

**Photochemical Cleavage with Release of Carboxylic Acids and Phenol from Pyrrolidino-Substituted 1,4-Benzoquinones Using Visible Light.**

**Supplementary Information**

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**2-Hydroxy-5-methoxy-3,6-dimethylbenzaldehyde (11).** The procedure was similar to one reported in the literature.<sup>16</sup> To a mixture of 5.0 g (32.8 mmol) of 2,5-dimethyl-4-methoxyphenol in 1L CH<sub>3</sub>CN (distilled over CaH<sub>2</sub>) containing 13 mL (93.3 mmol) triethylamine and 9.8 g (103 mmol) anhydrous MgCl<sub>2</sub> was added 3.5 g (117 mmol) of dry paraformaldehyde in portions. The mixture was refluxed 8 h, cooled, 5% aqueous HCl was added, and the mixture was extracted with ether. The extracts were dried over MgSO<sub>4</sub>, concentrated in vacuo, and the residue purified by MPLC, eluting with 11% EtOAc in hexane. This gave 3.67 g (62% yield) of yellow crystals, mp 94.5-95.5 °C. The spectral data were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.20 (s, 3 H), 2.42 (s, 3 H), 3.76 (s, 3 H), 6.98 (s, 1 H), 10.29 (s, 1 H), 11.73 (s, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 9.8, 15.6, 57.3, 118.1, 123.8, 124.5, 126.9, 149.4, 155.5, 195.9.

**2-Hydroxy-5-methoxy-3,6-dimethylbenzenemethanol (12).** The procedure was similar to one reported in the literature.<sup>17</sup> To a solution of 2.0 g (11 mmol) of benzaldehyde **11** in 20 mL of glacial acetic acid was added 1.7 g (44 mmol) of solid NaBH<sub>4</sub> in portions with cooling to 16-21°C. After 2 h, 10 ml of water was added and the mixture was neutralized with aq NaHCO<sub>3</sub>. The mixture was extracted with ethyl acetate, the extracts were dried over MgSO<sub>4</sub>, and concentrated in vacuo. The solid residue was crystallized from 10% ethyl acetate in hexane to give 1.06 g (52 % yield) of colorless crystals, mp 75.5-77.0 °C. The spectral data were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.02 (s, 3 H), 2.18(s, 3 H), 3.24(s, broad, 1 H), 3.73(s, 3 H), 4.79(s, 2 H), 6.58(s, 1 H), 7.57(s, broad,1 H); <sup>13</sup>C NMR(CDCl<sub>3</sub>): δ 11.5, 16.8, 56.7, 60.8, 113.5, 121.7, 122.5, 123.8, 148.2, 150.6. Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>: C, 65.92; H, 7.74. Found: C, 65.81 H, 7.57.

**2-Hydroxymethyl-3,6-dimethyl-2,5-cyclohexadiene-1,4-dione (13).** A procedure similar to one in the literature was followed.<sup>18</sup> To 2.0 g (1.0 mmol) of benzylic alcohol **12** in 10 mL of CH<sub>3</sub>CN was added, dropwise with, stirring, a solution of 18.0 g (33.0 mmol) Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> in 100 mL of deionized water with cooling in an ice bath. After stirring overnight at room temperature, the mixture was extracted with CHCl<sub>3</sub>, washed with saturated NaCl, dried over MgSO<sub>4</sub>, and concentrated in vacuo. MPLC of the residue, eluting with 50% EtOAc in hexane, gave crystalline product, which was crystallized from 10% EtOAc in hexane to obtain 1.63 g (63%) of yellow crystals, mp 52.0-53.5 °C. The spectral data were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.02(d, J = 1.5Hz, 3 H), 2.06(s, 3 H), 4.53(s, 2 H), 6.59(q, J = 1.5Hz, 1 H); <sup>13</sup>C NMR(CDCl<sub>3</sub>): δ 11.8, 15.9, 57.5, 133.6, 140.7, 142.1, 145.5, 187.7, 188.6. Anal. Calcd for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>: C, 65.05; H, 6.07. Found: C, 64.72 H, 6.11.

**2-Hydroxymethyl-3,6-dimethyl-5-pyrrolidino-2,5-cyclohexadiene-1,4-dione (14).** A procedure similar to one reported in the literature was followed.<sup>1b</sup> To 1.5 g (9.0 mmol) benzoquinone **13** in 100mL of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise with stirring a solution of 1.5 mL (18.0 mmol) of pyrrolidine in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> with cooling in an ice bath, while keeping the reaction in the dark. After 3 h at room temperature, the volatiles were removed in vacuo. MPLC of the residue, eluting with 50% EtOAc in hexane, gave 1.42 g (67 %) of the purple product, as a viscous oil. The spectral data were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.84 (m, 4 H), 1.94 (s, 3 H), 1.98(s, 3 H), 3.40(s, broad, 1 H), 3.63(m, 4 H), 4.47(s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 11.4, 12.9, 26.0, 53.4, 59.0, 111.3, 136.7, 141.0, 151.0, 186.9, 187.8.

**Preparation of Carboxylate Derivatives 3 (LG = PhCO<sub>2</sub><sup>-</sup>, PhCH<sub>2</sub>CO<sub>2</sub><sup>-</sup>, 4-CNC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>) of 2-Hydroxymethyl-3,6-dimethyl-5-pyrrolidino-2,5-cyclohexadiene-1,4-**

**dione.** To a solution of 40 mmol of 2-pyrrolidino-1,4-benzoquinone **14** in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> in an ice bath was added dropwise with stirring a solution of 80 mmol of acid chloride in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred at room temperature for 10-30 h, depending on the ester to be synthesized. In each case, the mixture was washed with 5% aq HCL, satd NaCl, dried over MgSO<sub>4</sub>, and concentrated in vacuo. MPLC of the residue, eluting with 30% EtOAc in hexane gave each ester product as purple crystals, generally in 70-80 % yields.

The spectral data for **3** (LG = PhCO<sub>2</sub><sup>-</sup>) were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.85 (m, 4 H), 2.03 (s, 3 H), 2.08 (s, 3 H), 3.63(m, 3 H), 5.26(s, 4 H), 7.38(t, J = 7.2 Hz, 2 H), 7.51(t, J = 7.2 Hz, 1 H), 7.98(d, J = 7.2 Hz, 2 H); <sup>13</sup>C NMR(CDCl<sub>3</sub>): δ 12.8, 13.5, 26.1, 53.3, 58.5, 112.1, 128.4, 129.8, 129.9, 133.1, 137.1, 141.1, 150.3, 166.3, 183.9, 187.4; Anal. Calcd for C<sub>20</sub>H<sub>21</sub>O<sub>4</sub>N: C, 70.78; H, 6.24; N, 4.13; UV-Vis (30% aqueous CH<sub>3</sub>CN) λ<sub>max</sub> 542 nm (ε 3150 M<sup>-1</sup> cm<sup>-1</sup>). Found: C, 70.88; H, 6.35; N, 4.12.

The spectral data for **3** (LG = PhCH<sub>2</sub>CO<sub>2</sub><sup>-</sup>) were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.85(m, 4 H), 1.92(s, 3 H), 2.02 (s, 3 H), 3.60(s, 2 H), 5.03(s, 2 H), 7.25(m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.3, 13.4, 26.1, 41.3, 53.3, 58.5, 112.2, 127.2, 128.6, 129.4, 133.89, 136.90, 141.1, 171.3, 183.9, 187.3; UV-Vis (30% aqueous CH<sub>3</sub>CN) λ<sub>max</sub> 542 nm (ε 2850 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>O<sub>4</sub>N: C, 71.37; H, 6.56; N, 3.96. Found: C, 71.17; H, 6.51; N, 3.84.

The spectral data for **3** (LG = 4-CNC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>) were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.86(m, 4 H), 2.03(s, 3 H), 2.08(s, 3 H), 3.64(m, 4 H), 5.28(s, 2 H), 7.07(d, J = 8.7 Hz, 2 H), 8.10(d, J = 8.6 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.5, 13.4, 26.1, 53.4, 59.2, 112.0, 116.5, 118.1, 130.3, 132.3, 133.8, 136.5, 141.4, 150.4, 164.7, 183.8, 187.2; UV-Vis (30% aqueous CH<sub>3</sub>CN) λ<sub>max</sub> 542 nm (ε 2990 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: C, 69.22; H, 5.53; N, 7.69. Found: C, 68.97; H, 5.58; N, 7.59.

**2,5-Dimethoxy-3,6-dimethylbenzenemethanol (15).** The procedure was similar to one reported in the literature.<sup>19</sup> To a stirred mixture of 2.0 g (11 mmol) of phenolic aldehyde **11** and 7.67 g (56 mmol) K<sub>2</sub>CO<sub>3</sub> in dry DMT (40 mL) was added dropwise 3.6 mL (56 mmol) of MeI over 5 min. Stirring was continued overnight and the solids were then removed by filtration. The filtrate was poured into brine (20 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40mL). The combined organic extracts were washed with water (2 x 10mL) and brine (10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo. MPLC of the residue, eluting with 6.2% EtOAc in hexane gave a crystalline solid, which was crystallized from 10% EtOAc in hexane to obtain 2.1 g (96% yield) of light yellow crystalline aldehyde, mp 87.0-88.5 °C.

To a solution of 1.5 g (7.72 mmol) of the above dimethoxybenzaldehyde in 20 mL of EtOH was added 0.30 g (7.9 mmol) of solid NaBH<sub>4</sub> in portions at room temperature. After 2 h, 10mL of water was added and most of the solvent was removed in vacuo. The mixture was neutralized with aqueous NaHCO<sub>3</sub> until the pH = 7.0, the mixture was extracted with EtOAc, and the combined organics were dried over MgSO<sub>4</sub> and concentrated in vacuo. Crystallization of the solid residue with 10% EtOAc in hexane gave 1.4 g (90 % yield based on aldehyde) of colorless crystalline alcohol **15**, mp 81.0-82.0°C. The spectral data for **14** were as follows: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.209 (s, 3 H), 2.26 (s, 3 H), 3.72 (s, 3 H), 3.77(s, 3 H), 4.71(s, 2 H), 6.61(s, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 11.4, 16.3, 56.0, 57.8, 61.7, 112.9, 124.4, 128.4, 132.8, 150.9, 154.0.

