

**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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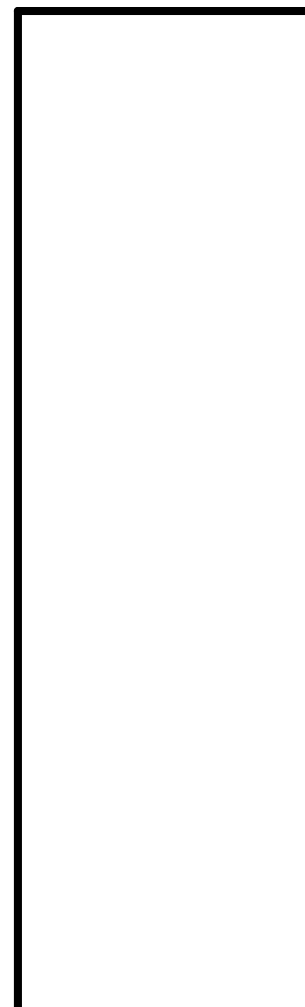
**An oxidative Prins and Prins/Friedel-Crafts cyclizations for the stereoselective synthesis of dioxabicycles and hexahydro-1*H*-benzo[*f*]isochromenes *via* the benzylic C-H activation**

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## 1. Preparation of starting materials



**General procedure A: Synthesis of homopropargylic alcohols via opening of ethylene oxide by terminal alkynes<sup>1,2</sup>**

To a cooled (-70 °C) solution of Li-amide (prepared from Li (60 mmol, 1.5 equiv.), 70 mL liquid ammonia and catalytic Fe(NO<sub>3</sub>)<sub>3</sub>, a solution of terminal alkyne (40 mmol, 1 equiv.) in dry diethyl ether (10 mL) was added dropwise with stirring. After additional stirring of 1h ethylene oxide (60 mmol, 1.5 equiv.) was added. The reaction mixture was stirred for 5-8h. After completion of the reaction as indicated by TLC, the reaction mixture was quenched with NH<sub>4</sub>Cl. Ammonia was allowed to evaporate and the reaction mixture was diluted with 25 mL water and extracted with ether (3x25 mL). The organic extract was washed with brine (2x10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford pure product.

**6-(Tetrahydro-2H-pyran-2-yloxy)hex-3-yn-1-ol<sup>1,5,6</sup>:**

The title compound was prepared in 70% yield according to general procedure A. Liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.65-4.58 (m, 1H), 3.91-3.69 (m, 2H), 3.63 (t, *J* = 6.0 Hz, 2H), 3.56-3.42 (m, 2H), 2.57-2.22 (m, 5H), 1.96-1.43 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 98.7, 79.3, 77.7, 65.9, 62.3, 61.1, 30.5, 25.3, 23.0, 20.1, 19.4; IR (neat): ν 3391, 2928, 2852, 1154, 1045, 748 cm<sup>-1</sup>; ESI-MS: *m/z* 199 (M+H)<sup>+</sup>; HRMS (ESI) calculated for C<sub>11</sub>H<sub>19</sub>O<sub>3</sub>: 199.1334 (M+H)<sup>+</sup>, Found 199.1321.

**7-(tetrahydro-2H-pyran-2-yloxy)hept-3-yn-1-ol<sup>8,9</sup>:**



The title compound was prepared in 72% yield according to general procedure A. Liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.60-4.53 (m, 1H), 3.90-3.73 (m, 2H), 3.63 (t, *J* = 6.0 Hz, 2H), 3.54-3.36 (m, 2H), 2.44-2.33 (m, 2H), 2.32-2.21 (m, 2H), 1.97 (broad s, 1H), 1.89-1.42 (m,

8H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  98.6, 81.8, 77.2, 65.8, 62.1, 61.3, 30.7, 29.0, 25.6, 23.3, 19.5, 15.7; IR (neat):  $\nu$  3382, 2946, 2839, 1158, 1043, 765  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  213 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{12}\text{H}_{21}\text{O}_3$ : 213.1491 ( $\text{M}+\text{H}$ ) $^+$ , Found 213.1484.

#### 6-Phenylhex-3-yn-1-ol<sup>2</sup>:



The title compound was obtained in 75% yield according to general procedure A. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30-7.22 (m, 2H), 7.21-7.13 (m, 3H), 3.57 (t,  $J = 6.2$  Hz, 2H), 2.79 (t,  $J = 7.5$  Hz, 2H), 2.49-2.40 (m, 2H), 2.39-2.31 (m, 2H), 1.59 (broad s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.6, 128.3, 128.2, 126.1, 81.5, 77.4, 61.1, 35.1, 22.9, 20.7; IR (neat):  $\nu$  3360, 2927, 1453, 1045, 749, 699  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  175 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{12}\text{H}_{15}\text{O}$ : 175.1123 ( $\text{M}+\text{H}$ ) $^+$ , Found 175.1130.

#### 6-(3-Methoxyphenyl)hex-3-yn-1-ol:



The title compound was obtained in 70% yield according to general procedure A. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.21-7.11 (m, 1H), 6.79-6.66 (m, 3H), 3.78 (s, 3H), 3.59 (t,  $J = 5.7$  Hz, 2H), 2.76 (t,  $J = 7.4$  Hz, 2H), 2.49-2.30 (m, 4H), 1.65 (broad s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5, 142.3, 129.3, 120.7, 114.3, 111.4, 81.7, 77.4, 61.2, 55.1, 35.2, 23.1, 20.8; IR (neat):  $\nu$  3391, 2939, 1594, 1489, 1459, 1262, 1158, 1047, 781, 695  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  205 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_{17}\text{O}_2$ : 205.1229 ( $\text{M}+\text{H}$ ) $^+$ , Found 205.1222.

**General procedure B: Synthesis of (*E*)-homoallylic alcohols via *trans*-reduction of homopropargylic alcohols<sup>1,2</sup>**

To a solution of homopropargylic alcohol obtained by general procedure A (20 mmol, 1 equiv.) in THF (10 mL) was added liquid NH<sub>3</sub> (45 mL) followed by sodium metal (80 mmol, 4 equiv.). The blue coloured reaction mixture was allowed to stir for 8-10h. After the completion of the reaction, the reaction was quenched by NH<sub>4</sub>Cl and ammonia was allowed to evaporate. The reaction mixture was diluted with 15 mL water and extracted with ether (3x15 mL). The organic layer was washed with brine (2x10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford pure product.

**(*E*)-6-(tetrahydro-2*H*-pyran-2-yloxy)hex-3-en-1-ol<sup>5</sup>:**



The title compound was prepared in 90% yield according to general procedure B. Liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.63-5.38 (m, 2H), 4.59-4.51 (m, 1H), 3.89-3.66 (m, 2H), 3.58 (t, *J* = 6.0 Hz, 2H), 3.53-3.34 (m, 2H), 2.36-2.19 (m, 4H), 1.91-1.42 (m, 7H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 129.4, 127.5, 98.8, 66.7, 62.2, 61.8, 30.7, 30.4, 27.9, 25.3, 19.4; IR (neat): ν 3384, 2926, 2848, 1155, 1042, 752 cm<sup>-1</sup>; ESI-MS: *m/z* 201 (M+H)<sup>+</sup>; HRMS (ESI) calculated for C<sub>11</sub>H<sub>21</sub>O<sub>3</sub>: 201.1491 (M+H)<sup>+</sup>, Found 201.1480.

**(*E*)-7-(tetrahydro-2*H*-pyran-2-yloxy)hept-3-en-1-ol<sup>9</sup>:**



The title compound was prepared in 90% yield according to general procedure B. Liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.61-5.47 (m, 1H), 5.46-5.32 (m, 1H), 4.56-4.49 (m, 1H), 3.89-3.65 (m, 2H), 3.59 (t, *J* = 6.0 Hz, 2H), 3.52-3.41 (m, 1H), 3.40-3.29 (m, 1H), 2.30-2.18 (m, 2H), 2.17-2.05 (m, 2H), 1.91-1.42 (m, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 132.8, 126.4,

98.7, 66.7, 62.2, 61.9, 35.8, 30.6, 29.2, 29.1, 25.3, 19.5; IR (neat):  $\nu$  3378, 2927, 2832, 1167, 1060, 754  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  215 (M+H)<sup>+</sup>; HRMS (ESI) calculated for C<sub>12</sub>H<sub>23</sub>O<sub>3</sub>: 215.1647 (M+H)<sup>+</sup>, Found 215.1657.

**(E)-6-(Phenyl)hex-3-en-1-ol<sup>2</sup>:**



The title compound was obtained in 90% yield according to general procedure B. Liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.14 (m, 5H), 5.61-5.45 (m, 1H), 5.40-5.24 (m, 1H), 3.52 (t,  $J$  = 6.2 Hz, 2H), 2.68 (t,  $J$  = 7.4 Hz, 2H), 2.41-2.28 (m, 2H), 2.27-2.15 (m, 2H), 1.47 (broad s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  141.7, 132.9, 128.4, 128.2, 126.7, 125.7, 61.8, 35.8, 35.7, 34.3; IR (neat):  $\nu$  3354, 2928, 1449, 1046, 970, 744, 699  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  177 (M+H)<sup>+</sup>; HRMS (ESI) calculated for C<sub>12</sub>H<sub>17</sub>O: 177.1279 (M+H)<sup>+</sup>, Found 177.1285.

**(E)-6-(3-Methoxyphenyl)hex-3-en-1-ol<sup>2</sup>:**



The title compound was obtained in 90% yield according to general procedure B. Viscous liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.18-7.09 (m, 1H), 6.74-6.60 (m, 3H), 5.60-5.44 (m, 1H), 5.42-5.25 (m, 1H), 3.77 (s, 3H), 3.53 (t,  $J$  = 6.0 Hz, 2H), 2.65 (t,  $J$  = 7.3 Hz, 2H), 2.40-2.27 (m, 2H), 2.26-2.15 (m, 2H), 1.28 (broad s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  159.5, 143.4, 132.9, 129.2, 126.7, 120.8, 114.2, 111.0, 61.8, 55.1, 35.9, 35.8, 34.2; IR (neat):  $\nu$  3375, 2936, 1593, 1488, 1458, 1261, 1156, 1047, 781, 696  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  207 (M+H)<sup>+</sup>; HRMS (ESI) calculated for C<sub>13</sub>H<sub>19</sub>O<sub>2</sub>: 207.1385 (M+H)<sup>+</sup>, Found 207.1378.

**General procedure C: Synthesis of (Z)-homoallylic alcohols via cis-reduction of homopropargylic alcohols<sup>3,4</sup>**

To a stirred solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (20 mmol, 1 equiv.) in ethanol (20 mL) under H<sub>2</sub> atmosphere, NaBH<sub>4</sub> (20 mmol, 1 equiv.) in ethanol (20 mL) was added at room temperature. After stirring for 0.5h, ethylenediamine (80 mmol, 4 equiv.) and homopropargylic alcohol obtained by general procedure A (20 mmol, 1 equiv.) in ethanol (20 mL) were added sequentially. The reaction mixture was allowed to stir for 4-6h. After completion of the reaction, ethanol was concentrated and reaction mixture was diluted with 20 mL 10% ethyl acetate in *n*-hexane and filtered through celite path, the residue was washed with *n*-hexane. The filtrate was concentrated in vacuo and the resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford pure product.

**(Z)-6-(tetrahydro-2H-pyran-2-yloxy)hex-3-en-1-ol<sup>4,5</sup>:**



The title compound was prepared in 95% yield according to general procedure C. Liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.68-5.37 (m, 2H), 4.61-4.51 (m, 1H), 3.89-3.70 (m, 2H), 3.66-3.30 (m, 4H), 2.45-2.27 (m, 4H), 2.20 (broad s, 1H), 1.91-1.41 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 129.8, 128.1, 98.7, 66.9, 62.3, 61.6, 35.8, 32.9, 30.5, 25.3, 19.5; IR (neat): ν 3380, 2925, 2845, 1157, 1046, 752 cm<sup>-1</sup>; ESI-MS: *m/z* 201 (M+H)<sup>+</sup>; HRMS (ESI) calculated for C<sub>11</sub>H<sub>21</sub>O<sub>3</sub>: 201.1491 (M+H)<sup>+</sup>, Found 201.1488.

**(Z)-7-(tetrahydro-2H-pyran-2-yloxy)hept-3-en-1-ol:**



The title compound was prepared in 95% yield according to general procedure C. Liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.58-5.45 (m, 1H), 5.44-5.31 (m, 1H), 4.57-4.50 (m, 1H), 3.88-3.77 (m, 1H), 3.72 (td, *J* = 9.8 and 6.0 Hz, 1H), 3.60 (t, *J* = 6.0 Hz, 2H), 3.52-3.42 (m, 1H),

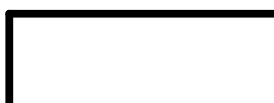
3.36 (td,  $J = 9.8$  and  $6.0$  Hz, 1H), 2.41-2.23 (m, 2H), 2.22-2.11 (m, 2H), 1.92-1.44 (m, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.2, 125.9, 98.9, 66.7, 62.4, 62.2, 30.7, 29.5, 25.4, 23.9, 19.6; IR (neat):  $\nu$  3375, 2930, 2824, 1161, 1057, 755  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  215 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{12}\text{H}_{23}\text{O}_3$ : 215.1647 ( $\text{M}+\text{H}$ ) $^+$ , Found 215.1635.

**(Z)-6-(Phenyl)hex-3-en-1-ol:**



The title compound was obtained in 95% yield according to general procedure C. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27-7.18 (m, 2H), 7.17-7.09 (m, 3H), 5.60-5.49 (m, 1H), 5.40-5.29 (m, 1H), 3.49 (t,  $J = 6.4$  Hz, 2H), 2.66 (t,  $J = 7.5$  Hz, 2H), 2.44-2.33 (m, 2H), 2.26-2.16 (m, 2H), 1.28 (broad s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.7, 131.8, 128.4, 128.2, 126.0, 125.7, 62.1, 35.8, 30.7, 29.2; IR (neat):  $\nu$  3360, 2925, 1446, 1045, 972, 745, 697  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  177 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{12}\text{H}_{17}\text{O}$ : 177.1279 ( $\text{M}+\text{H}$ ) $^+$ , Found 177.1270.

**(Z)-6-(3-Methoxyphenyl)hex-3-en-1-ol:**



The title compound was obtained in 95% yield according to general procedure C. Liquid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.15-7.10 (m, 1H), 6.74-6.70 (m, 1H), 6.69-6.63 (m, 2H), 5.58-5.50 (m, 1H), 5.39-5.31 (m, 1H), 3.77 (s, 3H), 3.52 (t,  $J = 7.0$  Hz, 2H), 2.63 (t,  $J = 8.0$  Hz, 2H), 2.42-2.34 (m, 2H), 2.26-2.19 (m, 2H), 1.20 (broad s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5, 143.4, 131.9, 129.2, 126.0, 120.8, 114.3, 111.0, 62.1, 55.1, 35.8, 30.7, 29.1; IR (neat):  $\nu$  3380, 2937, 1595, 1489, 1459, 1263, 1158, 1046, 780, 695  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  207 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_{19}\text{O}_2$ : 207.1385 ( $\text{M}+\text{H}$ ) $^+$ , Found 207.1392.



## **General procedure D: Synthesis of benzylic ethers of (*E*)- or (*Z*)-homoallylic alcohols**

### **1. Synthesis of benzylic ethers of the substrates containing tetrahydropyranyl group<sup>10,11</sup>**

To a stirring mixture of NaH (1.2 mmol, 1.2 equiv.) in THF (10 mL) was added a solution of (*E*)- or (*Z*)-homoallylic alcohol (obtained by general procedure B or C) in THF (5 mL) at 0 °C. After additional stirring for 0.5h at room temperature, benzylic bromide (1.1 mmol, 1.1 equiv.) and catalytic TBAI were added and reaction mixture was allowed to stir for 8-10h. After completion of the reaction as indicated by TLC, the reaction mixture was slowly quenched with saturated solution of NH<sub>4</sub>Cl (5-10 mL) and extracted with ethyl acetate (2x10 mL). The organic extracts were washed with brine (2x10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo and the crude product was obtained as a viscous liquid (Yield, 85-90%). Then to a solution of resulting crude product in methanol (15 mL) was added Amberlyst-15<sup>®</sup> (200 mg) and the reaction mixture was stirred for 2-4h at ambient temperature. After completion of the reaction as indicated by TLC, the reaction mixture was filtered, washed with methanol and the filtrate was concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradients to afford corresponding pure product.

### **2. Synthesis of benzylic ethers of the substrates without tetrahydropyranyl group<sup>10</sup>**

To a stirring mixture of NaH (1.2 mmol, 1.2 equiv.) in THF (10 mL) was added a solution of (*E*)- or (*Z*)-homoallylic alcohol (obtained by general procedure B or C) in THF (5 mL) at 0 °C. After additional stirring for 0.5h at room temperature, benzylic bromide (1.1 mmol, 1.1 equiv.) and catalytic TBAI were added and reaction mixture was allowed to stir for 8-10h. After completion of the reaction as indicated by TLC, the reaction mixture was slowly quenched with saturated solution of NH<sub>4</sub>Cl (5-10 mL) and extracted with ethyl acetate (2x10 mL). The organic extracts were washed with brine (2x10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, 100-200 mesh) using ethyl acetate/*n*-hexane gradients to afford corresponding pure product.

**(E)-6-(4-methoxybenzyloxy)hex-3-en-1-ol:**



The title compound was prepared in 86% yield according to general procedure D1. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22-7.15 (m, 2H), 6.85-6.78 (m, 2H), 5.59-5.36 (m, 2H), 4.40 (s, 2H), 3.78 (s, 3H), 3.57 (t,  $J = 6.2$  Hz, 2H), 3.42 (t,  $J = 6.6$  Hz, 2H), 2.34-2.18 (m, 4H), 1.67 (broad s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 130.4, 130.1, 129.2, 128.1, 113.7, 72.5, 69.5, 61.8, 55.2, 36.0, 33.1; IR (neat):  $\nu$  3389, 2929, 1471, 1265, 1156, 1036, 784, 699  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  237 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{20}\text{NaO}_3$ : 259.1310 ( $\text{M}+\text{H}$ ) $^+$ , Found 259.1296.

**(Z)-6-(4-methoxybenzyloxy)hex-3-en-1-ol:**



The title compound was prepared in 85% yield according to general procedure D1. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23-7.15 (m, 2H), 6.85-6.78 (m, 2H), 5.59-5.40 (m, 2H), 4.41 (s, 2H), 3.78 (s, 3H), 3.58 (t,  $J = 6.0$  Hz, 2H), 3.42 (t,  $J = 6.2$  Hz, 2H), 2.42-2.25 (m, 4H), 1.54 (broad s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 130.2, 129.4, 129.3, 127.7, 113.7, 72.6, 69.0, 61.9, 55.2, 30.7, 28.0; IR (neat):  $\nu$  3391, 2934, 1472, 1258, 1152, 1044, 785, 698  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  237 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{21}\text{O}_3$ : 237.1491 ( $\text{M}+\text{H}$ ) $^+$ , Found 237.1499.

**(E)-7-(4-methoxybenzyloxy)hept-4-en-1-ol:**



The title compound was prepared in 85% yield according to general procedure D1. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31-7.20 (m, 2H), 6.92-6.82 (m, 2H), 5.62-5.32 (m, 2H), 4.43 (s, 2H), 3.81 (s, 3H), 3.61 (t,  $J = 6.4$  Hz, 2H), 3.44 (t,  $J = 6.2$  Hz, 2H), 2.37-2.20 (m, 4H), 1.74-1.58 (m, 1H), 1.43 (broad s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 133.3, 130.5, 129.2, 127.1, 113.7, 72.5, 69.7, 62.4, 55.2, 35.9, 32.3, 29.1; IR (neat):  $\nu$  3389, 2929, 2857, 1480, 1275, 1170, 1042, 777, 702  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  251 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{23}\text{O}_3$ : 251.1647 ( $\text{M}+\text{H}$ ) $^+$ , Found 251.1641.

**(Z)-7-(benzyloxy)hept-4-en-1-ol:**



The title compound was prepared in 88% yield according to general procedure D1. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35-7.19 (m, 5H), 5.49-5.32 (m, 2H), 4.48 (s, 2H), 3.54 (t,  $J = 6.0$  Hz, 2H), 3.44 (t,  $J = 6.2$  Hz, 2H), 2.40-2.30 (m, 2H), 2.29-1.95 (m, 3H), 1.64-1.52 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.0, 130.9, 128.2, 127.6, 127.5, 126.4, 72.8, 69.5, 61.5, 31.9, 27.8, 23.3; IR (neat):  $\nu$  3365, 2925, 2842, 1254, 1172, 1046, 755, 692  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  221 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{21}\text{O}_2$ : 221.1542 ( $\text{M}+\text{H}$ ) $^+$ , Found 251.1555.

**(E)-1-(6-(4-methoxybenzyloxy)hex-3-enyl)benzene:**



The title compound was obtained in 90% yield according to general procedure D2. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29-7.06 (m, 7H), 6.87-6.76 (m, 2H), 5.57-5.33 (m, 2H), 4.39 (s, 2H), 3.78 (s, 3H), 3.38 (t,  $J = 6.8$  Hz, 2H), 2.65 (t,  $J = 7.3$  Hz, 2H), 2.37-2.19 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 142.0, 131.4, 130.6, 129.2, 128.4, 128.2, 127.1, 125.7, 113.7, 72.4, 69.8, 55.2, 35.9, 34.4, 33.0; IR (neat):  $\nu$  2926, 2837, 1498, 1260, 1080, 832, 749  $\text{cm}^{-1}$ ; MS (APCI):  $m/z$  297 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (APCI) calculated for  $\text{C}_{20}\text{H}_{25}\text{O}_2$ : 297.1855 ( $\text{M}+\text{H}$ ) $^+$ , Found 297.1842.

**(E)-5-((6-phenylhex-3-enyloxy)methyl)benzo[d][1,3]dioxole:**



The title compound was obtained in 86% yield according to general procedure D2. Liquid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24-7.18 (m, 2H), 7.15-7.08 (m, 3H), 6.80-6.77 (m, 1H), 6.73-6.59 (m, 2H), 5.92 (s, 2H), 5.54-5.34 (m, 2H), 4.35 (s, 2H), 3.38 (t,  $J = 7.0$  Hz, 2H), 2.65 (t,  $J = 7.5$  Hz, 2H), 2.34-2.22 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.7, 146.9, 142.0, 132.3, 131.5, 128.4, 128.2, 127.0, 125.7, 121.1, 108.4, 107.9, 100.9, 72.6, 69.8, 35.9, 34.4, 33.0; IR (neat):  $\nu$  2927, 2840, 1562, 1490, 1442, 1260, 1164, 1051, 780  $\text{cm}^{-1}$ ; MS (APCI):  $m/z$  311 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (APCI) calculated for  $\text{C}_{20}\text{H}_{23}\text{O}_3$ : 311.1647 ( $\text{M}+\text{H}$ ) $^+$ , Found 311.1633.

**(Z)-1-(6-(benzyloxy)hex-3-enyl)-3-methoxybenzene:**



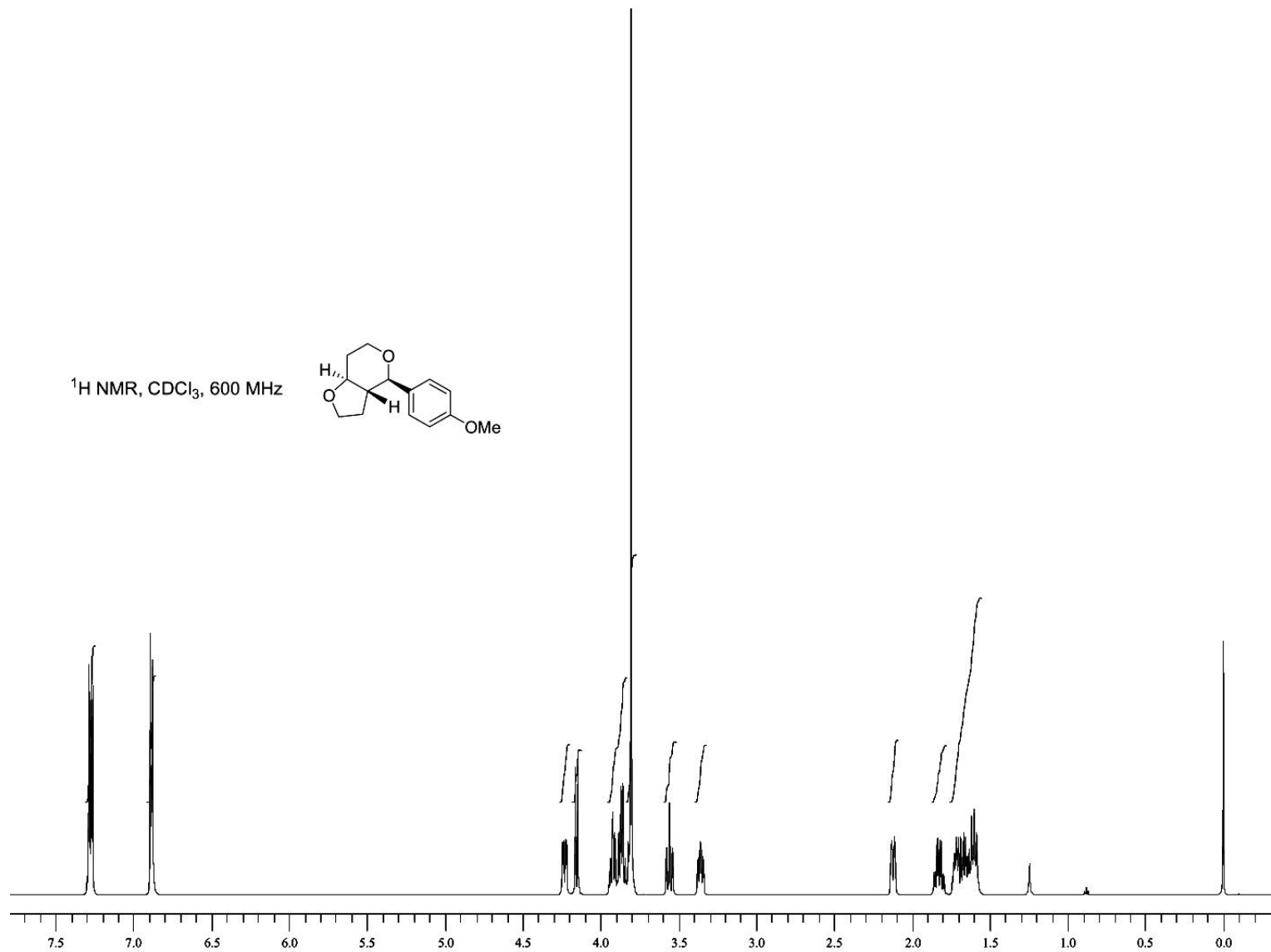
The title compound was obtained in 88% yield according to general procedure D2. Liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36-7.21 (m, 5H), 7.17-7.08 (m, 1H), 6.74-6.61 (m, 3H), 5.52-5.33 (m, 2H), 4.53(s, 2H), 3.76 (s, 3H), 3.35 (t,  $J = 6.8$  Hz, 2H), 2.62 (t,  $J = 7.5$  Hz, 2H), 2.40-2.23 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5, 143.6, 138.5, 130.7, 129.2, 128.3, 127.6, 127.5, 126.3, 120.9, 114.2, 111.0, 72.8, 69.8, 55.1, 35.8, 29.1, 27.9; IR (neat):  $\nu$  2922, 2833, 1582, 1487, 1455, 1263, 1168, 1042, 789  $\text{cm}^{-1}$ ; MS (APCI):  $m/z$  297 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (APCI) calculated for  $\text{C}_{20}\text{H}_{25}\text{O}_2$ : 297.1855 ( $\text{M}+\text{H}$ ) $^+$ , Found 297.1861.

