

*Electronic Supplementary Information Material*

# **Mechanistic Investigation of Energy Transfer in Perylene- cored Anthracene Dendrimers**

*Masaki Takahashi,<sup>a,\*</sup> Hironao Morimoto,<sup>b</sup> Kentaro Miyake,<sup>a</sup> Hideki Kawai,<sup>c</sup> Yoshihisa Sei,<sup>d</sup> Kentaro Yamaguchi,<sup>d</sup> Tetsuya Sengoku<sup>a</sup> and Hidemi Yoda<sup>a,\*</sup>*

<sup>a</sup> Department of Materials Science, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan

<sup>b</sup> Graduate School of Science and Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan

<sup>c</sup> Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8011, Japan

<sup>d</sup> Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, Shido, Sanuki, Kagawa 769-2193, Japan

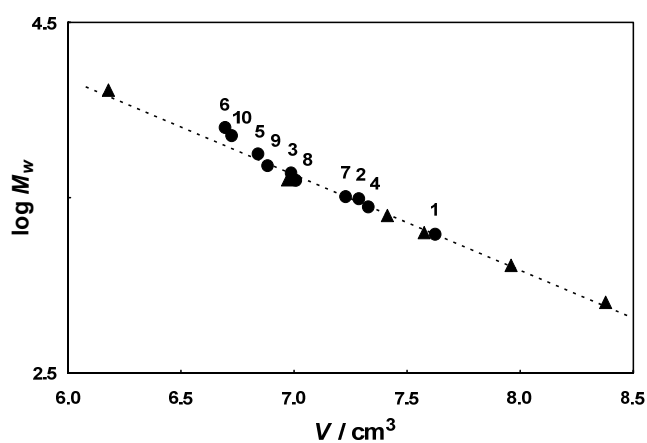
Tel: +81-53-478-1621; FAX: +81-53-478-1621; e-mail address: tmtakah@ipc.shizuoka.ac.jp

Tel: +81-53-478-1150; FAX: +81-53-478-1150; e-mail address: tchyoda@ipc.shizuoka.ac.jp

**Table S1** SEC results for **1-10**

Entry	Formula	$M_w/M_n^b$	$V^c / \text{cm}^3$	nominal $M_w$	$M_w^b$
1 <sup>a</sup>	C <sub>136</sub> H <sub>124</sub> O <sub>12</sub>	1.03	7.63	1950	1984
2 <sup>a</sup>	C <sub>224</sub> H <sub>188</sub> O <sub>20</sub>	1.04	7.23	3200	3266
3 <sup>a</sup>	C <sub>308</sub> H <sub>276</sub> O <sub>24</sub>	1.03	6.99	4361	4426
4 <sup>a</sup>	C <sub>220</sub> H <sub>212</sub> O <sub>16</sub>	1.03	7.29	3112	3034
5 <sup>a</sup>	C <sub>396</sub> H <sub>340</sub> O <sub>32</sub>	1.07	6.84	5611	5319
6 <sup>a</sup>	C <sub>564</sub> H <sub>516</sub> O <sub>40</sub>	1.03	6.70	7934	6389
7	C <sub>192</sub> H <sub>172</sub> O <sub>20</sub>	1.03	7.33	2799	2879
8	C <sub>276</sub> H <sub>260</sub> O <sub>24</sub>	1.03	7.01	3961	4311
9	C <sub>332</sub> H <sub>308</sub> O <sub>32</sub>	1.03	6.88	4810	5045
10	C <sub>500</sub> H <sub>484</sub> O <sub>40</sub>	1.03	6.73	7133	6160

<sup>a</sup> See ref. 6. <sup>b</sup> Calibrated with narrow-dispersity polystyrene standards. <sup>c</sup> Retention volume.



**Fig. S1** Semilogarithmic plot of average molecular weights ( $M_w$ ) vs. retention volumes ( $V$ ) for dendrimers (●) and polystyrenes (▲).

**Preparation and characterization of 12.** Although preparation of this compound (CAS 2417-72-3) has already been reported, a modification procedure was attempted to increase the product yield as follows. A solution of **11** (1.00 g, 6.66 mmol), *N*-bromosuccinimide (1.54 g, 8.65 mmol), and AIBN (0.10 g, *ca.* 10%) in chloroform (60 mL) was heated to reflux with vigorous stirring under argon. After 6 hours, the reaction mixture was cooled to room temperature and the solvent was then evaporated under vacuum. The residue was dissolved in ethyl acetate (50 mL) and the resulting solution was washed with water (20 mL) and brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. Purification of the residue by flash column chromatography on silica gel (eluent: chloroform) and recrystallization from CHCl<sub>3</sub>-hexane gave **12** (1.33 g, 87%) as colorless crystals: mp 50-51 °C; IR (KBr) 1610 cm<sup>-1</sup> (C=C), 1722 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 3.92 (s, 3H, OCH<sub>3</sub>), 4.50 (s, 2H, CH<sub>2</sub>Br), 7.46 (d, *J* = 8.4 Hz, 2H, ArH), 8.02 (d, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 32.1 (CH<sub>2</sub>), 52.1 (CH<sub>3</sub>), 129.0 (CH), 130.1 (CH), 142.6 (C), 166.5 (C).

**Preparation and characterization of 13L.** A solution containing **12** (0.85 g, 3.71 mmol), 3-(benzyloxy)phenol (0.72 g, 3.36 mmol), potassium carbonate (0.70 g, 5.06 mmol), and 18-crown-6 (0.5 g, 1.89 mmol) in acetone (5 mL) was refluxed with vigorous stirring under argon. After 4 hours, the reaction mixture was cooled to room temperature, poured into saturated ammonium chloride solution (5 mL), and extracted twice with ethyl acetate (20 mL). The extracts were washed with water (20 mL) and brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. Purification of the residue by flash column chromatography on silica gel (eluent: chloroform/hexane = 70/30) and recrystallization from CHCl<sub>3</sub>-hexane gave **13L** (1.11 g, 91%) as colorless crystals: mp 93-94 °C; IR (KBr) 1591 cm<sup>-1</sup> (C=C), 1716 cm<sup>-1</sup> (C=O); MS (FAB, positive) *m/z* 362 (*M*<sup>+</sup>), 363 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 3.91 (s, 3H, OCH<sub>3</sub>), 5.12 (s, 2H, CH<sub>2</sub>), 6.83-6.90 (m, 3H, ArH), 7.30-7.36 (m, 1H, ArH), 7.48-7.53 (m, 4H, ArH), 7.60-7.66 (m, 1H, ArH), 8.06 (d, *J* = 8.4 Hz, 2H, ArH), 8.20 (d, *J* = 8.4 Hz, 2H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 52.1 (CH<sub>3</sub>), 69.5 (CH<sub>2</sub>), 108.7 (CH), 112.5 (CH), 114.5 (CH), 127.0 (CH), 128.6 (CH), 129.5

(C), 129.8 (C), 129.9 (CH), 130.1 (CH), 130.2 (CH), 133.7 (CH), 141.9 (C), 152.0 (C), 159.5 (C), 165.1 (C), 166.9 (C). Anal Calcd for C<sub>22</sub>H<sub>18</sub>O<sub>5</sub>: C, 72.92; H, 5.01; N, 0.00. Found: C, 72.87; H, 4.89; N, 0.00.

**Preparation and characterization of 13B.** A solution containing **12** (0.82 g, 3.59 mmol), 3,5-di(benzoyloxy)phenol (1.20 g, 3.59 mmol), potassium carbonate (0.75 g, 5.43 mmol), and 18-crown-6 (0.48 g, 1.82 mmol) in acetone (8 mL) was refluxed with vigorous stirring under argon. After 4 hours, the reaction mixture was cooled to room temperature, poured into saturated ammonium chloride solution (5 mL), and extracted twice with ethyl acetate (20 mL). The extracts were washed with water (20 mL) and brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel (eluent: chloroform) and recrystallization from CHCl<sub>3</sub>-hexane gave **13B** (1.59 g, 92%) as colorless crystals: mp 138-139 °C; IR (KBr) 1599 cm<sup>-1</sup> (C=C), 1724 cm<sup>-1</sup> (C=O); MS (FAB, positive) *m/z* 482 (*M*<sup>+</sup>), 483 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 3.91 (s, 3H, OCH<sub>3</sub>), 5.14 (s, 2H, CH<sub>2</sub>), 6.82-6.84 (m, 3H, ArH), 7.48-7.53 (m, 6H, ArH), 7.61-7.66 (m, 2H, ArH), 8.07 (d, *J* = 8.1 Hz, 2H, ArH), 8.17-8.20 (m, 4H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 52.0 (CH<sub>3</sub>), 69.8 (CH<sub>2</sub>), 106.5 (CH), 108.8 (CH), 127.0 (CH), 128.7 (CH), 129.3 (C), 129.9 (C), 130.0 (CH), 130.3 (CH), 133.8 (CH), 141.4 (C), 152.2 (C), 159.8 (C), 164.8 (C), 166.9 (C). Anal Calcd for C<sub>29</sub>H<sub>22</sub>O<sub>7</sub>: C, 72.19; H, 4.60; N, 0.00. Found: C, 72.01; H, 4.51; N, 0.00.

**Preparation and characterization of 14L.** A solution containing **13L** (0.81 g, 2.24 mmol) and *n*-butylamine (2.22 mL, 22.5 mmol) in THF (10 mL) was refluxed with stirring under argon. After 18 hours, the reaction mixture was cooled to room temperature, and concentrated *in vacuo*. Purification of the residue by silica-gel column chromatography (eluent: chloroform/hexane = 50/50) and recrystallization from CHCl<sub>3</sub>-hexane gave **14L** (0.49 g, 85%) as white powders: mp 92-93 °C; IR (KBr) 1595 cm<sup>-1</sup> (C=C), 1695 cm<sup>-1</sup> (C=O), 3375 cm<sup>-1</sup> (OH); MS (FAB, positive) *m/z* 258 (*M*<sup>+</sup>), 259 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>) δ 3.89 (s, 3H, OCH<sub>3</sub>), 5.18 (s, 2H, CH<sub>2</sub>), 6.44-6.53 (m, 3H, ArH), 7.07-7.13 (m, 1H, ArH), 7.61 (d, *J* = 8.7 Hz, 2H, ArH), 8.04 (d, *J* = 8.7 Hz, 2H, ArH), 8.38 (s, 1H, OH); <sup>13</sup>C-NMR (acetone-*d*<sub>6</sub>) δ 53.4 (CH<sub>3</sub>), 70.7 (CH<sub>2</sub>), 104.2 (CH), 107.9 (CH), 110.2 (CH), 129.2 (CH), 131.5 (CH),

131.6 (C), 132.0 (CH), 145.1 (C), 160.7 (C), 162.0 (C), 168.2 (C). Anal Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>: C, 69.76; H, 5.46; N, 0.00. Found: C, 69.57; H, 5.39; N, 0.00.

**Preparation and characterization of 14B.** A solution containing **13B** (0.85 g, 1.76 mmol) and *n*-butylamine (3.49 mL, 35.4 mmol) in THF (15 mL) was refluxed with stirring under argon. After 18 hours, the reaction mixture was cooled to room temperature, and concentrated *in vacuo*. Purification of the residue by silica-gel column chromatography (eluent: chloroform/hexane = 50/50) gave **14B** (0.40 g, 83%) as white powders: mp 158-159 °C; IR (KBr) 1599 cm<sup>-1</sup> (C=C), 1684 cm<sup>-1</sup> (C=O), 3354 cm<sup>-1</sup> (OH); MS (FAB, positive) *m/z* 274 (*M*<sup>+</sup>), 275 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>) δ 3.89 (s, 3H, OCH<sub>3</sub>), 5.12 (s, 2H, CH<sub>2</sub>), 6.01-6.04 (m, 3H, ArH), 7.58 (d, *J* = 8.7 Hz, 2H, ArH), 8.03 (d, *J* = 8.7 Hz, 2H, ArH), 8.25 (s, 2H, OH); <sup>13</sup>C-NMR (acetone-*d*<sub>6</sub>) δ 53.3 (CH<sub>3</sub>), 70.6 (CH<sub>2</sub>), 96.0 (CH), 97.9 (CH), 129.1 (CH), 131.5 (CH), 131.6 (C), 145.2 (C), 161.3 (C), 162.7 (C), 168.2 (C). Anal Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>5</sub>: C, 65.69; H, 5.15; N, 0.00. Found: C, 65.62; H, 5.07; N, 0.00.

**Preparation and characterization of 15L.** A solution containing **14L** (0.17 g, 0.66 mmol), 9-(chloromethyl)-10-hexylanthracene (0.22 g, 0.71 mmol), potassium carbonate (0.12 g, 0.87 mmol), and 18-crown-6 (0.09 g, 0.34 mmol) in DMF (4 mL) was heated at 55 °C with stirring under argon. After 4 hours, the reaction mixture was cooled to room temperature, poured into saturated ammonium chloride solution (5 mL), and extracted with ethyl acetate (20 mL). The extracts were washed with water (20 mL) and brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. Purification of the residue by silica-gel column chromatography (eluent: chloroform/hexane = 80/20) gave **15L** (0.31 g, 88%) as pale yellow powders: mp 149-150 °C; IR (KBr) 1591 cm<sup>-1</sup> (C=C), 1718 cm<sup>-1</sup> (C=O); MS (FAB, positive) *m/z* 532 (*M*<sup>+</sup>), 533 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.93 (t, *J* = 7.0 Hz, 3H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.33-1.44 (m, 4H, (CH<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.57-1.63 (m, 2H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.78-1.84 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 3.62 (t, *J* = 8.1 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 3.91 (s, 3H, OCH<sub>3</sub>), 5.09 (s, 2H, CH<sub>2</sub>), 5.90 (s, 2H, CH<sub>2</sub>), 6.64-6.68 (m, 1H, ArH), 6.76-6.83 (m, 2H, ArH), 7.29 (t, *J* = 8.2 Hz, 1H, ArH), 7.48-7.54 (m, 6H, ArH), 8.05 (d, *J* = 8.1 Hz, 2H, ArH), 8.26-8.34 (m, 4H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 14.0 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 28.4

(CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 52.1 (CH<sub>3</sub>), 62.9 (CH<sub>2</sub>), 69.3 (CH<sub>2</sub>), 102.2 (CH), 107.4 (CH), 107.6 (CH), 124.7 (CH), 125.1 (CH), 125.1 (C), 125.2 (CH), 126.1 (CH), 127.0 (CH), 129.4 (C), 129.7 (C), 129.9 (CH), 130.2 (CH), 131.0 (C), 138.2 (C), 142.2 (C), 159.9 (C), 160.7 (C), 167.0 (C). Anal Calcd for C<sub>36</sub>H<sub>36</sub>O<sub>4</sub>: C, 81.17; H, 6.81; N, 0.00. Found: C, 81.33; H, 6.76; N, 0.00.

**Preparation and characterization of 15B.** A solution containing **14B** (0.20 g, 0.73 mmol), 9-(chloromethyl)-10-hexylanthracene (0.49 g, 1.58 mmol), potassium carbonate (0.27 g, 1.95 mmol), and 18-crown-6 (0.19 g, 0.72 mmol) in DMF (4 mL) was heated at 55 °C with stirring under argon. After 4 hours, the reaction mixture was cooled to room temperature, and poured into saturated ammonium chloride solution to form a precipitation of the product. The precipitate was collected by filtration, intensively washed with water, and dried *in vacuo* to afford a pale yellow solid. Purification of the residue by silica-gel column chromatography (eluent: chloroform/hexane = 50/50) and recrystallization from CHCl<sub>3</sub>-hexane solution gave **15B** (0.52 g, 87%) as pale yellow powders: mp 149-150 °C; IR (KBr) 1591 cm<sup>-1</sup> (C=C), 1718 cm<sup>-1</sup> (C=O); MS (FAB, positive) *m/z* 822 (*M*<sup>+</sup>), 823 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.92 (t, *J* = 7.1 Hz, 6H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.33-1.43 (m, 8H, (CH<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.56-1.63 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.79-1.84 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 3.63 (t, *J* = 8.1 Hz, 4H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 3.91 (s, 3H, OCH<sub>3</sub>), 5.08 (s, 2H, CH<sub>2</sub>), 5.91 (s, 4H, CH<sub>2</sub>), 6.50 (d, *J* = 2.1 Hz, 2H, ArH), 6.65 (t, *J* = 2.1 Hz, 1H, ArH), 7.48-7.56 (m, 10H, ArH), 8.05 (d, *J* = 8.4 Hz, 2H, ArH), 8.29-8.35 (m, 8H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 14.0 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 52.1 (CH<sub>3</sub>), 63.0 (CH<sub>2</sub>), 69.4 (CH<sub>2</sub>), 94.7 (CH), 94.9 (CH), 124.7 (CH), 125.0 (C), 125.1 (CH), 125.3 (CH), 126.2 (CH), 127.1 (CH), 129.4 (C), 129.7 (C), 129.9 (CH), 131.0 (C), 138.3 (C), 142.1 (C), 160.6 (C), 161.4 (C), 167.0 (C). Anal Calcd for C<sub>57</sub>H<sub>58</sub>O<sub>5</sub>: C, 83.18; H, 7.10; N, 0.00. Found: C, 82.97; H, 7.00; N, 0.00.

