

## SUPPORTING INFORMATION

### **C–C Coupling between trinitrothiophenes and triaminobenzenes: zwitterionic intermediates and new all-conjugated structures**

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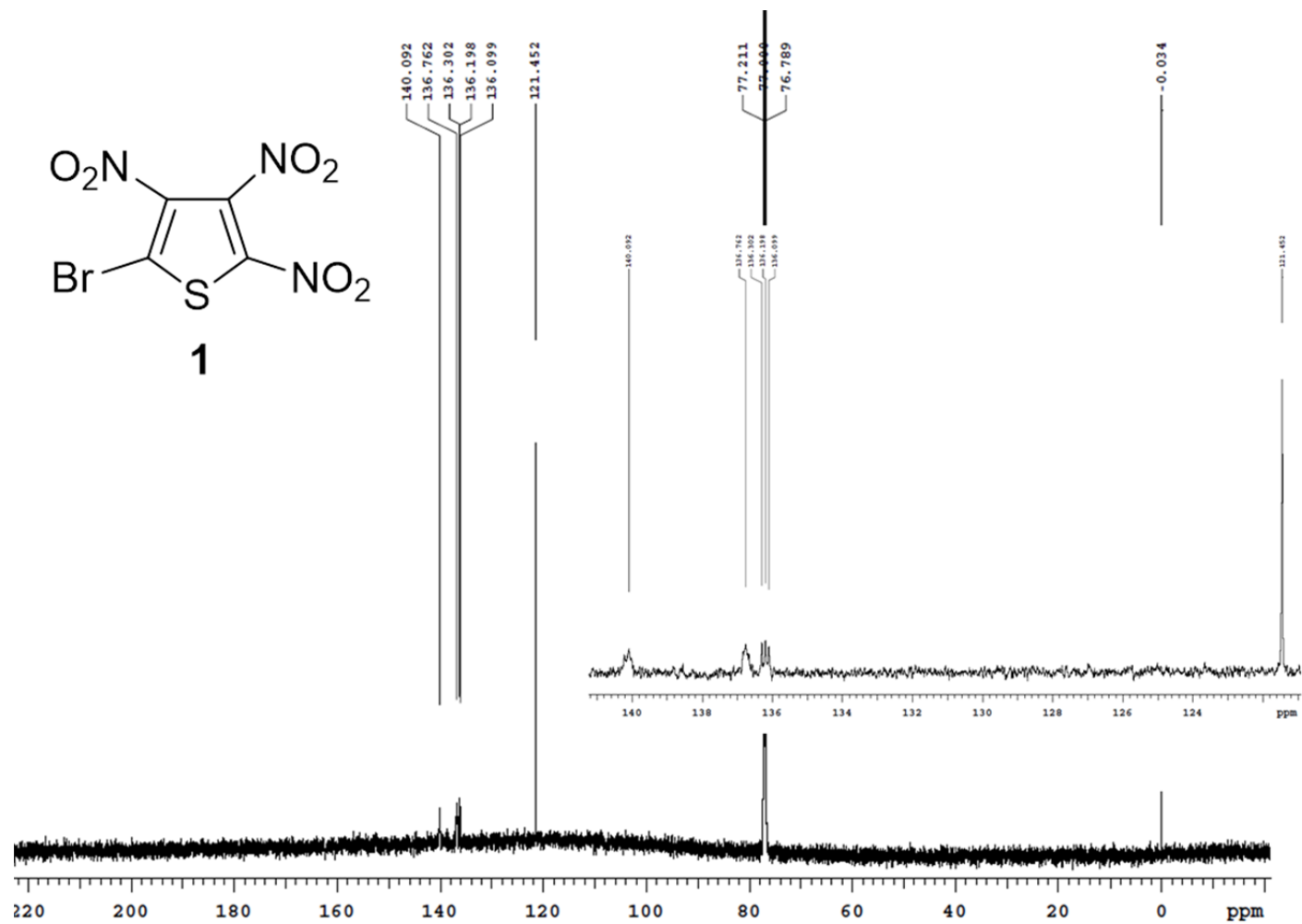


Figure SI-1. <sup>13</sup>C NMR spectrum (150.8 MHz, CDCl<sub>3</sub>, 25 °C) and related expanded view of compound **1**.

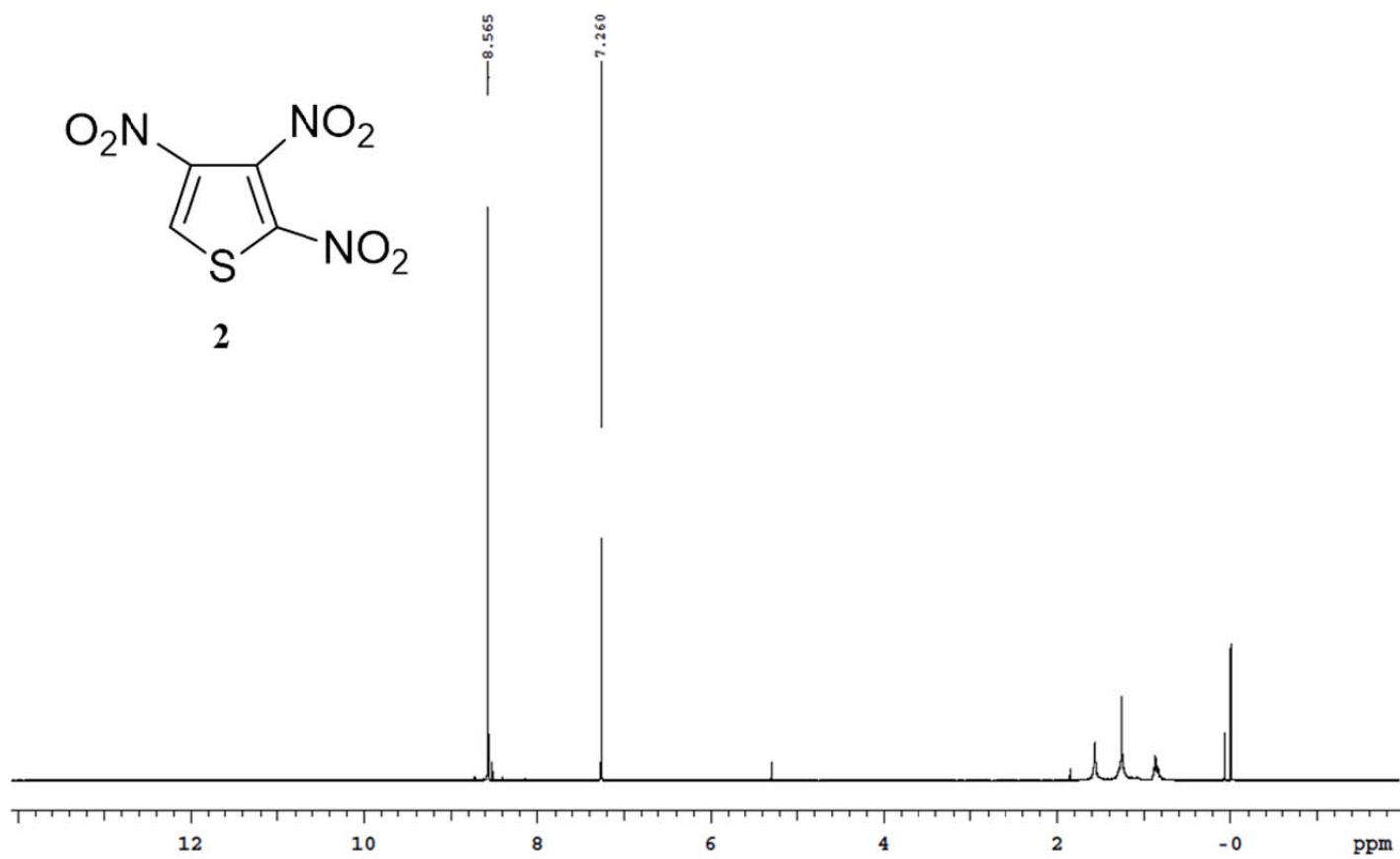


Figure SI-2. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 25 °C) of compound **2**.

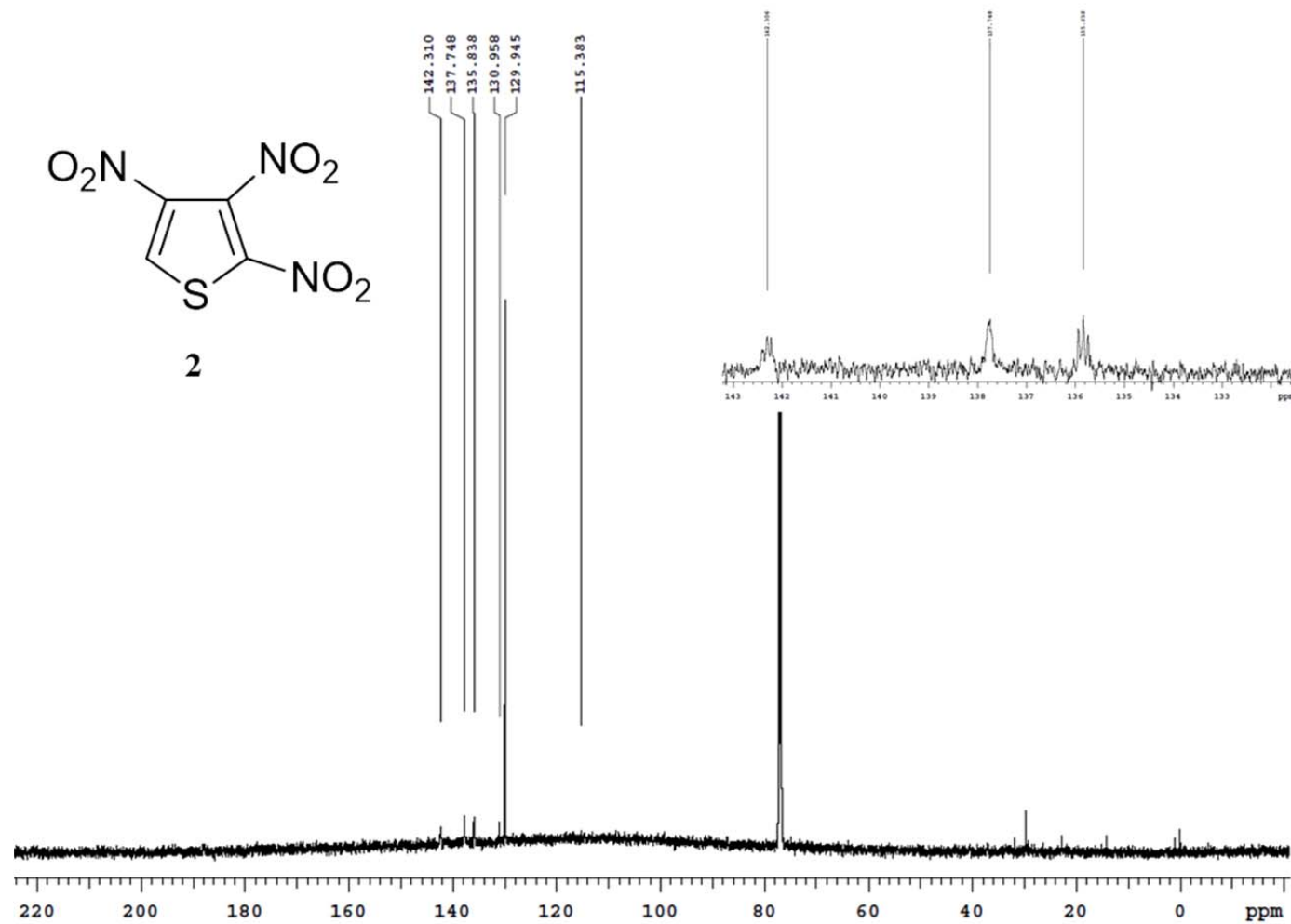


Figure SI-3. <sup>13</sup>C NMR spectrum (150.8 MHz, CDCl<sub>3</sub>, 25 °C) and related expanded view of compound **2**.

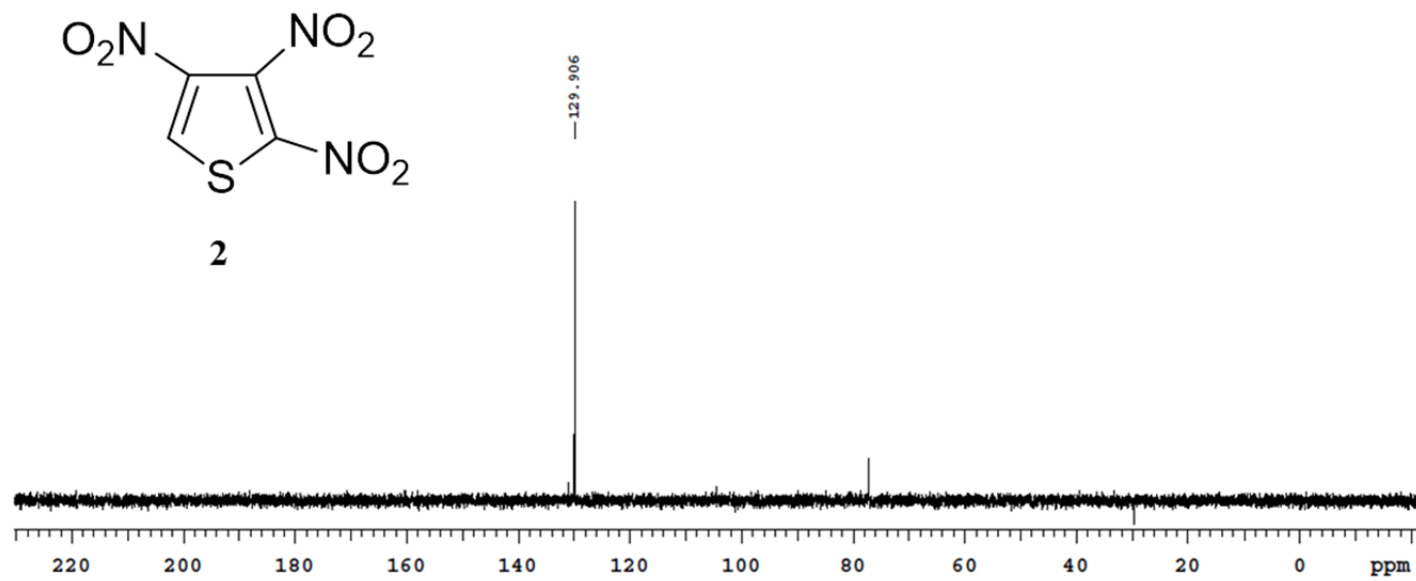


Figure SI-4. DEPT spectrum of compound **2**.

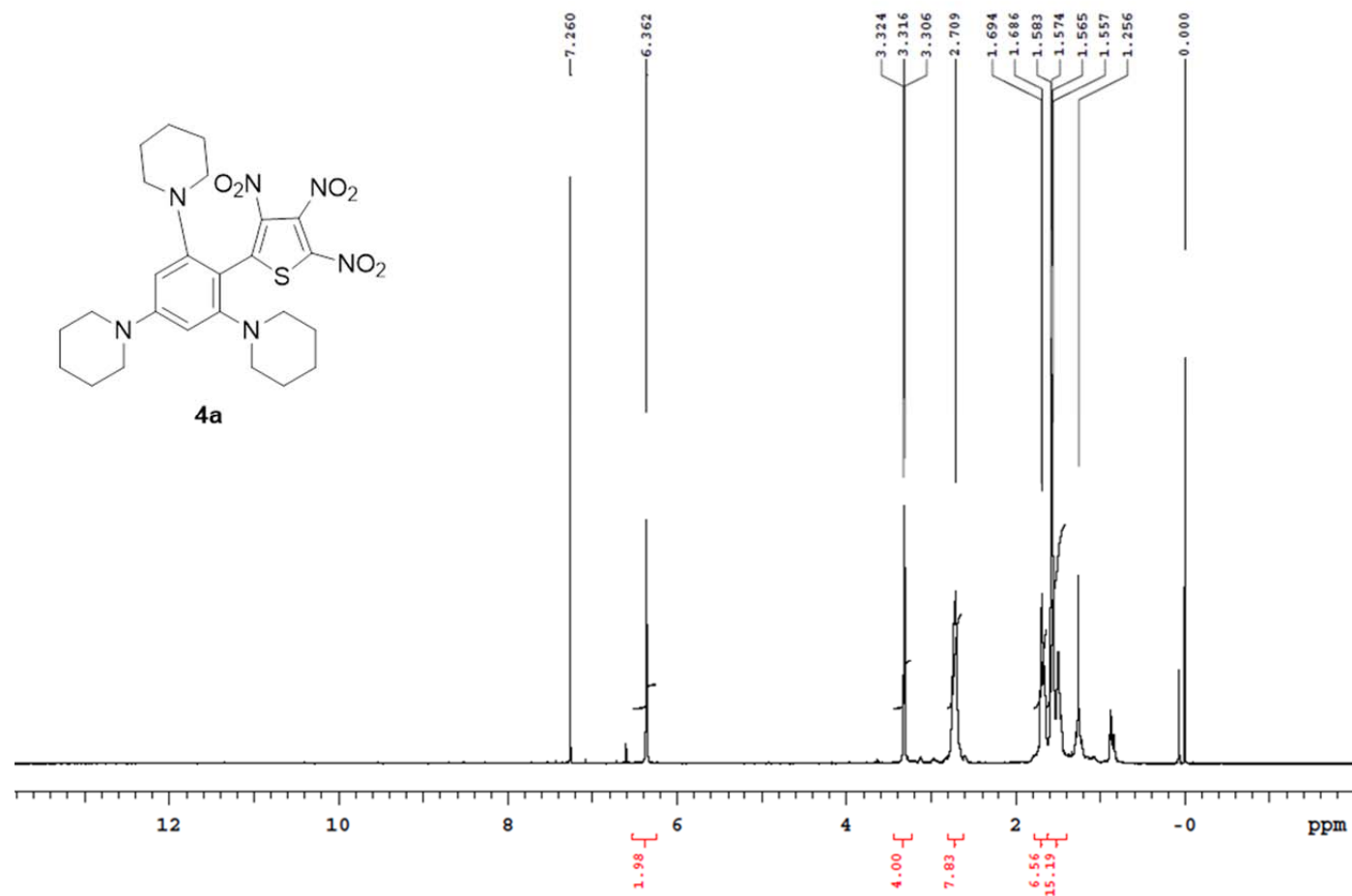


Figure SI-5.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) of compound **4a**.

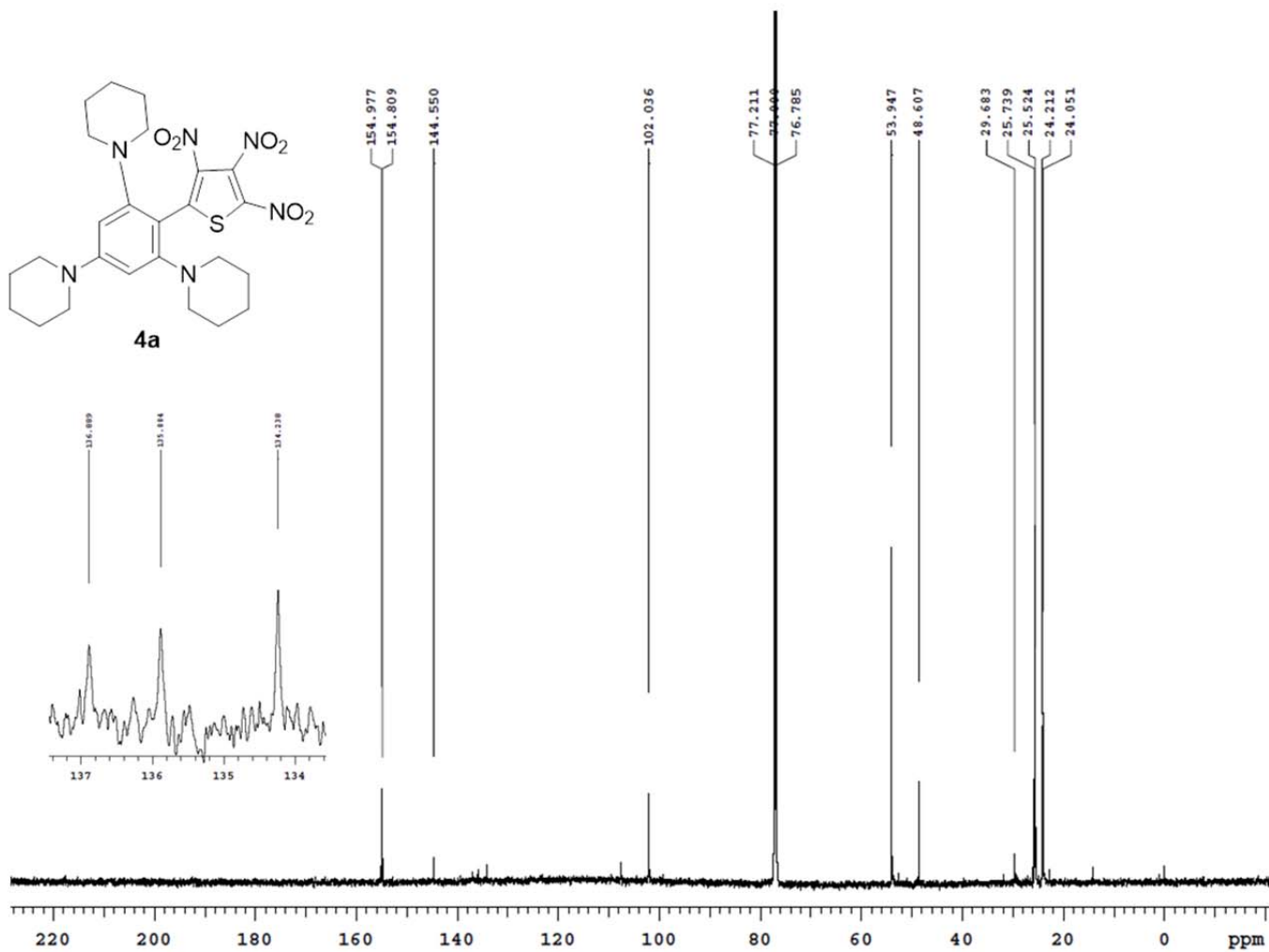


Figure SI-6.  $^{13}\text{C}$  NMR spectrum (150.8 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) of compound **4a**.

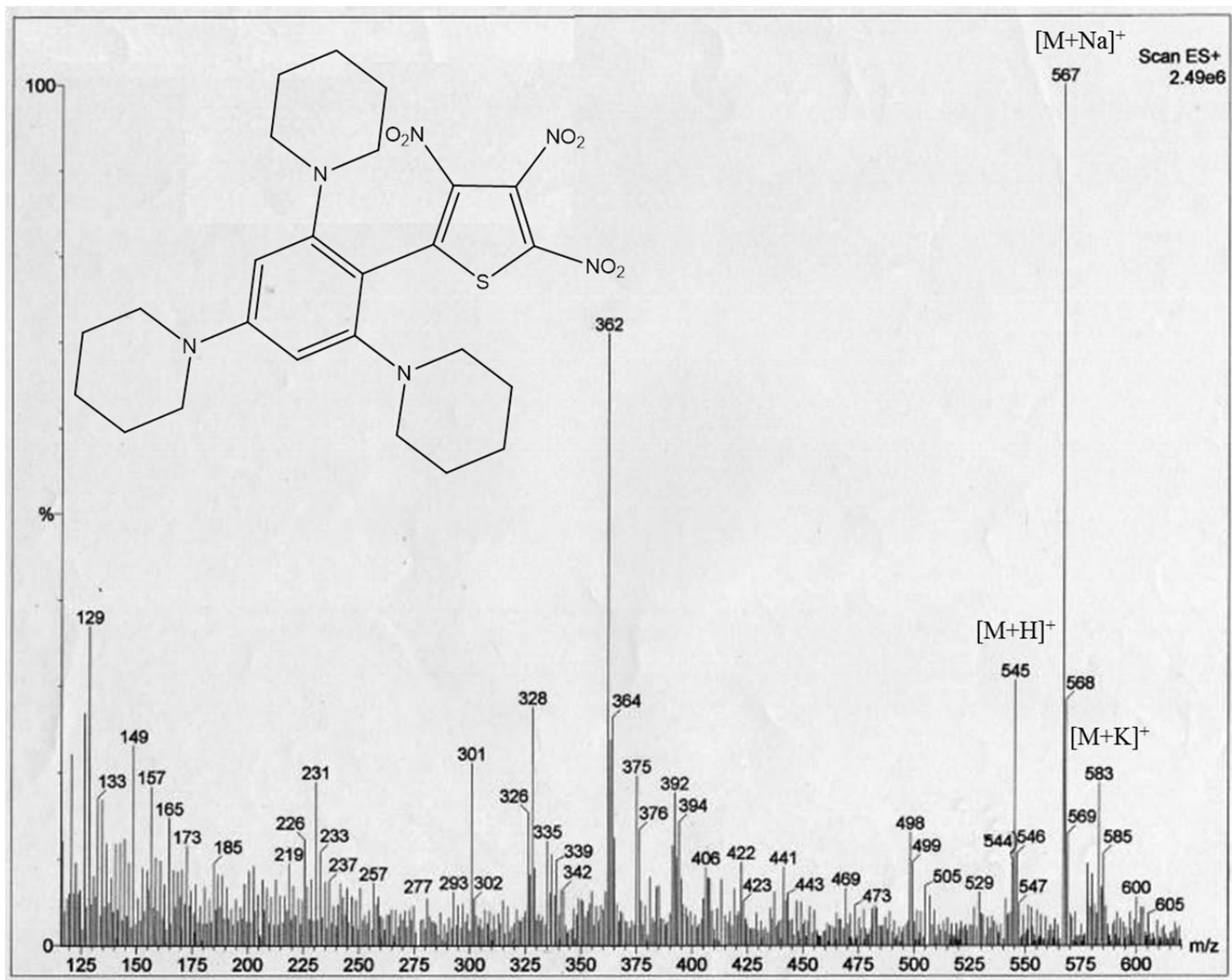


Figure SI-7: ESI-MS (ES<sup>+</sup>) spectrum of compound **4a**.