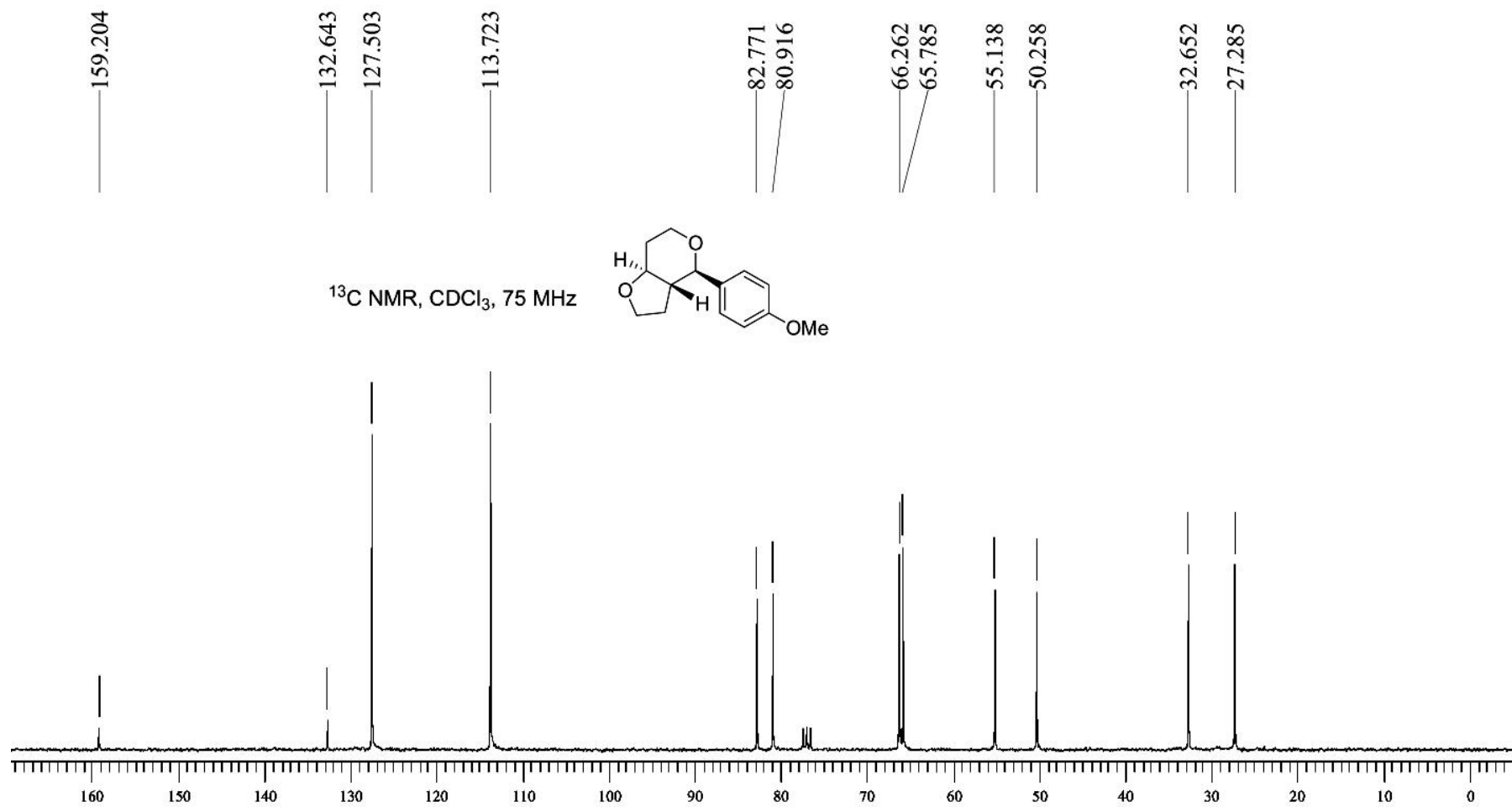
**References:**

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2. W. N. Speckai and J. Dukink, *Tetrahedron Lett.*, 1978, **34**, 173.
3. C. A. Brown and V. K. Ahuja, *J. Org. Chem.*, 1973, **38**, 2226.
4. G. Pohnert, S. Adolph and T. Wichard, *Chemistry and Physics of Lipids*, 2004, **131**, 159.
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7. S. Girard and P. Deslongchamps, *Can. J. Chem.*, 1992, **70**, 1265.
8. L. Crombie and A. G. Jacklin, *Lipids. Part V.*, 1957, 1622.
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10. (a) S. Czernecki, C. Georgoulis, and C. Provelenghiou, *Tetrahedron Lett.*, 1976, 3535; (b) J. L. Marco and J. A. Hueso-Rodriguez, *Tetrahedron Lett.*, 1988, **29**, 2459; (c) H. Takaku, T. Ito and K. Imai, *Chem. Lett.*, 1986, 1005.
11. (a) B. Richichi, S. Cicchi, U. Chiacchio, G. Romeo and A. Brandi, *Tetrahedron*, 2003, **59**, 5231; (b) F. M. Cordero, F. Pisaneschi, M. Gensini, A. Goti and A. Brandi, *Eur. J. Org. Chem.*, 2002, **2002**, 1941.

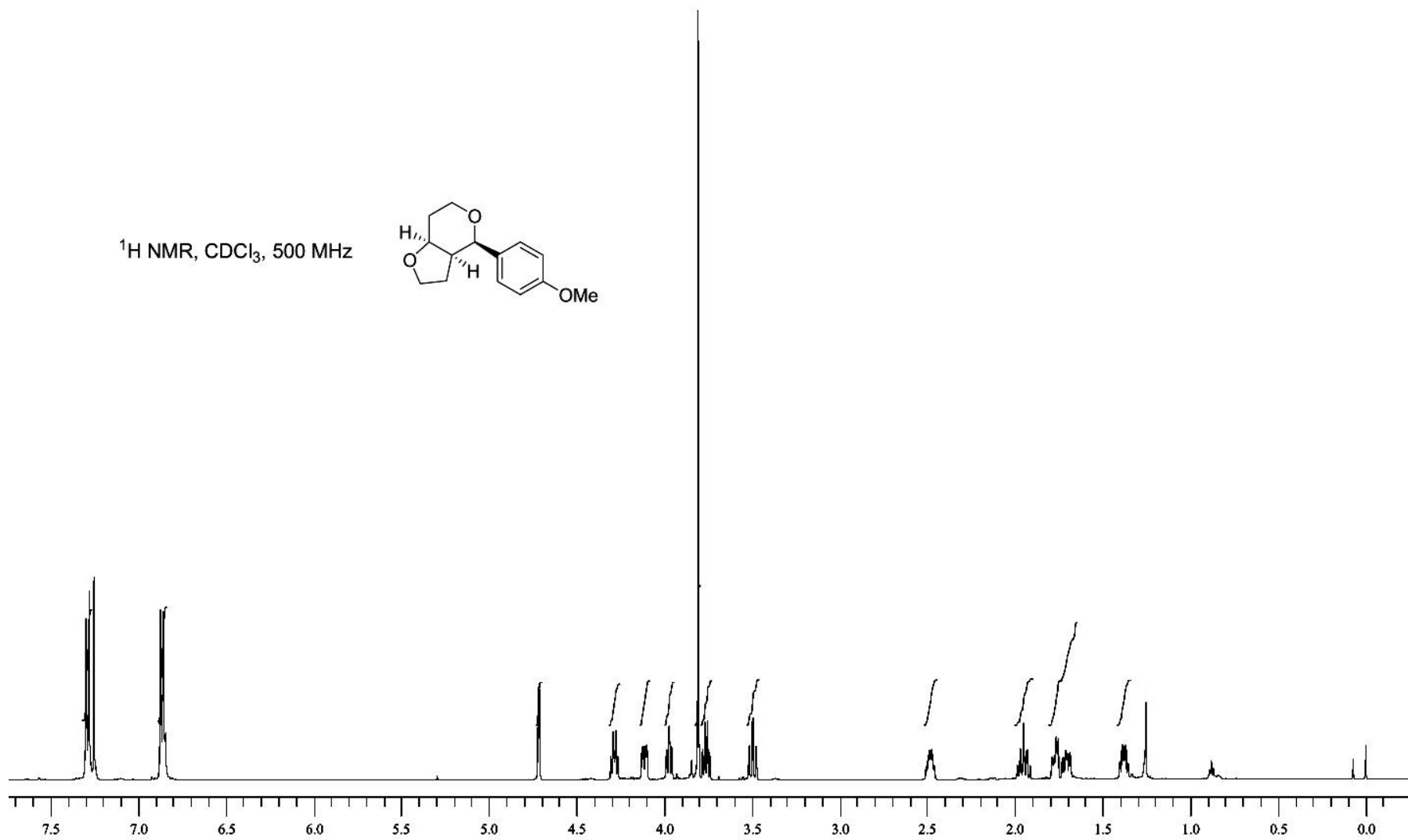
### 3. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products 2a-2i, 4a-4g, 5d, 5g and 7a-7h

Product 2a (Table 2, Entry a):

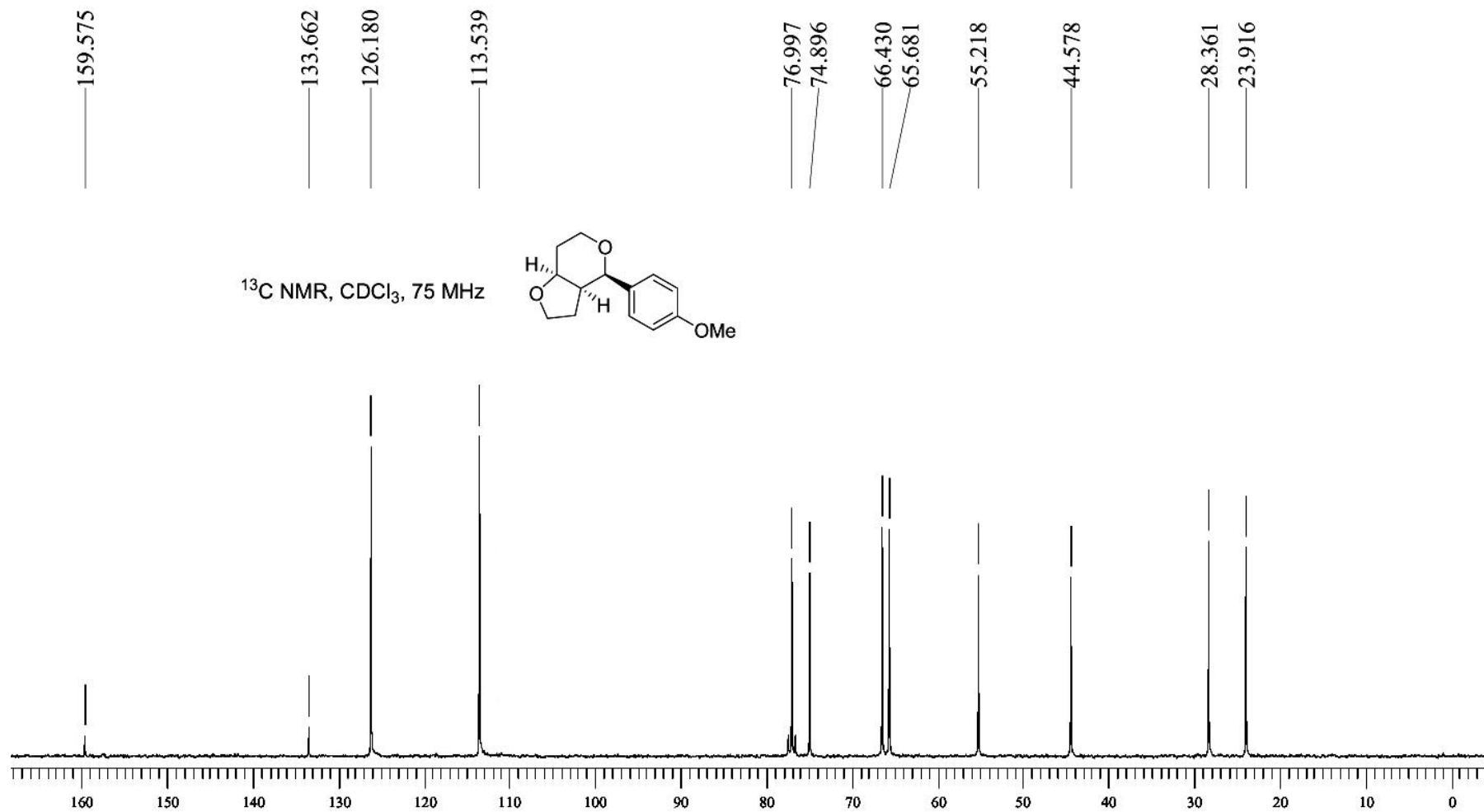




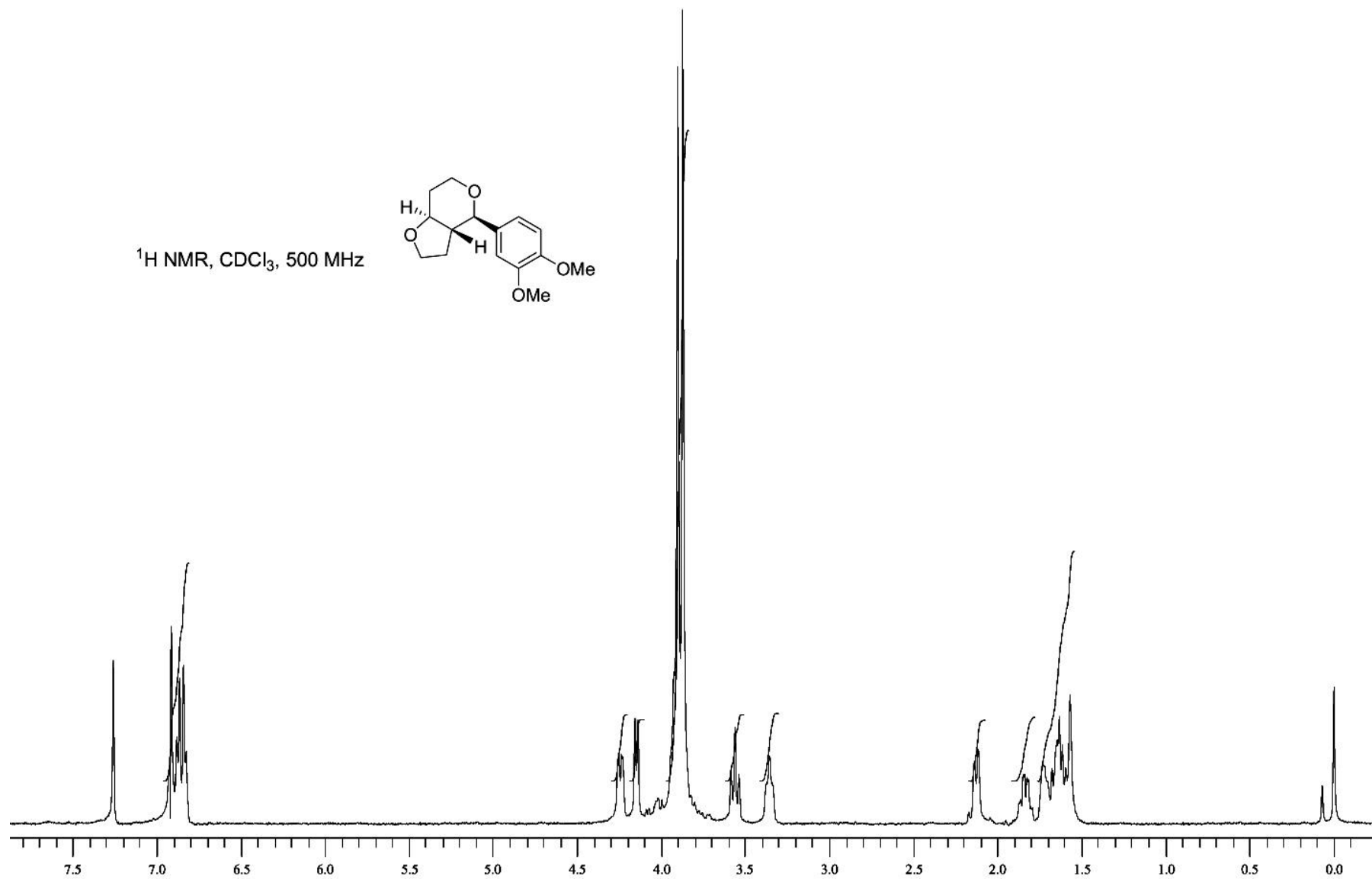
Product **2b** (Table 2, Entry **b**):