**Preparation and characterization of 16L.** To a solution of **15L** (0.14 g, 0.26 mmol) in anhydrous THF (10 mL) was added lithium aluminum hydride (0.01 g, 0.26 mmol) slowly at 0 °C with stirring under argon. The reaction mixture was stirred for additional 12 hours, cooled to 0 °C, quenched carefully with 5% aqueous hydrochloric acid (3 mL), extracted twice with ethyl acetate (20 mL). The extracts were washed with water (20 mL), saturated sodium bicarbonate (20 mL), and brine (20 mL),

dried over  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. Purification of the residue recrystallization from  $\text{CHCl}_3$ -hexane solution gave **16L** (0.13 g, 98%) as pale yellow powders: mp 148-151 °C; IR (KBr) 1587  $\text{cm}^{-1}$  (C=C), 3527  $\text{cm}^{-1}$  (OH); MS (FAB, positive)  $m/z$  504 ( $M^+$ ), 505 ( $MH^+$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.93 (t,  $J$  = 7.0 Hz, 3H,  $(\text{CH}_2)_5\text{CH}_3$ ), 1.33-1.44 (m, 4H,  $(\text{CH}_2)_3(\text{CH}_2)_2\text{CH}_3$ ), 1.55-1.68 (m, 2H, OH and  $(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ ), 1.76-1.88 (m, 2H,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ), 3.64 (t,  $J$  = 8.1 Hz, 2H,  $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 4.70 (d,  $J$  = 3.1 Hz, 2H,  $\text{CH}_2\text{OH}$ ), 5.05 (s, 2H,  $\text{CH}_2$ ), 5.93 (s, 2H,  $\text{CH}_2$ ), 6.66-6.69 (m, 1H, ArH), 6.79-6.82 (m, 2H, ArH), 7.29-7.32 (m, 1H, ArH), 7.38 (d,  $J$  = 8.2 Hz, 2H, ArH), 7.44 (d,  $J$  = 8.2 Hz, 2H, ArH), 7.49-7.55 (m, 4H, ArH), 8.27-8.37 (m, 4H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  14.0 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_2$ ), 28.4 ( $\text{CH}_2$ ), 30.0 ( $\text{CH}_2$ ), 31.4 ( $\text{CH}_2$ ), 31.7 ( $\text{CH}_2$ ), 62.9 ( $\text{CH}_2$ ), 65.1 ( $\text{CH}_2$ ), 69.8 ( $\text{CH}_2$ ), 102.2 (CH), 107.3 (CH), 107.7 (CH), 124.8 (CH), 125.1 (CH), 125.3 (CH), 126.1 (CH), 127.3 (CH), 127.9 (CH), 129.4 (C), 130.1 (CH), 131.0 (C), 136.5 (C), 138.2 (C), 140.7 (C), 160.2 (C), 160.7 (C). Anal Calcd for  $\text{C}_{35}\text{H}_{36}\text{O}_3$ : C, 83.30; H, 7.19; N, 0.00. Found: C, 83.11; H, 7.12; N, 0.00.

**Preparation and characterization of 16B.** To a solution of **15B** (0.82 g, 1.00 mmol) in anhydrous THF (5 mL) was added lithium aluminum hydride (0.04 g, 1.05 mmol) slowly at 0 °C with stirring under argon. The reaction mixture was stirred for additional 12 hours, cooled to 0 °C, quenched carefully with 5% aqueous hydrochloric acid (3 mL), extracted twice with ethyl acetate (20 mL). The extracts were washed with water (20 mL), saturated sodium bicarbonate (20 mL), and brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. Purification of the residue recrystallization from  $\text{CHCl}_3$ -hexane solution gave **16B** (0.72 g, 91%) as pale yellow powders: mp 180-181 °C; IR (KBr) 1579  $\text{cm}^{-1}$  (C=C), 3521  $\text{cm}^{-1}$  (OH); MS (FAB, positive)  $m/z$  794 ( $M^+$ ), 795 ( $MH^+$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J$  = 6.9 Hz, 6H,  $(\text{CH}_2)_5\text{CH}_3$ ), 1.29-1.45 (m, 8H,  $(\text{CH}_2)_3(\text{CH}_2)_2\text{CH}_3$ ), 1.55-1.64 (m, 5H, OH and  $(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ ), 1.76-1.86 (m, 4H,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ), 3.62 (t,  $J$  = 8.1 Hz, 4H,  $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 4.67 (s, 2H,  $\text{CH}_2\text{OH}$ ), 5.01 (s, 2H,  $\text{CH}_2$ ), 5.89 (s, 4H,  $\text{CH}_2$ ), 6.50 (d,  $J$  = 1.9 Hz, 2H, ArH), 6.63 (t,  $J$  = 1.9 Hz, 1H, ArH), 7.36 (d,  $J$  = 8.2 Hz, 2H, ArH), 7.42 (d,  $J$  = 8.2 Hz, 2H, ArH), 7.49-7.55 (m, 8H, ArH), 8.28-8.34 (m, 8H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  14.0 ( $\text{CH}_3$ ), 22.6 ( $\text{CH}_2$ ), 28.4 ( $\text{CH}_2$ ), 30.0 ( $\text{CH}_2$ ), 31.3

(CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 62.9 (CH<sub>2</sub>), 65.1 (CH<sub>2</sub>), 69.9 (CH<sub>2</sub>), 94.6 (CH), 95.0 (CH), 124.7 (CH), 125.1 (CH), 125.2 (CH), 126.1 (CH), 127.3 (CH), 127.9 (CH), 129.4 (C), 136.3 (C), 138.2 (C), 140.8 (C), 160.9 (C), 161.4 (C). Anal Calcd for C<sub>56</sub>H<sub>58</sub>O<sub>4</sub>: C, 84.60; H, 7.35; N, 0.00. Found: C, 84.46; H, 7.19; N, 0.00.

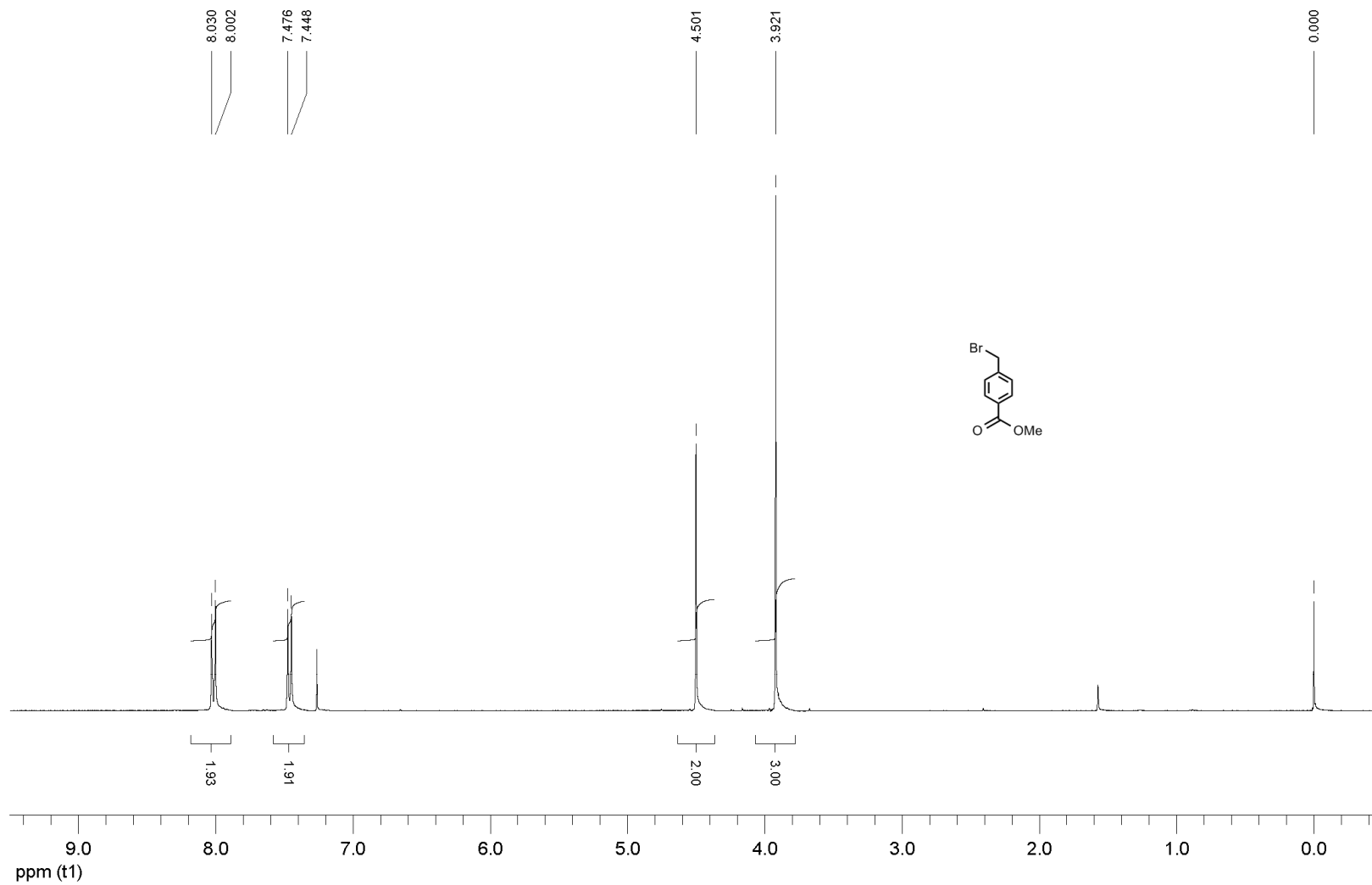
**Preparation and characterization of A1.** To a solution containing **16L** (0.69 g, 1.37 mmol), lithium chloride (1.74 g, 41.0 mmol), and triethylamine (0.86 mL, 6.20 mmol) in anhydrous THF (5 mL), a solution of methanesulfonyl chloride (0.32 mL, 4.13 mmol) in anhydrous THF (5 mL) was added slowly at 0 °C. After stirring for additional 12 hours at room temperature, the reaction mixture was quenched by slow addition of 5% aqueous hydrochloric acid (10 mL), and then extracted twice with chloroform (30 mL). The extracts were washed with water (20 mL) and brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. Purification of the residue by recrystallization from chloroform-hexane solution gave **A1** (0.69 g, 96%) as pale yellow powders: mp 139-141 °C; IR (KBr) 1587 cm<sup>-1</sup> (C=C); MS (FAB, positive) *m/z* 522 (*M*<sup>+</sup>), 523 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.93 (t, *J* = 7.0 Hz, 3H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.33-1.46 (m, 4H, (CH<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.55-1.63 (m, 2H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.77-1.85 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 3.63 (t, *J* = 8.1 Hz, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 4.58 (s, 2H, CH<sub>2</sub>Cl), 5.04 (s, 2H, CH<sub>2</sub>), 5.91 (s, 2H, CH<sub>2</sub>), 6.65-6.68 (m, 1H, ArH), 6.77-6.82 (m, 2H, ArH), 7.29 (t, *J* = 8.1 Hz, 1H, ArH), 7.38-7.44 (m, 4H, ArH), 7.49-7.54 (m, 4H, ArH), 8.27-8.35 (m, 4H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 14.0 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 31.7 (CH<sub>2</sub>), 45.9 (CH<sub>2</sub>), 62.9 (CH<sub>2</sub>), 69.5 (CH<sub>2</sub>), 102.2 (CH), 107.3 (CH), 107.6 (CH), 124.7 (CH), 125.1 (CH), 125.2 (CH), 126.0 (CH), 127.9 (CH), 128.9 (CH), 129.4 (C), 130.2 (CH), 131.0 (C), 137.25 (C), 137.34 (C), 138.2 (C), 160.1 (C), 160.7 (C). Anal Calcd for C<sub>35</sub>H<sub>35</sub>ClO<sub>2</sub>: C, 80.36; H, 6.74; N, 0.00. Found: C, 80.61; H, 6.63; N, 0.00.

**Preparation and characterization of A2.** To a solution containing **16B** (0.29 g, 0.36 mmol), lithium chloride (0.47 g, 11.1 mmol), and triethylamine (0.23 mL, 1.66 mmol) in anhydrous THF (5 mL), a solution of methanesulfonyl chloride (0.09 mL, 1.16 mmol) in anhydrous THF (5 mL) was added slowly at 0 °C. After stirring for additional 12 hours at room temperature, the reaction mixture was quenched by slow addition of 5% aqueous hydrochloric acid (5 mL), and then extracted twice with chloroform (20 mL). The extracts were washed with water (20 mL) and brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>,

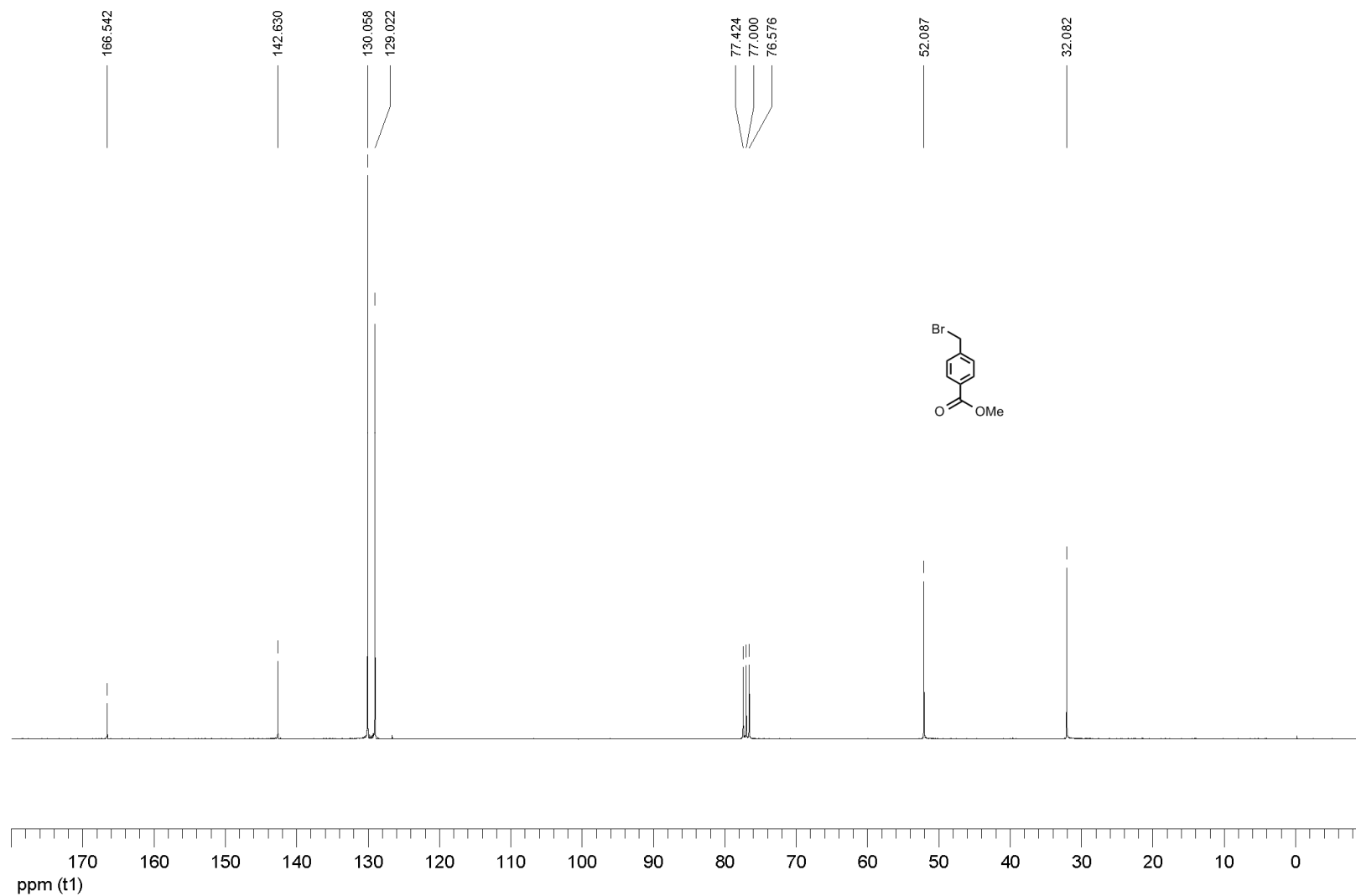


and concentrated *in vacuo*. Purification of the residue by recrystallization from chloroform-hexane solution gave **A2** (0.28 g, 94%) as pale yellow powders: mp 159-160 °C; IR (KBr) 1597 cm<sup>-1</sup> (C=C); MS (FAB, positive) *m/z* 812 (*M*<sup>+</sup>), 813 (*MH*<sup>+</sup>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.89 (t, *J* = 7.0 Hz, 6H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.28-1.37 (m, 8H, (CH<sub>2</sub>)<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.48-1.57 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.69-1.79 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 3.50 (t, *J* = 8.1 Hz, 4H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 4.45 (s, 2H, CH<sub>2</sub>Cl), 4.87 (s, 2H, CH<sub>2</sub>), 5.69 (s, 4H, CH<sub>2</sub>), 6.43 (d, *J* = 1.9 Hz, 2H, ArH), 6.55 (t, *J* = 1.9 Hz, 1H, ArH), 7.25-7.32 (m, 4H, ArH), 7.41-7.45 (m, 8H, ArH), 8.18-8.25 (m, 8H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 14.0 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 45.8 (CH<sub>2</sub>), 62.8 (CH<sub>2</sub>), 69.5 (CH<sub>2</sub>), 94.5 (CH), 94.9 (CH), 124.7 (CH), 125.0 (CH), 125.10 (C), 125.13 (CH), 126.0 (CH), 127.8 (CH), 128.8 (CH), 129.3 (C), 130.9 (C), 137.1 (C), 137.1 (C), 138.0 (C), 160.8 (C), 161.3 (C). Anal Calcd for C<sub>56</sub>H<sub>57</sub>ClO<sub>3</sub>: C, 82.68; H, 7.06; N, 0.00. Found: C, 82.40; H, 7.04; N, 0.00.

