



## Supporting Information

for

### Transition-metal-free decarbonylation–oxidation of 3-arylbenzofuran-2(3*H*)-ones: access to 2-hydroxybenzophenones

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**Characterization data of compounds 3aa–ma, 4aa–ma, and 5.  
<sup>1</sup>H and <sup>13</sup>C NMR spectra of 3aa–ma, 4aa–ma, and 5; single  
crystal data of 4ja, 4fb, and 4ma; UV–vis absorption spectra  
and optical properties of 4aa–ma**

| Page No. | Description                            |                                                                          |
|----------|----------------------------------------|--------------------------------------------------------------------------|
| S2–S11   |                                        | Analytical data of the synthesized compounds                             |
| S12      | <b>Fig. S1</b>                         | <sup>1</sup> H NMR showing formation of THF-hydroperoxide in situ in THF |
| S13      | <b>Fig. S2</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3bb</b> .          |
| S14      | <b>Fig. S3</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3ca</b> .          |
| S15      | <b>Fig. S4</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3cb</b> .          |
| S16      | <b>Fig. S5</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3dc</b> .          |
| S17      | <b>Fig. S6</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3fd</b> .          |
| S18      | <b>Fig. S7</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3ha</b> .          |
| S19      | <b>Fig. S8</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3ia</b> .          |
| S20      | <b>Fig. S9</b>                         | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3ka</b> .          |
| S21      | <b>Fig. S10</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3la</b> .          |
| S22      | <b>Fig. S11</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>3ma</b> .          |
| S23      | <b>Fig. S12</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4aa</b> .          |
| S24      | <b>Fig. S13</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ba</b> .          |
| S25      | <b>Fig. S14</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4bb</b> .          |
| S26      | <b>Fig. S15</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ca</b> .          |
| S27      | <b>Fig. S16</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4cb</b> .          |
| S28      | <b>Fig. S17</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4dc</b> .          |
| S29      | <b>Fig. S18</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ea</b> .          |
| S30      | <b>Fig. S19</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4eb</b> .          |
| S31      | <b>Fig. S20</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4fa</b> .          |
| S32      | <b>Fig. S21</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4fb</b> .          |
| S33      | <b>Fig. S22</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4fd</b> .          |
| S34      | <b>Fig. S23</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ga</b> .          |
| S35      | <b>Fig. S24</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ha</b> .          |
| S36      | <b>Fig. S25</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ia</b> .          |
| S37      | <b>Fig. S26</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ja</b> .          |
| S38      | <b>Fig. S27</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ka</b> .          |
| S39      | <b>Fig. S28</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>4ma</b> .          |
| S40      | <b>Fig. S29</b>                        | <sup>1</sup> H and <sup>13</sup> C NMR spectrum of <b>5</b> .            |
| S41–S44  | Single crystal XRD data for <b>4ja</b> |                                                                          |
| S45–S52  | Single crystal XRD data for <b>4fb</b> |                                                                          |
| S53–S58  | Single crystal XRD data for <b>4ma</b> |                                                                          |
| S59      | <b>Fig. S30</b>                        | UV–vis absorption spectra of synthesized compounds                       |
| S60      | Table S12                              | Optical properties of the compounds <b>4aa–ma</b> .                      |
| S61      | <b>Fig. S31</b>                        | Picture of the reaction set-up for the synthesis of <b>4aa–ma</b> .      |
| S62      | References                             |                                                                          |

## 1. Analytical data of the synthesized compounds

*3-(4-Methoxyphenyl)-5-methylbenzofuran-2(3H)-one (3bb)* [1]. Reaction of **1b** with **2b** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3bb** as a colourless solid (yield: 0.92 g, 72%). mp 137-138 °C; FT-IR (neat)  $\nu_{\max}$  2900, 1789, 1611, 1484, 1304, 1061  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.16-7.11 (m, 3H), 7.07-7.04 (m, 1H), 7.00 (s, 1H), 6.91-6.87 (m, 2H), 4.80 (s, 1H), 3.79 (s, 3H), 2.32 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 175.7, 159.4, 151.8, 134.1, 129.6, 129.3, 127.3, 127.2, 125.7, 114.5, 110.4, 55.3, 49.1, 21.0. Anal. Found: C, 75.30; H, 5.26. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_3$ : C, 75.58; H, 5.55 %.

*5-Ethyl-3-phenylbenzofuran-2(3H)-one (3ca)* [2]. Reaction of **1c** with **2a** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3ca** as a colourless solid (yield: 0.87 g, 73%). mp 66-67 °C; FT-IR (neat)  $\nu_{\max}$  2965, 1800, 1615, 1479, 1140  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.41-7.31 (m, 3H), 7.25-7.22 (m, 2H), 7.21-7.16 (m, 1H), 7.12-7.08 (m, 1H), 7.03 (s, 1H), 4.88 (s, 1H), 2.63 (q,  $J$  = 7.5 Hz, 2H), 1.20 (t,  $J$  = 8.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 175.4, 152.0, 140.7, 135.3, 129.1, 128.6, 128.3, 128.1, 127.0, 124.6, 110.5, 49.9, 28.5, 15.8. Anal. Found: C, 80.67; H, 5.53. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_2$ : C, 80.65; H, 5.92 %.

*5-Ethyl-3-(4-methoxyphenyl)benzofuran-2(3H)-one (3cb)*. Reaction of **1c** with **2b** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3cb** as a colourless solid (yield: 0.94 g, 70%). mp 113-114 °C; FT-IR (neat)  $\nu_{\max}$  2969, 1808, 1510, 1247, 1067  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.19-7.12 (m, 3H), 7.09-7.06 (m, 1H), 7.01 (s, 1H), 6.91-6.87 (m, 2H), 4.80 (s, 1H), 3.79 (s, 3H), 2.62 (q,  $J$  = 7.5 Hz, 2H), 1.19 (t,  $J$  = 7.5 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 175.7, 159.5, 151.9, 140.7, 129.4, 128.5, 127.3, 127.2, 124.6, 114.5, 110.5, 55.3, 49.2, 28.5, 15.8. Anal. Found: C, 76.29; H, 5.64. Calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_3$ : C, 76.10; H, 6.01 %.

*3-(4-Bromophenyl)-5-octylbenzofuran-2(3H)-one (3dc)*. Reaction of **1d** with **2c** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3dc** as a colourless viscous liquid (yield: 1.42 g, 71%). FT-IR (neat)  $\nu_{\max}$  2957, 1807, 1485, 1189, 1060  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.49 (d,  $J$  = 8.5 Hz, 2H), 7.19-7.15 (m, 1H), 7.14-7.07 (m, 3H), 6.99 (s, 1H), 4.82 (s, 1H), 2.58 (t,  $J$  = 7.5 Hz, 2H), 1.29-1.21 (m, 12H), 0.88 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 174.8, 152.0, 139.6, 134.3, 132.2, 130.0, 129.4, 126.2, 125.0, 122.3, 110.6, 49.3, 35.5, 31.8, 31.6, 29.3, 29.2, 29.1, 22.6, 14.0. Anal. Found: C, 65.73; H, 6.47. Calcd. for  $\text{C}_{22}\text{H}_{25}\text{BrO}_2$ : C, 65.84; H, 6.28 %.

*5-(tert-Butyl)-3-(4-fluorophenyl)benzofuran-2(3H)-one (3fd)*. Reaction of **1f** with **2d** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3fd** as a colourless viscous liquid (yield: 0.98 mg, 69%). FT-IR (neat)  $\nu_{\max}$  2960, 1813, 1559, 1508, 1056  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.41 (d,  $J$  = 8.5 Hz, 1H), 7.25-7.19 (m, 3H), 7.14-7.04 (m, 3H), 4.86 (s, 1H), 1.31 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 175.2, 163.5, 161.5, 151.7, 131.1, 131.0, 130.0, 129.8, 126.3, 126.2, 122.1, 116.1, 115.9, 49.2, 34.7, 31.5. Anal. Found: C, 76.31; H, 5.65. Calcd. for  $\text{C}_{18}\text{H}_{17}\text{FO}_2$ : C, 76.04; H, 6.03%.

*5-Ethoxy-3-phenylbenzofuran-2(3H)-one (3ha)*. Reaction of **1h** with **2a** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3ha** as a colourless solid (yield: 0.93 g, 73%). mp: 60 -61  $^{\circ}\text{C}$ ; FT-IR (neat)  $\nu_{\max}$  2982, 1797, 1486, 1144, 1038  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.38-7.31 (m, 3H), 7.24-7.21 (m, 2H), 7.07 (d,  $J$  = 9.0 Hz, 1H) 6.86 (dd,  $J$  = 2.5 and 3.0 Hz, 1H), 6.74 (d,  $J$  = 2.0 Hz, 1H), 4.86 (s, 1H), 3.98-3.93 (m, 2H), 1.38 (t, 6.5 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 175.4, 156.1, 147.7, 135.1, 129.1, 128.3, 128.2, 127.9, 115.2, 111.7, 111.3, 64.2, 50.4, 14.8. Anal. Found: C, 75.72; H, 5.21. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_3$ : C, 75.58; H, 5.55 %.

*5-(Nonyloxy)-3-phenylbenzofuran-2(3H)-one (3ia)*. Reaction of **1i** with **2a** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3ia** as a colourless viscous liquid (yield: 1.25 g, 71%); FT-IR (neat)  $\nu_{\max}$  2923, 1806, 1485, 1394, 1060  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.39–7.30 (m, 3H), 7.23 (d,  $J = 7.0$  Hz, 2H), 7.09 (d,  $J = 9.0$  Hz, 1H), 6.86 (dd,  $J = 2.5$  and 2.5 Hz, 1H), 7.0 (d,  $J = 2.0$  Hz, 1H), 4.85 (s, 1H), 3.87 (t, 6.5 Hz, 2H), 1.75–1.70 (m, 2H) 1.43–1.37 (m, 2H), 1.31–1.25 (m, 10H), 0.87 (t, 6.5 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 175.4, 156.4, 147.7, 135.2, 129.1, 128.3, 128.2, 127.8, 115.2, 111.7, 111.3, 68.8, 50.4, 31.8, 29.5, 29.3, 29.2, 26.0, 22.6, 14.1$ . Anal. Found: C, 78.62; H, 8.01. Calcd. for  $\text{C}_{23}\text{H}_{28}\text{O}_3$ : C, 78.38; H, 8.01 %.

*7-(tert-Butyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (3ka)*. Reaction of **1k** with **2a** following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3ka** as a colourless solid (yield: 1.04 g, 74%); mp: 160–161  $^{\circ}\text{C}$ ; FT-IR (neat)  $\nu_{\max}$  2959, 1781, 1453, 1267, 1072  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.40–7.30 (m, 3H), 7.27–7.22 (m, 2H), 7.11 (s, 1H), 6.86 (s, 1H), 4.83 (s, 1H), 2.33 (s, 3H), 1.45 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta = 175.5, 149.8, 135.6, 133.9, 133.7, 129.0, 128.3, 128.0, 127.4, 127.0, 123.1, 49.5, 34.1, 29.6, 21.2$ . Anal. Found: C, 81.69; H, 7.12. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_2$ : C, 81.40; H, 7.19 %.

*5-Chloro-4,6-dimethyl-3-phenylbenzofuran-2(3H)-one (3la)*. Reaction of 4-chloro-3,5-dimethylphenol (5 mmol) and mandelic acid (6 mmol) following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3la** as a colourless solid (yield: 0.98 g, 72%). mp: 138–139  $^{\circ}\text{C}$ ; FT-IR (neat)  $\nu_{\max}$  2964, 1794, 1452, 1393, 1027  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.39–7.34 (m, 3H), 7.18–7.16 (m, 2H), 6.97 (s, 1H), 4.82 (s, 1H), 2.45 (s, 3H), 2.04 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 174.8, 151.9, 137.9, 134.4, 133.9, 130.4, 129.3, 128.3, 128.1, 124.4, 110.6, 49.9, 21.5, 17.1$ . Anal. Found: C, 70.62; H, 4.45. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_2$ : C, 70.46; H, 4.80 %.

