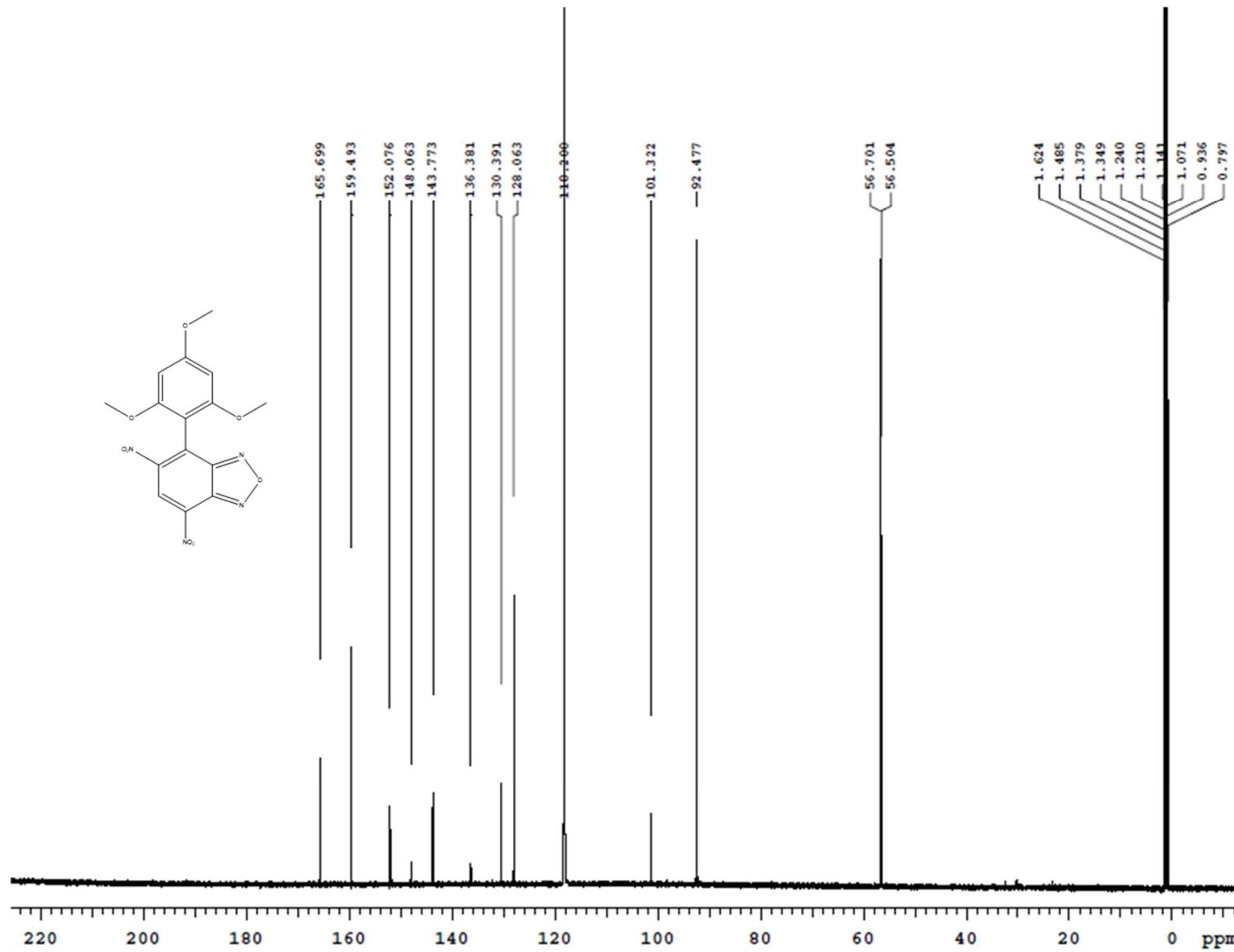
**Figure SI-22.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 600 MHz, 25 °C) of compound **16**.



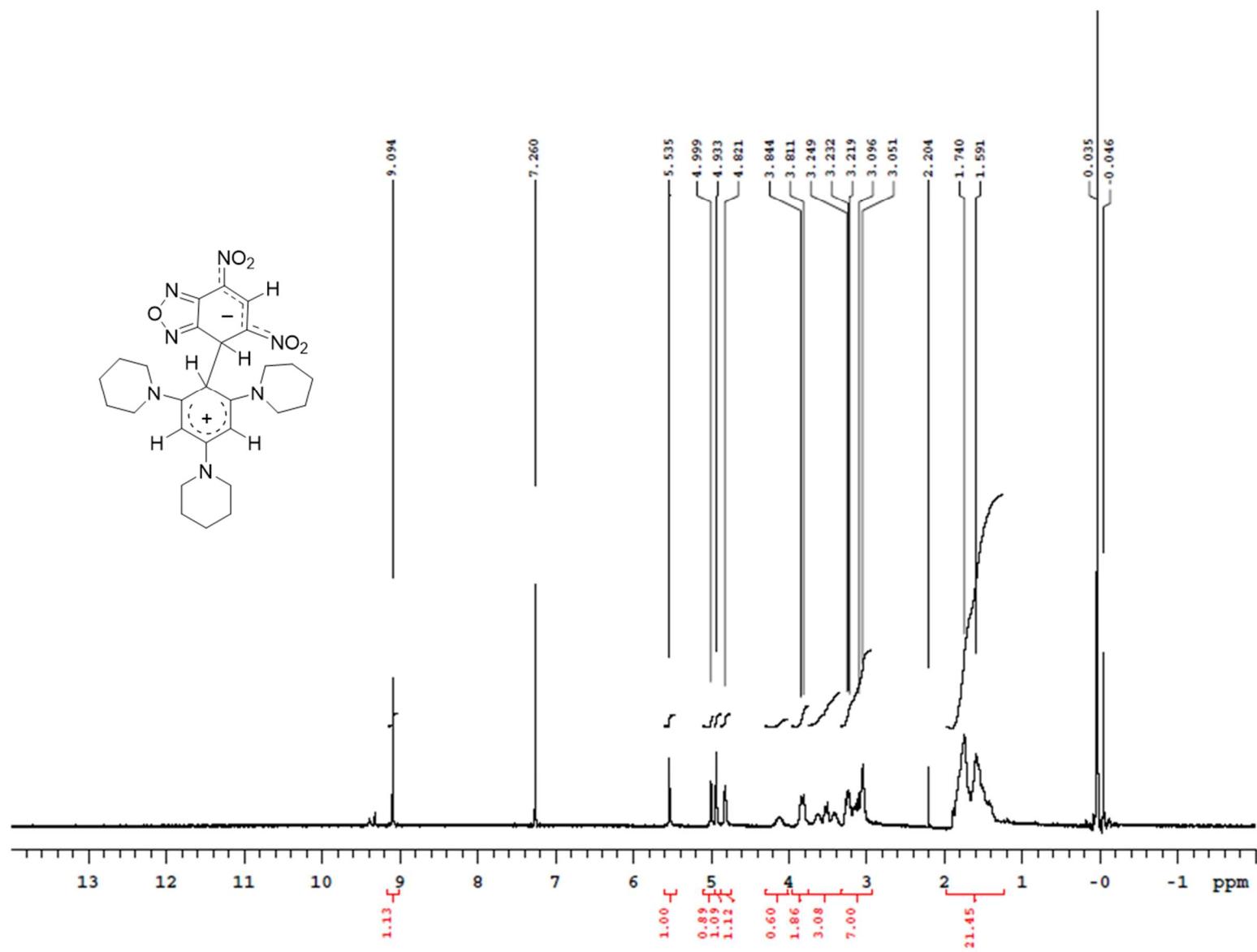
**Figure SI-23.**  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 150.80 MHz, 25 °C) of compound **16**; peaks at 159.7 and 95.3 ppm belong to phloroglucinol.



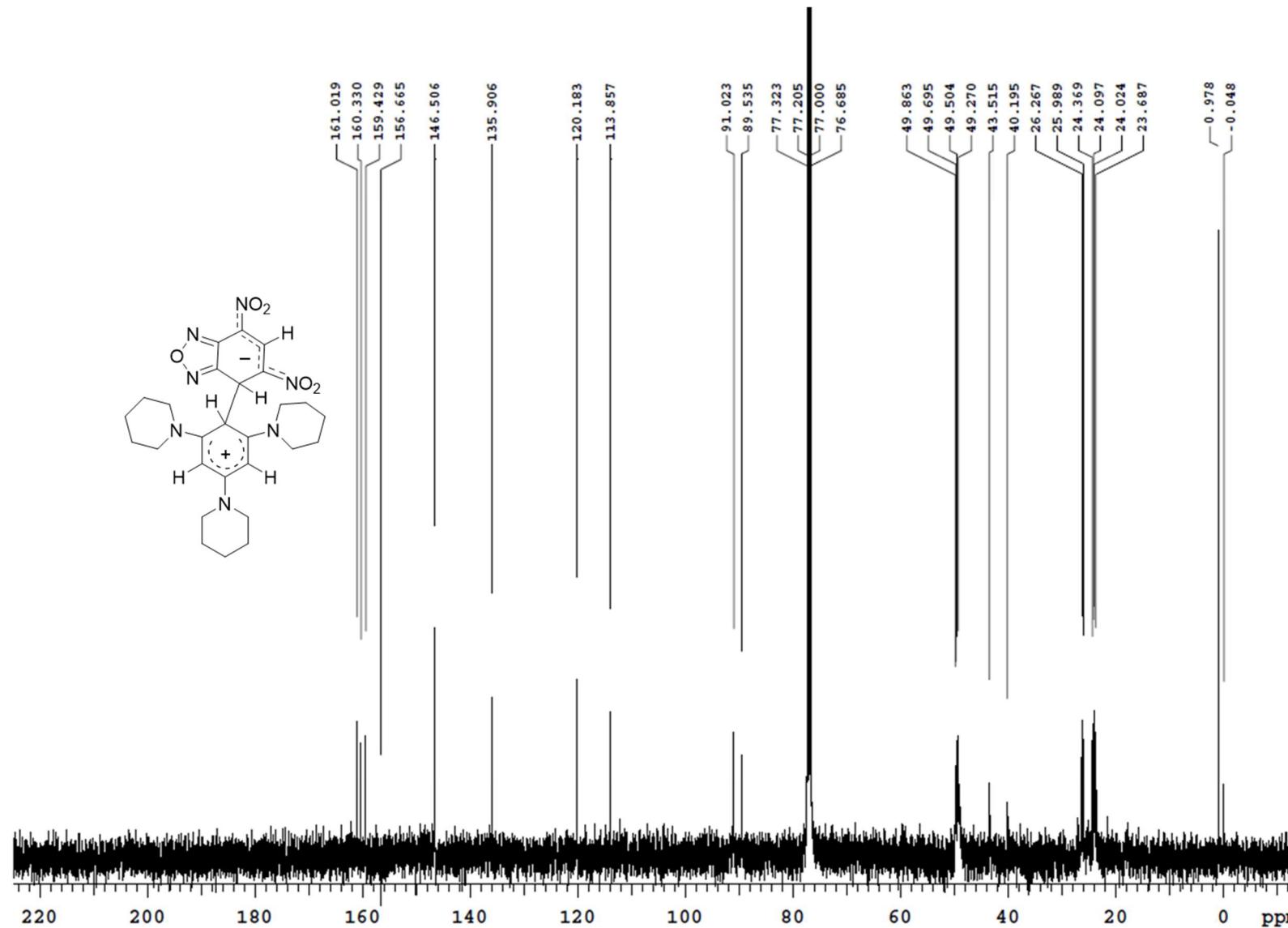
**Figure SI-24.** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 600 MHz, 25 °C) of compound 17.