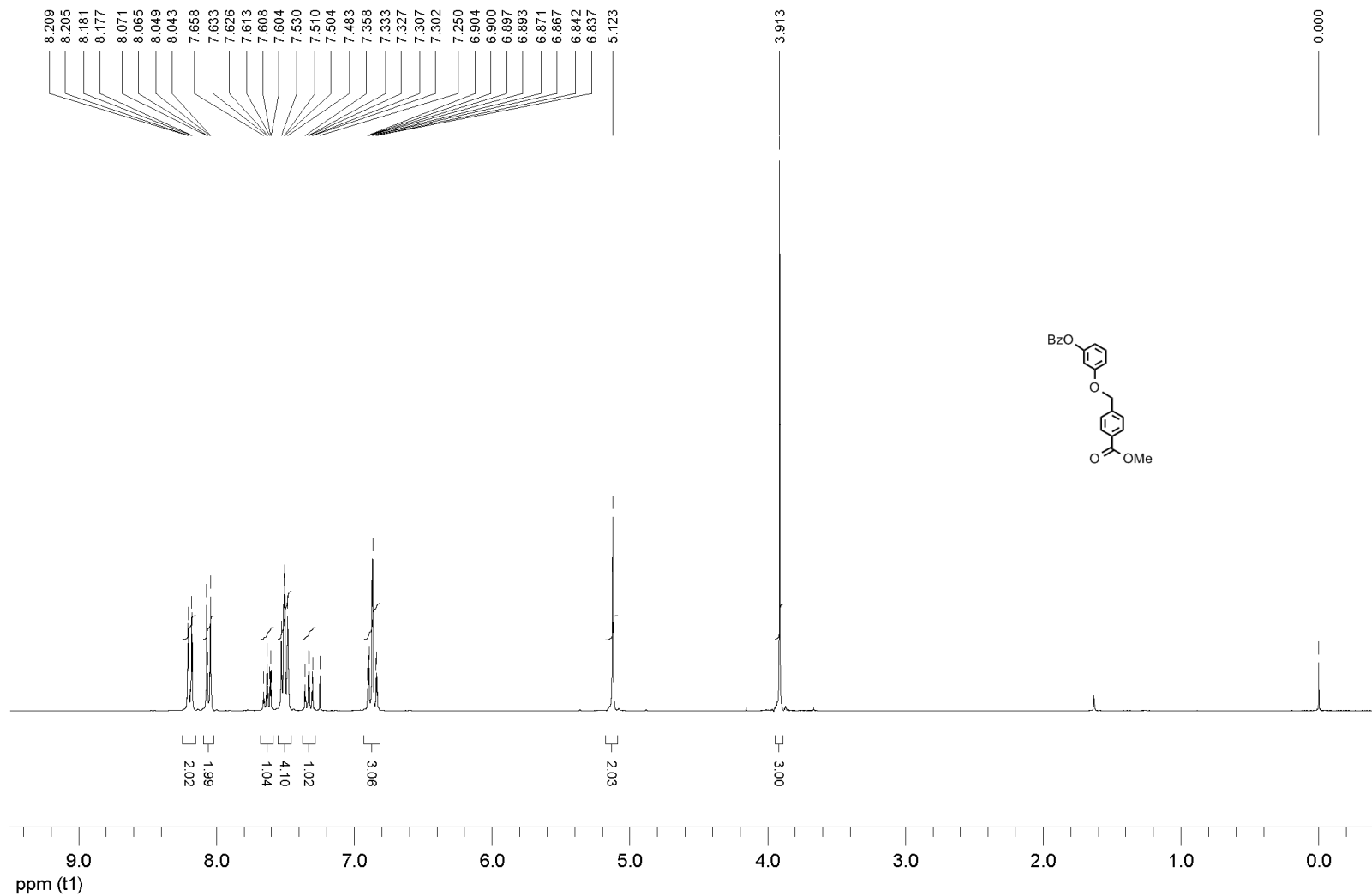
# <sup>1</sup>H-NMR spectrum of **12**



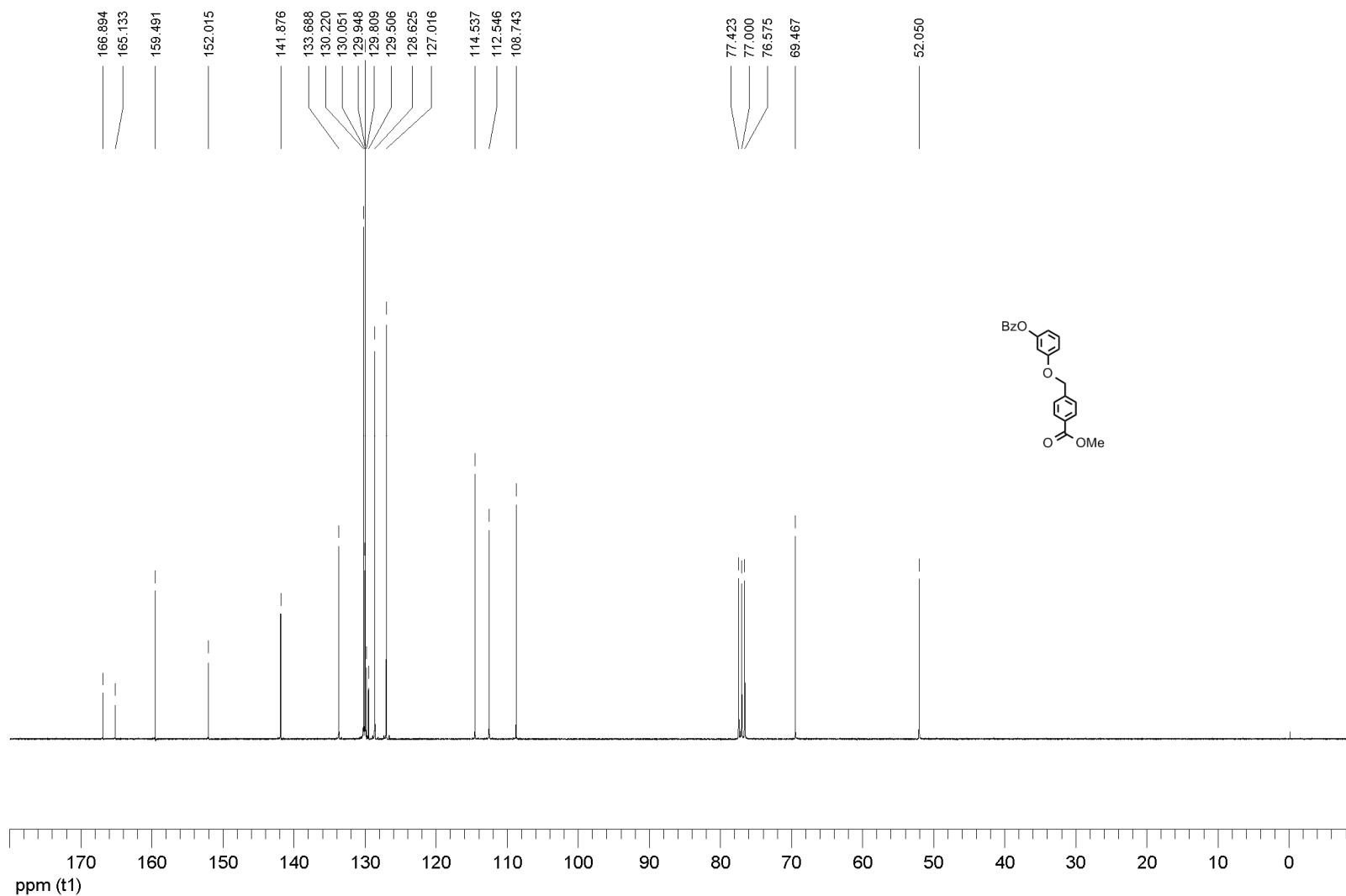
$^{13}\text{C}$ -NMR spectrum of **12**



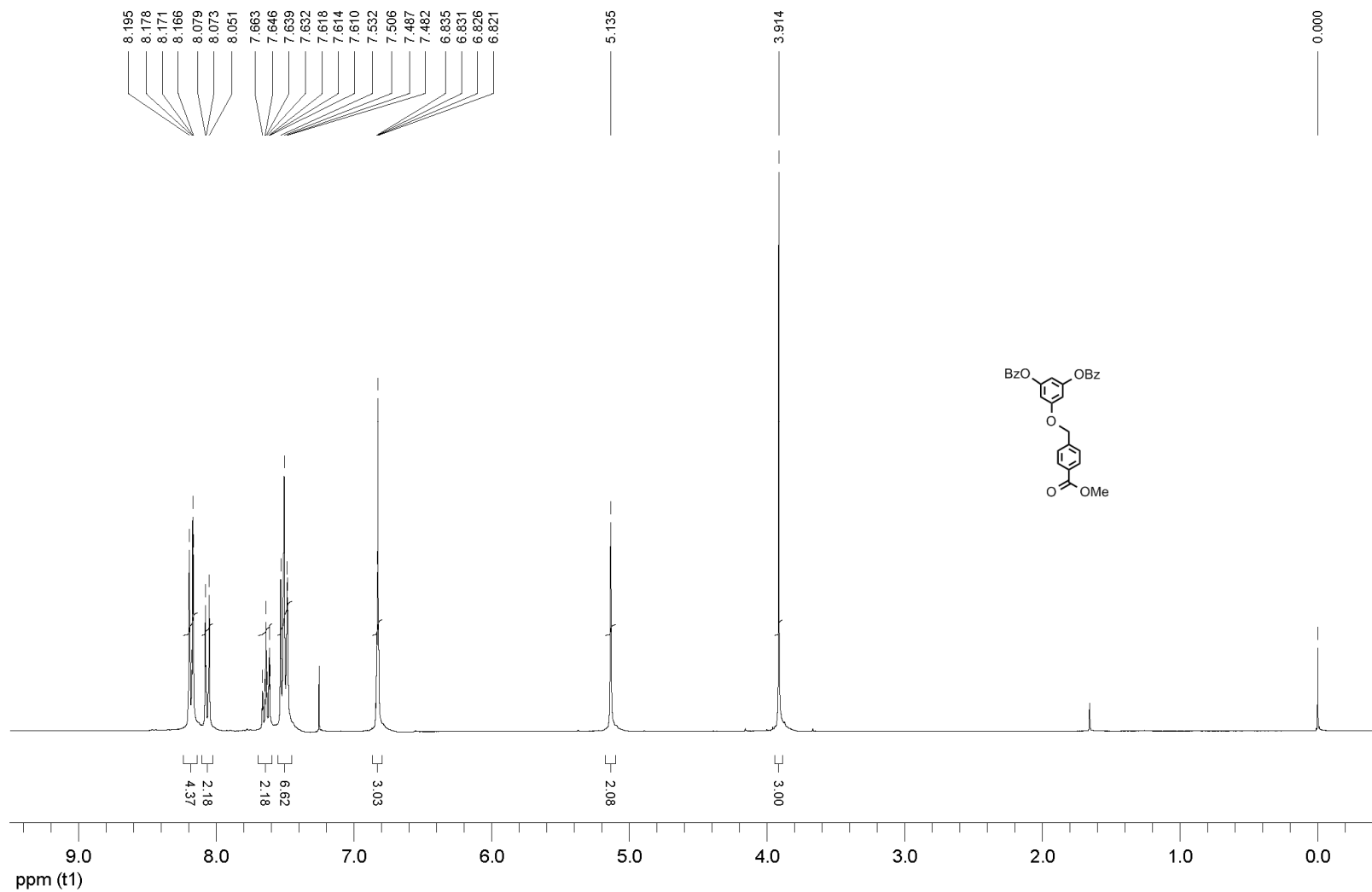
# <sup>1</sup>H-NMR spectrum of **13L**



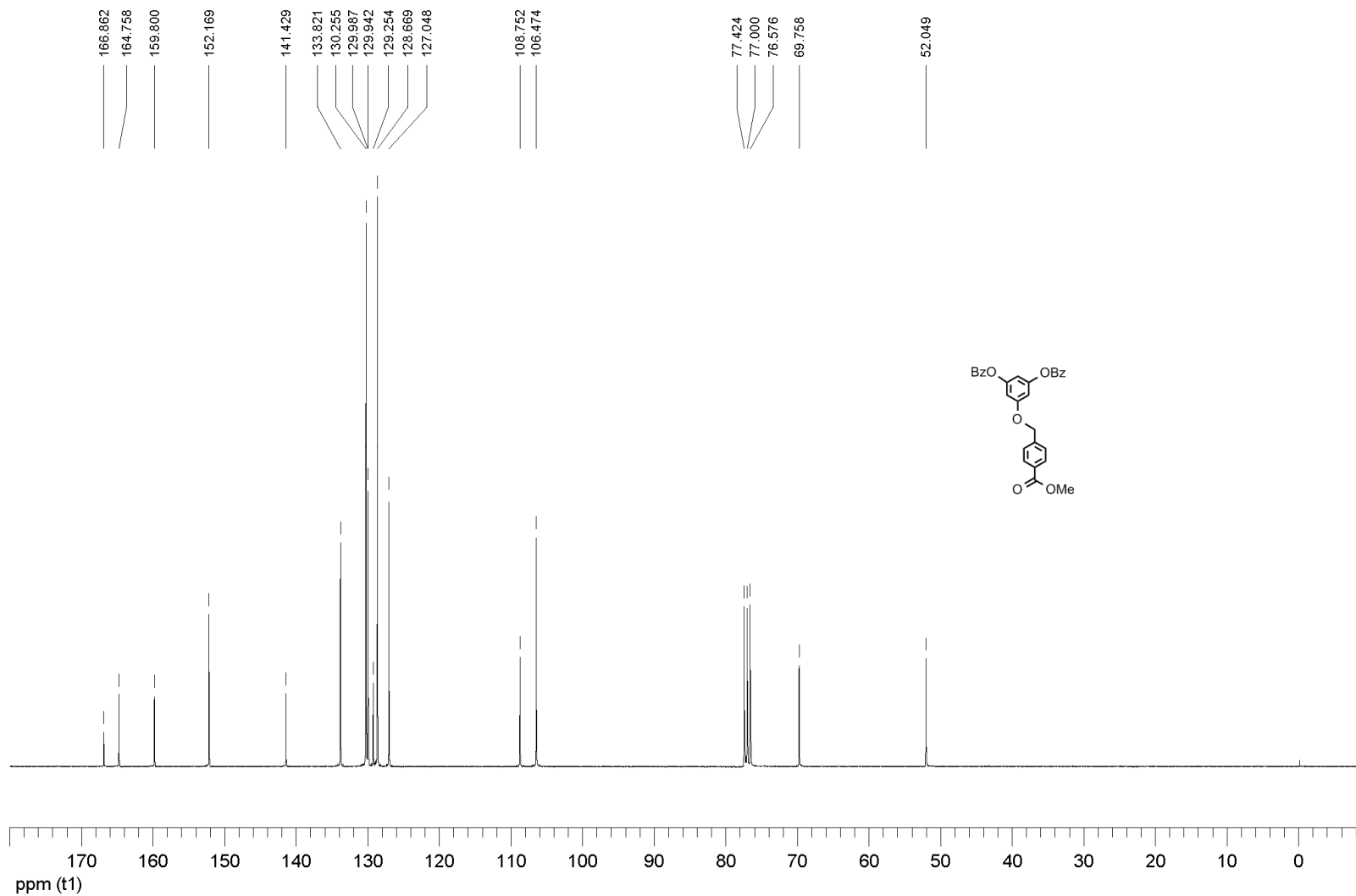
$^{13}\text{C}$ -NMR spectrum of **13L**