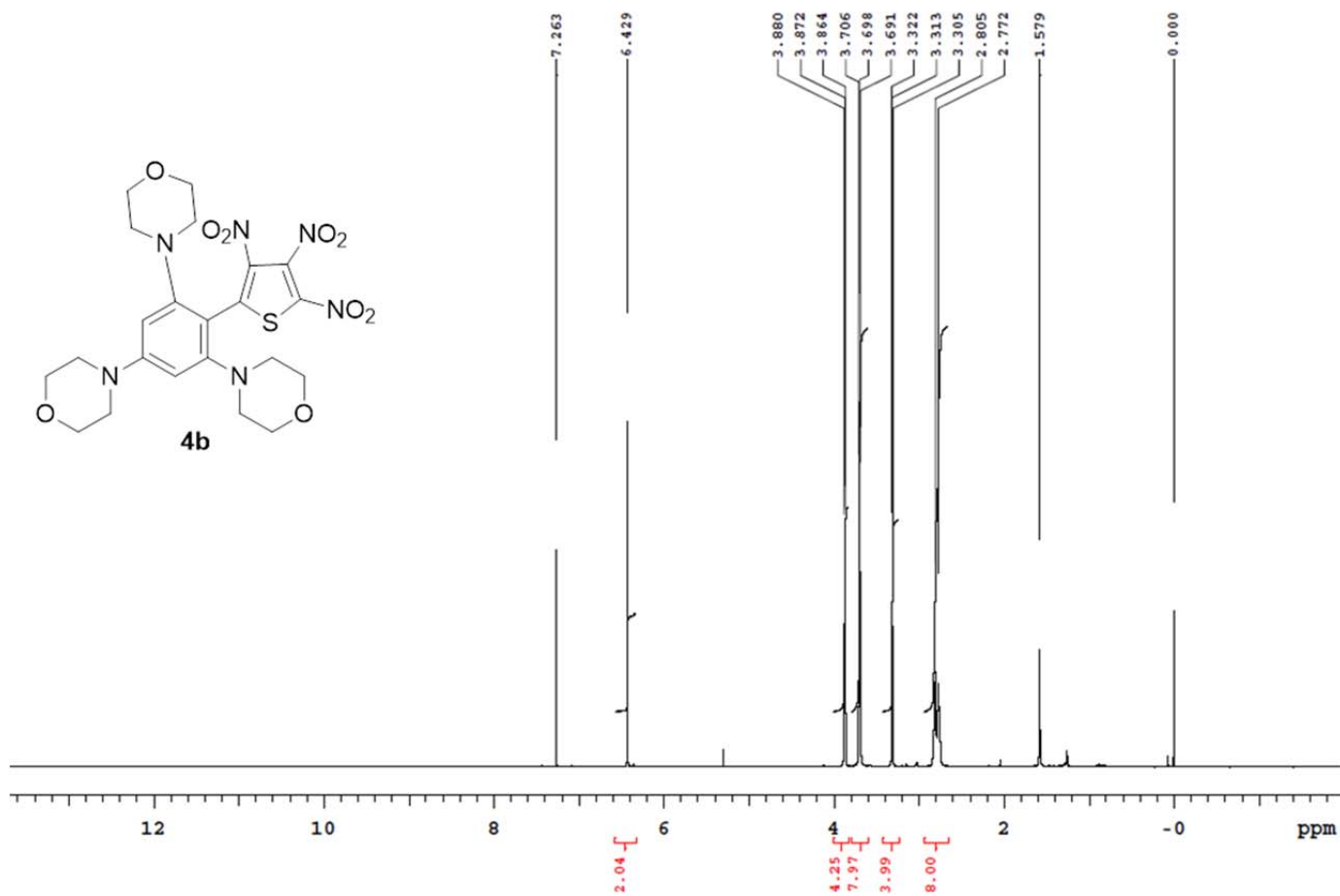


Figure SI-8.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) of compound **4b**.

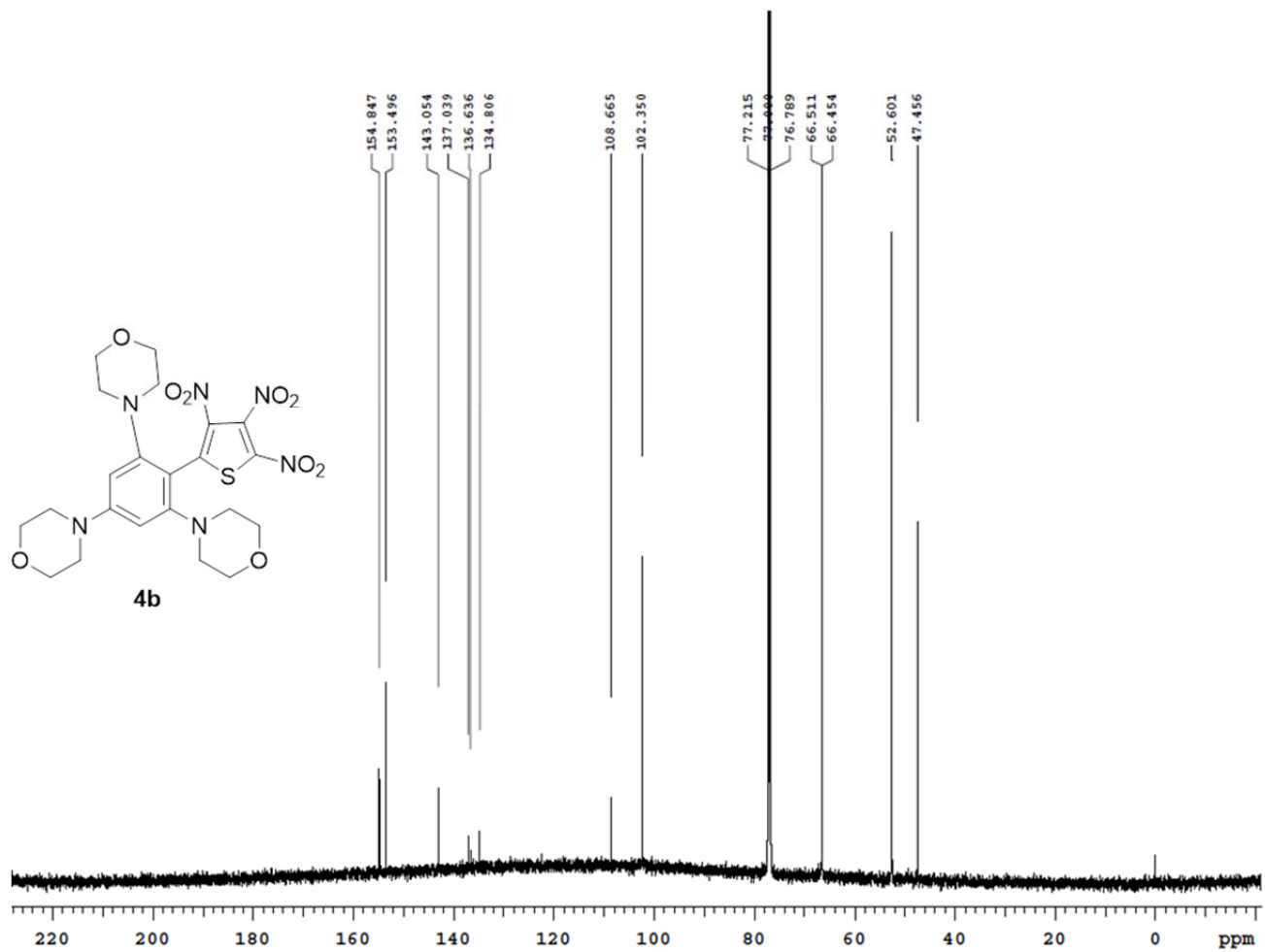


Figure SI-9.  $^{13}\text{C}$  NMR spectrum (150.8 MHz,  $\text{CDCl}_3$ , 25 °C) of compound **4b**.

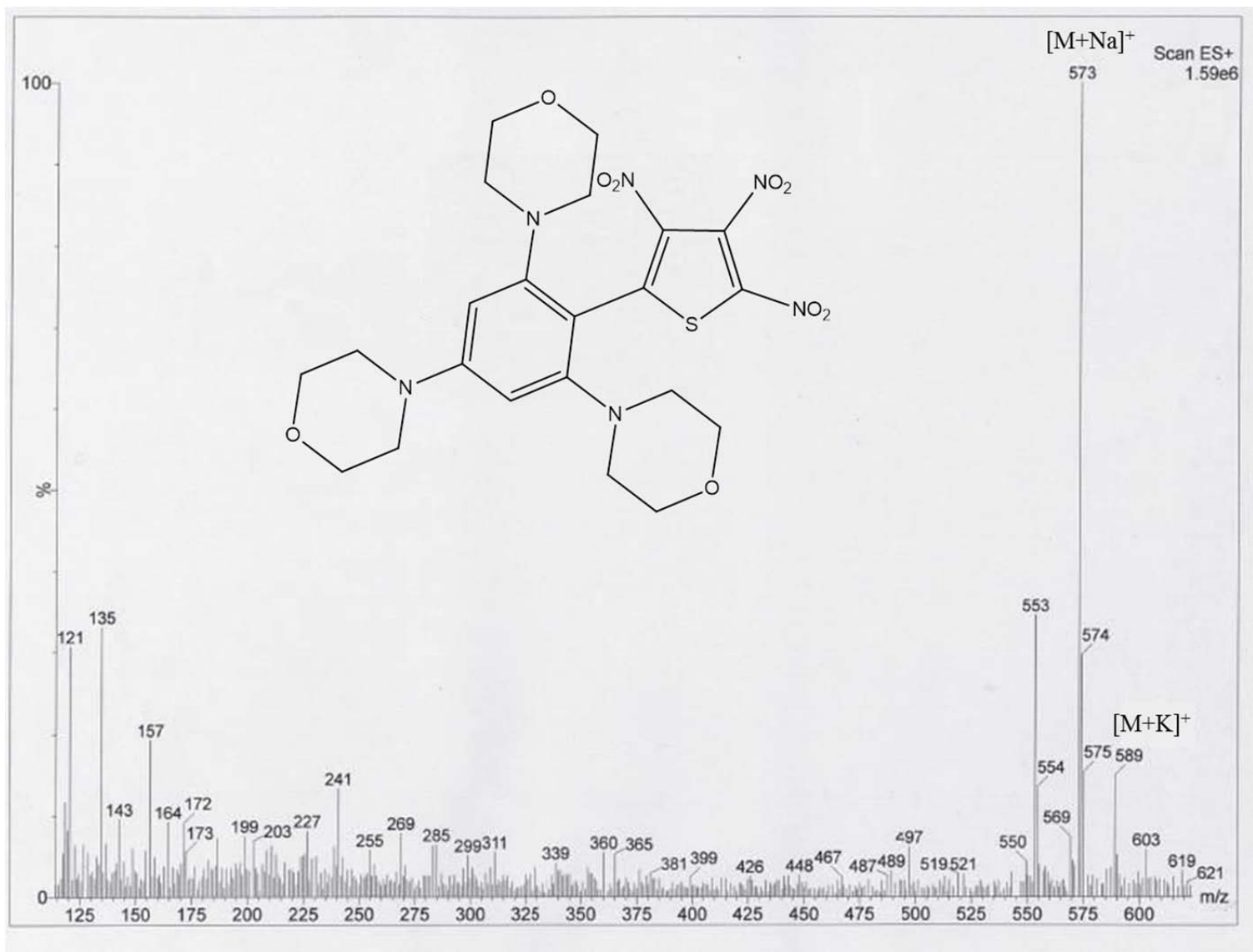


Figure SI-10: ESI-MS (ES<sup>+</sup>) spectrum of compound **4b**.

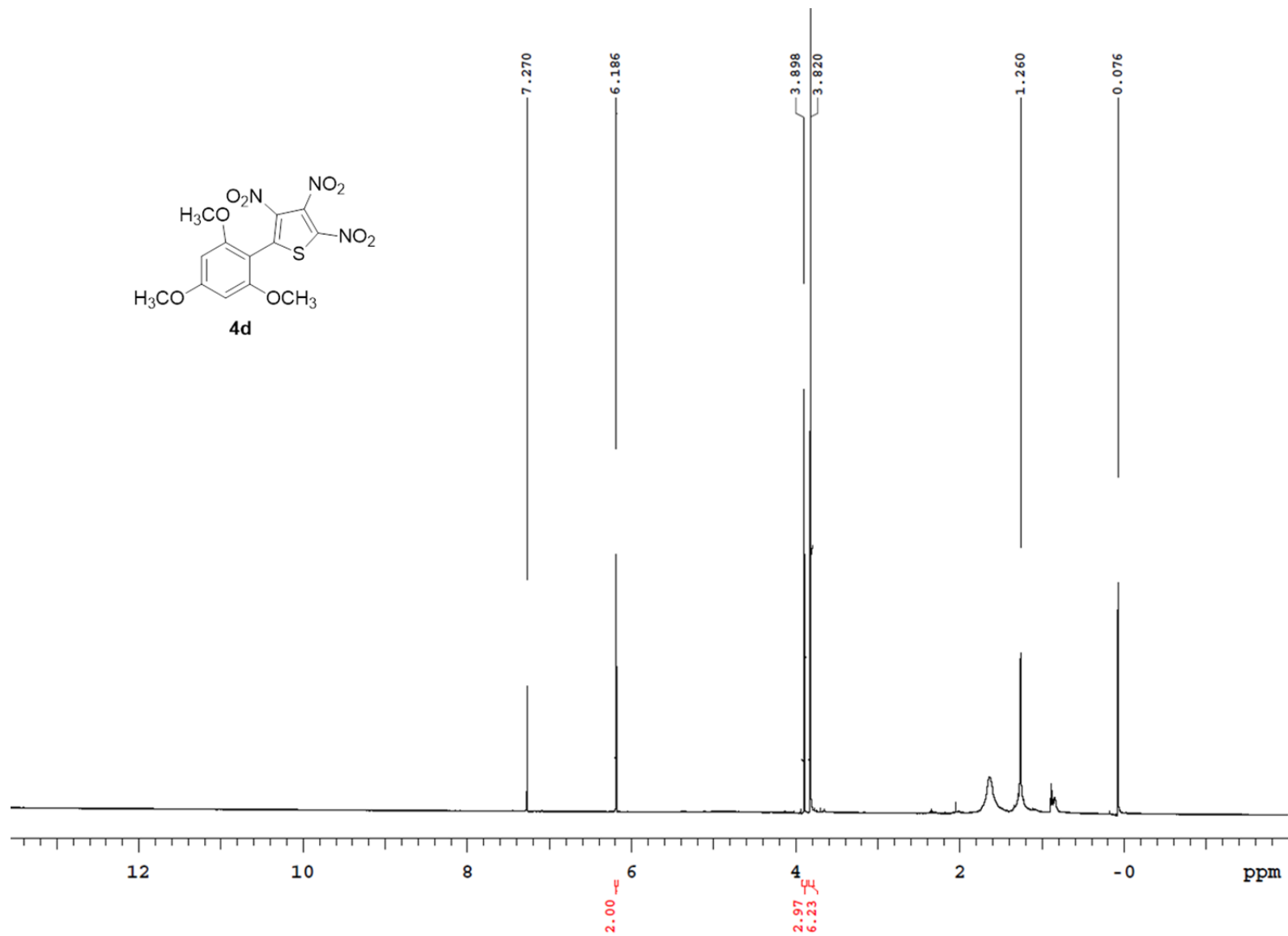


Figure SI-11: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C) of compound **4d**.

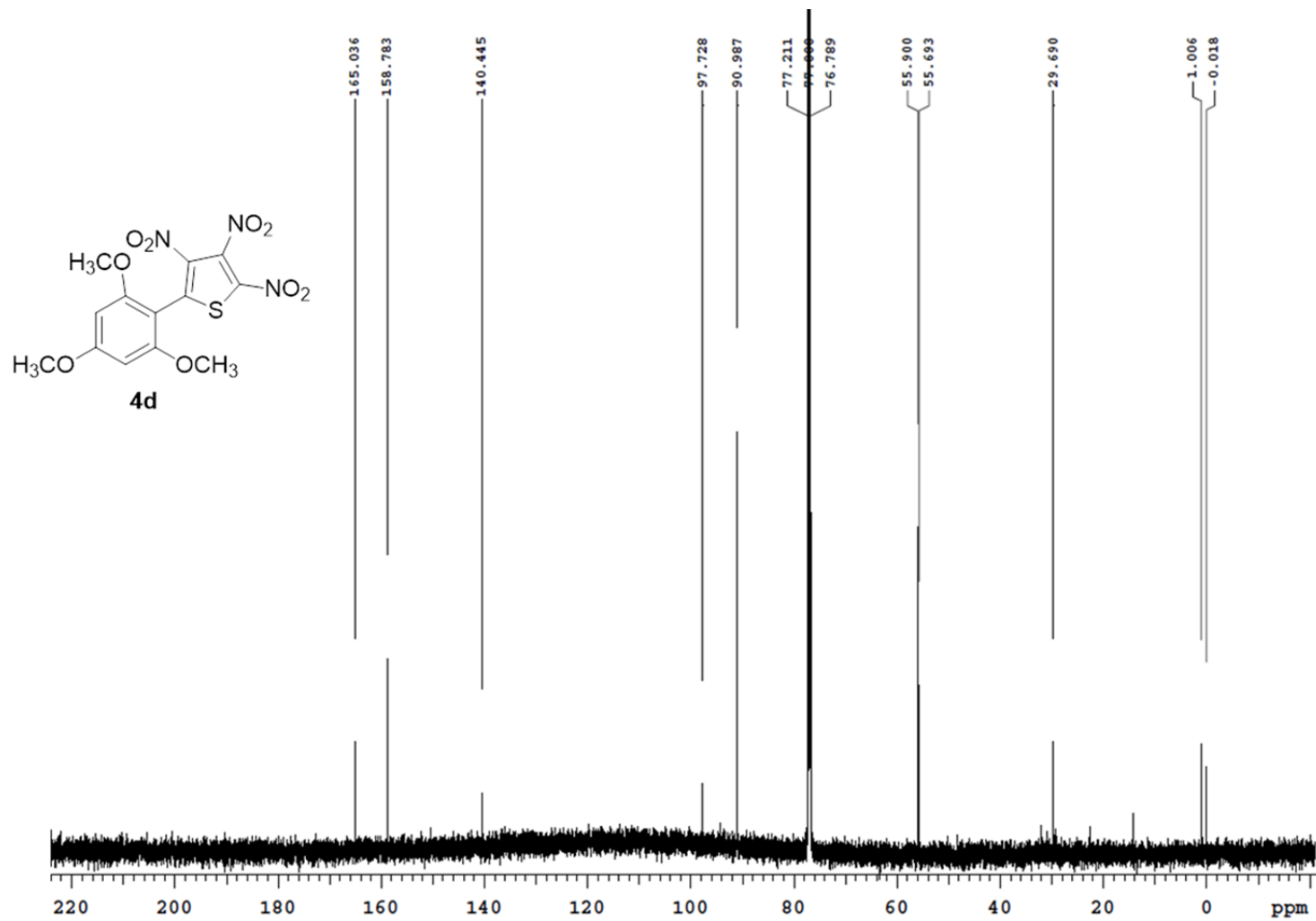


Figure SI-12: <sup>1</sup>H NMR (150.8 MHz, CDCl<sub>3</sub>, 25 °C) of compound **4d**.

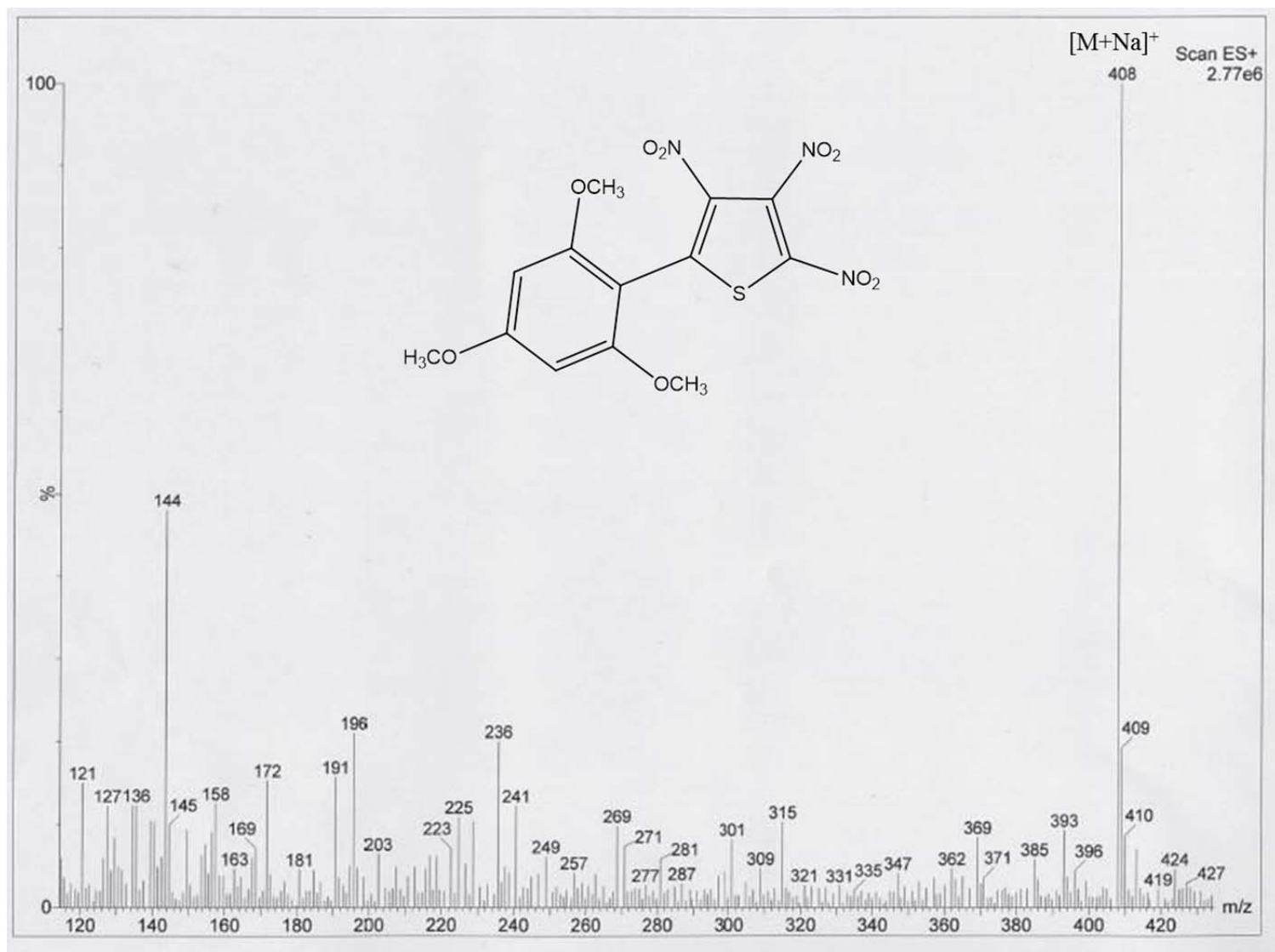


Figure SI-13: ESI-MS (ES<sup>+</sup>) spectrum of compound **4d**.

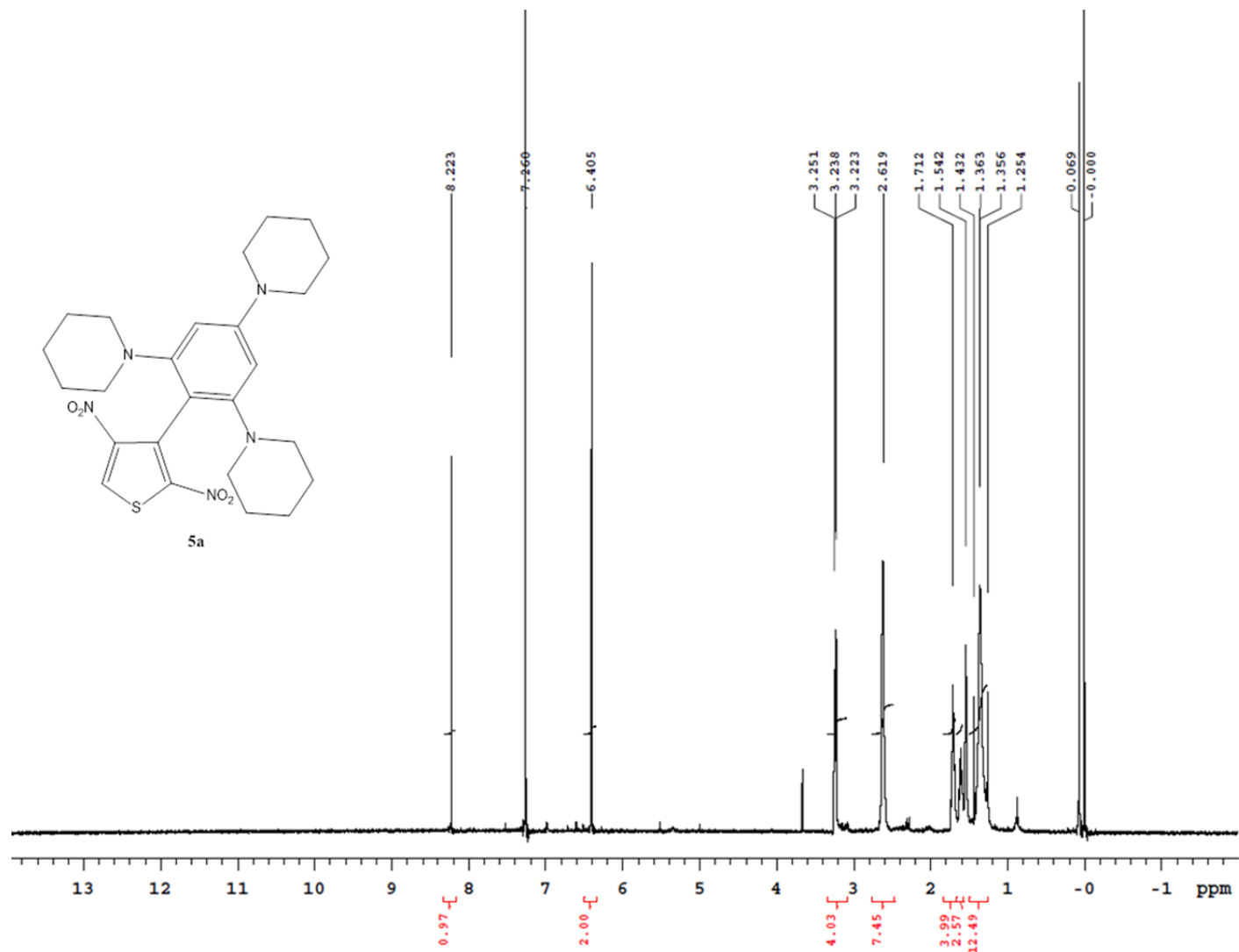


Figure SI-14.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) of compound **5a**.