**1-Phenoxymethyl-2,5-dimethoxy-3,6-dimethylbenzene (16).** In a 100 mL Schlenk flask 2.3 g (12 mmol) of benzylic alcohol **15** was dissolved in 50 mL of CHCl<sub>3</sub> under argon. The solution was cooled in an ice bath and a solution of 1.03 mL (14.1 mmol) of thionyl chloride in 25 mL CHCl<sub>3</sub> was slowly added over 30 min. The reaction mixture was stirred at room temperature for 10 h. To the reaction mixture was added 5% NaHCO<sub>3</sub>, and the phases were

separated. The aqueous phase was extracted with EtOAc (3x50mL), and the combined organics were dried over anhydrous  $\text{MgSO}_4$  and concentrated in vacuo. MPLC of the solid residue, eluting with 30% EtOAc in hexane, gave crystalline product, which was crystallized from 10% EtOAc in hexane to 2.4 g (98% yield) of colorless crystalline benzylic chloride product, mp 71.5-73.0 °C.

To 1.3 g (10 mmol) of potassium phenoxide dissolved in 25 mL of DME was added 1.8 g (8.4 mmol) of the above benzylic chloride in 10 mL of DME dropwise at 35 °C, and the mixture was heated at 40-50 °C for 12-24 h. The reaction mixture was poured into 50 mL of distilled water followed by extraction with EtOAc (3x30 mL). The combined organic extracts were washed with 1 N KOH and distilled water and dried over  $\text{MgSO}_4$ . After removing the solvent in vacuo, crystallization from ca. 50% aq MeOH gave 1.8 g (77% yield) of colorless crystalline **16**, mp 63.5-64.5°C. . The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.23(s, 3 H), 2.31 (s, 3 H), 3.71 (s, 3 H), 3.81(s, 3 H), 5.08(s, 2 H), 6.72(s, 1 H), 6.98(t, J = 7.5 Hz, 1 H), 7.06(d, J = 7.5 Hz, 2 H), 7.33 (t, J = 7.5 Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.8, 16.5, 56.1, 62.3, 62.6, 113.9, 114.9, 121.1, 126.1, 128.7, 129.0, 129.7, 151.5, 154.1, 159.3.

**2,5-Dimethyl-3-phenoxyethyl-2,5-cyclohexadiene-1,4-dione (17).**<sup>18</sup> To a solution of 2.3 g (8.5 mmol) of dimethoxy compound **16** in  $\text{CH}_3\text{CN}$  (20 mL) was added dropwise a solution of 13.9 g (25.5 mmol) of CAN in 20 mL of water while cooling in an ice bath. The reaction was stirred overnight at room temperature. Then  $\text{CH}_3\text{CN}$  was removed in vacuo and the mixture was extracted with EtOAc. The extracts were washed with saturated NaCl, dried over  $\text{MgSO}_4$ , and concentrated in vacuo. MPLC of the residue, eluting with 30% EtOAc in hexane, gave a crystalline product, which was crystallized from 10% EtOAc in hexane to obtain 1.3 g (64% yield) of yellow crystalline product **17**, mp 62.5-64.0 °C. The spectral data were as follows:

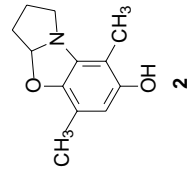
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.05(d,  $J = 1.8\text{Hz}$ , 3 H), 2.13 (s, 3H), 4.94 (s, 2H), 6.63(q,  $J=1.8\text{Hz}$ , 1H), 6.91(d,  $J = 7.5\text{Hz}$ , 2H), 6.95(t,  $J = 7.5\text{Hz}$ , 1H), 7.28(t,  $J = 7.5\text{Hz}$ , 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  12.5, 16.3, 60.5, 114.8, 121.5, 129.7, 133.5, 137.9, 145.7, 145.8, 158.5, 186.6, 187.7.

**2,5-Dimethyl-3-phenoxyethyl-6-pyrrolidino-2,5-cyclohexadiene-1,4-dione 3 (LG = PhO $^-$ ).**<sup>1b</sup> To a solution of 0.80 g (3.3 mmol) of 1,4-benzoquinone **17** in 50 mL of  $\text{CH}_2\text{Cl}_2$  was added, dropwise with stirring in an ice bath, a solution of 0.55 mL (6.6 mmol) of pyrrolidine in 20mL of  $\text{CH}_2\text{Cl}_2$  while bubbling  $\text{O}_2$  into the reaction mixture. Over the 4 h period of the reaction,  $\text{CH}_2\text{Cl}_2$  was added to replace solvent which had evaporated. The volatiles were then removed in vacuo. MPLC of the residue eluting with 10% EtOAc in hexane gave 31 mg (3% yield) of the 2-pyrrolidino-1,4-benzoquinone **3** (LG = PhO $^-$ ) as a viscous purple oil. The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  1.86(m, 4 H), 2.03 (s, 3 H), 2.04 (s, 3 H), 3.66(m, 4 H), 4.95(s, 2 H), 6.97(d,  $J = 7.2\text{Hz}$ , 1 H), 6.99(t,  $J = 7.2\text{Hz}$ , 2 H), 7.32(t,  $J = 7.2\text{Hz}$ , 2 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  12.4, 13.2, 26.4, 53.9, 62.0, 111.5, 115.6, 122.0, 130.6, 138.2, 142.4, 152.1, 159.8, 184.7, 188.7; UV-Vis  $\lambda_{\text{max}}$  542 nm ( $\epsilon$  1530  $\text{M}^{-1} \text{cm}^{-1}$ ).

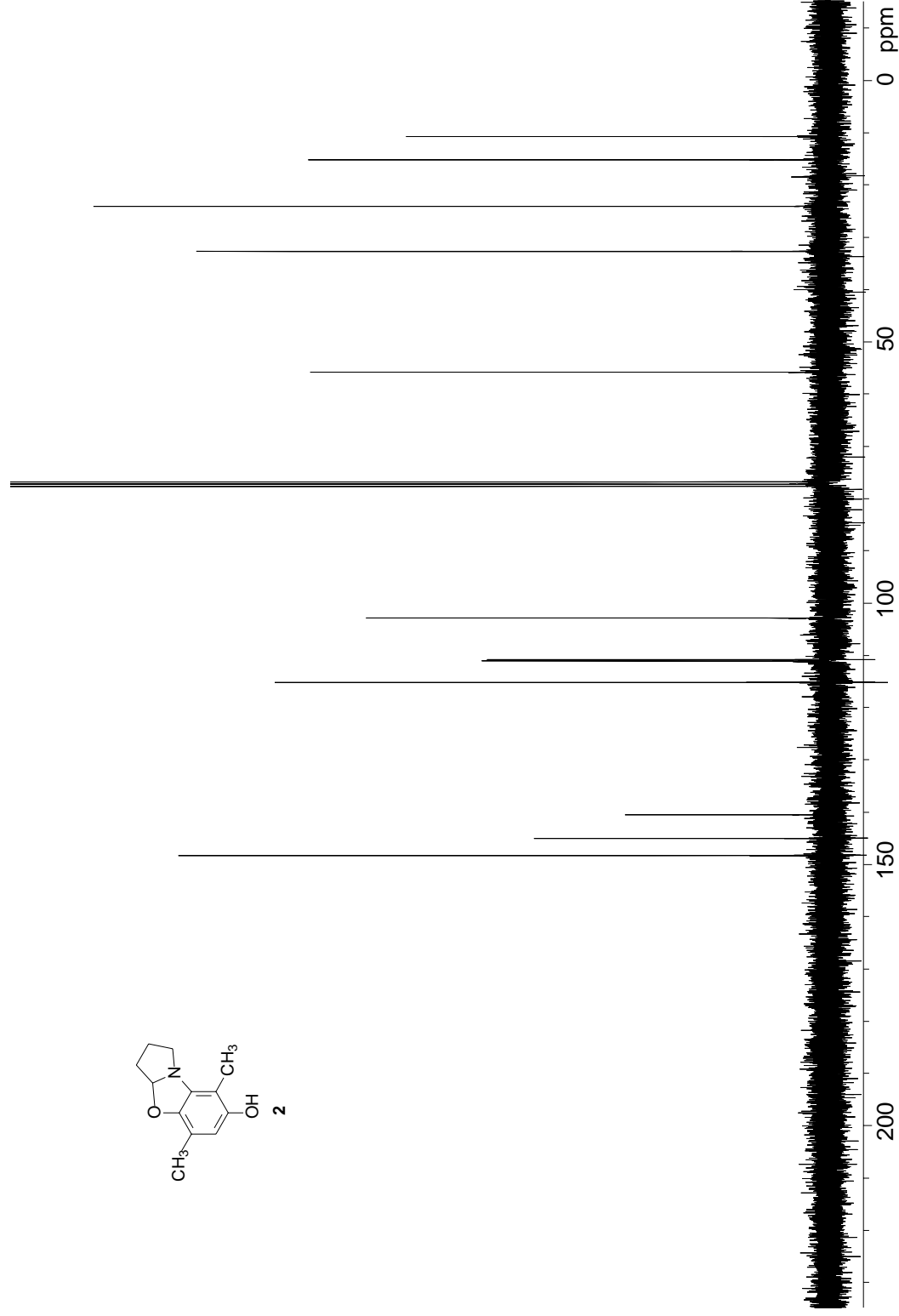
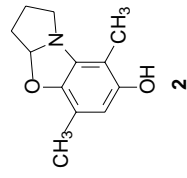
## Spectra

The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra are given for compounds **2**, **3** (LG = PhO $^-$ ), **4** (LG = PhO $^-$ ), **6** (LG = PhCO $_2^-$ ), and **8**.  $^1\text{H}$  NMR spectra are shown for **11-17**.