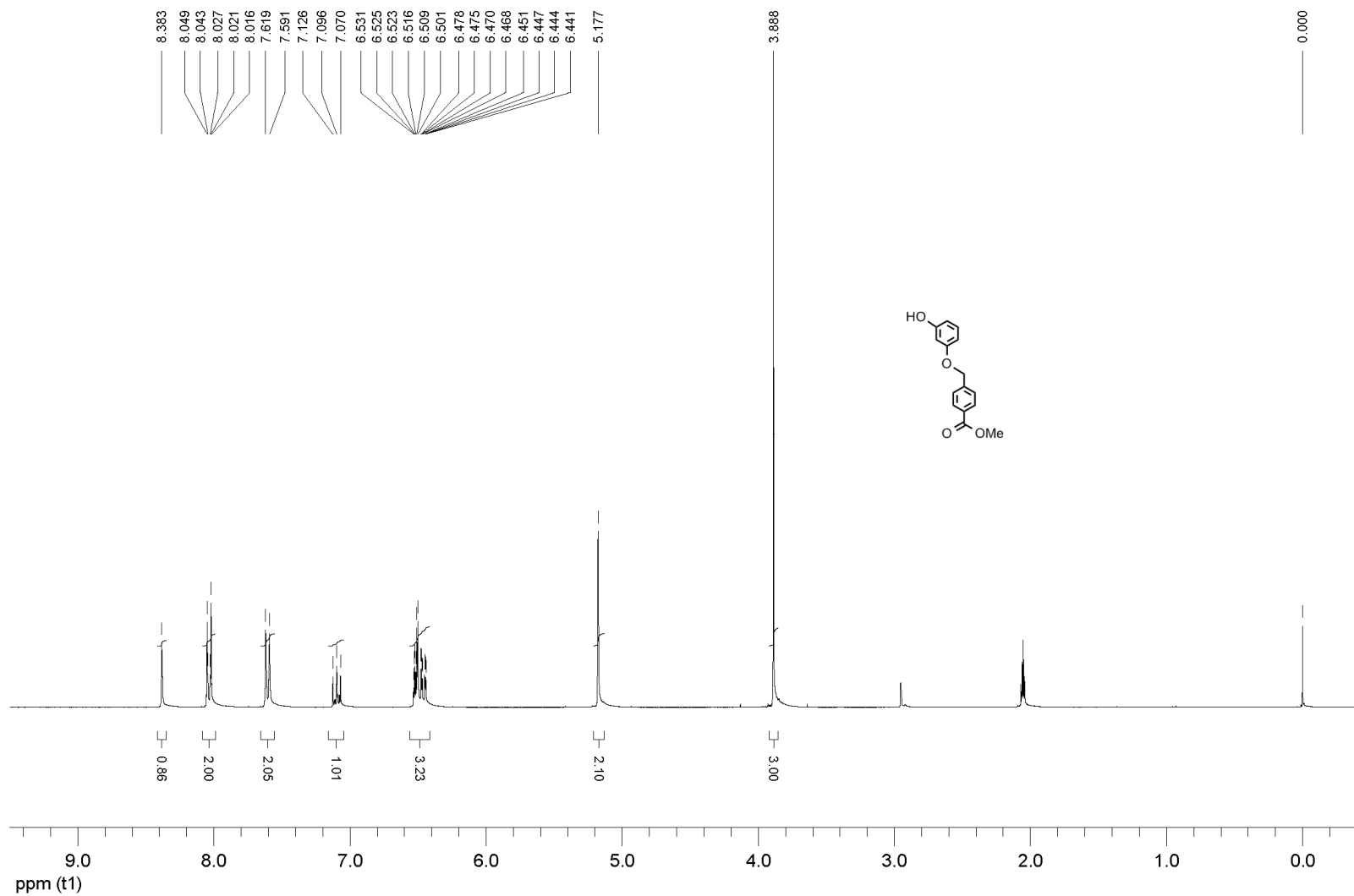
# $^1\text{H-NMR}$ spectrum of **13B**



$^{13}\text{C}$ -NMR spectrum of **13B**

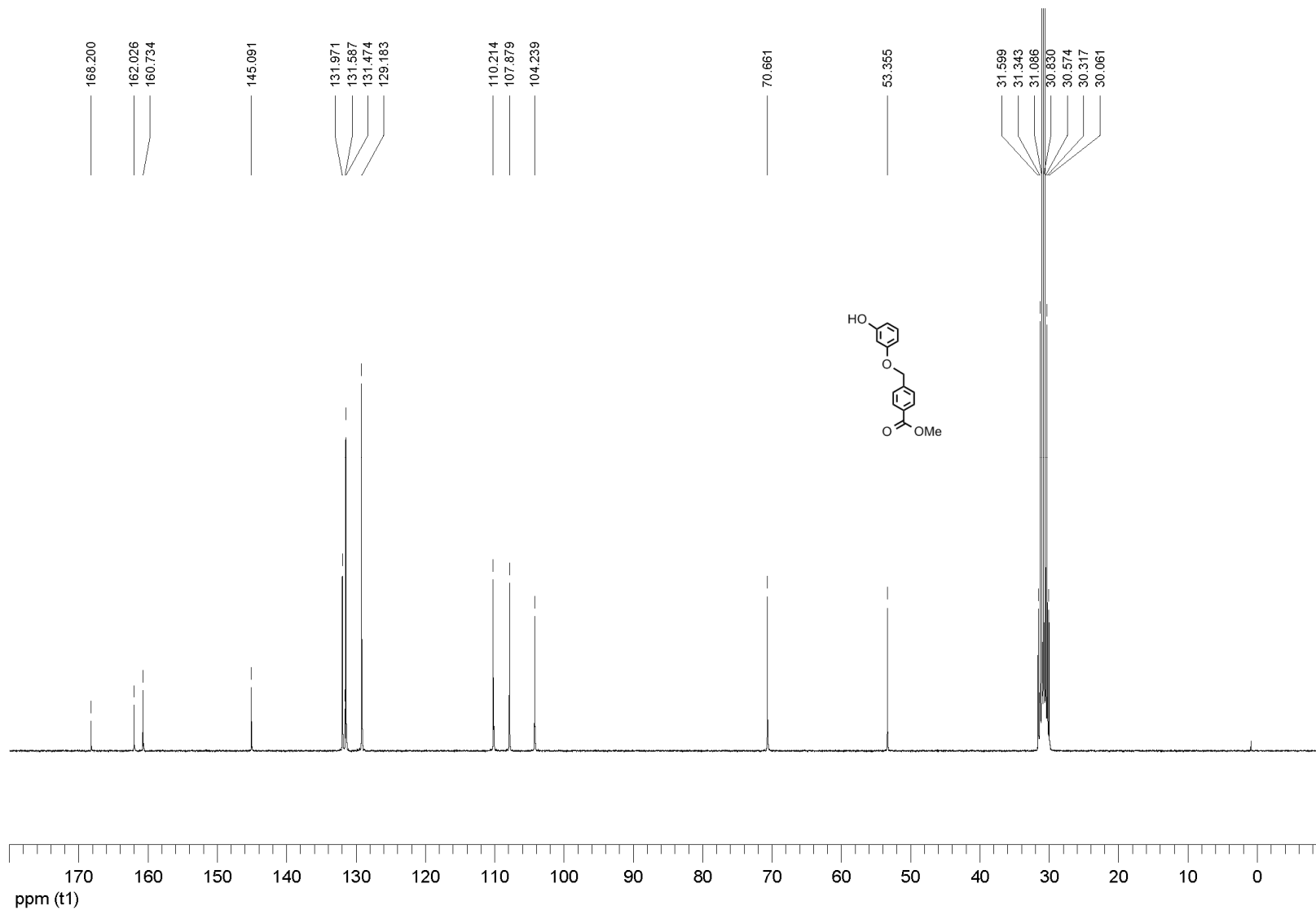


# $^1\text{H-NMR}$ spectrum of **14L**

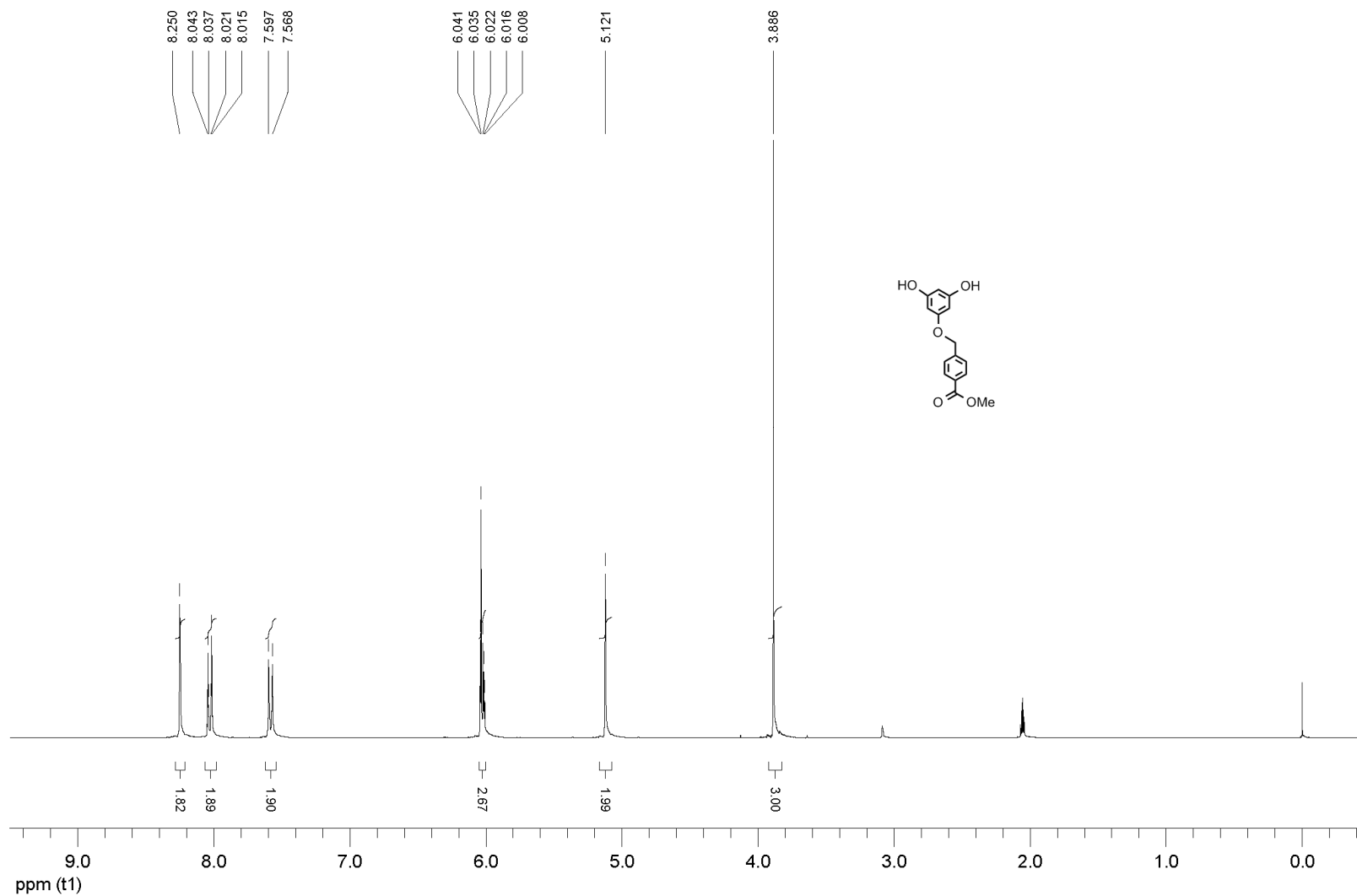




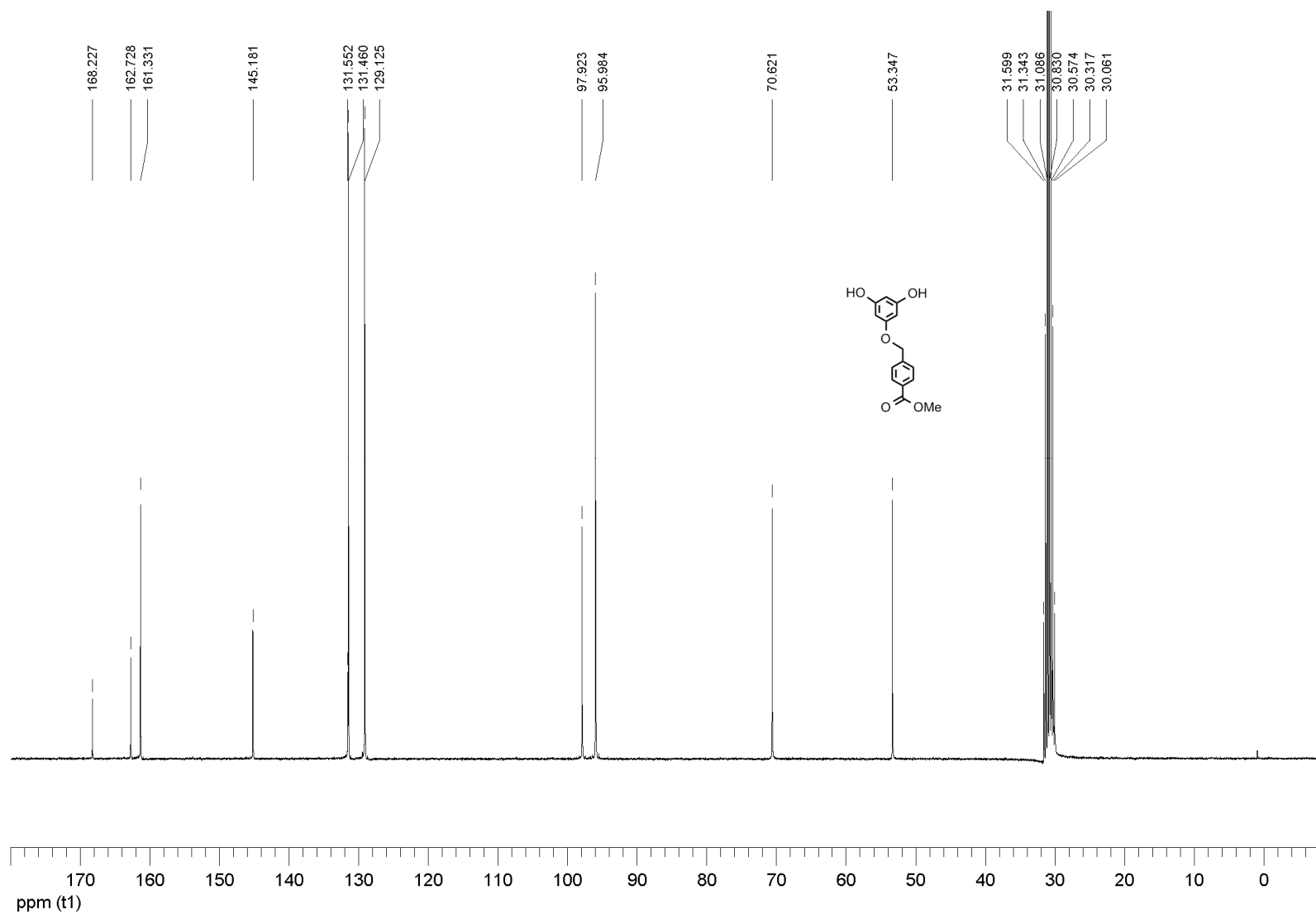
$^{13}\text{C}$ -NMR spectrum of **14L**