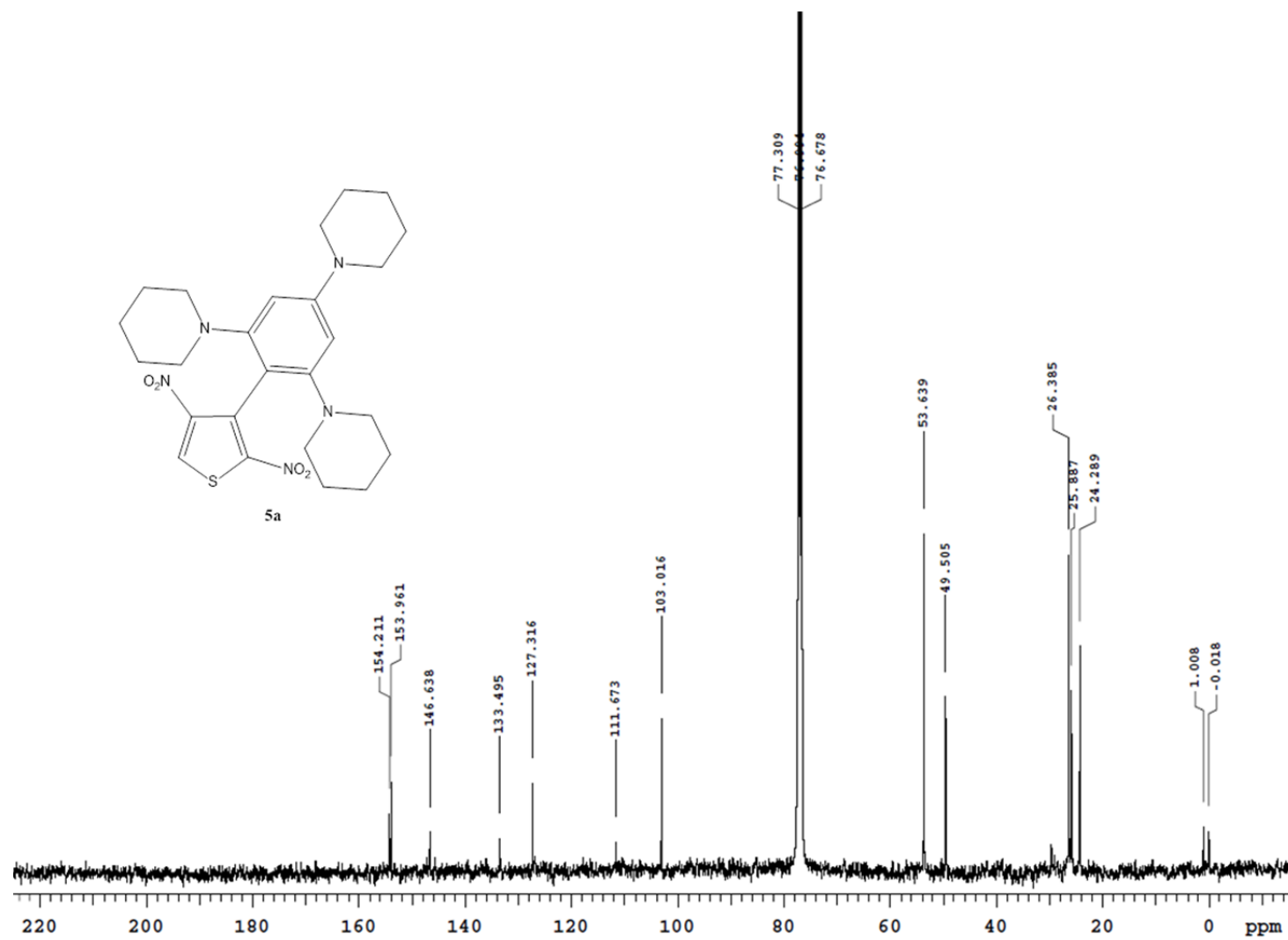


Figure SI-15.  $^{13}\text{C}$  NMR spectrum (100.56 MHz,  $\text{CDCl}_3$ , 25 °C) of compound **5a**.



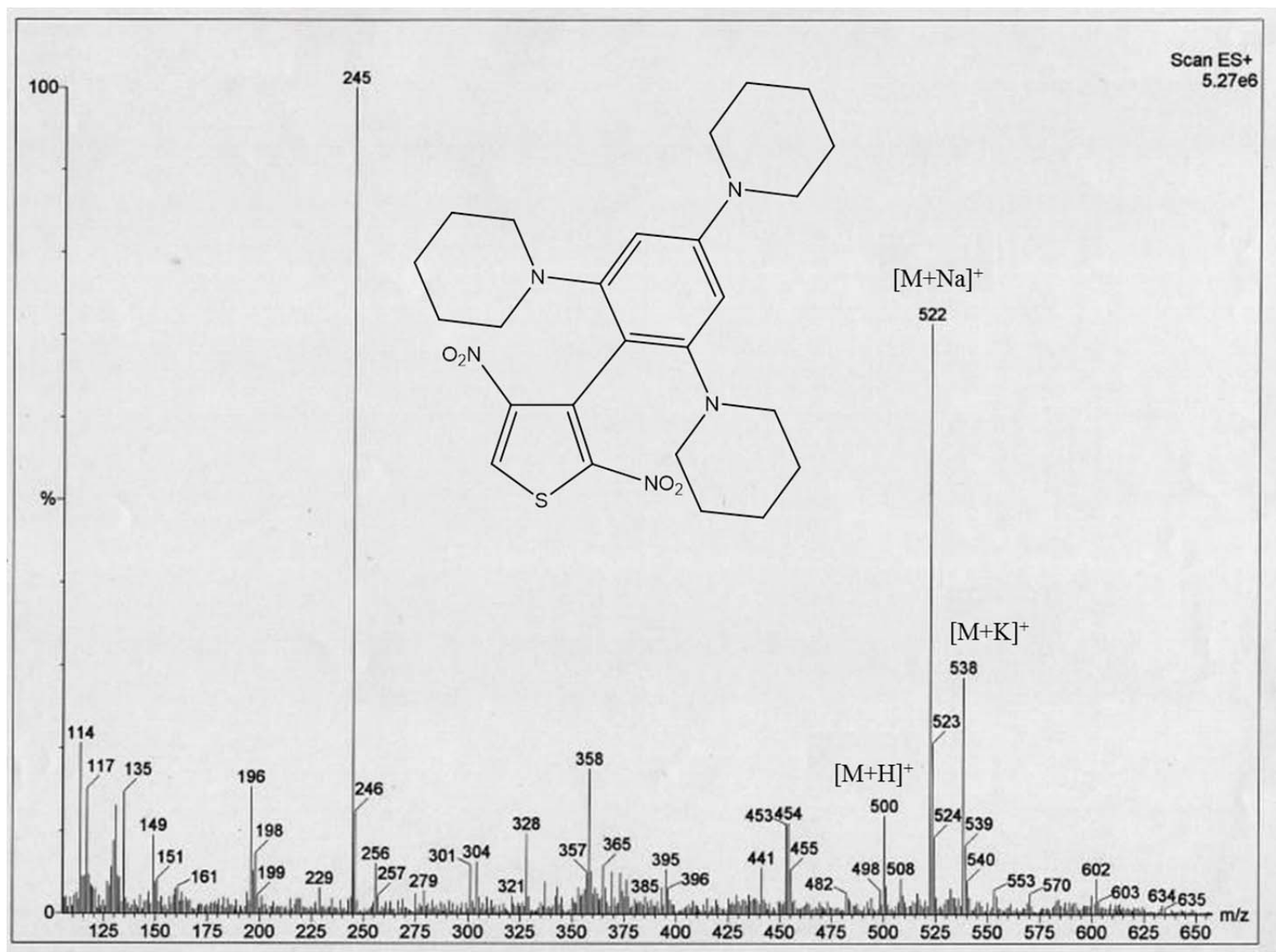


Figure SI-16: ESI-MS ( $\text{ES}^+$ ) spectrum of compound **5a**.

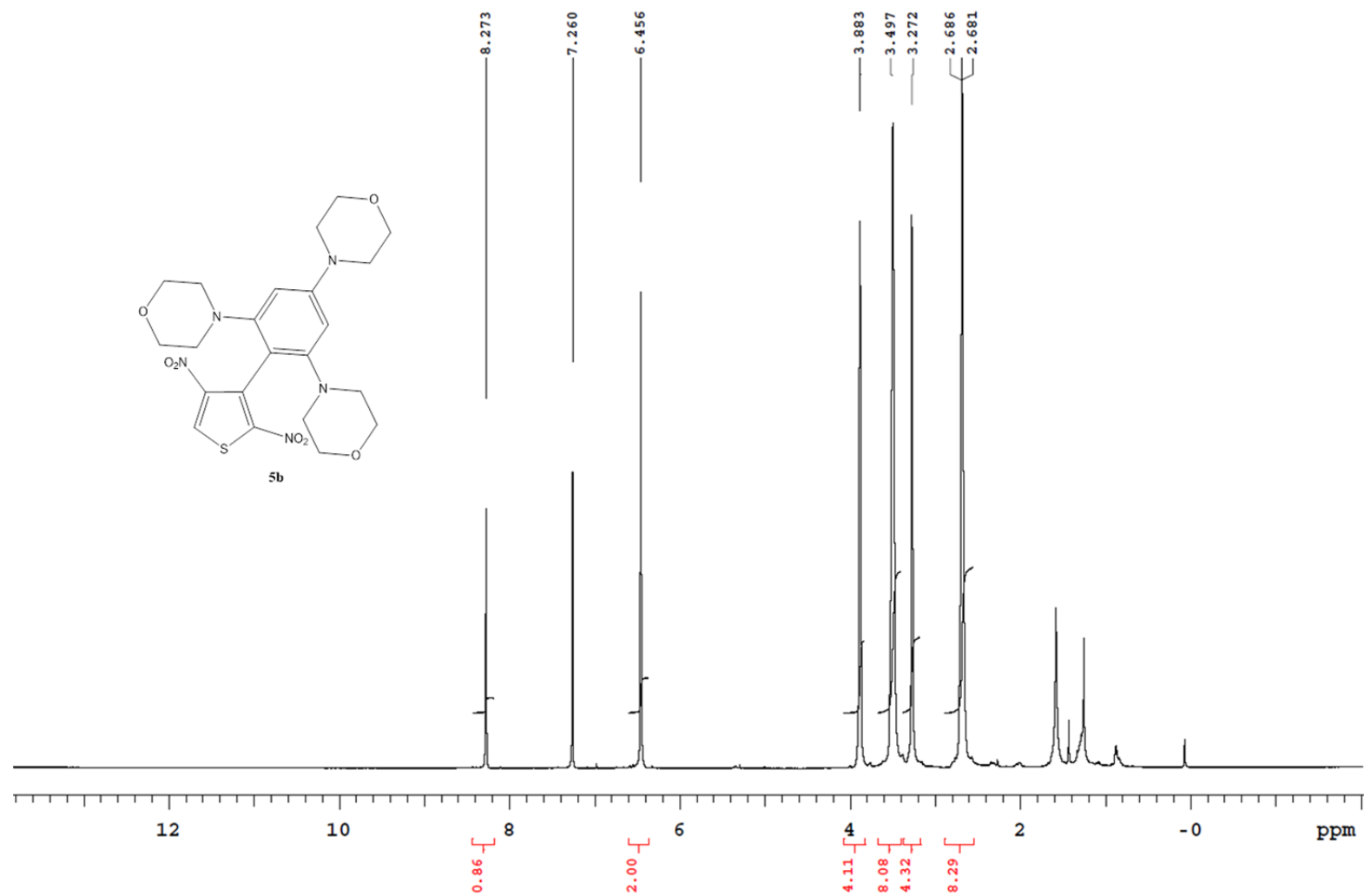


Figure SI-17.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) of compound **5b**.

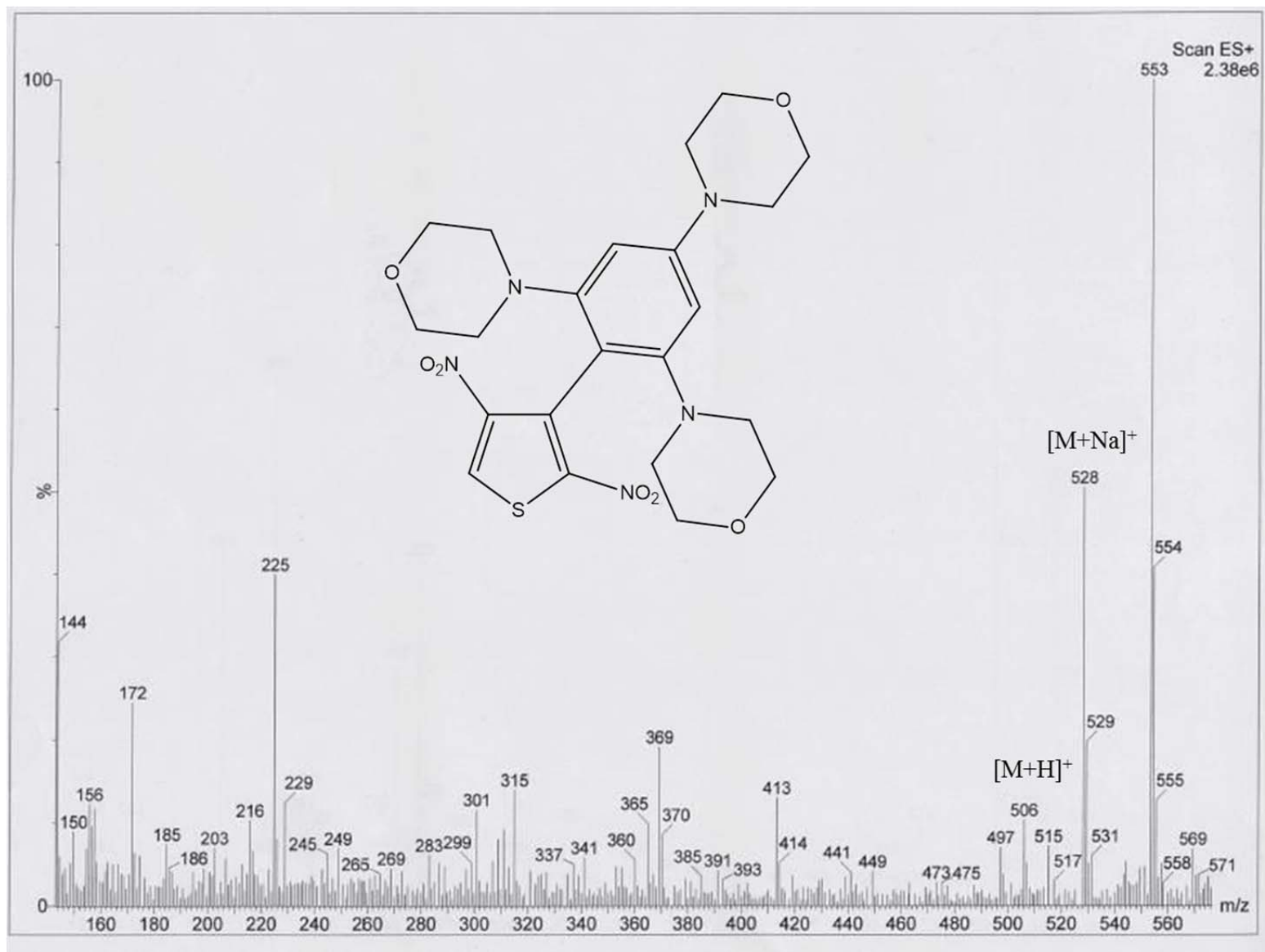


Figure SI-18: ESI-MS (ES<sup>+</sup>) spectrum of compound **5b**.

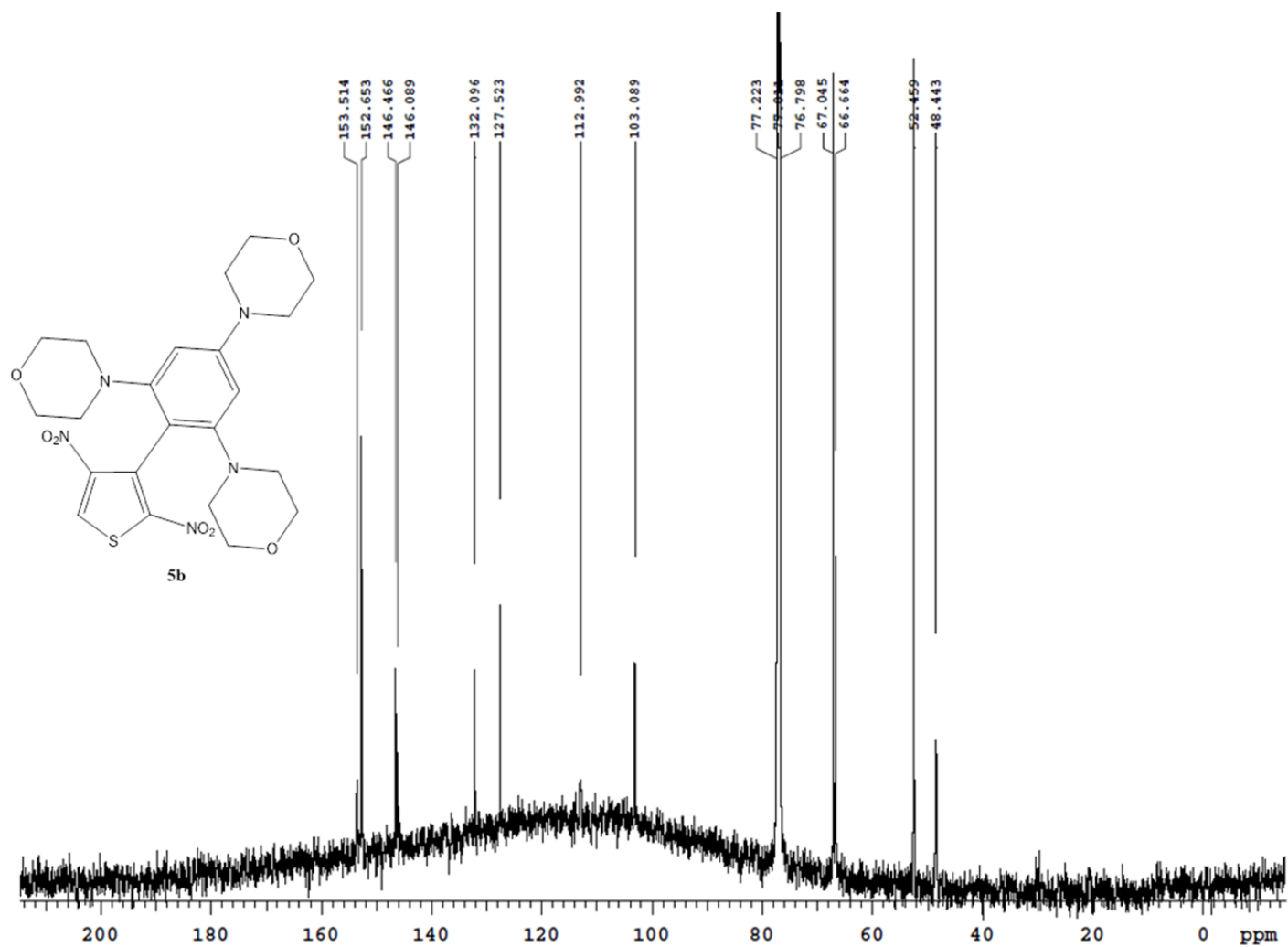


Figure SI-19. <sup>13</sup>C NMR spectrum (100.56 MHz, CDCl<sub>3</sub>, 25 °C) of compound **5b**.

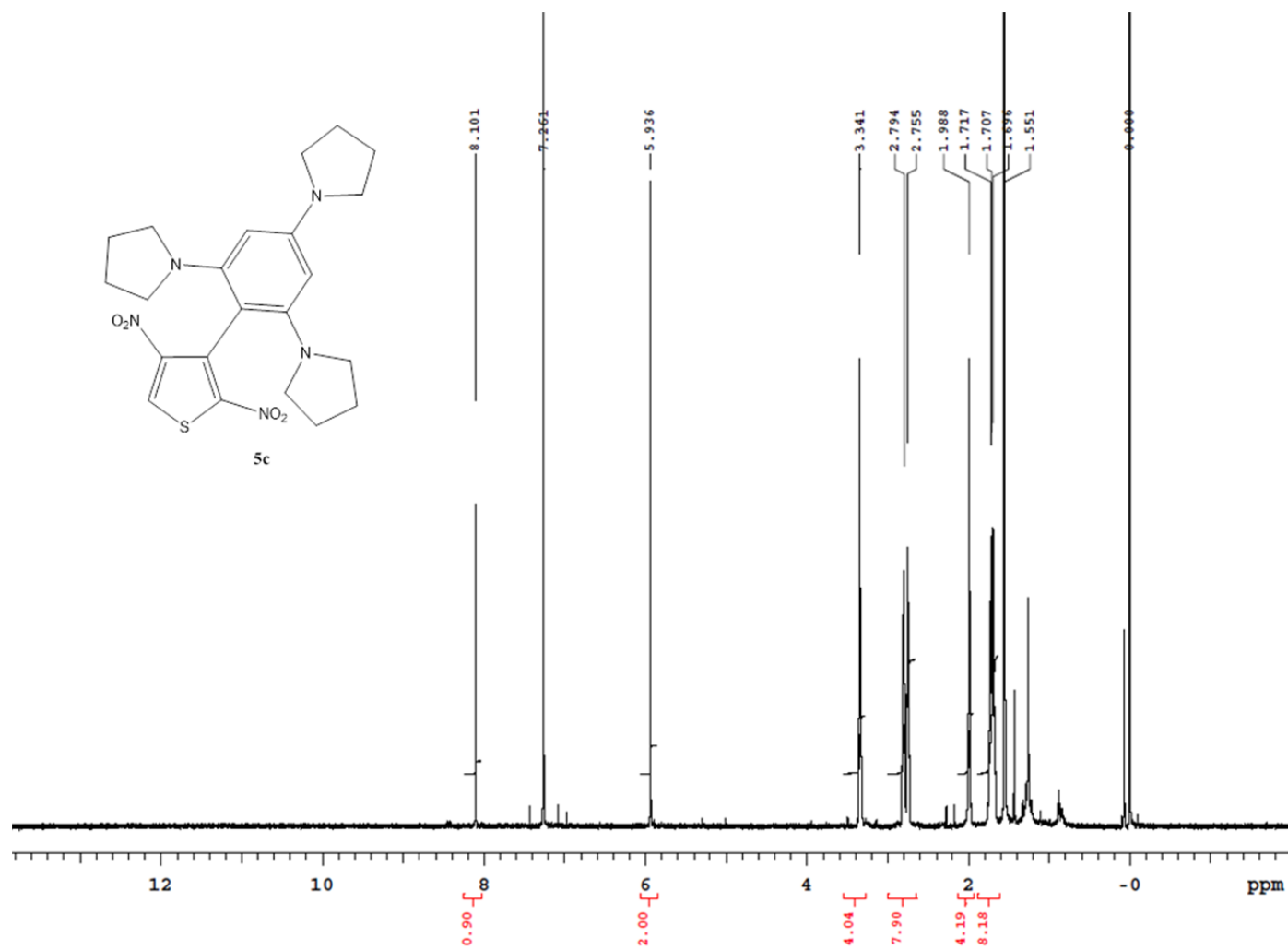


Figure SI-20.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) of compound **5c**.

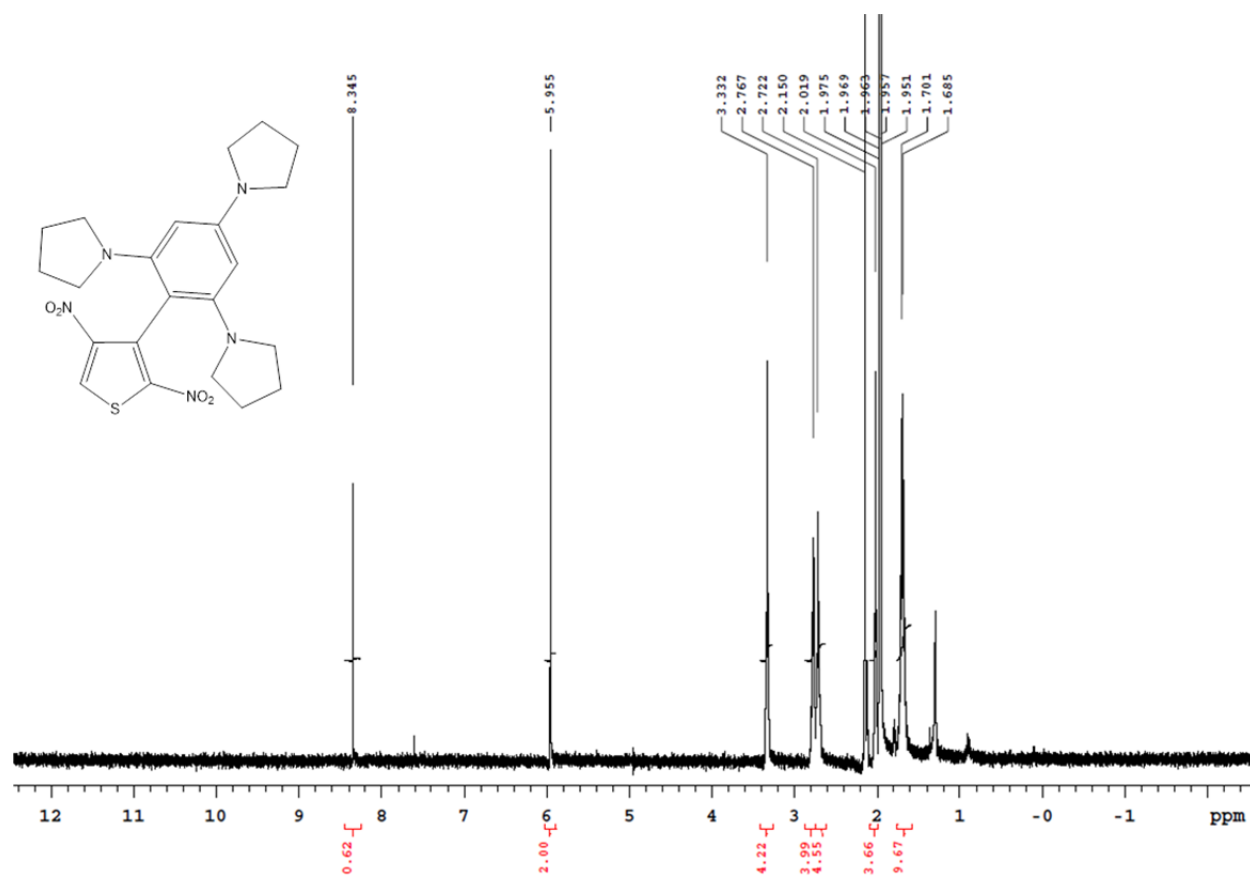


Figure SI-21. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 25 °C) of compound 5c.

