

**Sequential unsymmetrical aryl coupling of *o*-substituted aryl iodides with *o*-bromophenols and reaction with olefins: palladium-catalyzed synthesis of 6*H*-dibenzopyran derivatives**

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**Supporting information**

*General remarks*

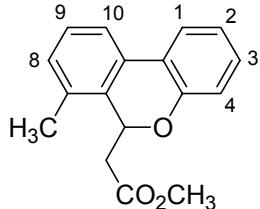
Most reagents were obtained from commercial sources and used without further purification. 1-Iodo-2,4-dimethylbenzene,<sup>1</sup> 2-bromo-4-nitrophenol,<sup>2</sup> 2-bromo-5-nitrophenol,<sup>3</sup> 2,6-dibromo-4-nitrophenol,<sup>4</sup> 2-bromo-5-methylphenol,<sup>5,6</sup> methyl 3-bromo-4-hydroxybenzoate,<sup>7</sup> methyl 4-bromo-3-hydroxybenzoate<sup>7,8</sup> were prepared according to reported procedures. DMF was dried and stored over 4 Å molecular sieves under nitrogen. Reactions were carried out under nitrogen using standard Schlenck technique. Gas chromatography analyses were performed with a Carlo Erba HRGC 5300 instrument using a 30 m SE-30 capillary column. Flash column chromatography was performed on Merck Kieselgel 60 and thin-layer chromatography on Merck 60F<sub>254</sub> plates. Melting points were determined with an Electrothermal apparatus and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AC-300 and AVANCE 300 spectrometers at 300.1 and 75.4 MHz, respectively, using the solvent as internal standard. The reported assignments are based on decoupling, COSY, NOESY, C-H, HMBC correlation experiments. Electron impact mass spectra (*m/z*, relative intensity (%)) were determined with a Hewlett Packard instrument working at 70 eV ionization energy (HP 6890 GC system and HP 5973 Mass selective detector). IR spectra were recorded on a Nicolet FT-IR 5700 spectrophotometer (Thermo Electron Corporation). Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

*General procedure for Table I*

To a Schlenck-type flask containing Pd(OAc)<sub>2</sub> (2.5 mg, 0.011 mmol) and K<sub>2</sub>CO<sub>3</sub> (125 mg, 0.90 mmol) was added a DMF solution (5 mL) of the *o*-substituted aryl iodide (0.28 mmol), the *o*-bromophenol (0.28 mmol), norbornene (22 mg, 0.23 mmol) and the terminal olefin (0.9 mmol). The reaction mixture was stirred at 80 °C for 24h. After cooling to room temperature the organic layer was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and extracted twice with a 5% solution of H<sub>2</sub>SO<sub>4</sub> (15 mL). The

organic layer was washed with water (20 mL) and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel using mixtures of hexane-EtOAc as eluent.

*6-Methoxycarbonylmethyl-7-methyl-6H-dibenzopyran (4a)*

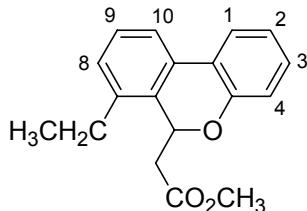


Yield: 83%. M.p. (cyclohexane): 85-86 °C. Eluent: hexane-ethyl acetate 95:5.

$^1\text{H}$  NMR:  $\delta$  7.72 (1H, dd,  $J = 7.7, 1.6$  Hz, H1), 7.59 (1H, br d,  $J = 7.8$  Hz, H10), 7.29 and 7.24 (2H, t,  $J = 7.7$  Hz, H9 and td,  $J = 7.7, 1.6$  Hz, H3), 7.13 (1H, br d,  $J = 7.6$  Hz, H8), 7.05 (1H, td,  $J = 7.6, 1.2$  Hz, H2), 6.96 (1H, dd,  $J = 8.0, 1.2$  Hz, H4), 5.95 (1H, dd,  $J = 10.7, 2.8$  Hz, H6), 3.75 (3H, s,  $\text{CO}_2\text{CH}_3$ ), 2.89 (1H, dd,  $J = 15.2, 10.7$  Hz, CH(C6)), 2.39 and 2.36 (4H, dd,  $J = 15.2, 2.8$  Hz, CH(C6) and s,  $\text{CH}_3(\text{C}7)$ );  $^{13}\text{C}$  NMR:  $\delta$  170.73 ( $\text{CO}_2\text{CH}_3$ ), 151.07 (C4a), 132.93 (C7), 131.47 (C6a), 129.95 (C8), 129.65 (C3), 128.79 (C10a), 128.26 (C9), 123.17 (C1), 122.23 (C2), 122.21 (C10b), 120.26 (C10), 118.52 (C4), 71.39 (C6), 51.86 ( $\text{CO}_2\text{CH}_3$ ), 38.07 (CH<sub>2</sub>(C6)), 18.19 ( $\text{CH}_3(\text{C}7)$ ); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  1725; MS: 268 (8,  $\text{M}^+$ ), 195 (100), 165 (12), 152 (7).

Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_3$ : C, 76.10; H, 6.01. Found: C, 75.98; H, 6.07.

*7-Ethyl-6-methoxycarbonylmethyl-6H-dibenzopyran (4b)*



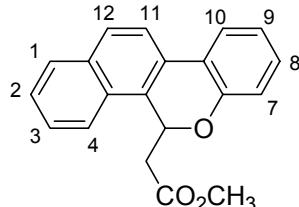
Yield: 64%. M.p. (hexane): 50-51 °C. Eluent: hexane-ethyl acetate 97:3.

$^1\text{H}$  NMR:  $\delta$  7.74 (1H, dd,  $J = 7.8, 1.6$  Hz, H1), 7.60 (1H, br d,  $J = 7.4$  Hz, H10), 7.35 (1H, t,  $J = 7.7$  Hz, H9), 7.25 (1H, dd further split, H3), 7.20 (1H, br d,  $J = 7.5$  Hz, H8), 7.06 (1H, td,  $J = 7.6, 1.3$  Hz, H2), 6.97 (1H, dd,  $J = 8.0, 1.3$  Hz, H4), 6.01 (1H, dd,  $J = 10.9, 2.7$  Hz, H6), 3.76 (3H, s,  $\text{CO}_2\text{CH}_3$ ), 2.92 (1H, dd,  $J = 15.4, 10.9$  Hz, CH(C6)), 2.82-2.53 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 2.39 (1H, dd,  $J = 15.4, 1.5$  Hz, CH(C6)), 1.32 (3H, t,  $J = 7.6$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR:  $\delta$  170.8 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 150.9 (C4a), 138.9 (C7), 130.6 (C6a), 129.6 (C3), 128.8 (C10a), 128.5 (C9), 128.0 (C8), 123.2 (C1), 122.4 (C10b), 122.2 (C2), 120.3 (C10), 118.5 (C4), 71.0 (C6), 51.9 ( $\text{CO}_2\text{CH}_3$ ), 38.6 (CH<sub>2</sub>(C6)),

24.3 (CH<sub>2</sub>CH<sub>3</sub>), 14.9 (CH<sub>2</sub>CH<sub>3</sub>); IR (KBr, cm<sup>-1</sup>):  $\nu$  1733; MS: 282 (8, M<sup>+</sup>), 209 (100), 194 (12), 165 (16).

Anal. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>: C, 76.57; H, 6.43. Found: C, 76.65; H, 6.38.

*5-Methoxycarbonylmethyl-5H-benzo-a-9-oxaphenanthrene (4c)*

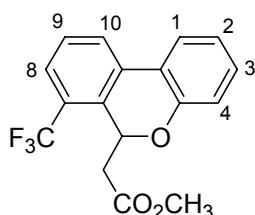


Yield: 69%. M.p. (hexane): 91 °C. Eluent: hexane-ethyl acetate 95:5.

<sup>1</sup>H NMR:  $\delta$  7.96 (1H, br d, *J* = 8.4 Hz, H4), 7.90-7.85 (3H, m, H1, H11, H12), 7.82 (1H, dd, *J* = 7.7, 1.6 Hz, H10), 7.60 (1H, m, H3), 7.51 (1H, m, H2), 7.31 (1H, td, *J* = 7.6, 1.6 Hz, H8), 7.12 (1H, td, *J* = 7.6, 1.2 Hz, H9), 7.06 (1H, dd, *J* = 8.0, 1.2 Hz, H7), 6.61 (1H, dd, *J* = 10.7, 2.8 Hz, H5), 3.80 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.01 (1H, dd, *J* = 15.3, 10.7 Hz, CH(C6)), 2.60 (1H, dd, *J* = 15.3, 2.8 Hz, CH(C6)); <sup>13</sup>C NMR:  $\delta$  170.84 (CO<sub>2</sub>CH<sub>3</sub>), 151.04 (C6a), 132.99 (C12b), 129.88 (C8), 128.92 and 128.89, (C1 and C12), 128.52 (C4a), 127.30 (C4b), 127.24 (C3), 126.14 (C10b), 125.87 (C2), 123.31 (C10), 122.25 (C9), 122.03 (C10a), 121.98 (C4), 120.32 (C11), 118.33 (C7), 71.25 (C5), 51.94 (CO<sub>2</sub>CH<sub>3</sub>), 38.44 (CH<sub>2</sub>(C6)); IR (KBr, cm<sup>-1</sup>):  $\nu$  1727; MS: 304 (13, M<sup>+</sup>), 231 (100), 215 (7), 202 (27).

Anal. Calcd for C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>: C, 79.50; H, 6.06. Found: C, 79.72; H, 5.98.

*6-Methoxycarbonylmethyl-7-trifluoromethyl-6H-dibenzopyran (4d)*



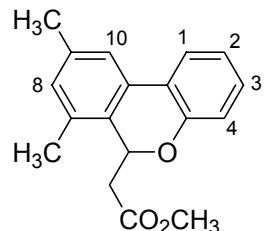
Yield: 92%. M.p. (hexane): 82 °C. Eluent: hexane-ethyl acetate 97:3.

<sup>1</sup>H NMR:  $\delta$  7.93 (1H, br d, *J* = 7.8 Hz, H10), 7.75 (1H, dd, *J* = 7.8, 1.6 Hz, H1), 7.63 (1H, d, *J* = 7.7 Hz, H8), 7.50 (1H, t, *J* = 7.8 Hz, H9), 7.32 (1H, td, *J* = 7.7, 1.6 Hz, H3), 7.11 (1H, td, *J* = 7.6, 1.2 Hz, H2), 7.00 (1H, dd, *J* = 8.1, 1.2 Hz, H4), 6.18 (1H, d further split, *J* = 11.0 Hz, H6), 3.75 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.91 (1H, dd, *J* = 15.6, 11.0 Hz, CH(C6), 2.50 (1H, dd, *J* = 15.6, 2.4 Hz, CH(C6)); <sup>13</sup>C NMR:  $\delta$  170.05 (CO<sub>2</sub>CH<sub>3</sub>), 150.95 (C4a), 130.87 (C10a), 130.81 (C3, C6a), 128.52 (C9), 126.37 (C10), 126.04 (quart, *J*<sub>C,F</sub> = 30.4 Hz, C7), 125.14 (quart, *J*<sub>C,F</sub> = 5.8 Hz, C8), 123.94 (quart, *J*<sub>C,F</sub> =

273.6 Hz, CF<sub>3</sub>), 123.19 (C1), 122.61 (C2), 121.18 (C10b), 118.76 (C4), 70.55 (quart,  $J_{C,F} = 2.7$  Hz, C6), 51.89 (CO<sub>2</sub>CH<sub>3</sub>), 38.06 (CH<sub>2</sub>(C6)); IR (KBr, cm<sup>-1</sup>):  $\nu$  1740; MS: 322 (7, M<sup>+</sup>), 249 (100), 201 (10), 165 (8), 152 (7).