*3,7-Diphenylbenzofuran-2(3H)-one (3ma)*. Reaction of [1,1'-biphenyl]-2-ol (5 mmol) and mandelic acid (6 mmol) following the general procedure followed by purification by column chromatography (silica gel, 0–15% EtOAc-hexane) yielded pure **3ma** as a highly viscous liquid (yield: 1.07 g, 75%). FT-IR (neat)  $\nu_{\max}$  2961, 1792, 1293, 1058  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.77-7.65 (two d, 3H,  $J$  = 7.5 Hz), 7.57-7.51 (d, 1H,  $J$  = 8.0 Hz), 7.51-7.46 (t, 2H,  $J$  = 7.5 Hz), 7.43-7.32 (m, 4H), 7.31-7.23 (m, 2H), 7.21-7.16 (m, 1H), 4.97 (s, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 175.1, 152.4, 150.9, 137.1, 135.3, 135.1, 130.6, 130.3, 129.5, 129.4, 129.3, 129.3=2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 125.1, 124.9, 124.2, 120.8, 115.9, 115.8, 49.8. Anal. Found: C, 83.72; H, 4.68. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_2$ : C, 83.90; H, 4.93 %.

*(2-Hydroxyphenyl)(phenyl)methanone (4aa)* [3]. Reaction of **3aa** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4aa** as a colourless viscous liquid (yield: 168 mg, 85%). FT-IR (neat)  $\nu_{\max}$  3059, 2957, 1625, 1444, 1032  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 12.03 (s, 1H), 7.70-7.66 (m, 2H), 7.62-7.56 (m, 2H), 7.51 (t,  $J$  = 7.0 Hz, 3H), 7.07 (d,  $J$  = 8.5 Hz, 1H), 6.88 (t,  $J$  = 7.5 Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 201.6, 163.2, 137.9, 136.3, 133.6, 131.9, 129.1, 128.3, 119, 118.6, 118.4. Anal. Found: C, 78.44; H, 5.14. Calcd. for  $\text{C}_{13}\text{H}_{10}\text{O}_2$ : C, 78.77; H, 5.09 %.

*(2-Hydroxy-5-methylphenyl)(phenyl)methanone (4ba)* [3]. Reaction of **3ba** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ba** as a colourless solid (Yield: 193 mg, 91%). mp: 81-82  $^{\circ}\text{C}$ ; FT-IR (neat)  $\nu_{\max}$  3200, 2918, 1625, 1445, 1225, 958  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.85 (s, 1H), 7.69-7.64 (m, 2H), 7.62-7.56 (m, 1H), 7.54-7.48 (m, 2H), 7.37-7.30 (m, 2H), 6.98 (d,  $J$  = 9.0 Hz, 1H), 2.25 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 201.6, 161.1, 138.0, 137.3, 131.2, 131.7, 129.1, 128.3, 127.7, 118.7, 118.1, 20.4. Anal. Found: C, 79.30; H, 5.47. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{O}_2$ : C, 79.23; H, 5.70 %.

*3-(4-Methoxyphenyl)-5-methylbenzofuran-2(3H)-one (4bb)* [4]. Reaction of **3bb** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4bb** as a colourless solid (yield: 199 mg, 82%). mp: 109–110 °C; FT-IR (neat)  $\nu_{max}$  2917, 1631, 1478, 1248, 1024  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.75 (s, 1H), 7.70 (d,  $J$  = 8.5 Hz, 2H), 7.39 (s, 1H), 7.29 (d,  $J$  = 8.5 Hz, 1H), 7.00–6.95 (m, 3H), 3.89 (s, 3H), 2.26 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.0, 162.8, 160.8, 136.7, 132.9, 131.7, 130.5, 127.6, 119.1, 118.0, 113.6, 55.4, 20.5. Anal. Found: C, 74.30; H, 5.65. Calcd. for  $\text{C}_{15}\text{H}_{14}\text{O}_3$ : C, 74.36; H, 5.82 %.

*(5-Ethyl-2-hydroxyphenyl)(phenyl)methanone (4ca)* [3]. Reaction of **3ca** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ca** as a colourless viscous liquid (yield: 190 mg, 84%). mp: 109–110 °C; FT-IR (neat)  $\nu_{max}$  2964, 1630, 1481, 950  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.86 (s, 1H), 7.68 (d,  $J$  = 7.5 Hz, 2H), 7.59 (t,  $J$  = 7.5 Hz, 1H), 7.52 (t,  $J$  = 7.5 Hz, 2H), 7.40–7.34 (m, 2H), 7.01 (d,  $J$  = 8.0 Hz, 1H), 2.55 (q,  $J$  = 7.5 Hz, 2H), 1.16 (t,  $J$  = 7.5 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.6, 161.3, 138.1, 136.2, 134.3, 132.1, 131.8, 129.1, 128.3, 118.8, 118.2, 27.9, 15.7. Anal. Found: C, 79.35; H, 6.25. Calcd. for  $\text{C}_{15}\text{H}_{14}\text{O}_2$ : C, 79.62; H, 6.24%.

*(5-Ethyl-2-hydroxyphenyl)(4-methoxyphenyl)methanone (4cb)*. Reaction of **3cb** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4cb** as a colourless viscous liquid (yield: 184 mg, 72%); FT-IR (neat)  $\nu_{max}$  2959, 1627, 1481, 1243, 1028  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.77 (s, 1H), 7.72 (d,  $J$  = 8.5 Hz, 2H), 7.42 (d,  $J$  = 2.0 Hz, 1H), 7.34 (dd,  $J$  = 2.0 and 6.5 Hz, 1H), 7.03–6.97 (m, 3H), 3.90 (s, 3H), 2.57 (q,  $J$  = 6.5 Hz, 2H), 1.18 (t,  $J$  = 7.5 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.0, 162.8, 160.9, 135.6, 134.1, 131.8, 131.7, 130.5, 119.1, 118.1, 113.6, 55.5, 27.9, 15.7. Anal. Found: C, 74.97; H, 6.31. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_3$ : C, 74.98; H, 6.29 %.

(4-Bromophenyl)(2-hydroxy-5-octylphenyl)methanone (**4dc**). Reaction of **3dc** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4dc** as a colourless viscous liquid (yield: 284 mg, 73%); FT-IR (neat)  $\nu_{\max}$  2923, 1630, 1480, 1244, 1012  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.68 (s, 1H), 7.65 (d,  $J$  = 8.5 Hz, 2H), 7.54 (d,  $J$  = 8.5 Hz, 2H), 7.34 (dd,  $J$  = 1.5 and 8.5 Hz, 1H), 7.29-7.27 (m, 1H), 7.26-7.25 (m, 1H), 2.49 (t,  $J$  = 7.5 Hz, 2H), 1.64-1.47 (m, 2H), 1.33-1.19 (m, 10H), 0.86 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.3, 161.3, 137.0, 136.8, 133.2, 132.3, 130.7, 126.7, 118.6, 118.3, 34.9, 31.8, 31.5, 29.3, 29.2, 29.0, 22.6, 14.0. Anal. Found: C, 64.66; H, 6.51. Calcd. for  $\text{C}_{21}\text{H}_{25}\text{BrO}_2$ : C, 64.79; H, 6.47 %.

(2-Hydroxy-5-isopropylphenyl)(phenyl)methanone (**4ea**) [3]. Reaction of **3ea** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ea** as a colourless viscous liquid (yield: 185 mg, 77%); FT-IR (neat)  $\nu_{\max}$  3300, 2956, 1809, 1597, 1244, 1074  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.87 (s, 1H), 7.69 (d,  $J$  = 7.5 Hz, 2H), 7.60 (t, 7.5 Hz, 1H), 7.52 (t, 7.0 Hz, 2H), 7.44-7.38 (m, 2H), 7.02 (d,  $J$  = 8.0 Hz, 1H) 2.84-2.79 (m, 1H), 1.18 (d,  $J$  = 7.0 Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 201.5, 161.3, 138.9, 138.0, 134.7, 131.8, 130.8, 129.2, 128.3, 118.7, 118.2, 33.2, 23.9. Anal. Found: C, 80.15; H, 6.56. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_2$ : C, 79.97; H, 6.71 %.

(2-Hydroxy-5-isopropylphenyl)(4-methoxyphenyl)methanone (**4eb**). Reaction of **3eb** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4eb** as a colourless viscous liquid (Yield: 195 mg, 72%). mp: 108-109 °C; FT-IR (neat)  $\nu_{\max}$  2959, 1627, 1337, 1028  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.78 (s, 1H), 7.21 (d,  $J$  = 9.0 Hz, 2H), 7.45 (d,  $J$  = 2.0 Hz, 1H), 7.38-7.35 (m, 1H), 7.00-6.98 (m, 3H), 3.89 (s, 3H), 2.85-2.8(m, 1H), 1.19 (d,  $J$  = 6.5 Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 199.9, 162.8, 160.9, 138.7, 134.2, 131.8, 130.5, 130.4, 118.9, 118.0, 113.6, 55.4, 33.2, 23.9. Anal. Found: C, 75.22; H, 6.45. Calcd. for  $\text{C}_{17}\text{H}_{18}\text{O}_3$ : C, 75.53; H, 6.71 %.



(5-(*tert*-Butyl)-2-hydroxyphenyl)(phenyl)methanone (**4fa**) [3]. Reaction of **3fa** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4fa** as a colourless viscous liquid (yield: 214 mg, 84%); FT-IR (neat)  $\nu_{\max}$  3400, 2959, 1629, 1482, 968  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.86 (s, 1H), 7.69 (d,  $J$  = 7.5 Hz, 2H), 7.63–7.55 (m, 3H), 7.52 (t,  $J$  = 7.5 Hz, 2H), 7.02 (d,  $J$  = 8.0 Hz, 1H), 1.25 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 201.6, 160.9, 141.3, 138.1, 133.9, 131.9, 129.8, 129.2, 128.3, 118.4, 117.9, 34.0, 31.2. Anal. Found: C, 80.50; H, 7.10. Calcd. for  $\text{C}_{17}\text{H}_{18}\text{O}_2$ : C, 80.28; H, 7.13 %.

(5-(*tert*-Butyl)-2-hydroxyphenyl)(4-methoxyphenyl)methanone (**4fb**). Reaction of **3fb** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4fb** as a colourless solid (yield: 245 mg, 86%). mp: 92–93 °C; FT-IR (neat)  $\nu_{\max}$  2919, 1626, 1565, 1029  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.76 (s, 1H), 7.73 (d,  $J$  = 9.0 Hz, 2H), 7.62 (d,  $J$  = 2 Hz, 1H), 7.56–7.53 (m, 1H), 7.01 (d,  $J$  = 8.5 Hz, 3H), 3.91 (s, 3H), 1.27 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.1, 162.9, 160.6, 141.1, 133.3, 131.8, 130.6, 129.6, 118.7, 117.8, 113.6, 55.5, 34.1, 31.3. Anal. Found: C, 75.87; H, 6.88. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{O}_3$ : C, 76.03; H, 7.09 %.

(5-(*tert*-Butyl)-2-hydroxyphenyl)(4-fluorophenyl)methanone (**4fd**). Reaction of **3fd** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4fd** as a colourless solid (yield: 150 mg, 55%). mp: 168–169 °C; FT-IR (neat)  $\nu_{\max}$  3402, 2918, 1784, 1319, 1027  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.69 (s, 1H), 7.74–7.72 (m, 2H), 7.58–7.56 (m, 1H), 7.53 (d,  $J$  = 2.5 Hz, 1H), 7.21 (t,  $J$  = 9.0 Hz, 2H), 7.02 (d,  $J$  = 9.0 Hz, 1H), 1.25 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.0, 166.0, 163.9, 160.9, 141.4, 133.9, 131.8, 131.7, 129.4, 118.3, 118.0, 115.6, 115.4, 34.1, 31.2. Anal. Found: C, 75.17; H, 6.52. Calcd. for  $\text{C}_{17}\text{H}_{17}\text{FO}_2$ : C, 74.98; H, 6.29 %.

(2-Hydroxy-5-methoxyphenyl)(phenyl)methanone (**4ga**) [3]. Reaction of **3ga** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ga** as a colourless solid (yield: 178 mg, 78%). mp: 81-82 °C; FT-IR (neat)  $\nu_{\max}$  2917, 1633, 1483, 1039  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.59 (s, 1H), 7.69 (d,  $J$  = 8.0 Hz, 2H), 7.60 (t,  $J$  = 8.5 Hz, 1H), 7.51 (t,  $J$  = 7.5 Hz, 2H), 7.14 (d,  $J$  = 8.5, Hz, 1H), 7.08-6.99 (m, 2H), 3.70 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 201.1, 157.5, 151.4, 137.9, 131.9, 129.1, 128.4, 124.0, 119.2, 118.7, 116.3, 55.9. Anal. Found: C, 73.54; H, 5.29. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{O}_3$ : C, 73.67; H, 5.30 %.