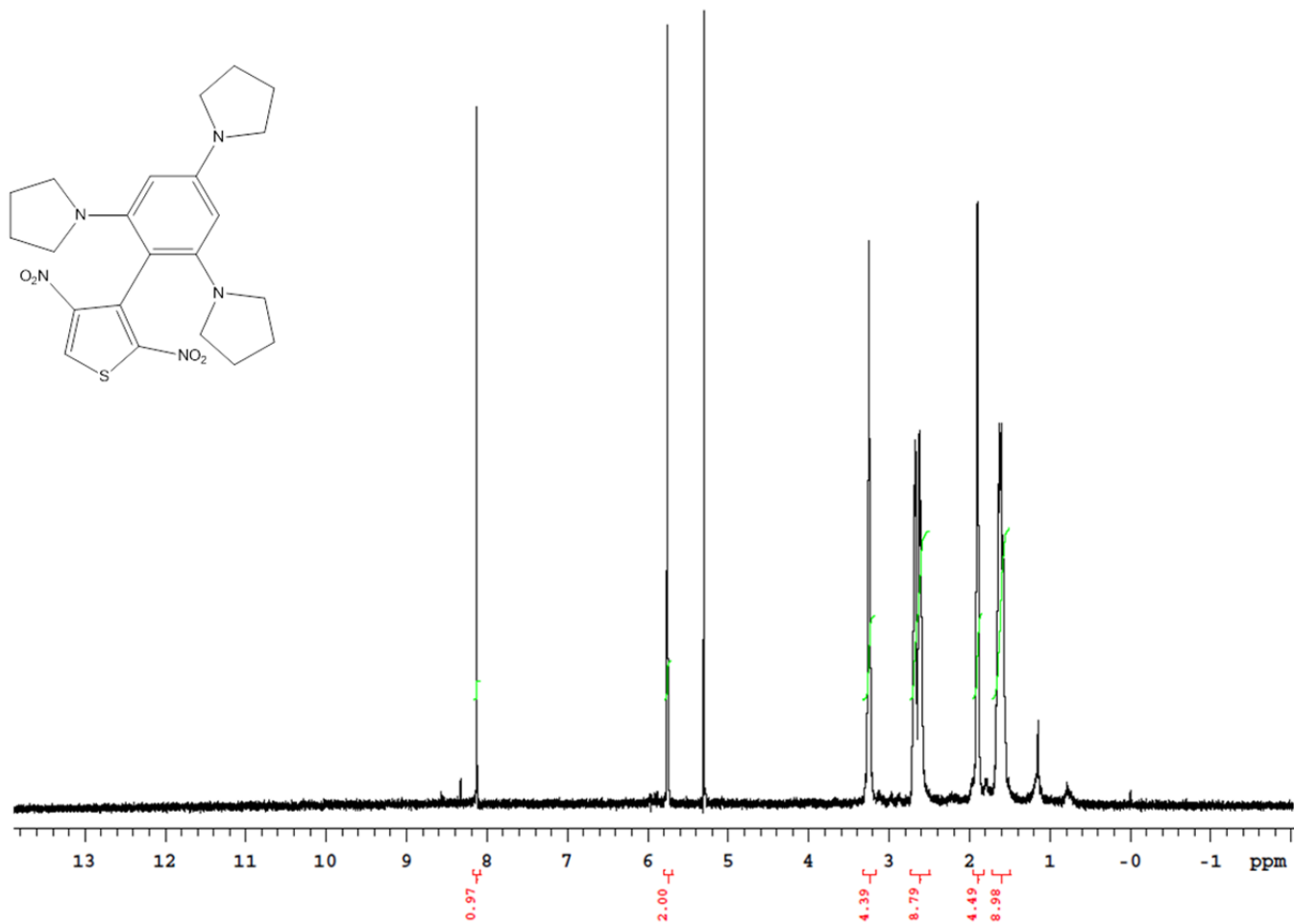


Figure SI-22. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -60 °C) of compound **5c**.

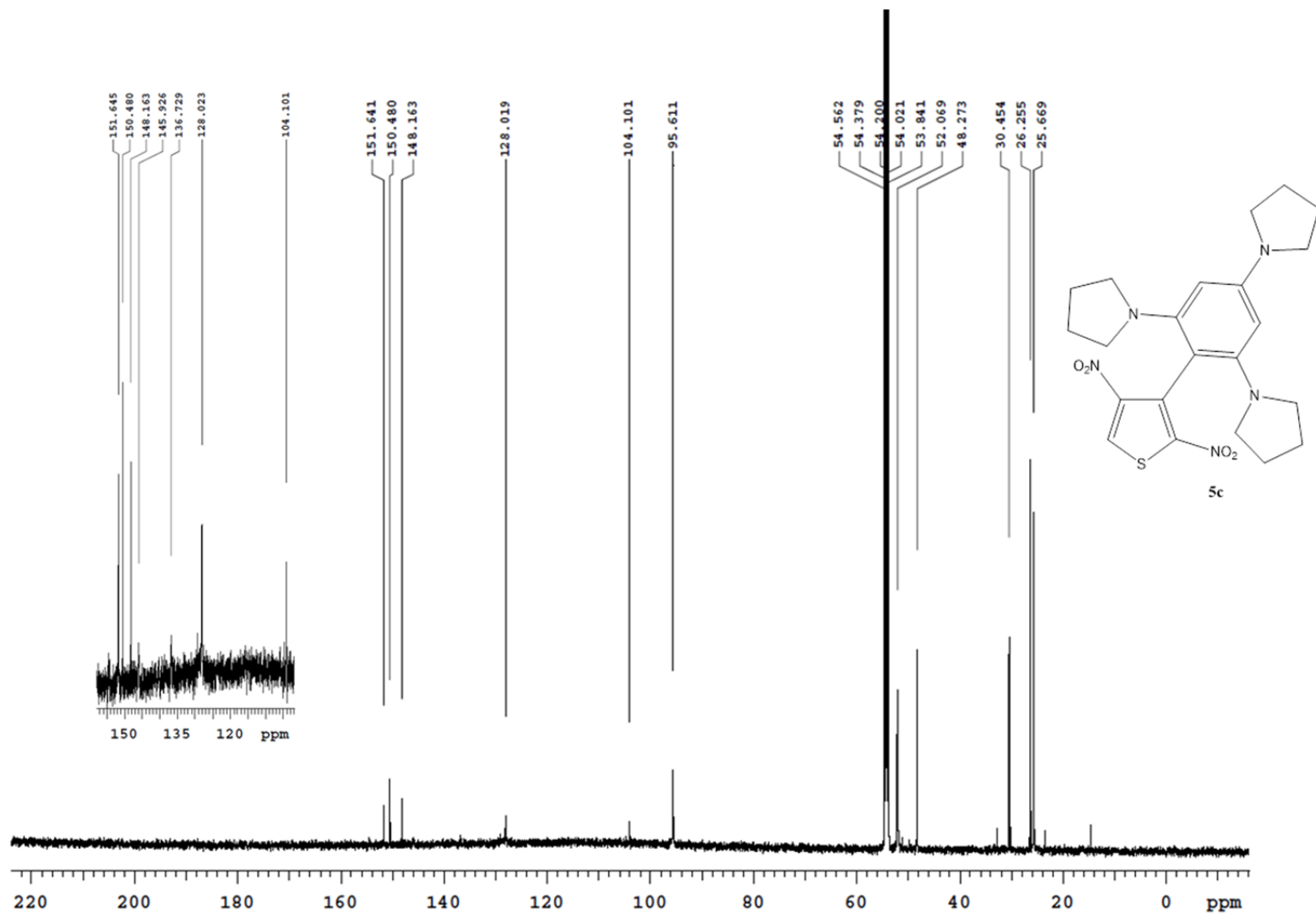


Figure SI-23.  $^{13}\text{C}$  NMR spectrum (100.56 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C) of compound **5c**.



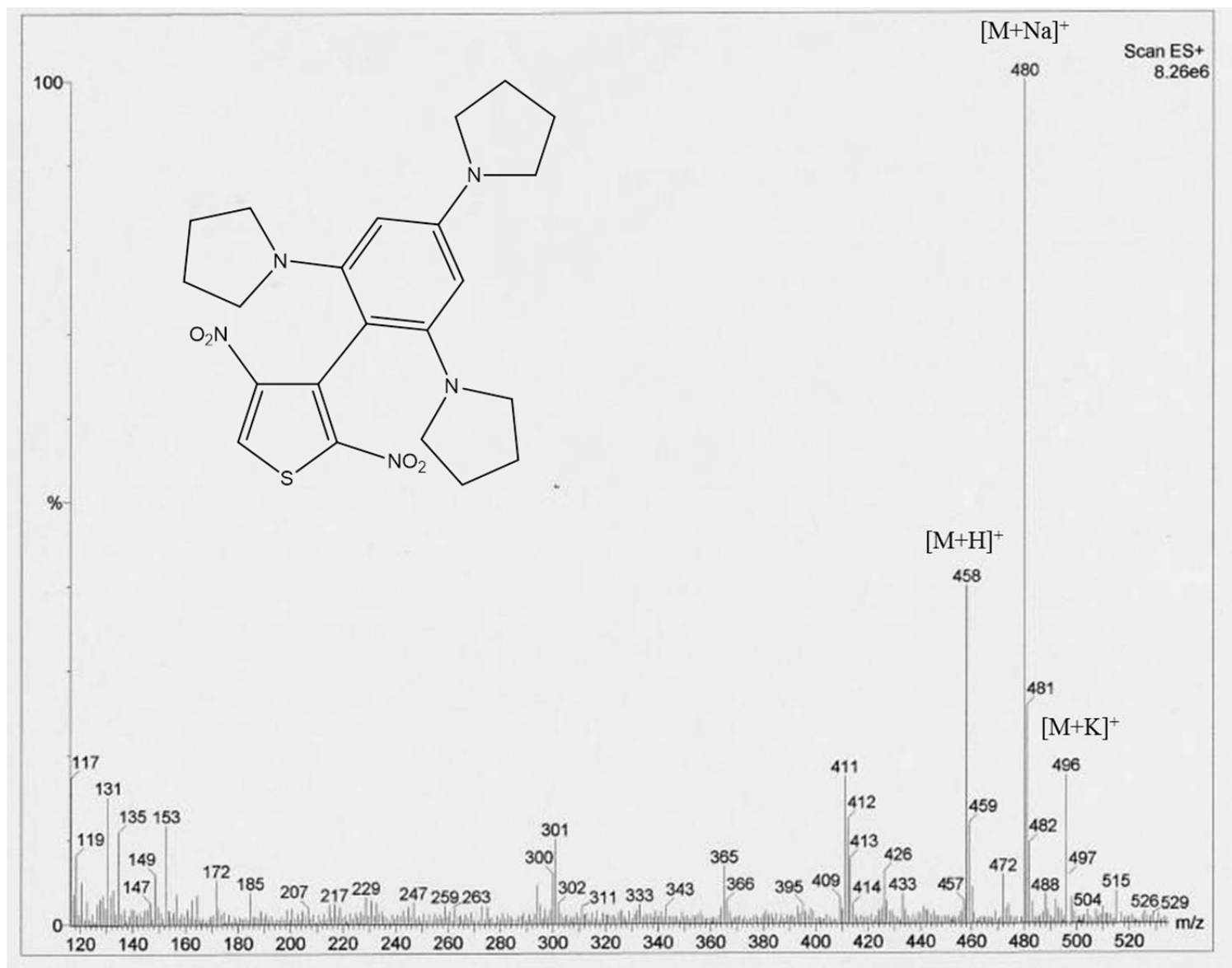


Figure SI-24: ESI-MS ( $ES^+$ ) spectrum of compound **5c**.

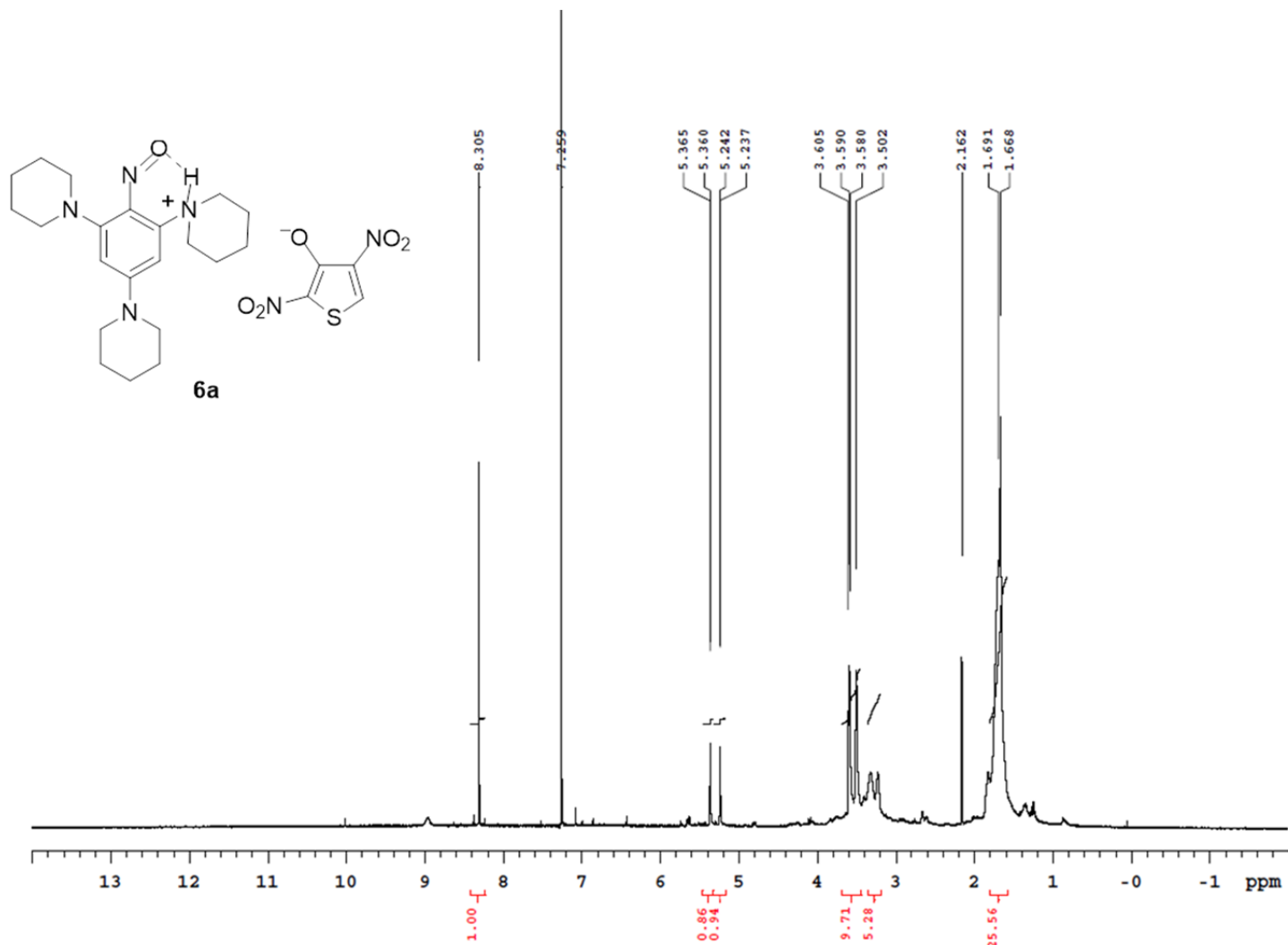


Figure SI-25. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) of crude salt **6a** precipitated from the reaction mixture.

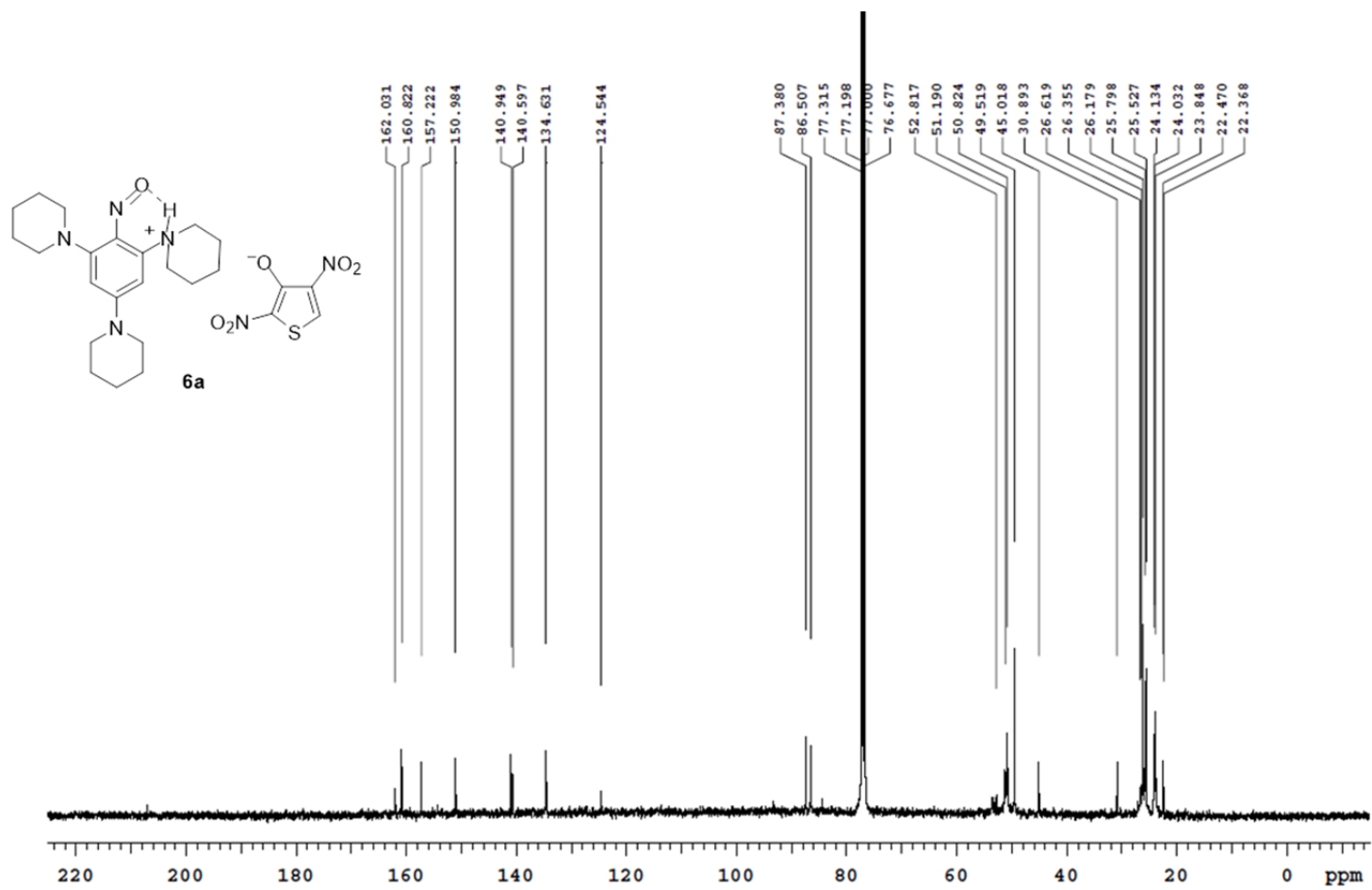


Figure SI-26. <sup>13</sup>C NMR (100.56 MHz, CDCl<sub>3</sub>, 25 °C) of crude salt **6a** precipitated from the reaction mixture.

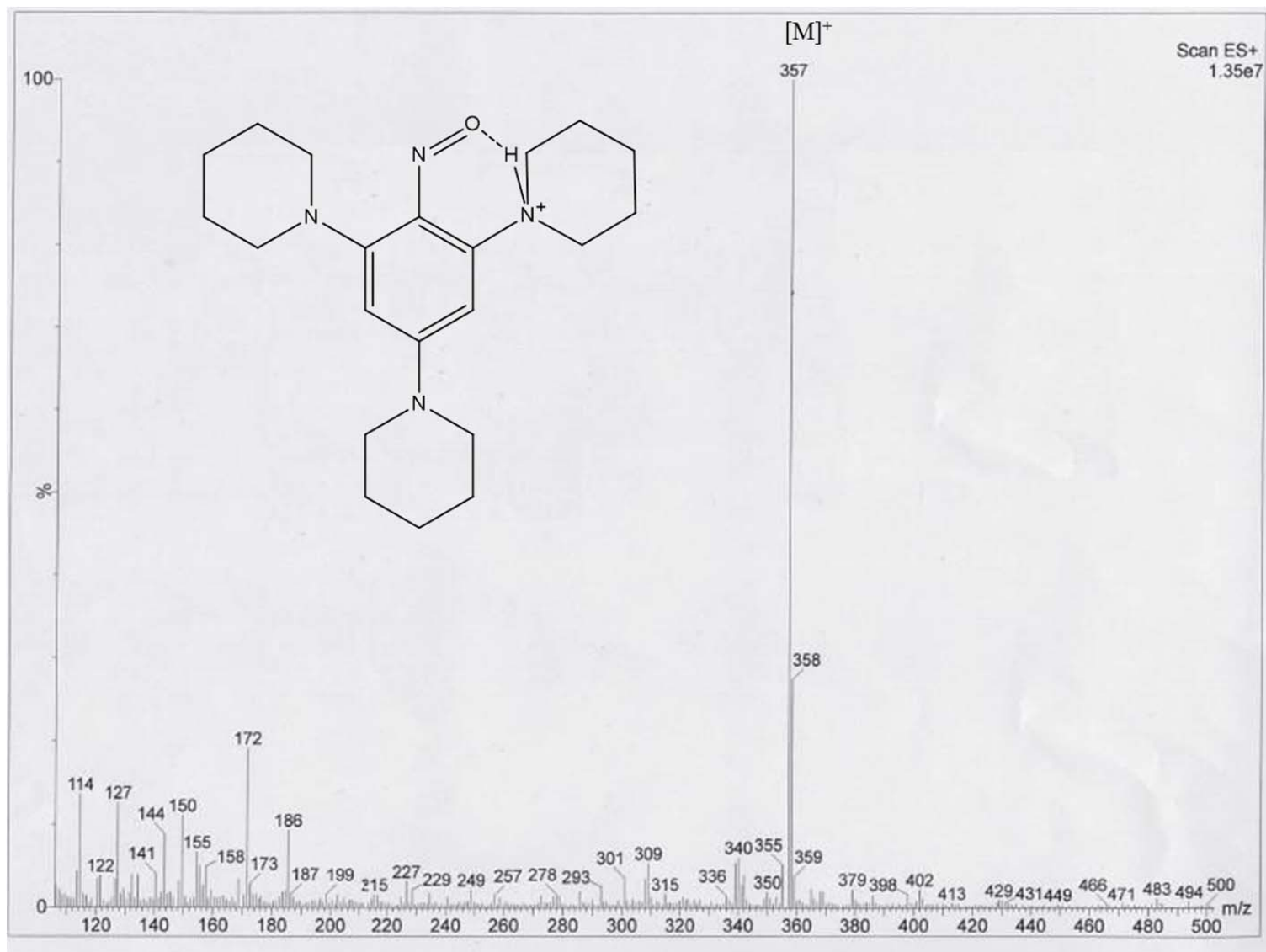


Figure SI-27: ESI-MS (ES<sup>+</sup>) spectrum of compound **6a**.

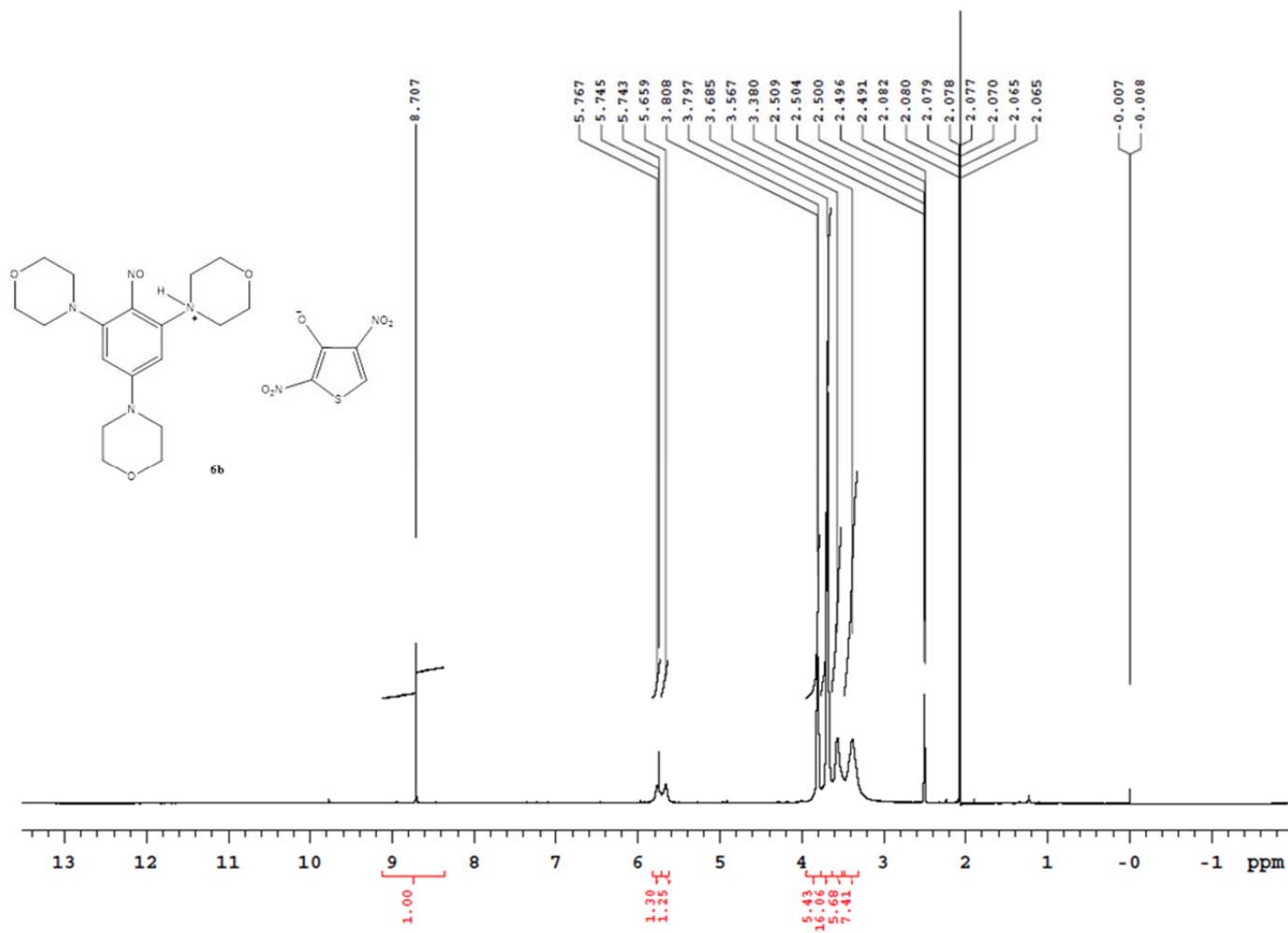


Figure SI-28. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C) of crude salt **6b** precipitated from the reaction mixture, with traces of solvents<sup>1</sup> (CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN).