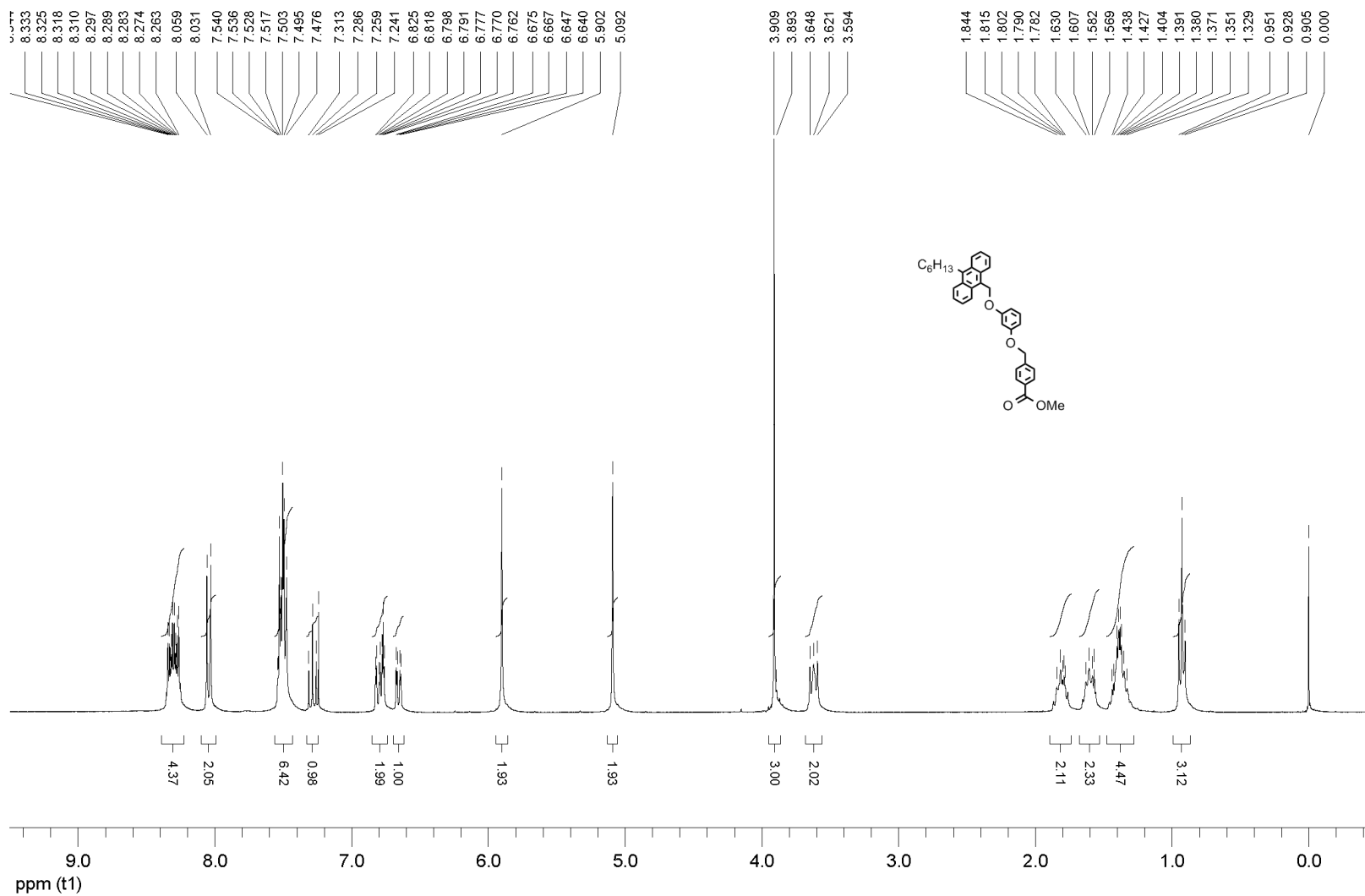
# <sup>1</sup>H-NMR spectrum of **14B**



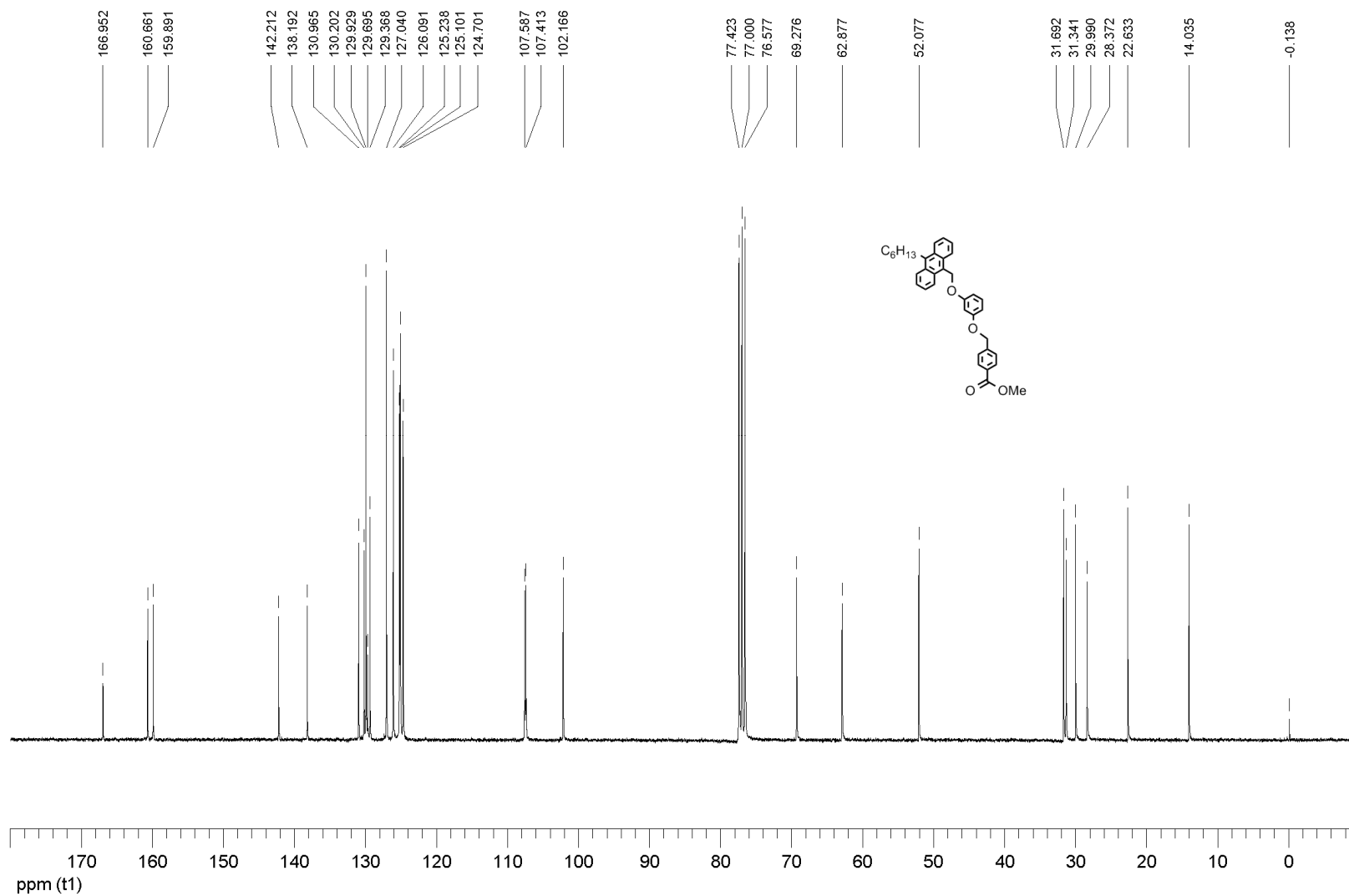
$^{13}\text{C}$ -NMR spectrum of **14B**



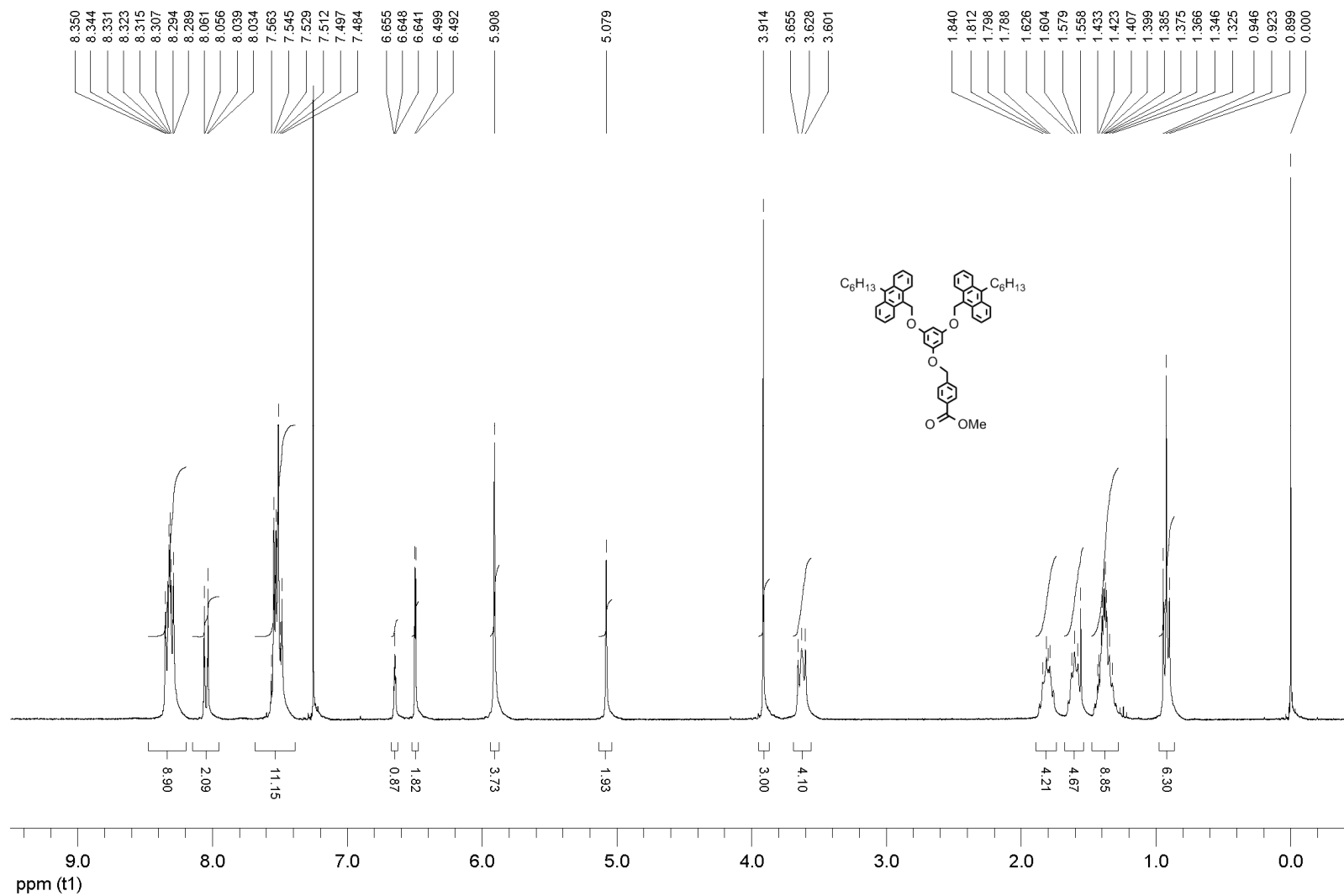
# $^1\text{H-NMR}$ spectrum of **15L**



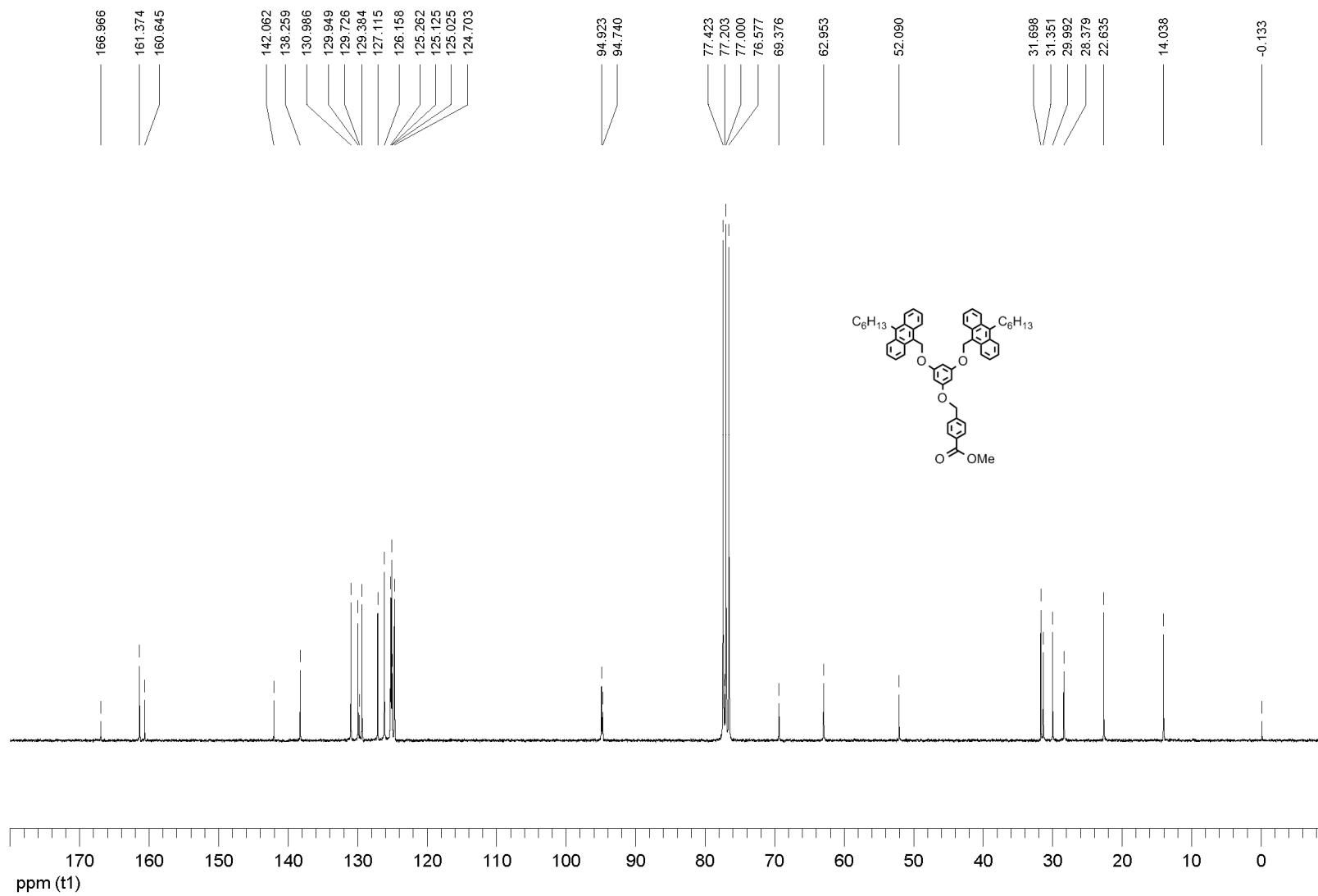
$^{13}\text{C}$ -NMR spectrum of **15L**