Anal. Calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>: C, 63.36; H, 4.07. Found: C, 63.27; H, 4.01.

#### *6-Methoxycarbonylmethyl-7,9-dimethyl-6H-dibenzopyran (4e)*

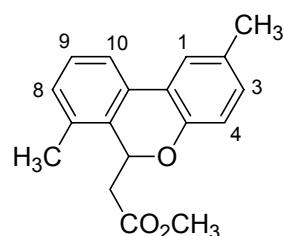


Yield: 88%. M.p. (hexane): 99 °C. Eluent: hexane-ethyl acetate 98:2.

<sup>1</sup>H NMR:  $\delta$  7.73 (1H, dd,  $J = 7.8, 1.6$  Hz, H1), 7.42 (1H, br s, H10), 7.25 (1H, m, H3), 7.06 (1H, td,  $J = 7.5, 1.3$  Hz, H2), 6.98 and 6.97 (2H, dd,  $J = 8.0, 1.3$  Hz, H4 and s further split, H8), 5.94 (1H, dd,  $J = 10.7, 2.8$  Hz, H6), 3.76 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.88 (1H, dd,  $J = 15.2, 10.7$  Hz, CH(C6)), 2.38 and 2.37 (4H, dd,  $J = 15.2, 2.8$  Hz, CH(C6) and s, CH<sub>3</sub>(C9)), 2.32 (3H, s, CH<sub>3</sub>(C7)); <sup>13</sup>C NMR:  $\delta$  170.71 (CO<sub>2</sub>CH<sub>3</sub>), 151.07 (C4a), 137.76 (C7), 132.72 (C9), 130.74 (C8), 129.41 (C3), 128.59 (C6a), 128.56 (C10a), 123.03 (C1), 122.18 (C10b), 122.07 (C2), 120.74 (C10), 118.41 (C4), 71.33 (C6), 51.75 (CO<sub>2</sub>CH<sub>3</sub>), 38.21 (CH<sub>2</sub>(C6)), 21.23 (CH<sub>3</sub>(C9)), 18.01 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>):  $\nu$  1733; MS: 282 (7, M<sup>+</sup>), 209 (100), 178 (5), 165 (9).

Anal. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>: C, 76.57; H, 6.43. Found: C, 76.24; H, 6.67.

#### *2,7-Dimethyl-6-methoxycarbonylmethyl-6H-dibenzopyran (4f)*



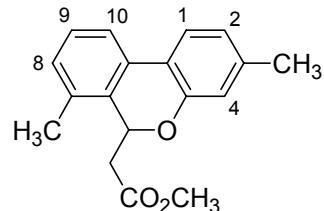
Yield: 46%. M.p. (hexane): 41 °C. Eluent: hexane-ethyl acetate 97:3.

<sup>1</sup>H NMR:  $\delta$  7.59 (1H, br d,  $J = 7.7$  Hz, H10), 7.54 (1H, d,  $J = 2.1$  Hz, H1), 7.29 (1H, t,  $J = 7.7$  Hz, H9), 7.13 (1H, br d,  $J = 7.6$  Hz, H8), 7.06 (1H, dd,  $J = 8.2, 2.1$  Hz, H3), 6.88 (1H, d,  $J = 8.2$  Hz, H4), 5.93 (1H, dd,  $J = 10.8, 2.8$  Hz, H6), 3.76 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.90 (1H, dd,  $J = 15.2, 10.9$  Hz, CH(C6)), 2.37, 2.37 and 2.36 (7H, dd,  $J = 15.2, 2.8$  Hz, CH(C6), s, CH<sub>3</sub>(C2) and s, CH<sub>3</sub>(C7)); <sup>13</sup>C NMR:  $\delta$  170.8 (CO<sub>2</sub>CH<sub>3</sub>), 148.7 (C4a), 132.8 (C7), 131.5 (C6a), 131.4 (C2), 130.3 (C3), 129.8

(C8), 128.8 (C10a), 128.1 (C9), 123.5 (C1), 121.8 (C10b), 120.1 (C10), 118.2 (C4), 71.2 (C6), 51.8 (CO<sub>2</sub>CH<sub>3</sub>), 37.8 (CH<sub>2</sub>(C6)), 20.9 (CH<sub>3</sub>(C2)), 18.2 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>):  $\nu$  1739; MS: 282 (8, M<sup>+</sup>), 209 (100), 178 (8), 165 (23).

Anal. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>: C, 76.57; H, 6.43. Found: C, 76.50; H, 6.41.

### 3,7-Dimethyl-6-methoxycarbonylmethyl-6H-dibenzopyran (4g)

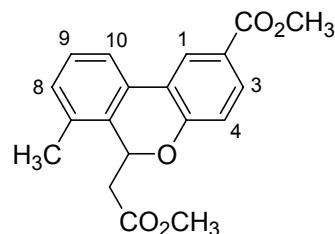


Yield: 52%. M.p. (hexane): 104 °C. Eluent: hexane-ethyl acetate 95:5.

<sup>1</sup>H NMR:  $\delta$  7.61 (1H, d, *J* = 7.9 Hz, H1), 7.56 (1H, d, *J* = 7.8 Hz, H10), 7.27 (1H, t, *J* = 7.7 Hz, H9), 7.11 (1H, d further split, *J* = 7.5 Hz, H8), 6.88 (1H, d further split, *J* = 8.2 Hz, H2), 6.80 (1H, br s, H4), 5.95 (1H, dd, *J* = 10.7, 2.7 Hz, H6), 3.77 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.91 (1H, dd, *J* = 15.3, 10.7 Hz, CH(C6)), 2.38 and 2.35 (7H, dd, *J* = 15.3, 2.7 Hz, CH(C6), s, 2CH<sub>3</sub>); <sup>13</sup>C NMR,  $\delta$ : 170.7 (CO<sub>2</sub>CH<sub>3</sub>), 150.9 (C4a), 139.9 (C3), 132.8 (C7), 130.9 (C6a), 129.4 (C8), 128.3 (C10a), 128.1 (C9), 123.1 (C2), 122.9 (C1), 119.8 (C10), 119.3 (C10b), 118.8 (C4), 71.3 (C6), 51.8 (CO<sub>2</sub>CH<sub>3</sub>), 37.9 (CH<sub>2</sub>(C6)), 21.3 (CH<sub>3</sub>(C3)), 18.1 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>):  $\nu$  1744; MS: 282 (12, M<sup>+</sup>), 209 (100), 178 (7), 165 (15).

Anal. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>: C, 76.57; H, 6.43. Found: C, 76.34; H, 6.29.

### 2-Methoxycarbonyl-6-methoxycarbonylmethyl-7-methyl-6H-dibenzopyran (4h)



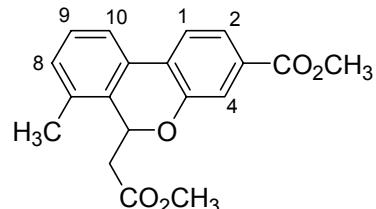
Yield: 40%. M.p. (hexane): 89 °C. Eluent: hexane-ethyl acetate 95:5.

<sup>1</sup>H NMR:  $\delta$  8.45 (1H, d, *J* = 2.0 Hz, H1), 7.92 (1H, dd, *J* = 8.5, 2.0 Hz, H3), 7.67 (1H, br d, *J* = 7.7 Hz, H10), 7.31 (1H, t, *J* = 7.7 Hz, H9), 7.16 (1H, br d, *J* = 7.5 Hz, H8), 6.98 (1H, d, *J* = 8.5 Hz, H4), 6.00 (1H, dd, *J* = 10.8, 2.8 Hz, H6), 3.92 (3H, s, CH<sub>3</sub>O<sub>2</sub>C(C2)), 3.74 (3H, s, CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 2.82 (1H, dd, *J* = 15.4, 10.8 Hz, CH(C6)), 2.40 (1H, dd, *J* = 15.3, 2.8 Hz, CH(C6)), 2.35 (3H, s, CH<sub>3</sub>(C7)); <sup>13</sup>C NMR:  $\delta$  170.4 (CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 166.7 (CH<sub>3</sub>O<sub>2</sub>C(C2)), 155.2 (C4a), 133.0 (C7), 131.1

(C3), 130.9 (C6a), 130.5 (C8), 128.5 (C9), 127.8 (C10a), 125.2 (C1), 124.2 (C2), 121.9 (C10b), 120.5 (C10), 118.4 (C4), 71.9 (C6), 52.0 ( $\text{CH}_3\text{O}_2\text{C}(\text{C}2)$ ), 51.9 ( $\text{CH}_2\text{CO}_2\text{CH}_3$ ), 38.5 ( $\text{CH}_2(\text{C}6)$ ), 18.1 ( $\text{CH}_3(\text{C}7)$ ); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  1733, 1716; MS: 326 (10,  $\text{M}^+$ ), 253 (100), 194 (10), 165 (15).

Anal. Calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_5$ : C, 69.93; H, 5.56. Found: C, 70.04; H, 5.43.

### *3-Methoxycarbonyl-7-methyl-6-methoxycarbonylmethyl-6H-dibenzopyran (4i)*

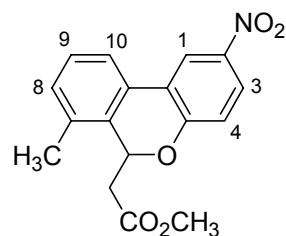


Yield: 72%. M.p. (hexane): 96 °C. Eluent: hexane-ethyl acetate 95:5.

$^1\text{H}$  NMR:  $\delta$  7.77 (1H, d,  $J = 8.2$  Hz, H1), 7.72 (1H, dd,  $J = 8.1, 1.7$  Hz, H2), 7.62 and 7.61 (2H, d,  $J = 7.8$  Hz, H10 and d,  $J = 1.7$  Hz, H4), 7.31 (1H, t,  $J = 7.7$  Hz, H9), 7.19 (1H, br d,  $J = 7.6$  Hz, H8), 5.98 (1H, dd,  $J = 10.8, 2.7$  Hz, H6), 3.91 (3H, s,  $\text{CH}_3\text{O}_2\text{C}(\text{C}3)$ ), 3.76 (3H, s,  $\text{CH}_2\text{CO}_2\text{CH}_3$ ), 2.84 (1H, dd,  $J = 15.4, 10.8$  Hz, CH(C6)), 2.38 and 2.35 (4H, dd,  $J = 15.4, 2.7$  Hz, CH(C6) and s, CH<sub>3</sub>(C7));  $^{13}\text{C}$  NMR:  $\delta$  170.4 ( $\text{CH}_2\text{CO}_2\text{CH}_3$ ), 166.5 ( $\text{CH}_3\text{O}_2\text{C}(\text{C}3)$ ), 150.9 (C4a), 133.1 (C7), 131.9 (C6a), 131.1 (C8, C3), 128.4 (C9), 127.8 (C10a), 126.4 (C10b), 123.4 (C2), 123.1 (C1), 120.9 (C10), 119.7 (C4), 71.5 (C6), 52.1 ( $\text{CH}_3\text{O}_2\text{C}(\text{C}3)$ ), 52.0 ( $\text{CH}_2\text{CO}_2\text{CH}_3$ ), 38.1 ( $\text{CH}_2(\text{C}6)$ ), 18.2 ( $\text{CH}_3(\text{C}7)$ ); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  1723; MS: 326 (5,  $\text{M}^+$ ), 254 (17), 253 (100), 194 (7), 165 (12).