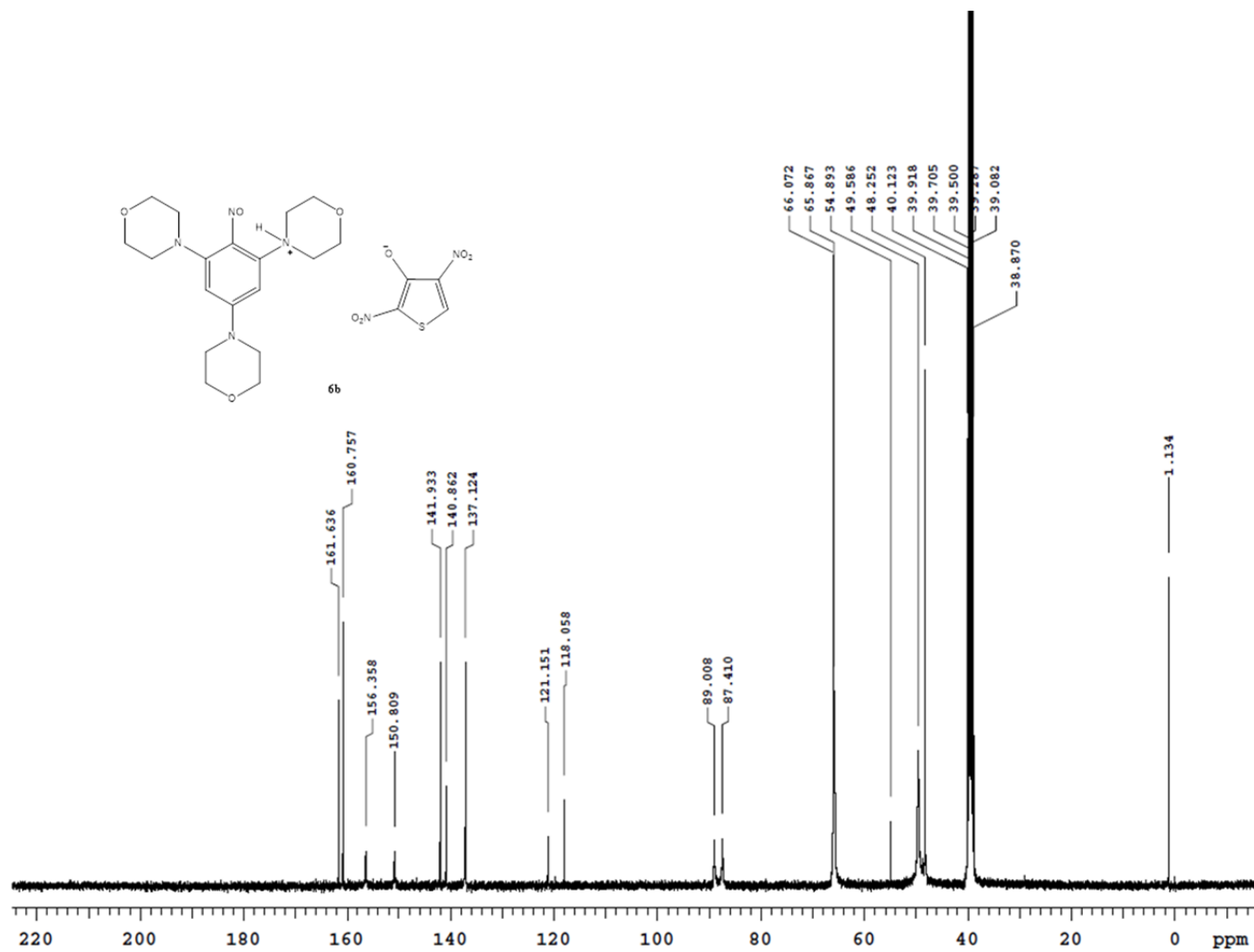


Figure SI-29. <sup>13</sup>C NMR (100.56 MHz, DMSO-d<sub>6</sub>, 25 °C) of crude salt **6b** precipitated from the reaction mixture, with traces of solvents<sup>1</sup> (CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN).

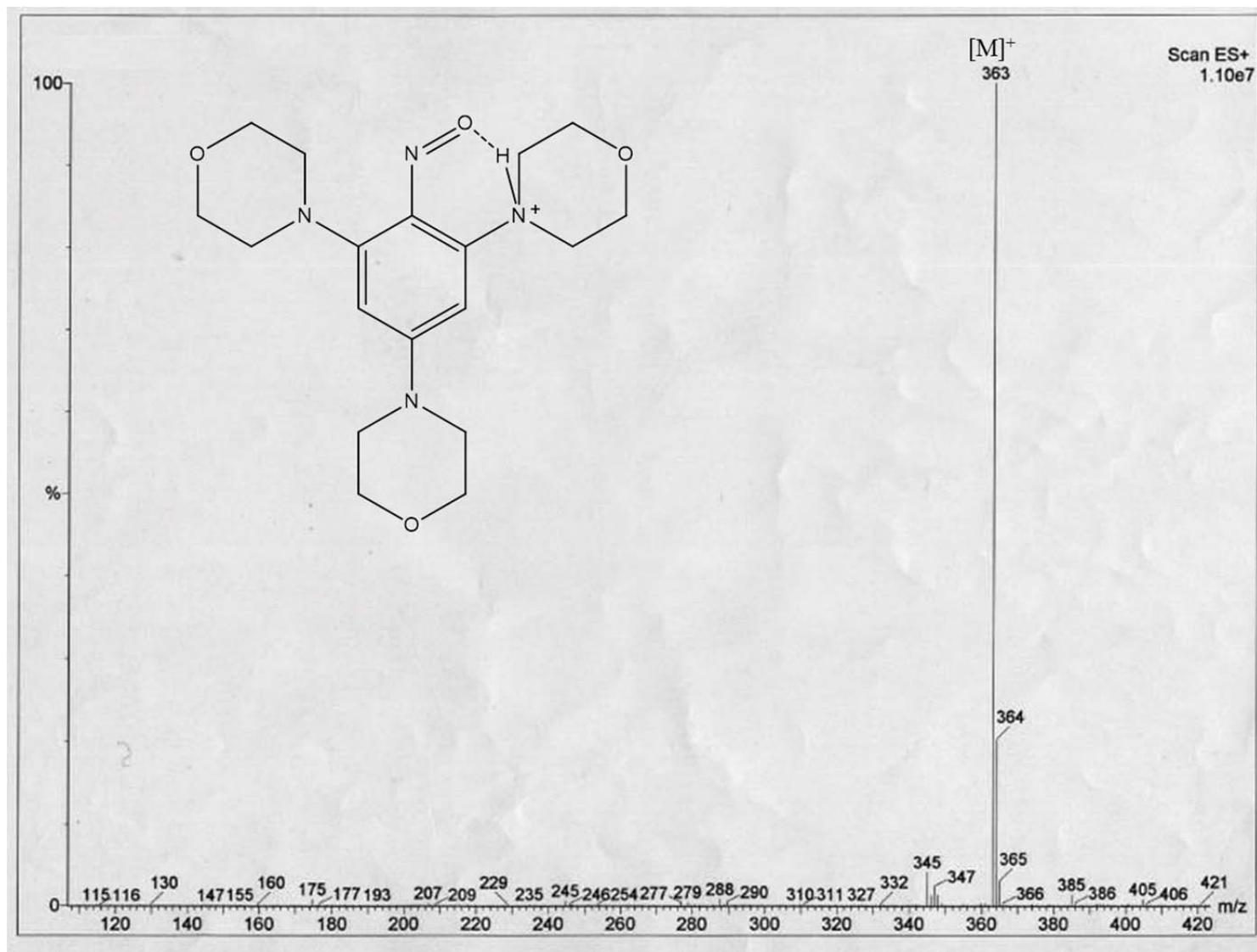


Figure SI-30: ESI-MS (ES<sup>+</sup>) spectrum of compound **6b**.

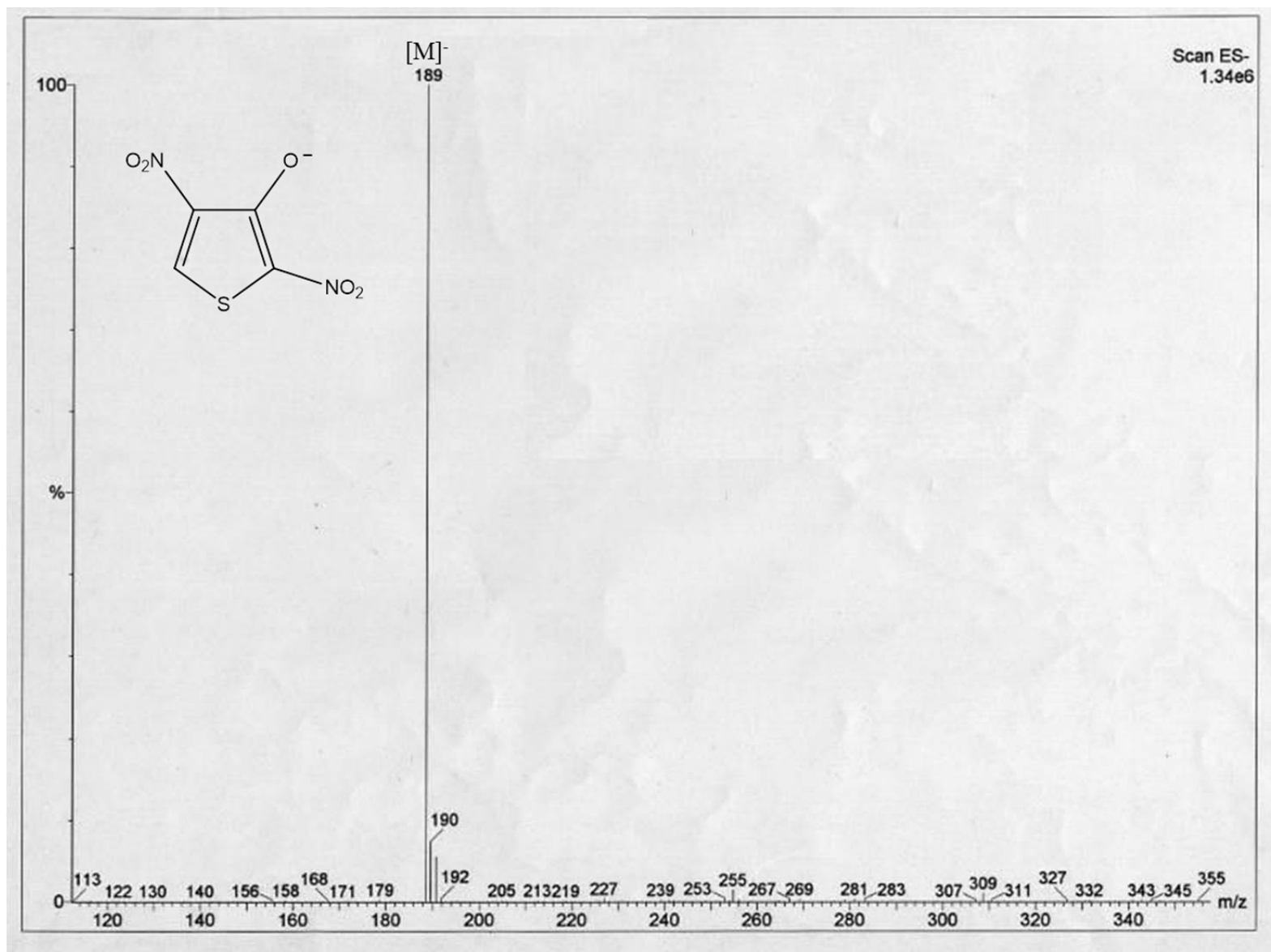


Figure SI-31: ESI-MS (ES<sup>-</sup>) spectrum of compound **6b**



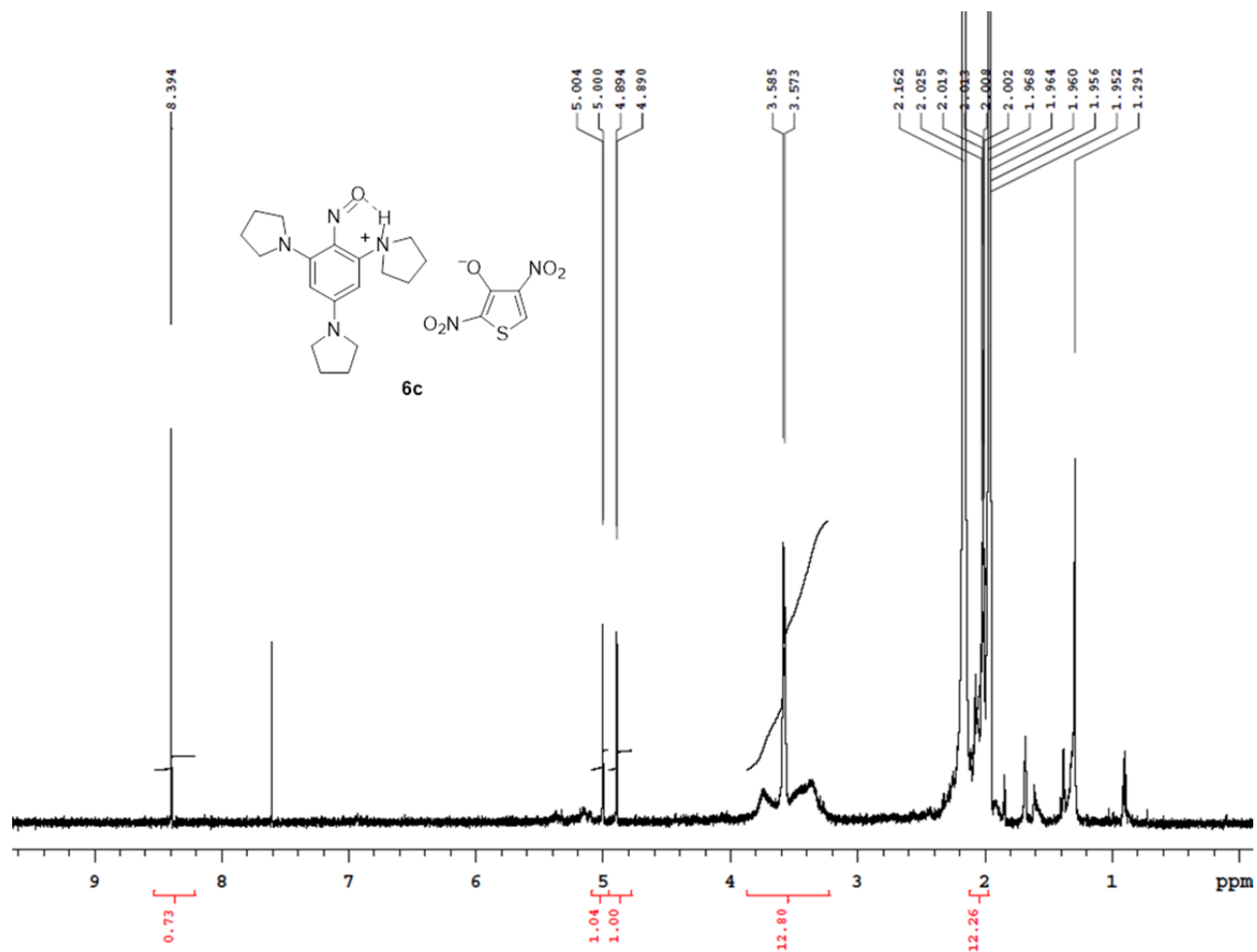


Figure SI-32.  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ , 25 °C) of crude salt **6c** precipitated from the reaction mixture, with traces of chloroform and water.<sup>1</sup>

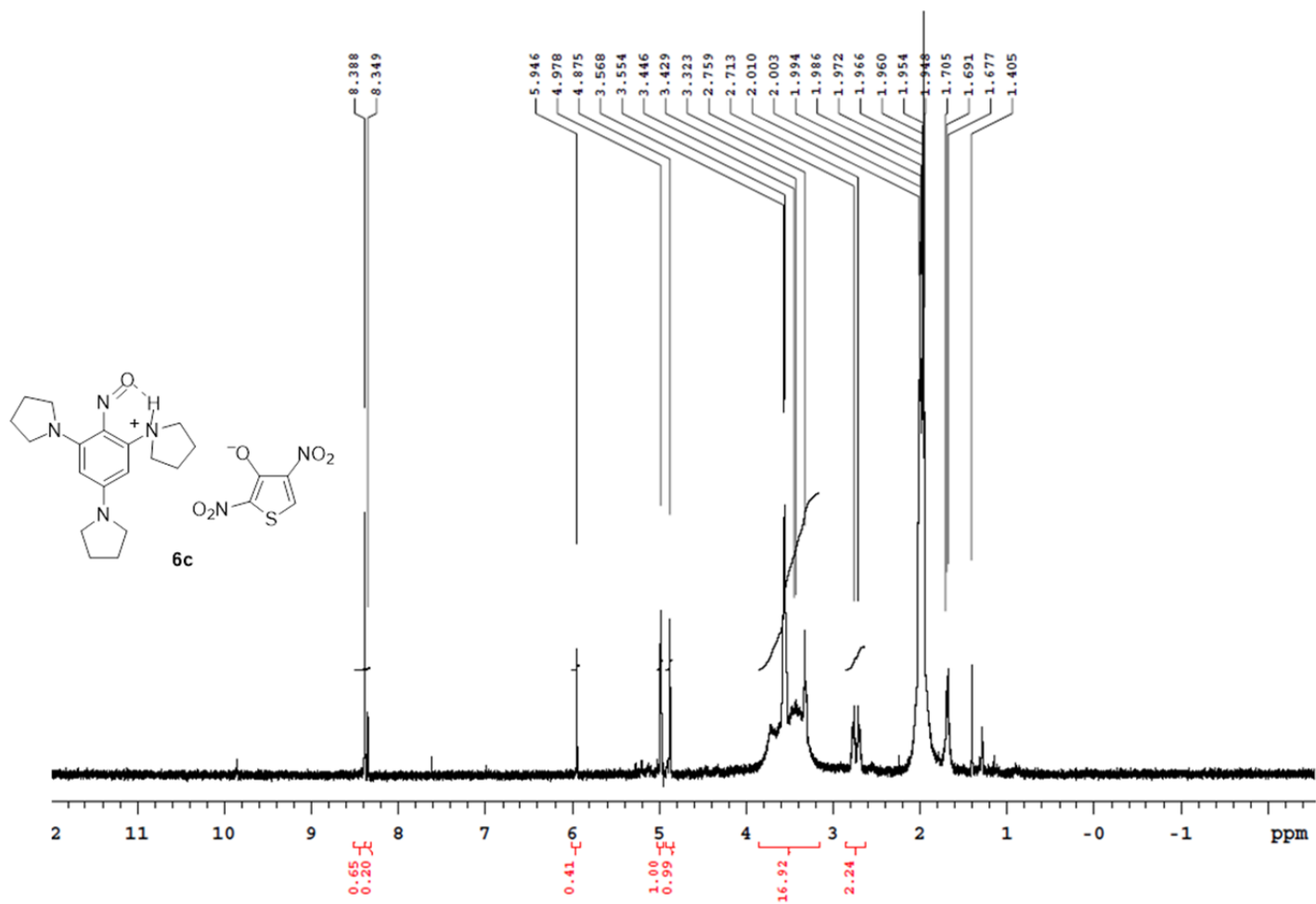


Figure SI-33. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C) of crude salt **6c** precipitated from the reaction mixture, with about 20% of **5c**, sample used to collect <sup>13</sup>C MR spectra of **6c** reported below.

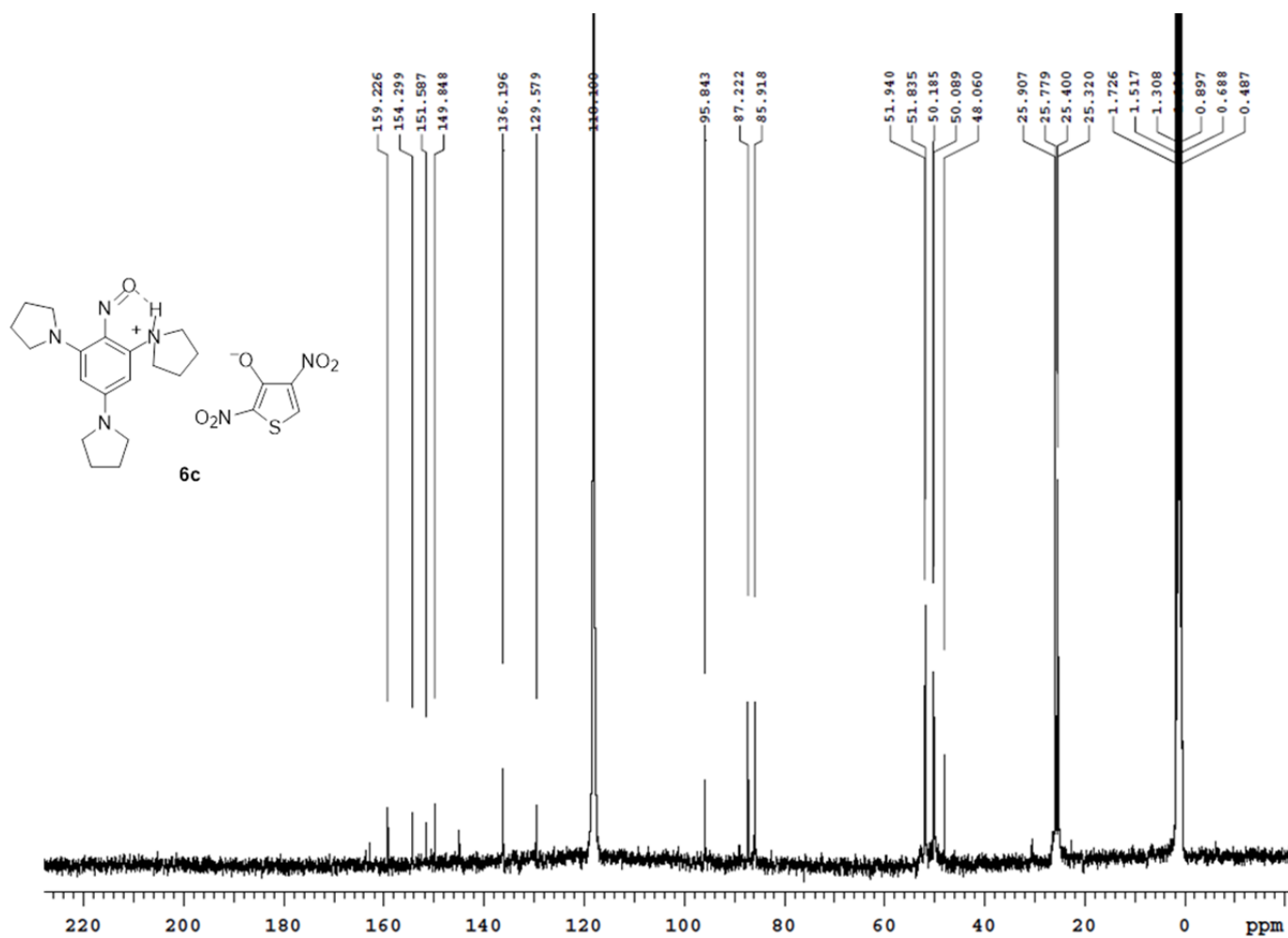


Figure SI-34. <sup>13</sup>C NMR (100.56 MHz, CD<sub>3</sub>CN, 25 °C) of crude salt **6c** precipitated from the reaction mixture (peaks at 129.6, 95.9, 51.9, 48.1, 25.9 belong to traces of **5c**).

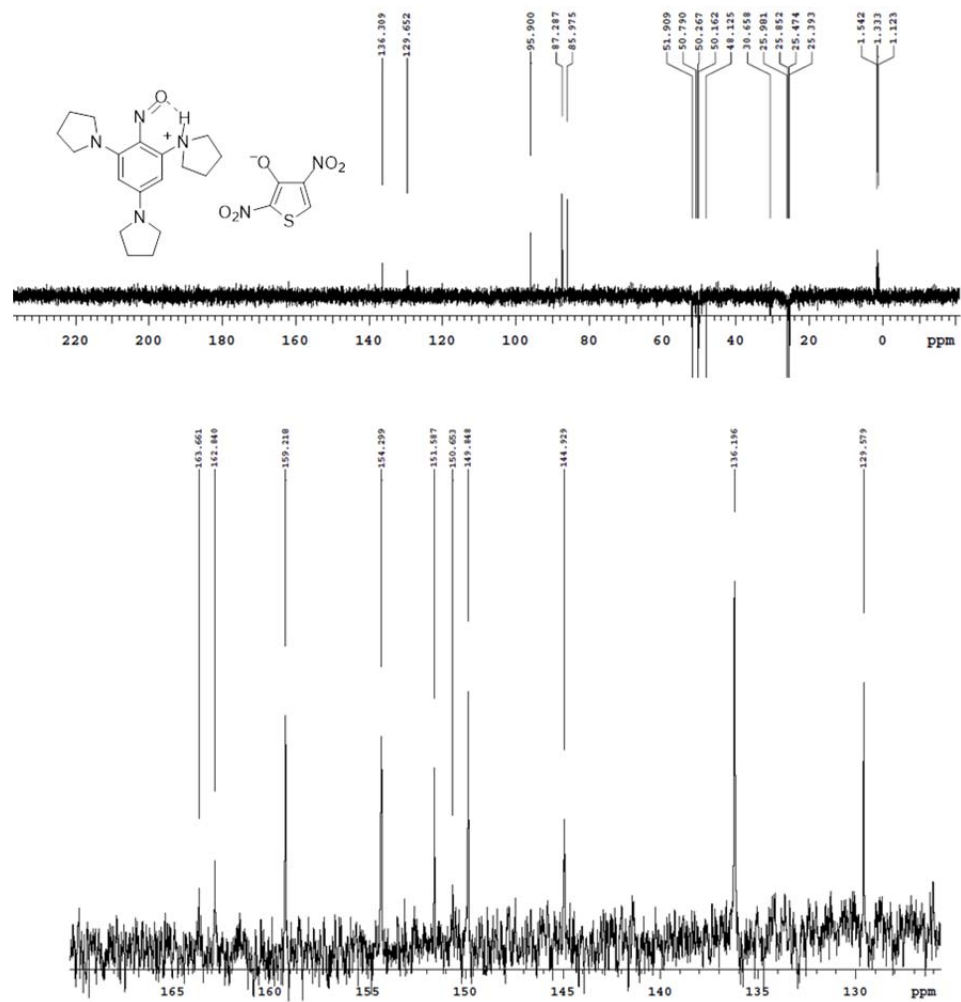


Figure SI-35. Up: DEPT spectrum of crude **6c** precipitated from the reaction mixture (peaks at 129.6 and 95.9, 51.9, 48.1, 25.9 belong to traces of **5c**).