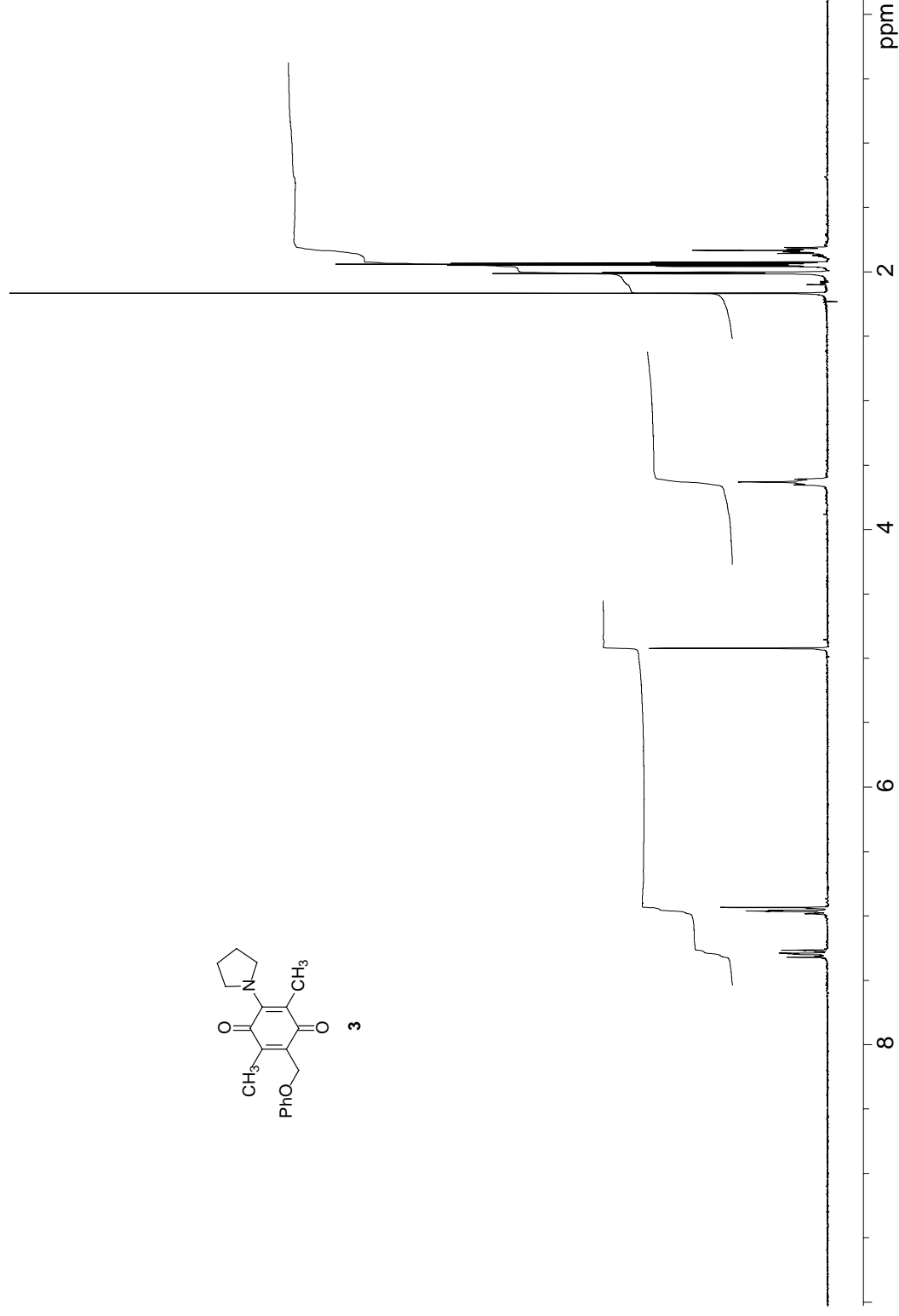
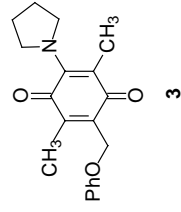




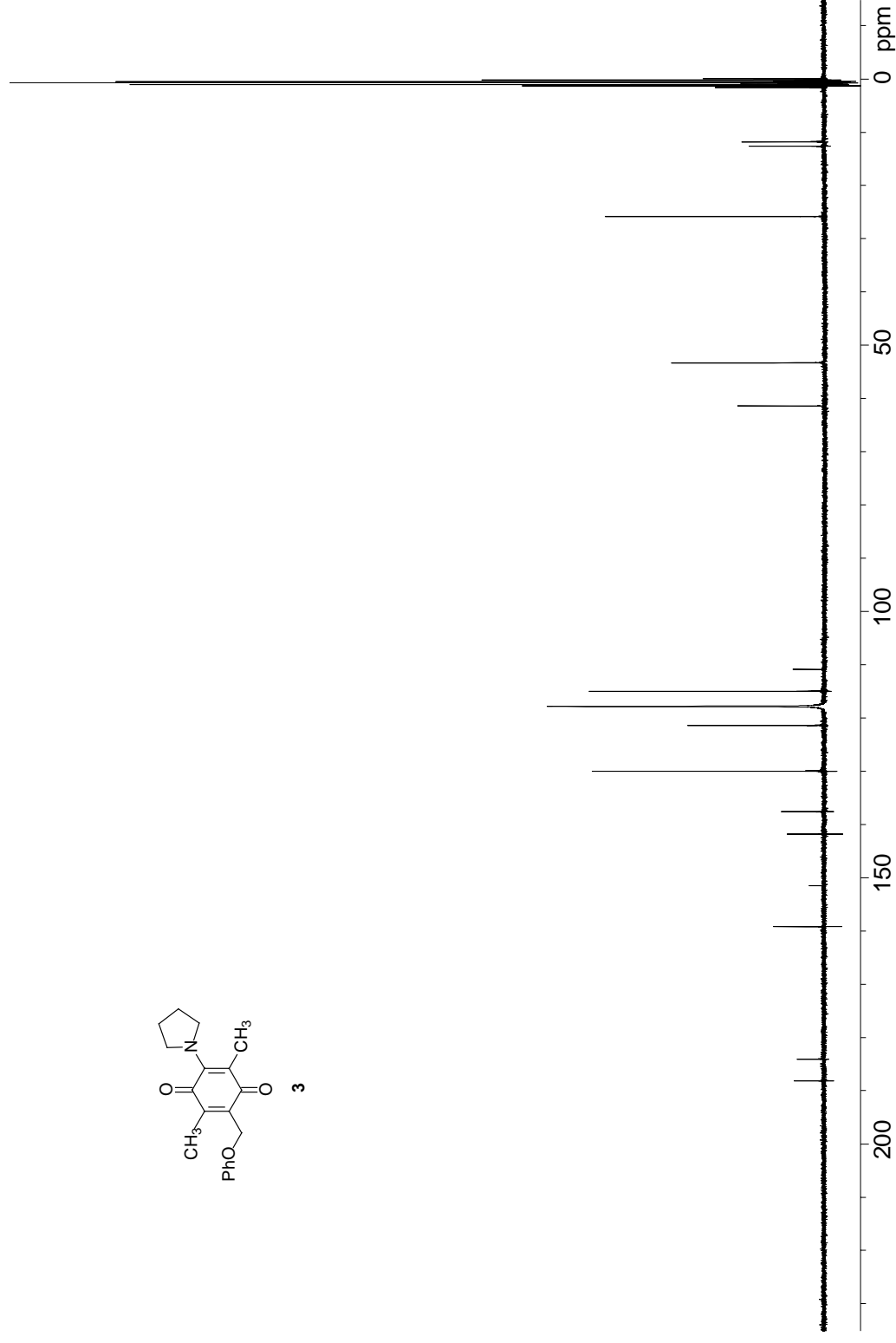
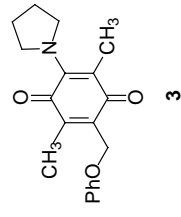
**Figure 3.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .



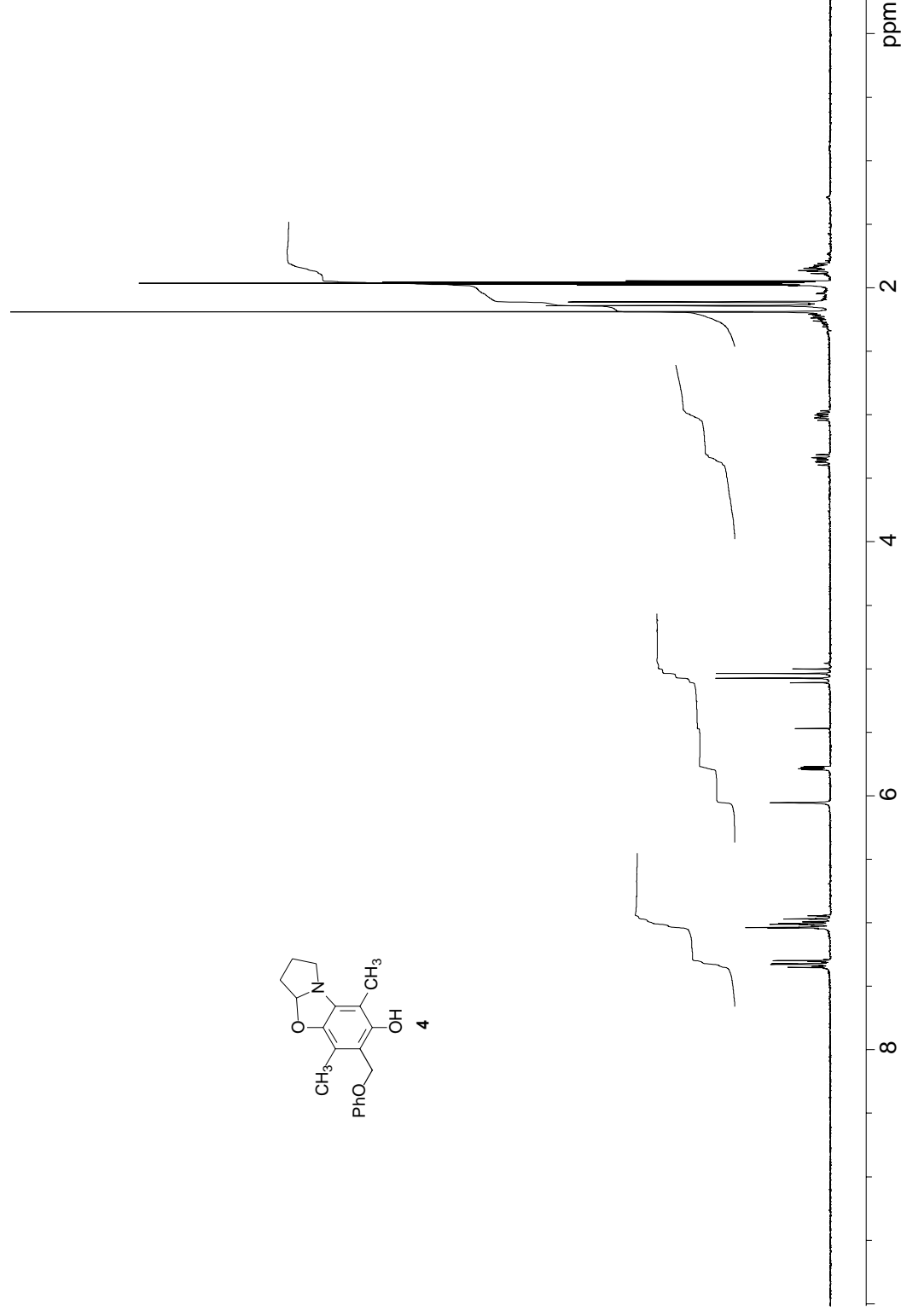
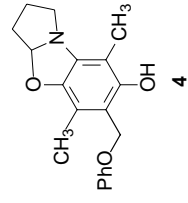
**Figure 4.**  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .



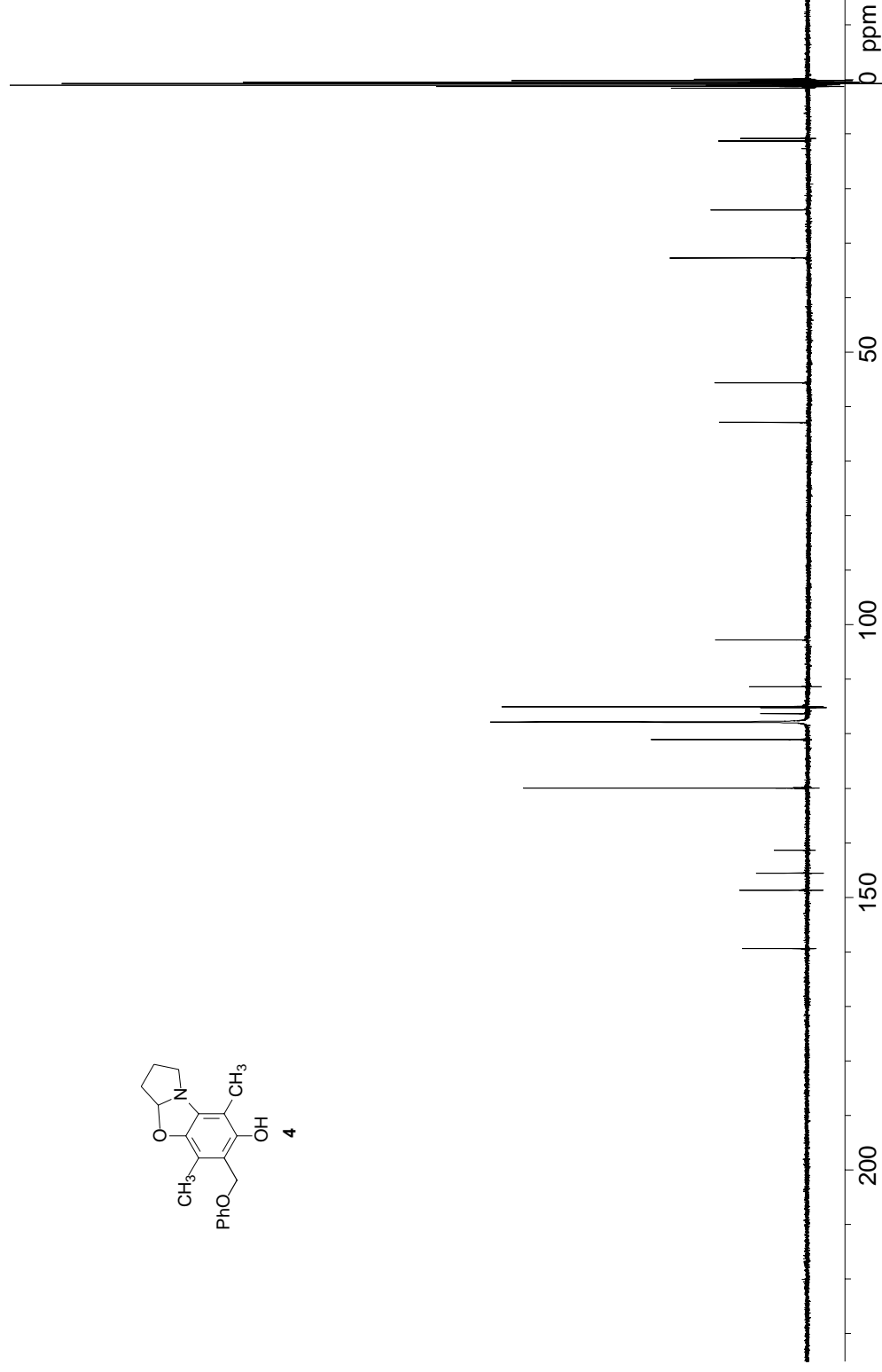
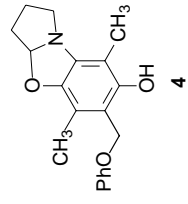
**Figure 5.**  $^1\text{H}$  NMR spectrum for 2-pyrrolidino-1,4-benzoquinone **3** ( $\text{LG} = \text{C}_6\text{H}_5\text{O}^-$ ) in  $\text{CD}_3\text{CN}$ .



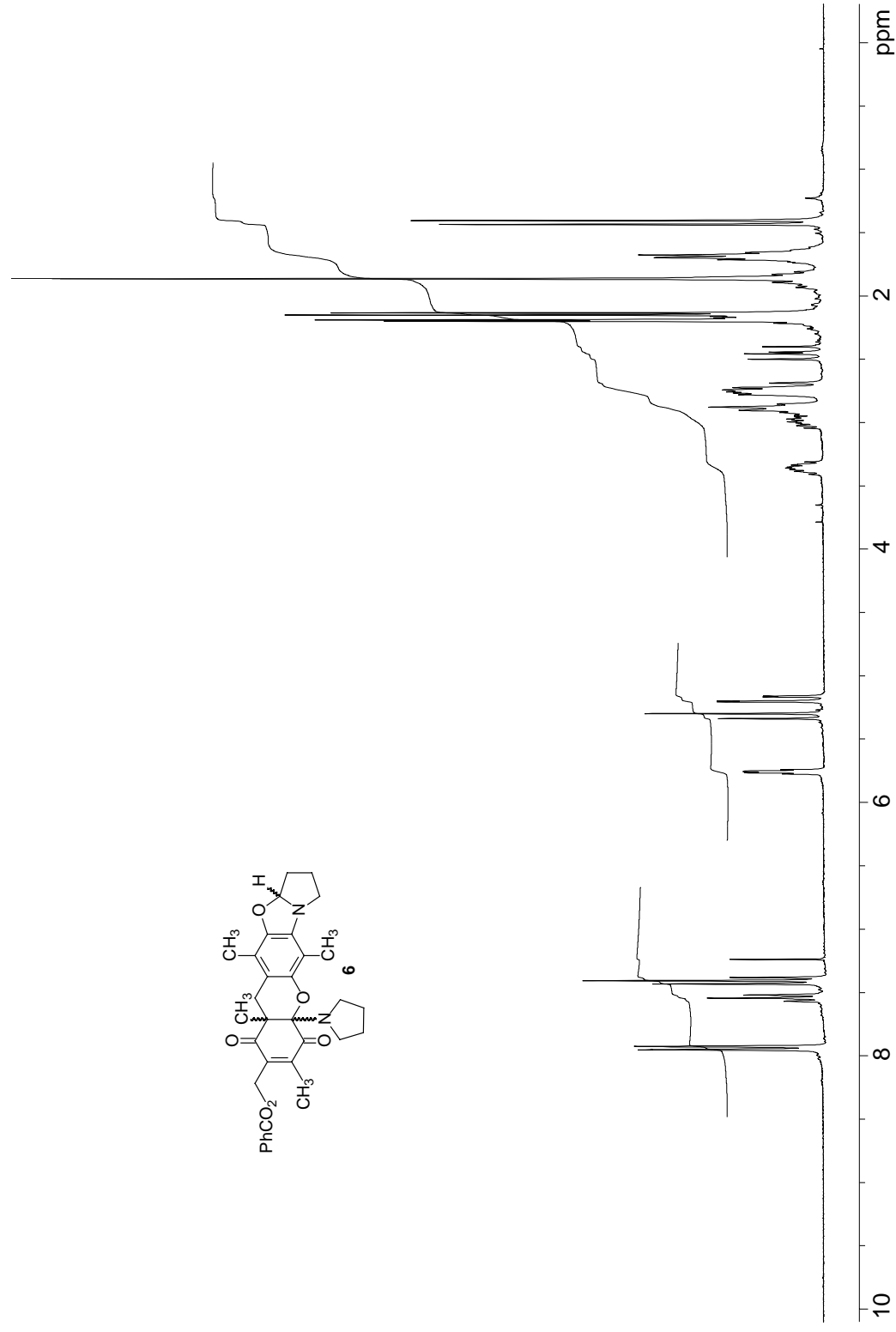
**Figure 6.** <sup>13</sup>C NMR spectrum of 2-pyrrolidino-1,4-benzoquinone **3** (LG = C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>) in CD<sub>3</sub>CN.