(5-Ethoxy-2-hydroxyphenyl)(phenyl)methanone (**4ha**). Reaction of **3ha** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ha** as a colourless viscous liquid (yield: 174 mg, 72%). FT-IR (neat)  $\nu_{\max}$  2980, 1632, 1445, 1046  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.58 (s, 1H), 7.69 (d,  $J$  = 7.5 Hz, 2H), 7.59 (t,  $J$  = 7.5 Hz, 1H), 7.51 (t,  $J$  = 8.0 Hz, 2H), 7.14 (dd,  $J$  = 9.0 Hz, 1H), 7.05 (d,  $J$  = 3.0, Hz, 1H), 7.00 (d,  $J$  = 9.0 Hz, 1H), 3.89, (q,  $J$  = 7.0 Hz, 2H), 1.35 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 201.2, 157.4, 150.7, 137.9, 131.9, 129.0, 128.3, 124.7, 119.1, 118.7, 117.3, 64.3, 14.7. Anal. Found: C, 74.51; H, 6.02. Calcd. for  $\text{C}_{15}\text{H}_{14}\text{O}_3$ : C, 74.36; H, 5.82 %.

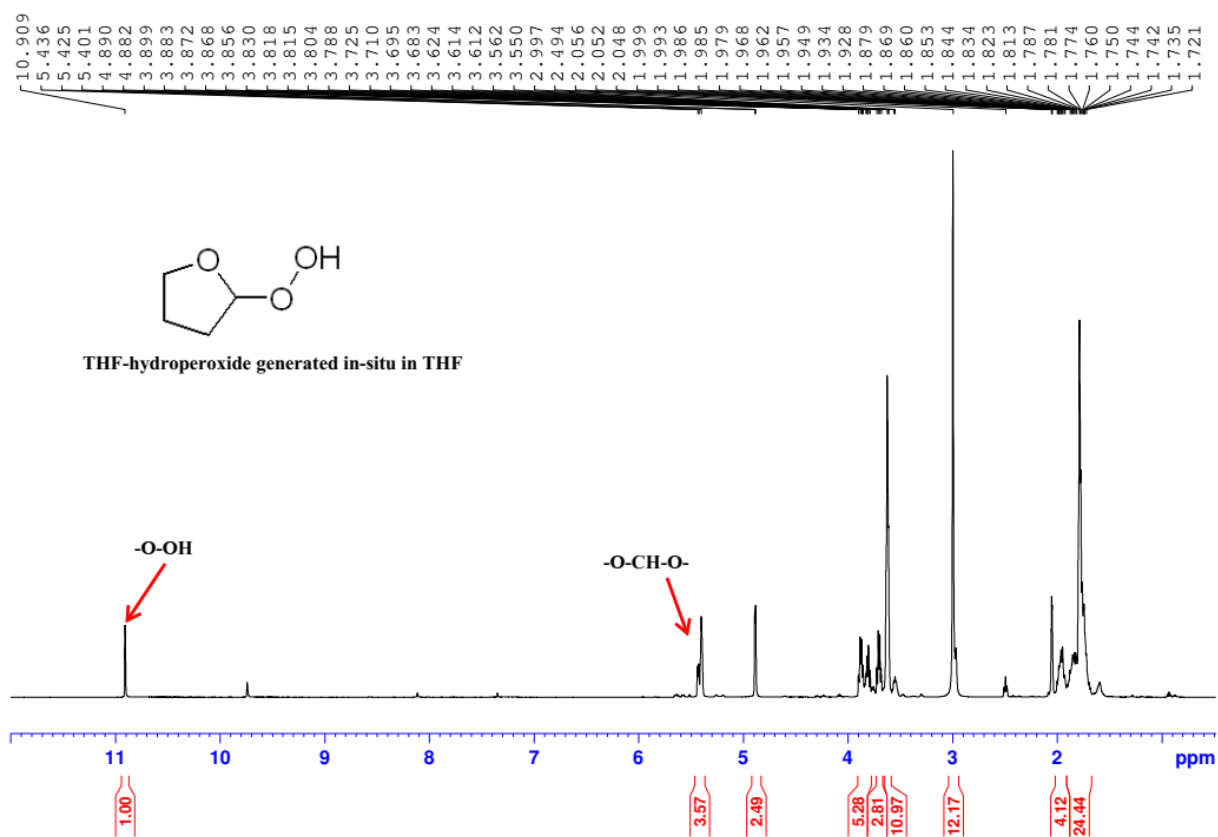
(2-Hydroxy-5-(nonyloxy)phenyl)(phenyl)methanone (**4ia**). Reaction of **3ia** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ia** as a colourless viscous liquid (Yield: 249 mg, 73%). FT-IR (neat)  $\nu_{\max}$  2925, 1603, 1483, 1029  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.56 (s, 1H), 7.68 (d,  $J$  = 7.0 Hz, 2H), 7.59 (t,  $J$  = 7.5 Hz, 1H), 7.51 (t,  $J$  = 8.0 Hz, 2H), 7.13 (dd,  $J$  = 3.0 and 9.0 Hz, 1H), 7.04 (d,  $J$  = 3.0 Hz, 1H), 7.99 (d,  $J$  = 4.0 Hz, 1H), 3.81, (t,  $J$  = 6.5 Hz, 2H), 1.72-1.66 (m, 2H), 1.41-1.35 (m, 2H), 1.32-1.24 (m, 10H), 0.86 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 201.2, 157.4, 150.9, 137.9, 131.9, 129.1, 128.3, 124.7, 119.1, 118.7, 117.3, 69.0, 31.8, 29.4, 29.3, 29.2, 29.1, 26.0, 22.6, 14.1. Anal. Found: C, 77.26; H, 8.07. Calcd. for  $\text{C}_{22}\text{H}_{28}\text{O}_3$ : C, 77.61; H, 8.29 %.

(5-Bromo-2-hydroxyphenyl)(phenyl)methanone (**4ja**). Reaction of **3ja** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ja** as a colourless solid (yield: 233 mg, 94%); mp: 111 -112 °C; IR (neat)  $\nu_{\max}$  3300, 2917, 1620, 1466, 1080  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 11.93 (s, 1H), 7.72-7.65 (m, 3H), 7.64-7.51 (m, 4H), 6.99 (d,  $J$  = 8.5 Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.5, 162.1, 138.9, 137.2, 135.3, 132.4, 129.1, 128.6, 120.5, 120.4, 110.2. Anal. Found: C, 56.41; H, 3.64. Calcd. for  $\text{C}_{13}\text{H}_9\text{BrO}_2$ : C, 56.35; H, 3.27 %.

(3-(*tert*-Butyl)-2-hydroxy-5-methylphenyl)(phenyl)methanone (**4ka**). Reaction of **3ka** following the general procedure followed by purification by column chromatography (silica gel, 0–20% EtOAc-hexane) yielded pure **4ka** as a colourless viscous liquid (yield: 225 mg, 84%). FT-IR (neat)  $\nu_{\max}$  3556, 2956, 1621, 1431, 986  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 12.7 (s, 1H), 7.64 (d,  $J$  = 7.5, Hz, 2H), 7.58 (t,  $J$  = 7.5, Hz, 1H), 7.50 (t,  $J$  = 8, Hz, 2H), 7.32 (d,  $J$  = 1.5, Hz, 1H), 7.20 (s, 1H), 2.23 (s, 3H), 1.45 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 202.4, 160.8, 138.7, 138.4, 134.8, 131.4, 131.2, 128.2, 126.4, 118.6, 34.8, 29.3, 20.8. Anal. Found: C, 80.42; H, 7.32. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{O}_2$ : C, 80.56; H, 7.51 %.

(2-Hydroxy-[1,1'-biphenyl]-3-yl)(phenyl)methanone (**4ma**). A solution of **3ma** in 2 mL of freshly distilled THF was heated at 50 °C in the presence of 1.0 mmol  $\text{Cs}_2\text{CO}_3$  under open atmosphere. After completion of the reaction (cf. TLC), the mixture was cooled to room temperature and THF was evaporated under vacuum. The residue was purified by preparative TLC (hexane/EtOAc) to obtain pure **4ma** as a colourless solid (yield: 217 mg, 53% in two steps). mp: 102-103 °C; FT-IR (neat)  $\nu_{\max}$  2921, 1608, 1446, 1024  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 12.56 (s, 1H), 7.74-7.69 (m, 2H), 7.66-7.57 (m, 5H), 7.53 (t,  $J$  = 8.5 Hz, 2H), 7.47 (t,  $J$  = 8.5 Hz, 2H), 7.38 (t,  $J$  = 6.5 Hz, 1H), 6.95 (t,  $J$  = 8.0 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 202.0, 160.5, 138.1, 137.2, 137.0, 133.0, 131.9, 131.2, 129.4, 129.2, 128.3, 128.2, 127.5, 119.3, 118.5. Anal. Found: C, 83.30; H, 5.23. Calcd. for  $\text{C}_{19}\text{H}_{14}\text{O}_2$ : C, 83.19 H, 5.14 %.

**Synthesis of 5-chloro-3-hydroxy-4,6-dimethyl-3-phenylbenzofuran-2(3H)-one (5).** As described before, a solution of **3na** (1.0 mmol) in 2 mL of freshly distilled THF was heated at 50 °C in the presence of 1.0 mmol Cs<sub>2</sub>CO<sub>3</sub> under open atmosphere. After completion of the reaction (cf. TLC), the mixture was cooled to room temperature and THF was evaporated under vacuum. The residue was purified by preparative TLC (hexane/EtOAc) to obtain pure **5** as a colourless solid (yield: 216 mg, 75%). mp: 161-162 °C; FT-IR (neat)  $\nu_{max}$  3480, 2956, 1787, 1451, 1027 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.38-7.31 (m, 4H), 6.97 (s, 1H), 3.34 (s, 1H), 2.44 (s, 3H), 2.13 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 175.9, 151.4, 139.8, 137.5, 135.5, 131.3, 129.2, 128.9, 128.8, 126.1, 125.1, 111.0, 77.7, 21.6, 15.8. Anal. Found: C, 65.71; H, 4.25. Calcd. for C<sub>16</sub>H<sub>13</sub>ClO<sub>3</sub>: C, 66.56 H, 4.54 %.