Down: Expanded view of  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 25 °C) spectrum of crude salt **6c**.

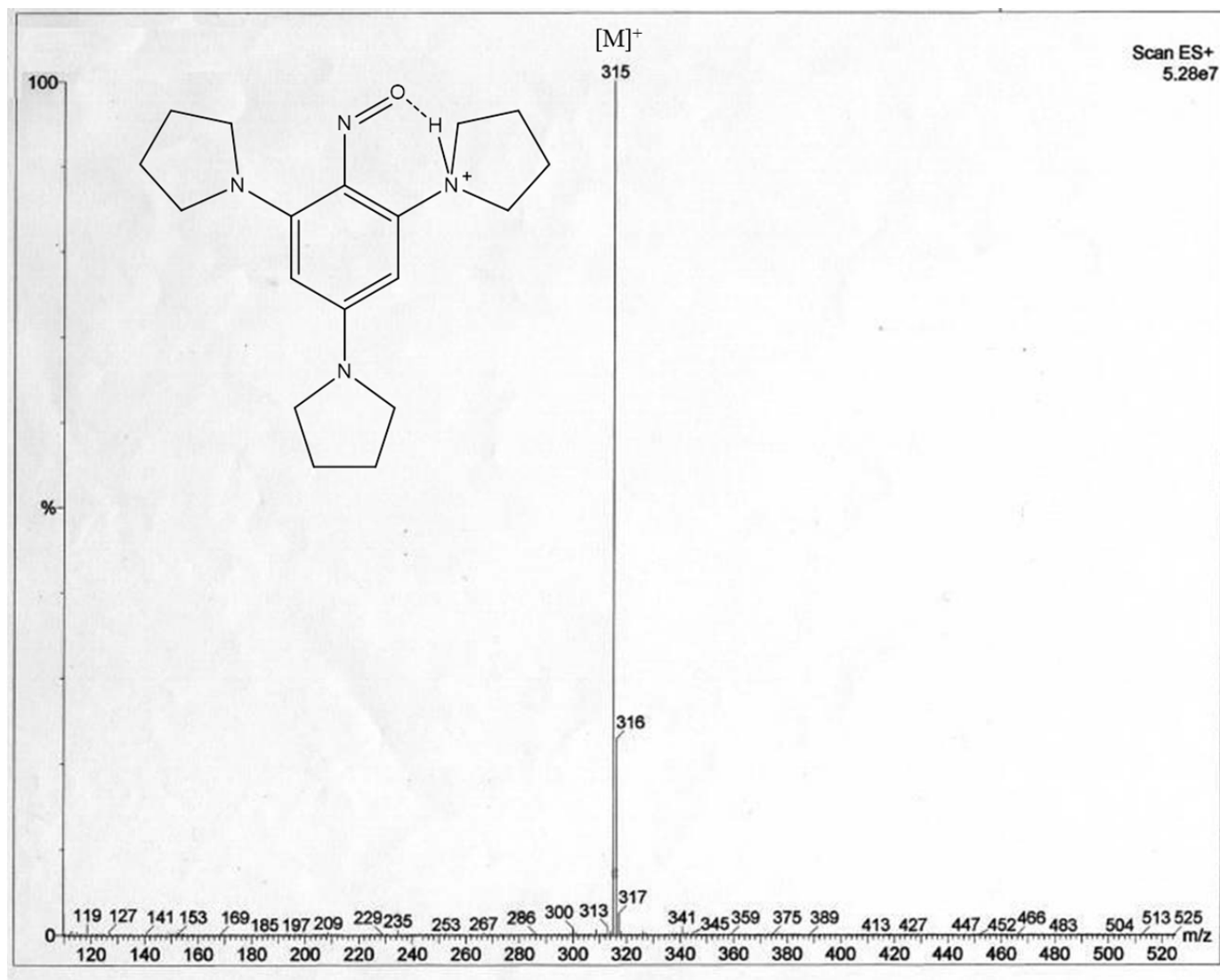


Figure SI-36: ESI-MS (ES<sup>+</sup>) spectrum of compound **6c**.

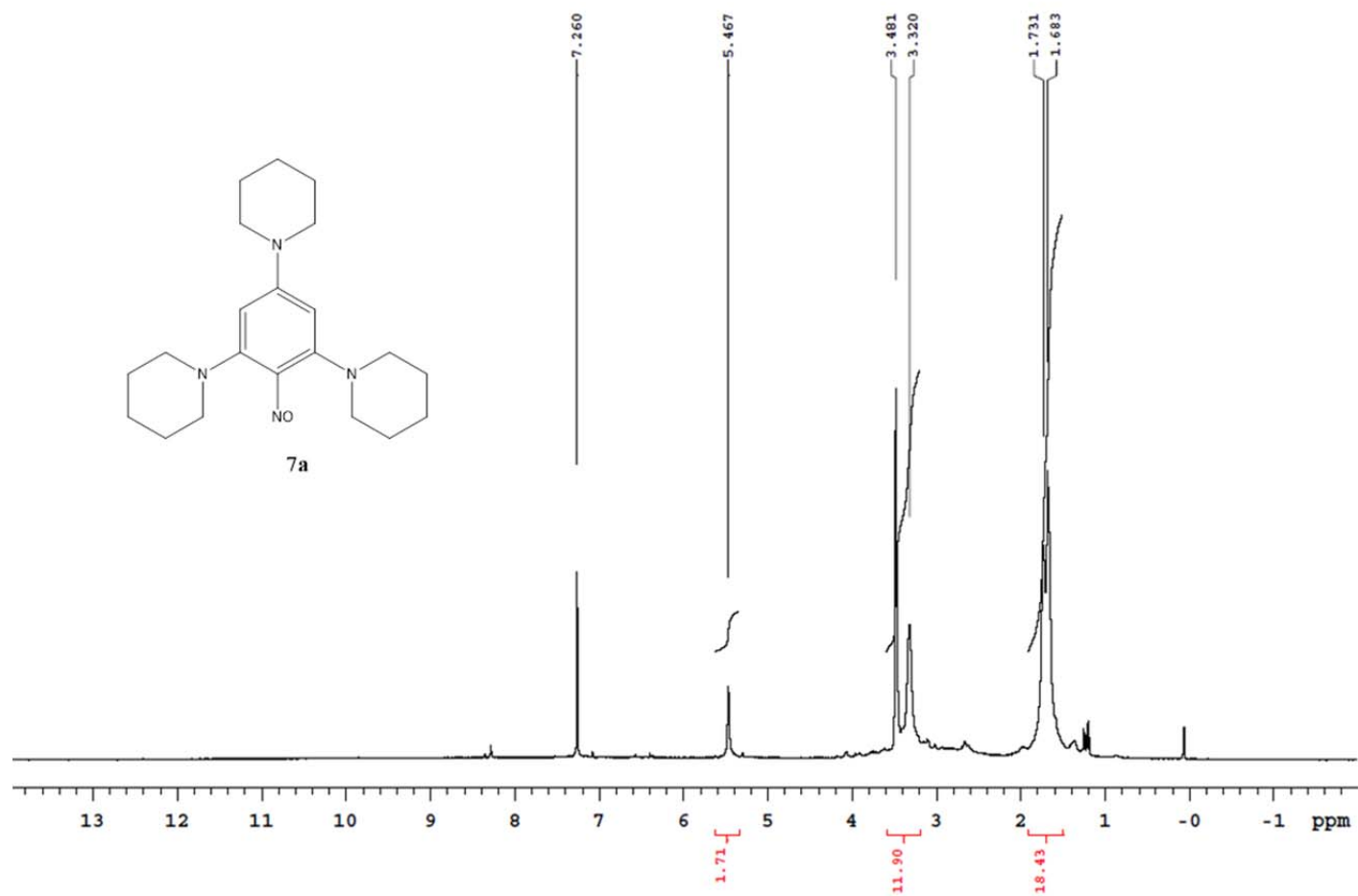


Figure SI-37. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) of compound **7a**.

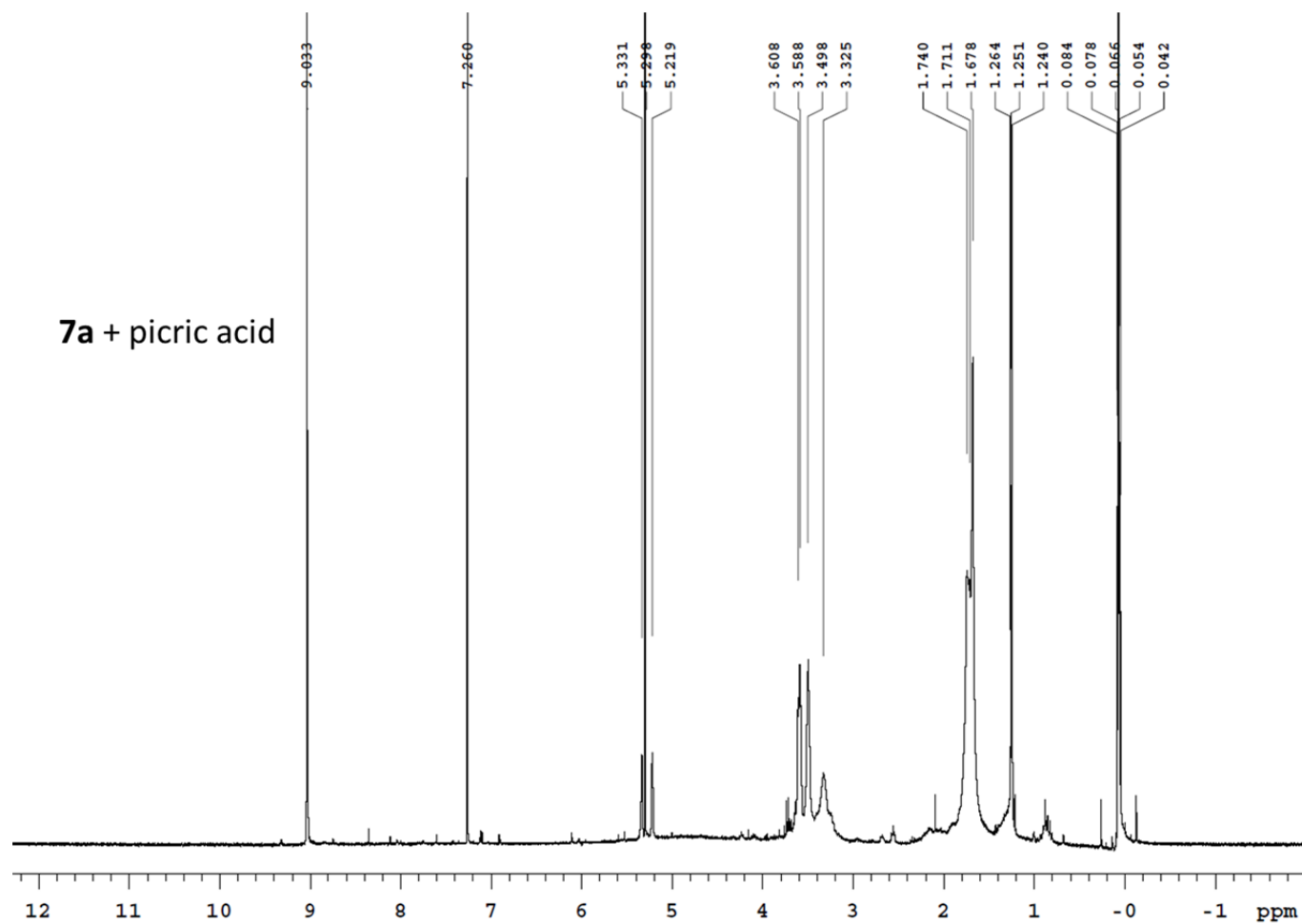


Figure SI-38.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of the solution obtained adding picric acid to compound **7a** (with traces of  $\text{CH}_2\text{Cl}_2$ ) with formation of related salt, very similar to spectrum of **6a**.

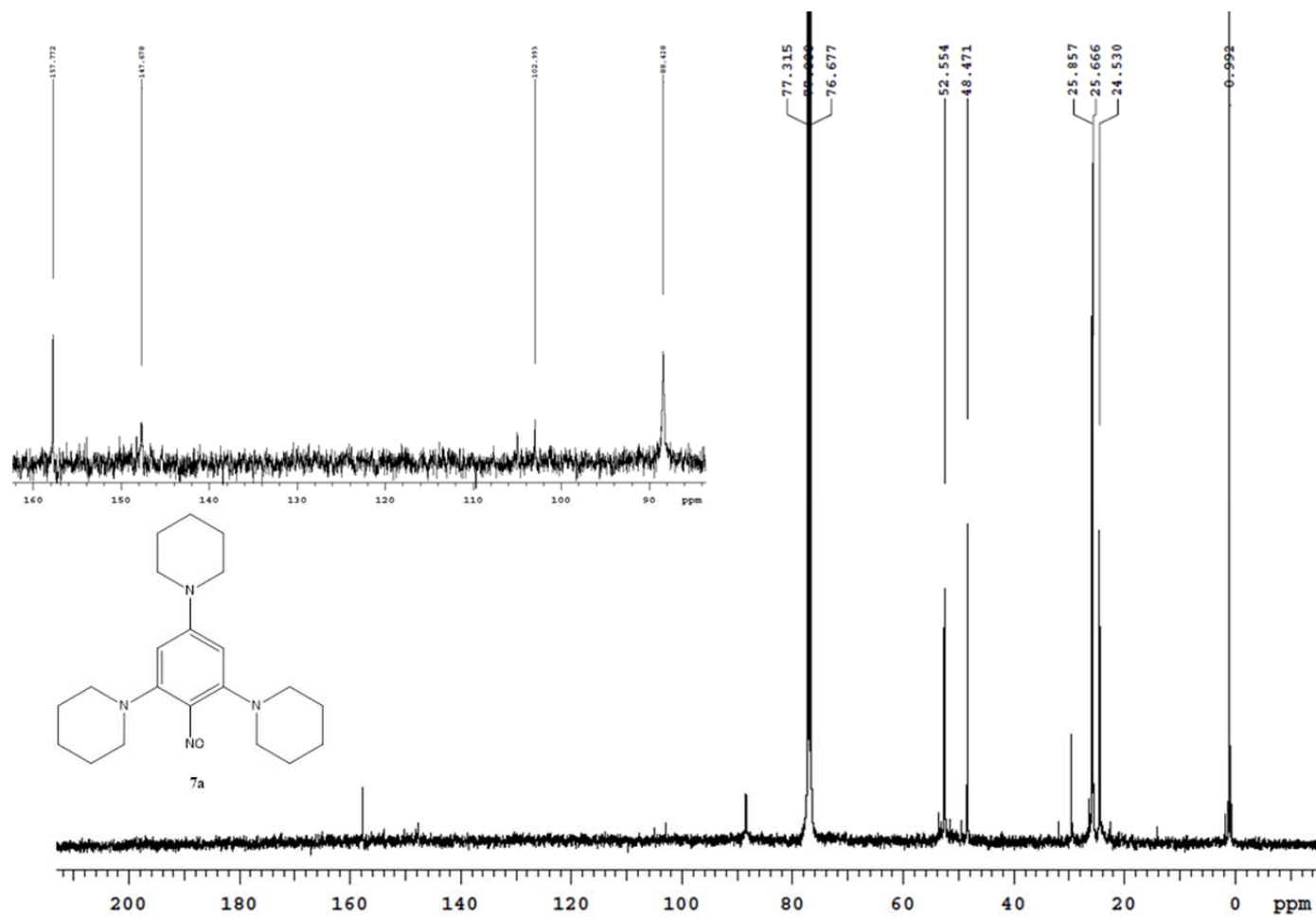


Figure SI-39.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) of compound **7a**.



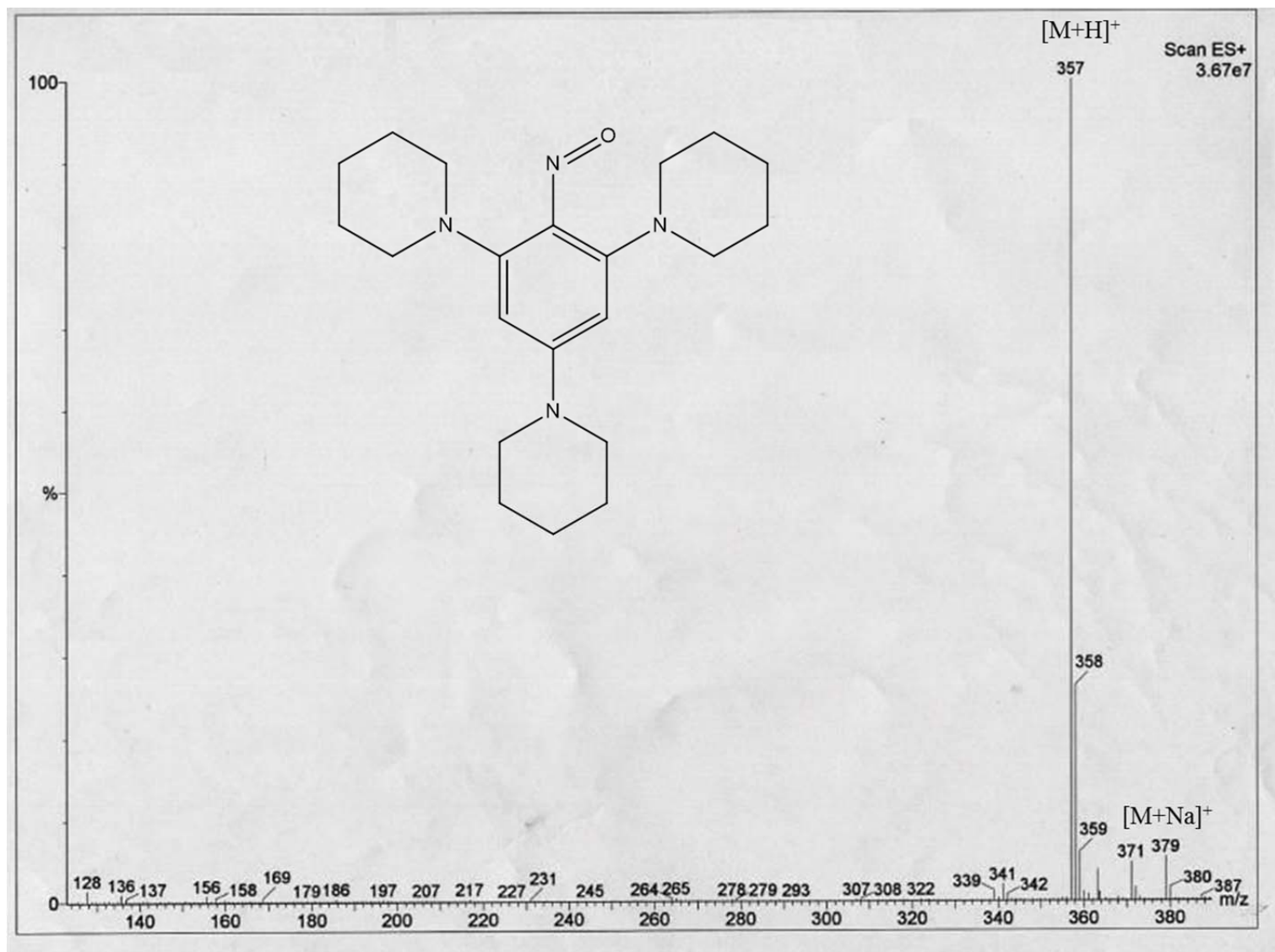


Figure SI-40: ESI-MS (ES<sup>+</sup>) spectrum of compound **7a**.

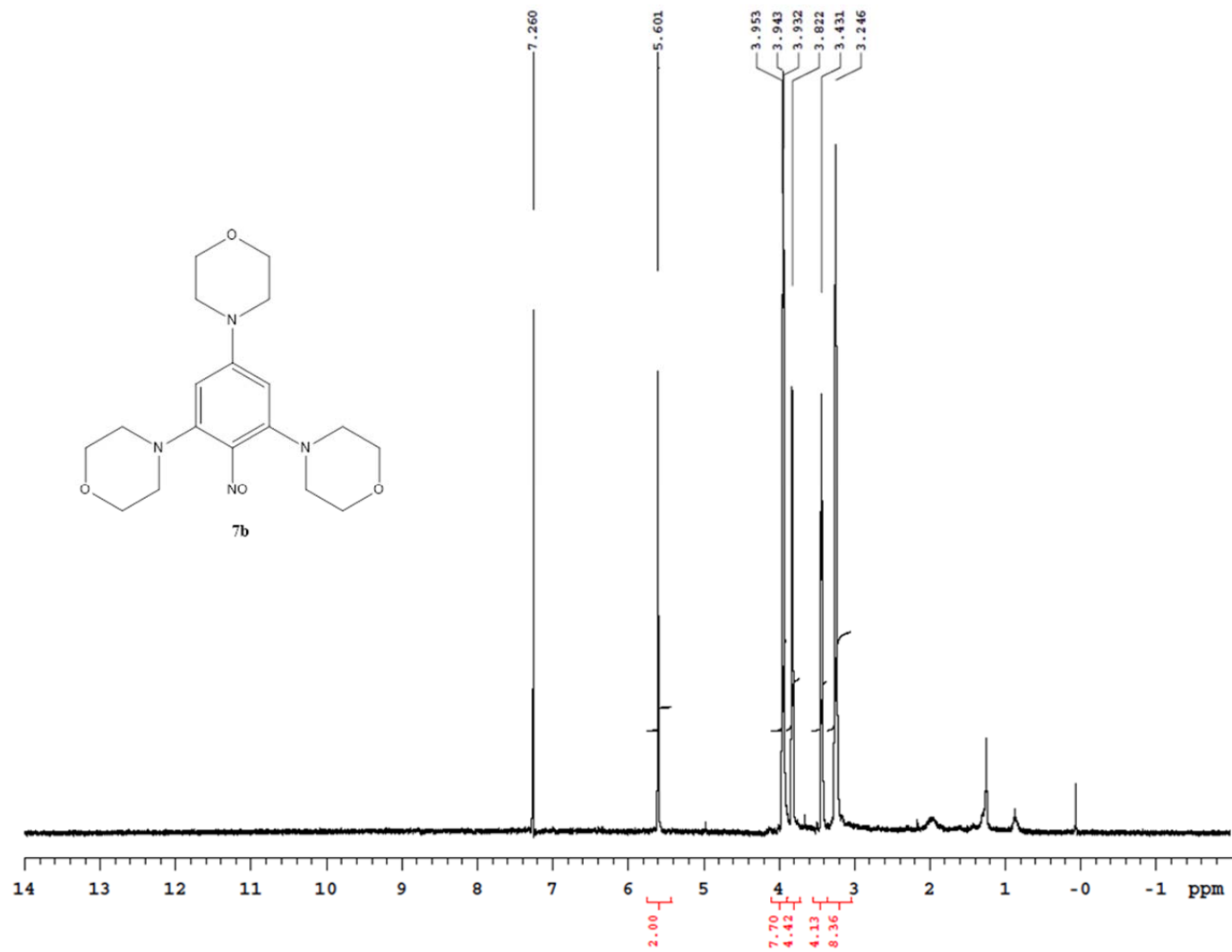


Figure SI-41. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) of compound **7b**.

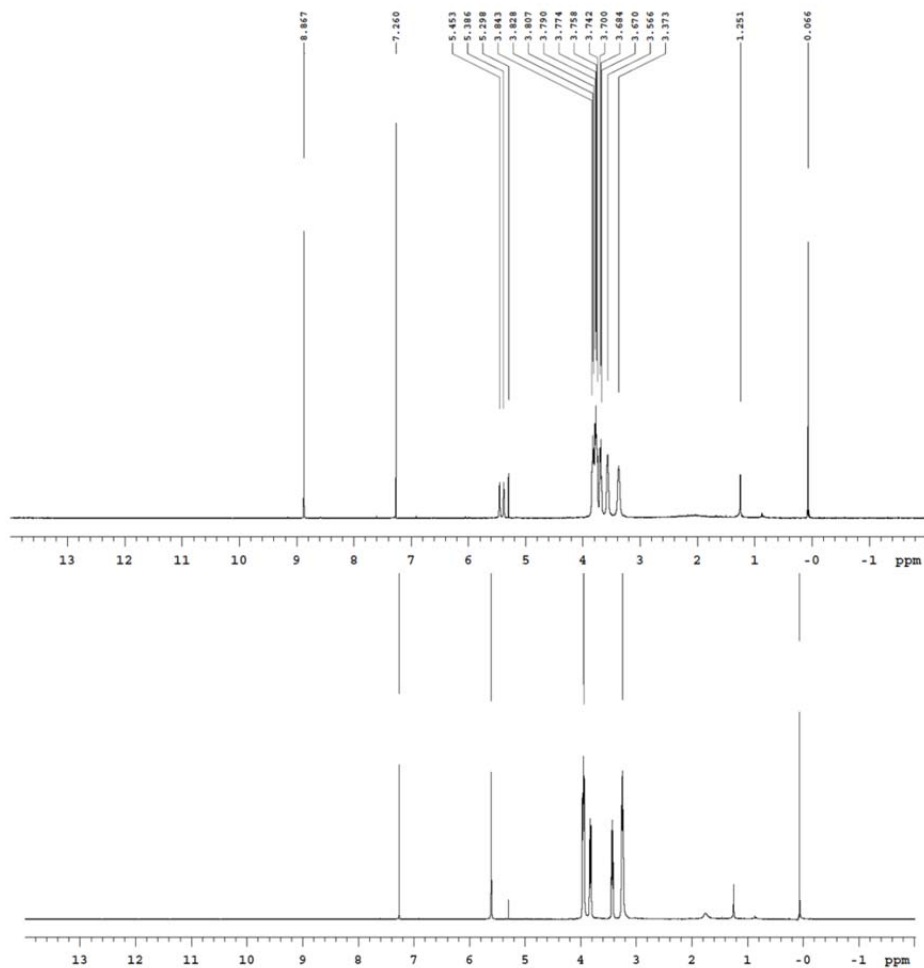


Figure SI-42.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of a solution of **7b** (with traces of  $\text{CH}_2\text{Cl}_2$ )

before (down) and after (up) addition of picric acid with formation of related salt, very similar to spectrum of **6b**.