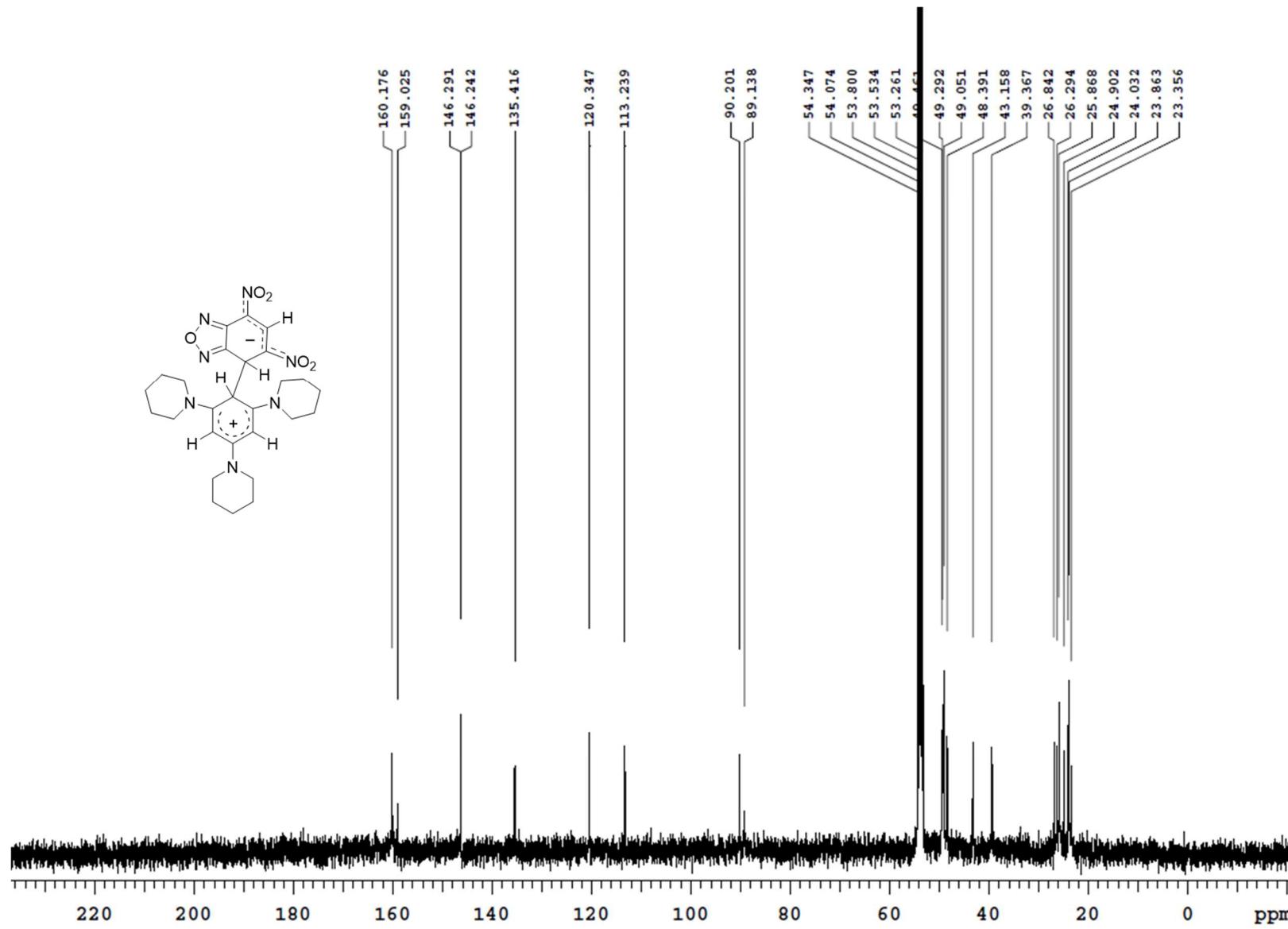
**Figure SI-25.**  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 150.80 MHz, 25 °C) of compound 17



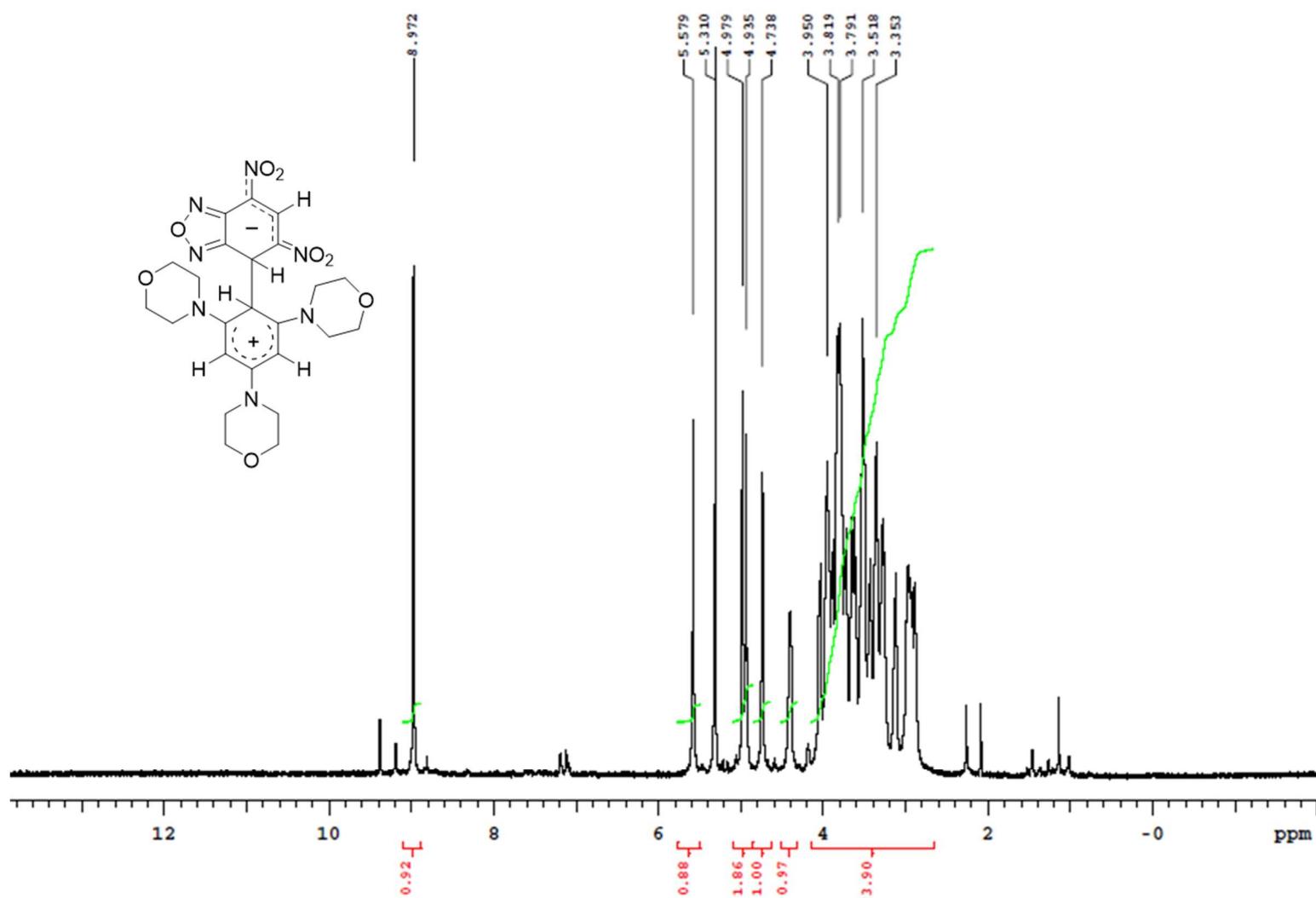
**Figure SI-26.** <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, -60 °C) of compound WM1



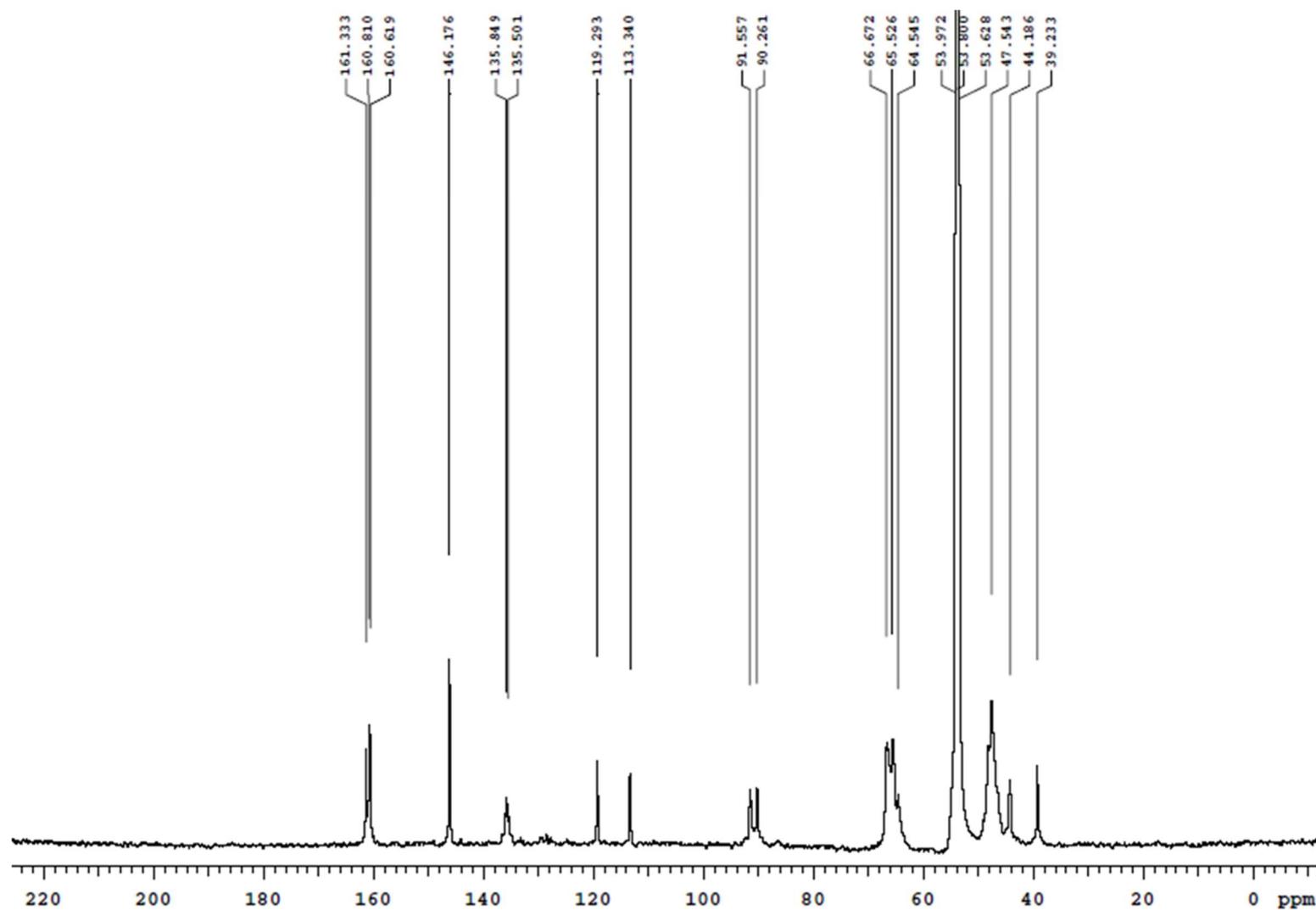
**Figure SI-27.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100.6 MHz,  $-43\text{ }^\circ\text{C}$ ) of compound **WM1**