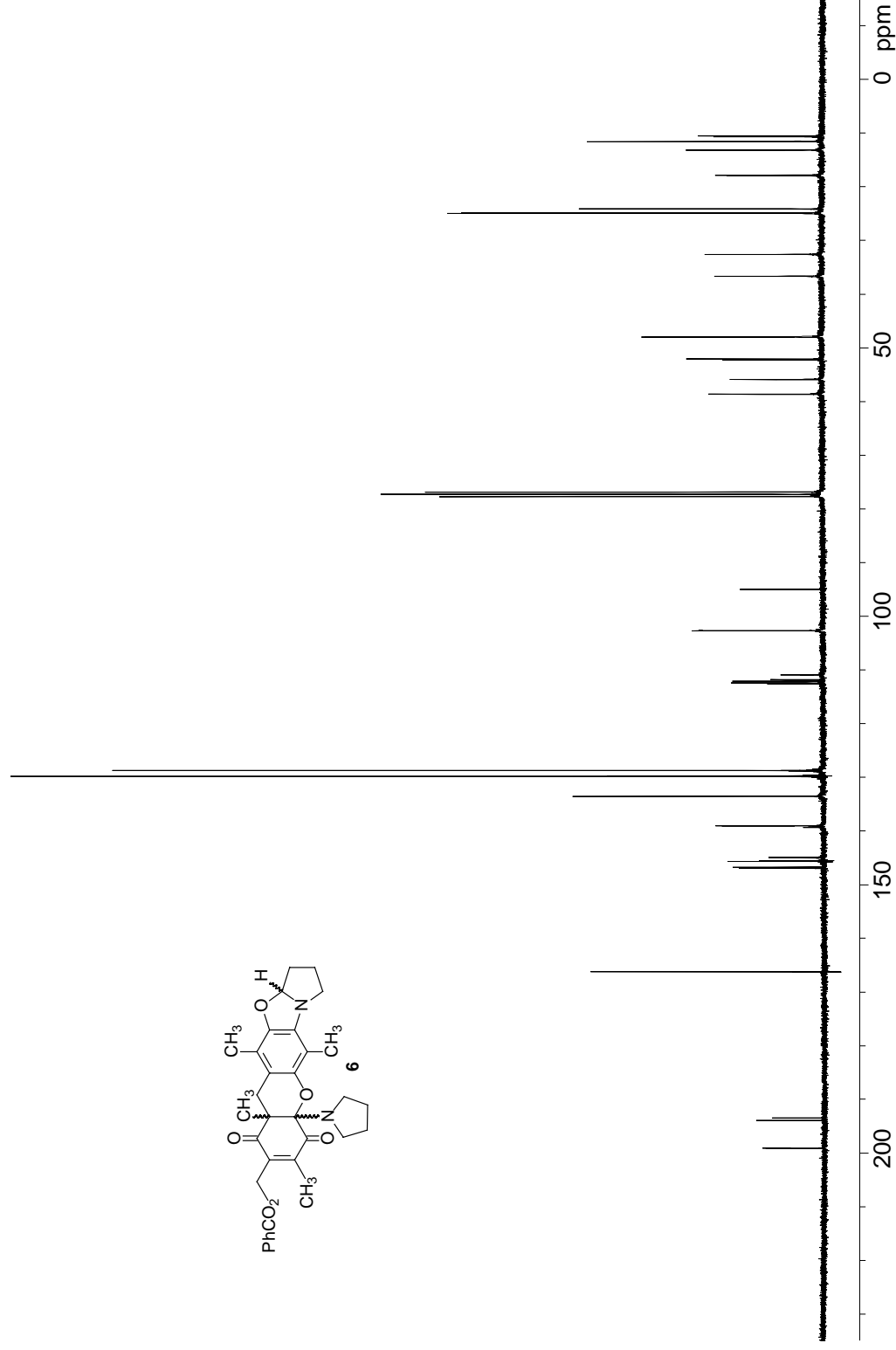
**Figure 7.**  $^1\text{H}$  NMR spectrum of **4** (LG =  $\text{C}_6\text{H}_5\text{O}^-$ ) in  $\text{CD}_3\text{CN}$  (the peak at 5.47  $\delta$  is an impurity).



**Figure 8.**  $^{13}\text{C}$  NMR spectrum of **4** (LG =  $\text{C}_6\text{H}_5\text{O}^-$ ) in  $\text{CD}_3\text{CN}$ .

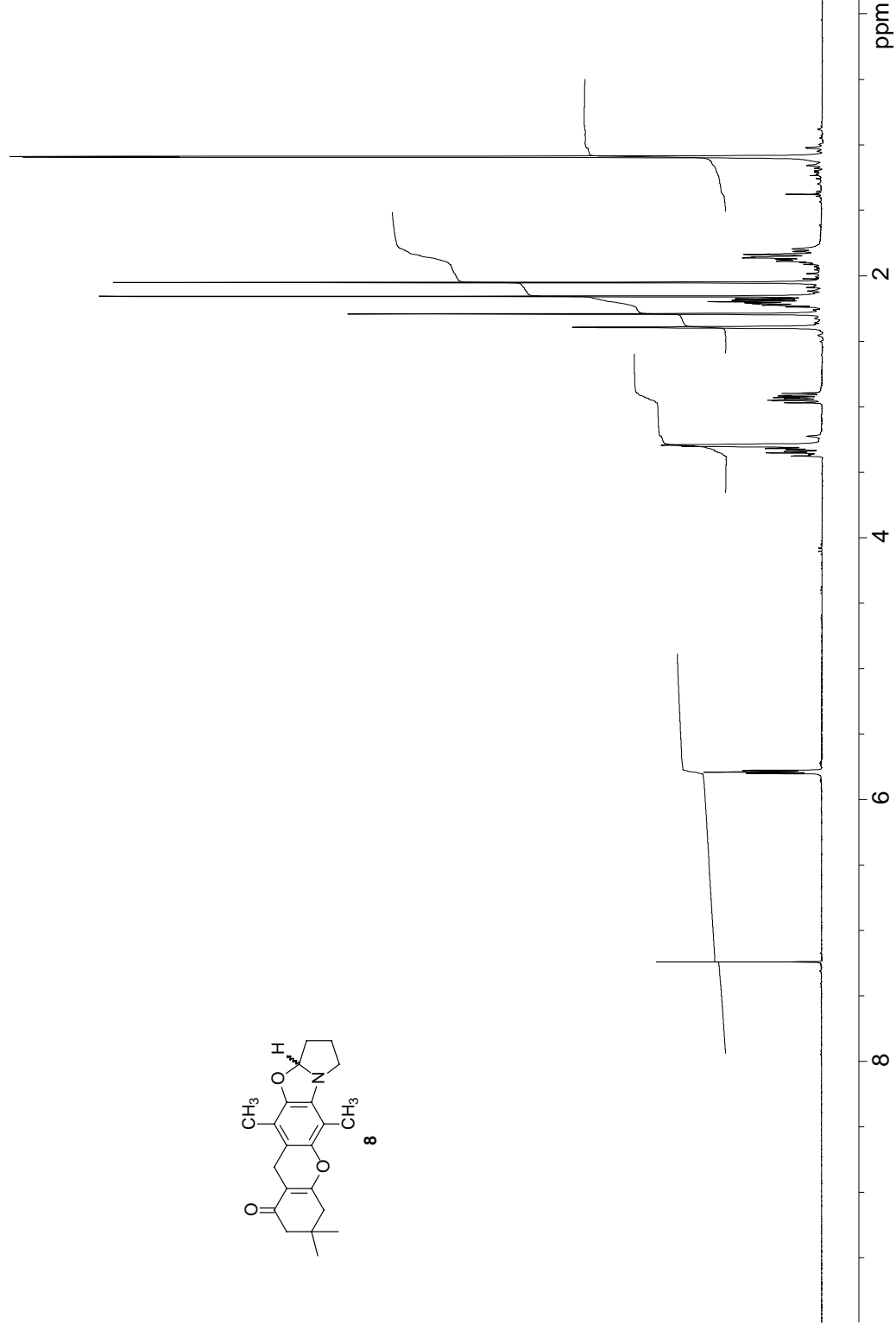
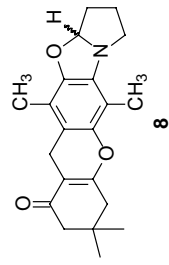


**Figure 9.** <sup>1</sup>H NMR spectrum of self-trapping product **6** (LG = PhCO<sub>2</sub><sup>-</sup>) in CDCl<sub>3</sub>.