Anal. Calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_5$ : C, 69.93; H, 5.56. Found: C, 69.69; H, 5.71.

### *6-Methoxycarbonylmethyl-7-methyl-2-nitro-6H-dibenzopyran(4j)*



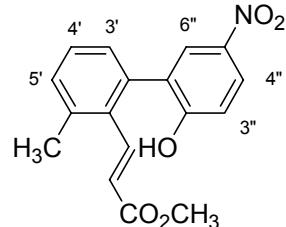
Yield: 52%. M.p. (hexane:  $\text{CH}_2\text{Cl}_2 = 1:1$ ): 130 °C. Eluent: hexane- ethyl acetate 9:1.

$^1\text{H}$  NMR:  $\delta$  8.65 (1H, d,  $J = 2.7$  Hz, H1), 8.13 (1H, dd,  $J = 8.9, 2.6$  Hz, H3), 7.67 (1H, br d,  $J = 7.7$  Hz, H10), 7.37 (1H, t,  $J = 7.7$  Hz, H9), 7.23 (1H, br d,  $J = 7.7$  Hz, H8), 7.04 (1H, d,  $J = 8.9$  Hz, H4), 6.06 (1H, dd,  $J = 10.9, 2.7$  Hz, H6), 3.76 (3H, s,  $\text{CO}_2\text{CH}_3$ ), 2.81 (1H, dd,  $J = 15.4, 10.9$  Hz, CH(C6)), 2.45 (1H, dd,  $J = 15.4, 2.7$  Hz, CH(C6)), 2.37 (3H, s, CH<sub>3</sub>(C7));  $^{13}\text{C}$  NMR:  $\delta$  170.0 ( $\text{CO}_2\text{CH}_3$ ), 156.6 (C4a), 142.9 (C2), 133.3 (C7), 131.5 (C8), 130.7 (C6a), 128.9 (C9), 126.7 (C10a), 125.1 (C3), 122.5 (C10b), 120.7 (C10), 119.3 (C1), 119.0 (C4), 72.5 (C6), 52.1 ( $\text{CO}_2\text{CH}_3$ ), 38.8

(CH<sub>2</sub>(C6)), 18.2 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>):  $\nu$  1733; MS: 313 (9, M<sup>+</sup>), 240 (100), 194 (35), 165 (15).

Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>: C, 65.17; H, 4.83; N, 4.47. Found: C, 65.30; H, 4.80; N, 4.71.

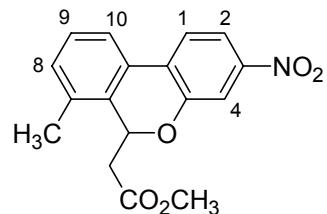
*Methyl E-3-[6'-methyl-2'-(2''-hydroxy-5''-nitrophenyl)phenyl]propenoate (10j)*



The product **10j** was obtained as an unseparable mixture together with 2-bromo-4-nitrophenol (15 mg, 3:1 based on NMR). Yield: 13%. Eluent: hexane-ethyl acetate 9:1.

<sup>1</sup>H NMR:  $\delta$  8.17 (1H, dd, *J* = 8.9, 2.8 Hz, H4''), 8.07 (1H, d, *J* = 2.8 Hz, H6''), 7.64 (1H, d, *J* = 16.3 Hz, H3), 7.39-7.33 (2H, m, H4', H5'), 7.16 (1H, dd, *J* = 6.8, 1.9 Hz, H3'), 6.99 (1H, d, *J* = 8.9 Hz, H3''), 5.75 (1H, d, *J* = 16.3, H2), 3.68 (3H, s, CH<sub>3</sub>O(C1)), 2.44 (3H, s, CH<sub>3</sub>(C6'')); <sup>13</sup>C NMR:  $\delta$  166.8 (C1), 158.0 (C2''), 141.8 (C3, C5''), 138.2 (C6'), 134.0 (C1'), 133.8 (C2'), 131.7 (C5'), 129.4 (C4'), 128.7 (C3'), 128.3 (C1''), 126.7 (C6''), 125.6 (C4''), 124.1 (C2), 116.1 (C3''), 51.8 (CH<sub>3</sub>O(C1)), 21.1 (CH<sub>3</sub>(C6'')); IR (KBr, cm<sup>-1</sup>):  $\nu$  1708; MS: 313 (18, M<sup>+</sup>), 240 (100), 194 (40), 165 (21).

*6-Methoxycarbonylmethyl-7-methyl-3-nitro-6H-dibenzopyran (4k)*

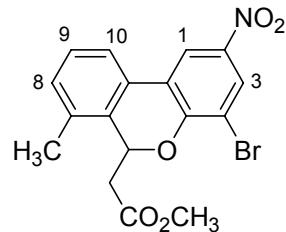


Yield: 83%. M.p. (hexane): 117 °C. Eluent: hexane-ethyl acetate 9:1.

<sup>1</sup>H NMR:  $\delta$  7.89 (1H, dd, *J* = 8.6, 2.2 Hz, H2), 7.83 (1H, d, *J* = 8.6 Hz, H1), 7.78 (1H, br d, *J* = 2.2 Hz, H4), 7.62 (1H, br d, *J* = 7.6 Hz, H10), 7.34 (1H, t, *J* = 7.7 Hz, H9), 7.24 (1H, br d, *J* = 7.6 Hz, H8), 6.01 (1H, dd, *J* = 10.8, 2.7 Hz, H6), 3.76 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.81 (1H, dd, *J* = 15.4, 10.8 Hz, CH(C6)), 2.42 (1H, dd, *J* = 15.4, 2.7 Hz, CH(C6)), 2.36 (3H, s, CH<sub>3</sub>(C7)); <sup>13</sup>C NMR:  $\delta$  170.1 (CO<sub>2</sub>CH<sub>3</sub>), 151.4 (C4a), 148.3 (C3), 133.4 (C7), 132.0 (C8), 131.8 (C6a), 128.7 (C9), 128.3 (C10b), 126.7 (C10a), 123.6 (C1), 121.2 (C10), 117.3 (C2), 113.9 (C4), 72.0 (C6), 52.1 (CO<sub>2</sub>CH<sub>3</sub>), 38.4 (CH<sub>2</sub>(C6)), 18.1 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>):  $\nu$  1746; MS: 313 (14, M<sup>+</sup>), 240 (100), 194 (35), 165 (15).

Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>: C, 65.17; H, 4.83; N, 4.47. Found: C, 65.34; H, 4.80; N, 4.67.

*4-Bromo-6-methoxycarbonylmethyl-7-methyl-2-nitro-6H-dibenzopyran (4l)*

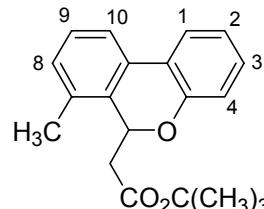


Yield: 86%. M.p. (hexane): 112 °C. Eluent: hexane-ethyl acetate 85:15.

<sup>1</sup>H NMR: δ 8.59 (1H, d, *J* = 2.6 Hz, H1), 8.39 (1H, d, *J* = 2.6 Hz, H3), 7.66 (1H, br d, *J* = 7.7 Hz, H10), 7.38 (1H, t, *J* = 7.7 Hz, H9), 7.26 (1H, br d, *J* = 7.6 Hz, H8), 6.20 (1H, dd, *J* = 11.2, 2.9 Hz, H6), 3.79 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.76 (1H, dd, *J* = 15.2, 11.2 Hz, CH(C6)), 2.48 (1H, dd, *J* = 15.2, 2.9 Hz, CH(C6)), 2.39 (3H, s, CH<sub>3</sub>(C7)); <sup>13</sup>C NMR: δ 169.6 (CO<sub>2</sub>CH<sub>3</sub>), 153.5 (C4a), 142.8 (C2), 133.4 (C7), 132.0 (C8), 130.5 (C6a), 129.1 (C9), 128.2 (C3), 126.3 (C10a), 123.5 (C10b), 121.0 (C10), 118.0 (C1), 112.9 (C4), 73.7 (C6), 52.3 (CO<sub>2</sub>CH<sub>3</sub>), 39.0 (CH<sub>2</sub>(C6)), 18.1 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>): ν 1726; MS: 393 (10, M<sup>+</sup>), 391 (10, M<sup>+</sup>), 320 (100), 318 (100), 274 (30), 272 (30), 193 (25).

Anal. Calcd for C<sub>17</sub>H<sub>14</sub>BrNO<sub>5</sub>: C, 52.06; H, 3.60; N, 3.57. Found: C, 52.31; H, 3.52; N, 3.69.

*6-t-Butoxycarbonylmethyl-7-methyl-6H-dibenzopyran (4m)*

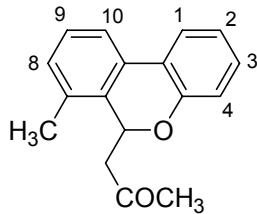


Yield: 8%. M.p. (hexane): 43 °C. Eluent: hexane-ethyl acetate 98:2.

<sup>1</sup>H NMR: δ 7.73 (1H, dd, *J* = 7.8, 1.6 Hz, H1), 7.59 (1H, br d, *J* = 7.8 Hz, H10), 7.28 and 7.25 (2H, t, *J* = 7.8 Hz, H9 and td, H3), 7.13 (1H, d further split, *J* = 7.5 Hz, H8), 7.06 (1H, td, *J* = 7.5, 1.3 Hz, H2), 6.98 (1H, dd, *J* = 8.1, 1.3 Hz, H4), 5.93 (1H, dd, *J* = 10.9, 2.7 Hz, H6), 2.78 (1H, dd, *J* = 15.0, 10.9 Hz, CH(C6)), 2.36 (3H, s, CH<sub>3</sub>(C7)), 2.30 (1H, dd, *J* = 15.0, 2.7 Hz, CH(C6)), 1.52 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR: δ 169.6 (CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 151.2 (C4a), 132.8 and 131.7 (C7 and C6a), 129.8 (C8), 129.5 (C3), 128.7 (C10a), 128.1 (C9), 123.1 (C1), 122.2 (C10b), 122.0 (C2), 120.1 (C10), 118.4 (C4), 80.9 (C(CH<sub>3</sub>)<sub>3</sub>), 71.8 (C6), 39.4 (CH<sub>2</sub>(C6)), 28.0 (C(CH<sub>3</sub>)<sub>3</sub>), 18.1 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>): ν 1730; MS: 310 (9, M<sup>+</sup>), 253 (30), 195 (100), 165 (9).

Anal. Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>: C, 77.39; H, 7.14. Found: C, 77.45; H, 7.23.

*6-Methylcarbonylmethyl-7-methyl-6H-dibenzopyran (4n)*

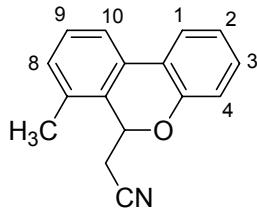


Yield: 93%. M.p. (hexane): 65 °C. Eluent: hexane-ethyl acetate 97:3.