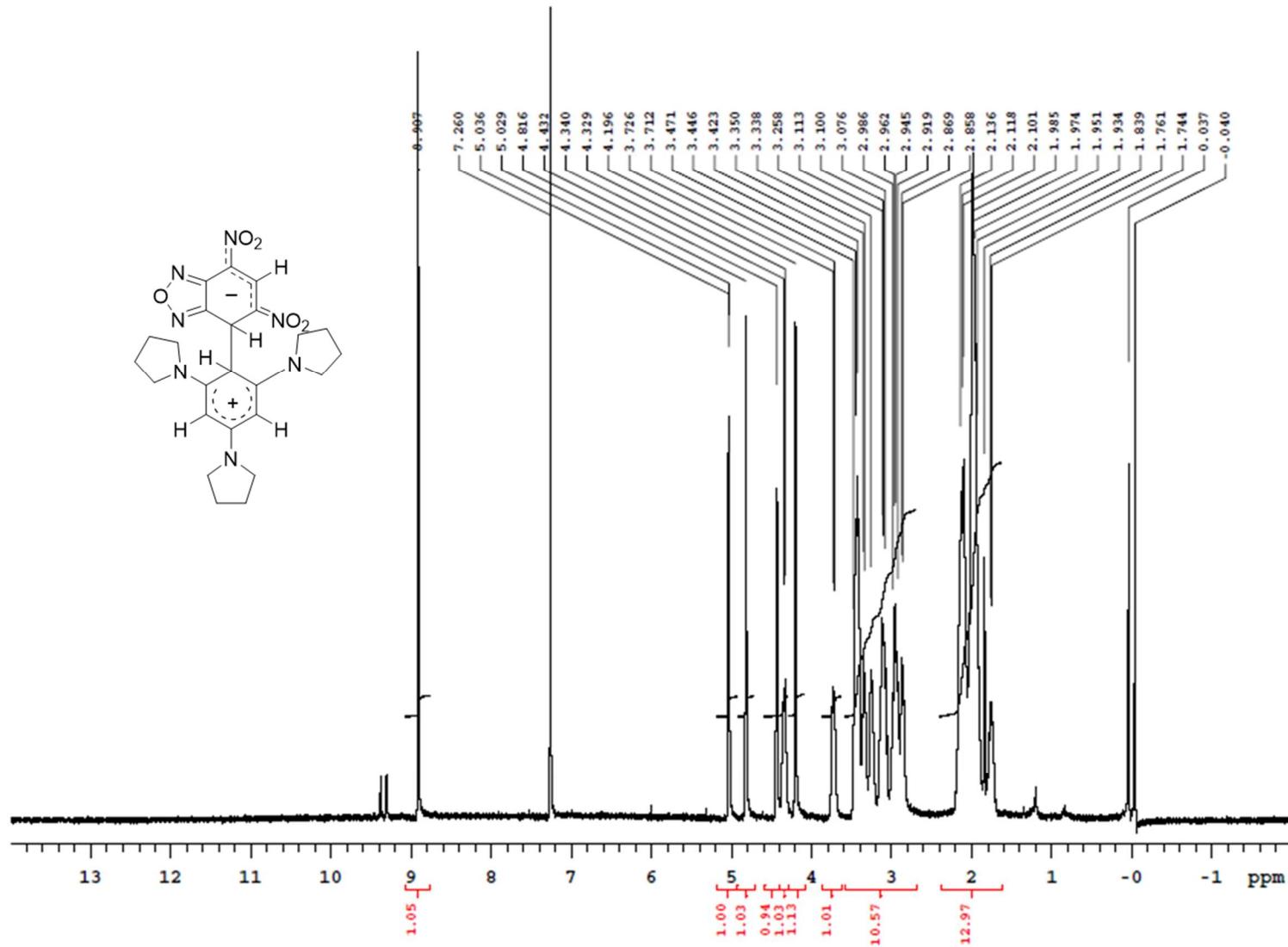
**Figure SI-28.**  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 100.6 MHz,  $-80^\circ\text{C}$ ) of compound WM1



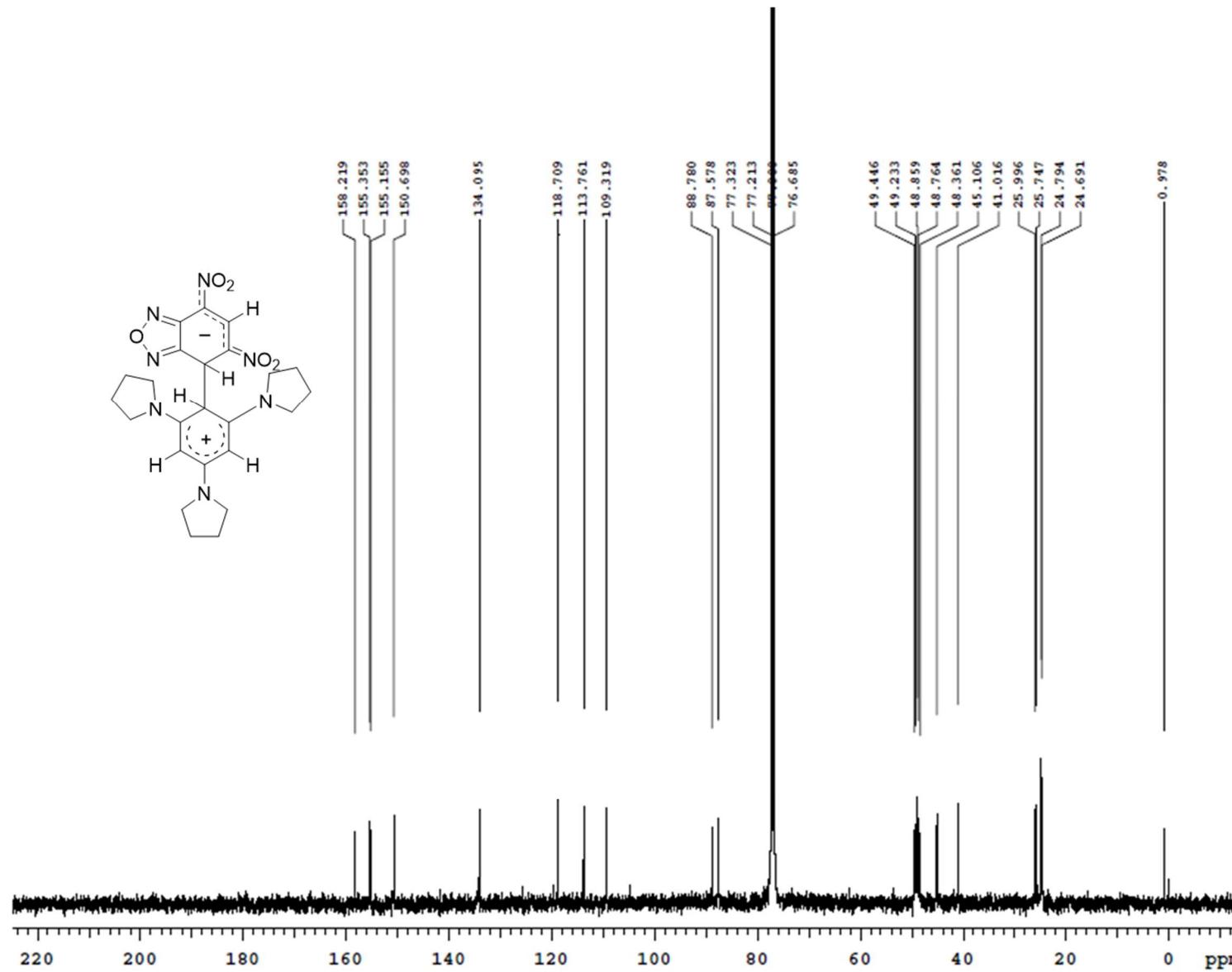
**Figure SI-29.** <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, -60 °C) of compound WM2



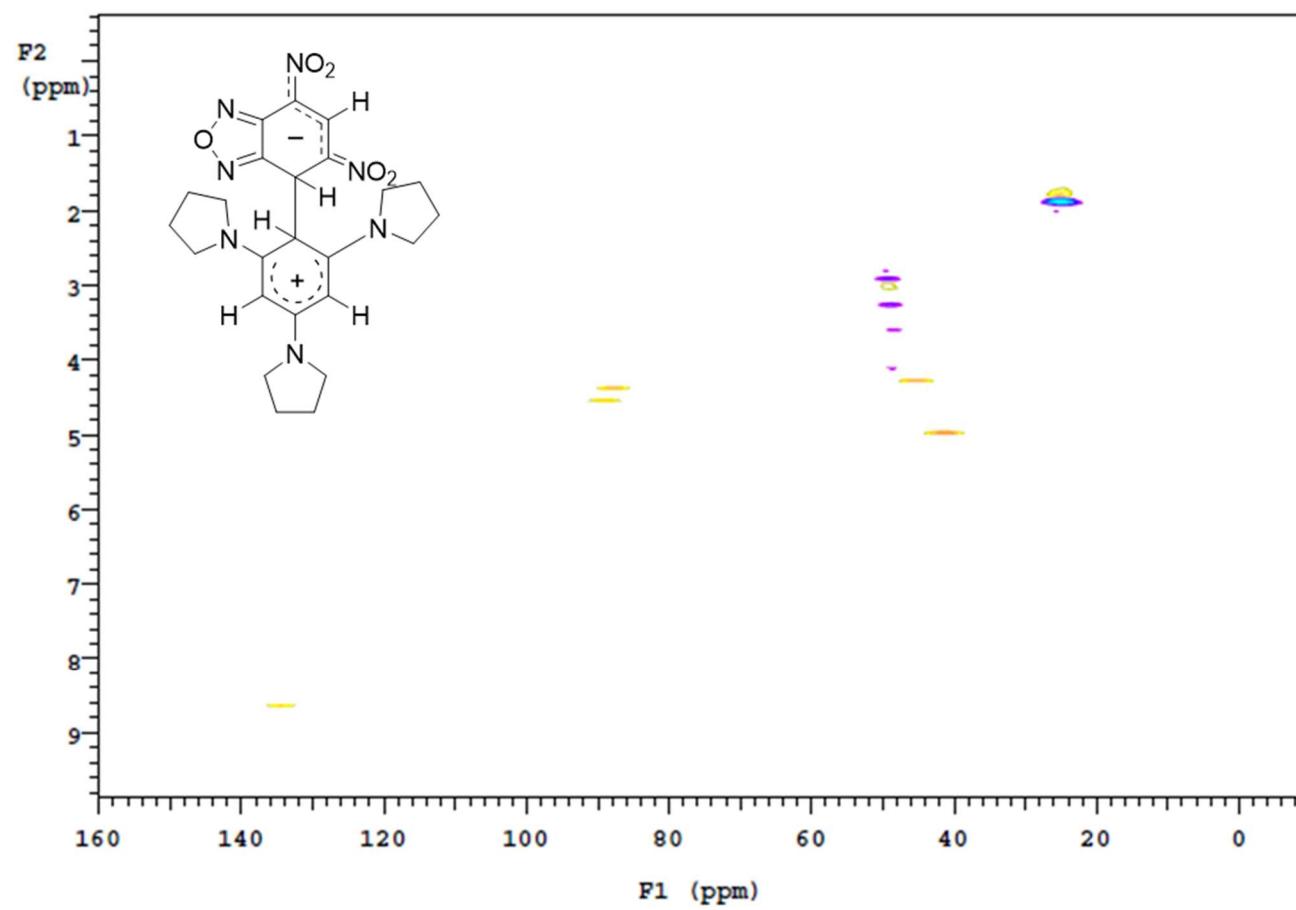
**Figure SI-30.** <sup>13</sup>C NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 100.6 MHz, -80 °C) of compound WM2