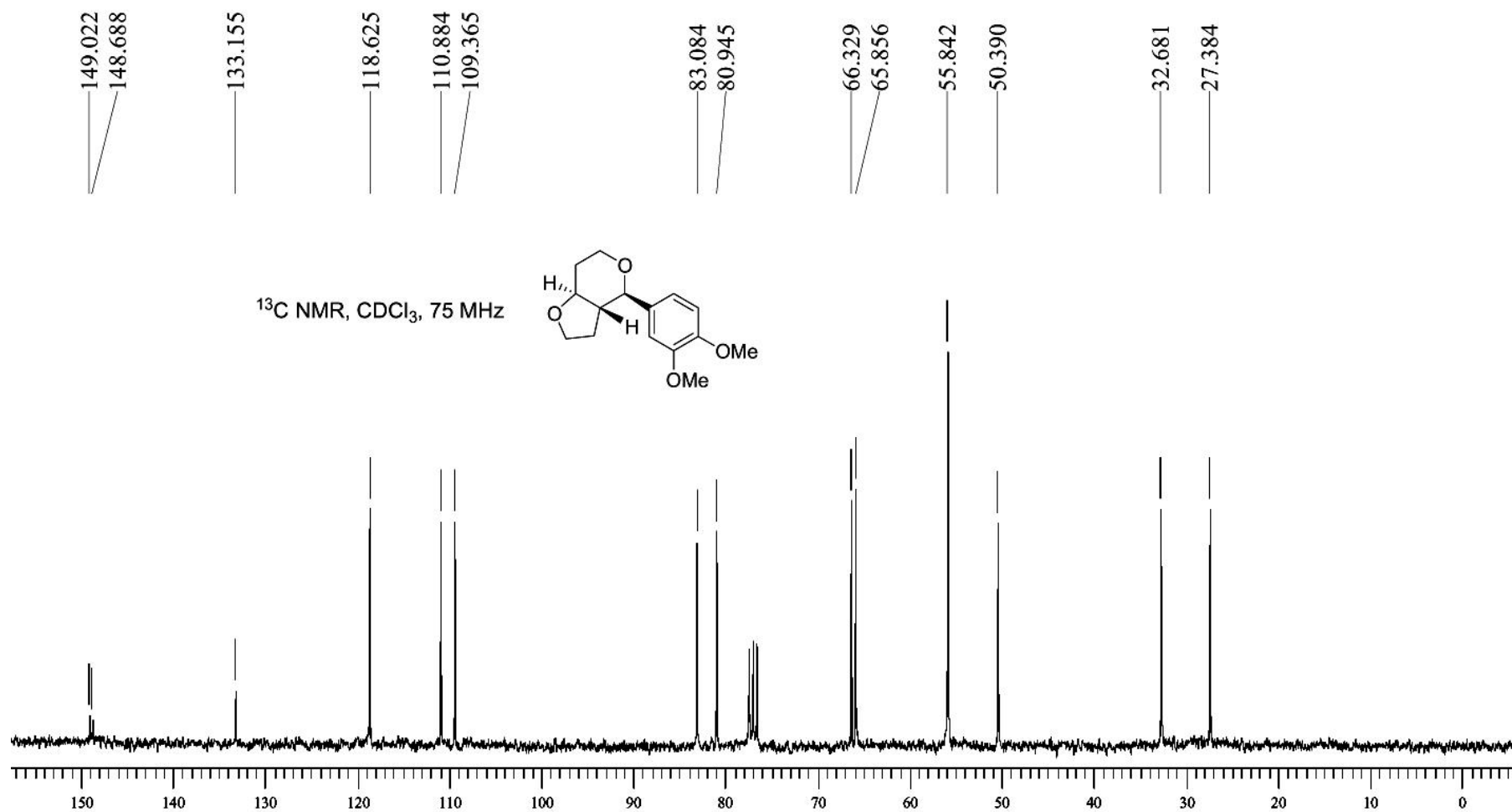




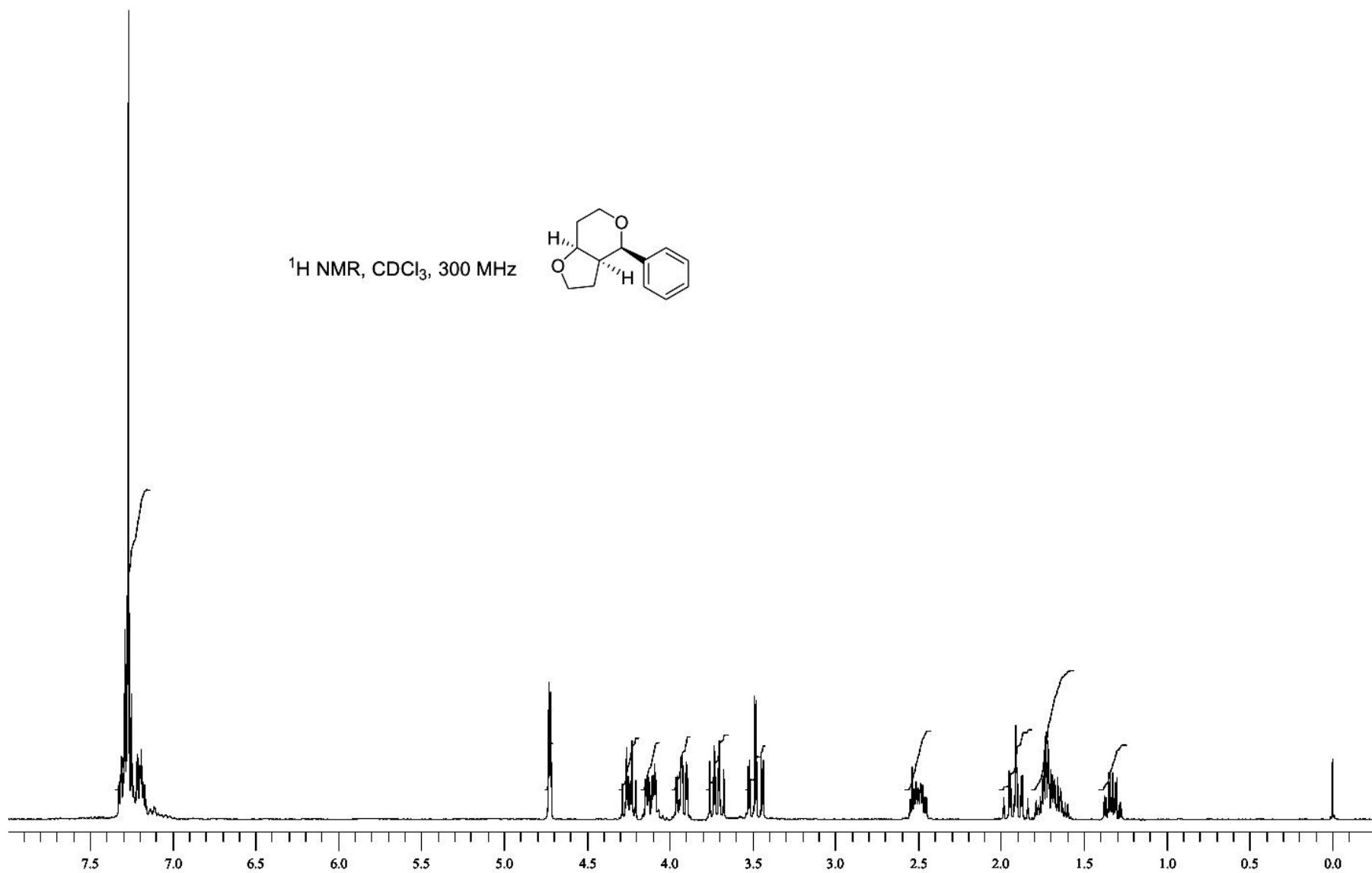


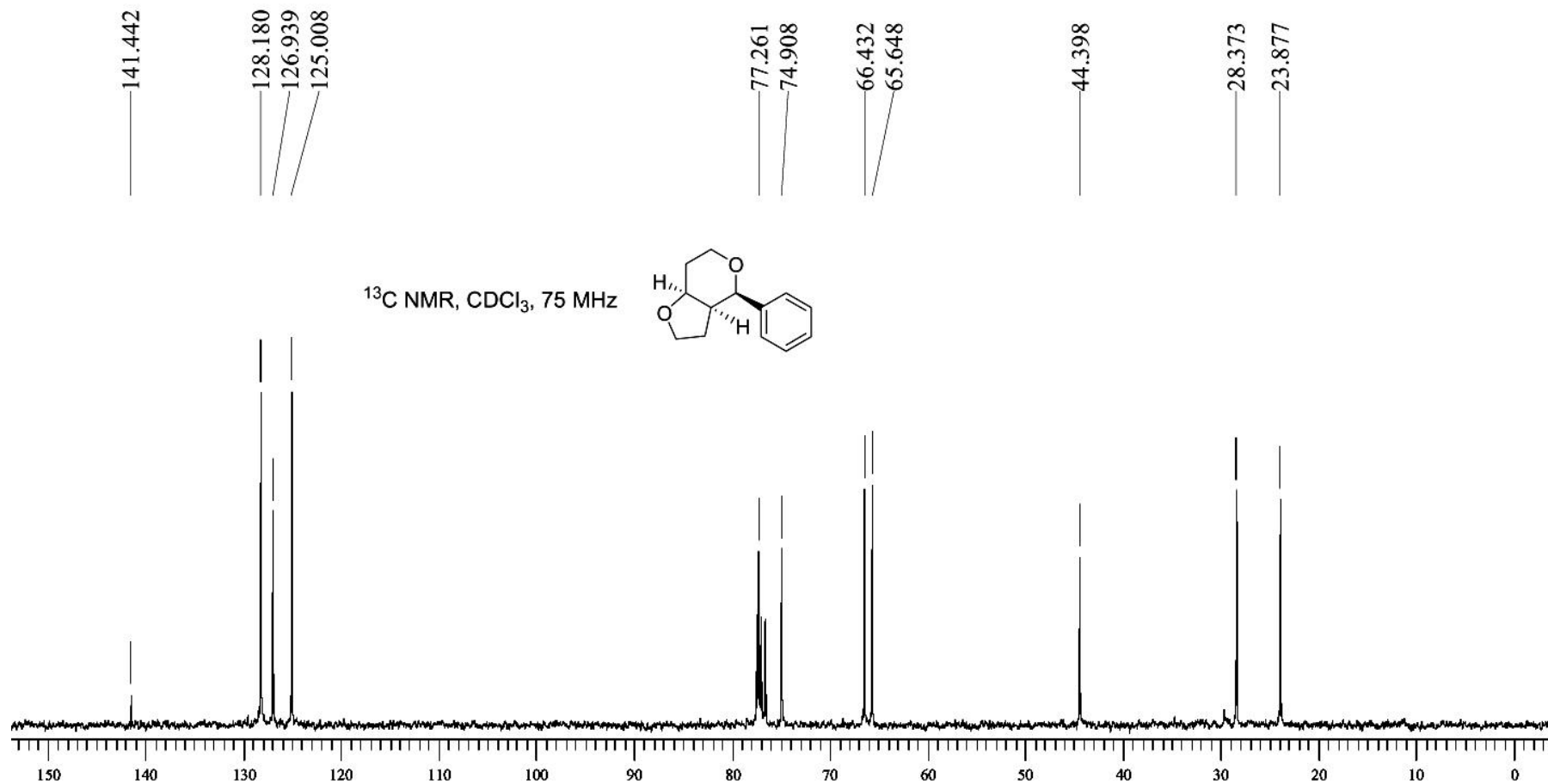
Product **2c** (Table 2, Entry c):



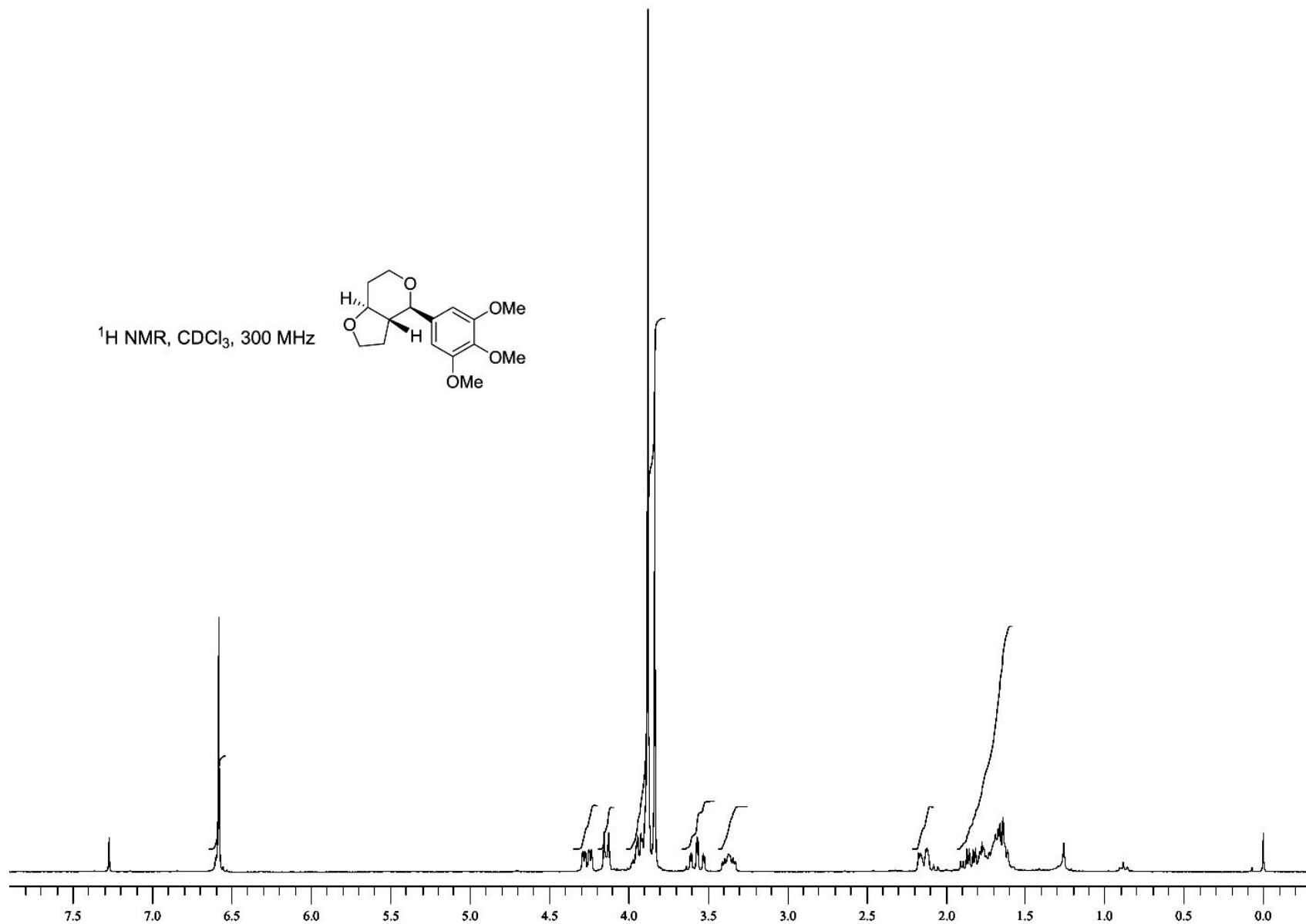


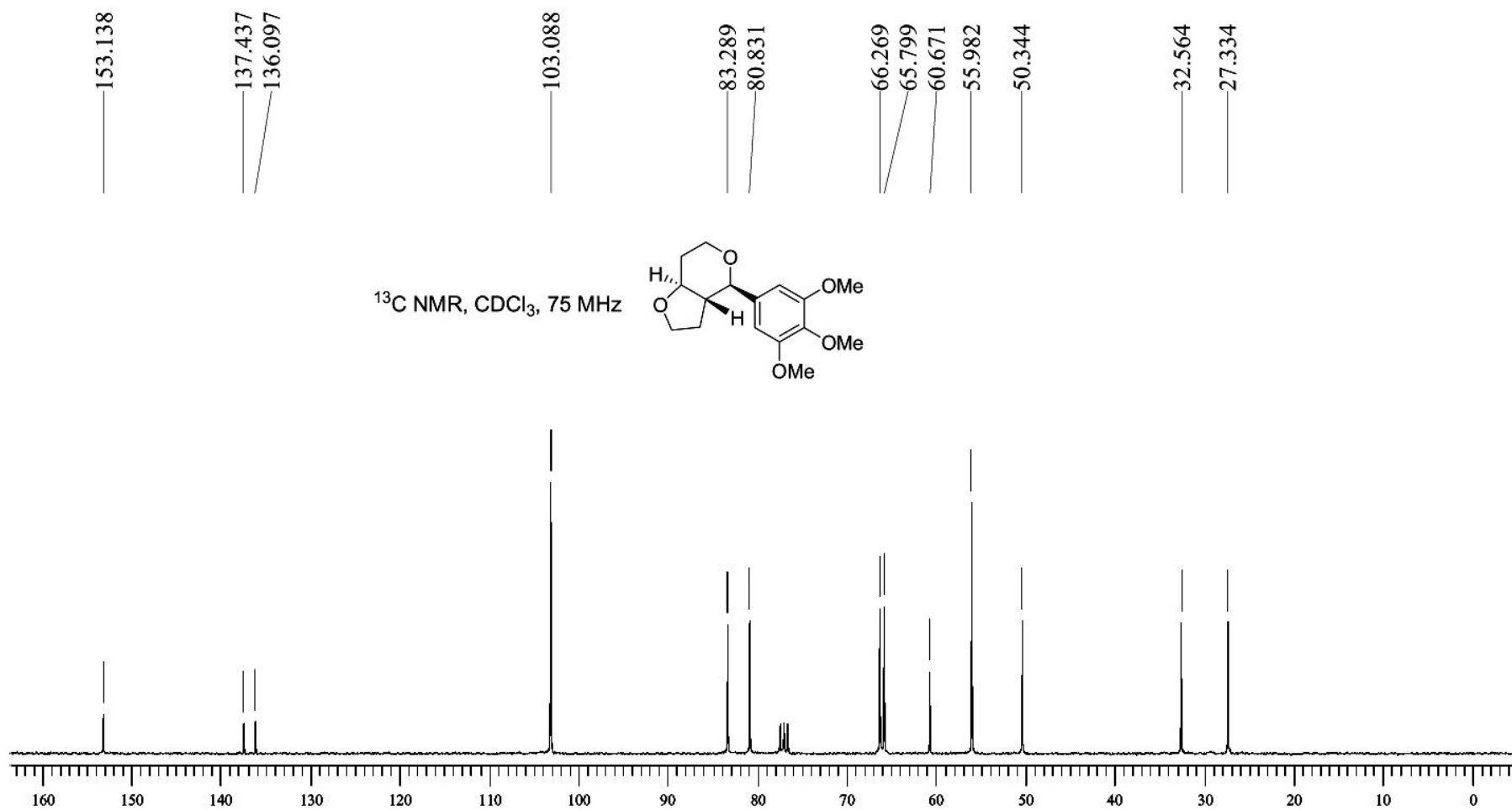
Product **2d** (Table 2, Entry **d**):



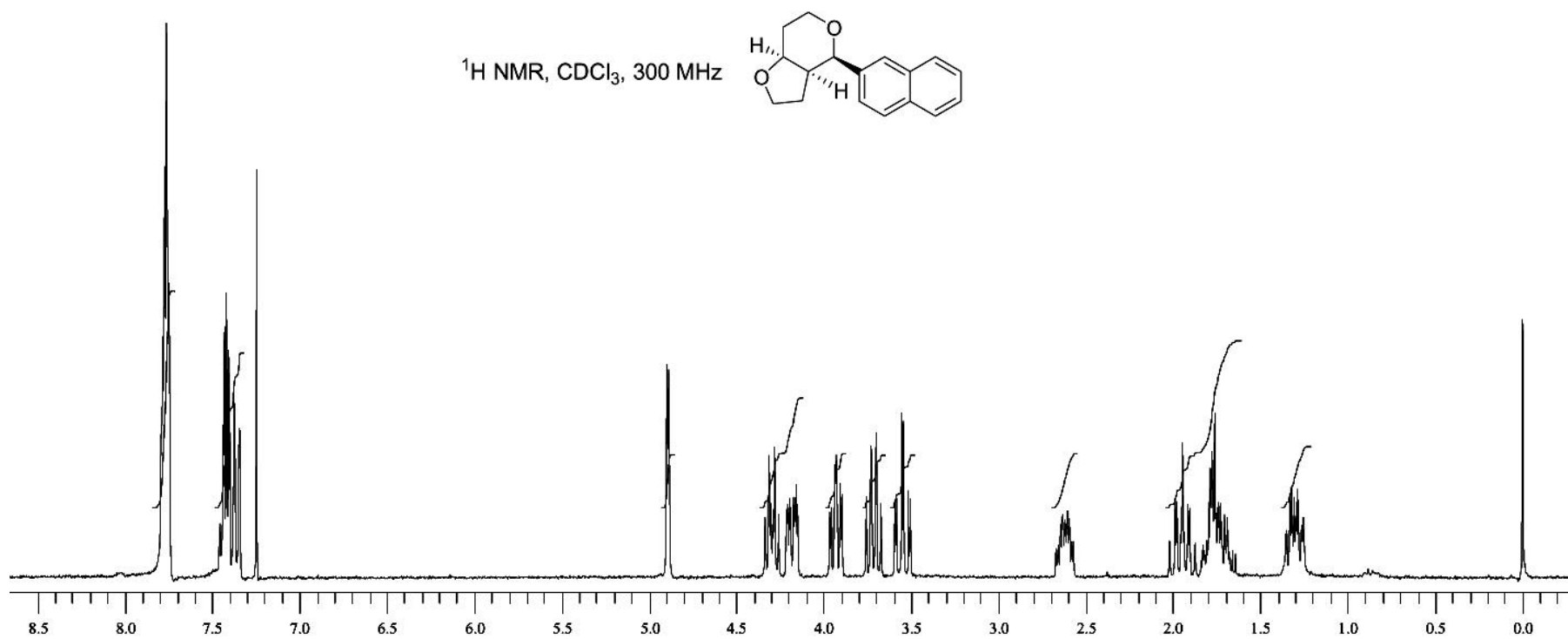


Product **2e** (Table 2, Entry e):

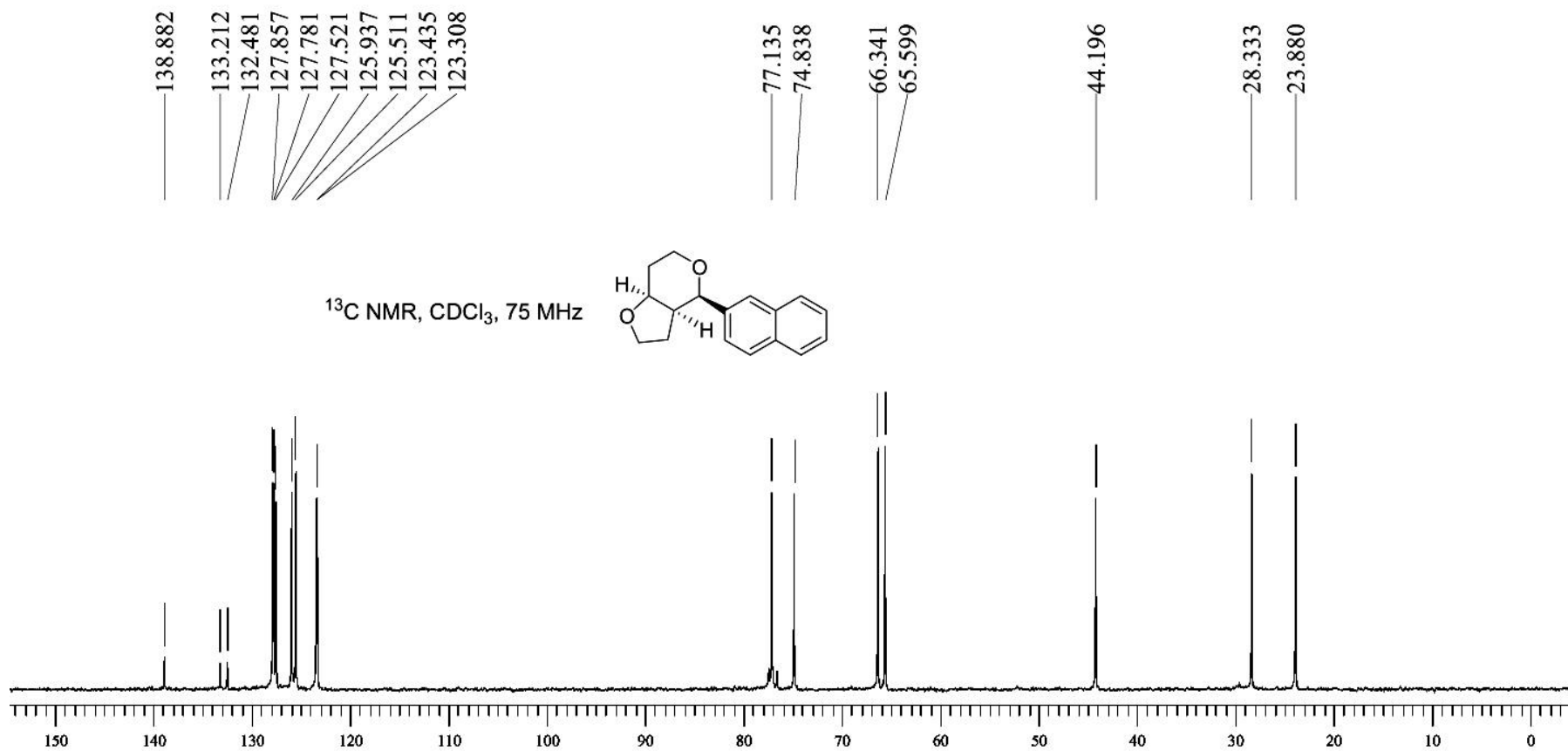




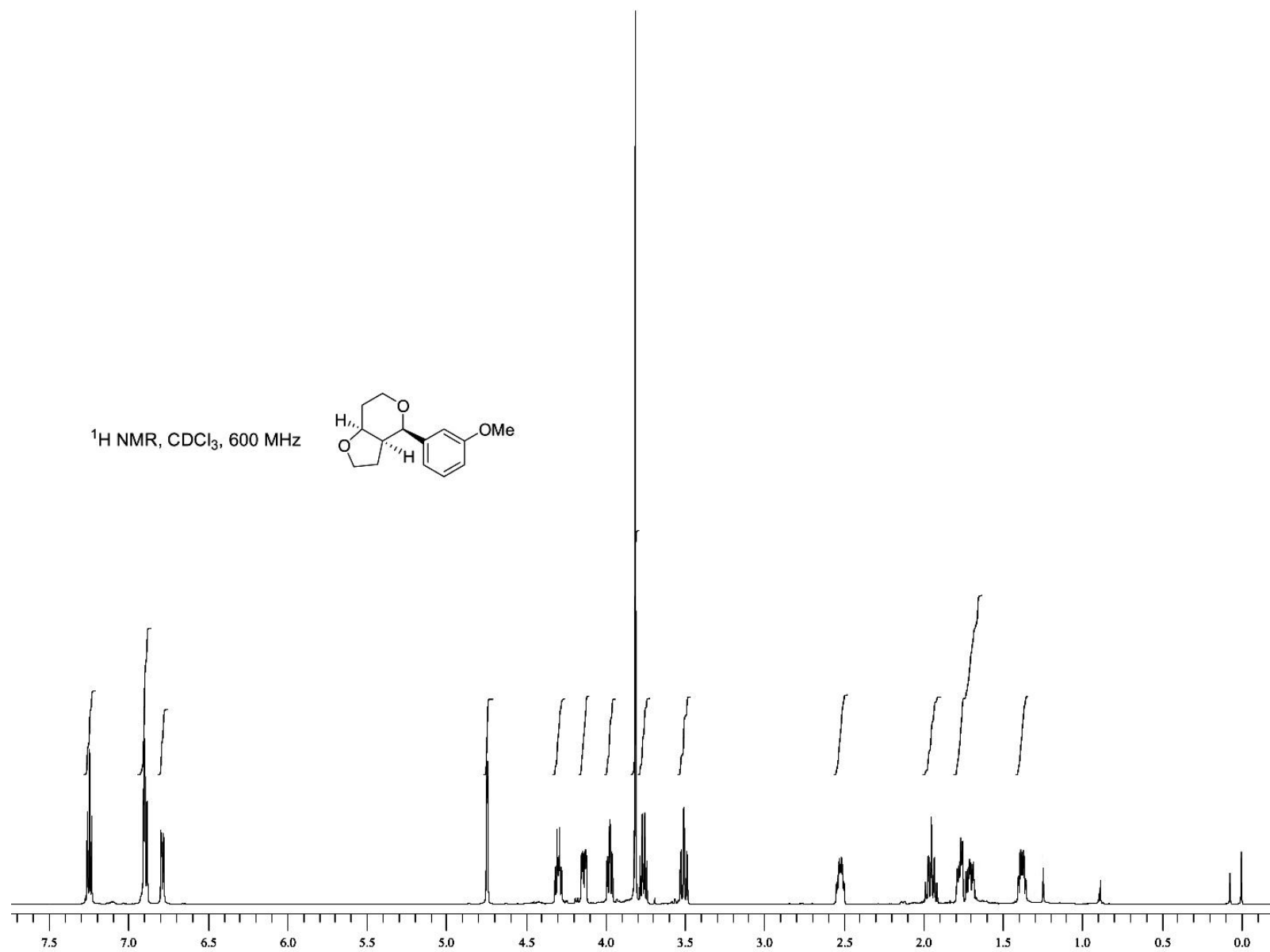
Product **2f** (Table 2, Entry f):