**Figure S1.**  $^1\text{H}$  NMR showing formation of THF-hydroperoxide in situ in THF.

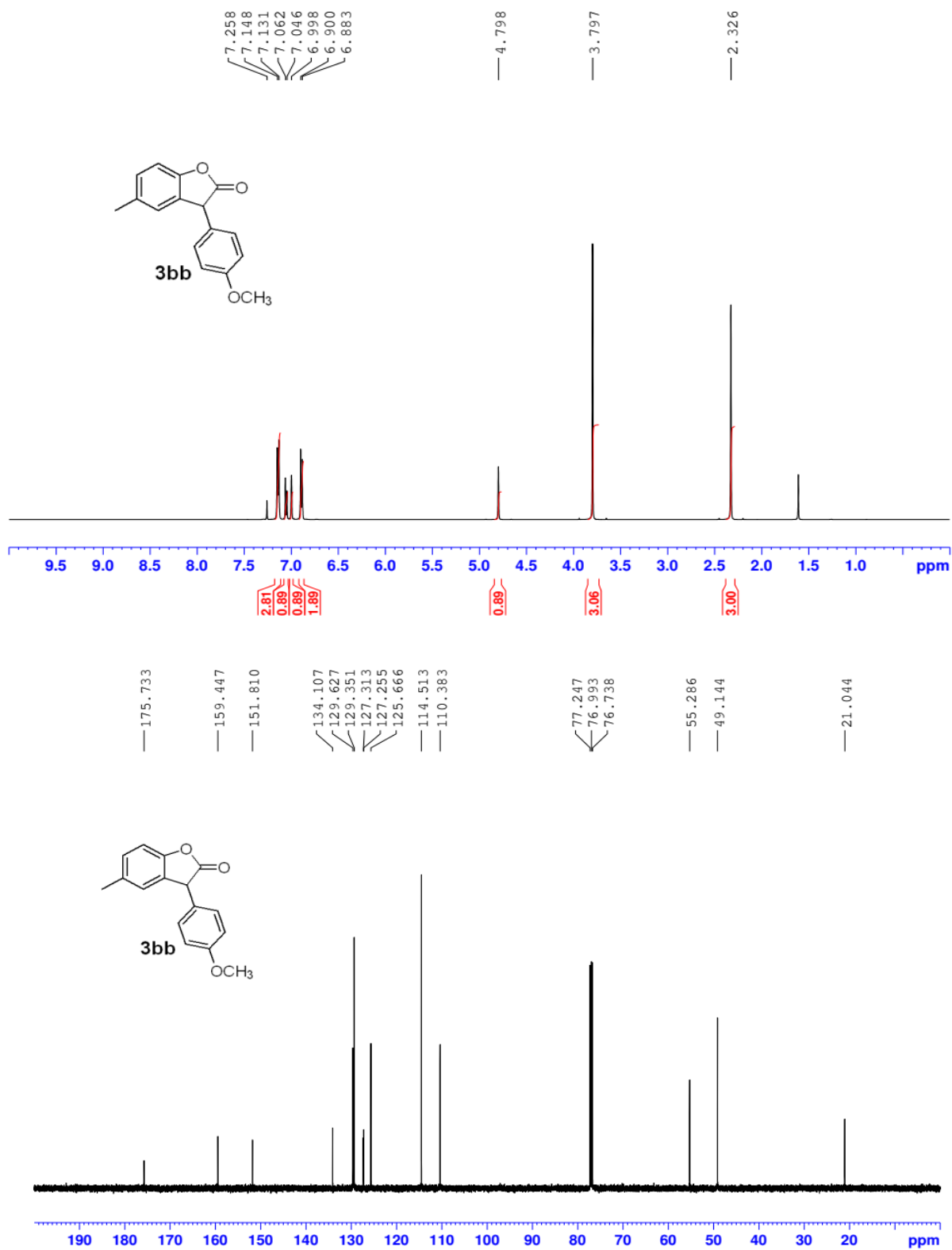
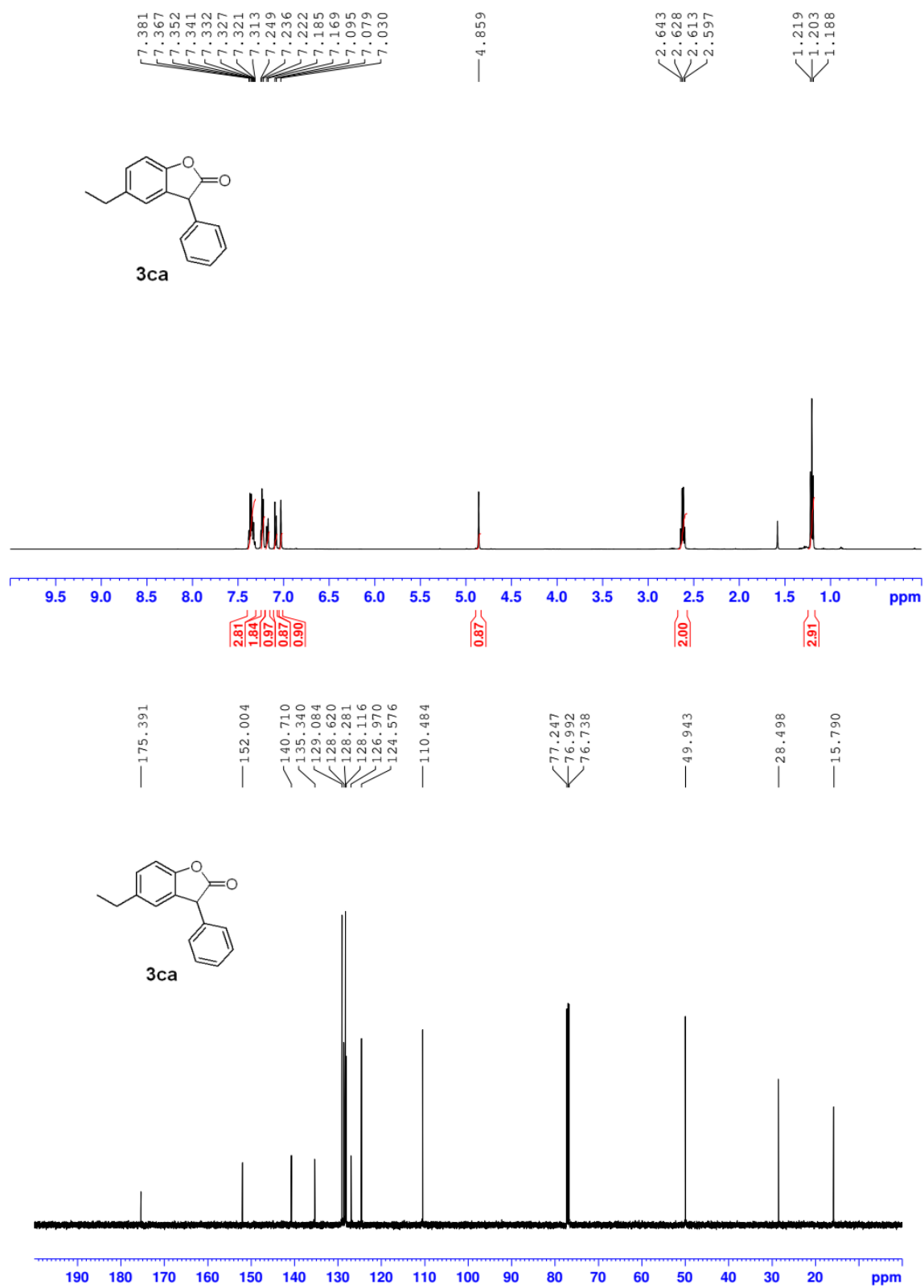


Figure S2. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **3bb**.



**Figure S3.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **3ca**.

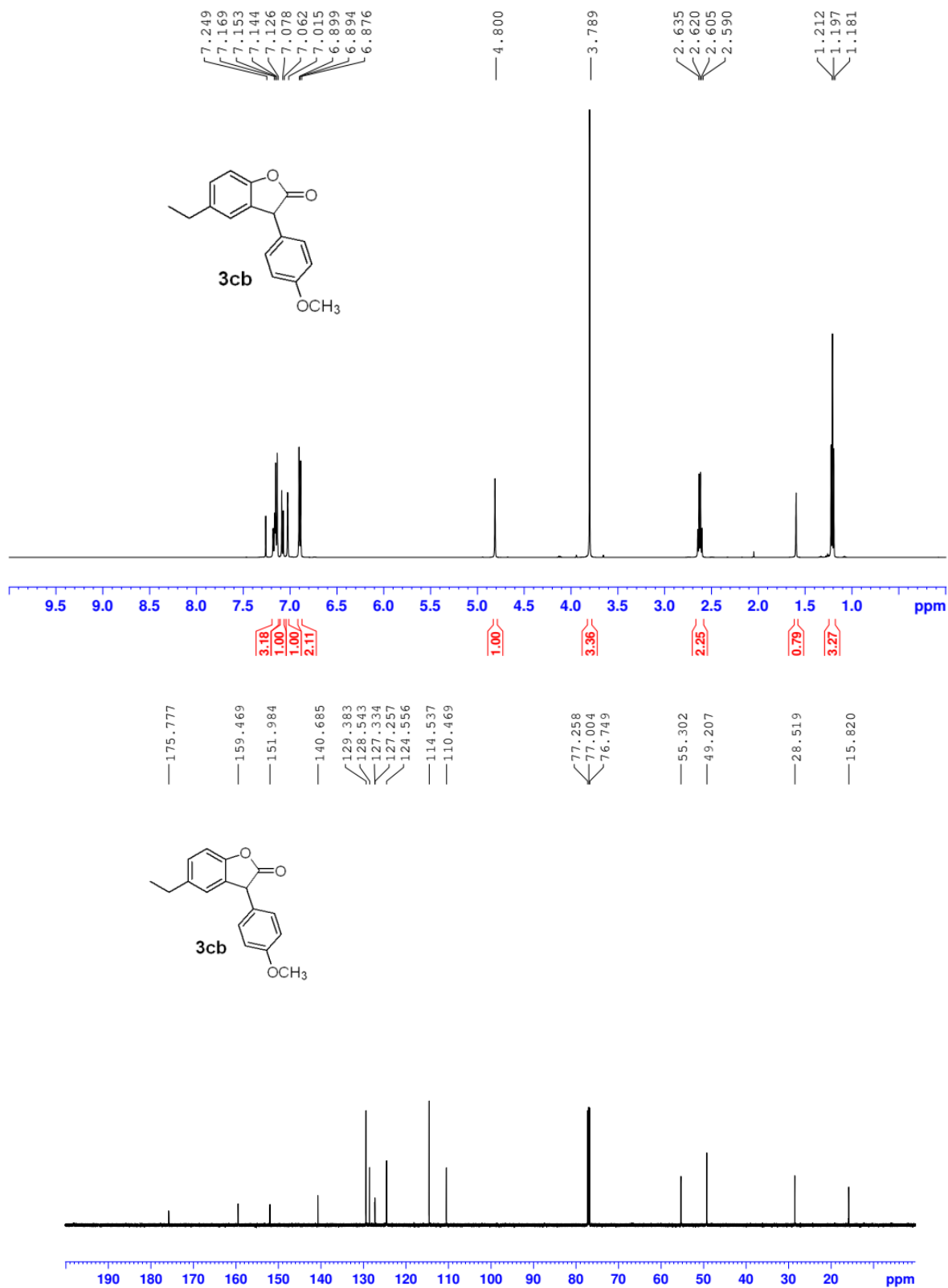


Figure S4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **3cb**.



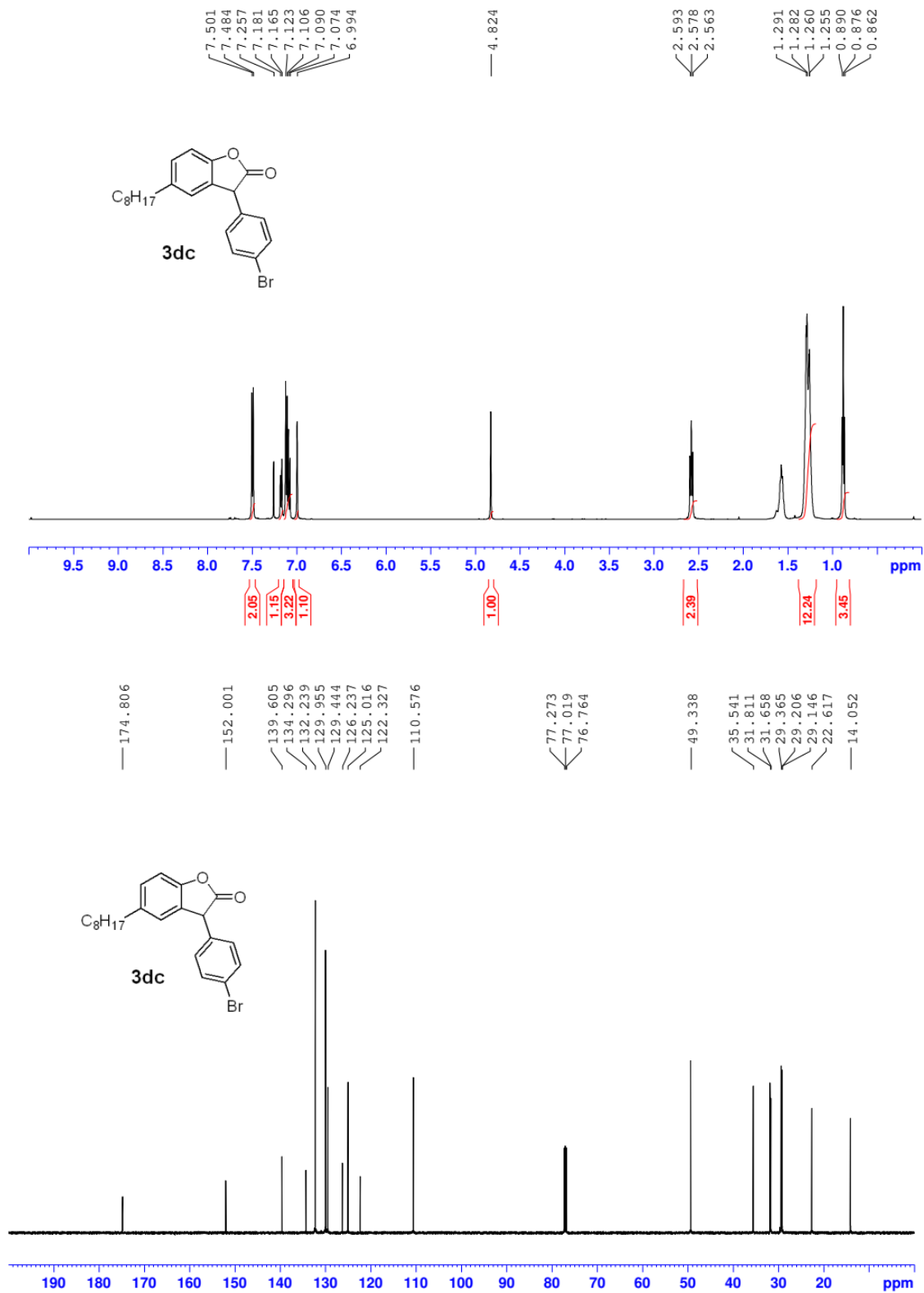


Figure S5.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **3dc**.