<sup>1</sup>H NMR: δ 7.74 (1H, dd, *J* = 7.8, 1.6 Hz, H1), 7.59 (1H, br d, *J* = 7.8 Hz, H10), 7.28 and 7.24 (2H, t, *J* = 7.7 Hz, H9 and m, H3), 7.13 (1H, br d, *J* = 7.7 Hz, H8), 7.06 (1H, td, *J* = 7.6, 1.3 Hz, H2), 6.95 (1H, dd, *J* = 8.0, 1.3 Hz, H4), 5.98 (1H, dd, *J* = 10.6, 2.4 Hz, H6), 3.15 (1H, dd, *J* = 15.8, 10.6 Hz, CH(C6)), 2.33 and 2.29 (4H, s, CH<sub>3</sub>(C7) and dd, *J* = 15.8, 2.4 Hz, CH(C6)), 2.19 (3H, s, COCH<sub>3</sub>); <sup>13</sup>C NMR: δ 205.9 (COCH<sub>3</sub>), 151.0 (C4a), 132.8 (C7), 131.8 (C6a), 130.0 (C8), 129.6 (C3), 128.6 (C10a), 128.1 (C9), 123.2 (C1), 122.3 (C10b), 122.2 (C2), 120.12 (C10), 118.3 (C4), 71.0 (C6), 45.9 (CH<sub>2</sub>(C6)), 30.9 (CH<sub>3</sub>CO), 18.2 (CH<sub>3</sub>(C7)); IR (KBr, cm<sup>-1</sup>): ν 1714; MS: 252 (6, M<sup>+</sup>), 195 (100), 165 (17), 152 (10).

Anal. Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>: C, 80.93; H, 6.39. Found: C, 80.89; H, 6.51.

*6-Cyanomethyl-7-methyl-6H-dibenzopyran (4o)*



Yield: 72%. M.p. (hexane): 89 °C. Eluent: hexane-ethyl acetate 98:2.

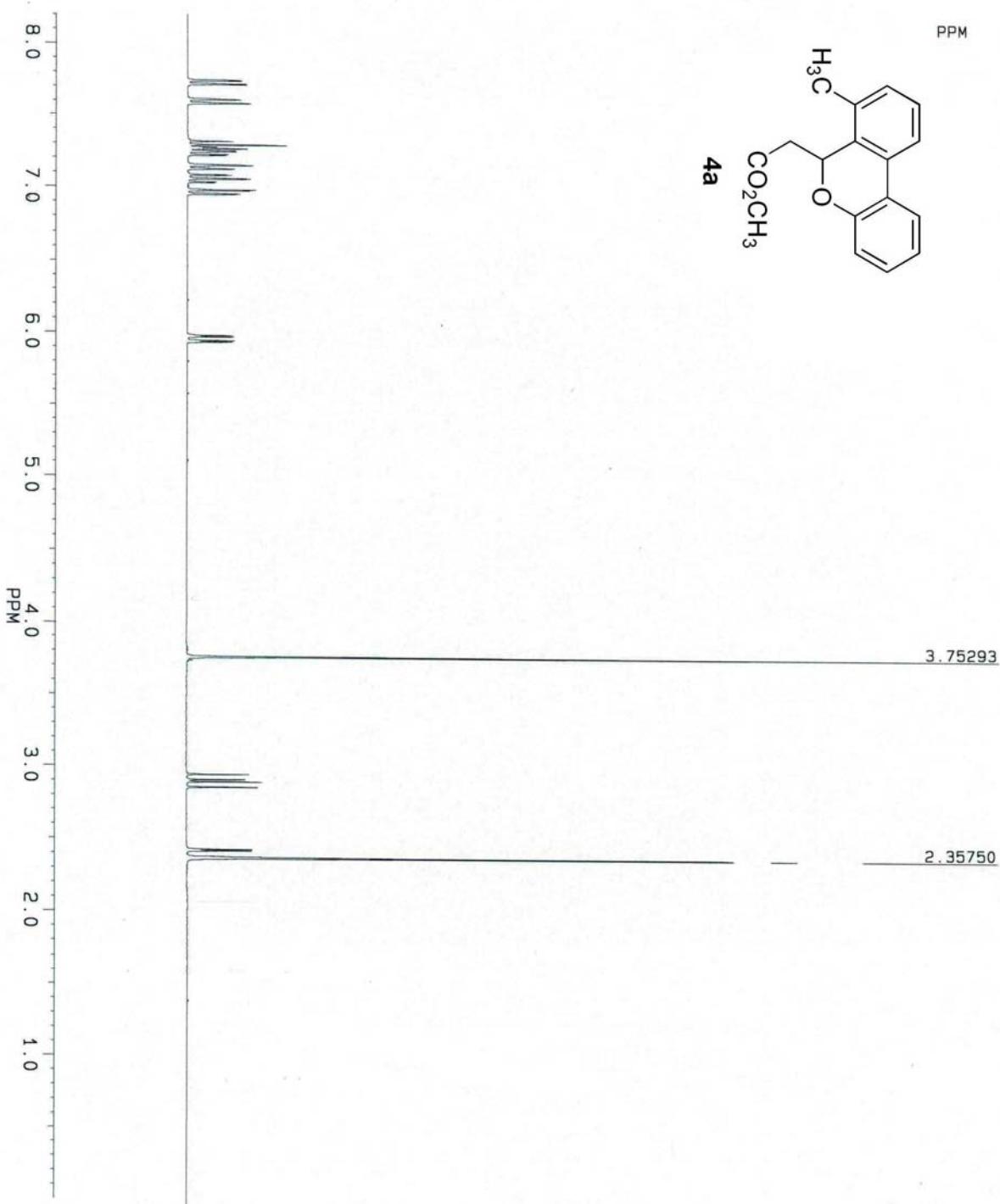
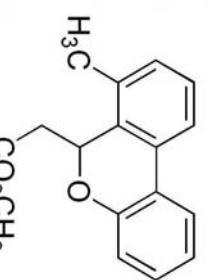
<sup>1</sup>H NMR: δ 7.75 (1H, dd, *J* = 8.1, 1.5 Hz, H1), 7.61 (1H, br d, *J* = 7.8 Hz, H10), 7.34 and 7.30 (2H, t, *J* = 7.8 Hz, H9 and td, H3), 7.17 (1H, d further split, *J* = 7.4 Hz, H8), 7.15-7.08 (2H, m, H2, H4), 5.78 (1H, dd, *J* = 9.5, 4.3 Hz, H6), 2.82 (1H, dd, *J* = 17.1, 9.5 Hz, CH(C6)), 2.53 (1H, dd, *J* = 17.1, 4.3 Hz, CH(C6), 2.37 (3H, s, CH<sub>3</sub>); <sup>13</sup>C NMR: δ 149.9 (C4a), 133.2 (C7), 130.2 (C8), 130.0 (C3), 129.5 (C6a), 128.9 (C9), 128.4 (C10a), 123.3 (C1), 122.8 (C2), 121.7 (C10b), 120.5 (C10), 118.5 (C4), 116.6 (CN), 69.7 (C6), 21.8 (CH<sub>2</sub>(C6)), 18.3 (CH<sub>3</sub>); IR (KBr, cm<sup>-1</sup>): ν 2249; MS: 235 (8, M<sup>+</sup>), 195 (100), 165 (14), 152 (8).

Anal. Calcd for C<sub>16</sub>H<sub>13</sub>NO: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.74; H, 5.51; N, 6.13.

*References:*

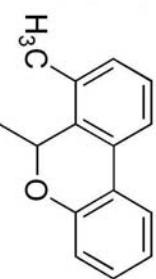
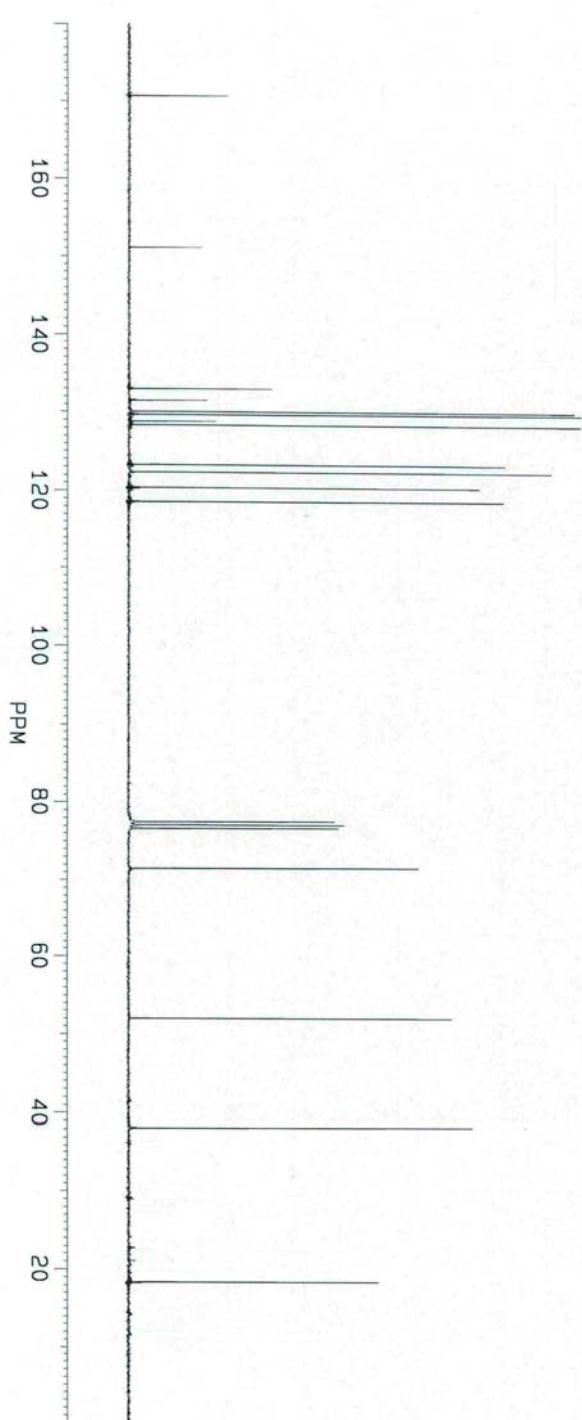
1. Morgan, G. T.; Coulson, E. A. *J. Chem. Soc.* **1929**, 2203.