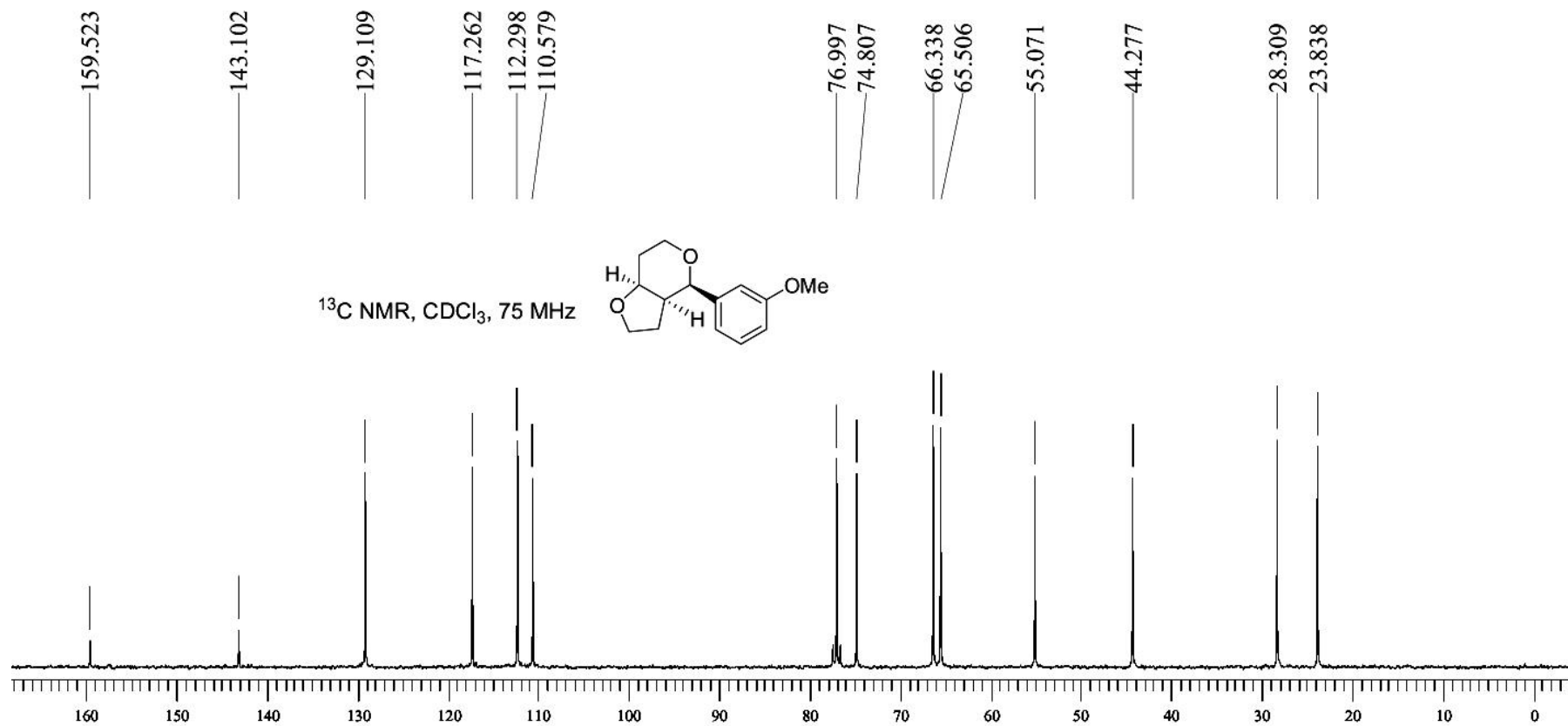






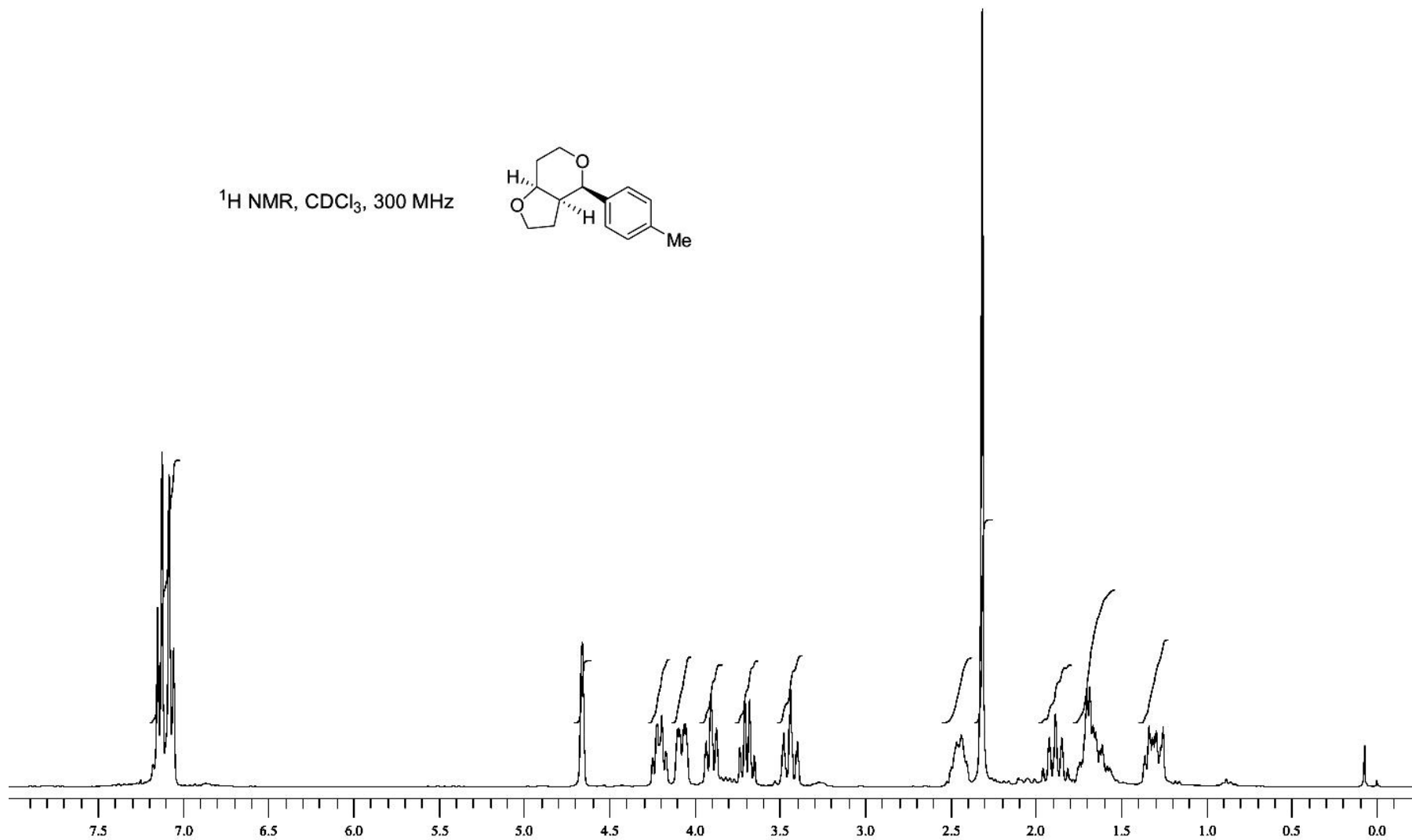
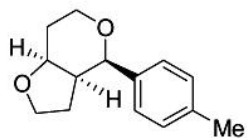
Product **2g** (Table 2, Entry **g**):

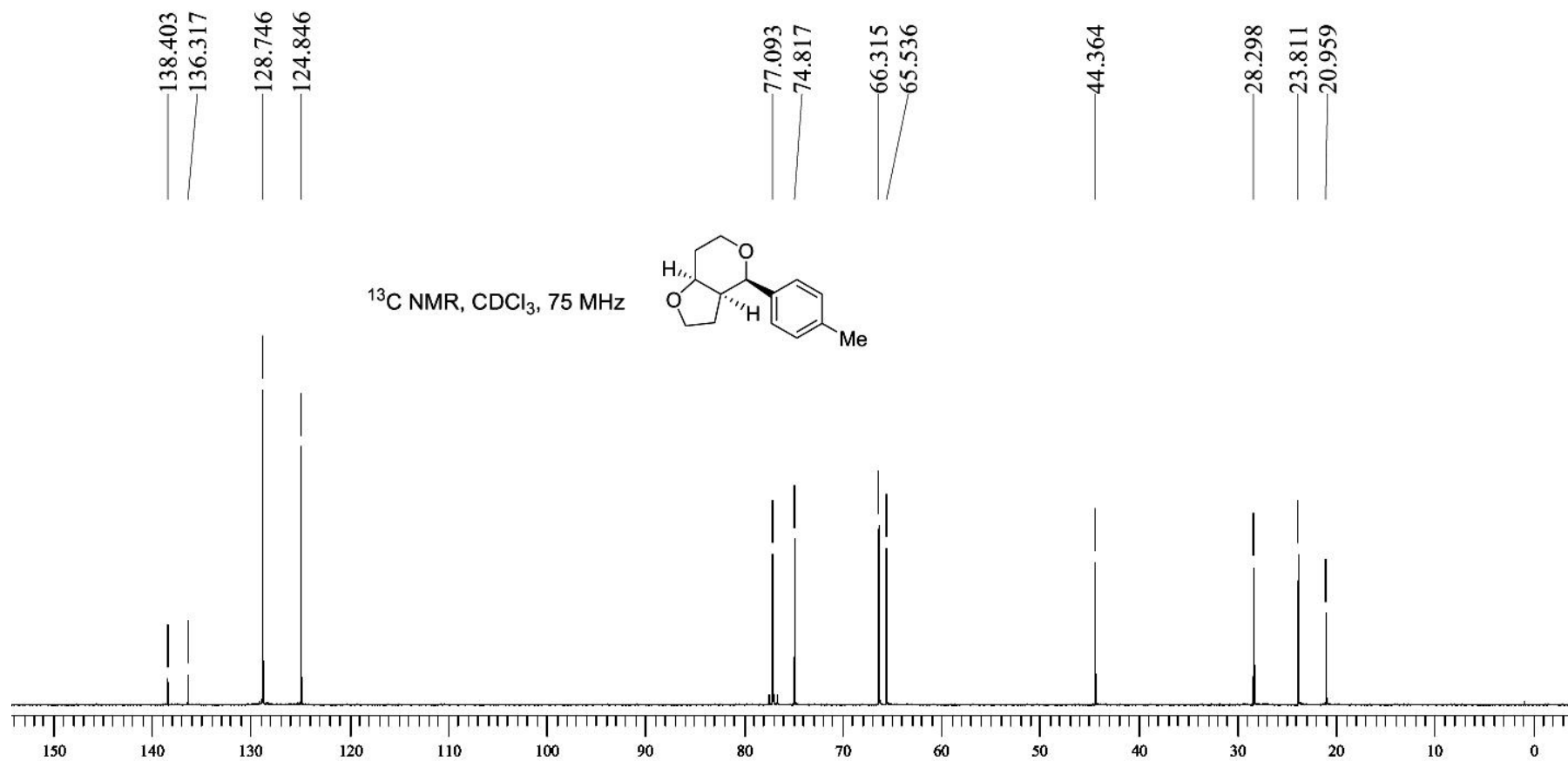




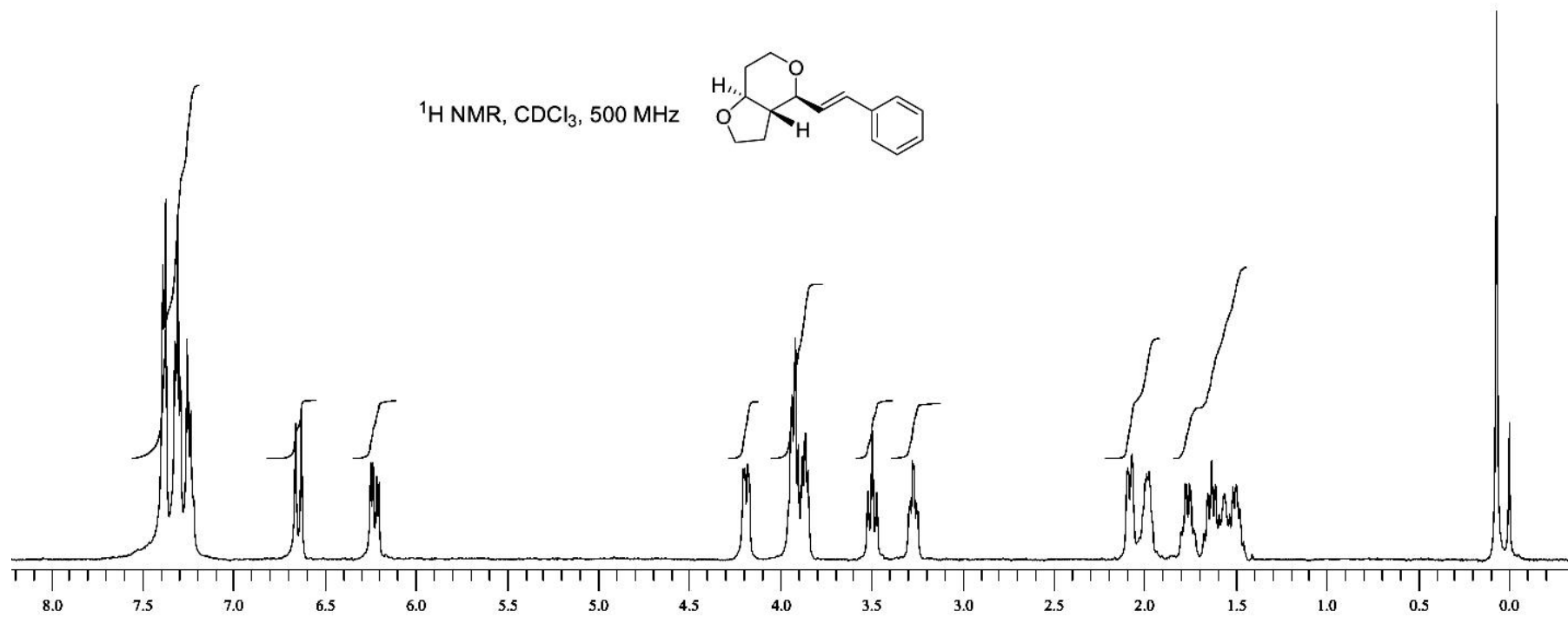
Product **2h** (Table 2, Entry **h**):

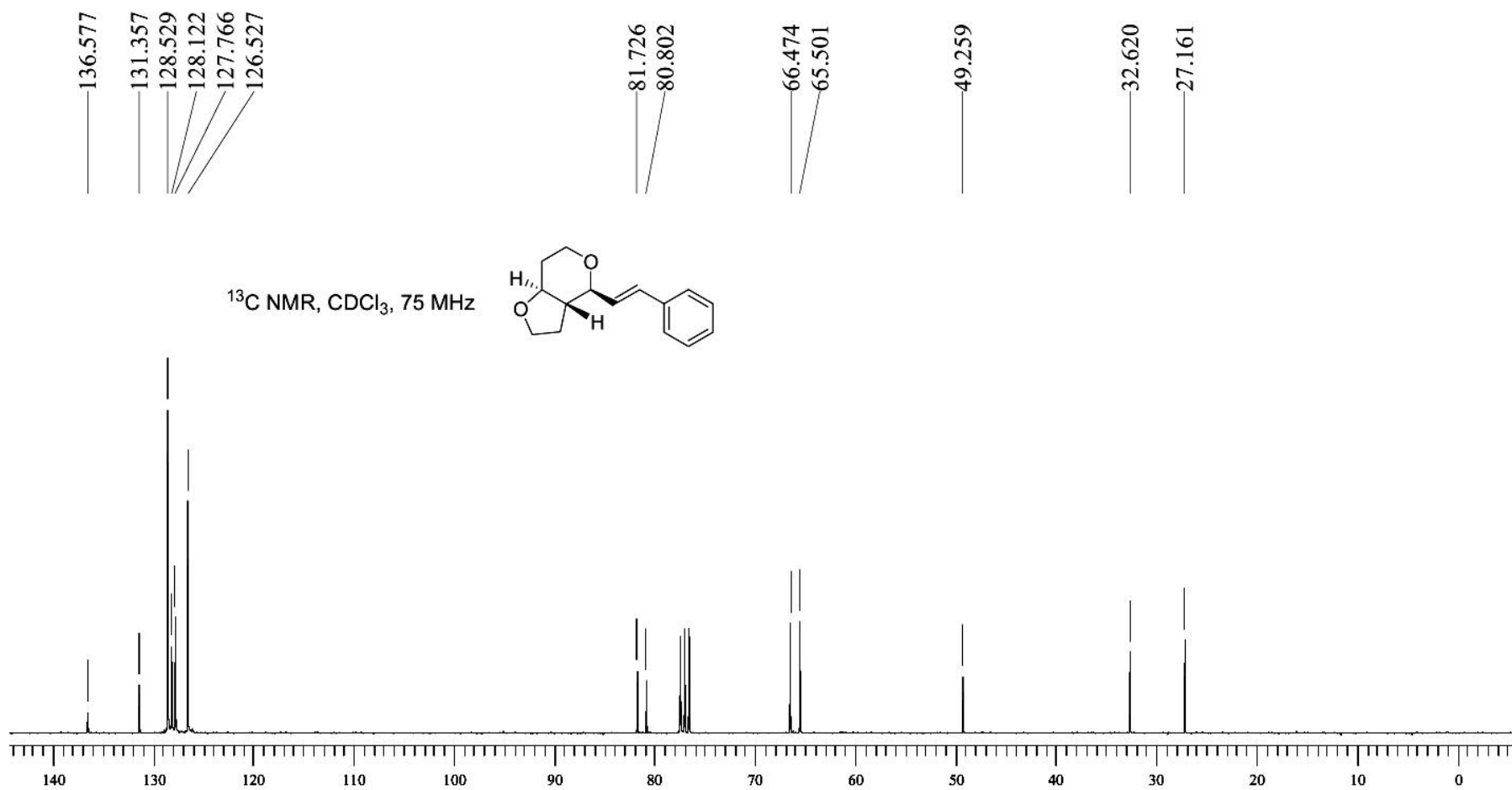
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 300 MHz



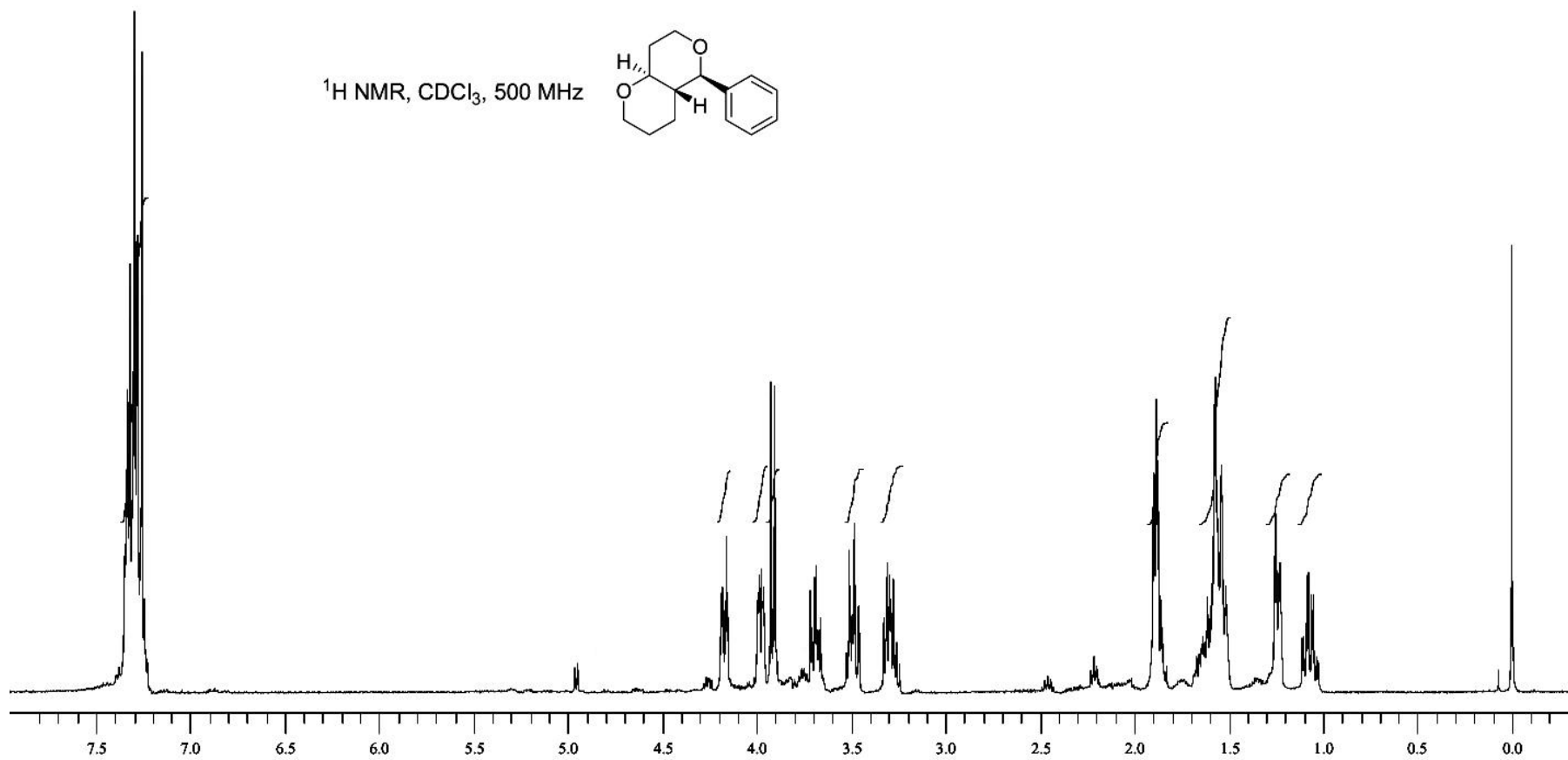


Product **2i** (Table 2, Entry **i**):

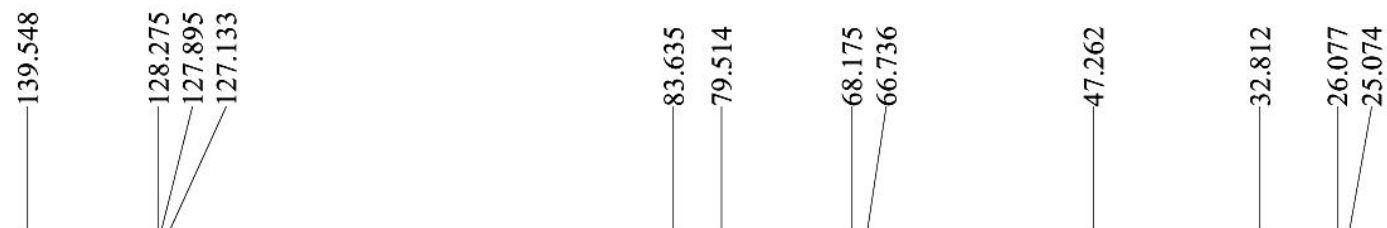




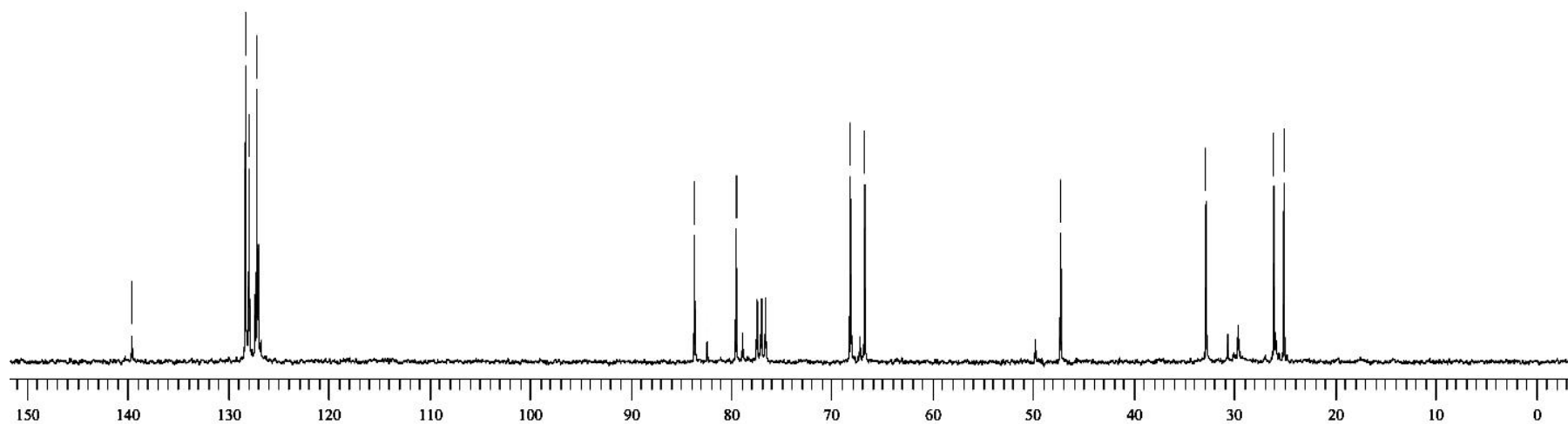
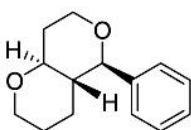
Product **4a** (Table 3, Entry a):





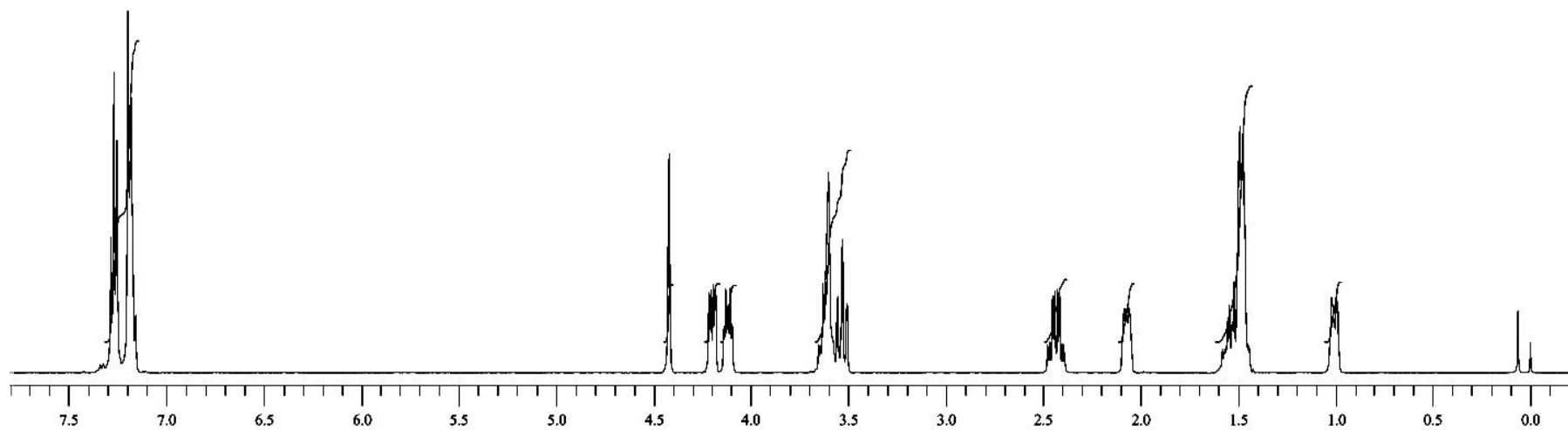
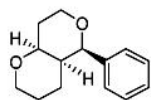