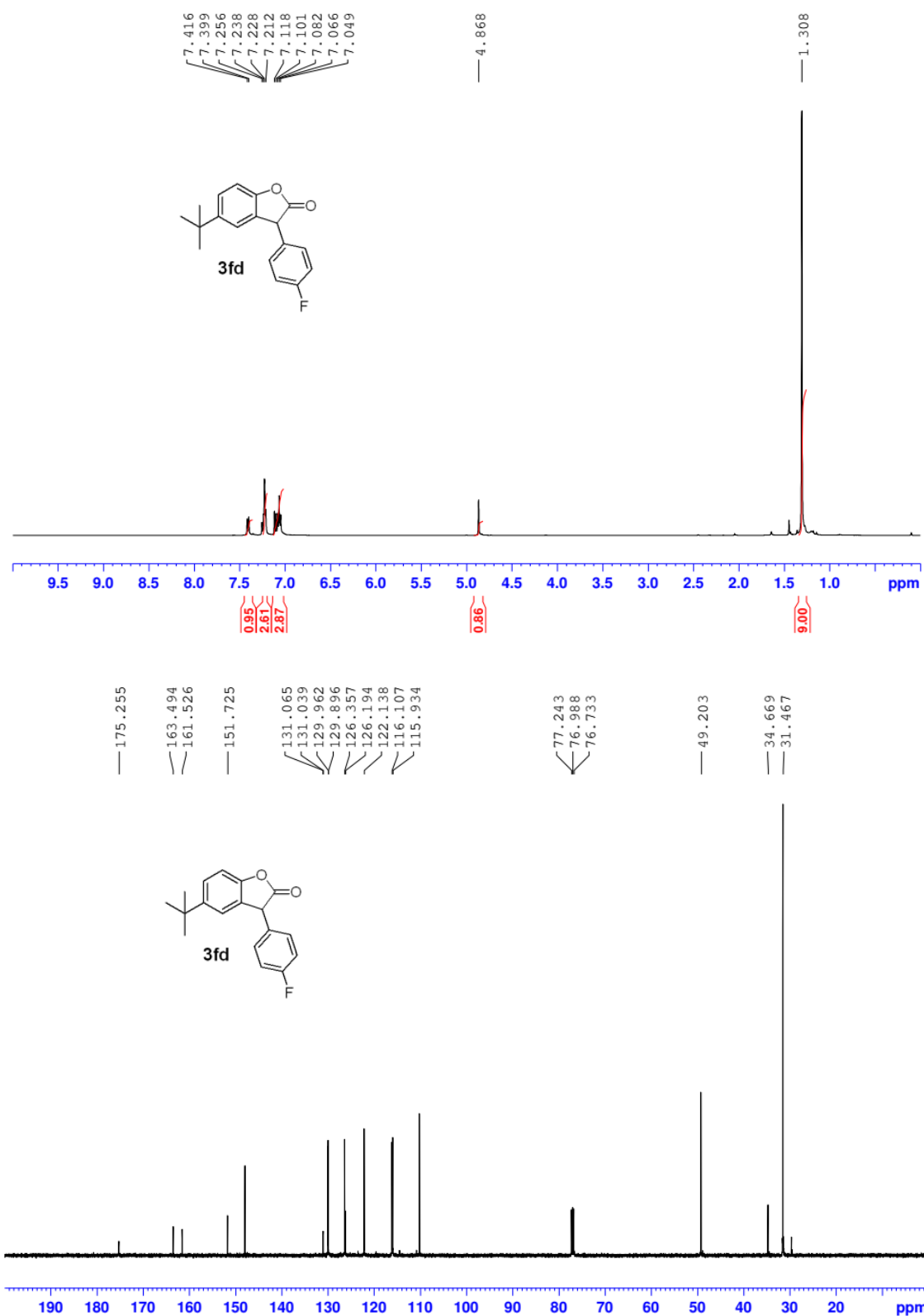


Figure S6.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **3fd**.

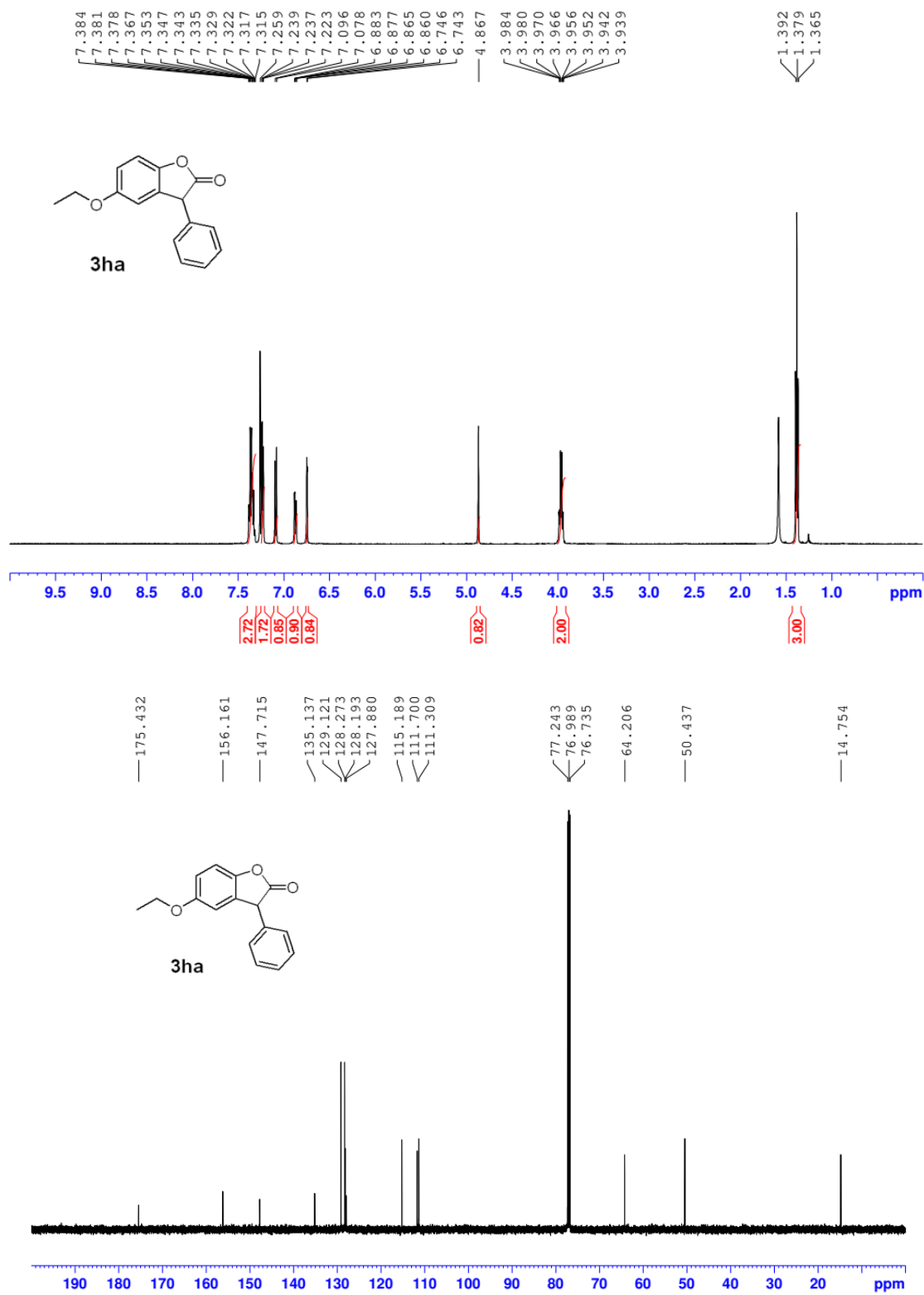


Figure S7.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **3ha**.

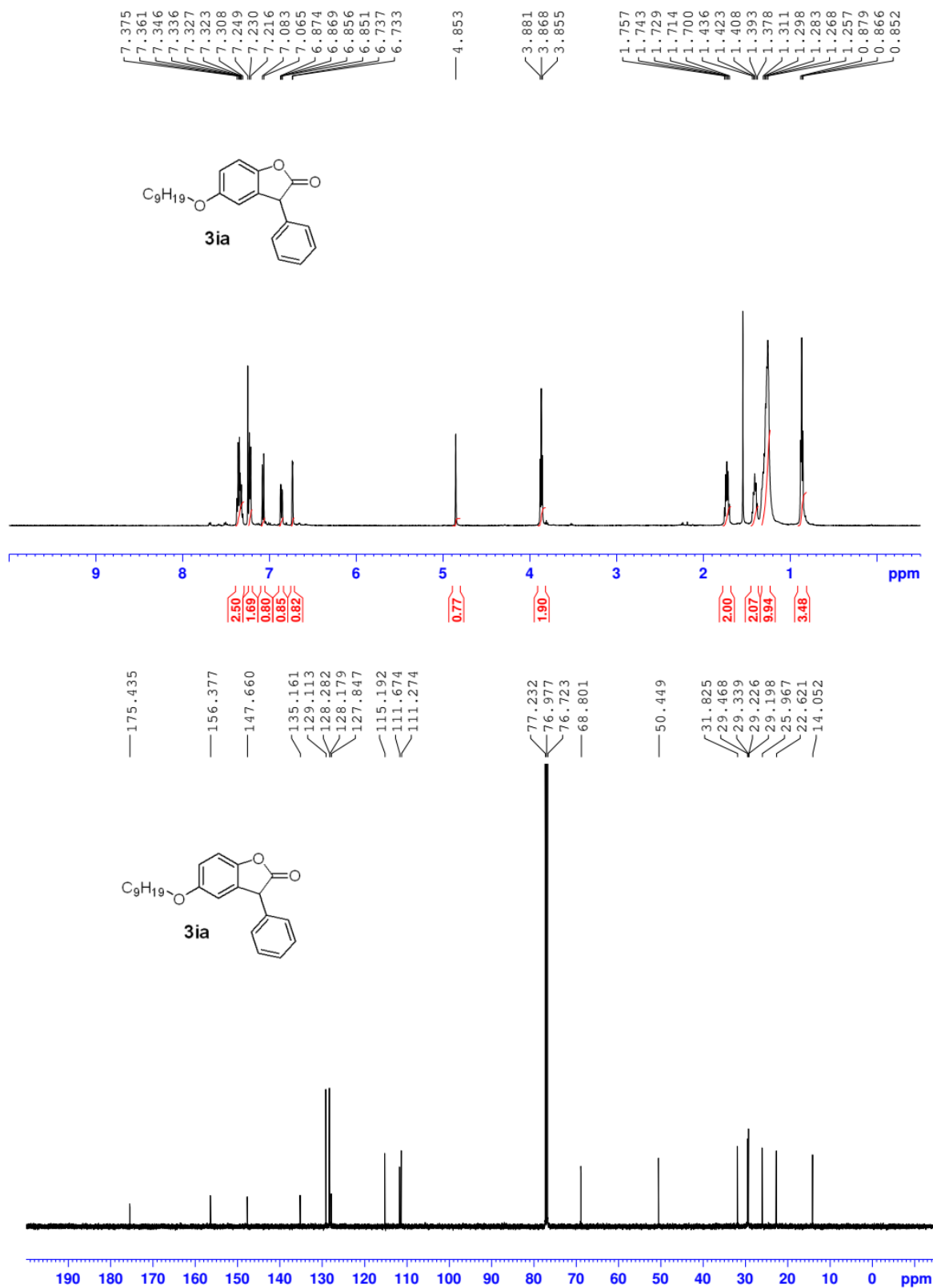


Figure S8. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **3ia**.