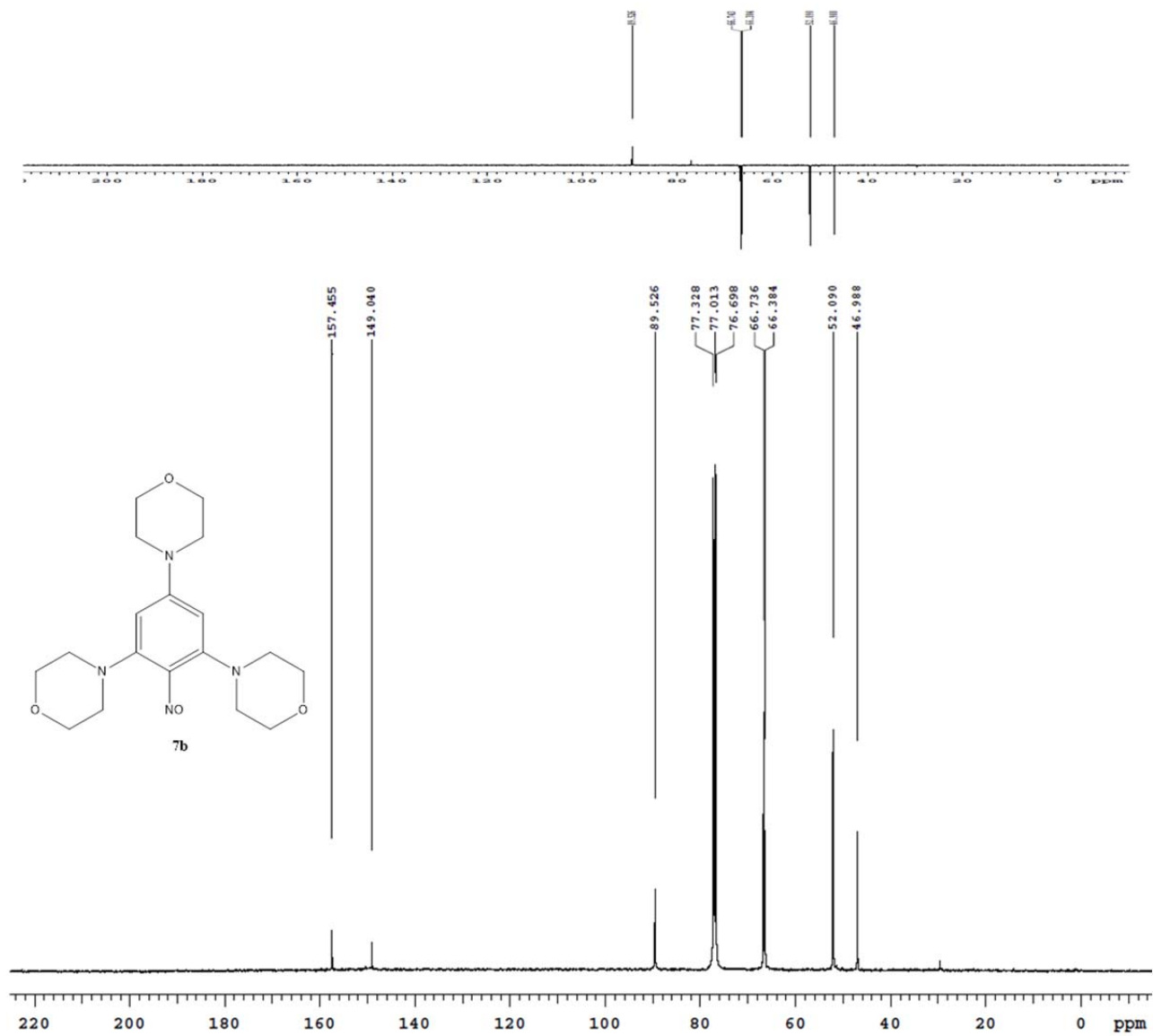


Figure SI-43.  $^{13}\text{C}$  NMR (100.56 MHz,  $\text{CDCl}_3$ , 25 °C) and DEPT of compound **7b**.

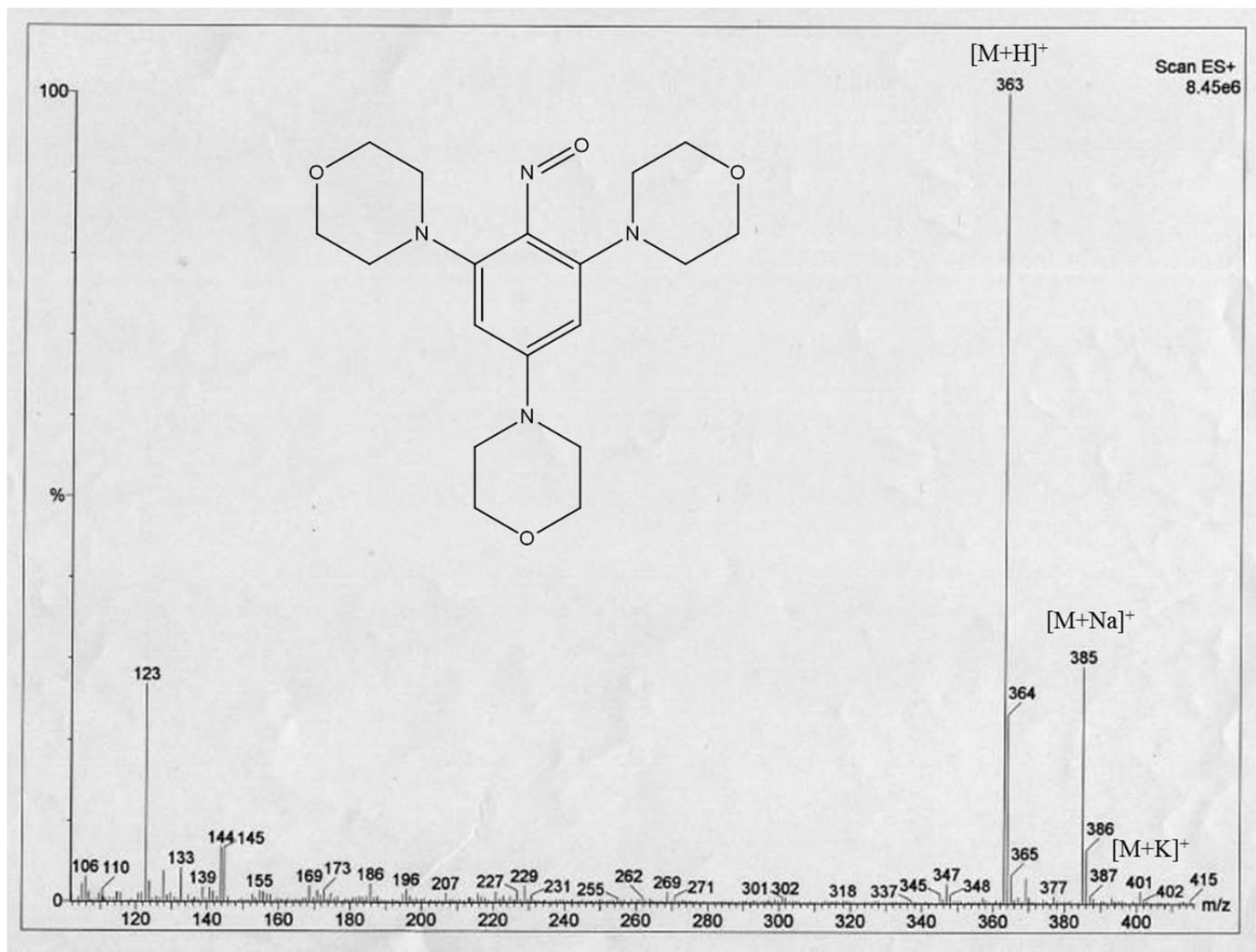


Figure SI-44: ESI-MS (ES<sup>+</sup>) spectrum of compound **7b**.

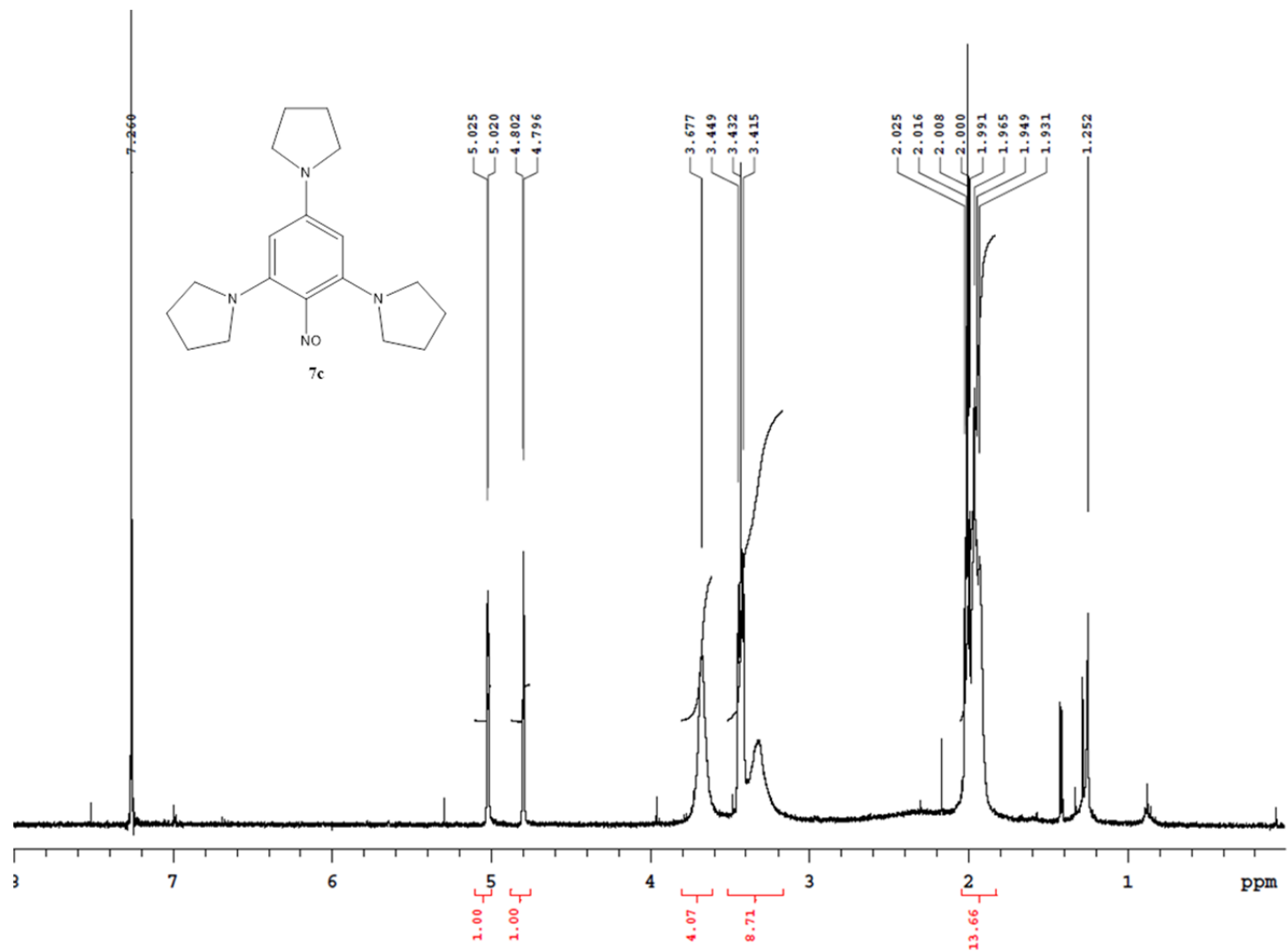


Figure SI-45: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) of compound 7c.

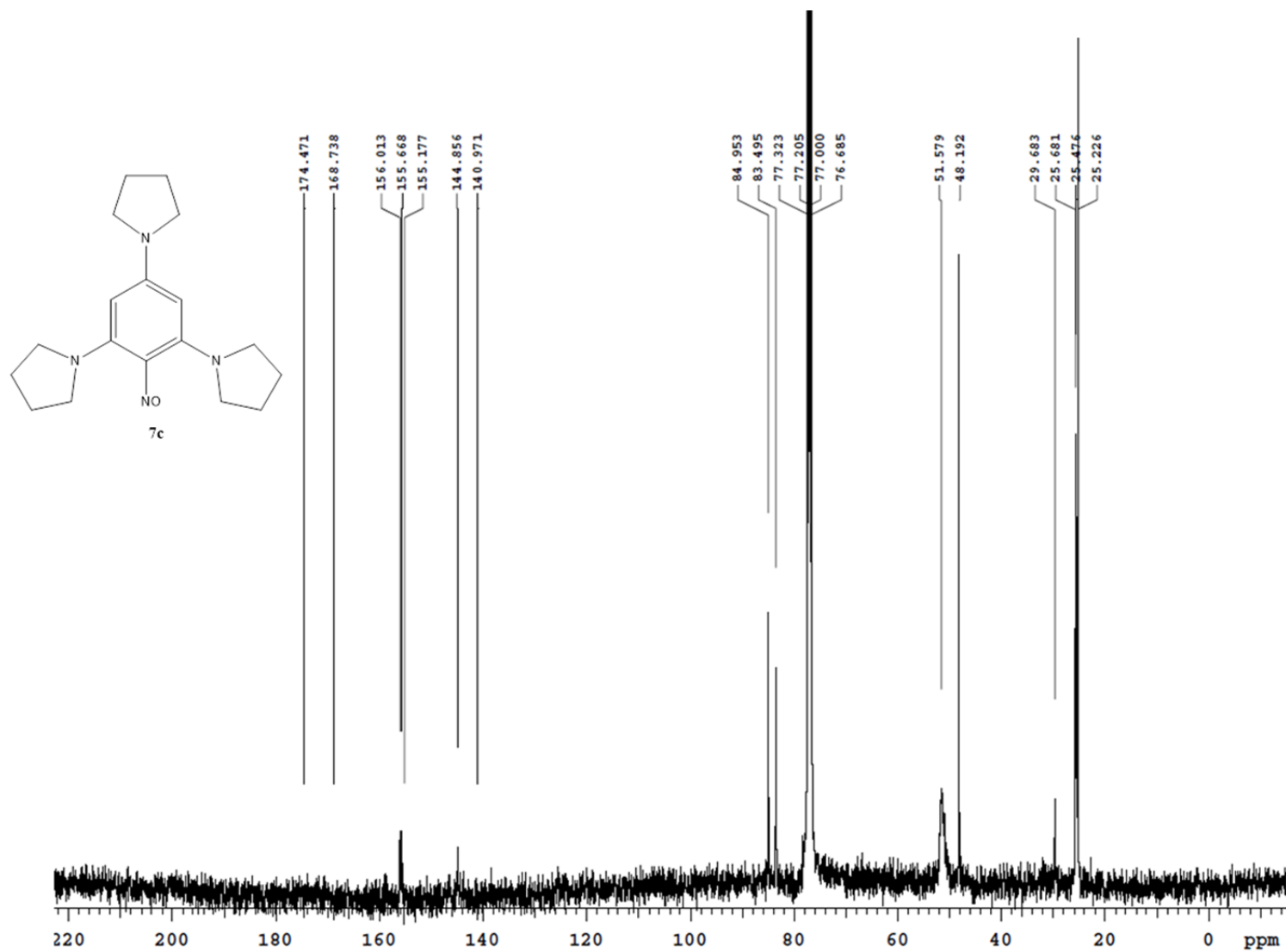


Figure SI-46:  $^{13}\text{C}$  NMR (100.56 MHz,  $\text{CDCl}_3$ , 25 °C) of compound **7c**.

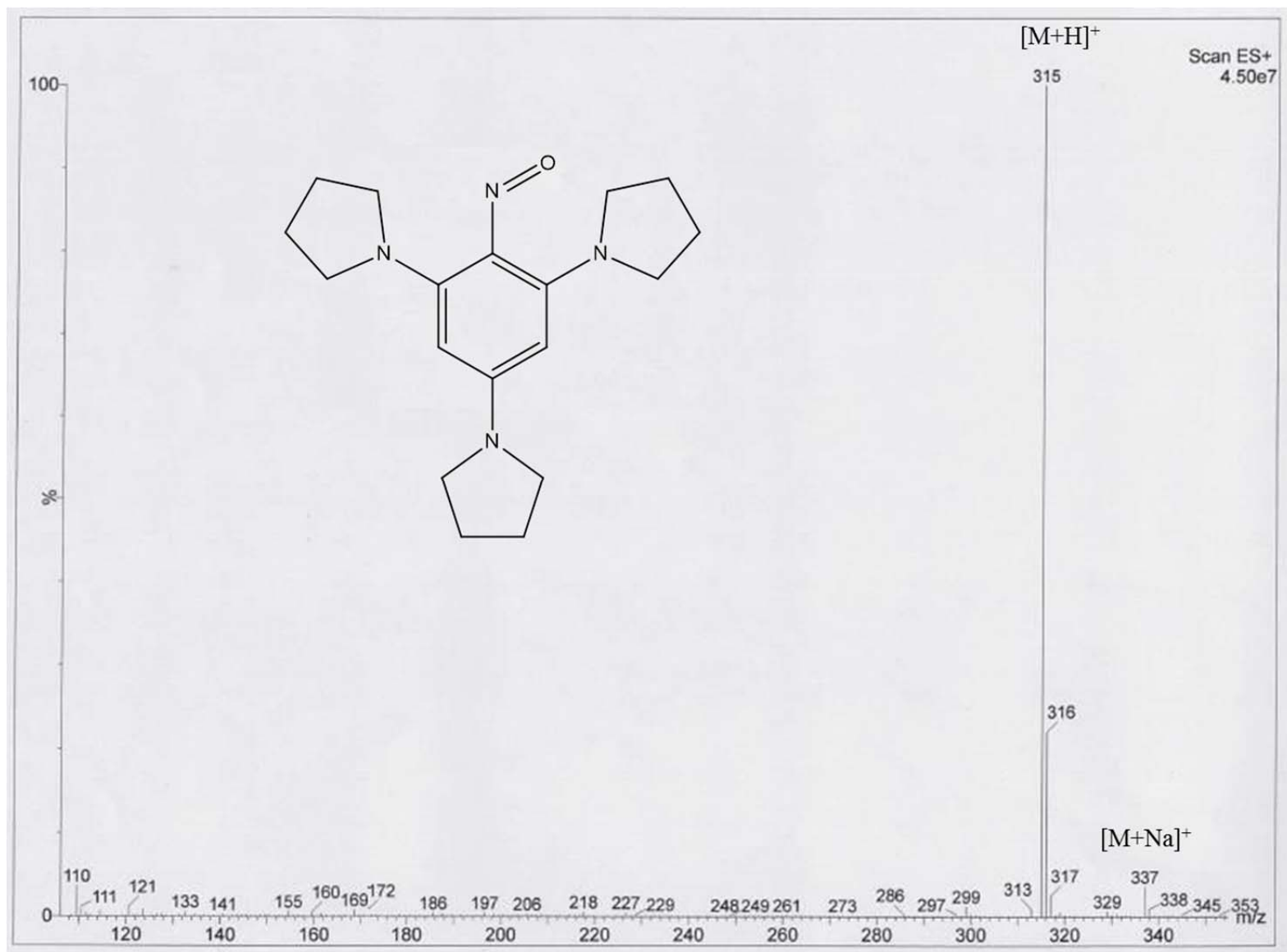


Figure SI-47: ESI-MS (ES<sup>+</sup>) spectrum of compound 7c.



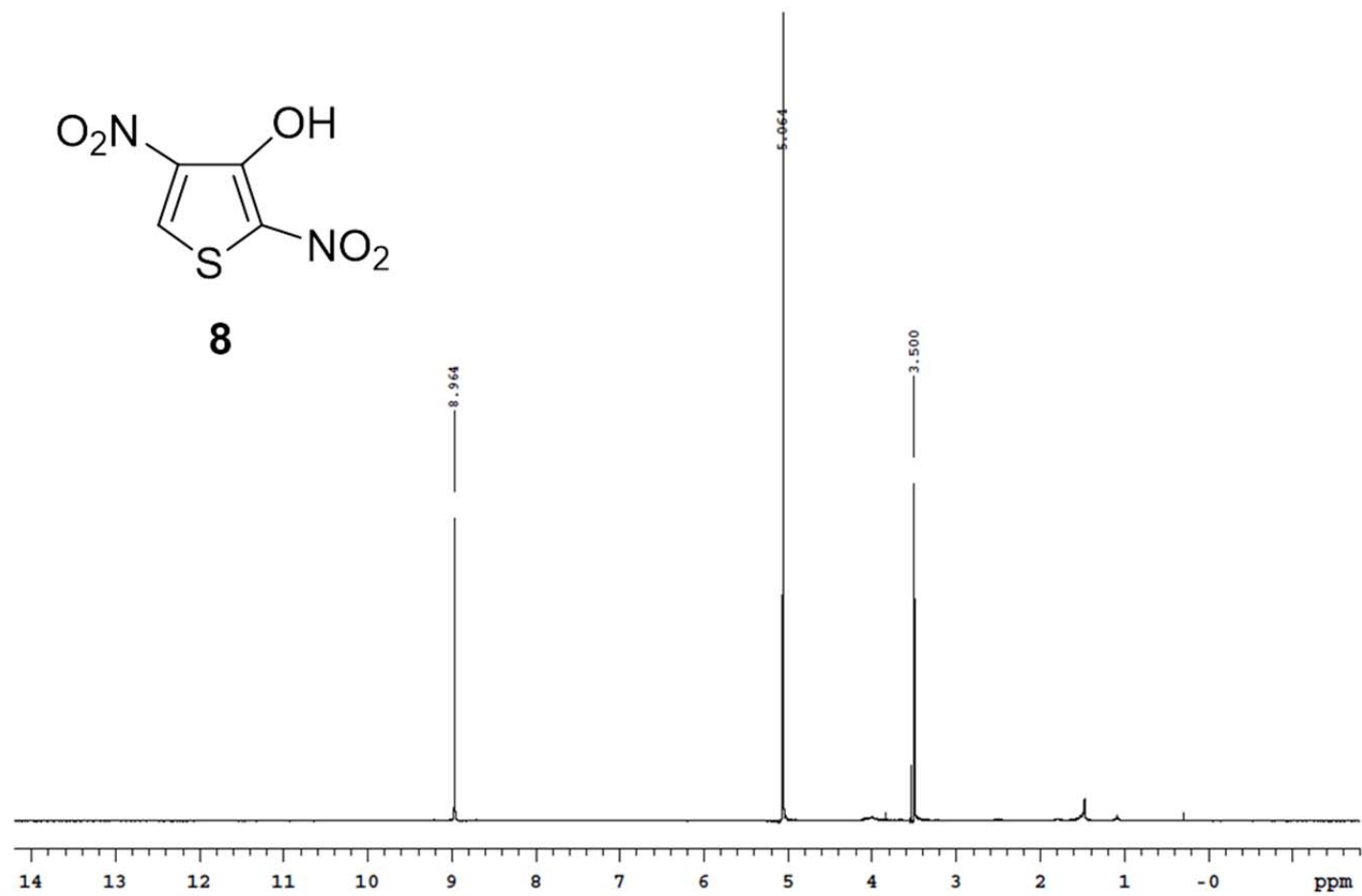


Figure SI-48: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, 25 °C) of compound **8**.

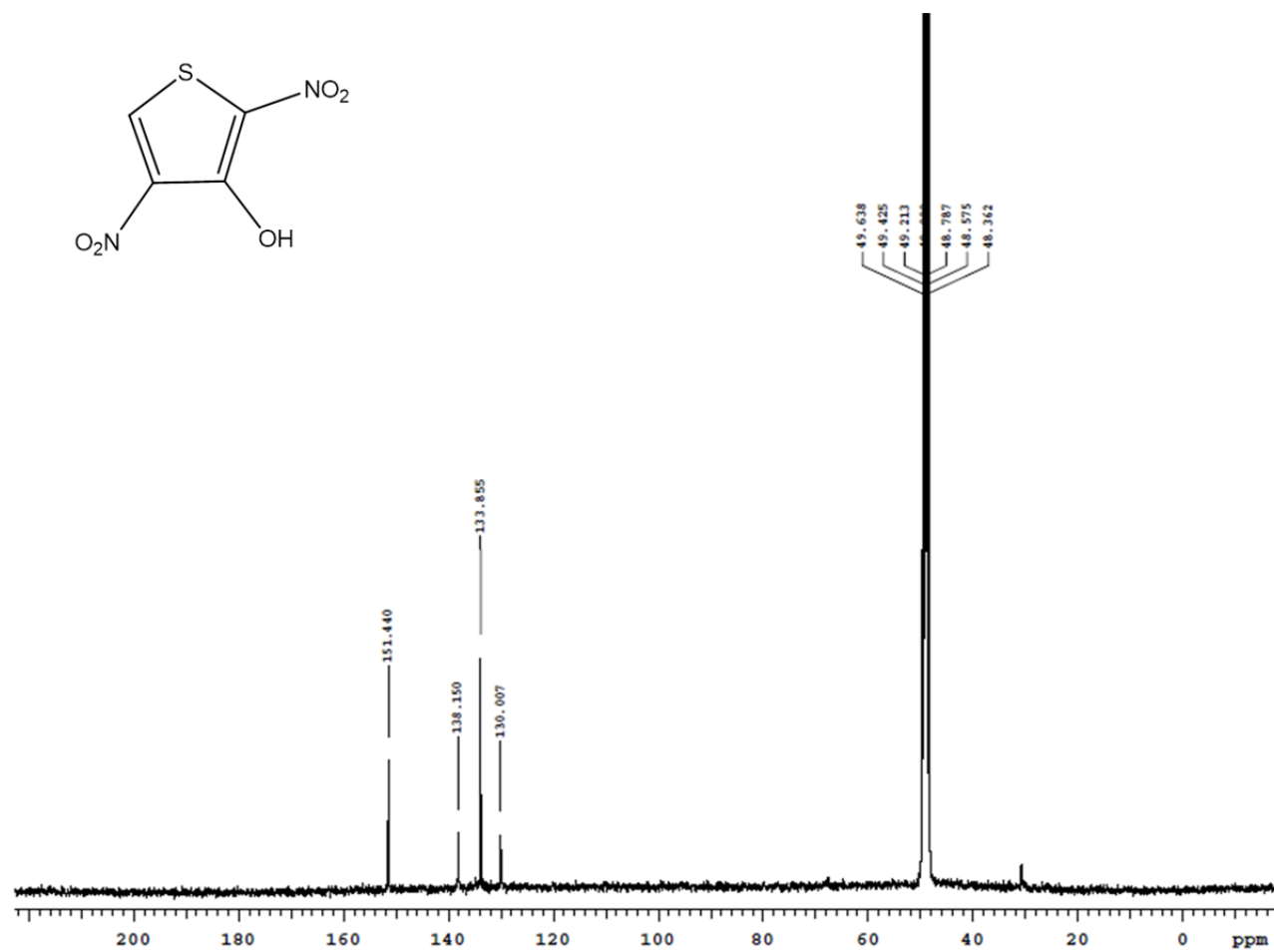


Figure SI-49:  $^{13}\text{C}$  NMR (100.56 MHz,  $\text{CD}_3\text{OD}$ , 25 °C) of compound **8**.