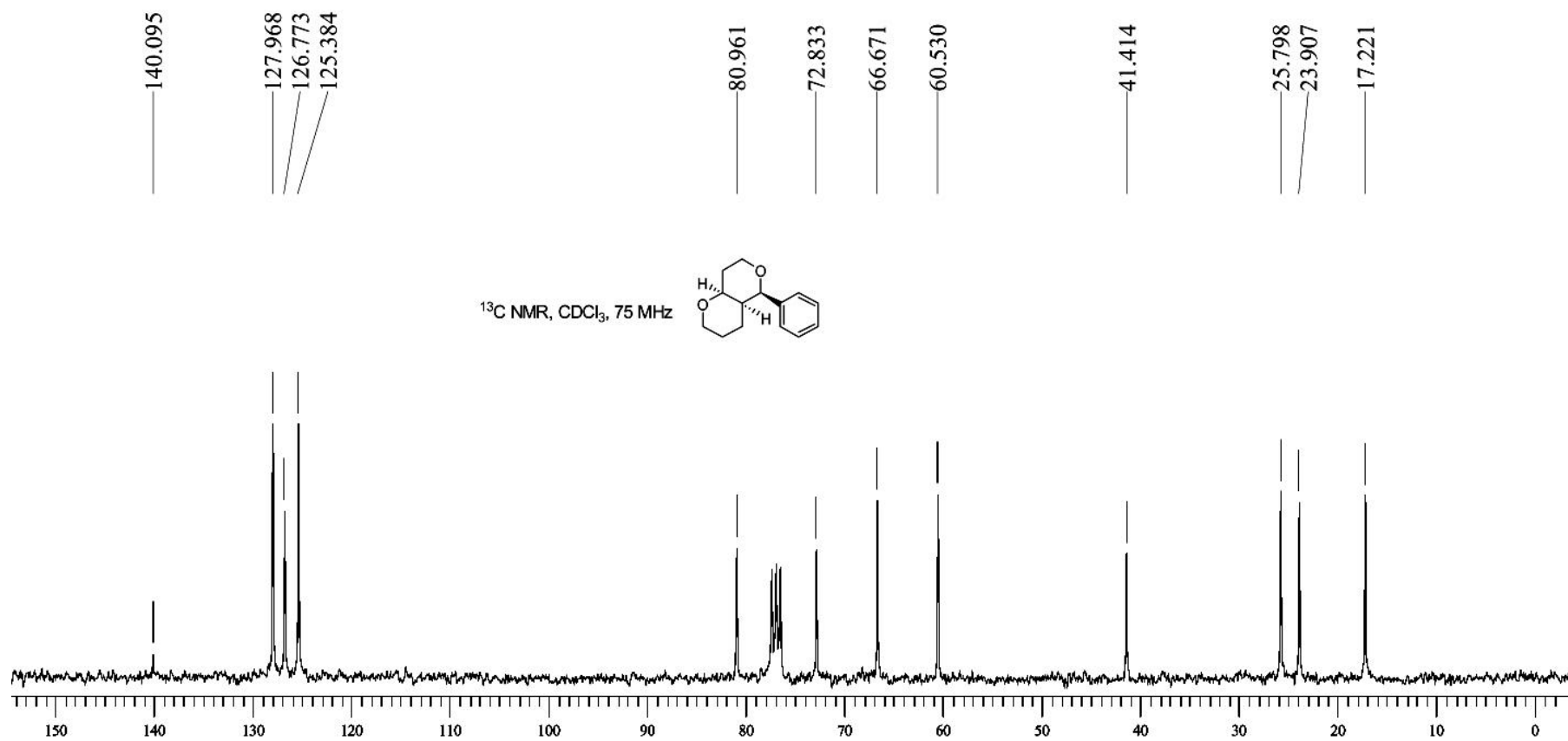
<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz



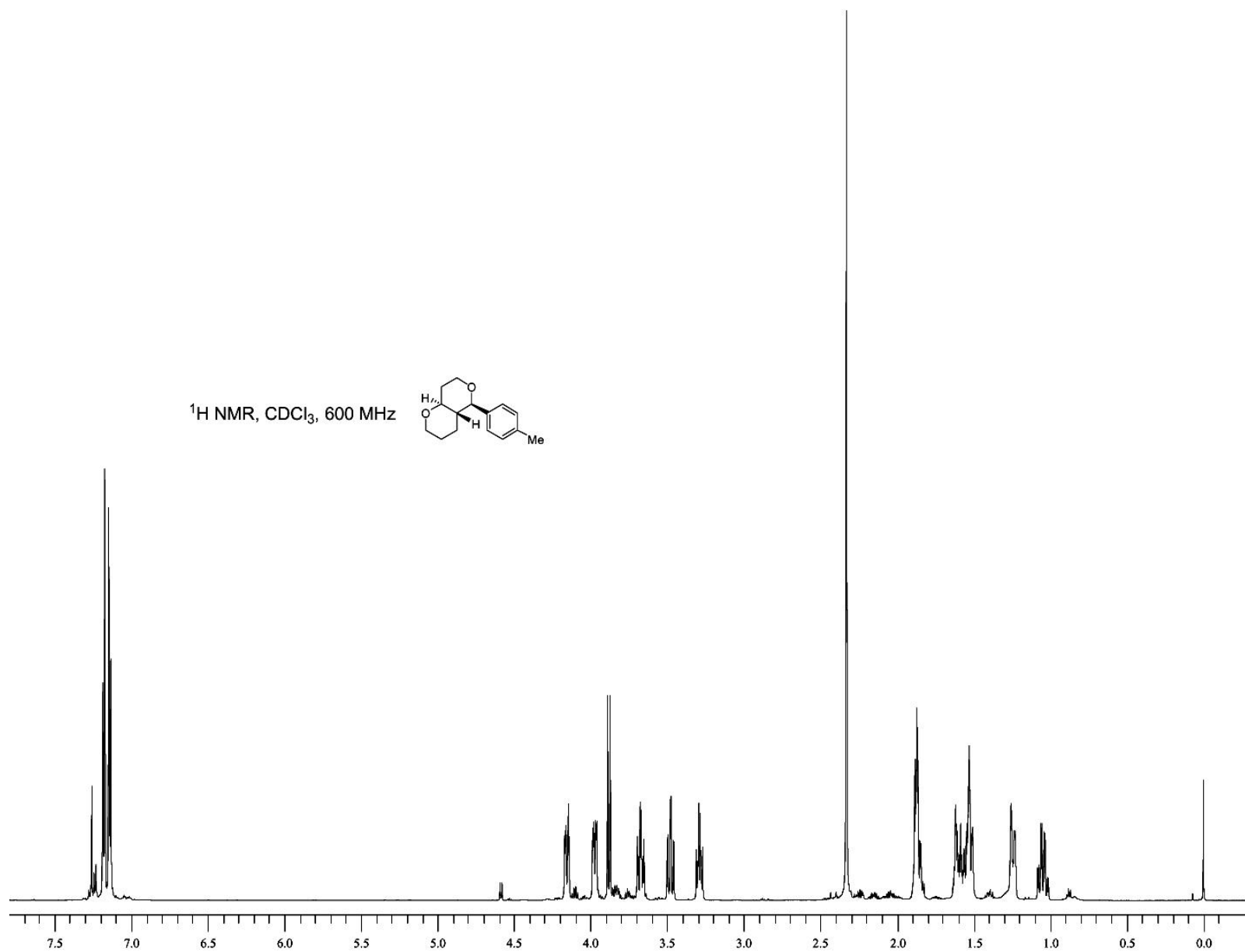
Product **4b** (Table 3, Entry **b**):

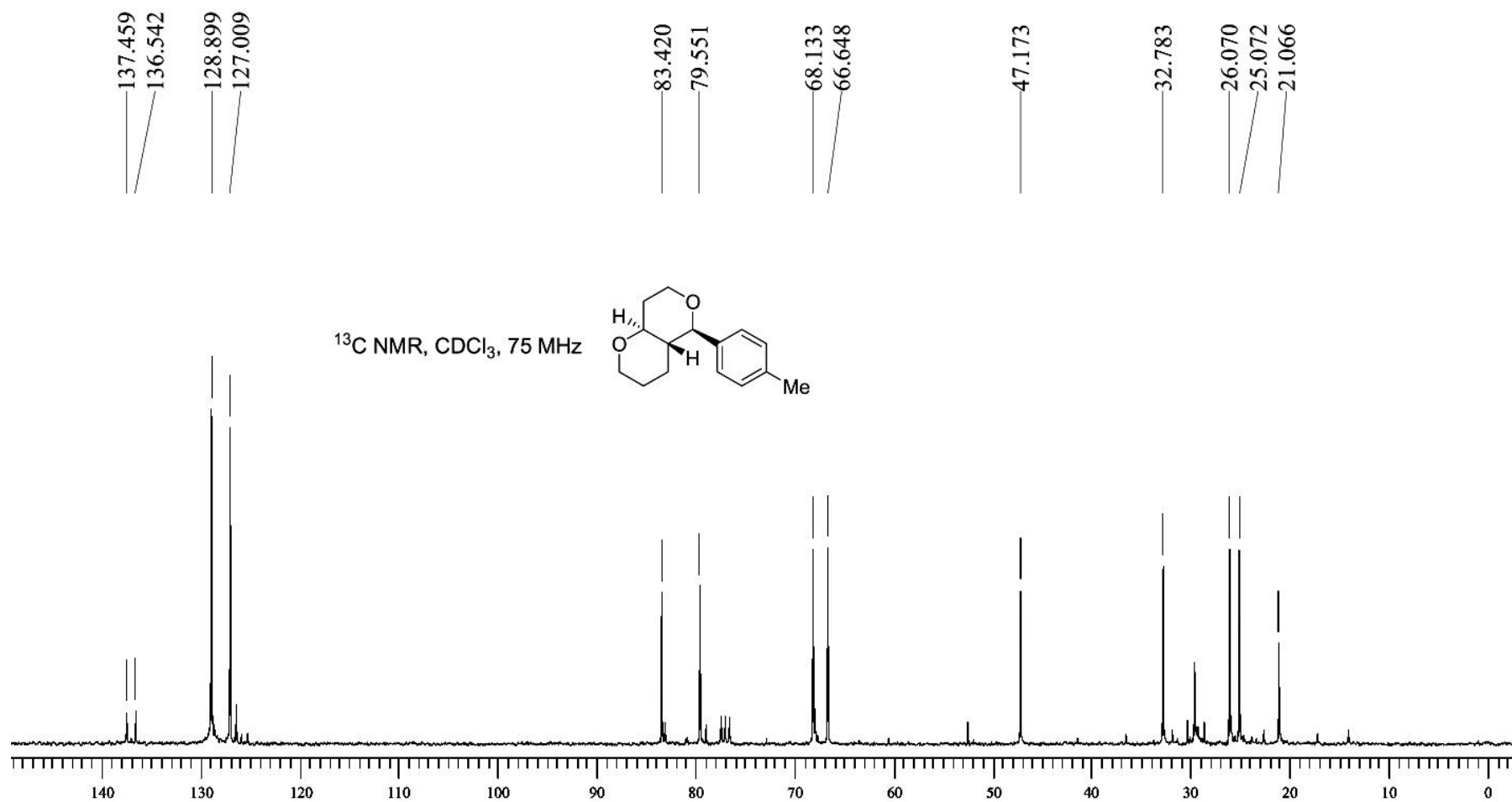
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 500 MHz



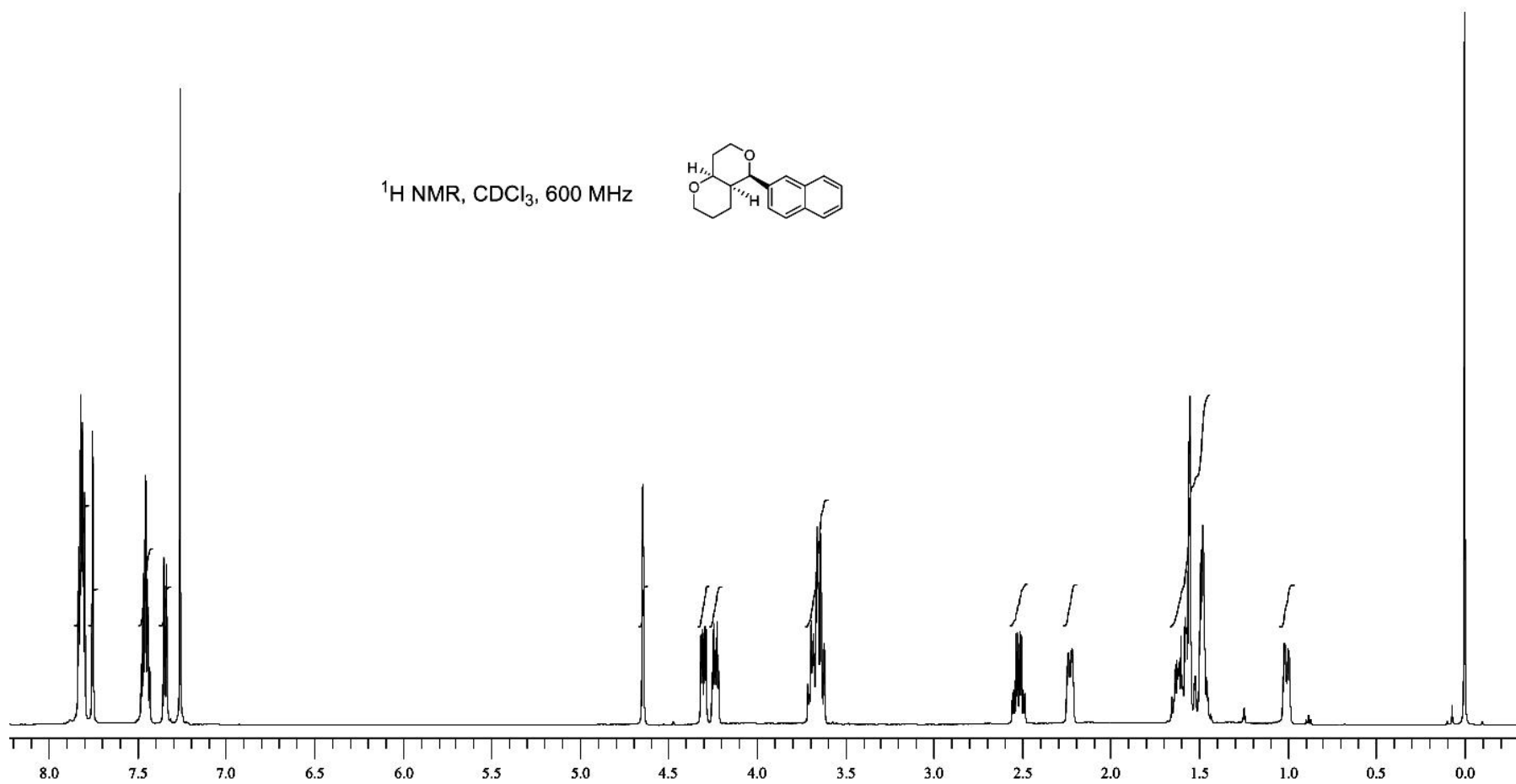


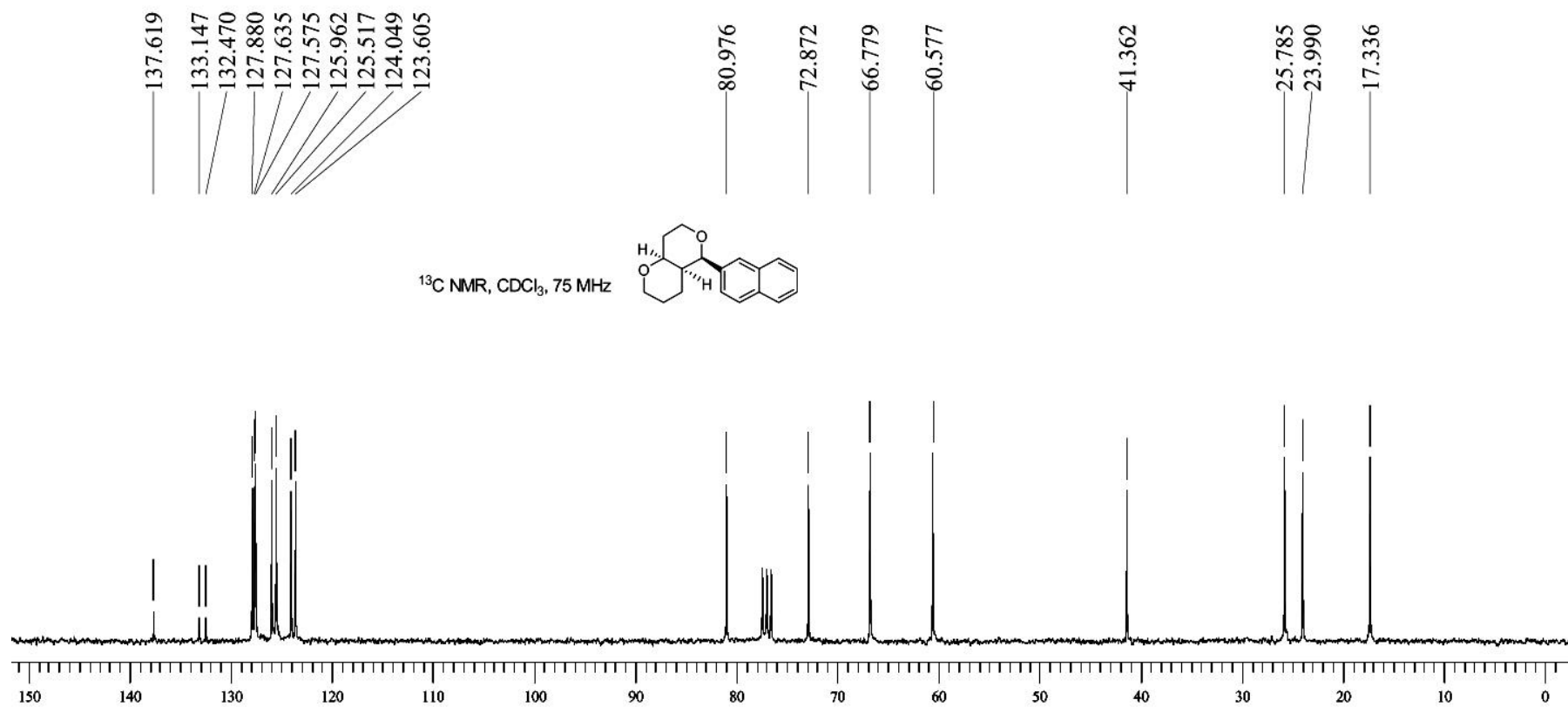
Product **4c** (Table 3, Entry c):



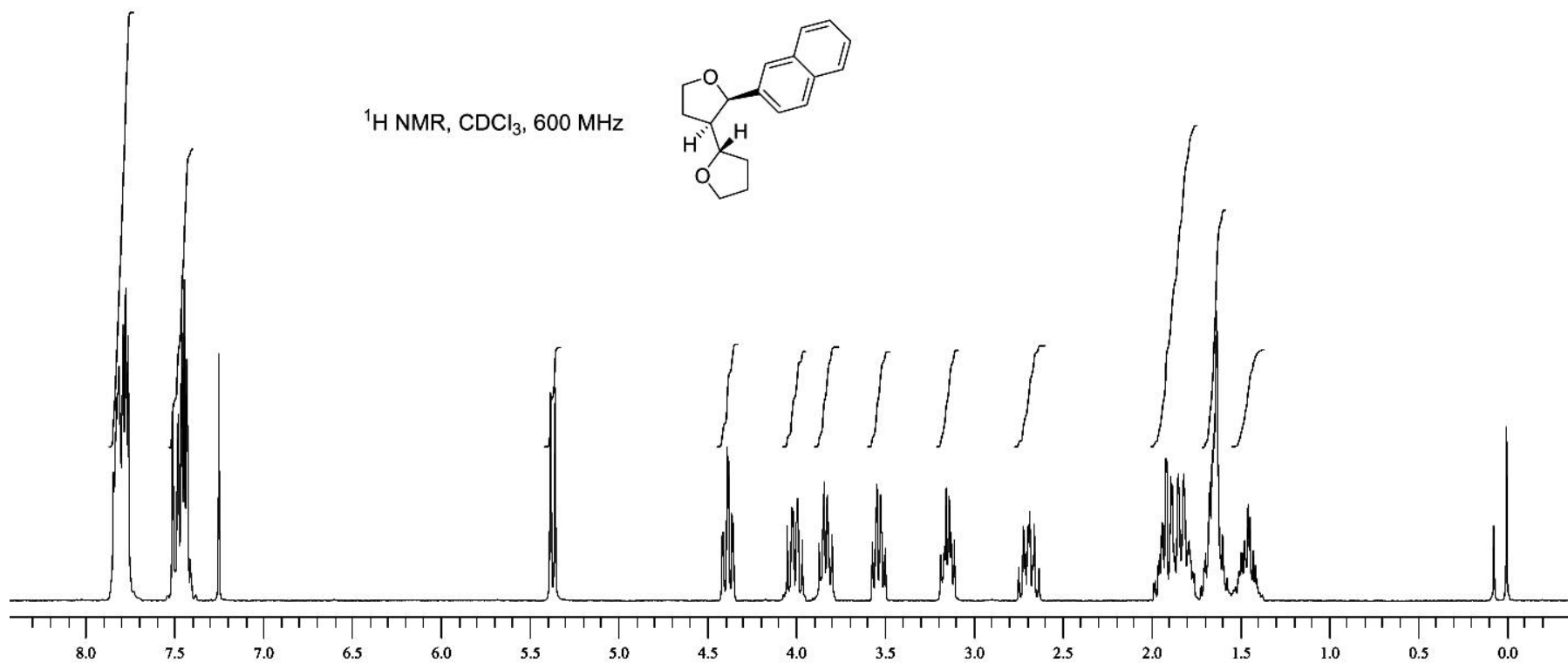


Product **4d** (Table 3, Entry **d**):

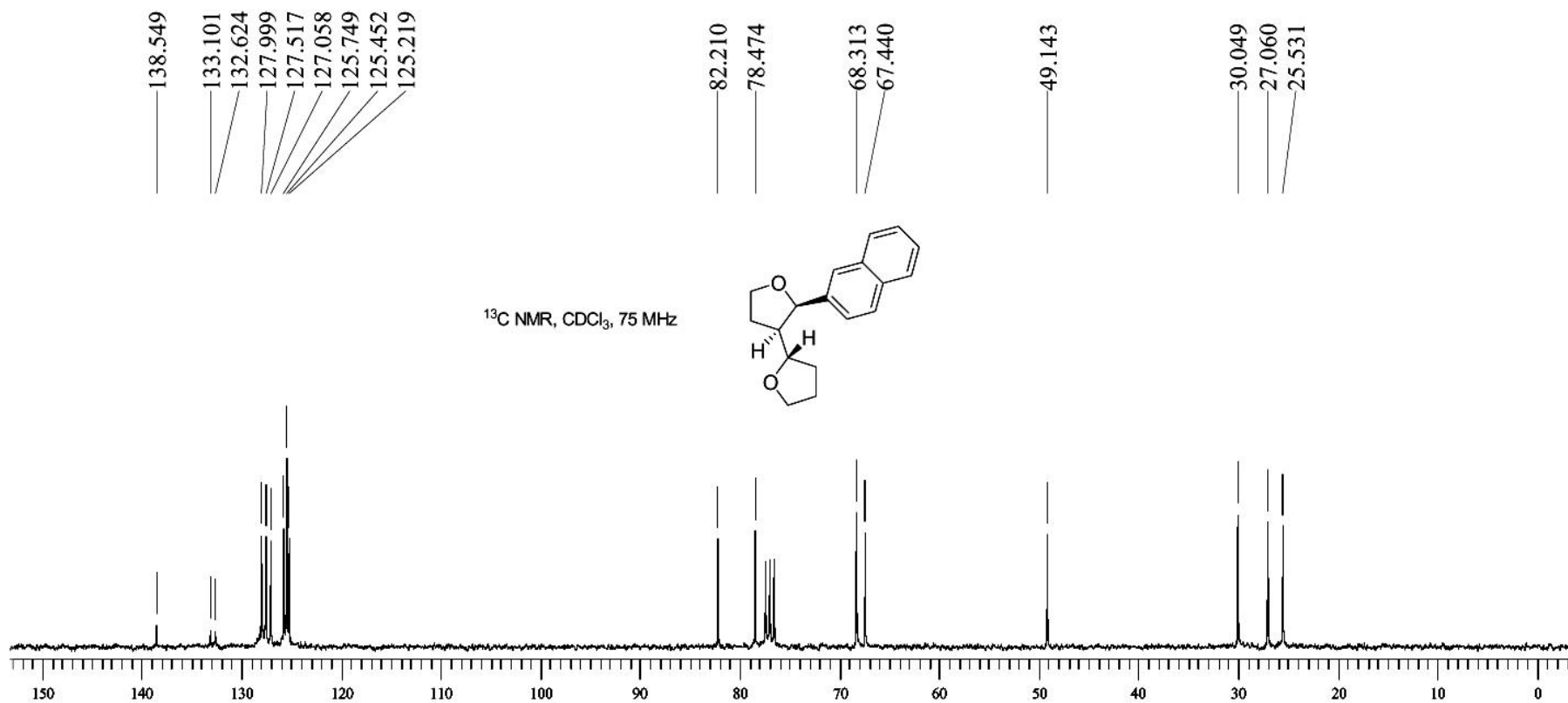




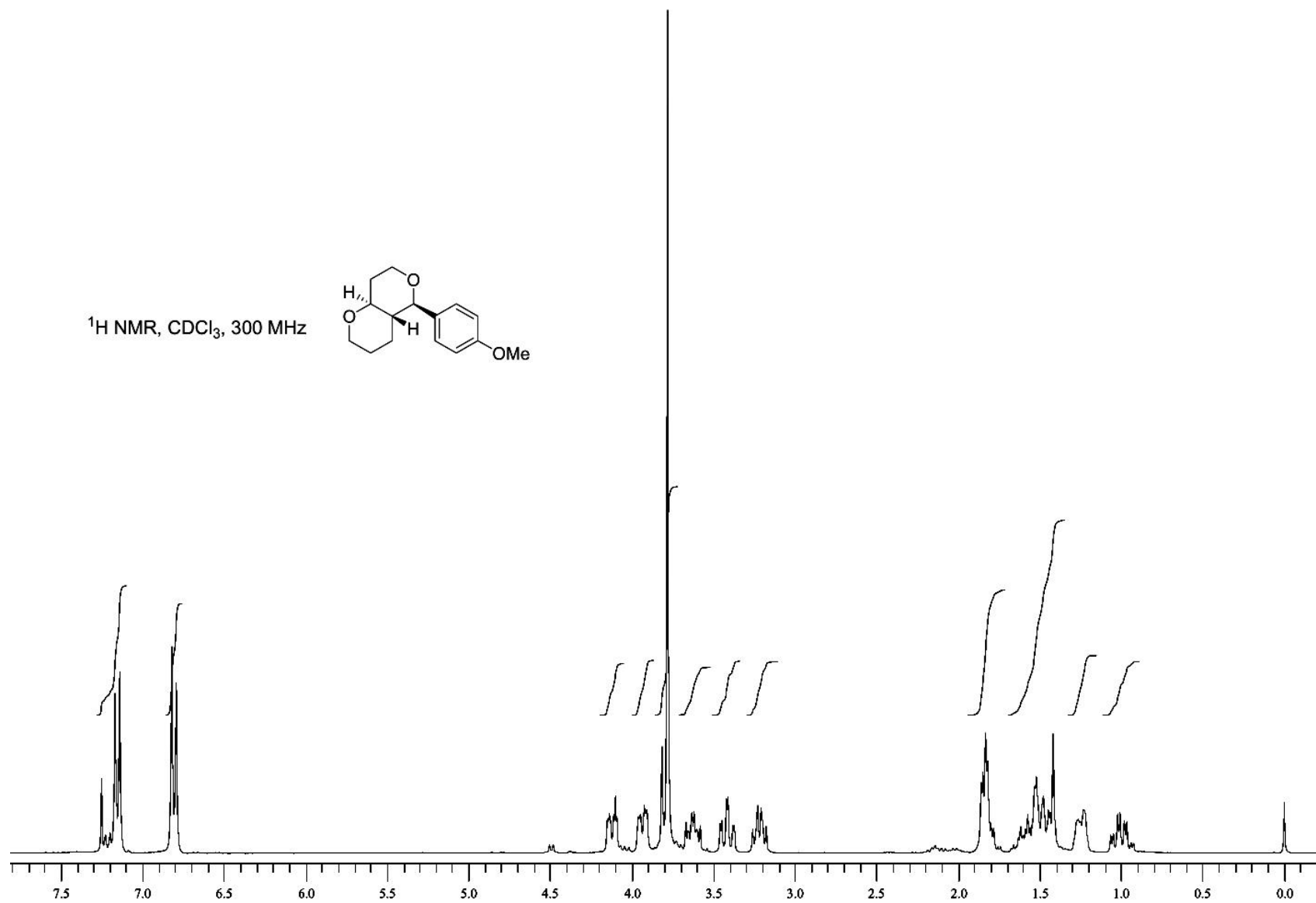
Minor Product **5d** (Table 3, Entry **d**):