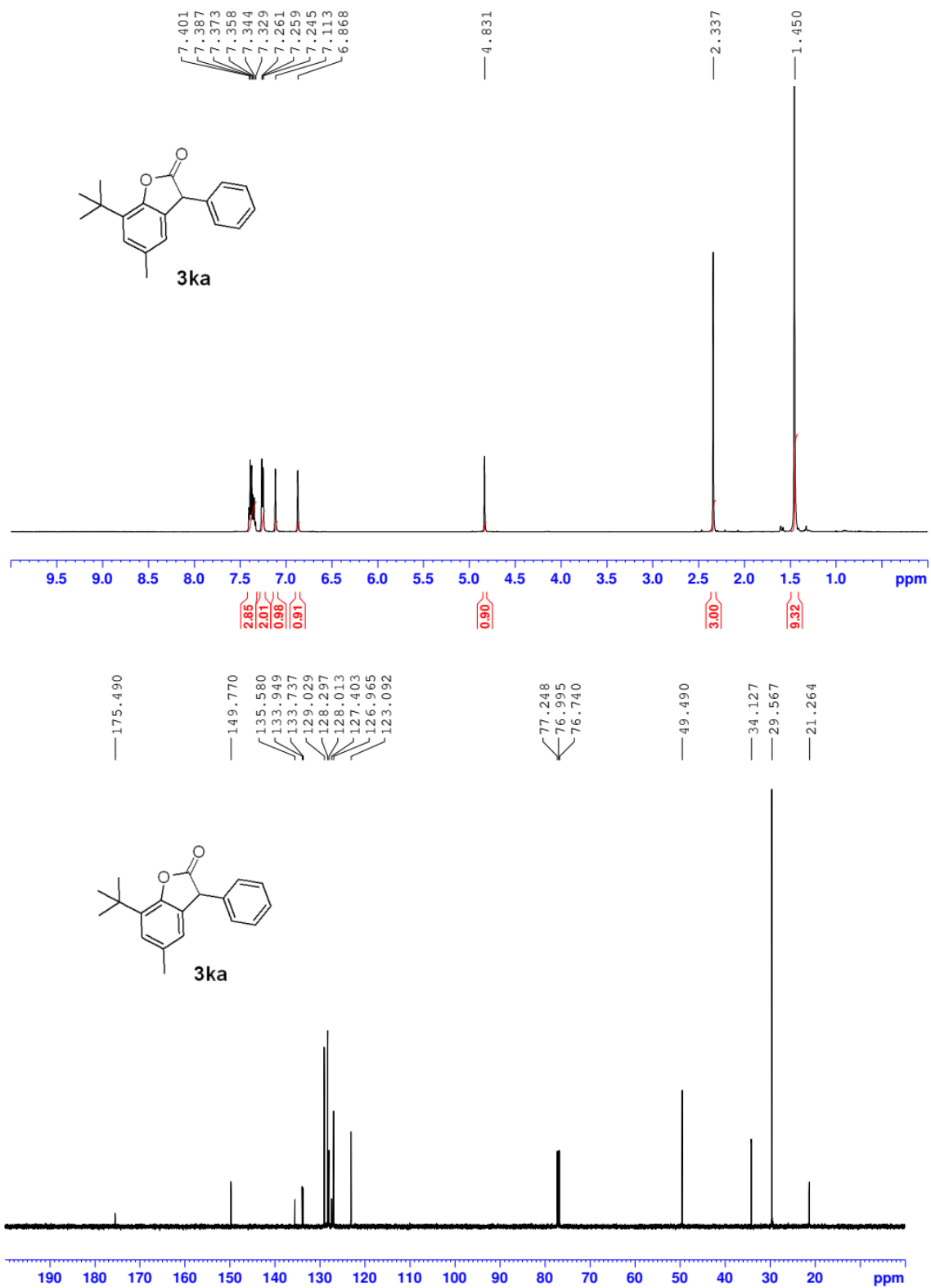


Figure S9. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 3ka.

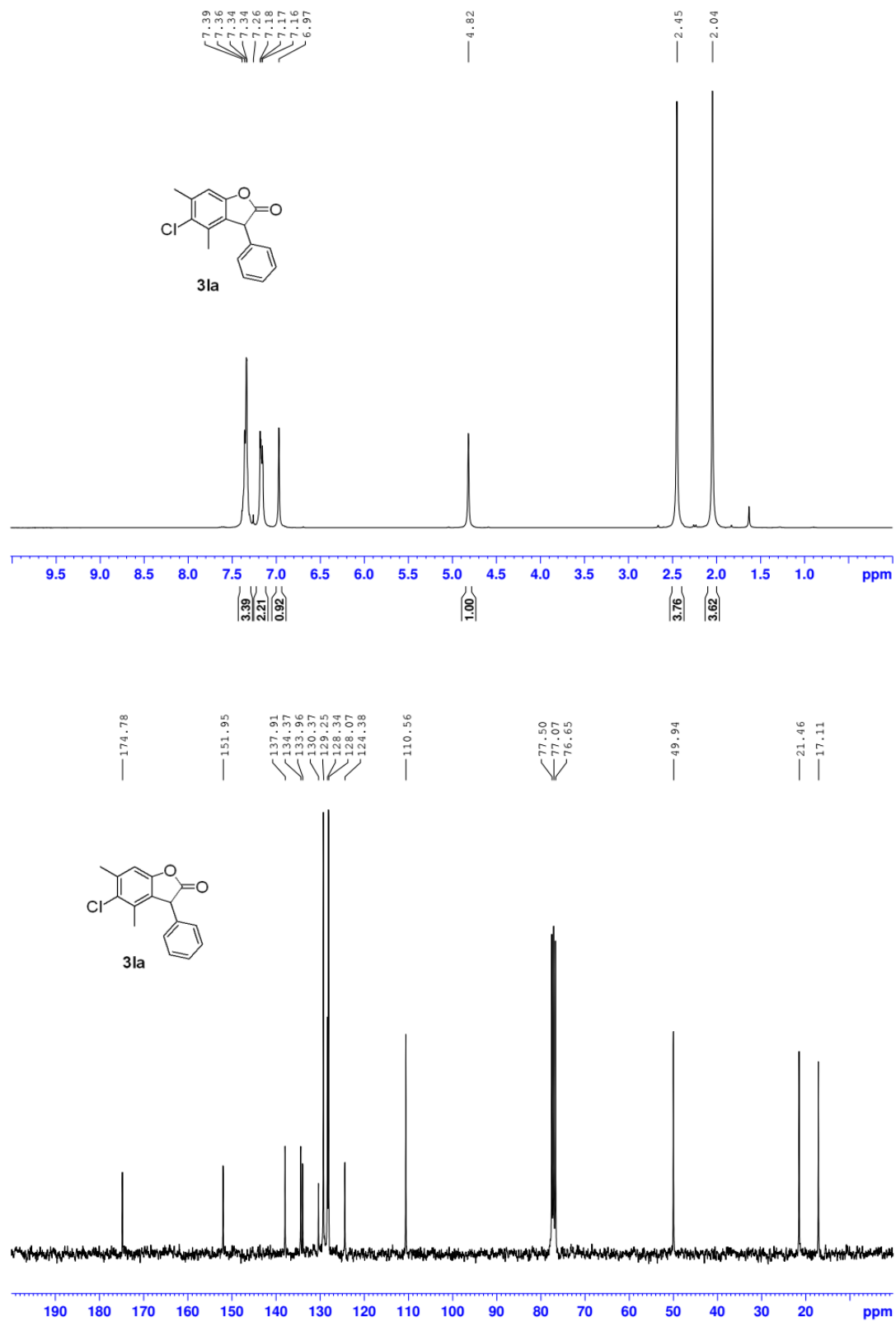
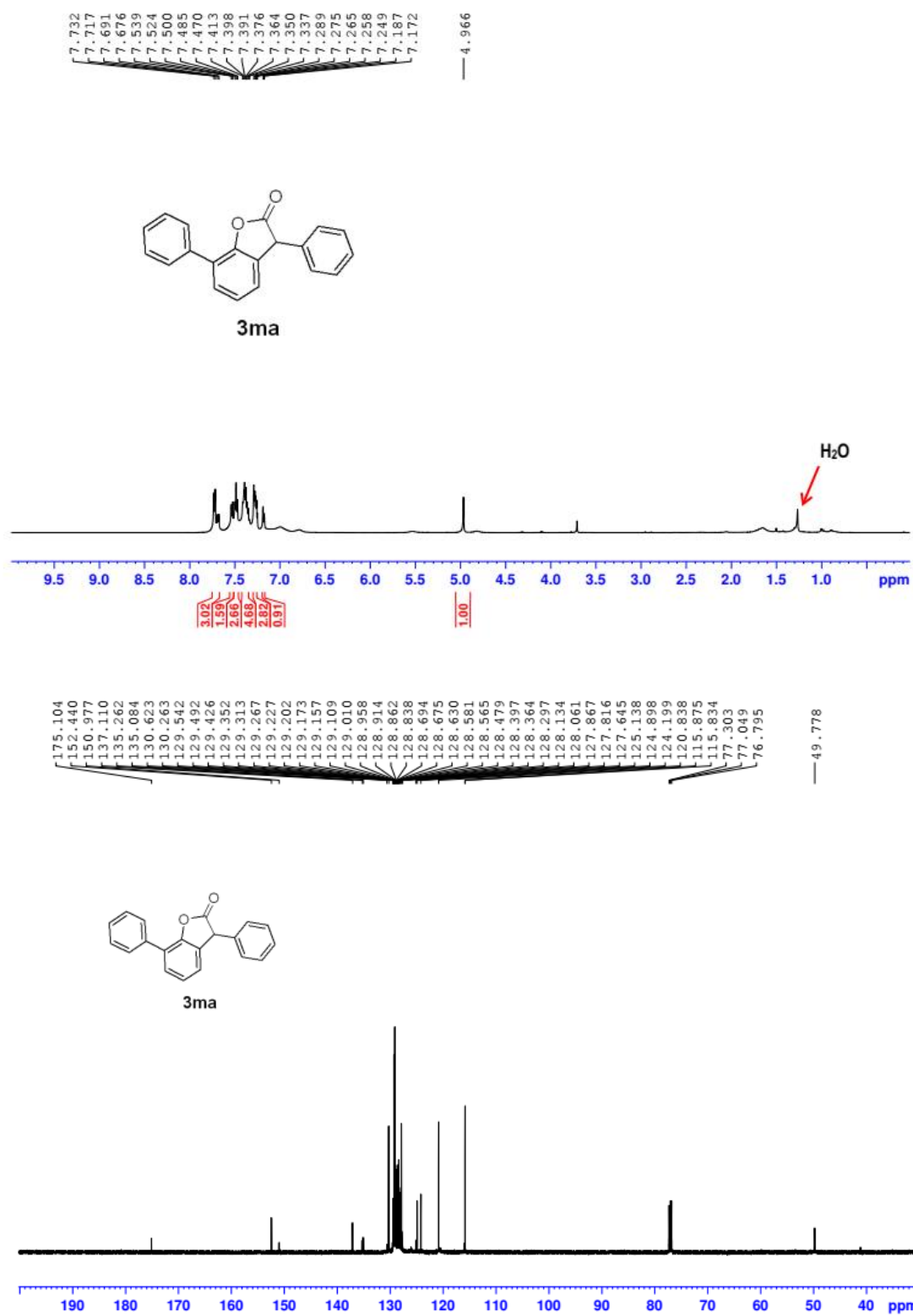
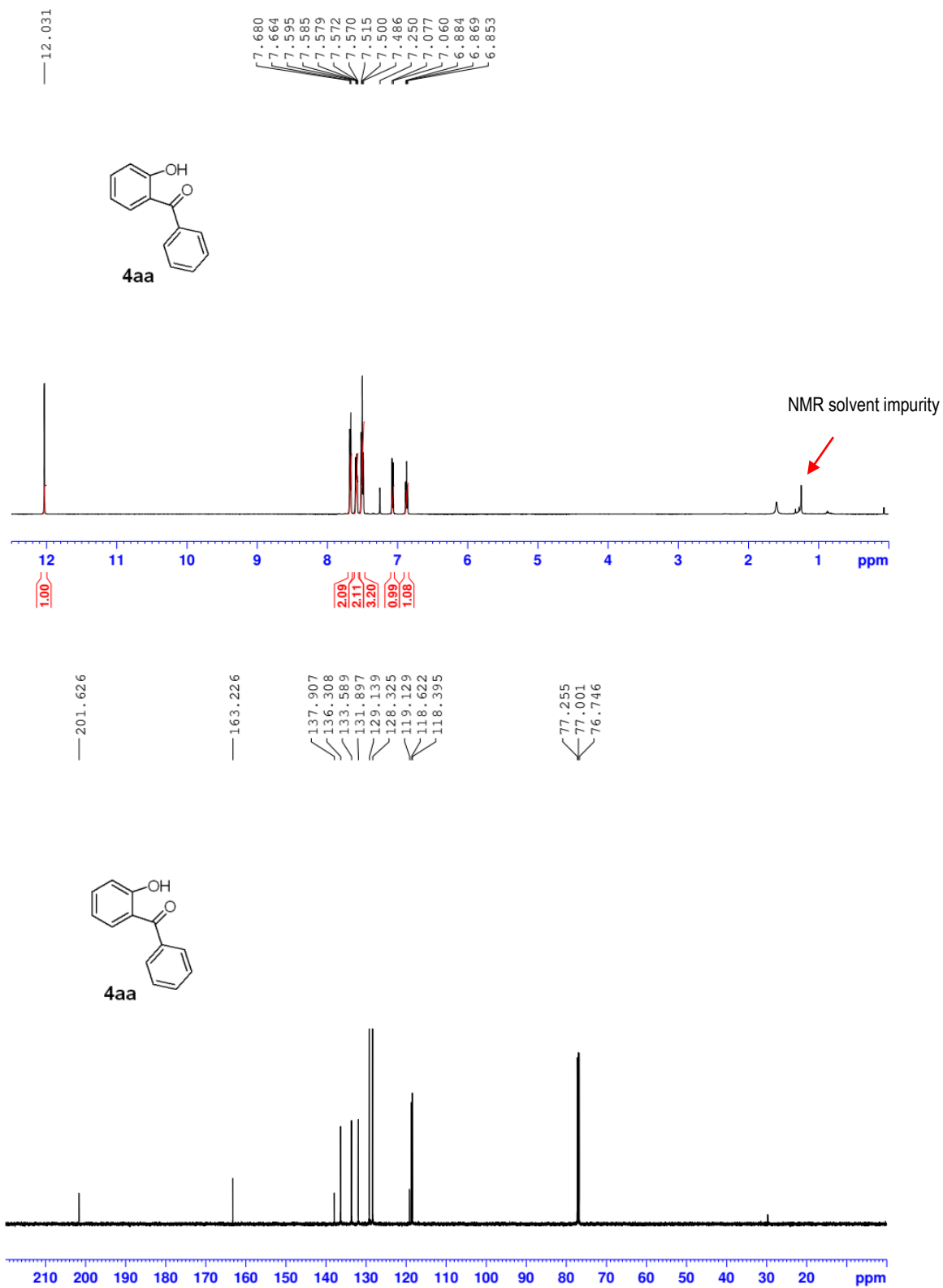