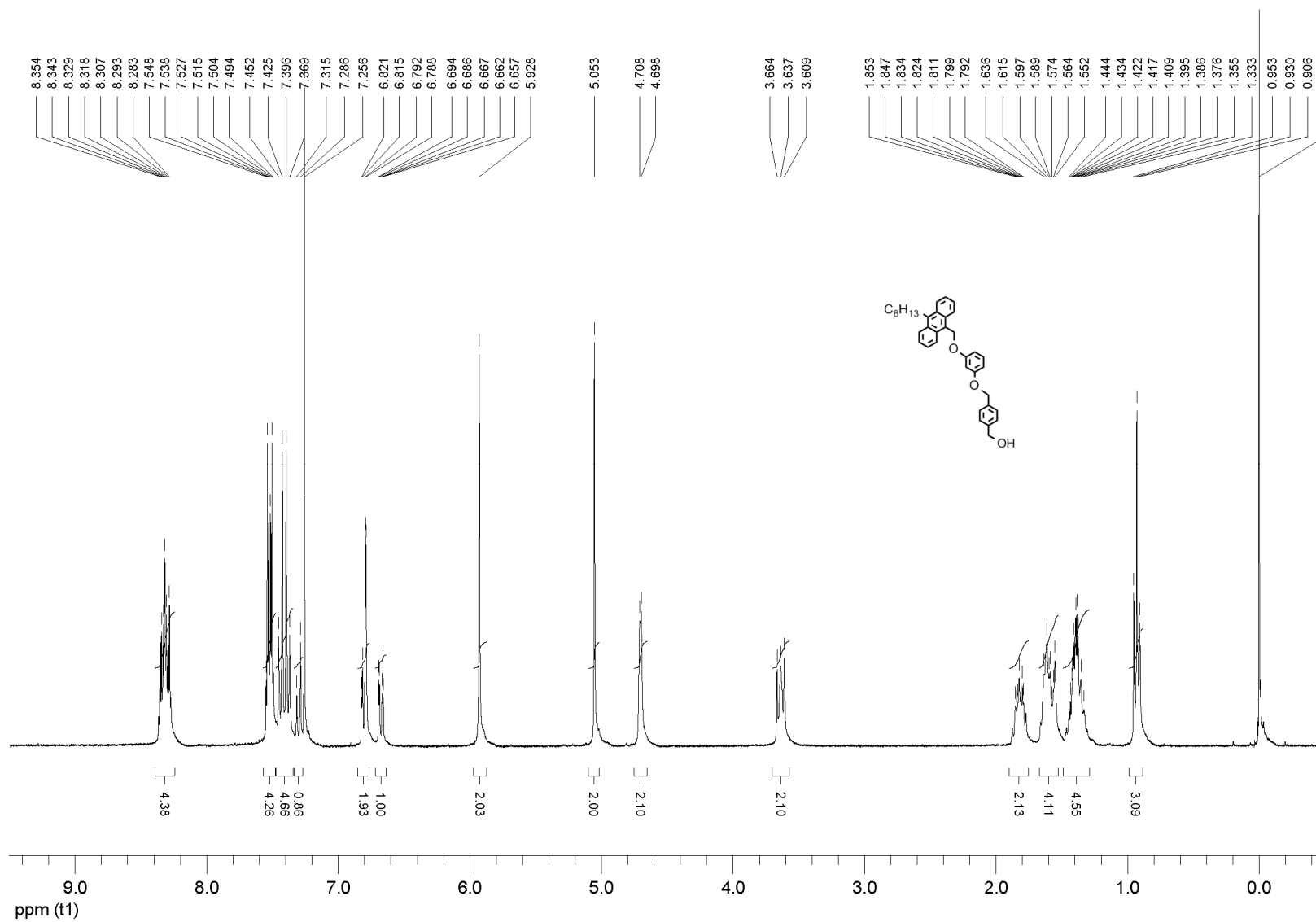
# $^1\text{H-NMR}$ spectrum of **15B**



$^{13}\text{C}$ -NMR spectrum of **15B**



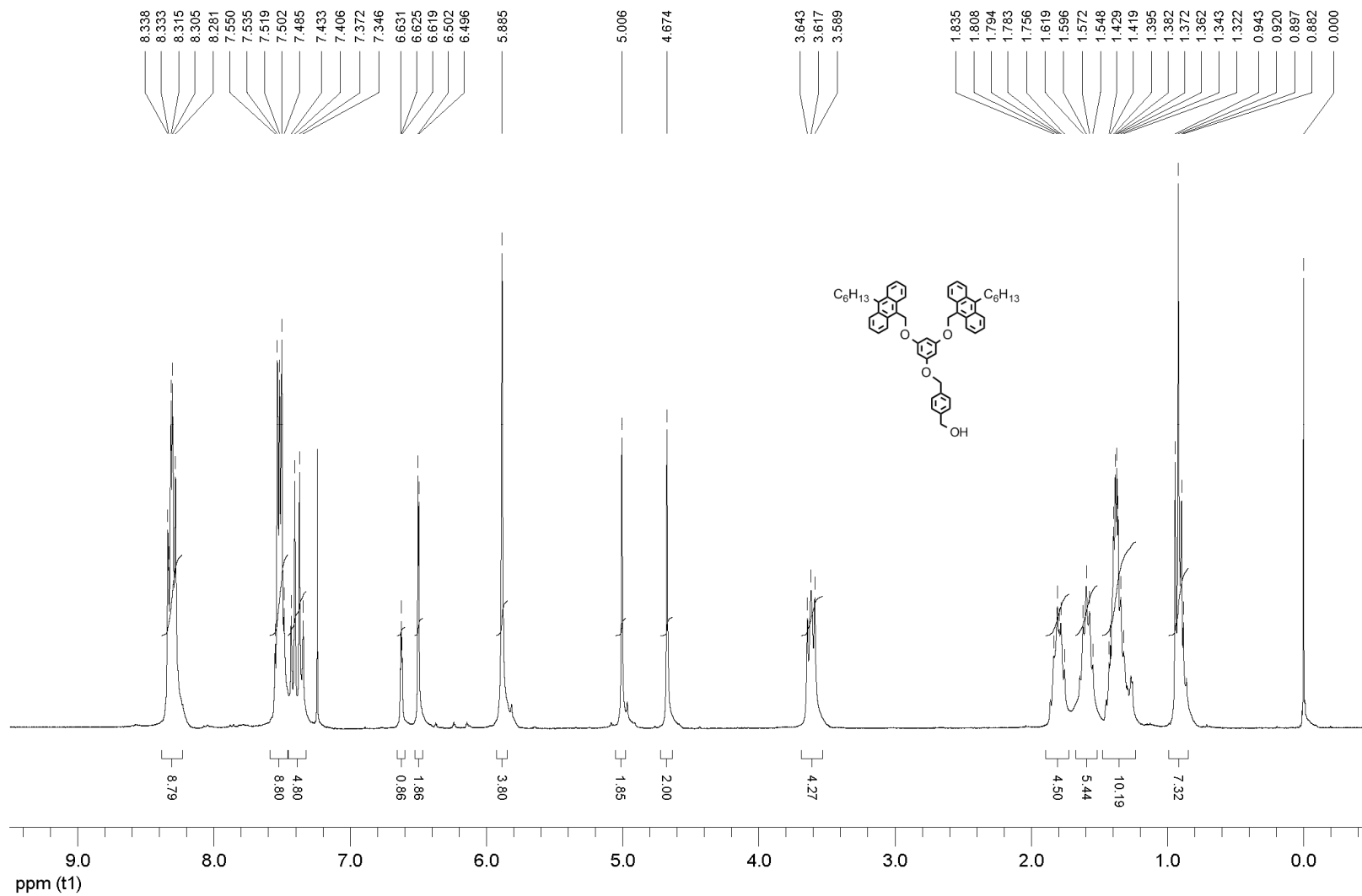
# $^1\text{H-NMR}$ spectrum of **16L**



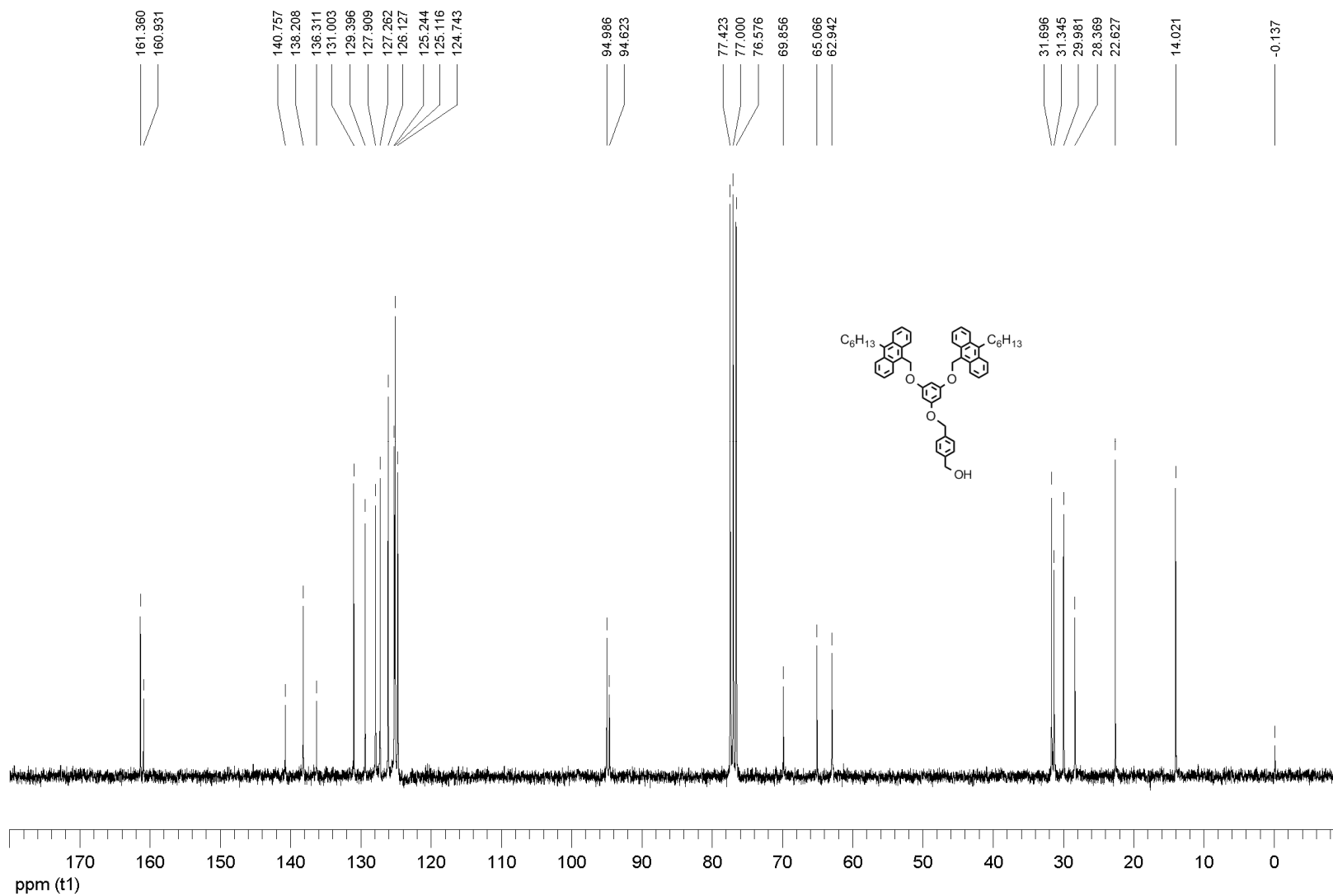




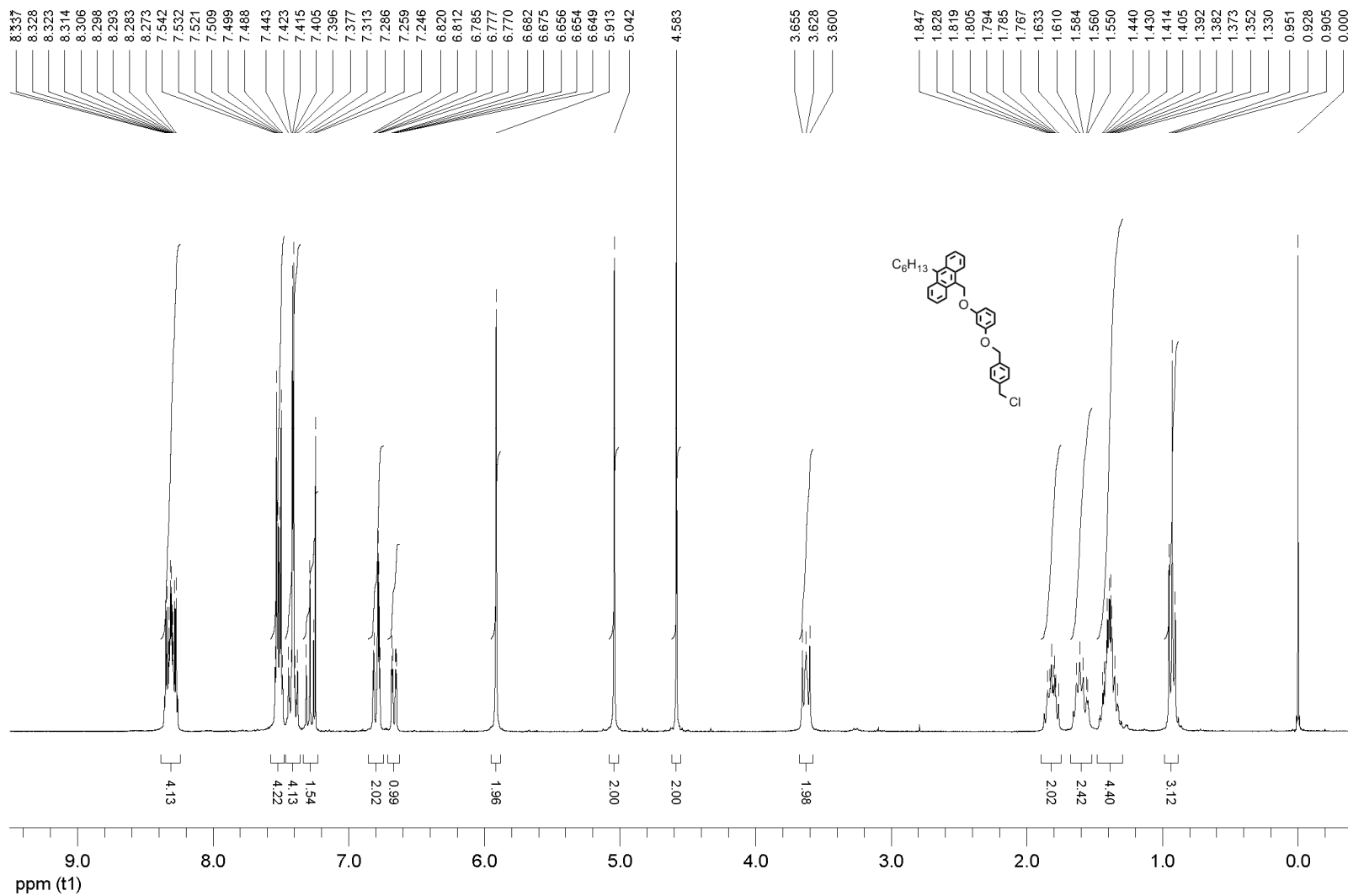
# <sup>1</sup>H-NMR spectrum of 16B



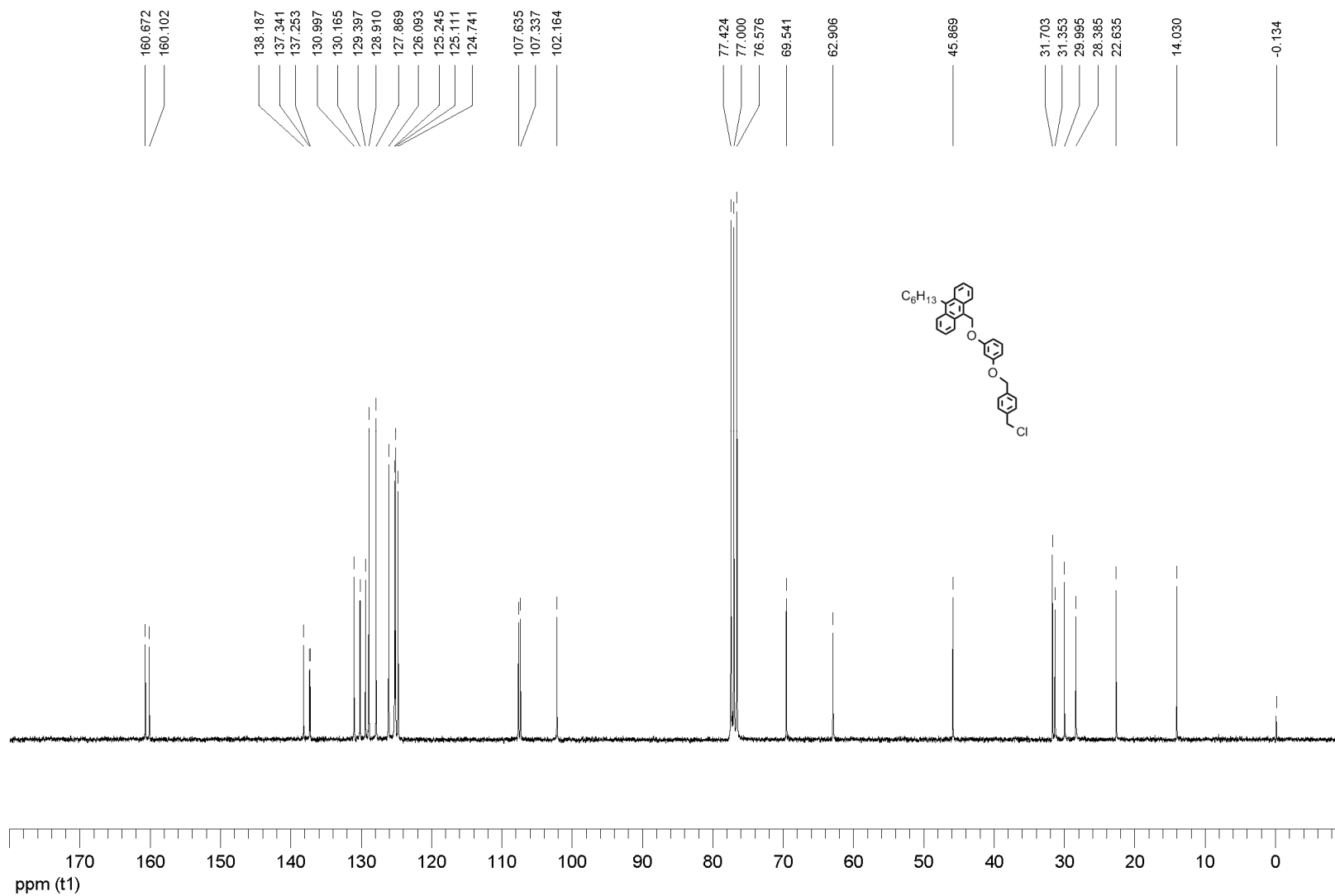
$^{13}\text{C}$ -NMR spectrum of **16B**