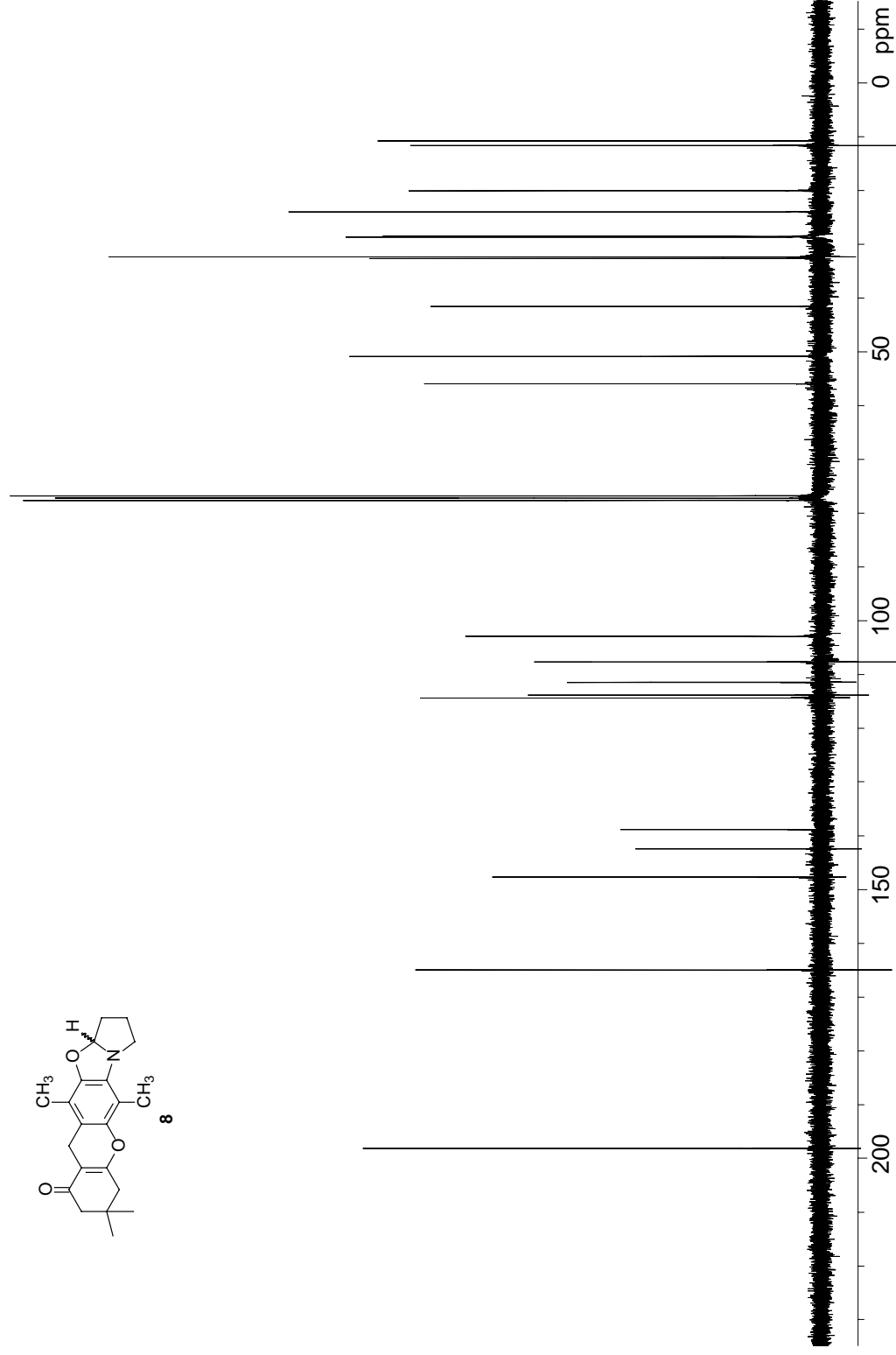


**Figure 10.**  $^{13}\text{C}$  NMR spectrum of self-trapping product **6** ( $\text{LG} = \text{PhCO}_2^-$ ) in  $\text{CDCl}_3$ .

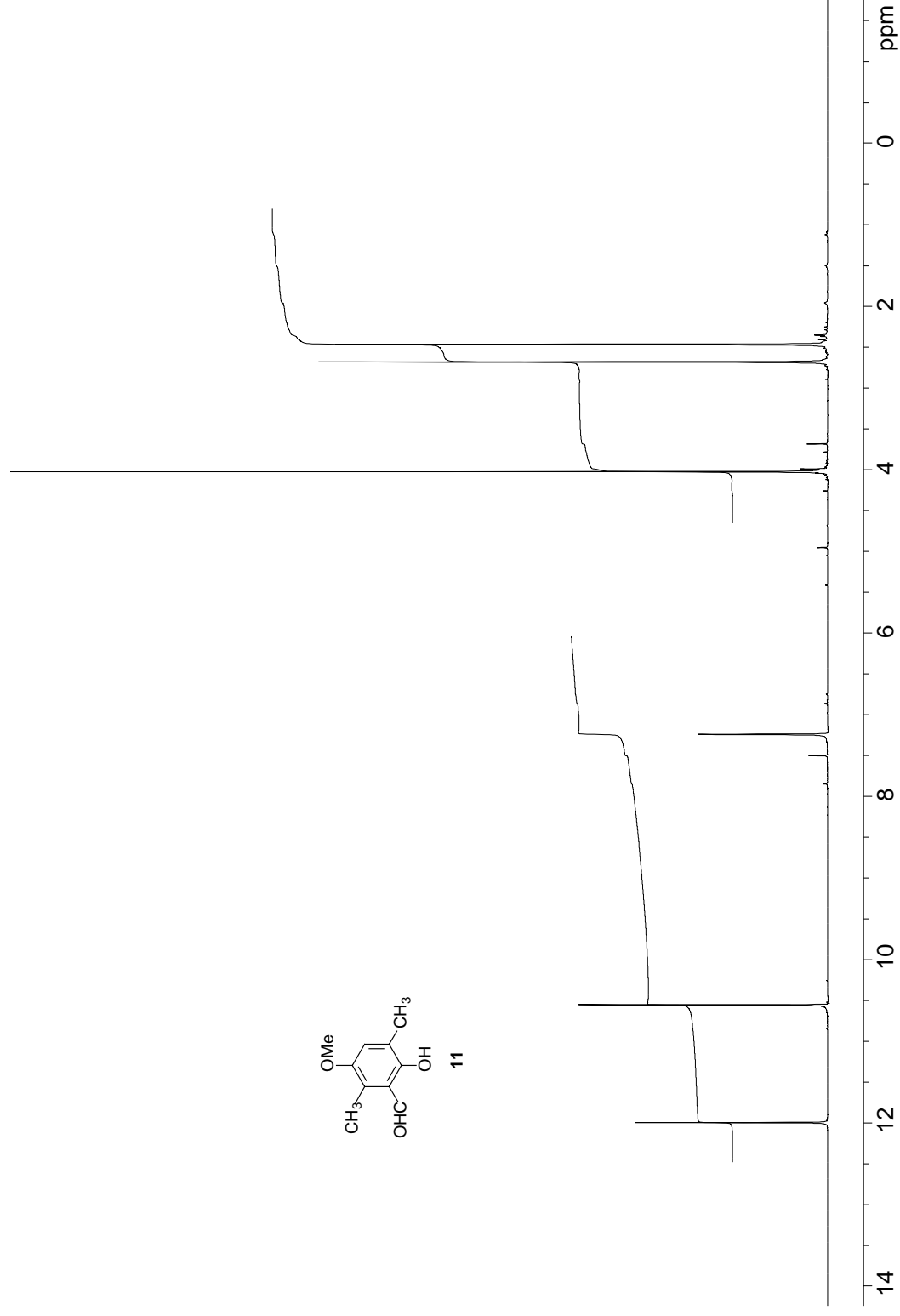




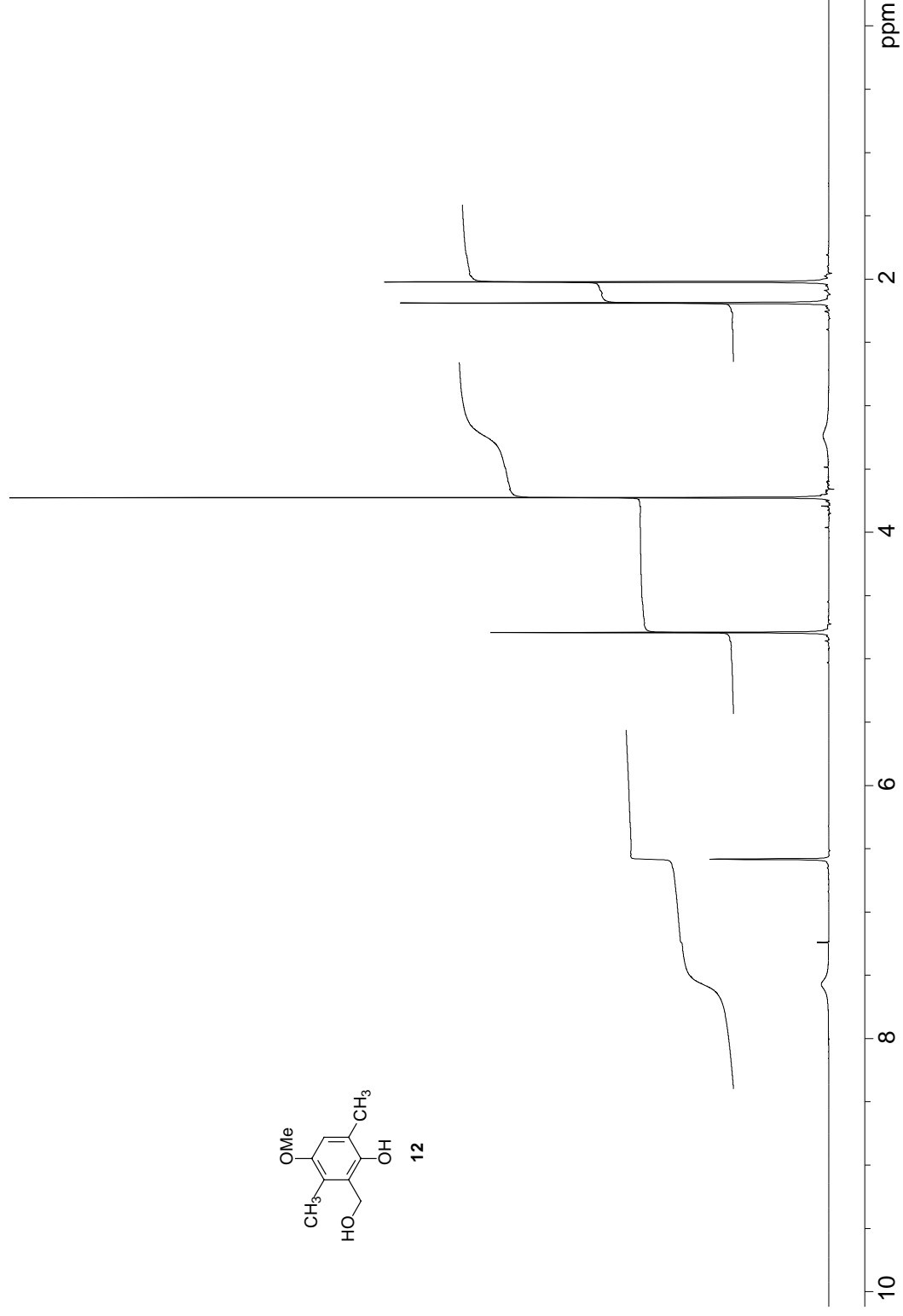
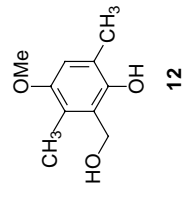
**Figure 11.**  $^1\text{H}$  NMR spectrum of trapping product **8** in  $\text{CDCl}_3$ .