Figure SI-50: ESI-MS (ES<sup>-</sup>) spectrum of compound 8.

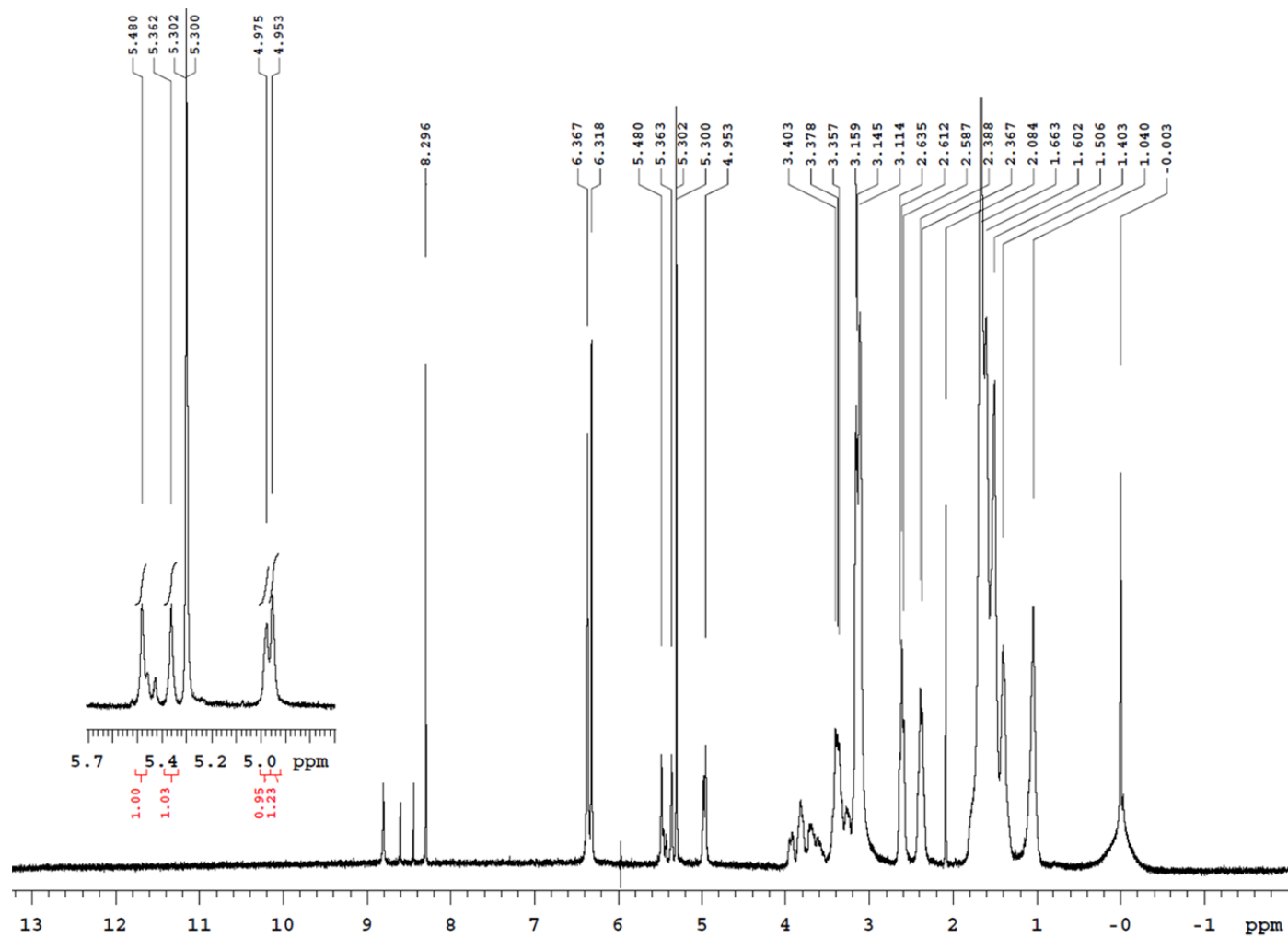


Figure SI-51:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-70^\circ\text{C}$ ) spectrum of the reaction mixture from **2** and **3a**

with expanded view of diagnostic signals belonging to **WMa** (solvent peak at 5.3 ppm).

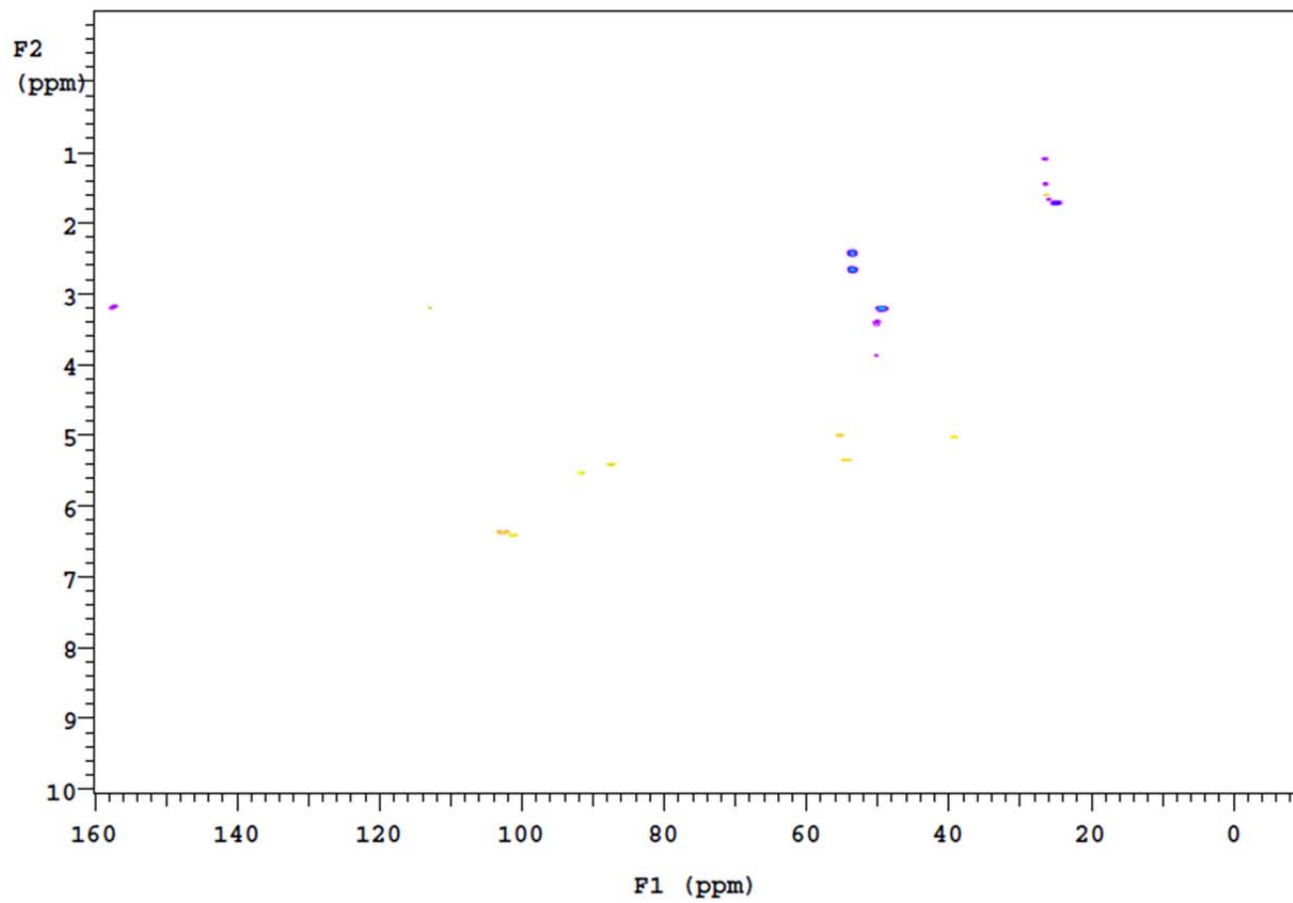


Figure SI-52: g-HSQC spectrum ( $\text{CD}_2\text{Cl}_2$ ,  $-70^\circ\text{C}$ ) of the reaction mixture from **2** and **3a**.

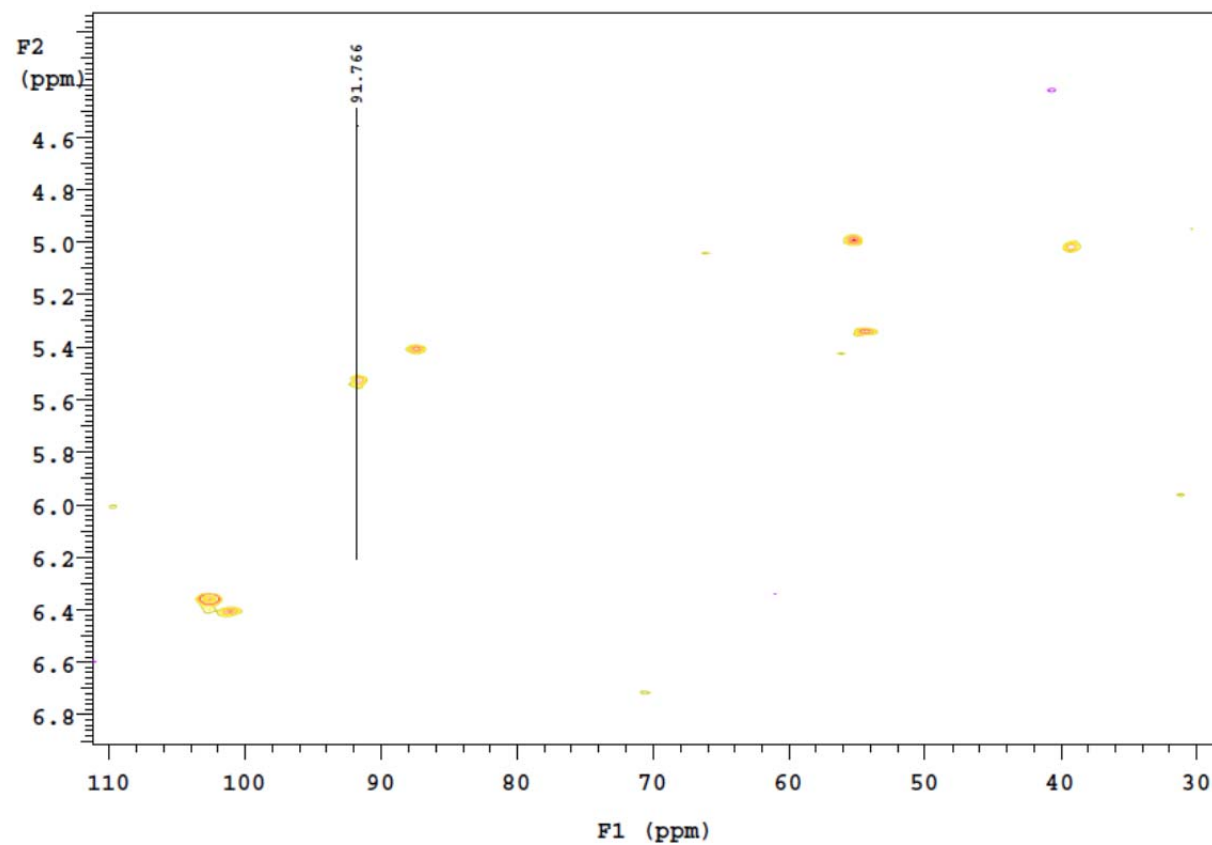


Figure SI-53: g-HSQC spectrum ( $\text{CD}_2\text{Cl}_2$ ,  $-70$  °C) of the reaction mixture from **2** and **3a** with expanded view of diagnostic signals belonging to **WMa**.

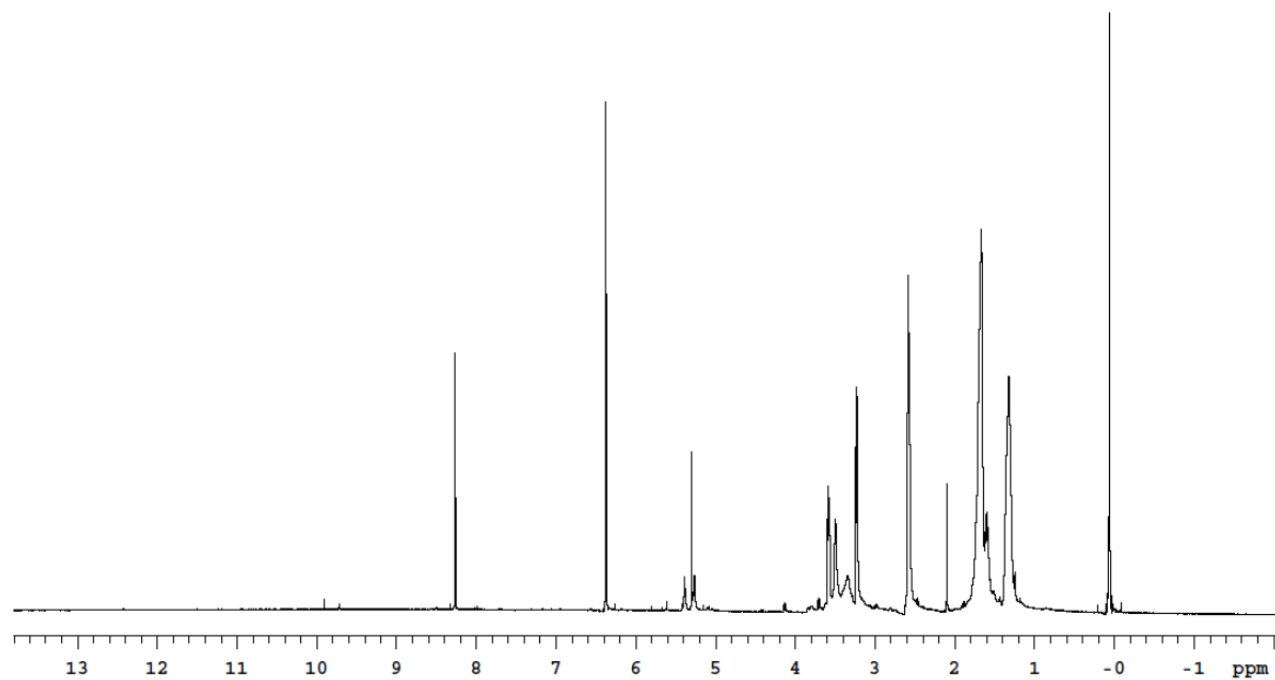


Figure SI-54:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ ) of the crude reaction mixture from **2** and **3a** after 1 day at 25  $^\circ\text{C}$ .

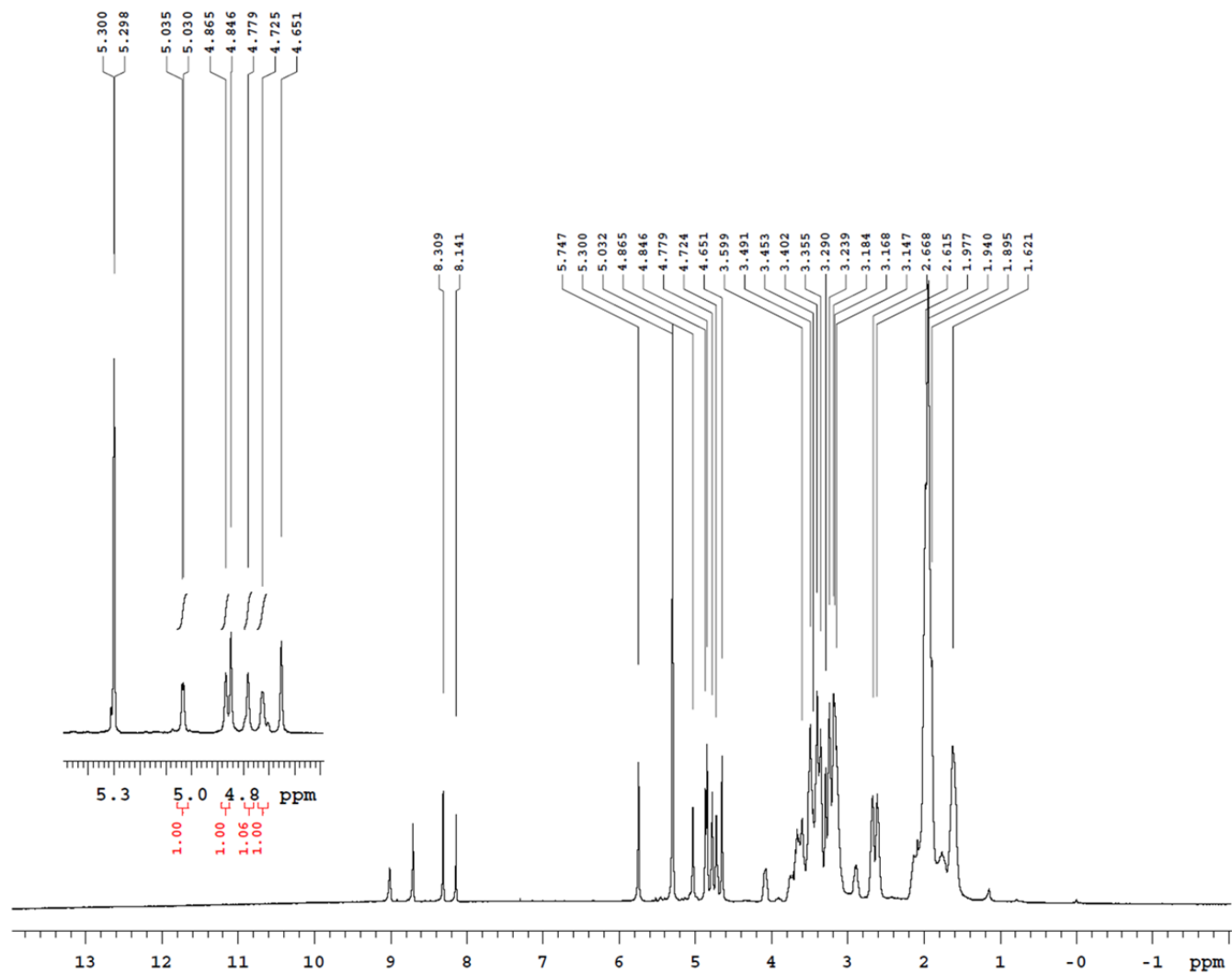


Figure SI-55:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-70^\circ\text{C}$ ) spectrum of the reaction mixture from **2** and **3c** with expanded view of diagnostic signals belonging to **WMc** (solvent peak at 5.3 ppm).



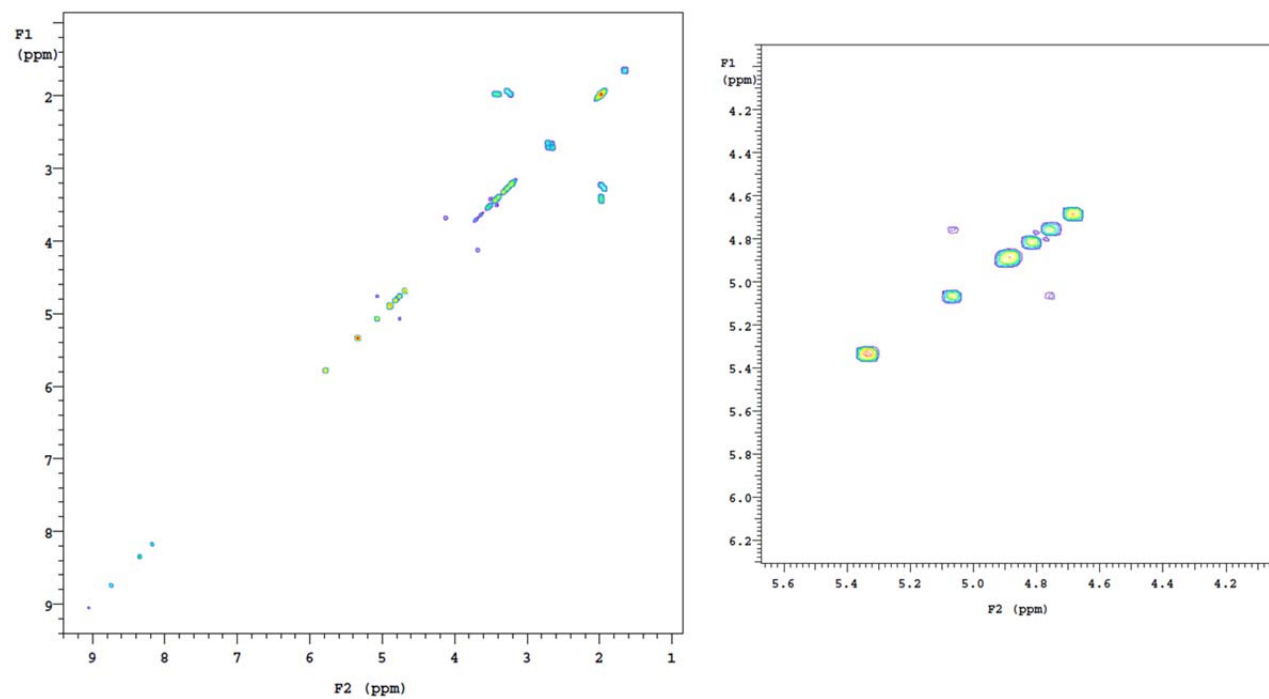


Figure SI-56: g-COSY spectra ( $\text{CD}_2\text{Cl}_2$ ,  $-70\text{ }^\circ\text{C}$ ) of the reaction mixture from **2** and **3c**. Left: full; right: expanded view.

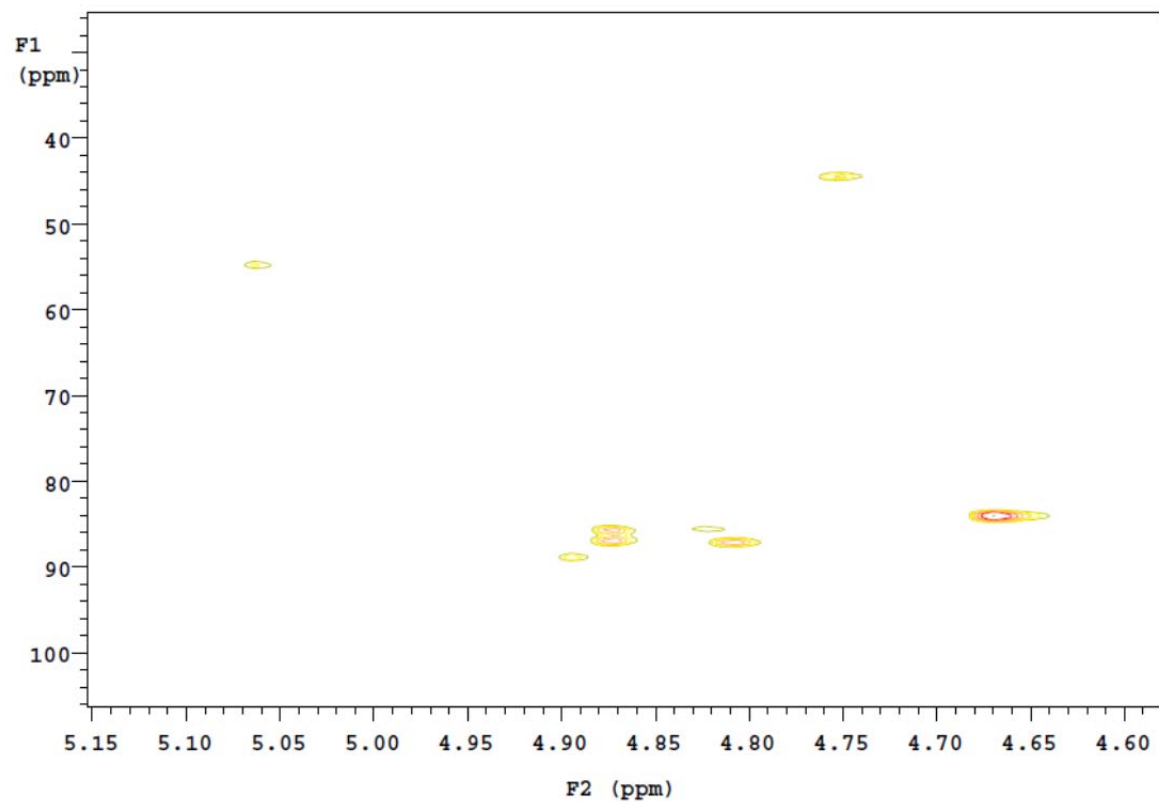


Figure SI-57: g-HSQC spectrum ( $\text{CD}_2\text{Cl}_2$ ,  $-70^\circ\text{C}$ , expanded view) of the reaction mixture from **2** and **3c**.

#### Reference

1. Fulmer, G. R.; Miller, A. J. M.; Sherden, Nathaniel H.; Gottlieb, Hugo E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I.

*Organometallics* **2010**, *29*, 2176–2179.