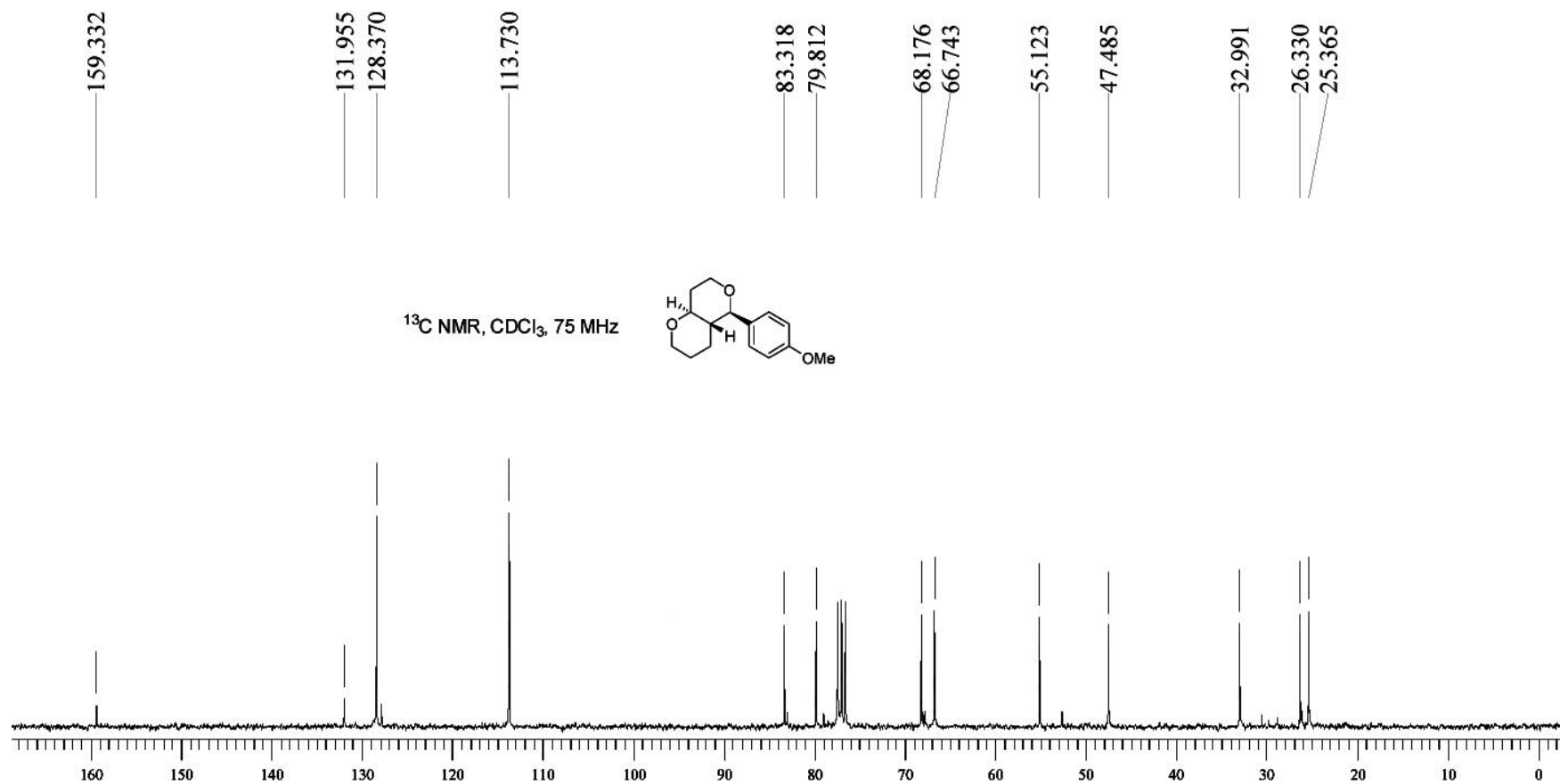




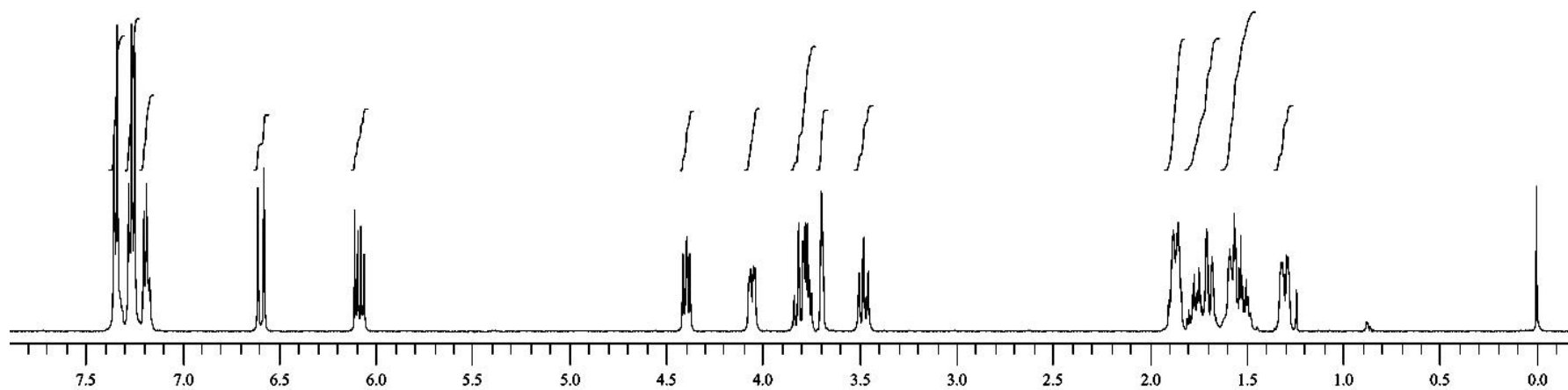
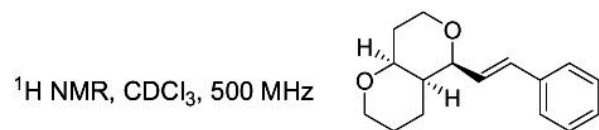


Product **4e** (Table 3, Entry e):





Product **4f** (Table 3, Entry **f**):

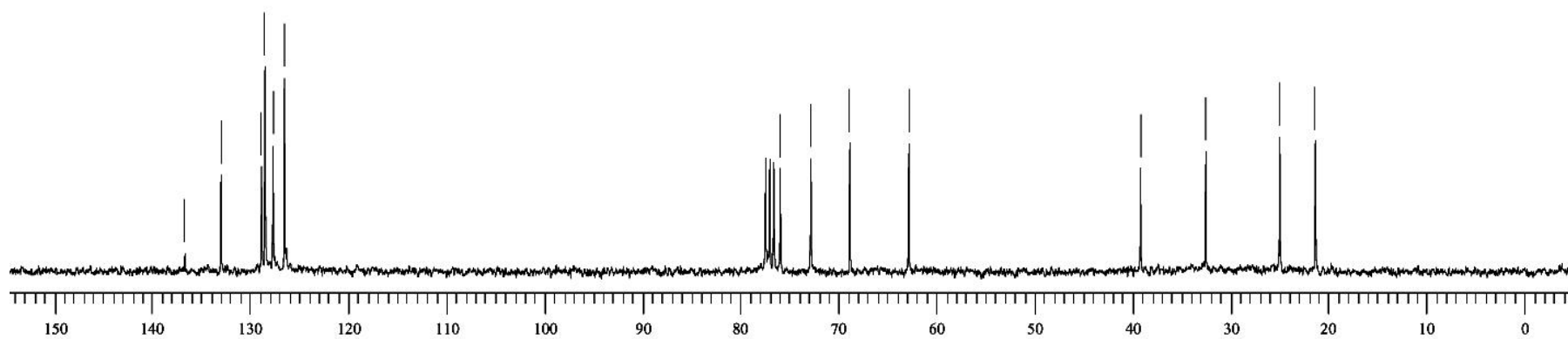
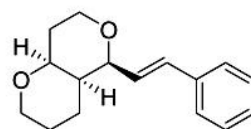


136.657  
132.980  
128.828  
128.478  
127.669  
126.508

75.922  
72.810  
68.824  
62.817

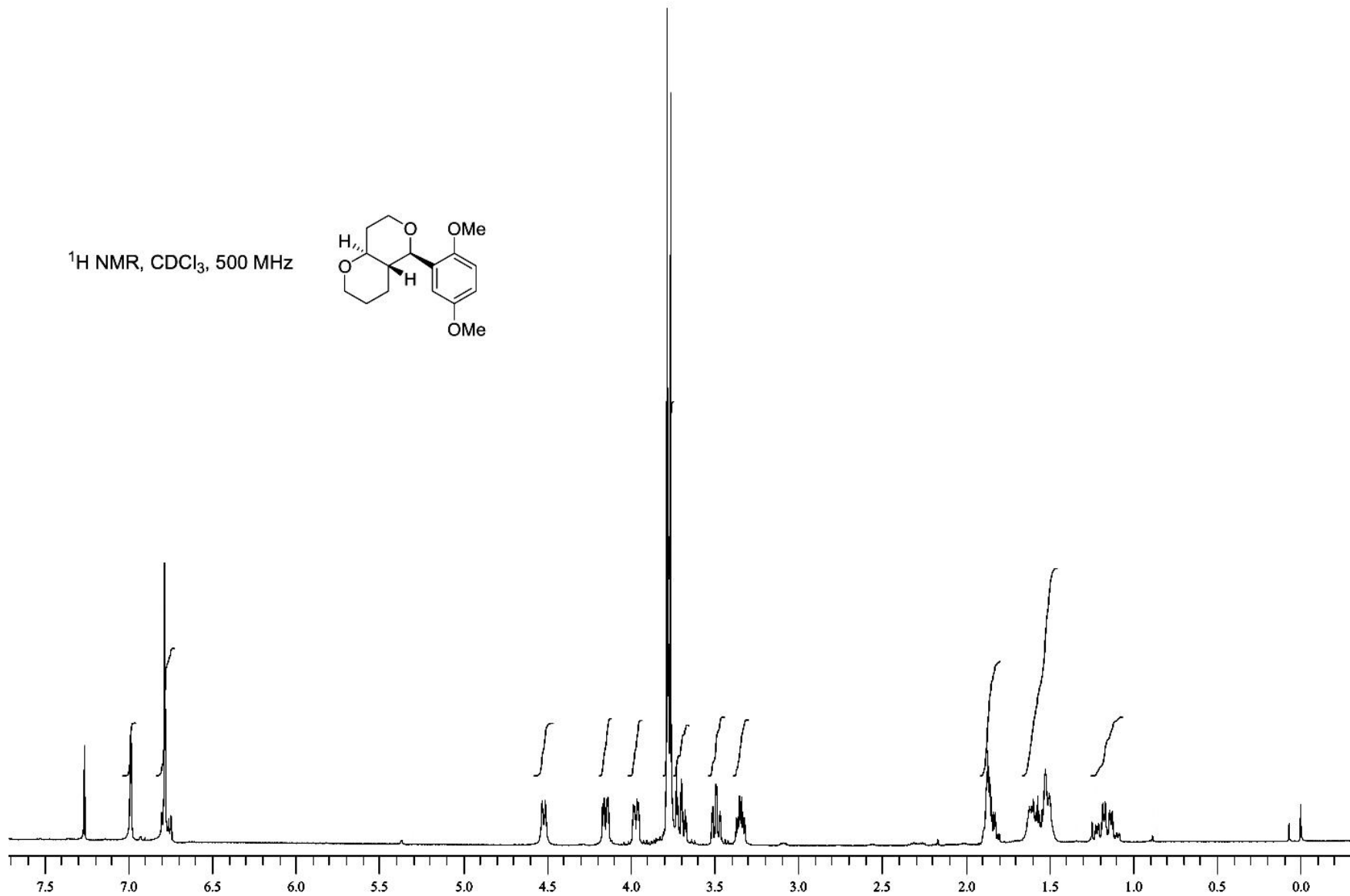
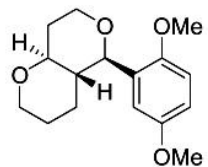
39.166  
32.511  
24.970  
21.327

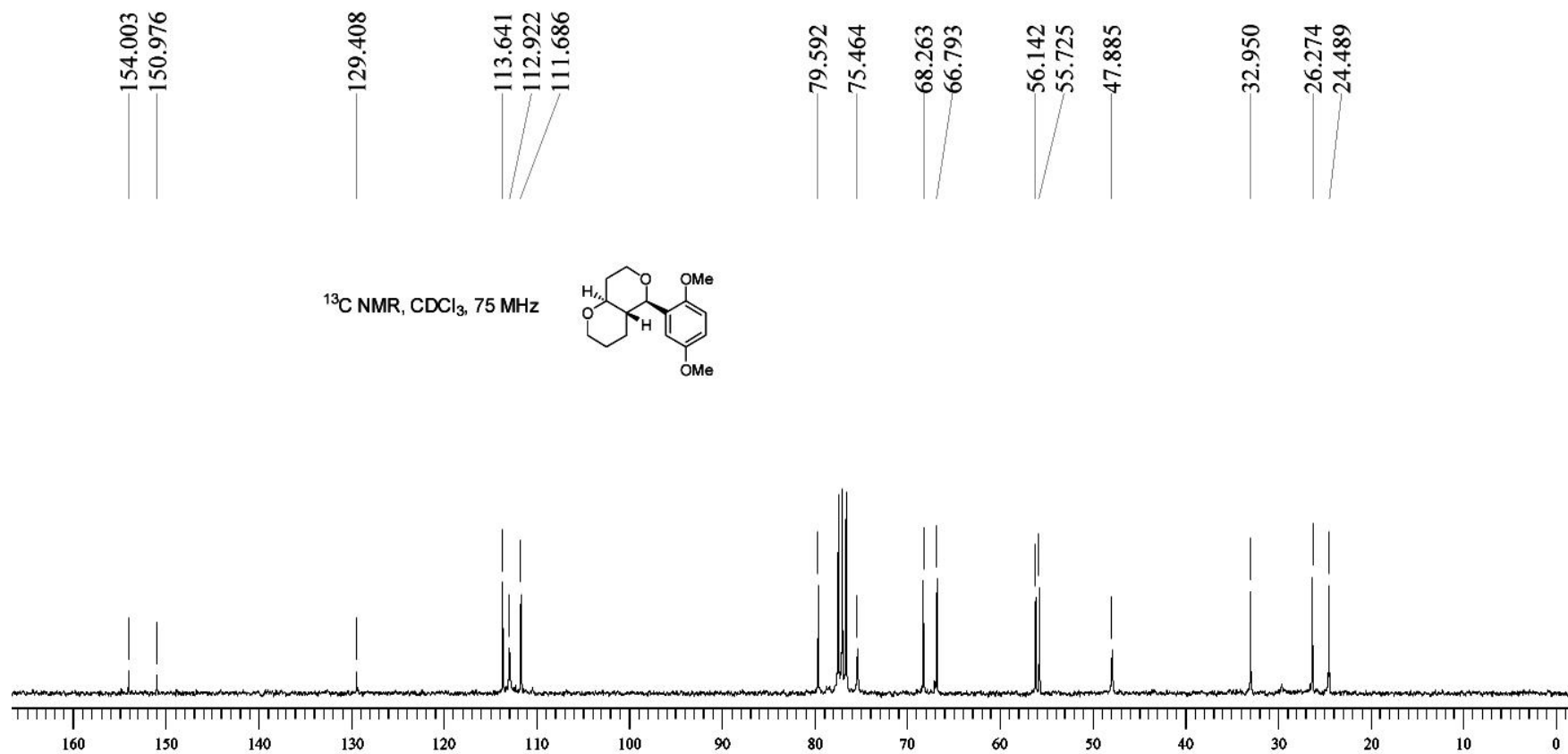
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz



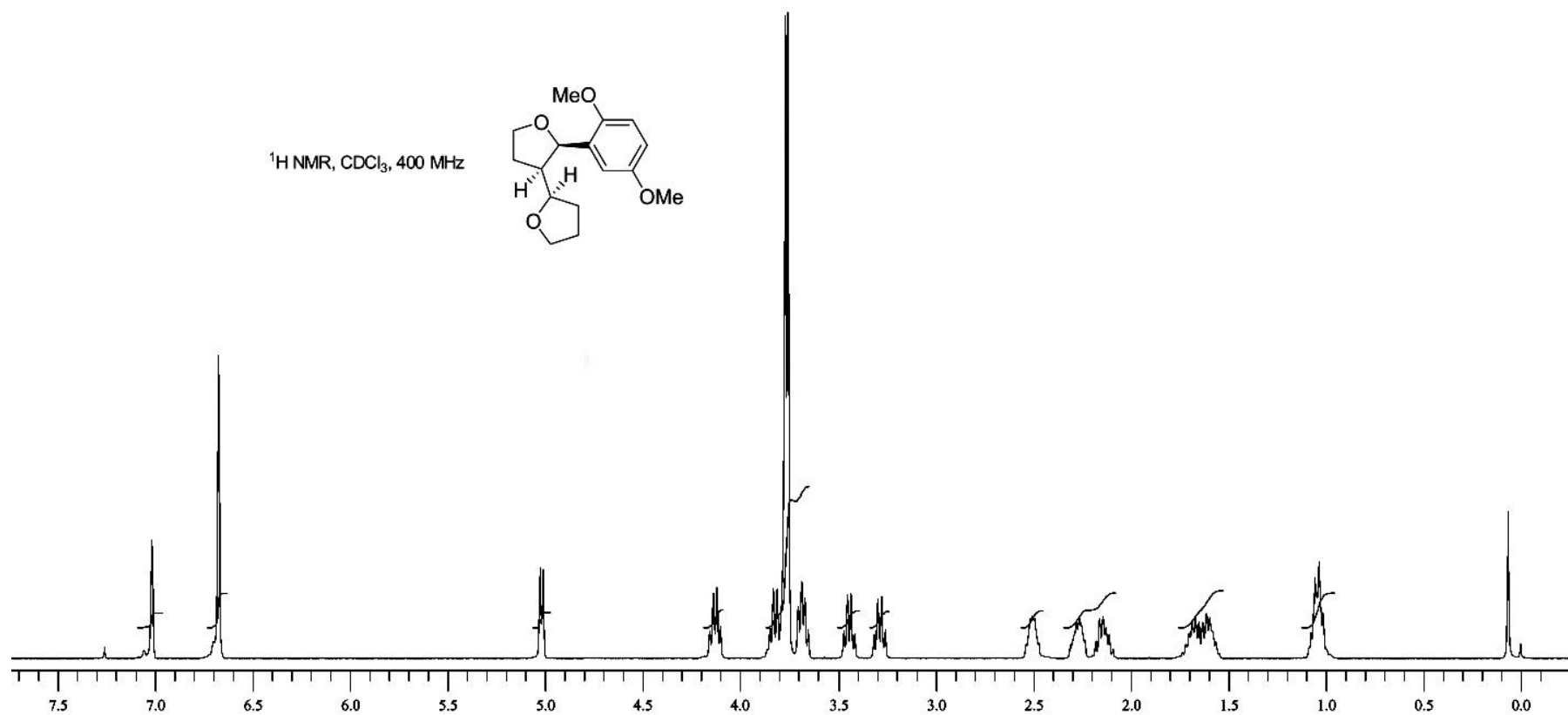
Product **4g** (Table 3, Entry **g**):