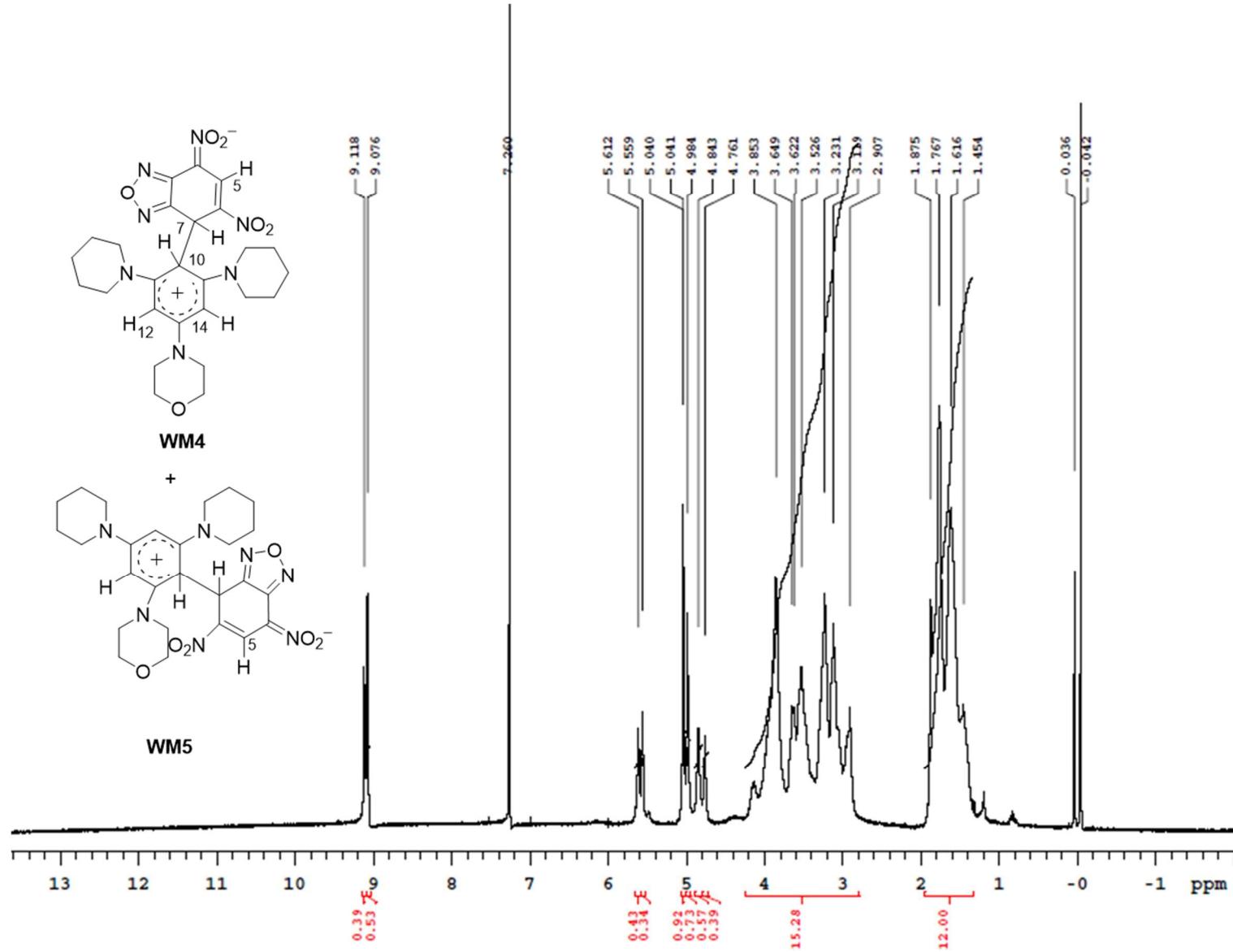
**Figure SI-31.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz,  $-37^\circ\text{C}$ ) of compound WM3



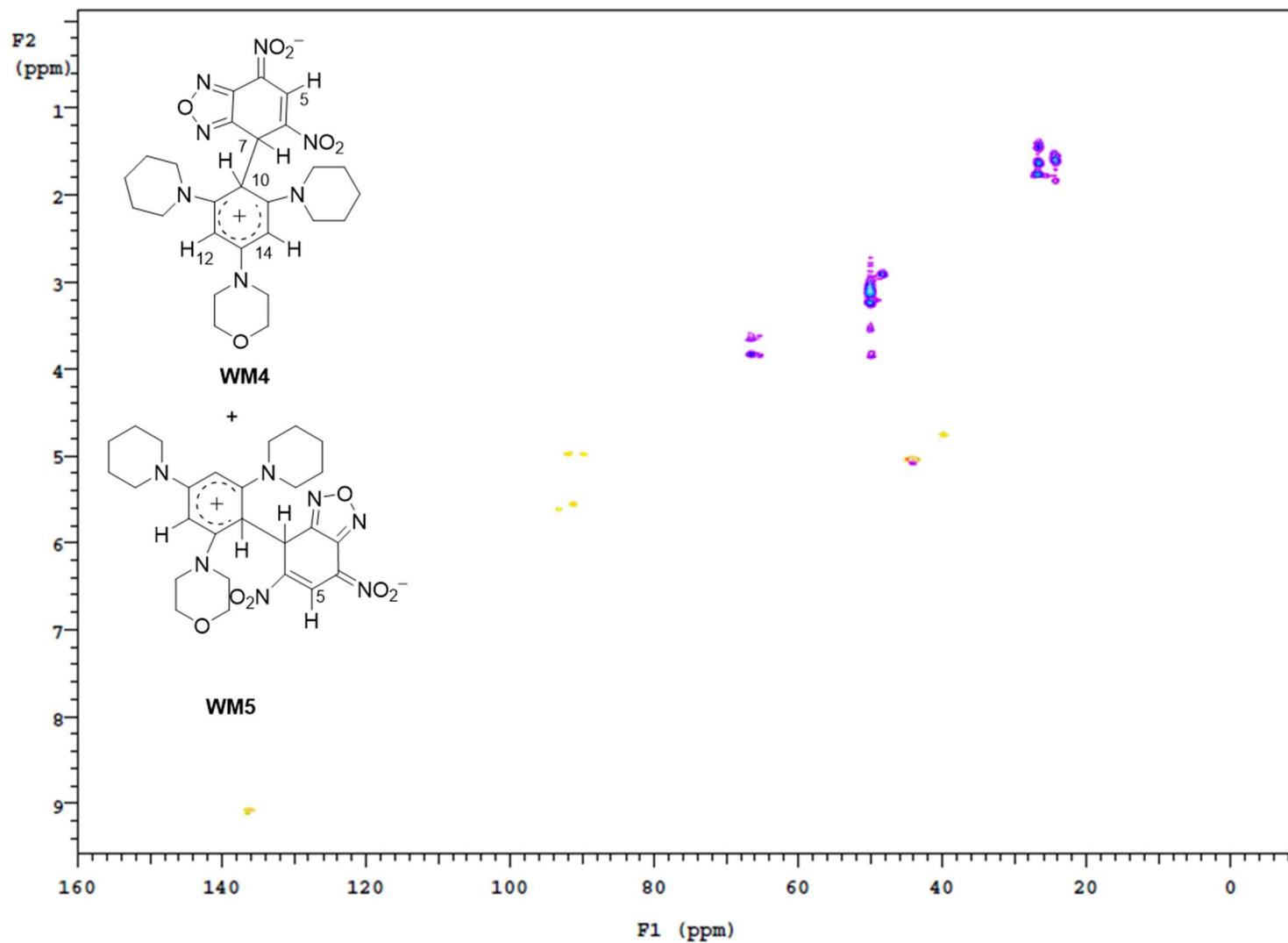
**Figure SI-32.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100.6 MHz, -37 °C) of compound WM3



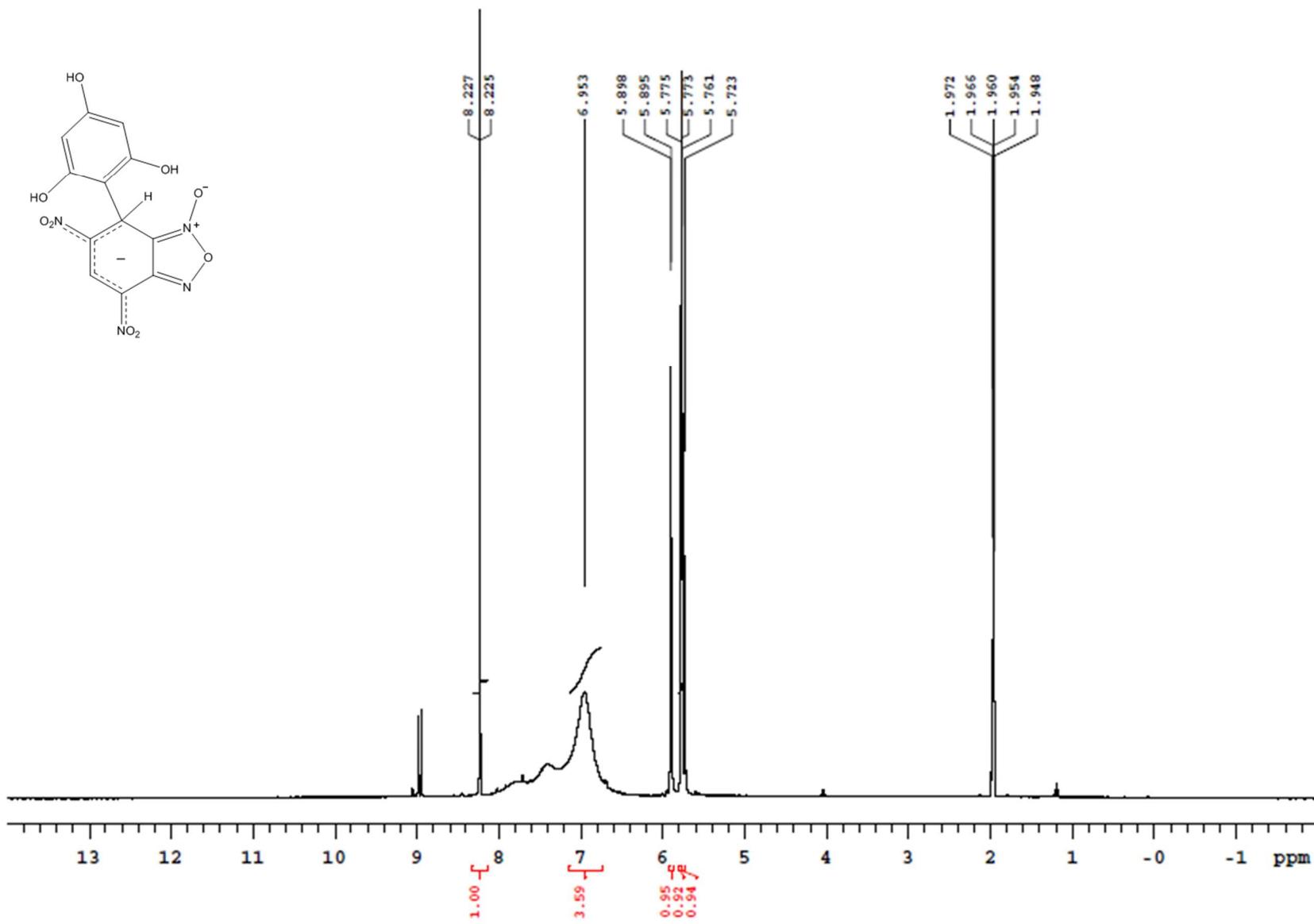
**Figure SI-33.** g-HSQC spectrum ( $\text{CDCl}_3$ , 100.6 MHz,  $-37^\circ\text{C}$ ) of compound WM3