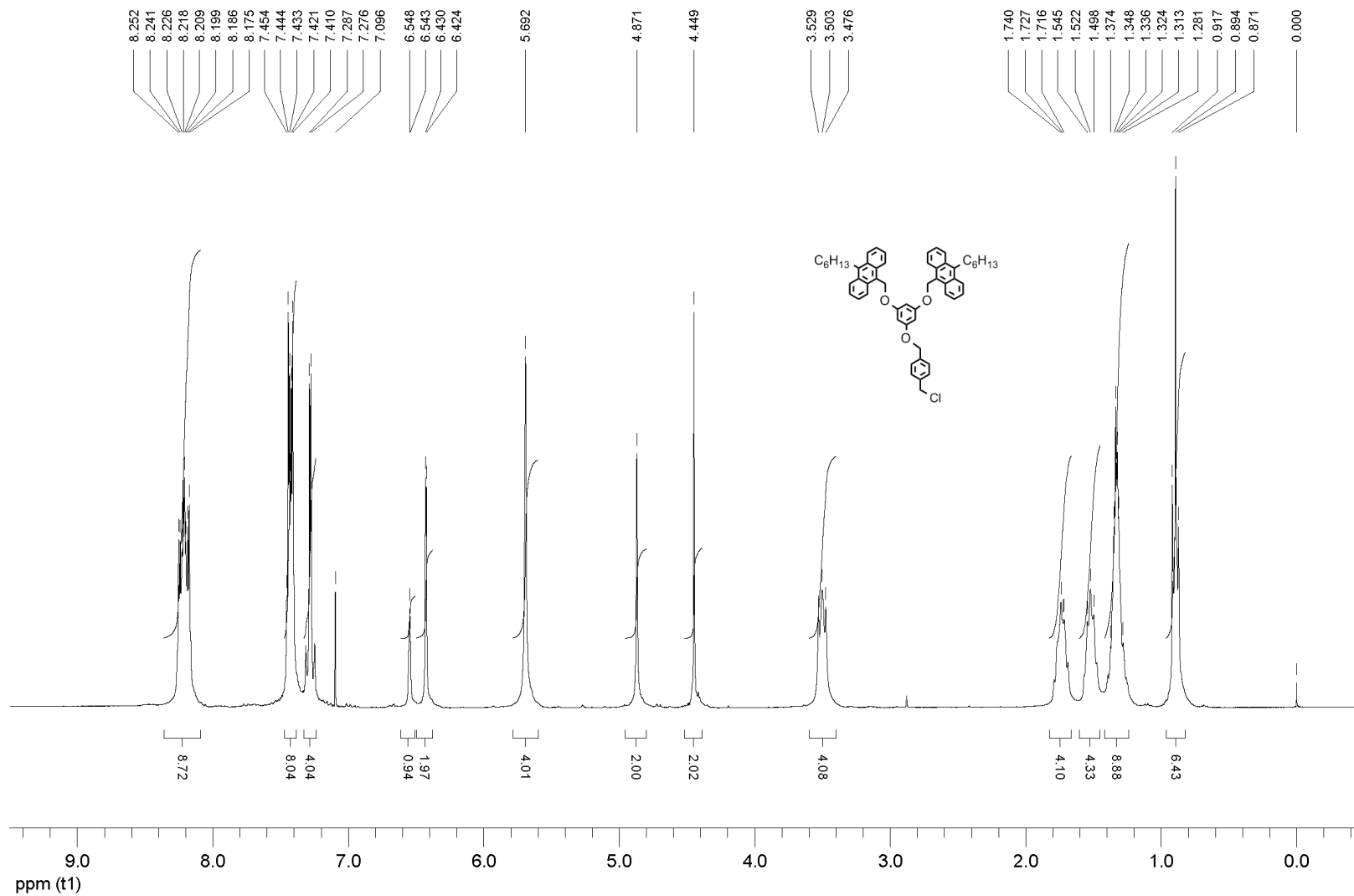
# $^1\text{H-NMR}$ spectrum of **A1**



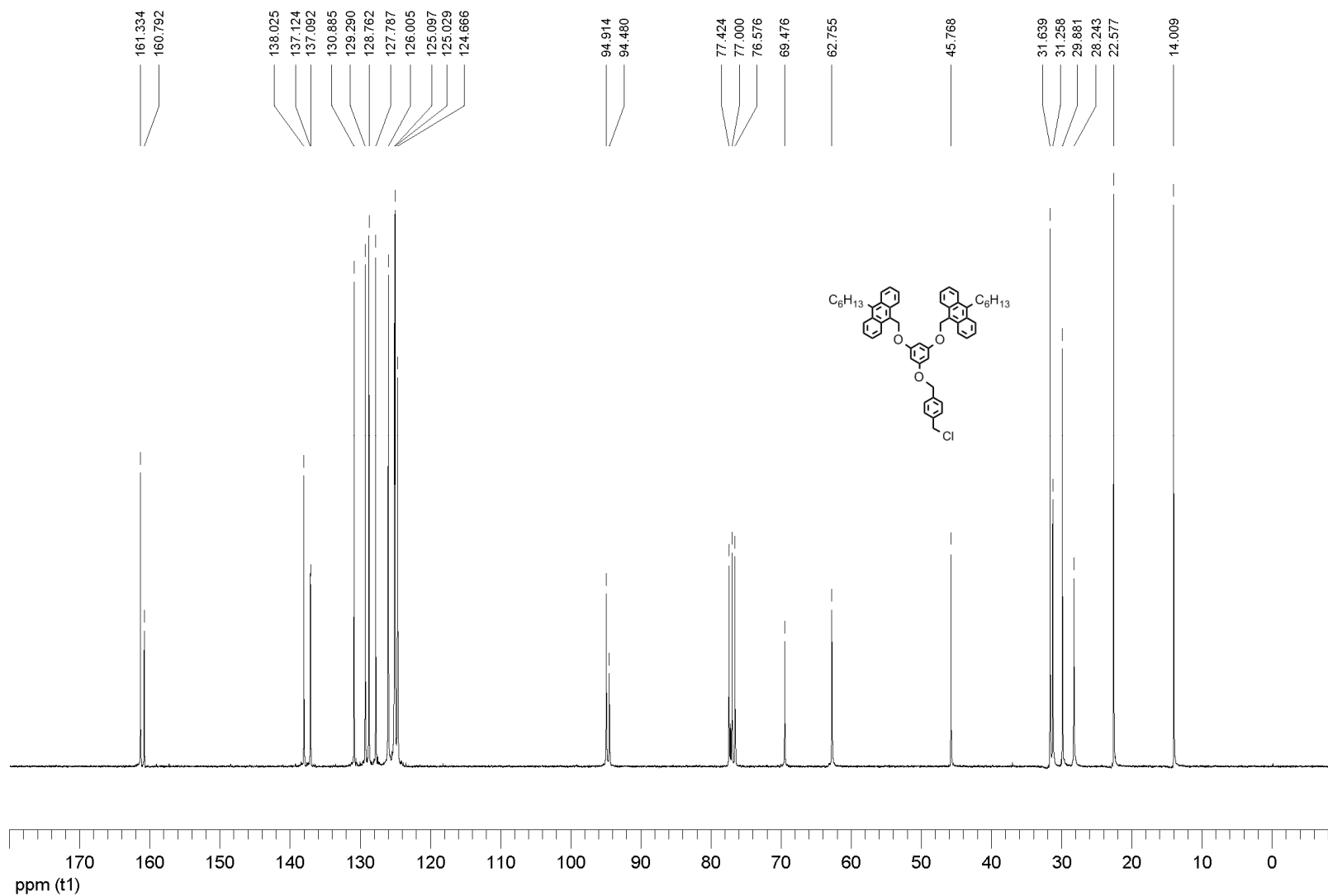
### $^{13}\text{C}$ -NMR spectrum of A1



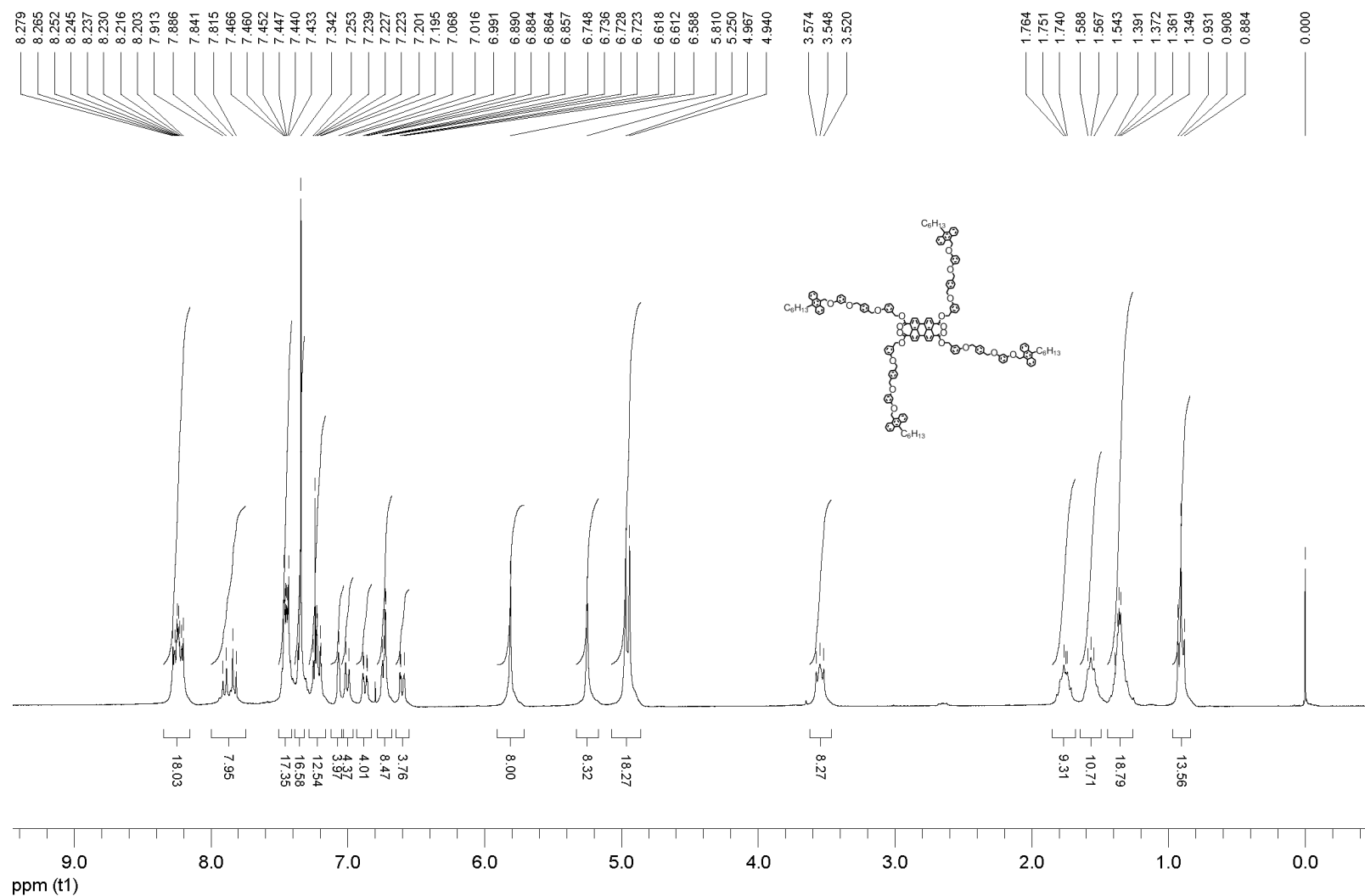
# <sup>1</sup>H-NMR spectrum of A2



### $^{13}\text{C}$ -NMR spectrum of A2

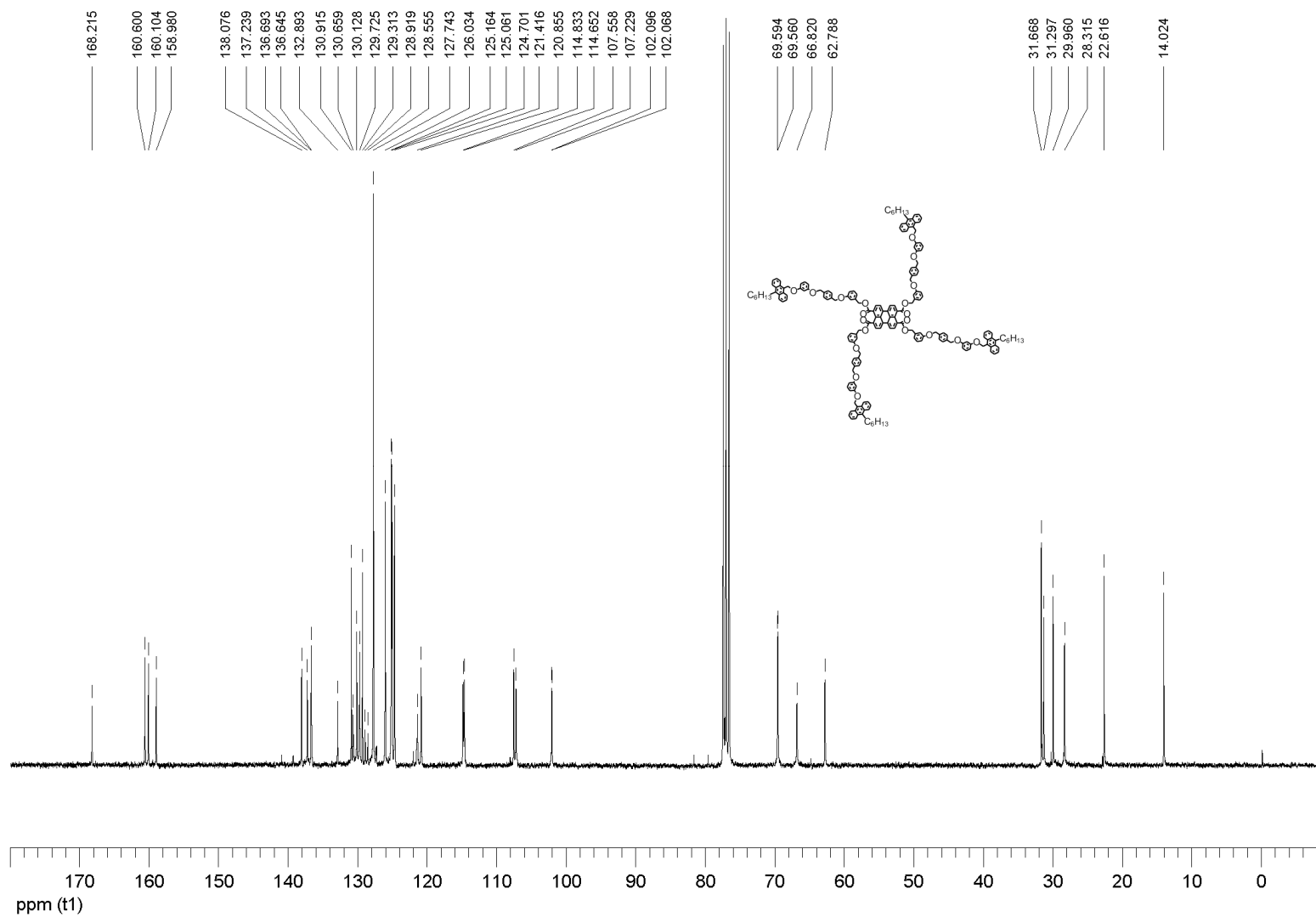


# $^1\text{H-NMR}$ spectrum of **7**

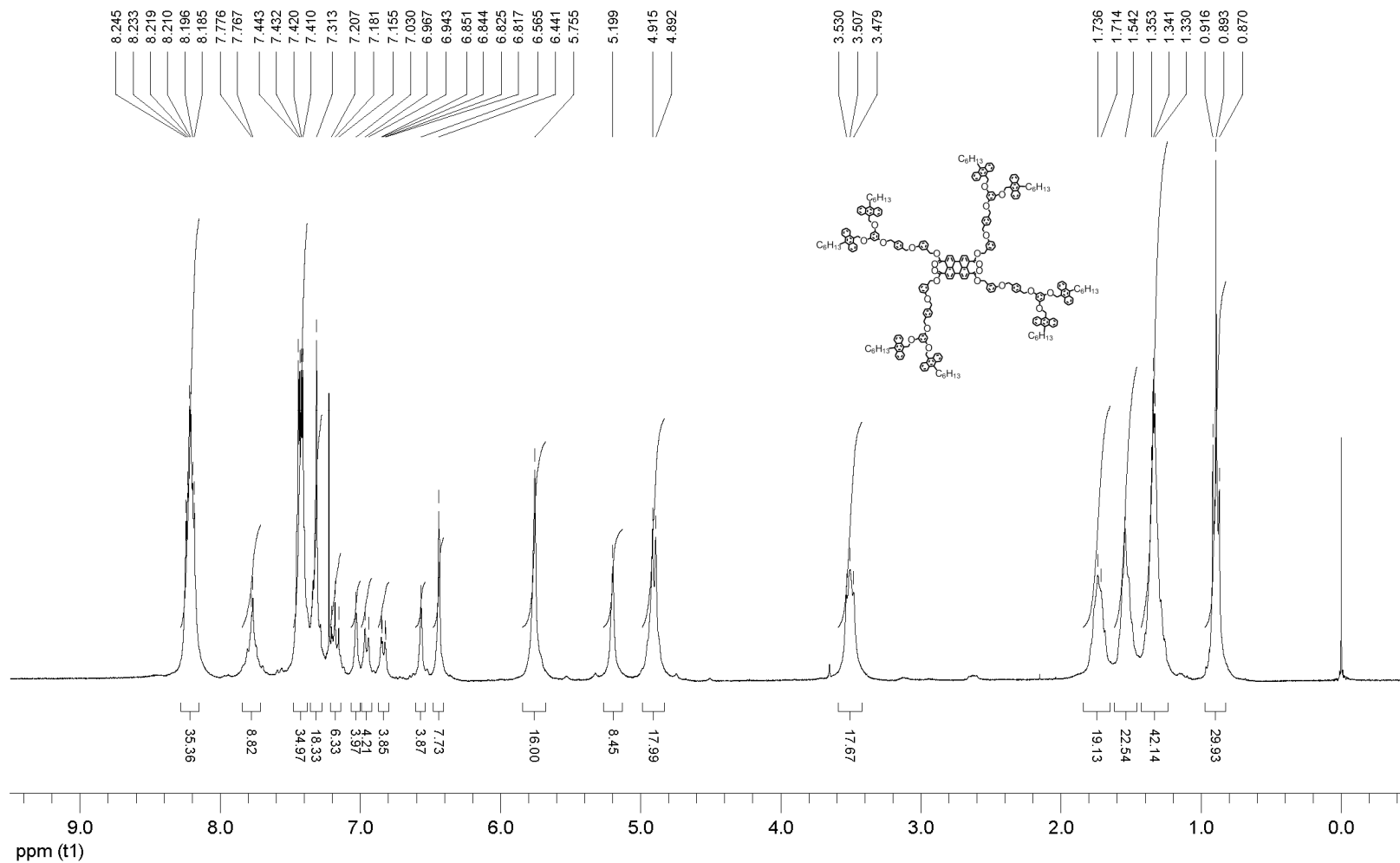




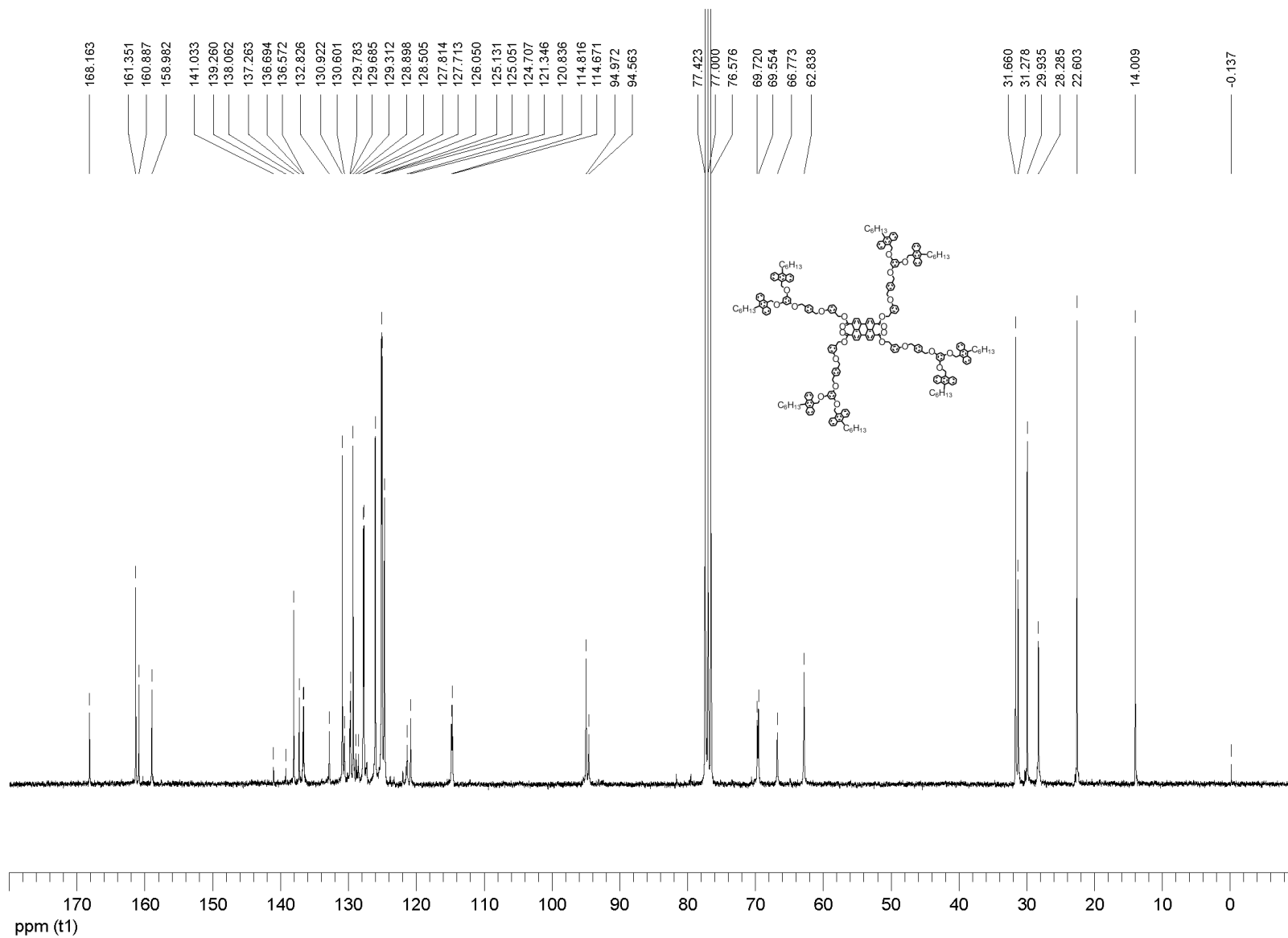