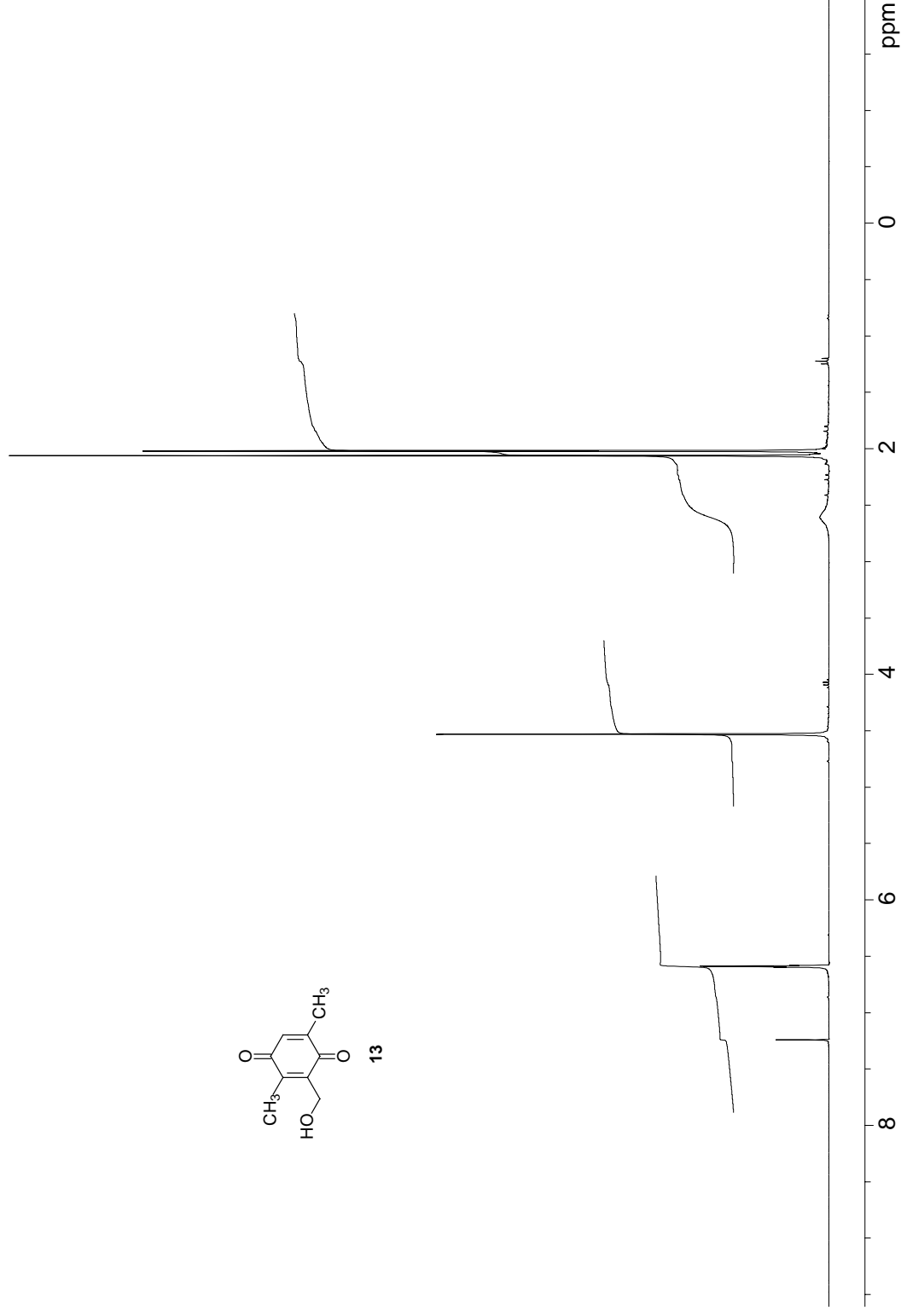
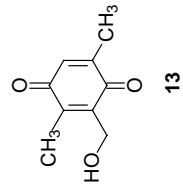
**Figure 12.**  $^{13}\text{C}$  NMR spectrum of trapping product **8** in  $\text{CDCl}_3$ .



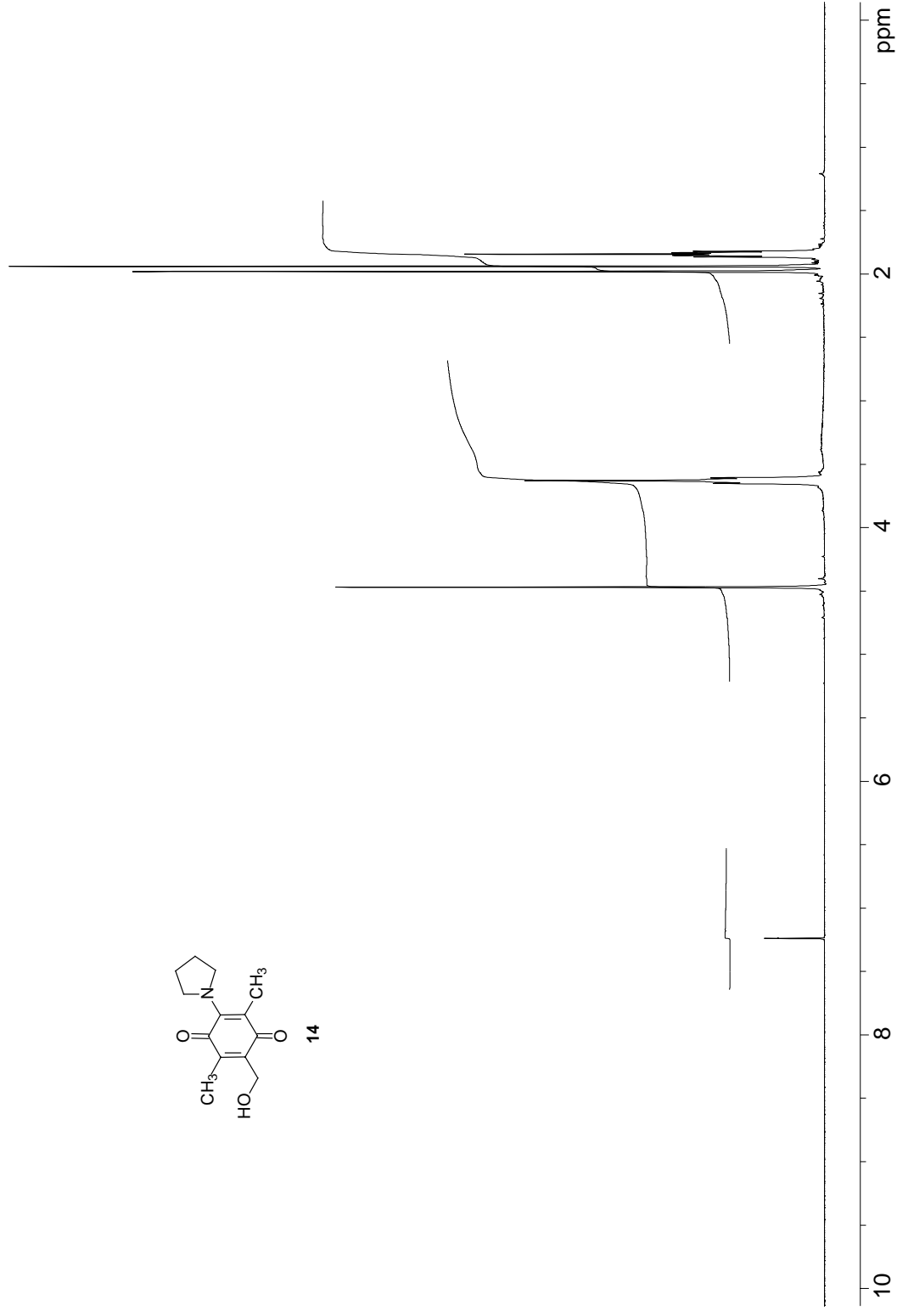
**Figure 13.**  $^1\text{H}$  NMR spectrum of benzaldehyde **11** in  $\text{CDCl}_3$ .



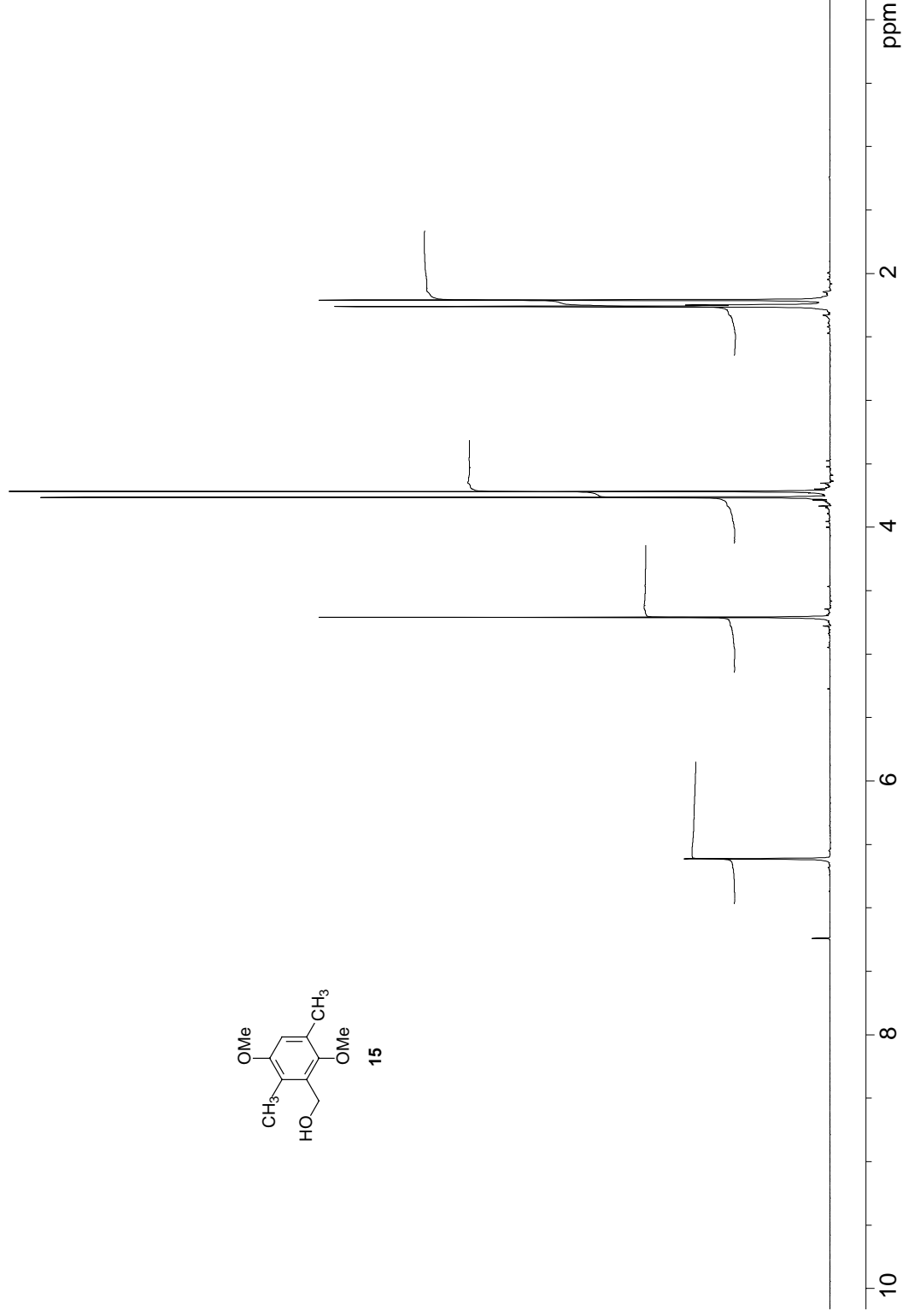
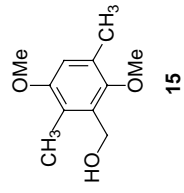
**Figure 14.** <sup>1</sup>H NMR spectrum of benzylic alcohol **12** in CDCl<sub>3</sub>.