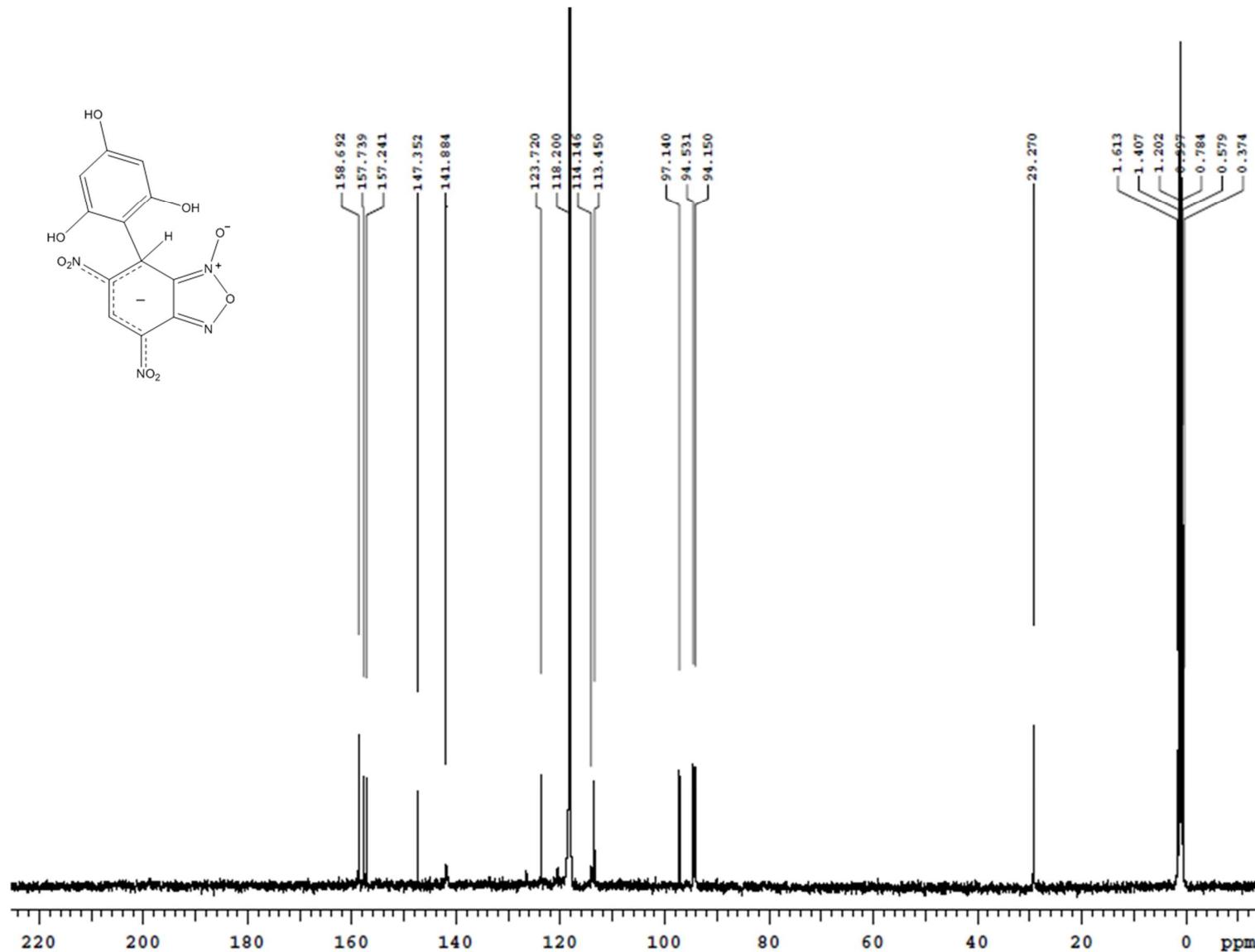
**Figure SI-34.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz, -37 °C) of compound WM4 and WM5



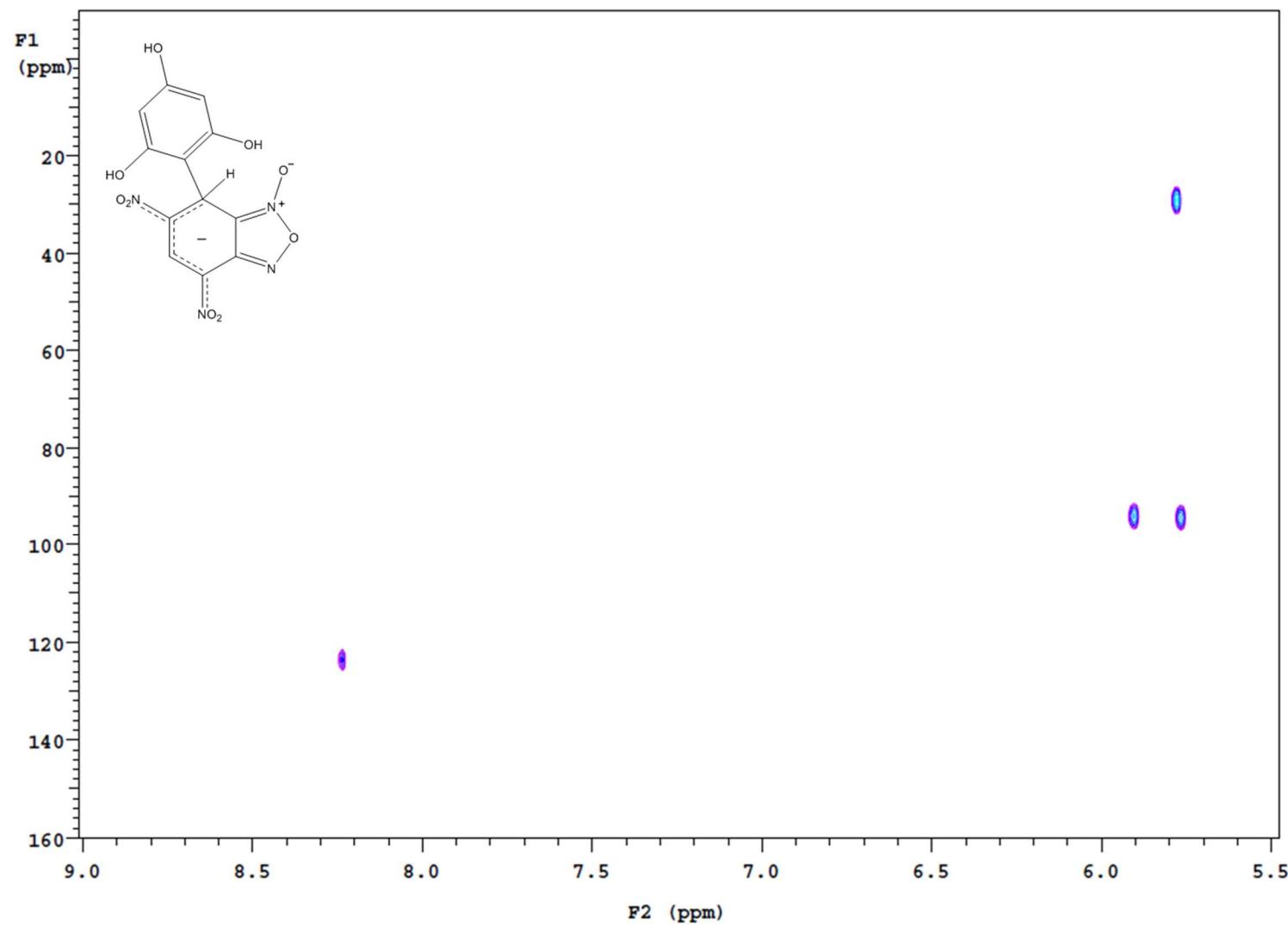
**Figure SI-35.** g-HSQC spectrum ( $\text{CDCl}_3$ , 100.6 MHz,  $-37^\circ\text{C}$ ) of compound WM4 and WM5



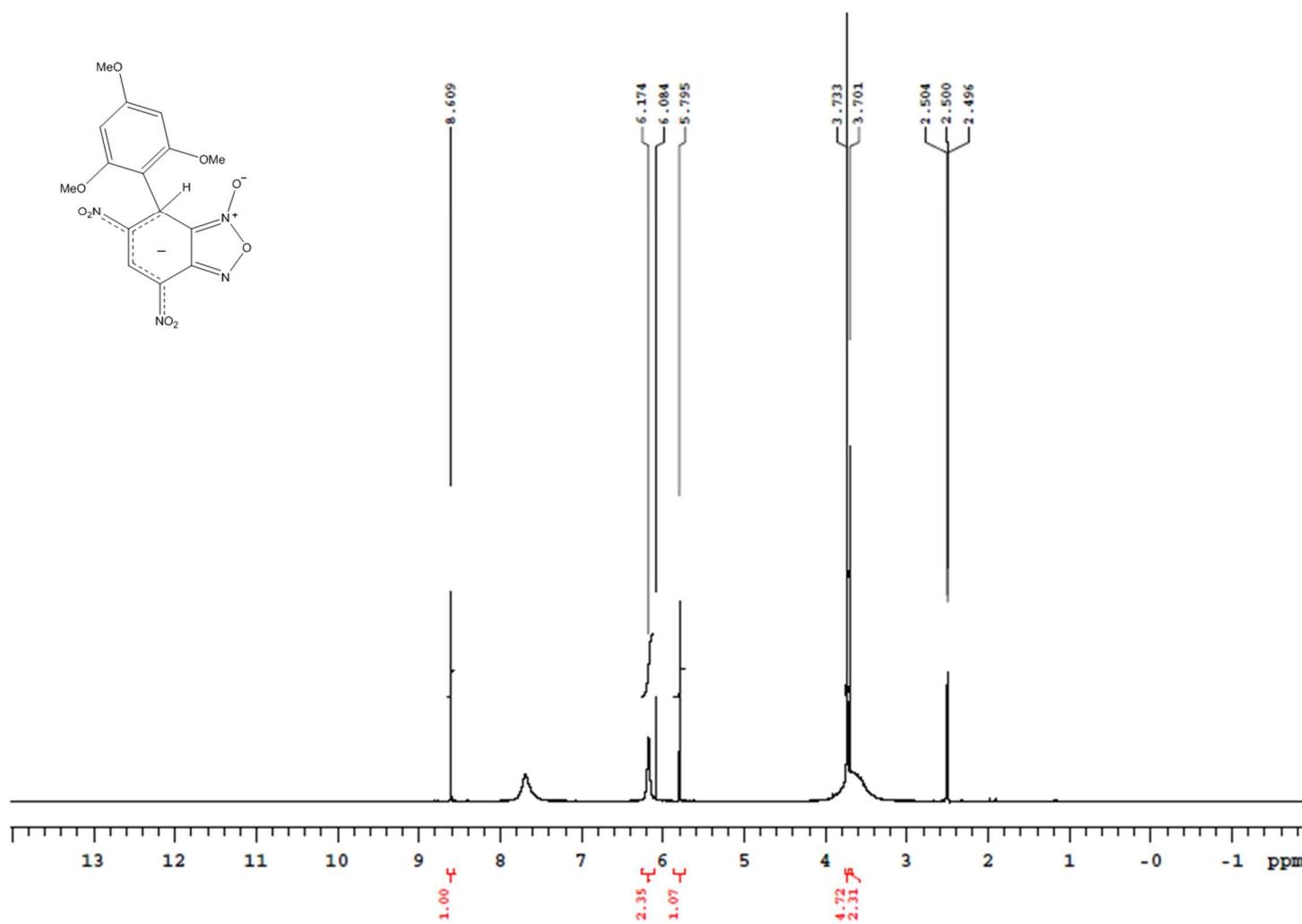
**Figure SI-36.** <sup>1</sup>H NMR spectrum ( $\text{CD}_3\text{CN}$ , 400 MHz, -35 °C) of compound **M1**