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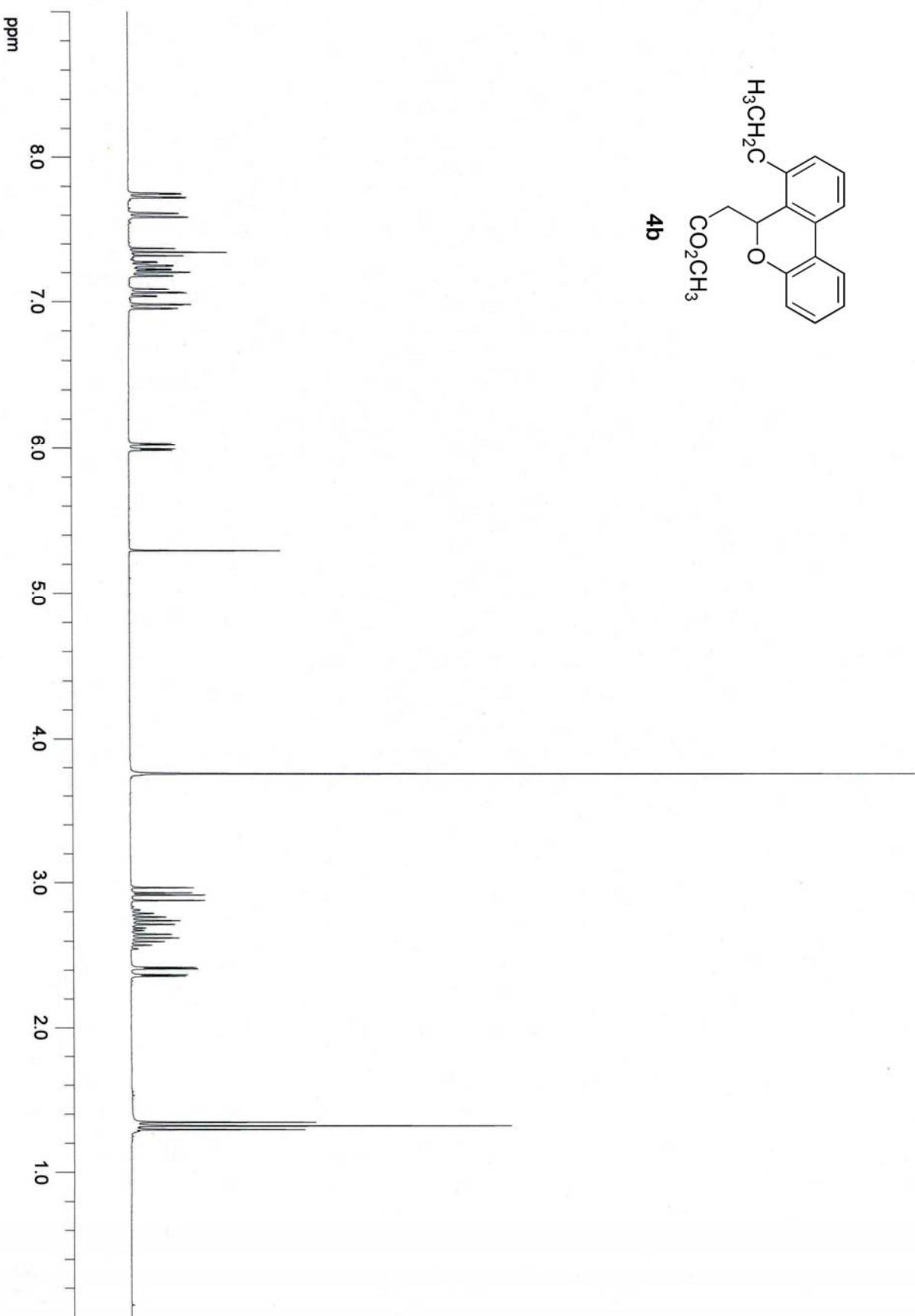
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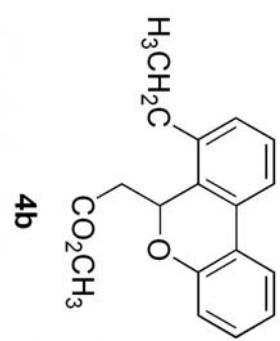
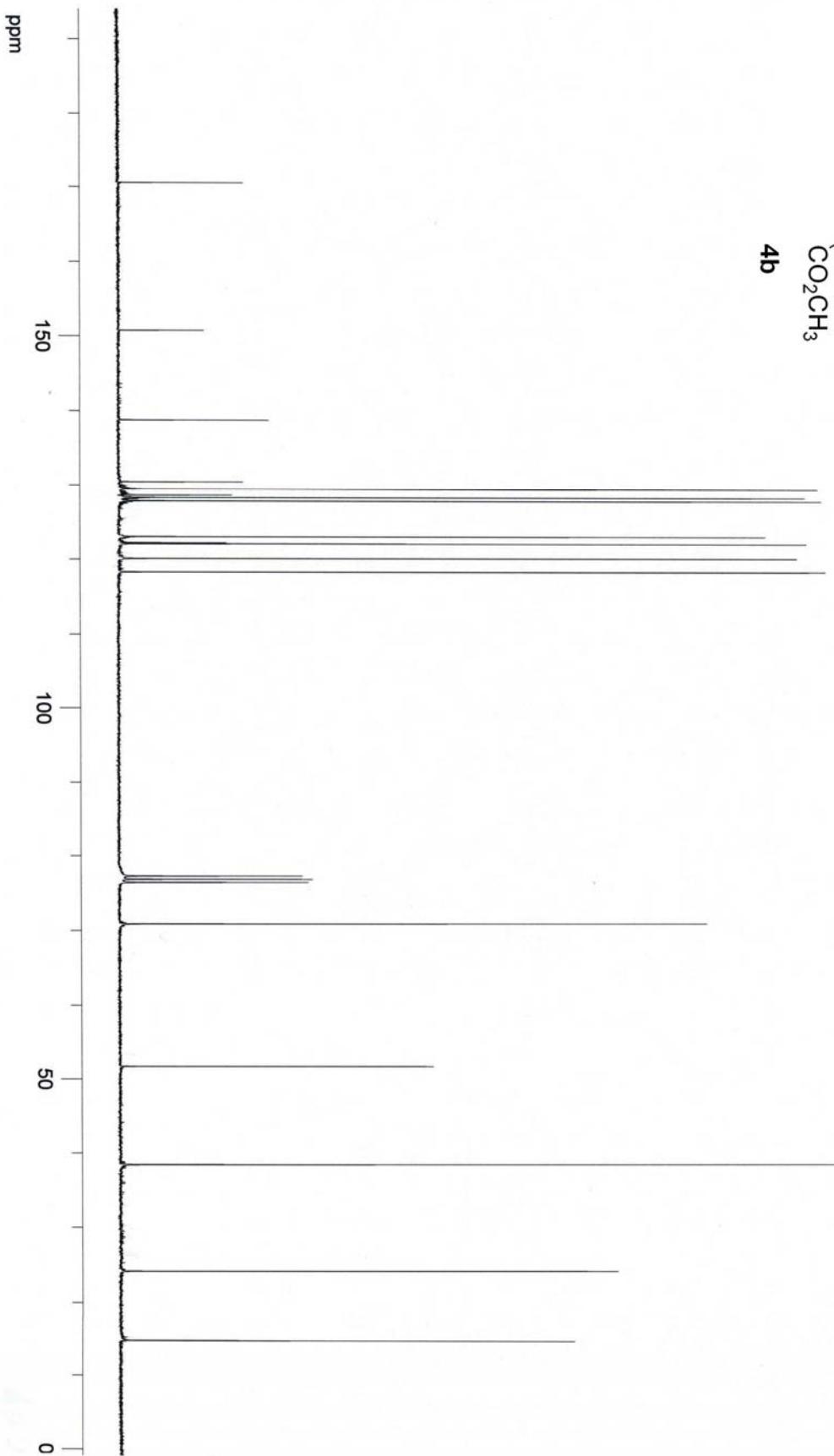
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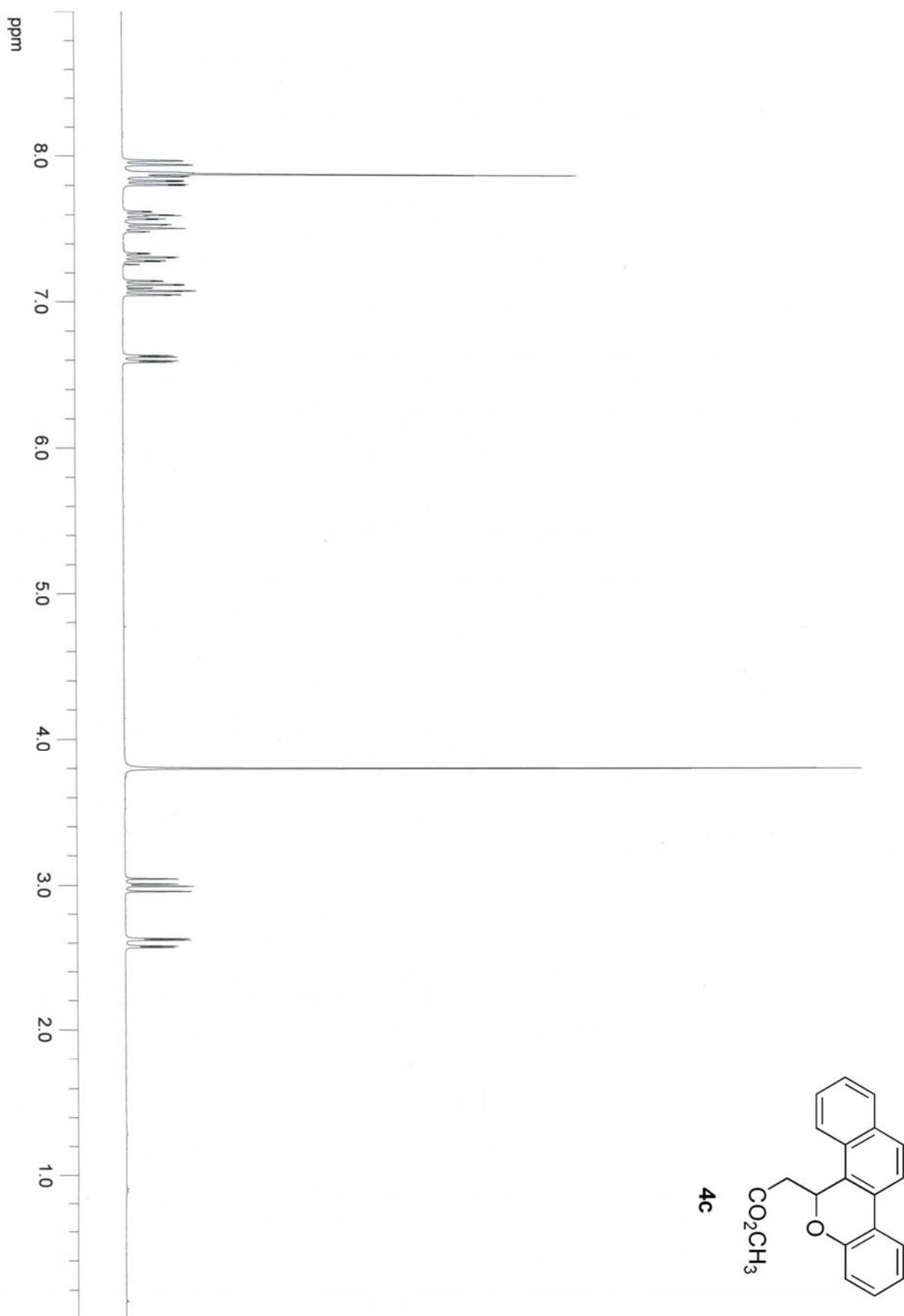