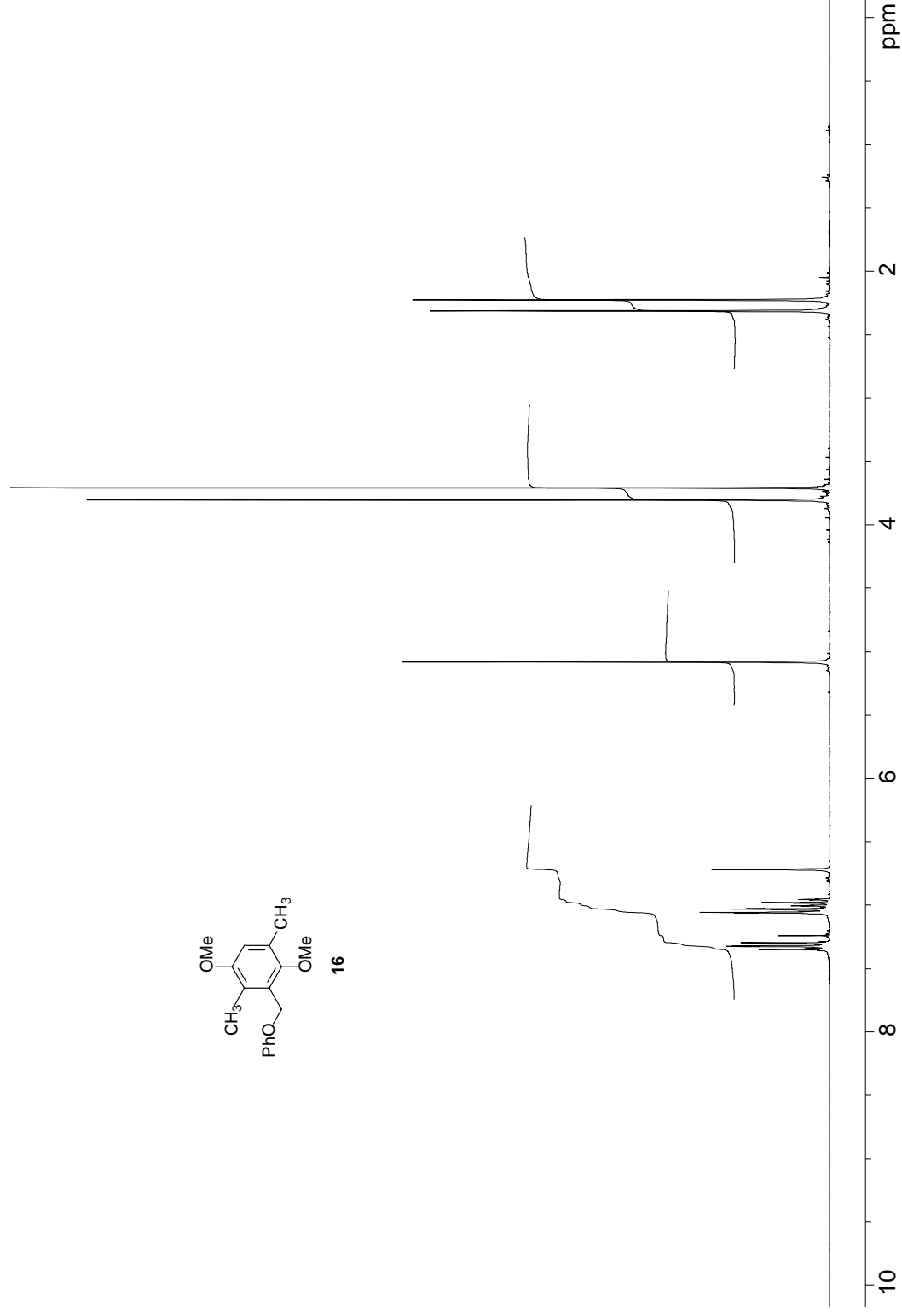
**Figure 15.**  $^1\text{H}$  NMR spectrum of hydroxymethyl-1,4-benzoquinone **13** in  $\text{CDCl}_3$



**Figure 16.** <sup>1</sup>H NMR spectrum of 5-hydroxymethyl-2-pyrrolidino-1,4-benzoquinone **14** in CDCl<sub>3</sub>.

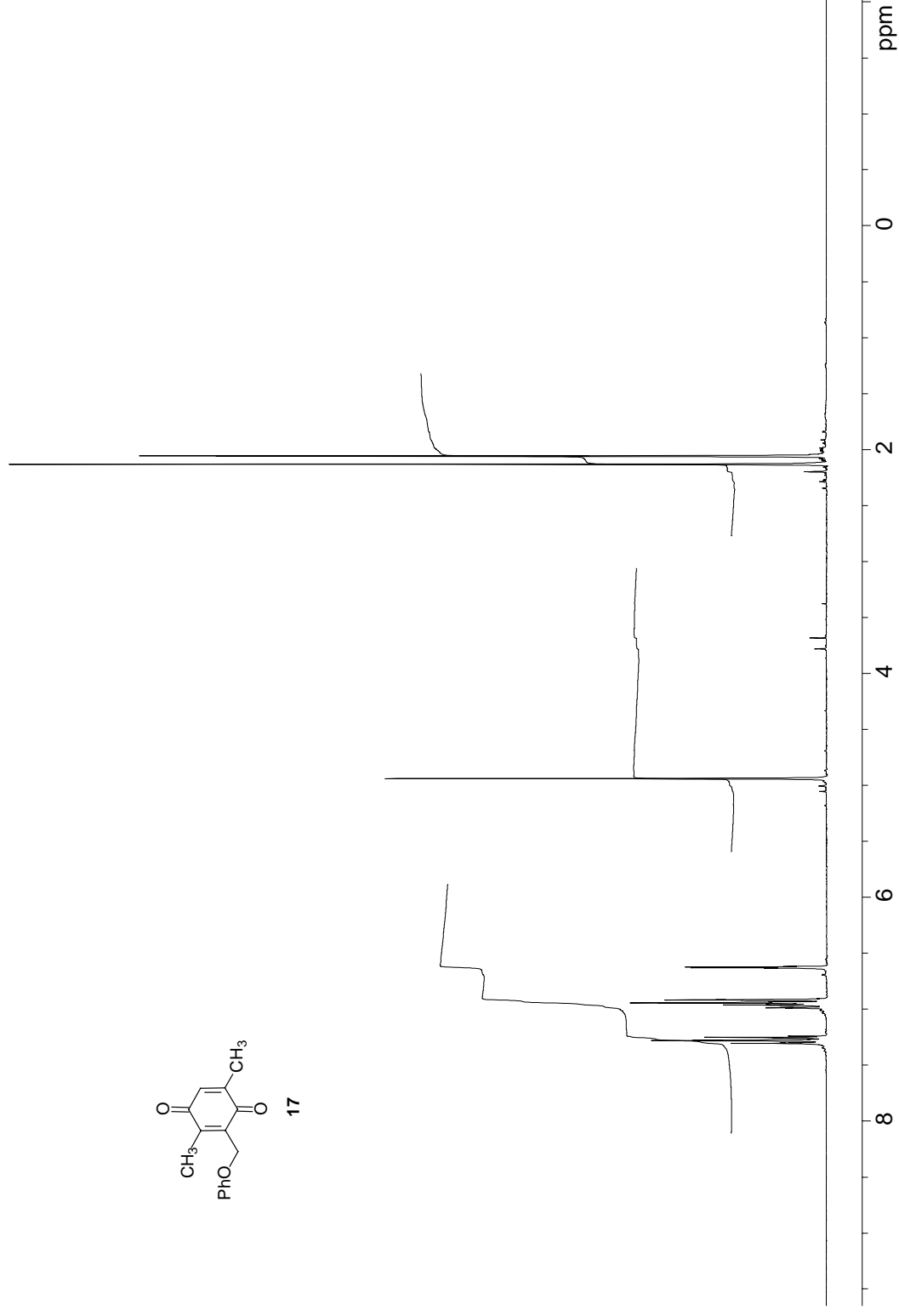
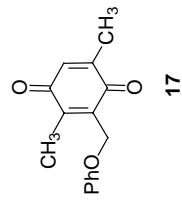


**Figure 17.** <sup>1</sup>H NMR spectrum of dimethoxybenzyl alcohol **15** in CDCl<sub>3</sub>.



**Figure 18.** <sup>1</sup>H NMR spectrum of phenoxyethylbenzene compound **16** in CDCl<sub>3</sub>.





**Figure 19.** <sup>1</sup>H NMR spectrum of phenoxyethyl-1,4-benzoquinone **17** in CDCl<sub>3</sub>.

## References for Supplementary Information

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