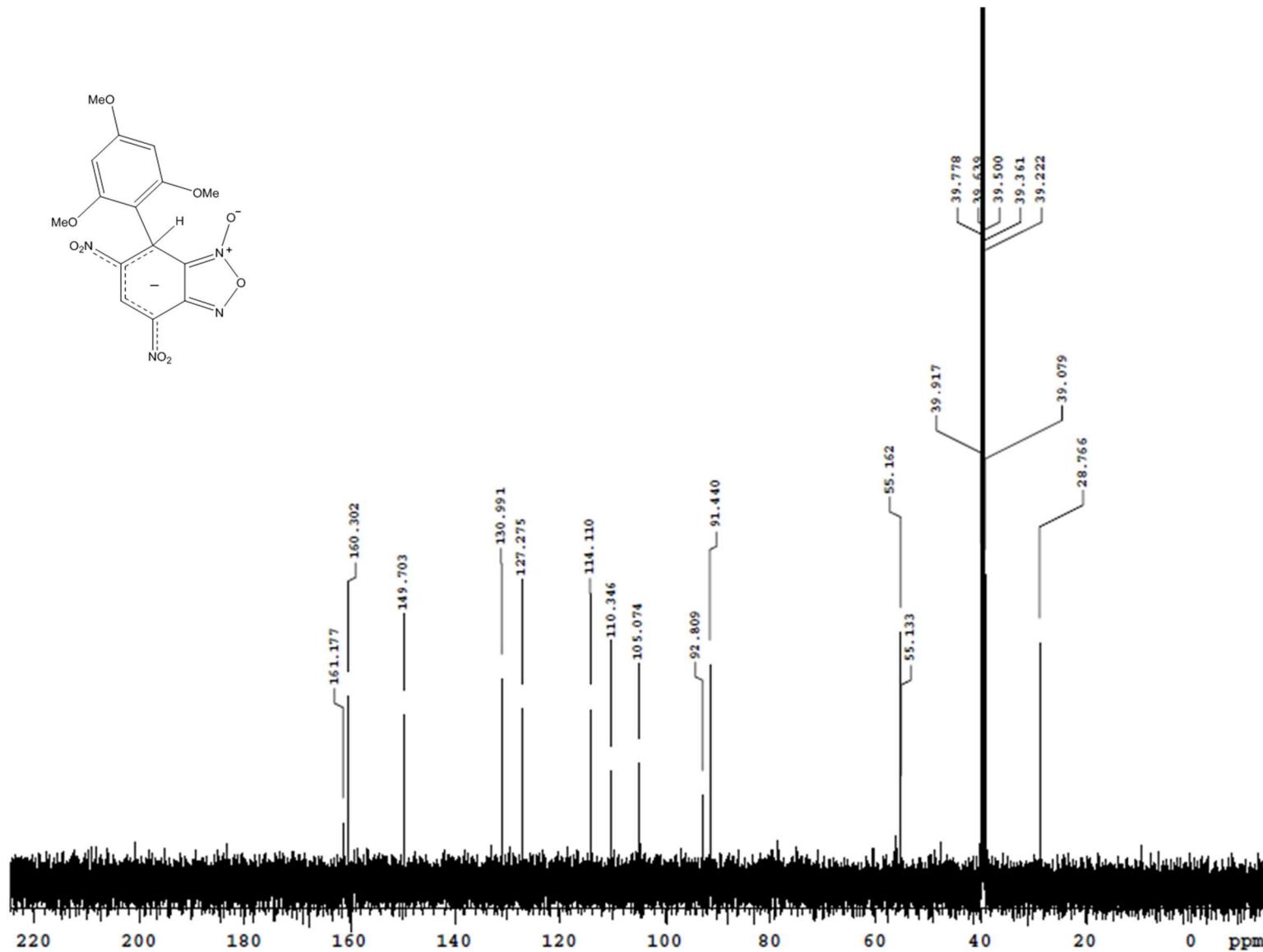
**Figure SI-37.**  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 100.56 MHz,  $-35^\circ\text{C}$ ) of compound **M1**



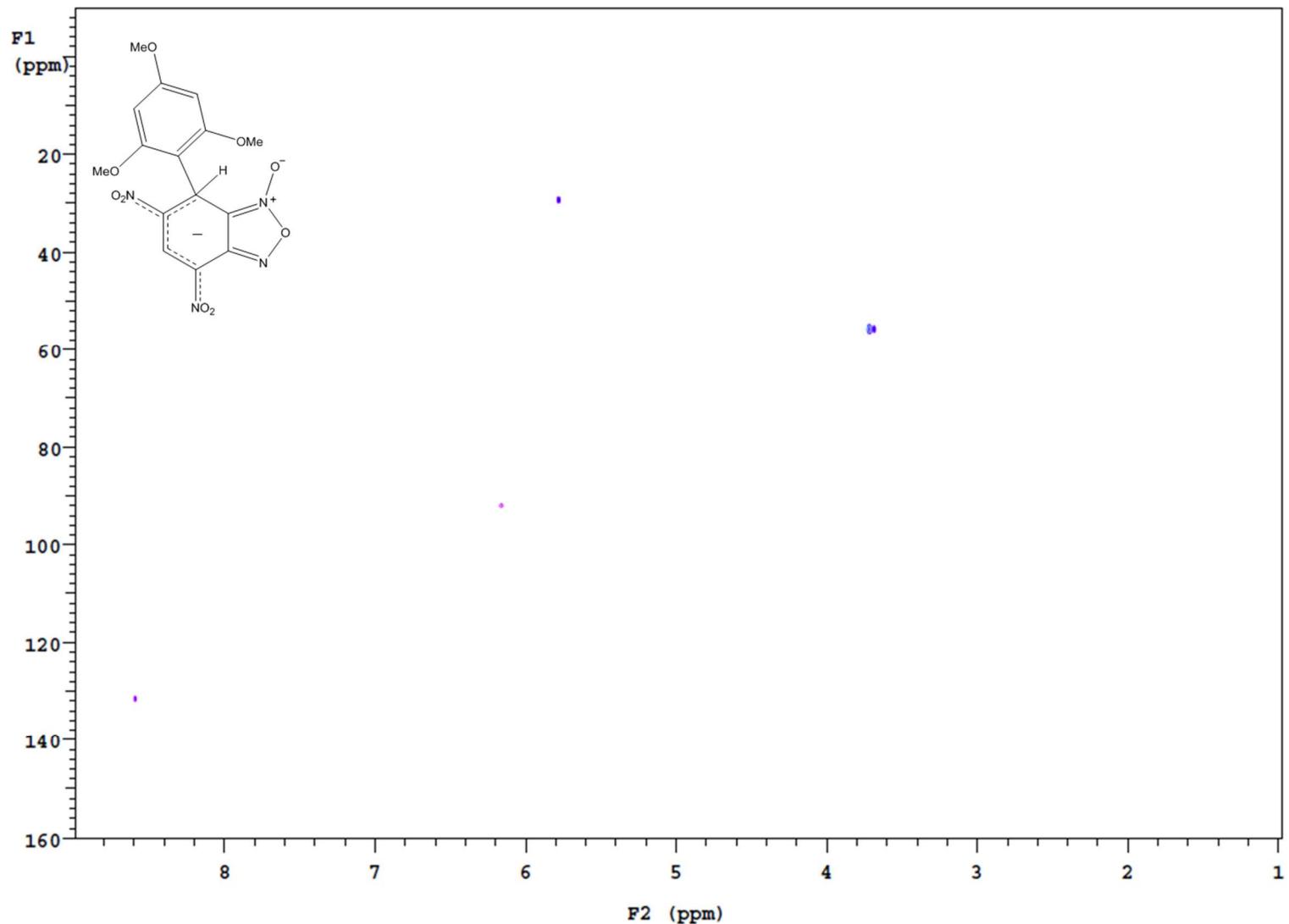
**Figure SI-38.** HSQC spectrum ( $\text{CD}_3\text{CN}$ , 400 MHz,  $-35^\circ\text{C}$ ) of compound **M1**



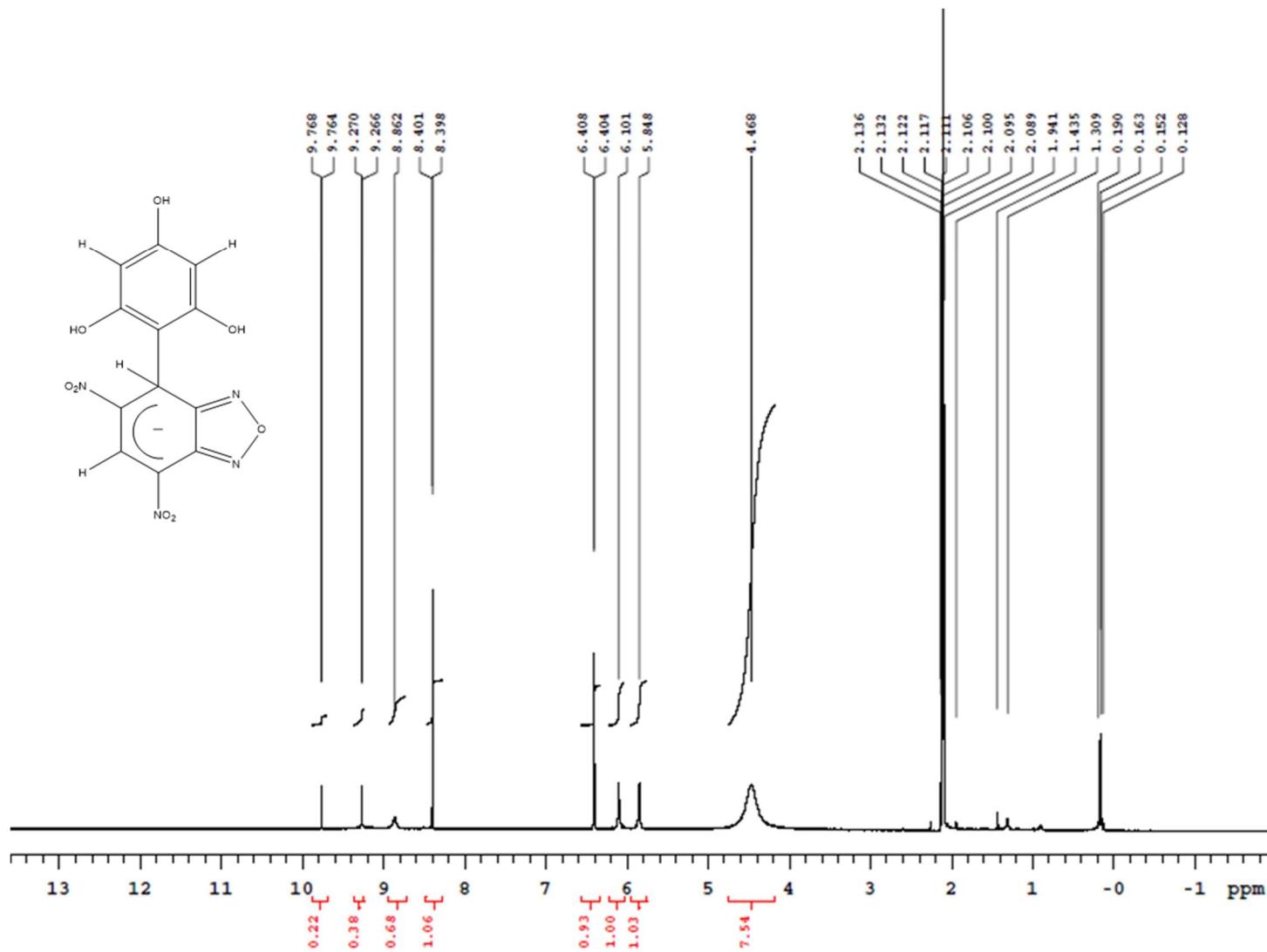
**Figure SI-39.** <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>, 400 MHz, 25 °C) of compound **M2**