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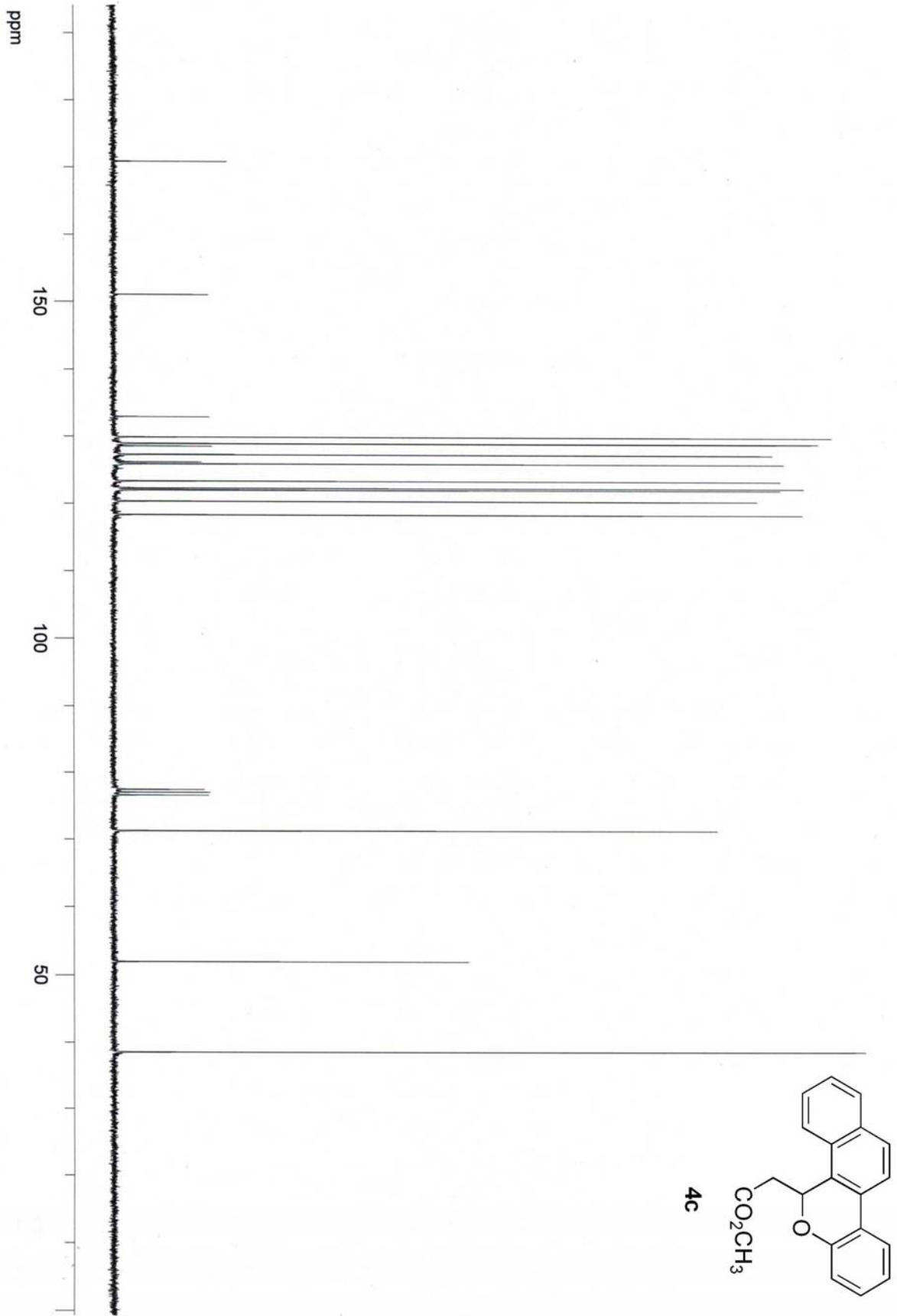
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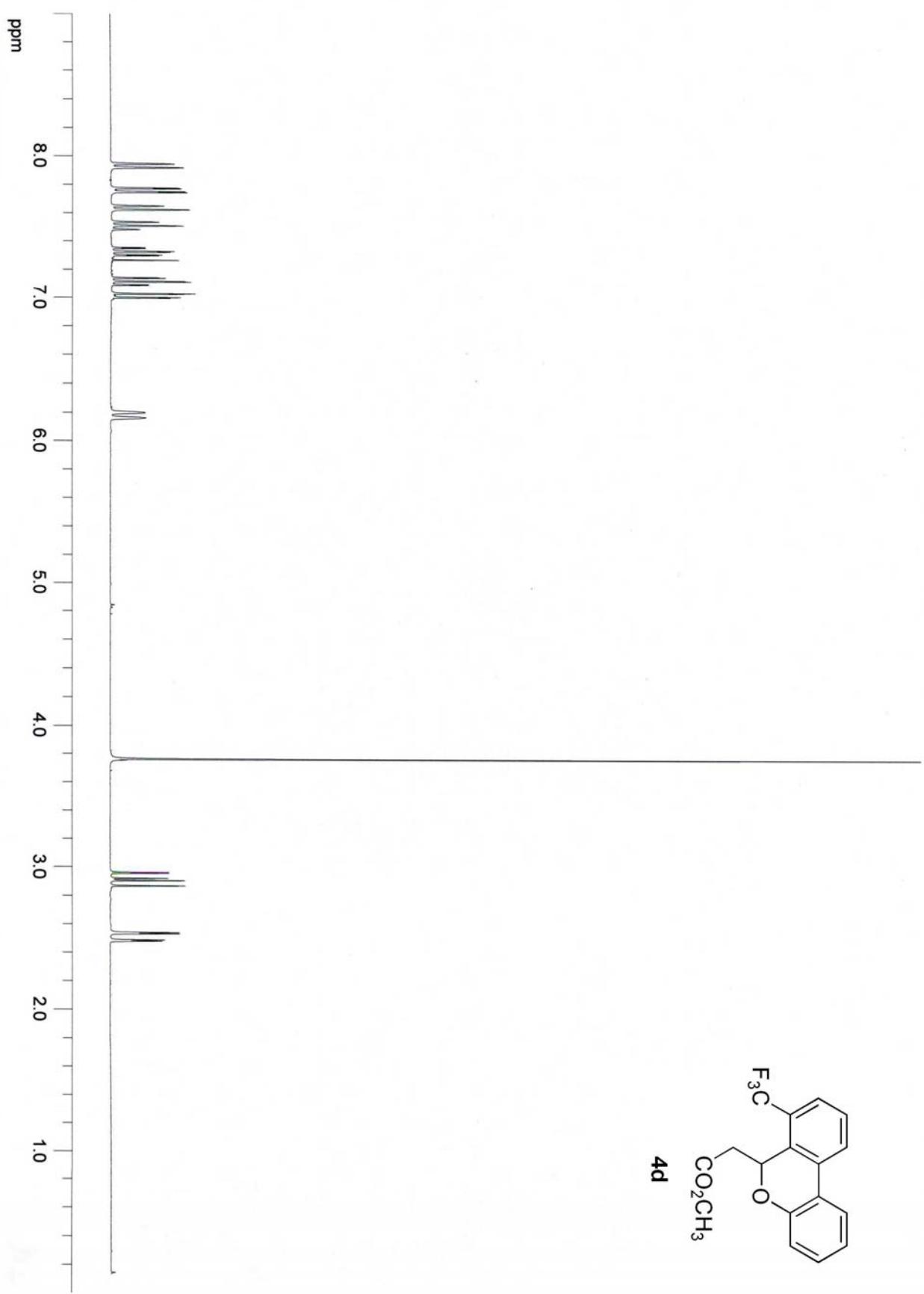
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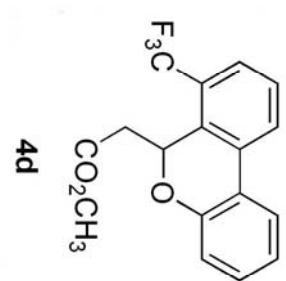