$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 500 MHz

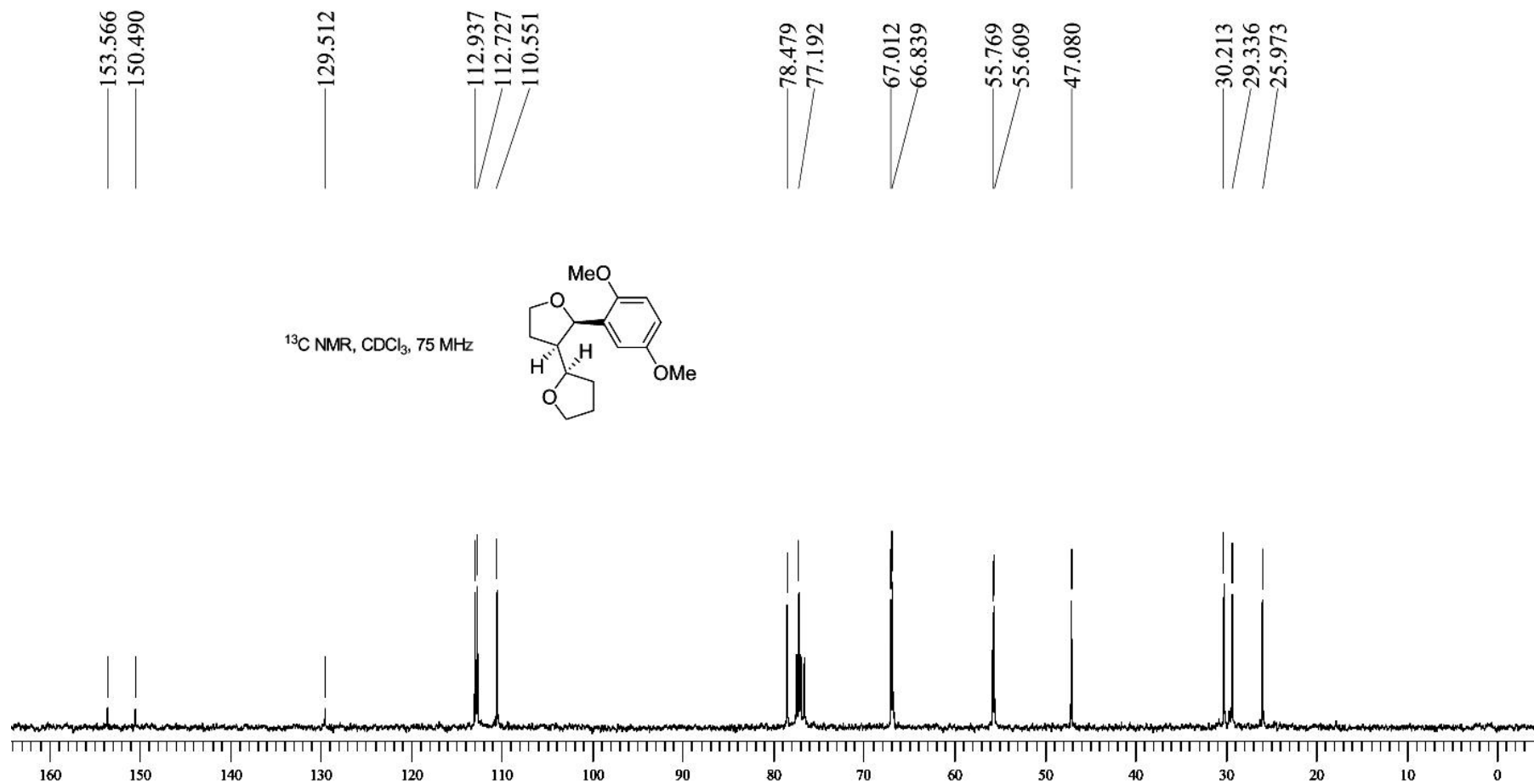




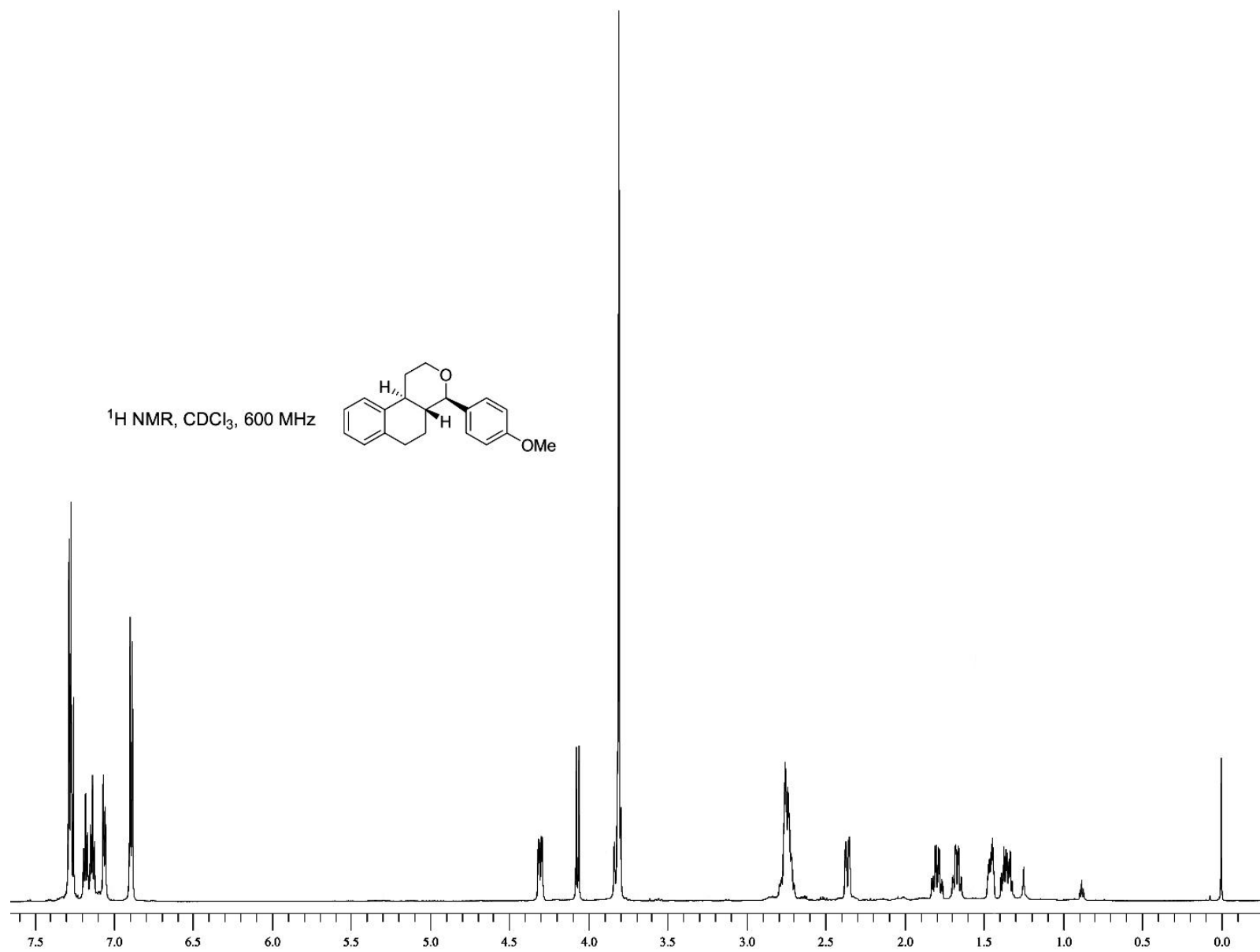
Minor Product **5g** (Table 3, Entry g):

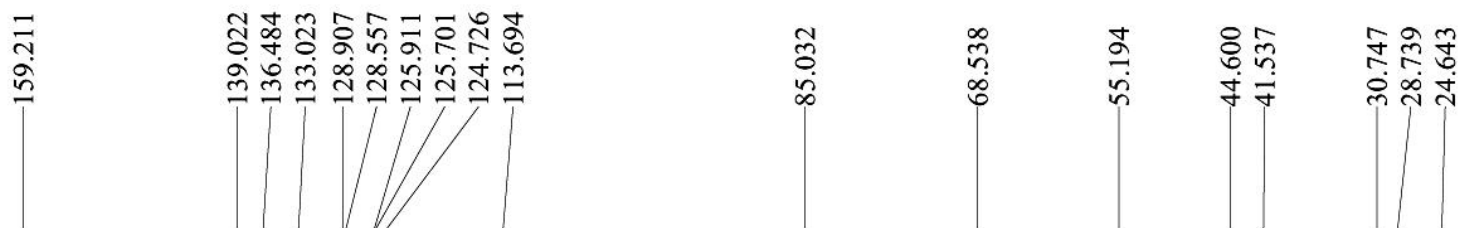




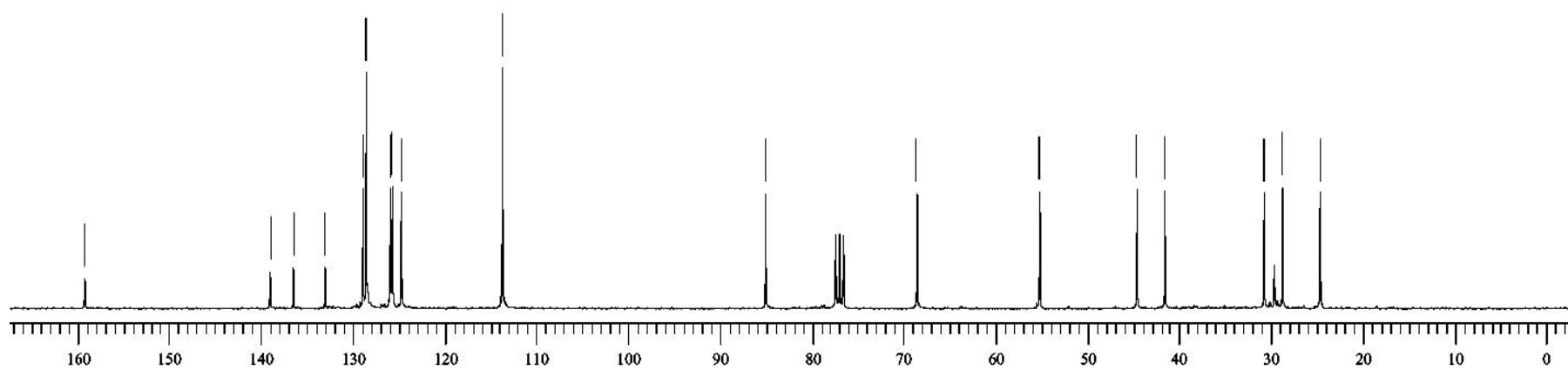
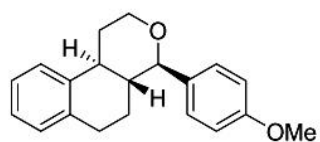


Product **7a** (Table 4, Entry a):

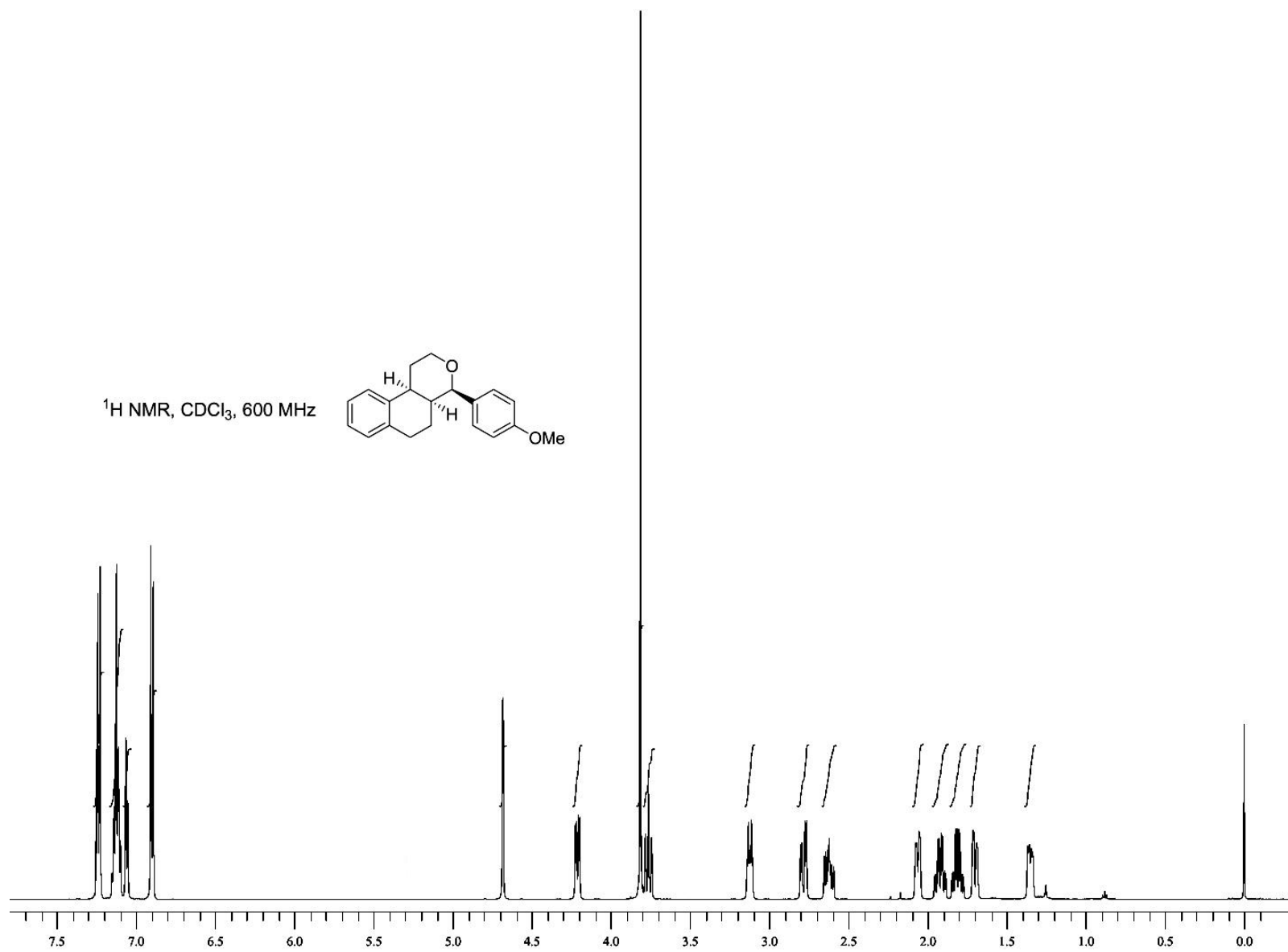


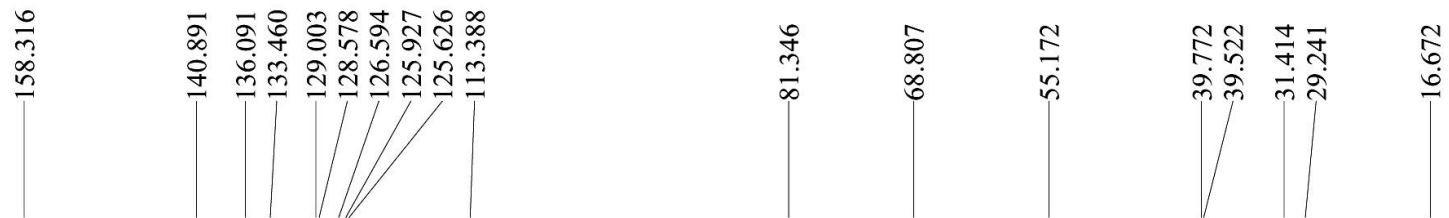


<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz

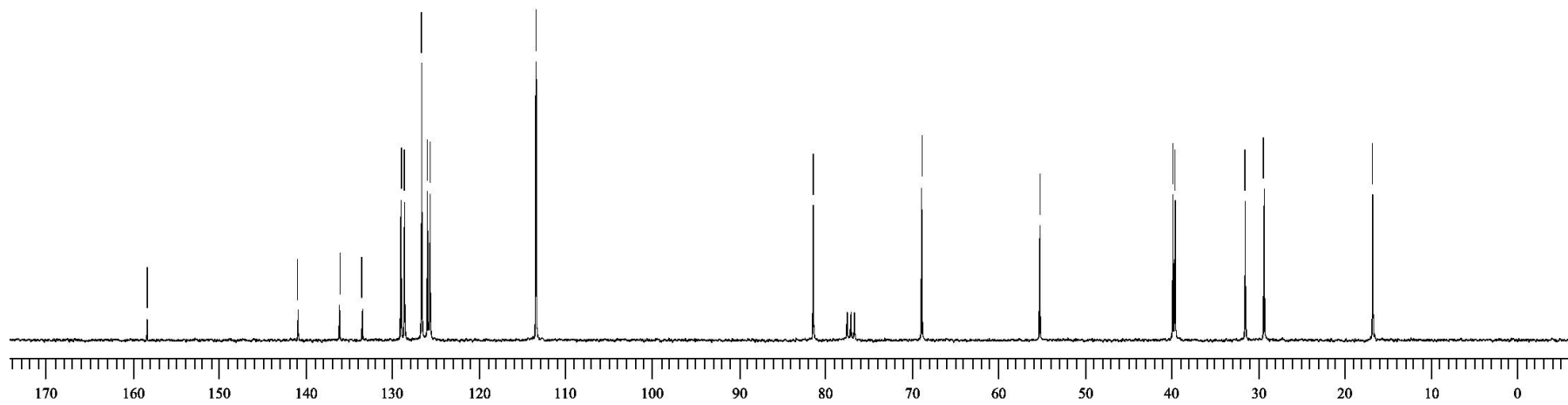
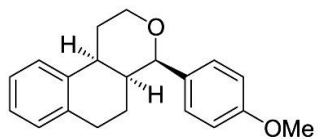


Product **7b** (Table 4, Entry **b**):

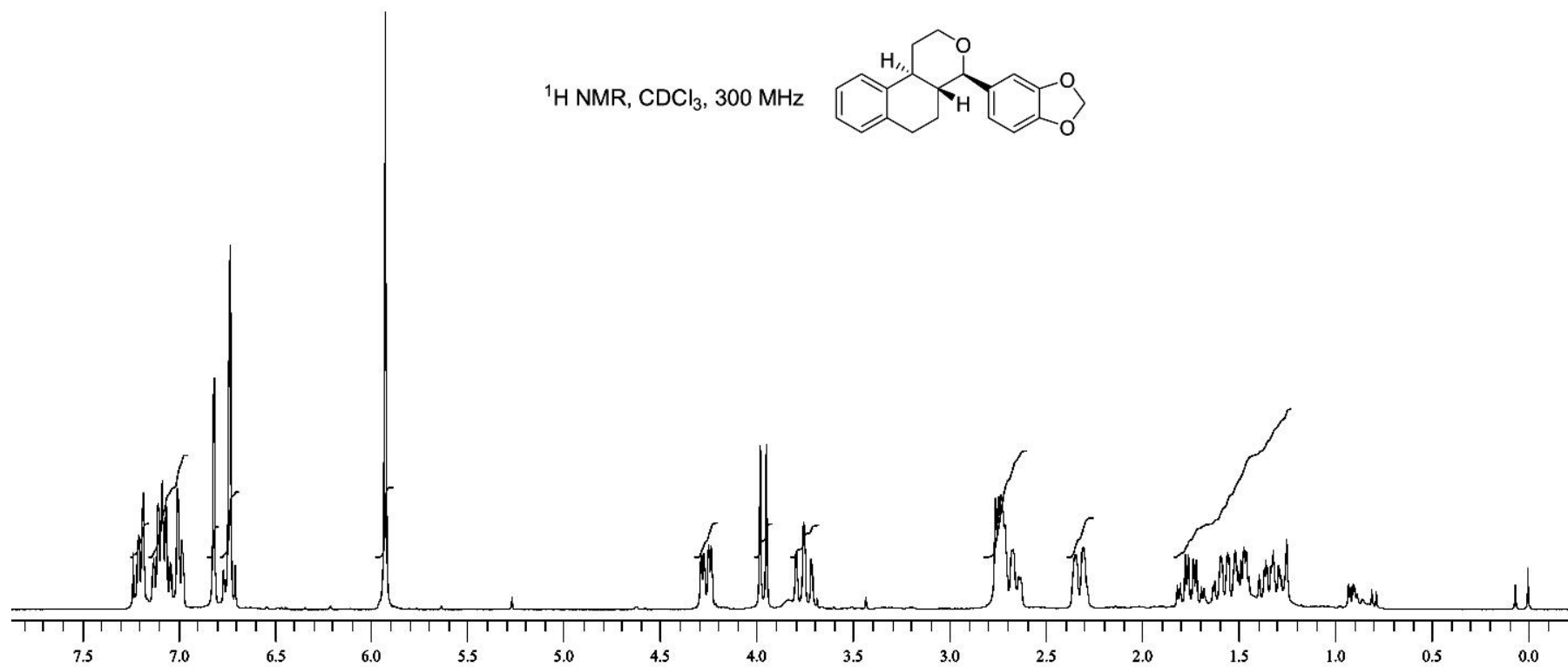


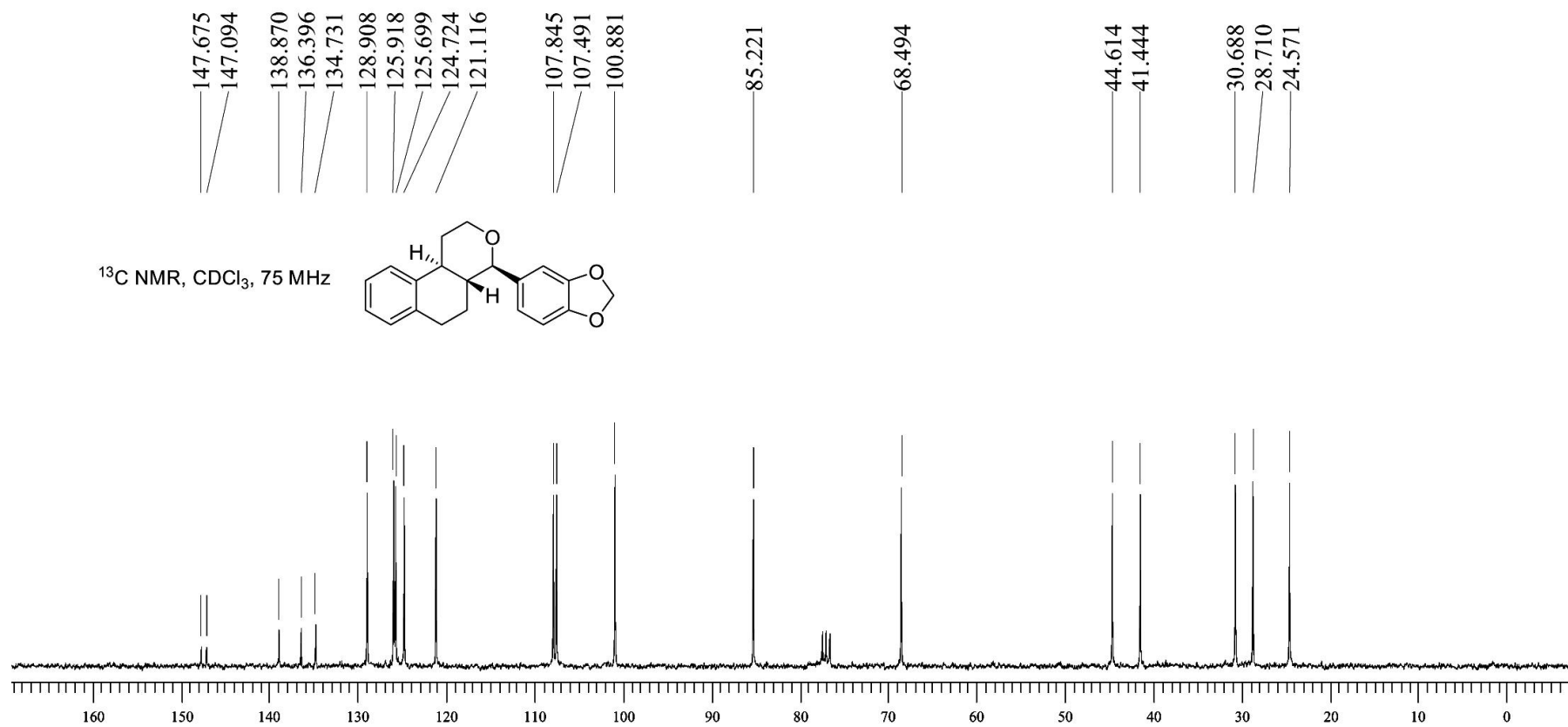


$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 75 MHz

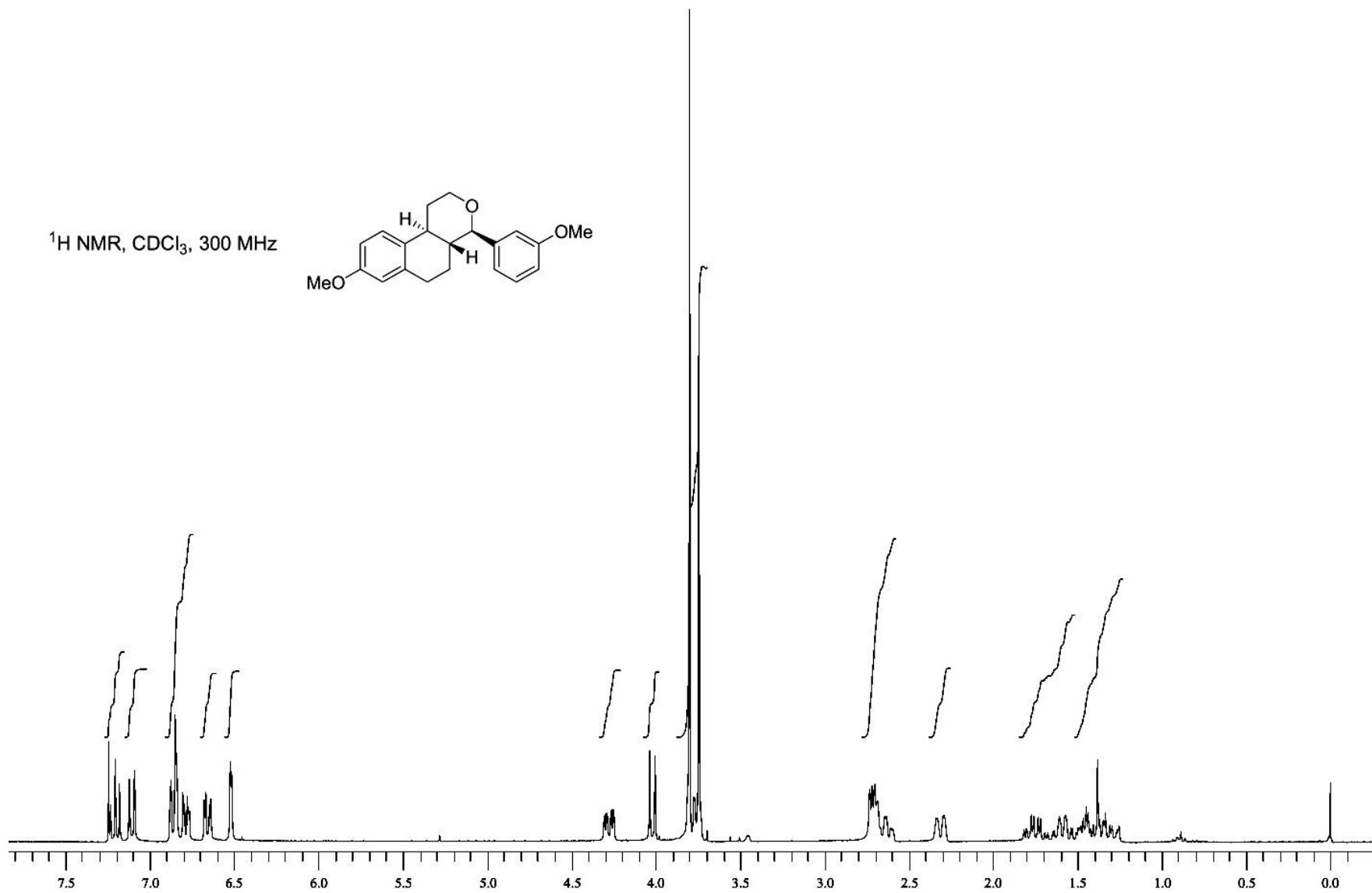


Product **7c** (Table 4, Entry c):