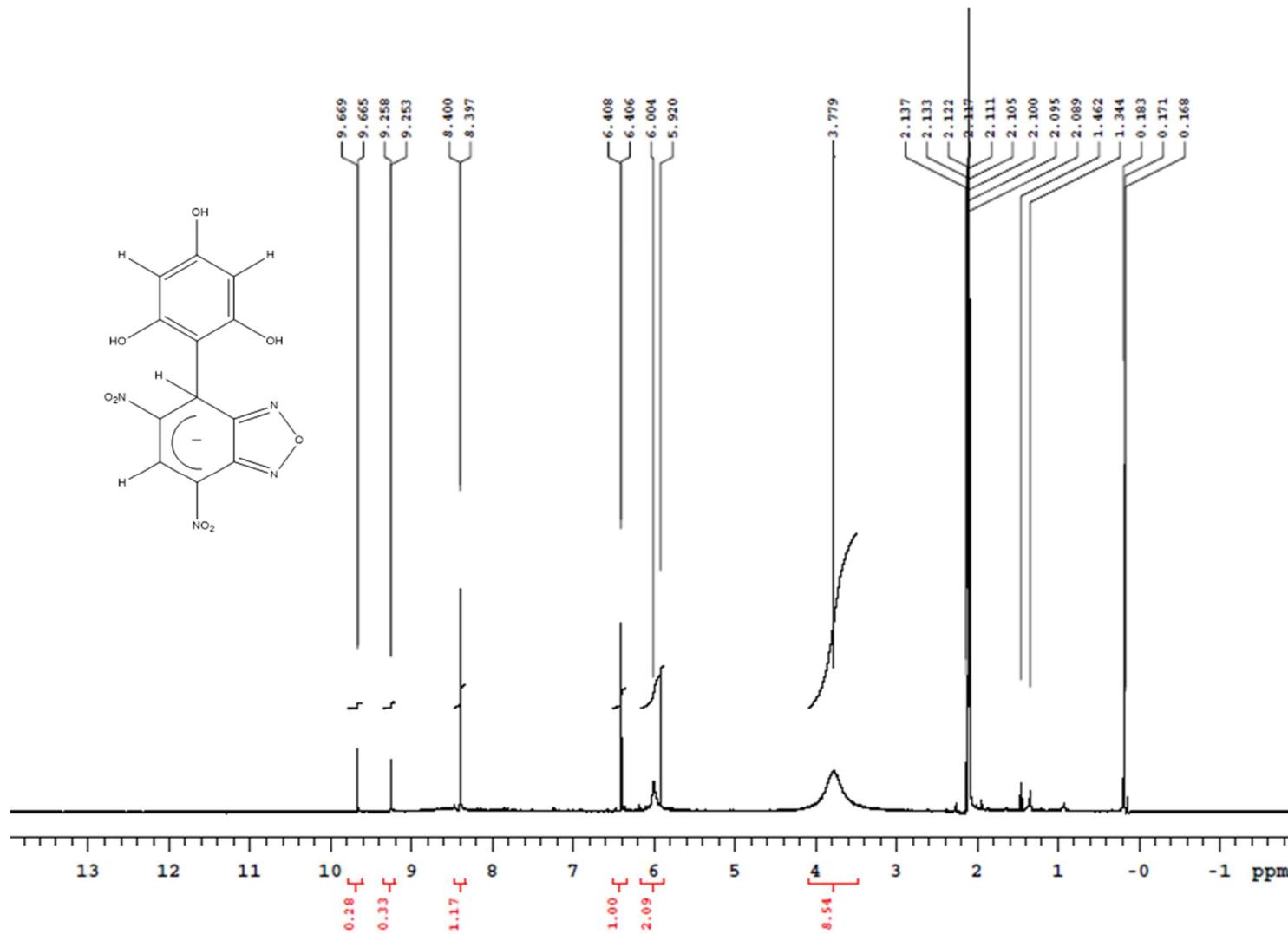
**Figure SI-40.**  $^{13}\text{C}$  NMR spectrum ( $\text{DMSO}-d_6$ , 150.80 MHz, 25 °C) of compound M2



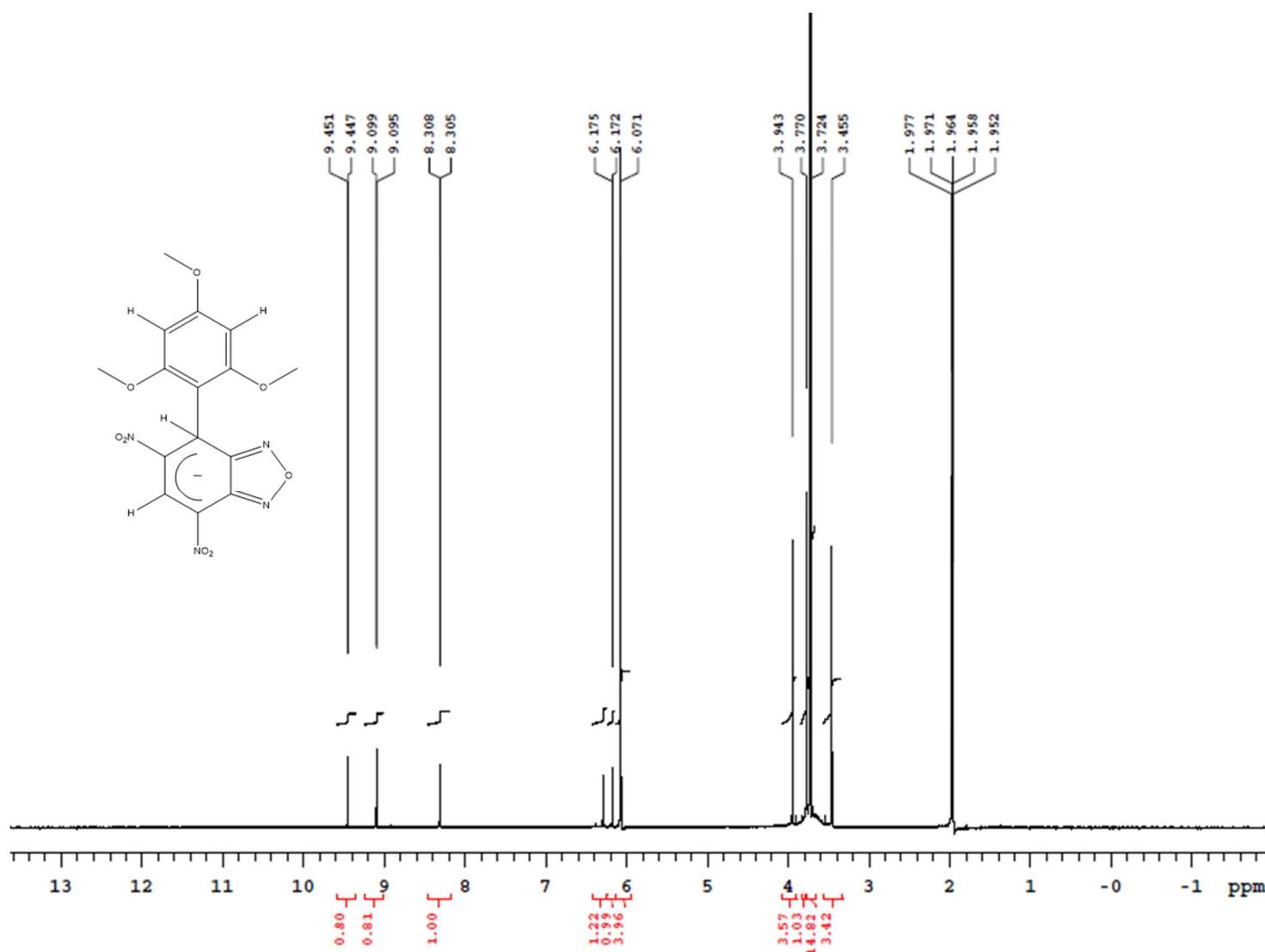
**Figure SI-41.** HSQC spectrum ( $\text{DMSO}-d_6$ , 400 MHz, 25 °C) of compound **M2**.



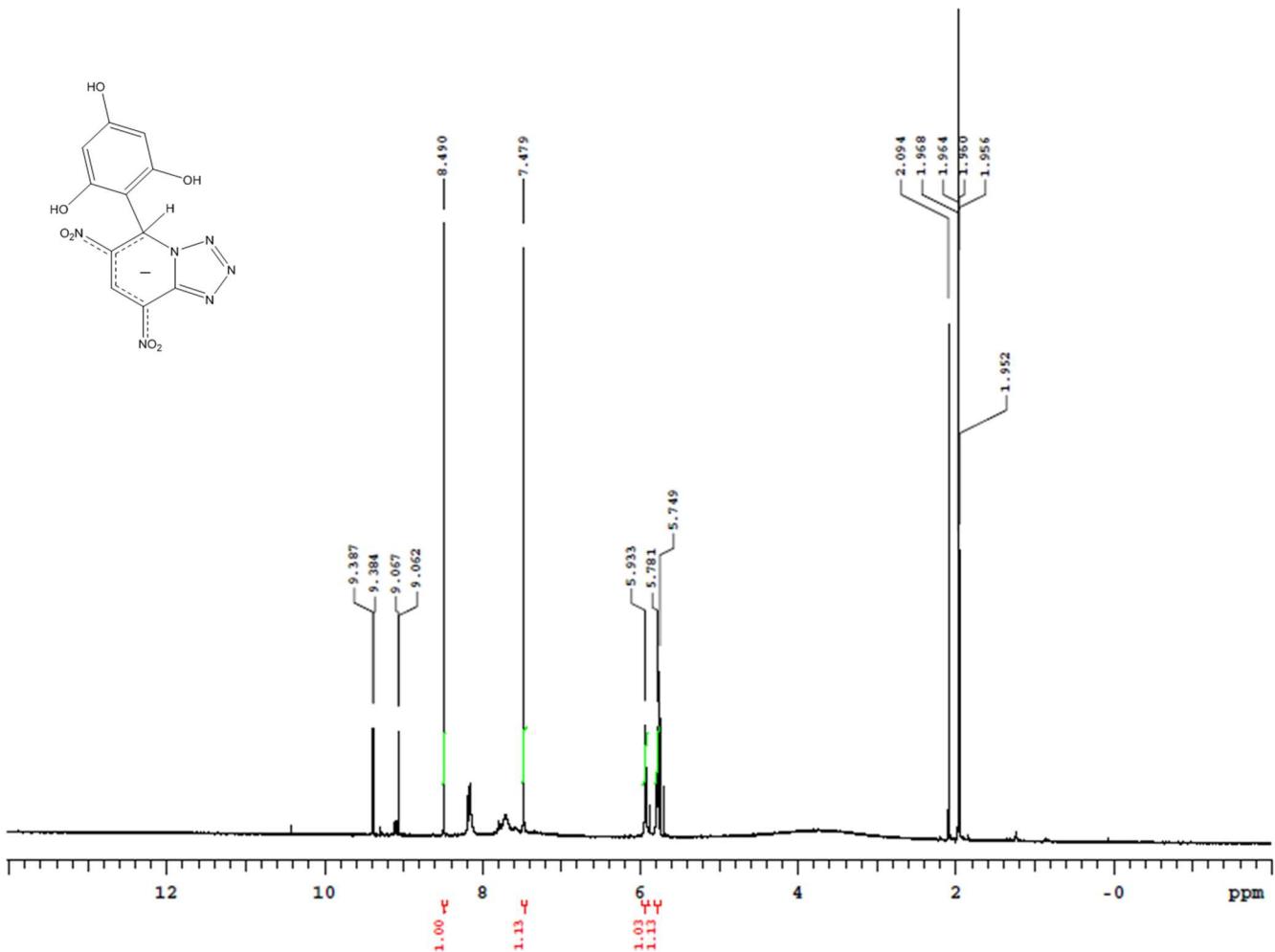
**Figure SI-42.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{COCD}_3$ , 400 MHz,  $-10^\circ\text{C}$ ) of compound **M3**; signals at 9.27 and 9.76 ppm belong to unreacted starting DNBZ, likely added in excess.