Figure S10. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **3la**.



**Figure S11.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **3ma**.



F

Figure S12. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 4aa.



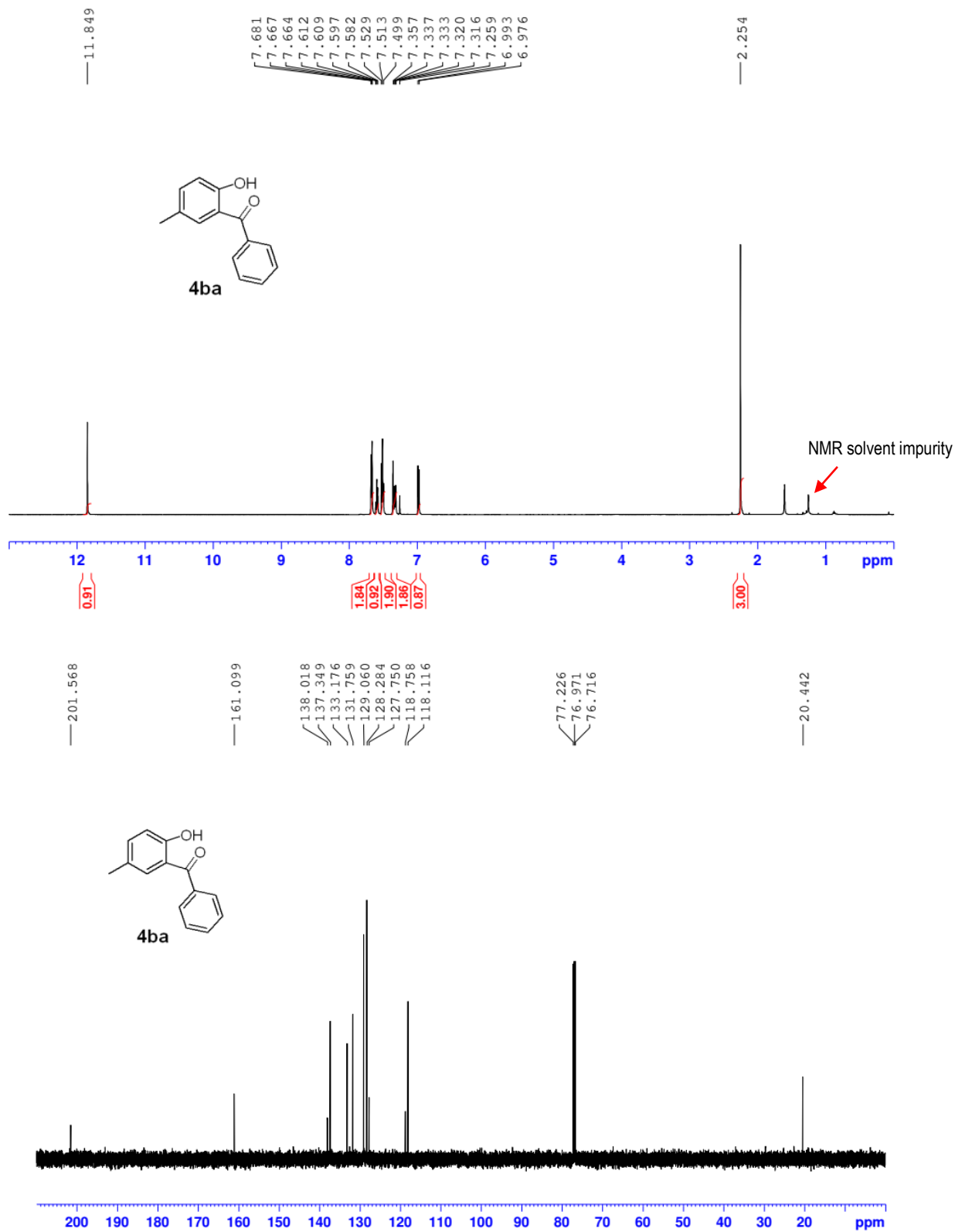
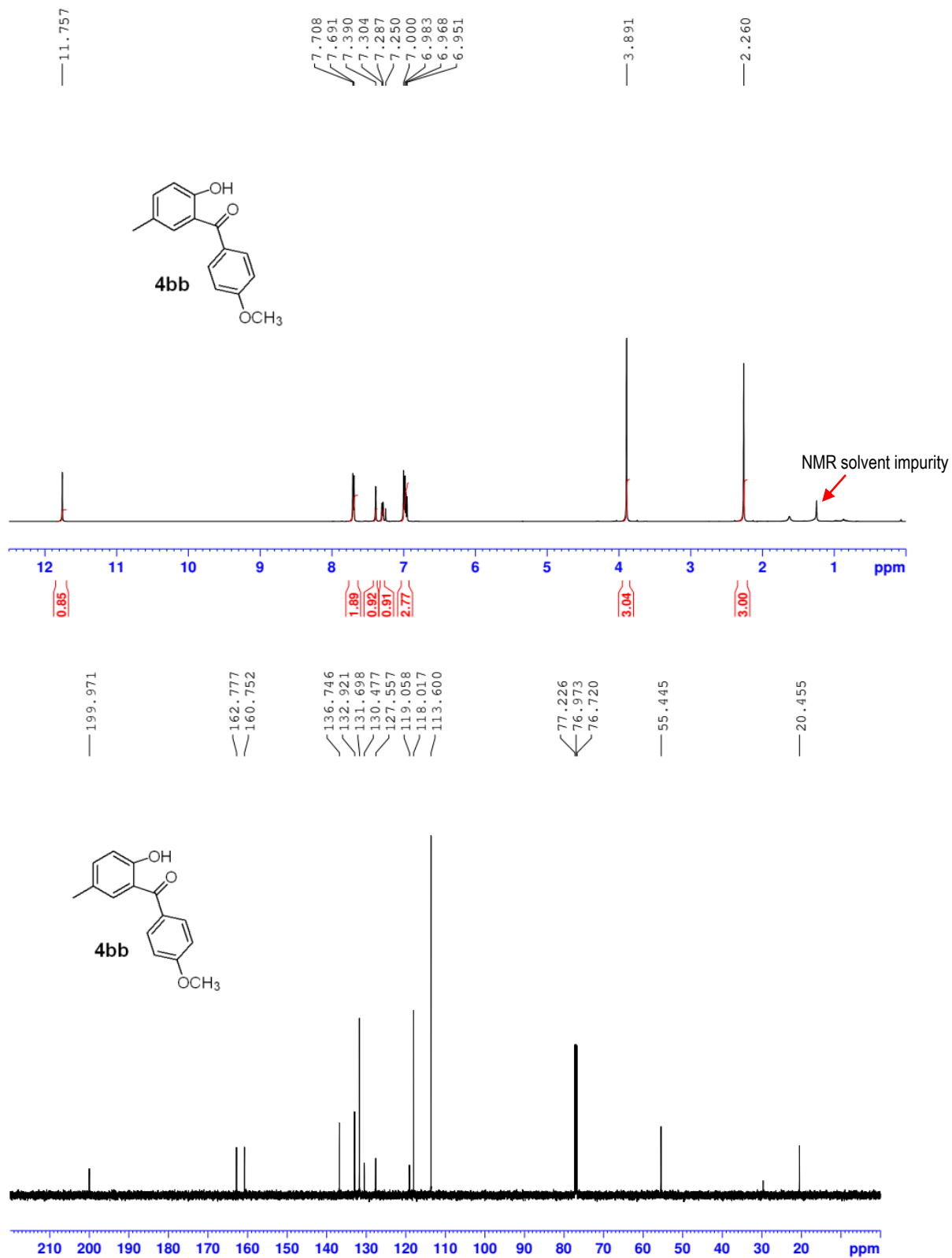


Figure S13. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4ba**.