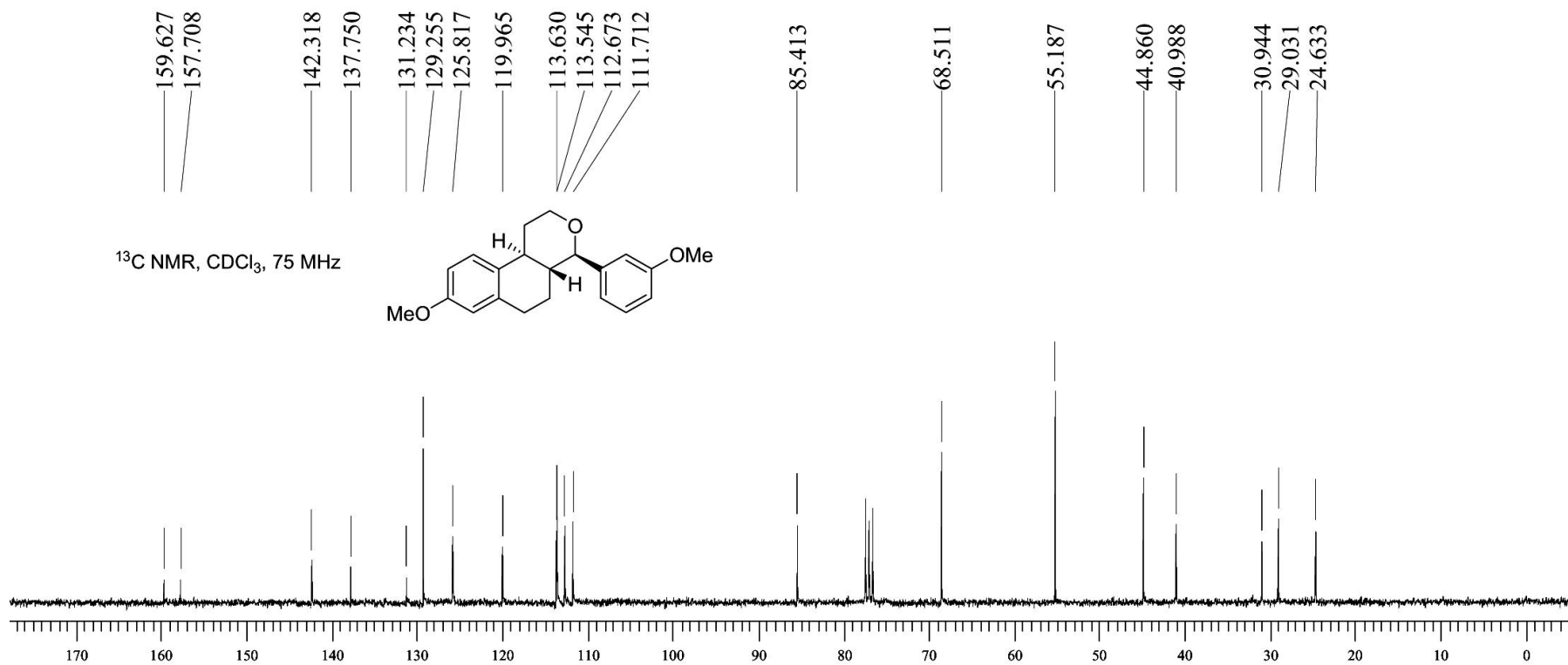




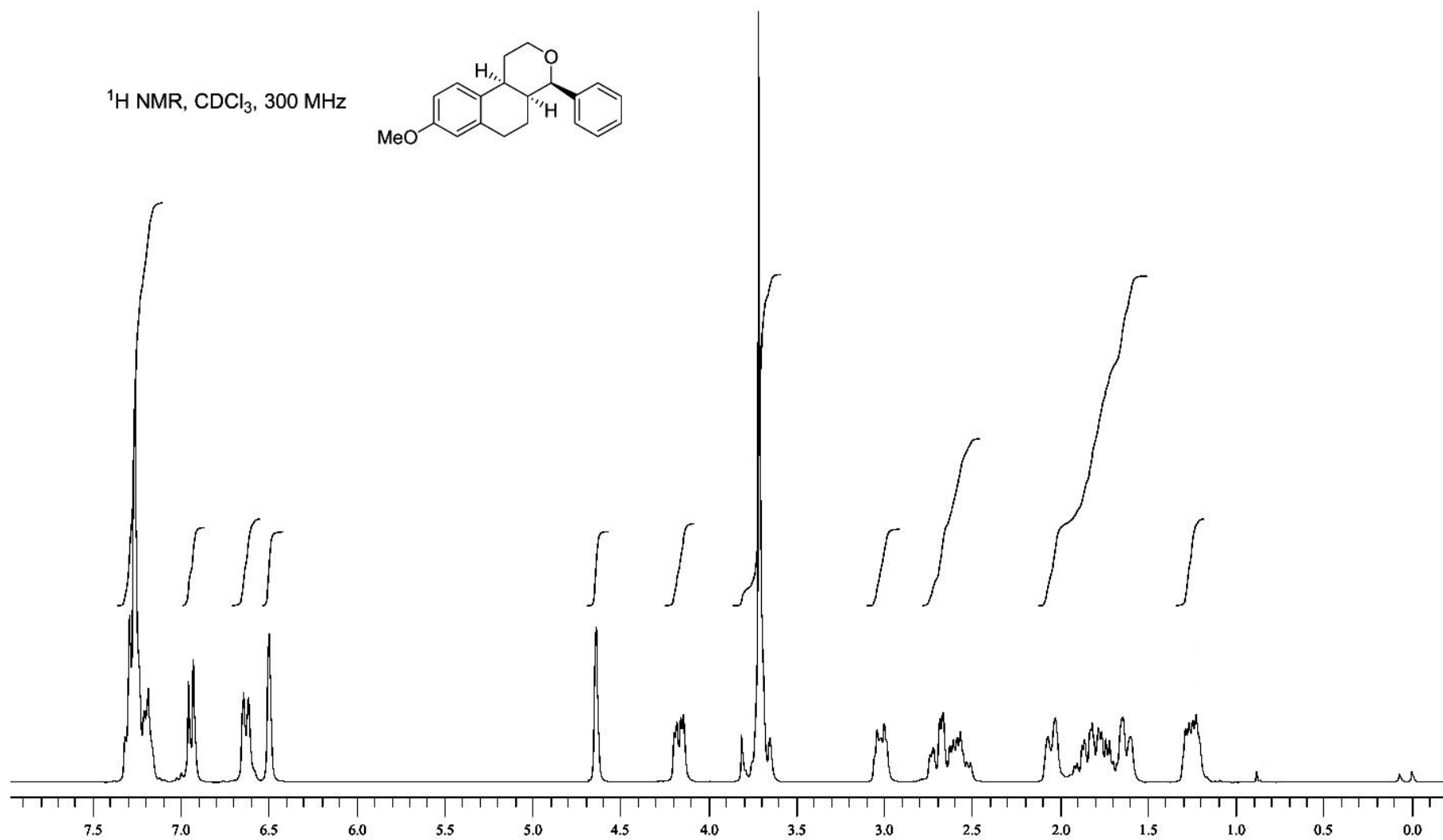
Product **7d** (Table 4, Entry **d**):

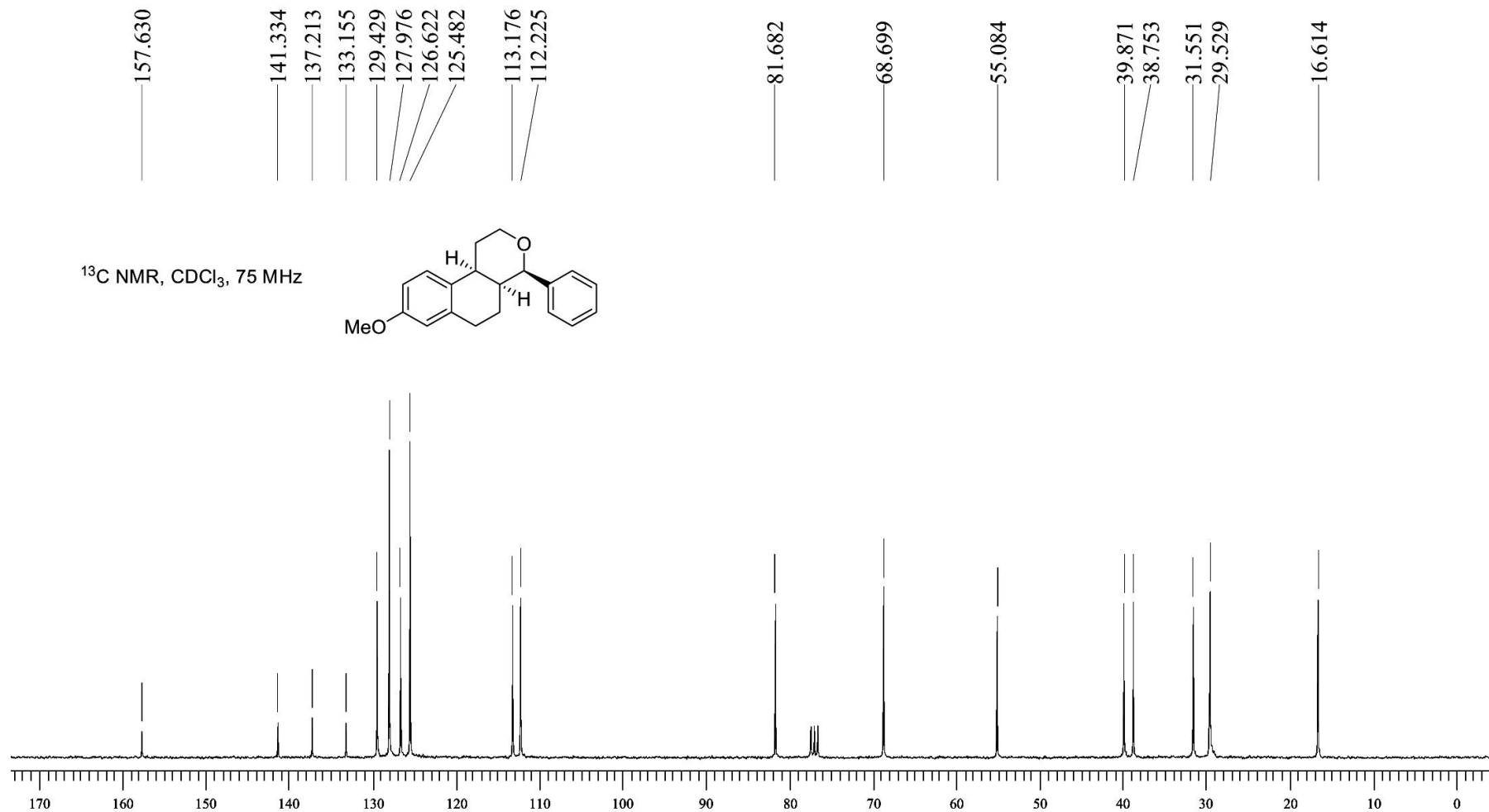




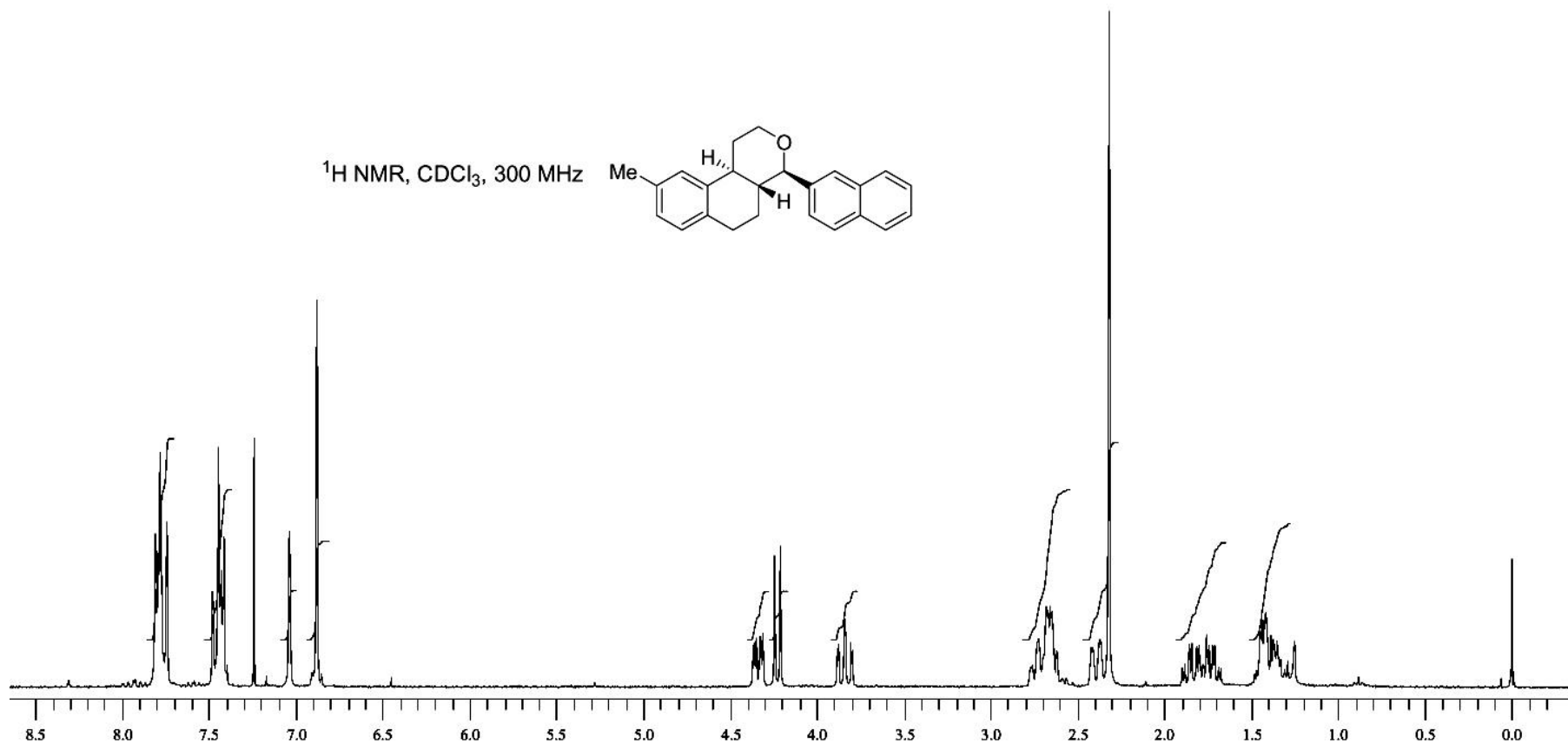
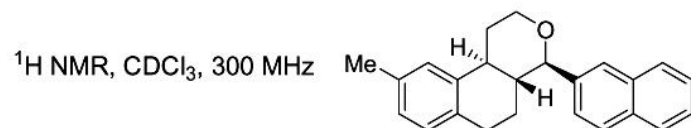


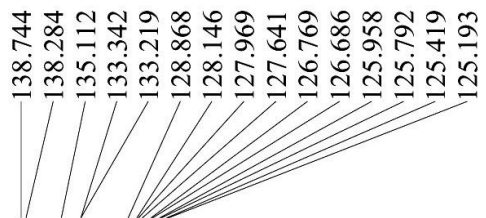
Product **7e** (Table 4, Entry e):





Product **7f** (Table 4, Entry **f**):





85.718

68.684

44.830

41.552

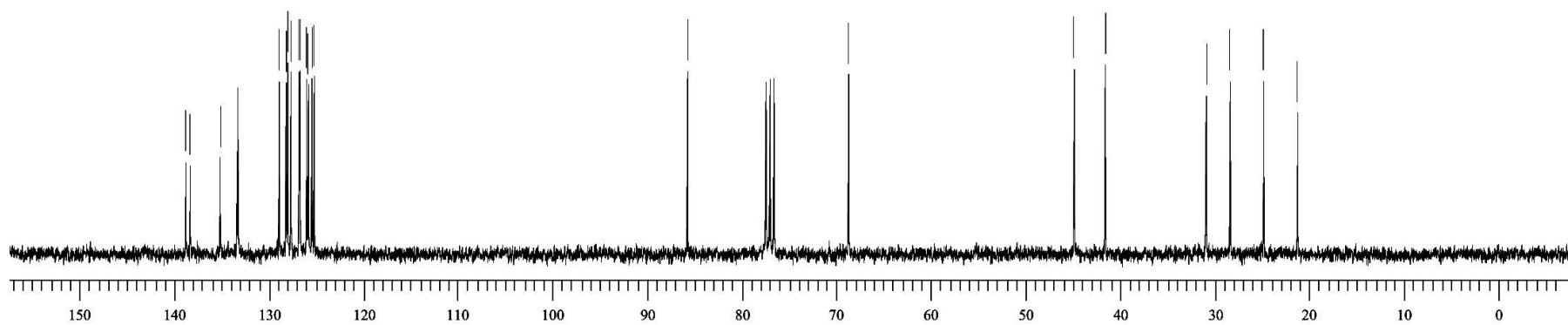
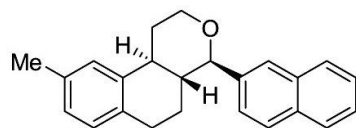
30.885

28.350

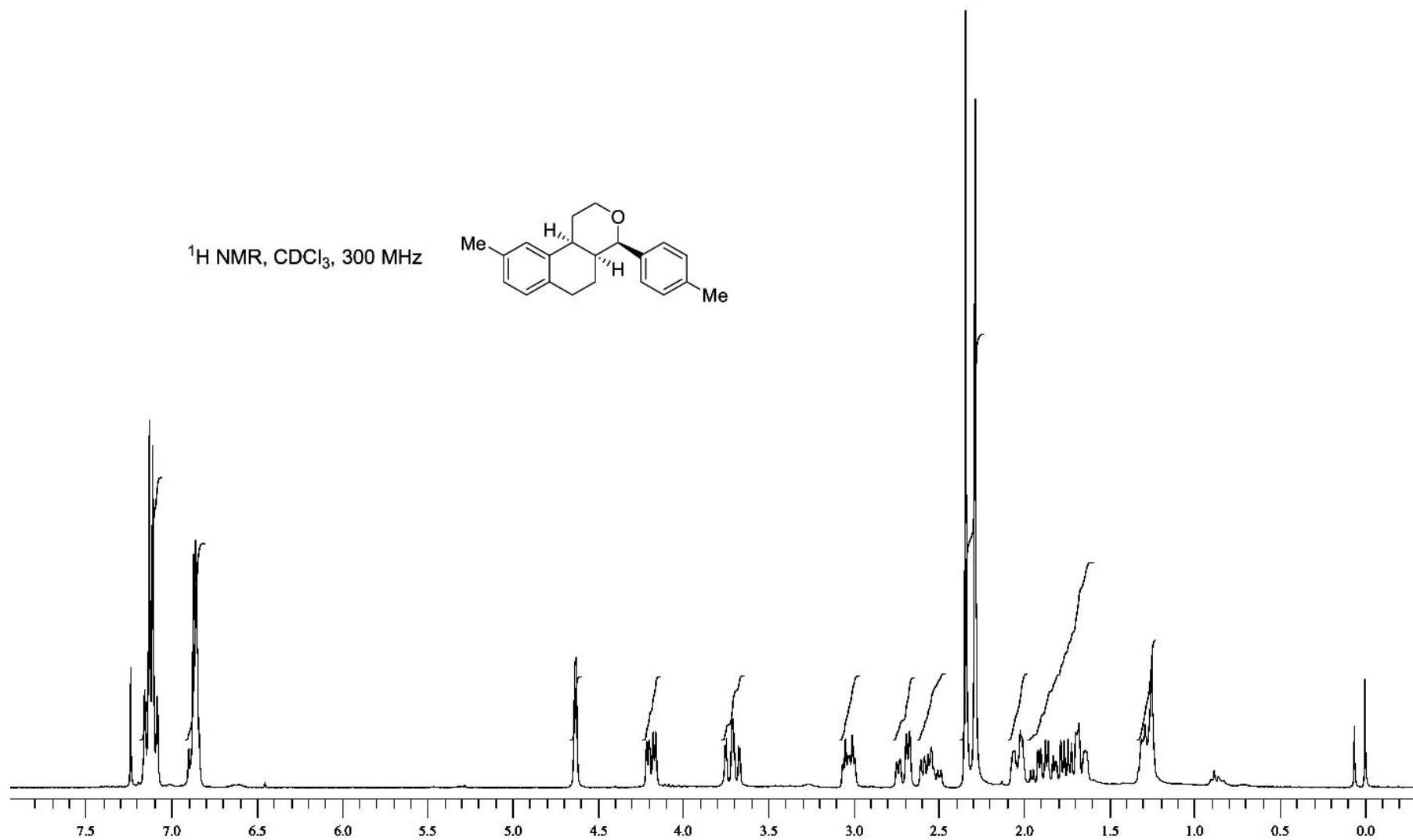
24.790

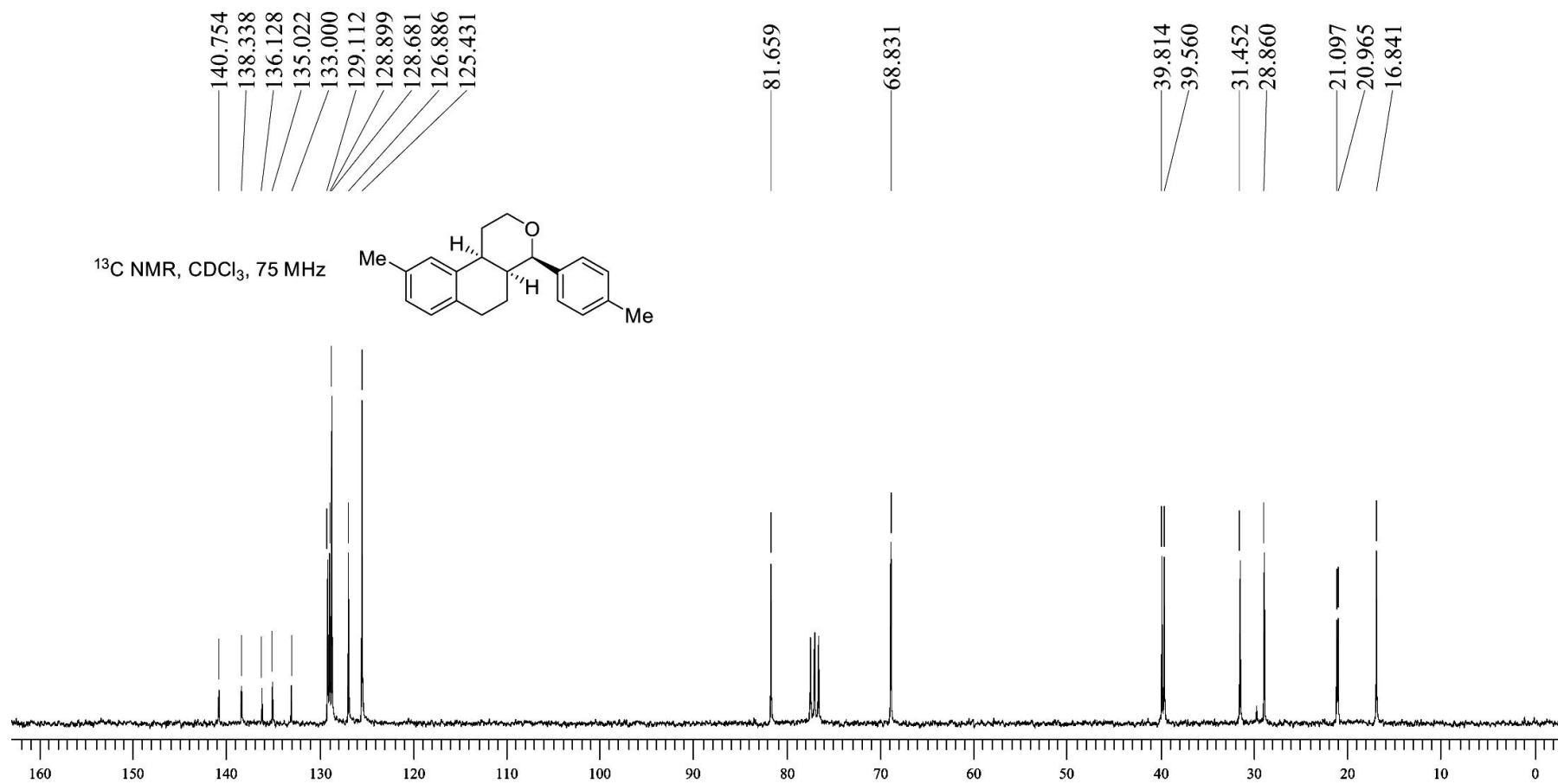
21.220

<sup>13</sup>C NMR, CDCl<sub>3</sub>, 75 MHz



Product **7g** (Table 4, Entry g):





Product **7g** (Table 4, Entry **g**):