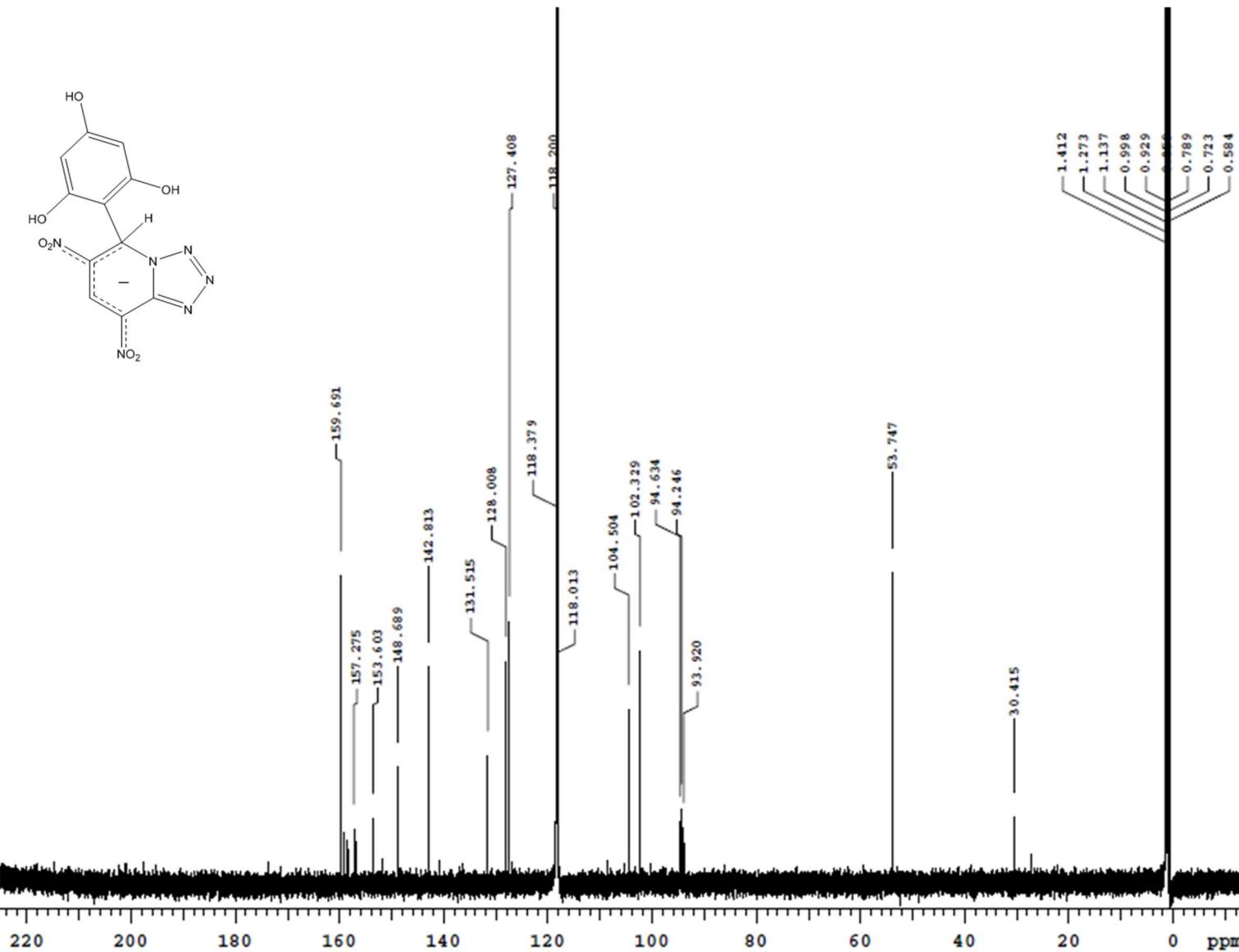
**Figure SI-43.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{COCD}_3$ , 400 MHz, +35 °C) of compound **M3**; signals at 9.27 and 9.76 ppm belong to unreacted starting DNBZ, likely added in excess.



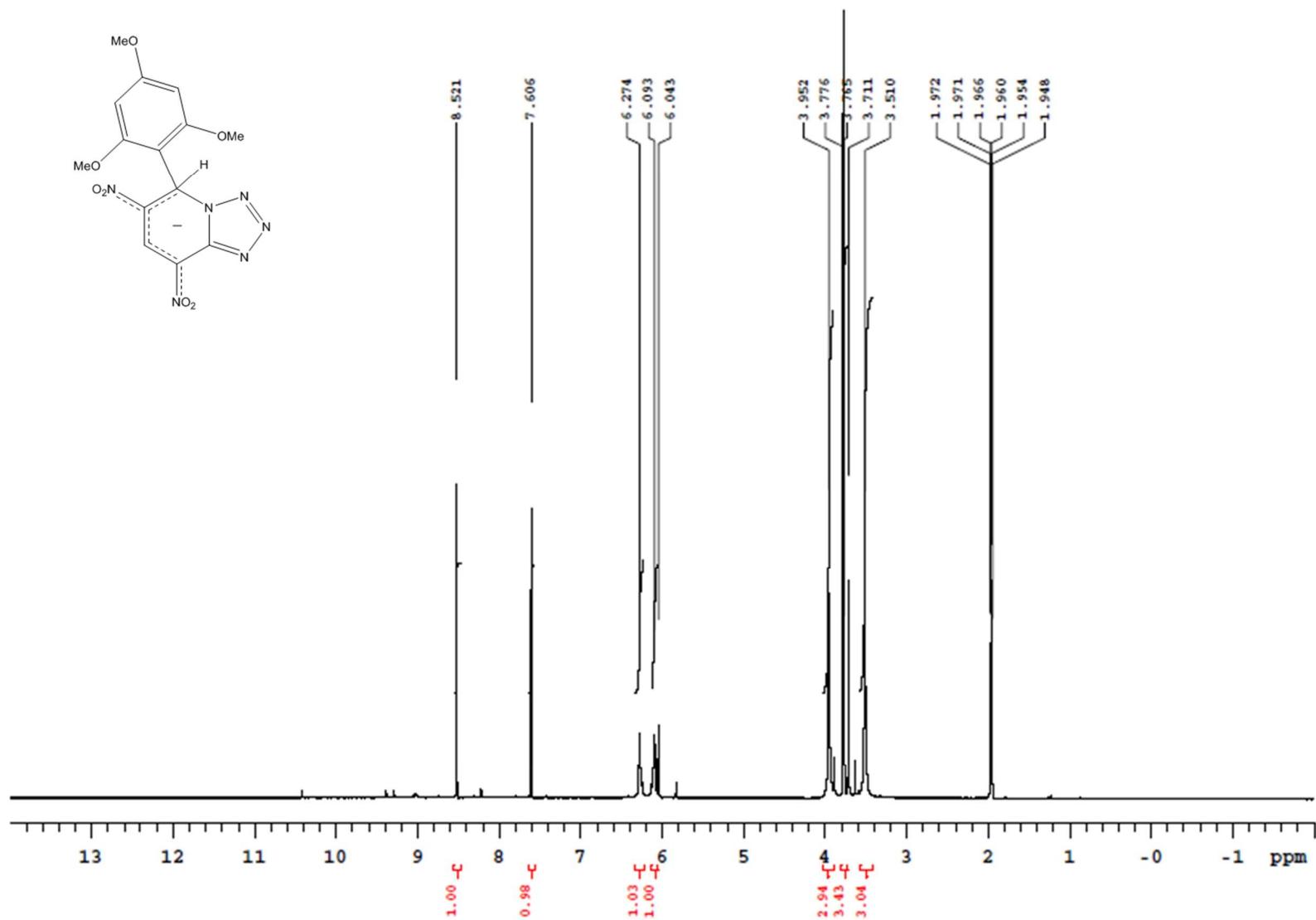
**Figure SI-44.**  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ , 400 MHz,  $-35^\circ\text{C}$ ) of compound **M4**; signals at 9.45, 9.10, 6.07, and 3.72 ppm belong to unreacted starting materials.



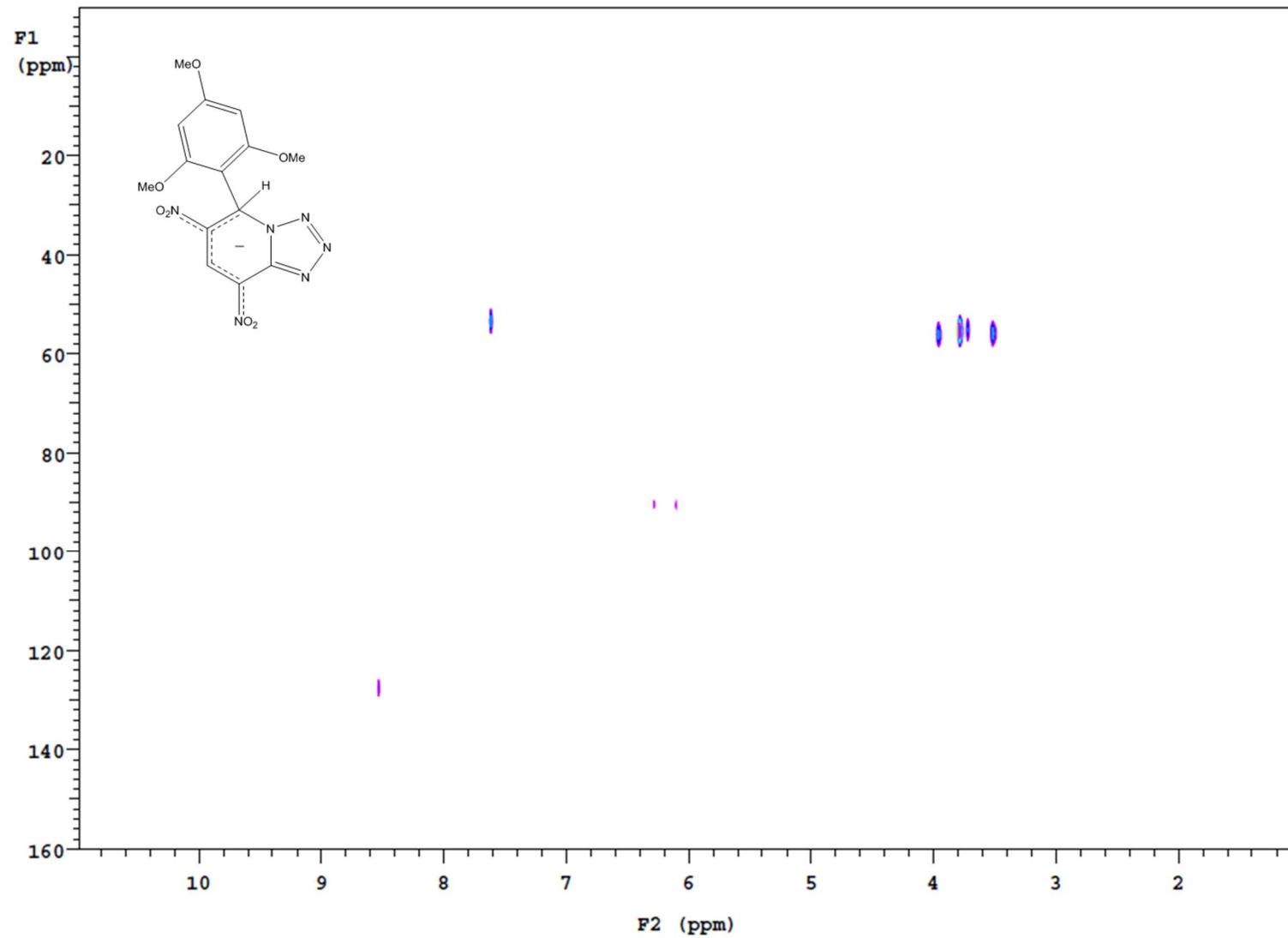
**Figure SI-45.** <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 600 MHz, -35 °C) of compound **M5**, together with signals belonging to unreacted starting materials



**Figure SI-46.**  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ , 150.80 MHz,  $-35^\circ\text{C}$ ) of compound **M5** together with signals belonging to unreacted starting materials.



**Figure SI-47.**  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 400 MHz,  $-35^\circ\text{C}$ ) spectrum of compound **M6**.



**Figure SI-48.** HSQC ( $\text{CD}_3\text{CN}$ , 400 MHz, -35 °C) of compound **M6**.