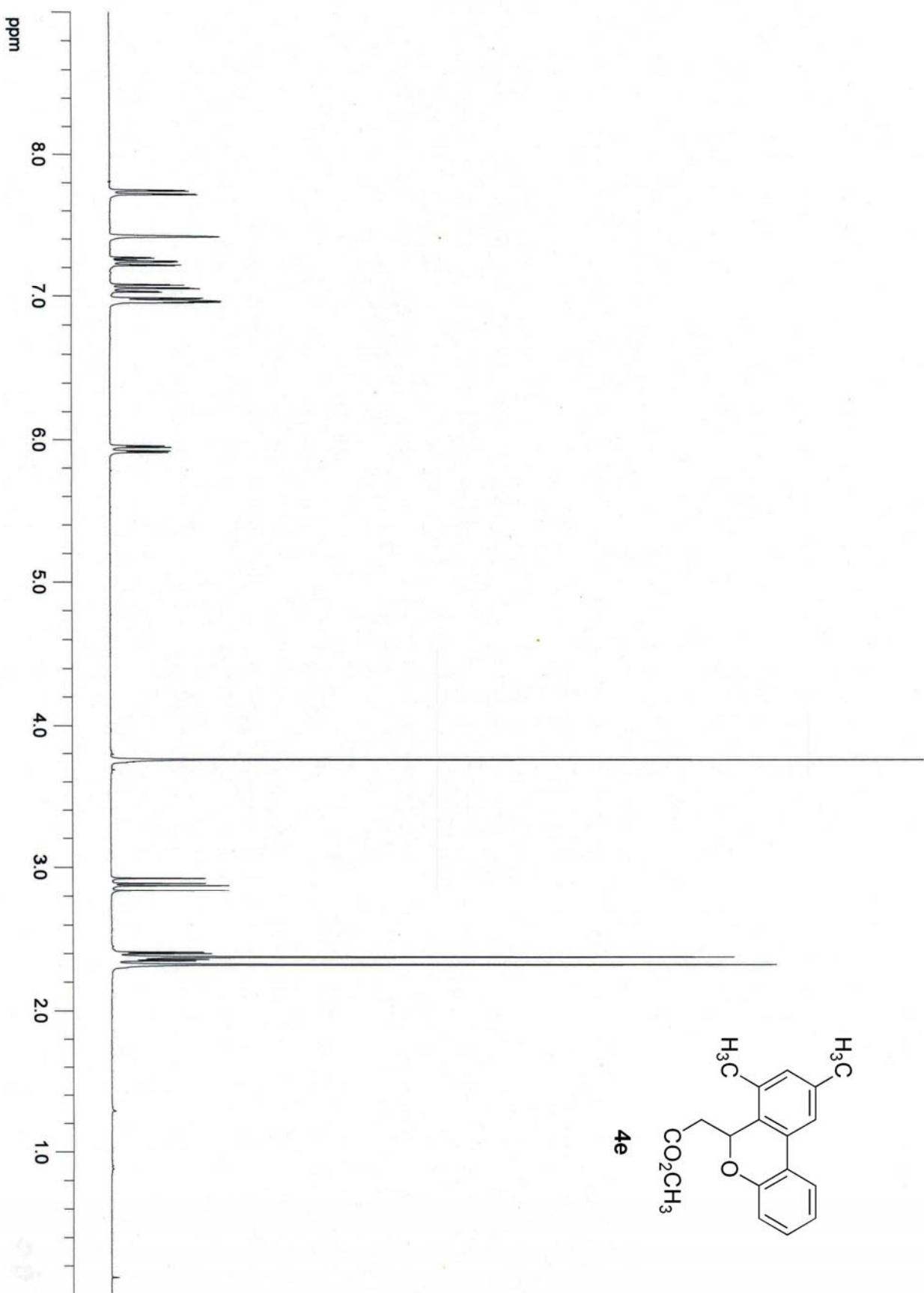
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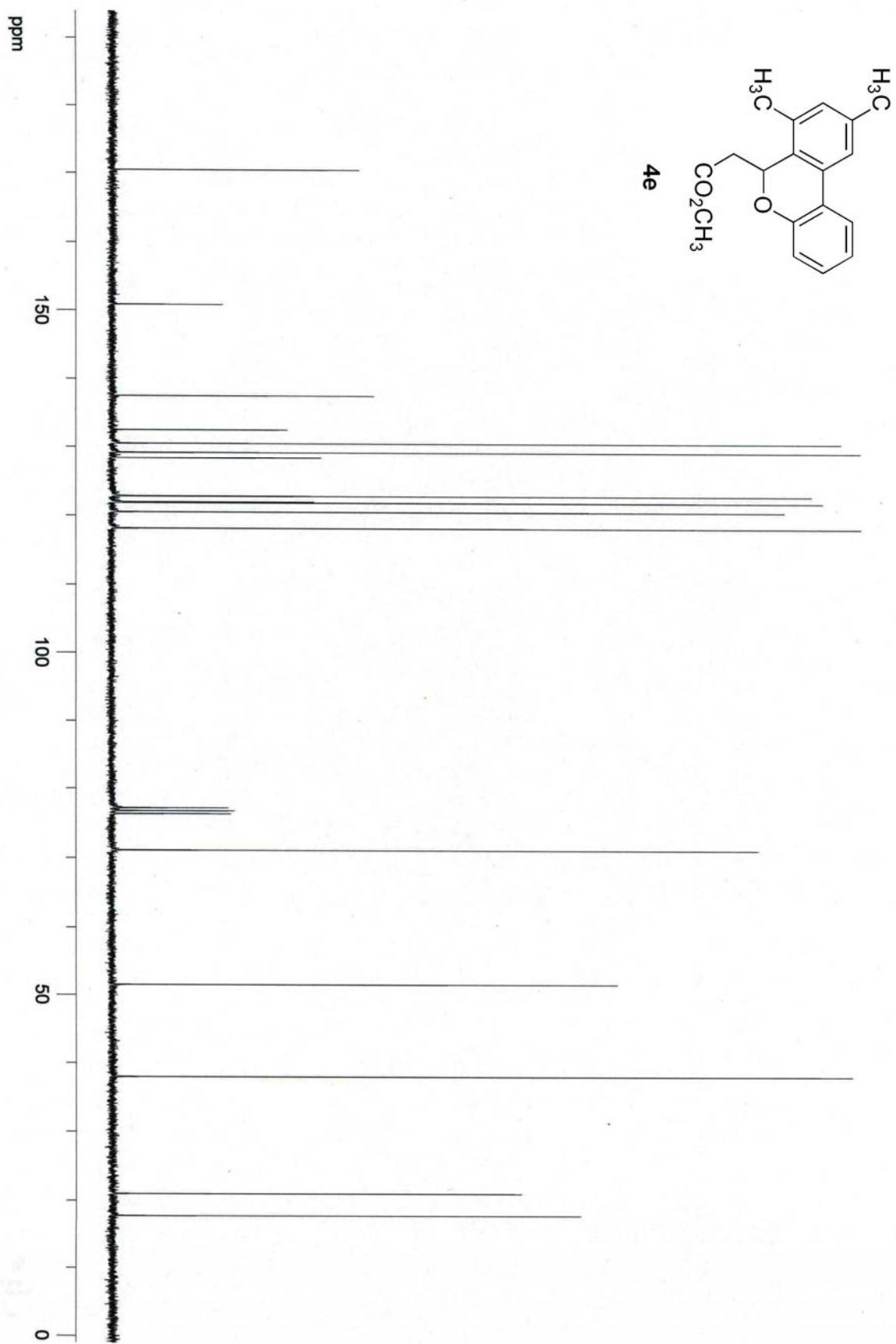
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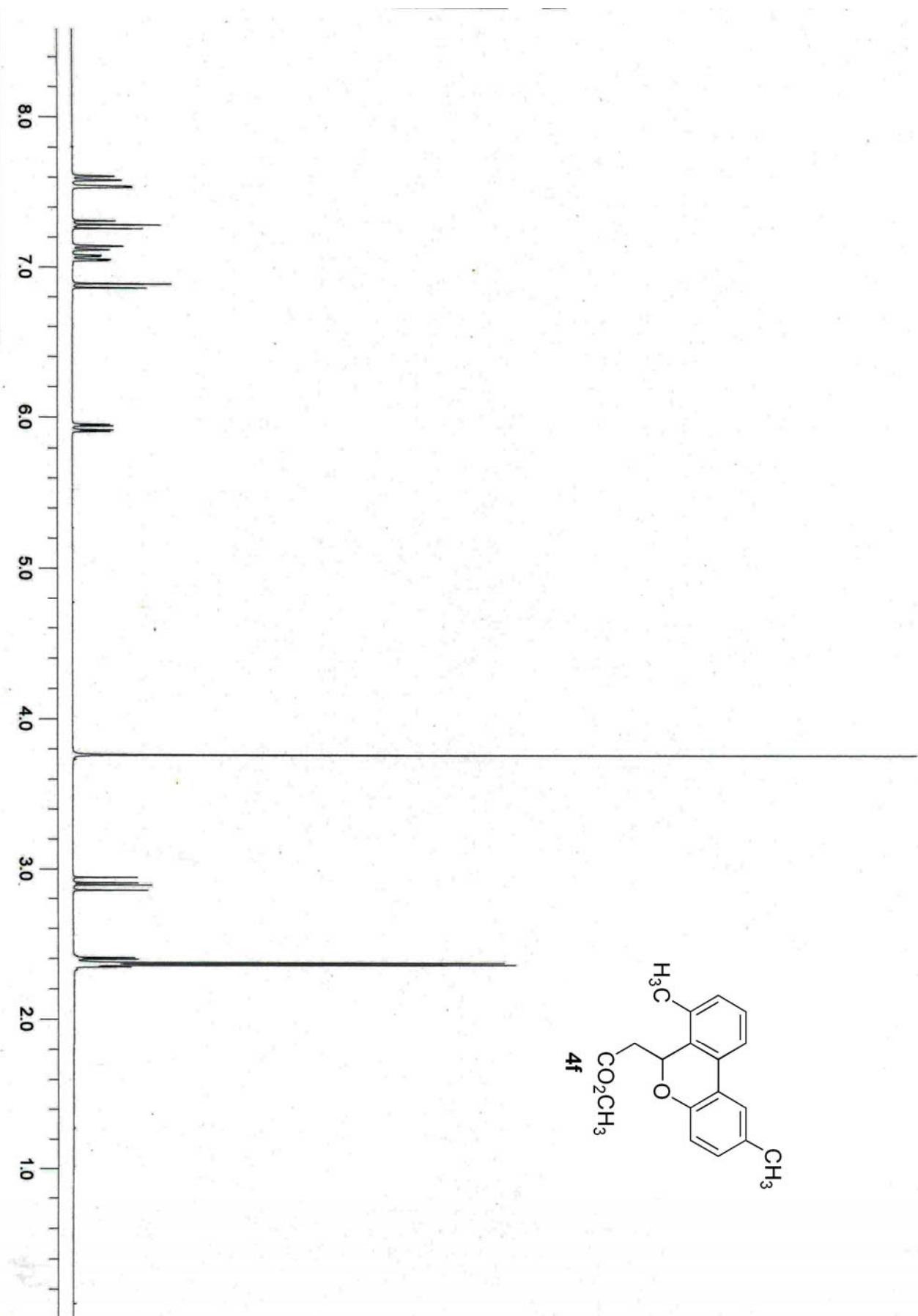
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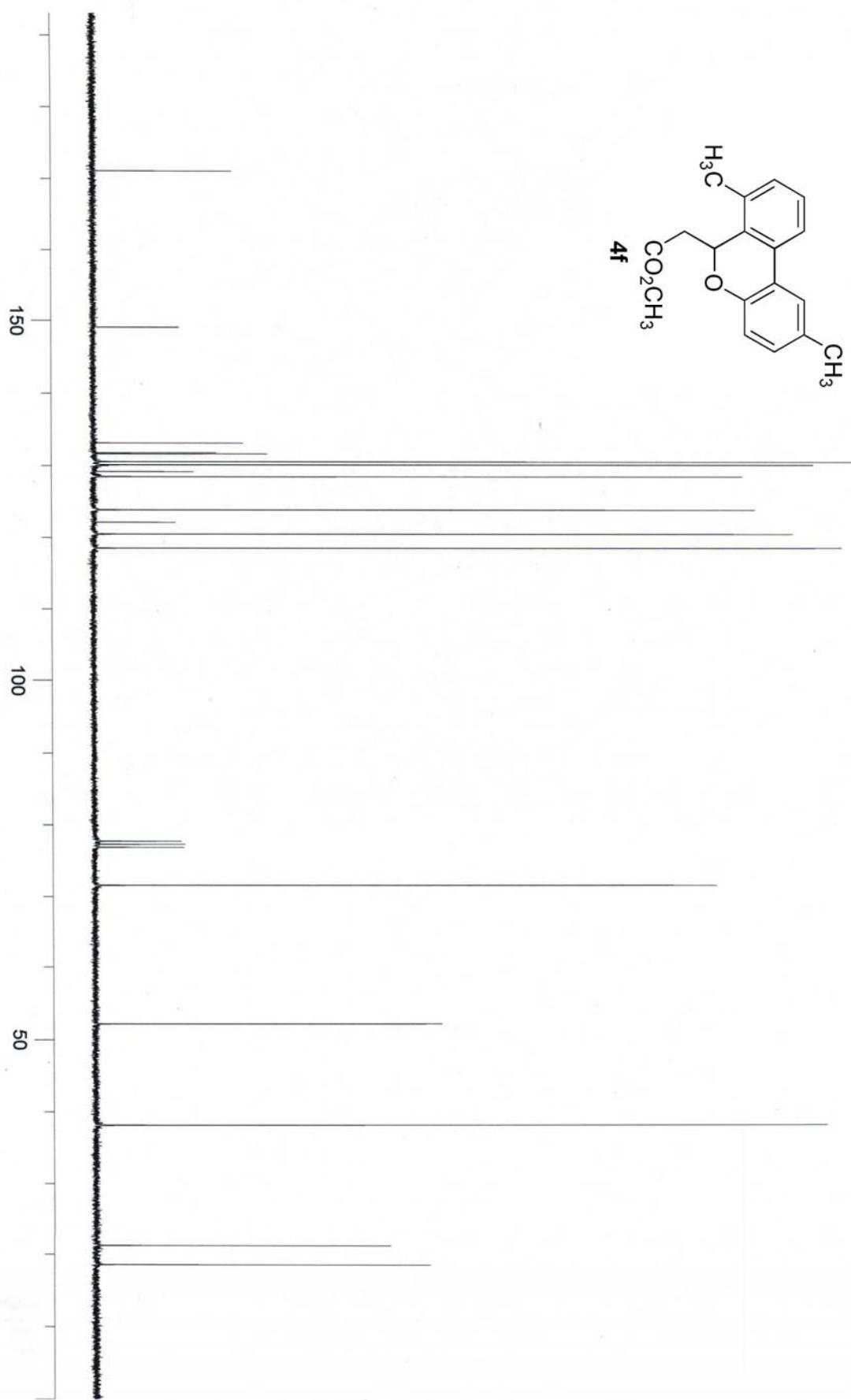
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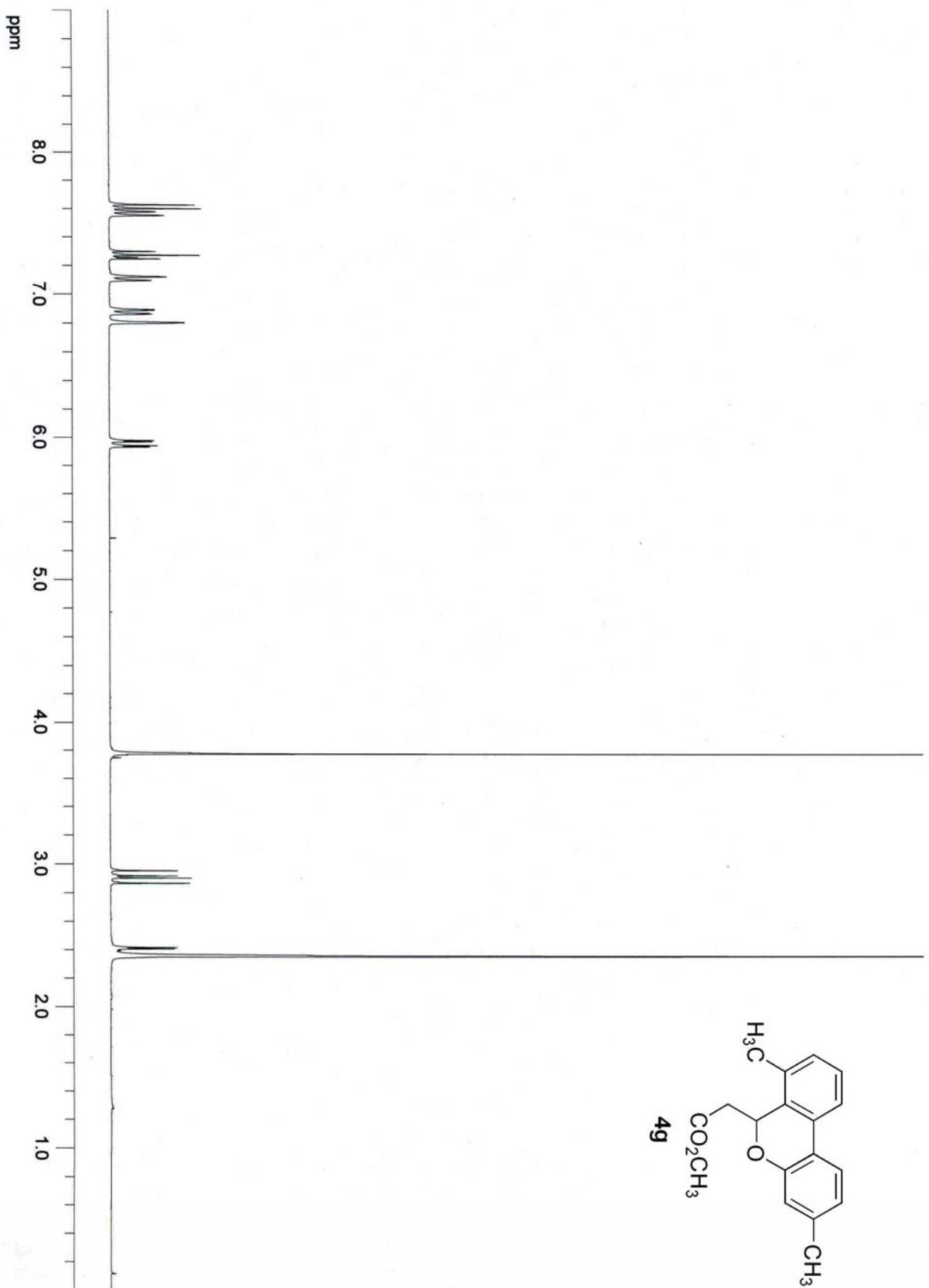