### $^{13}\text{C}$ -NMR spectrum of 7



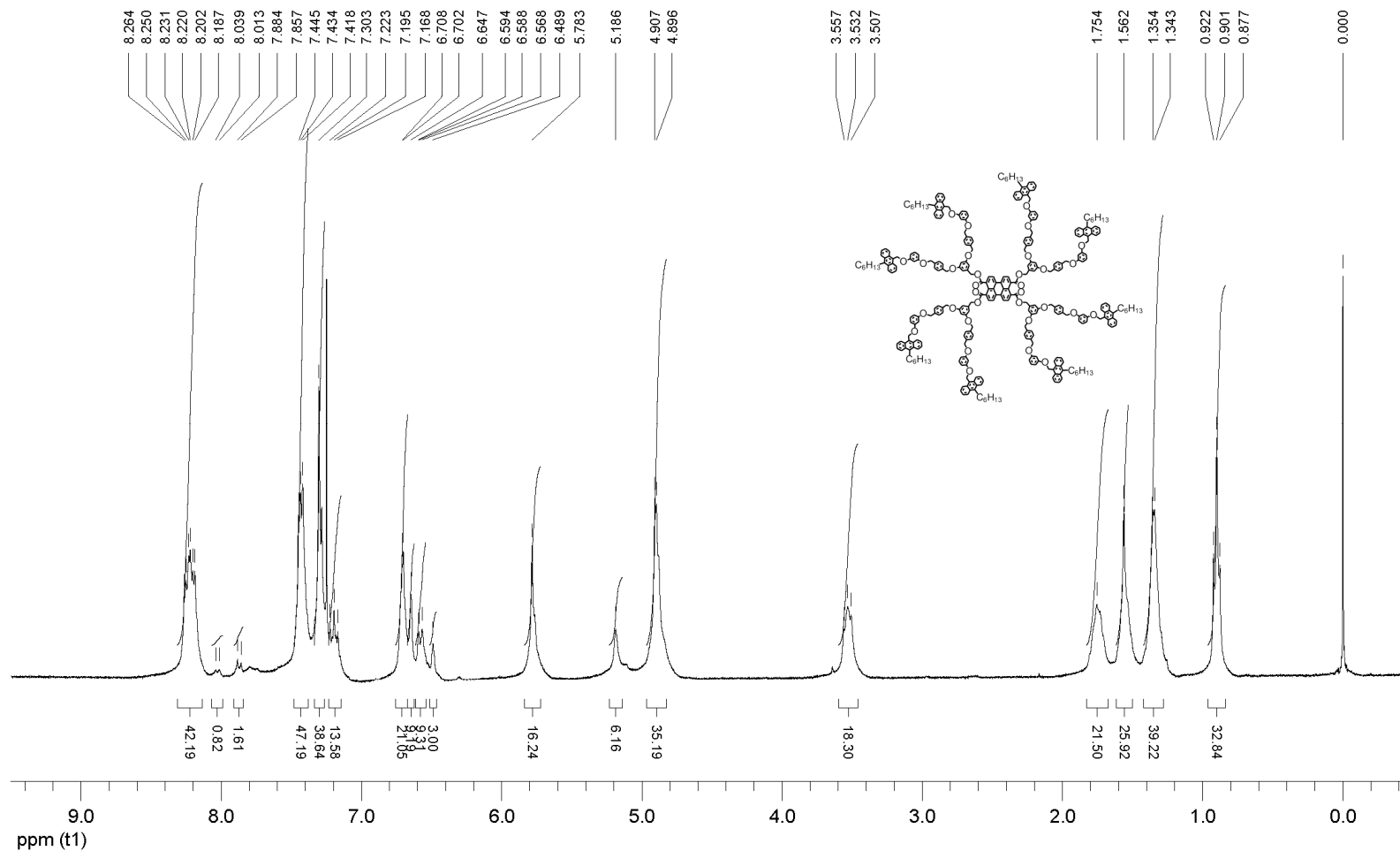
# $^1\text{H-NMR}$ spectrum of **8**



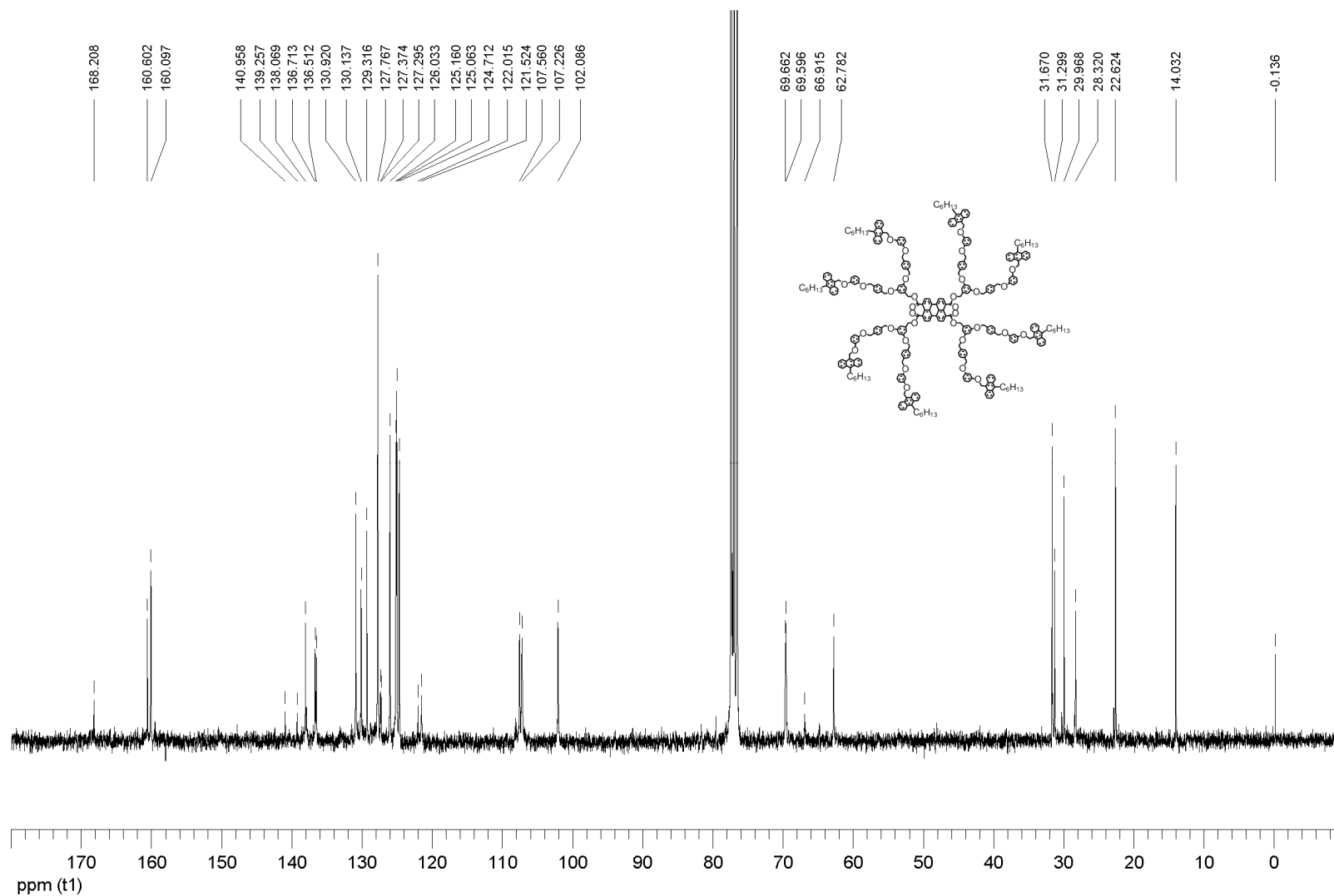
$^{13}\text{C}$ -NMR spectrum of **8**



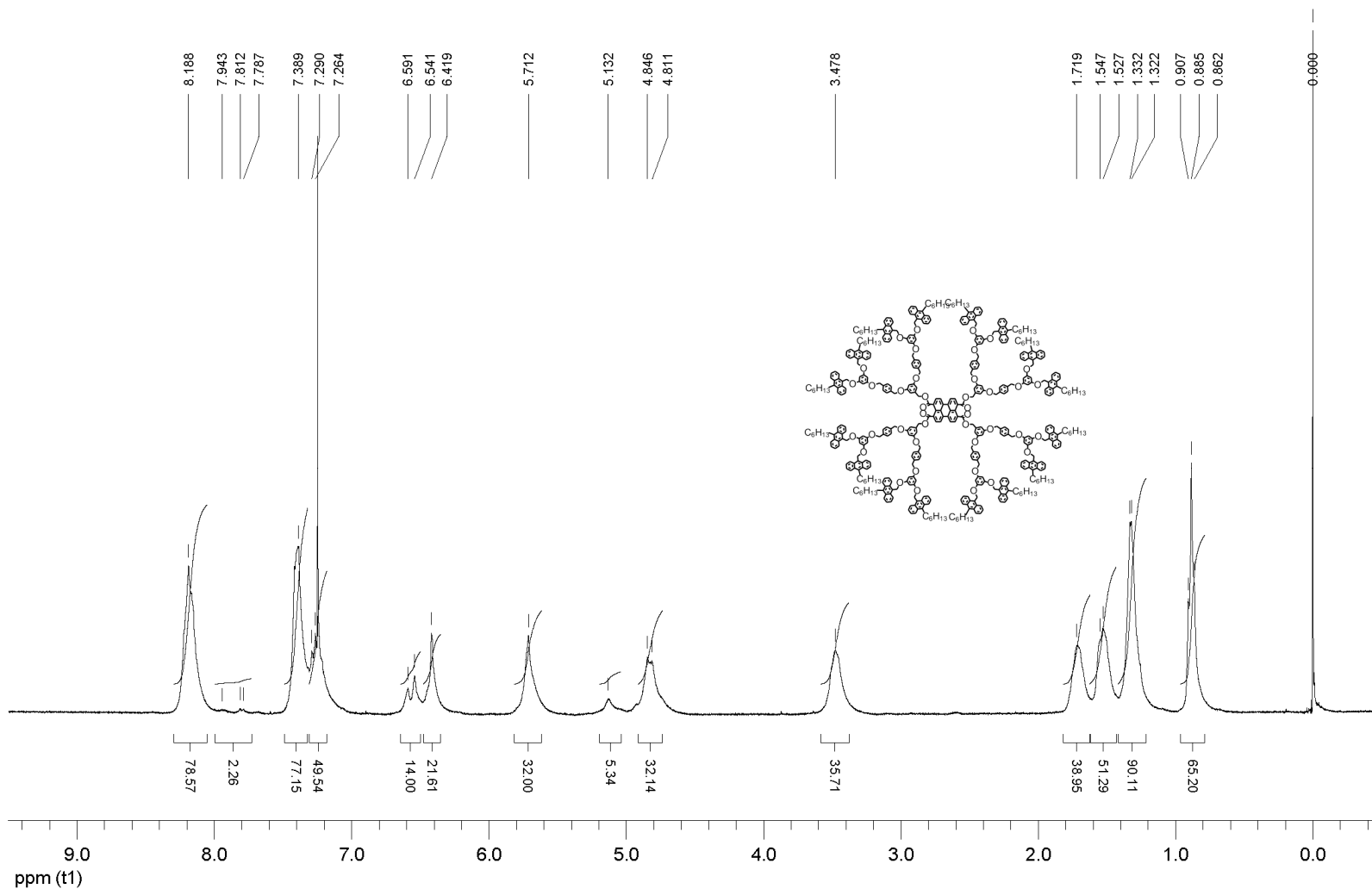
# $^1\text{H-NMR}$ spectrum of **9**



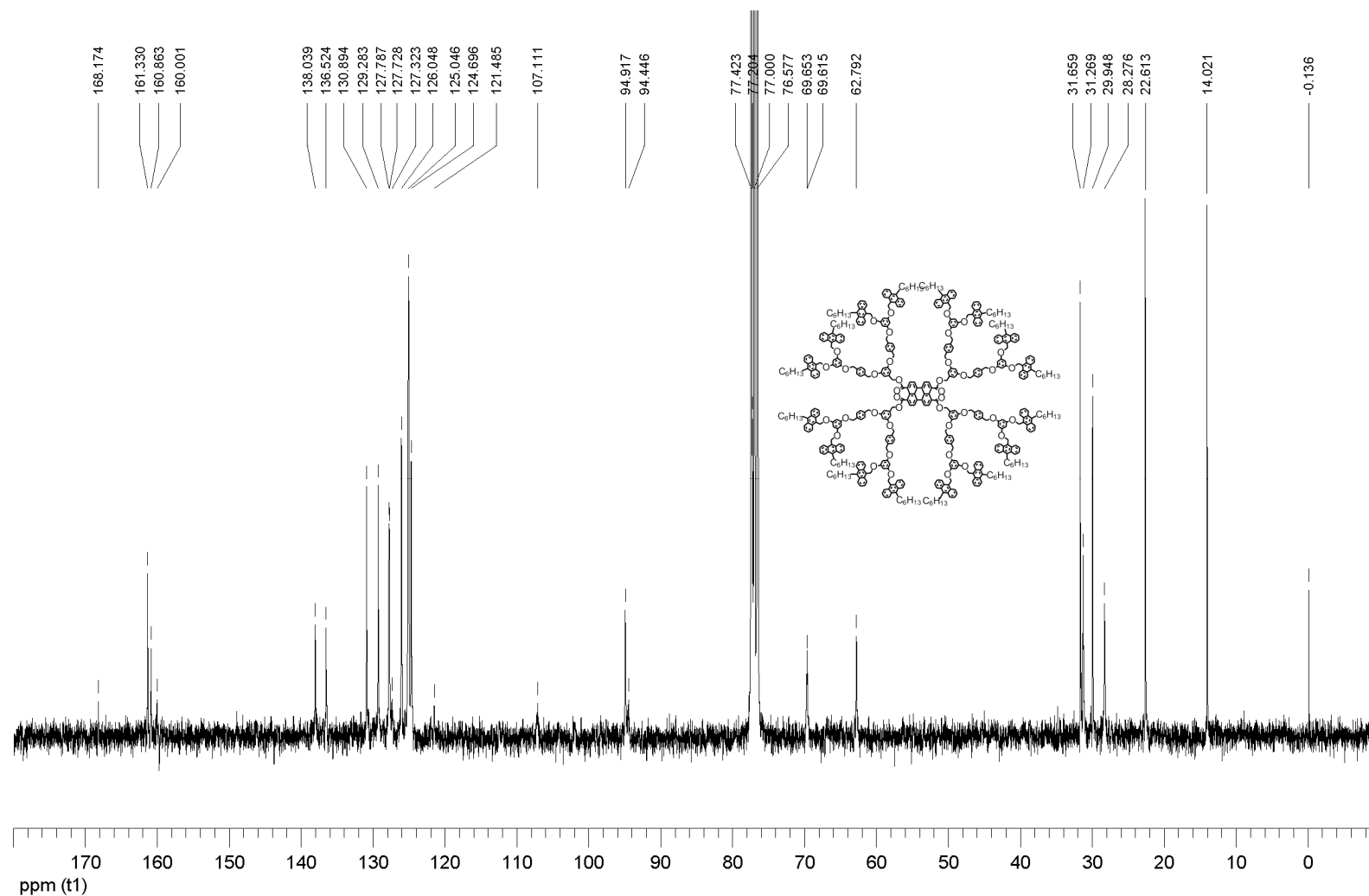
### $^{13}\text{C}$ -NMR spectrum of **9**



# $^1\text{H-NMR}$ spectrum of **10**



$^{13}\text{C}$ -NMR spectrum of **10**



### SEC traces of 7-10