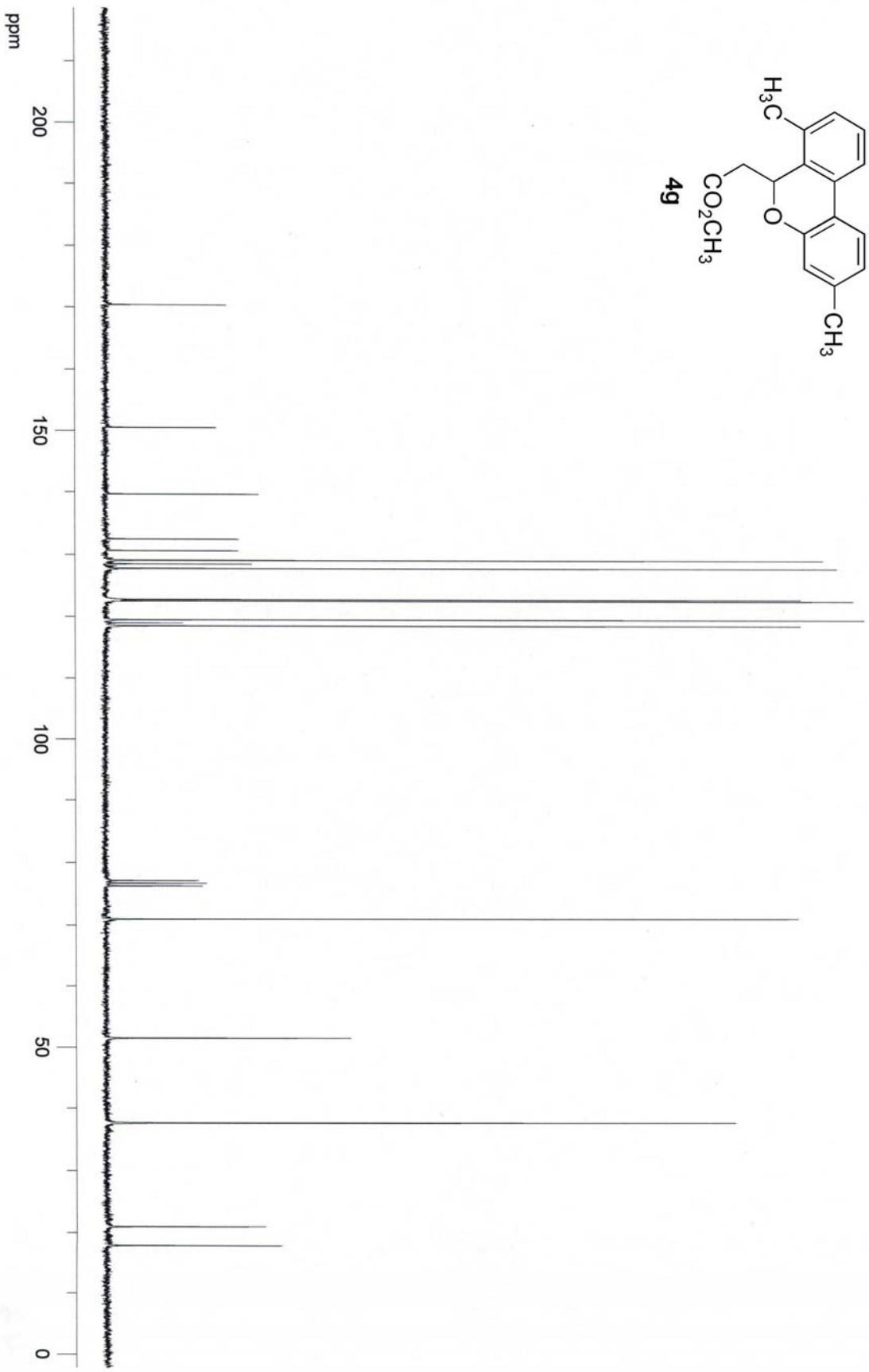


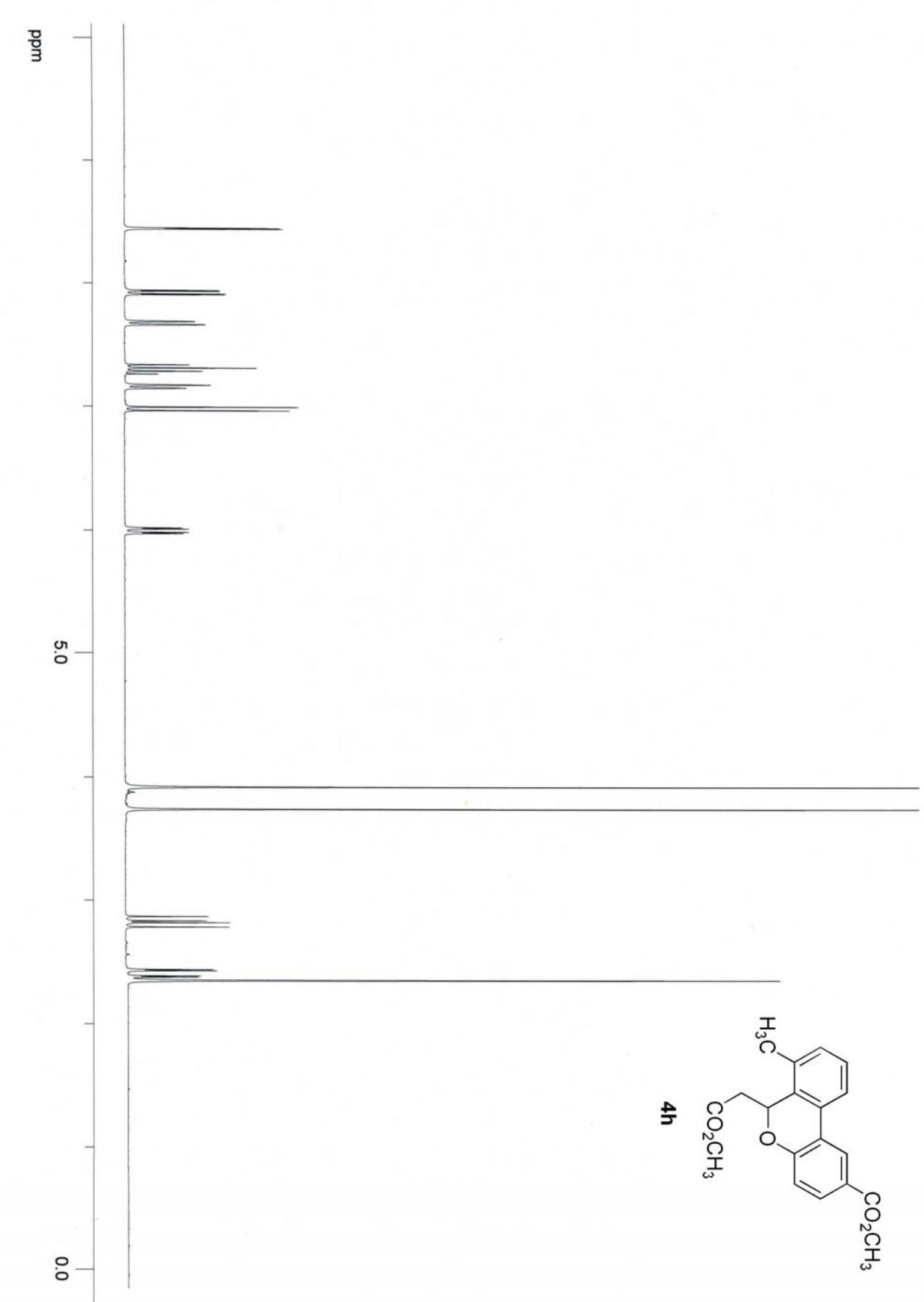












ppm

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