**Figure S14.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4bb**.

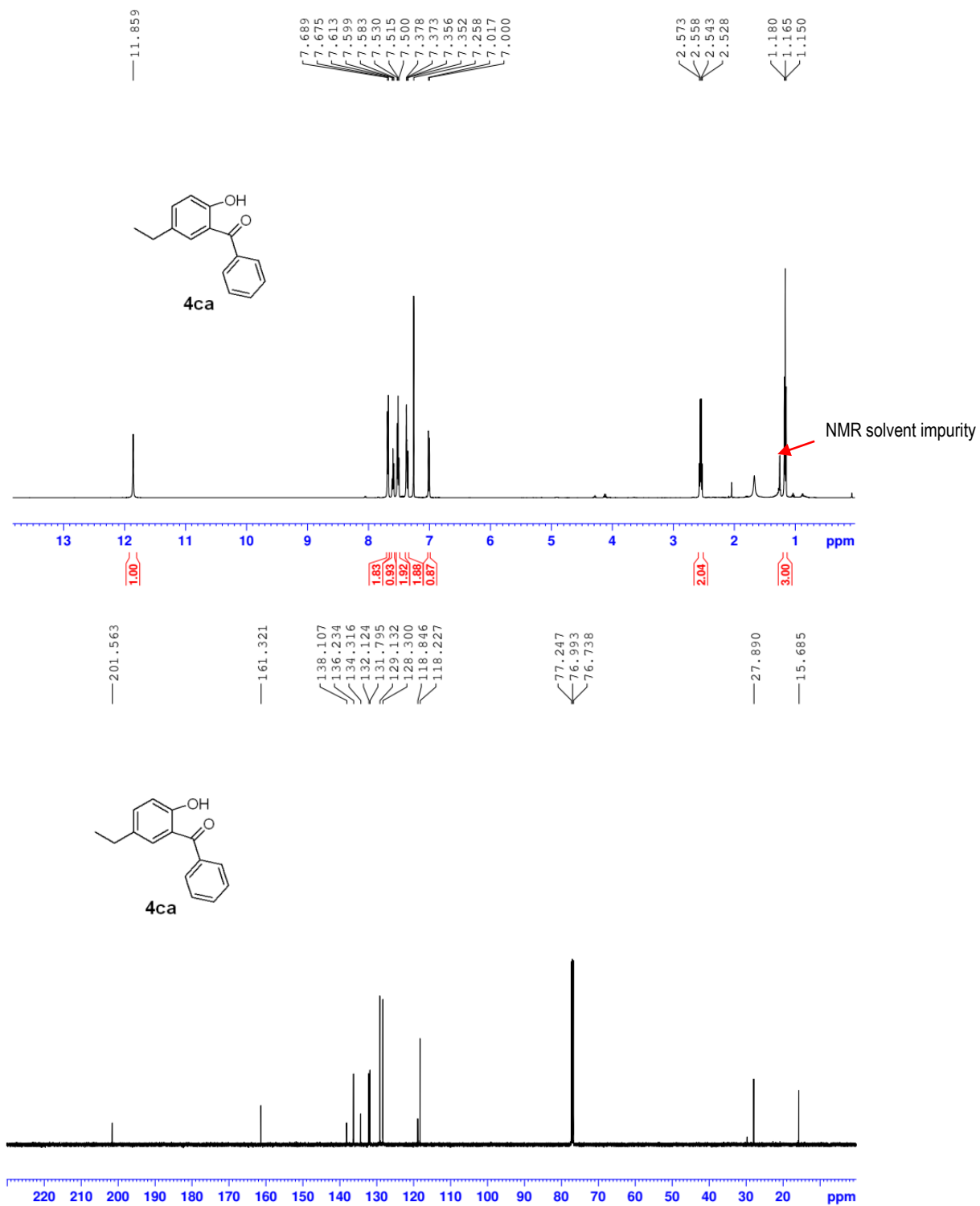
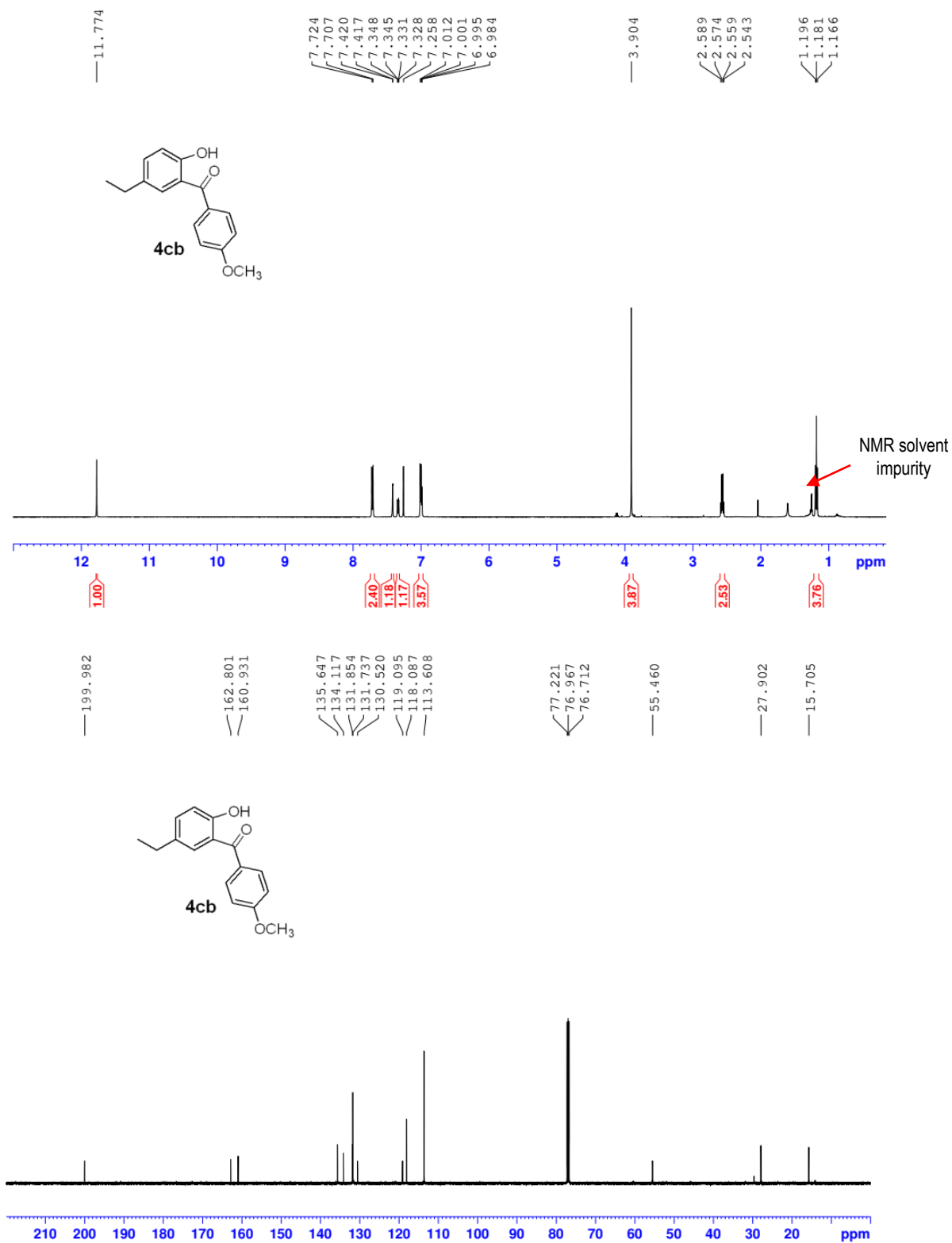
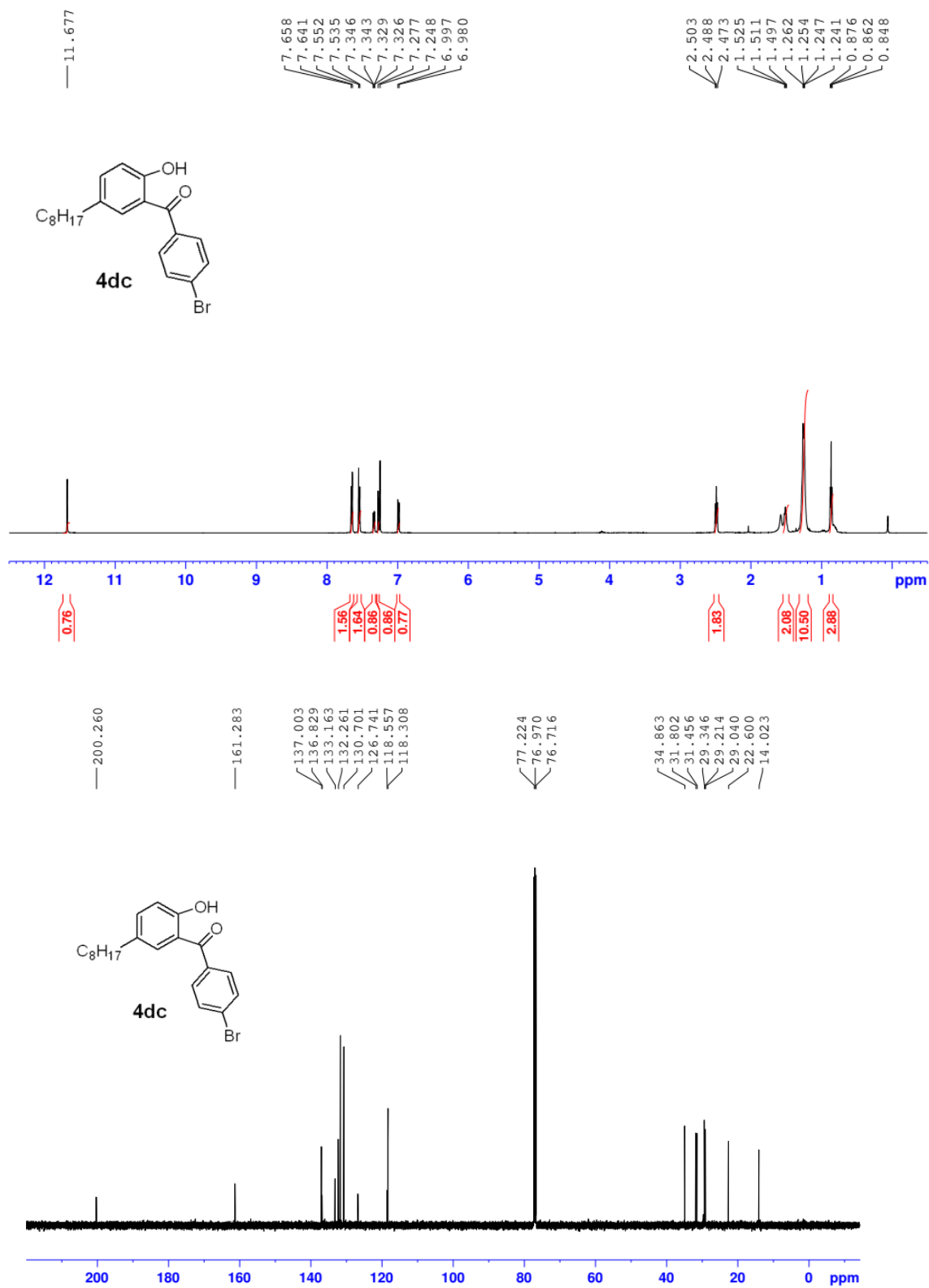


Figure S15. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4ca**.



**Figure S16.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **4cb**



**Figure S17.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4dc**.

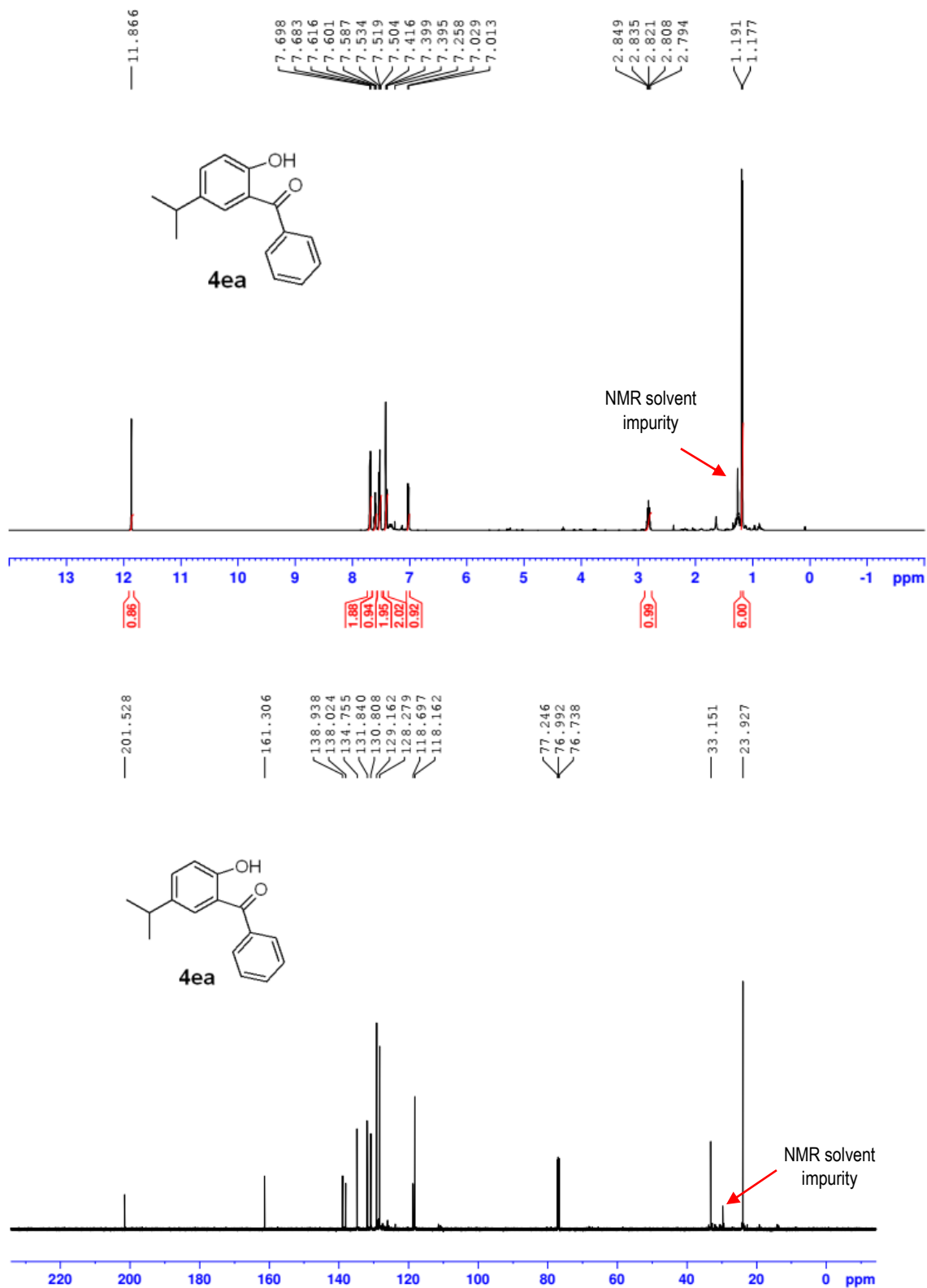


Figure S18. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 4ea.

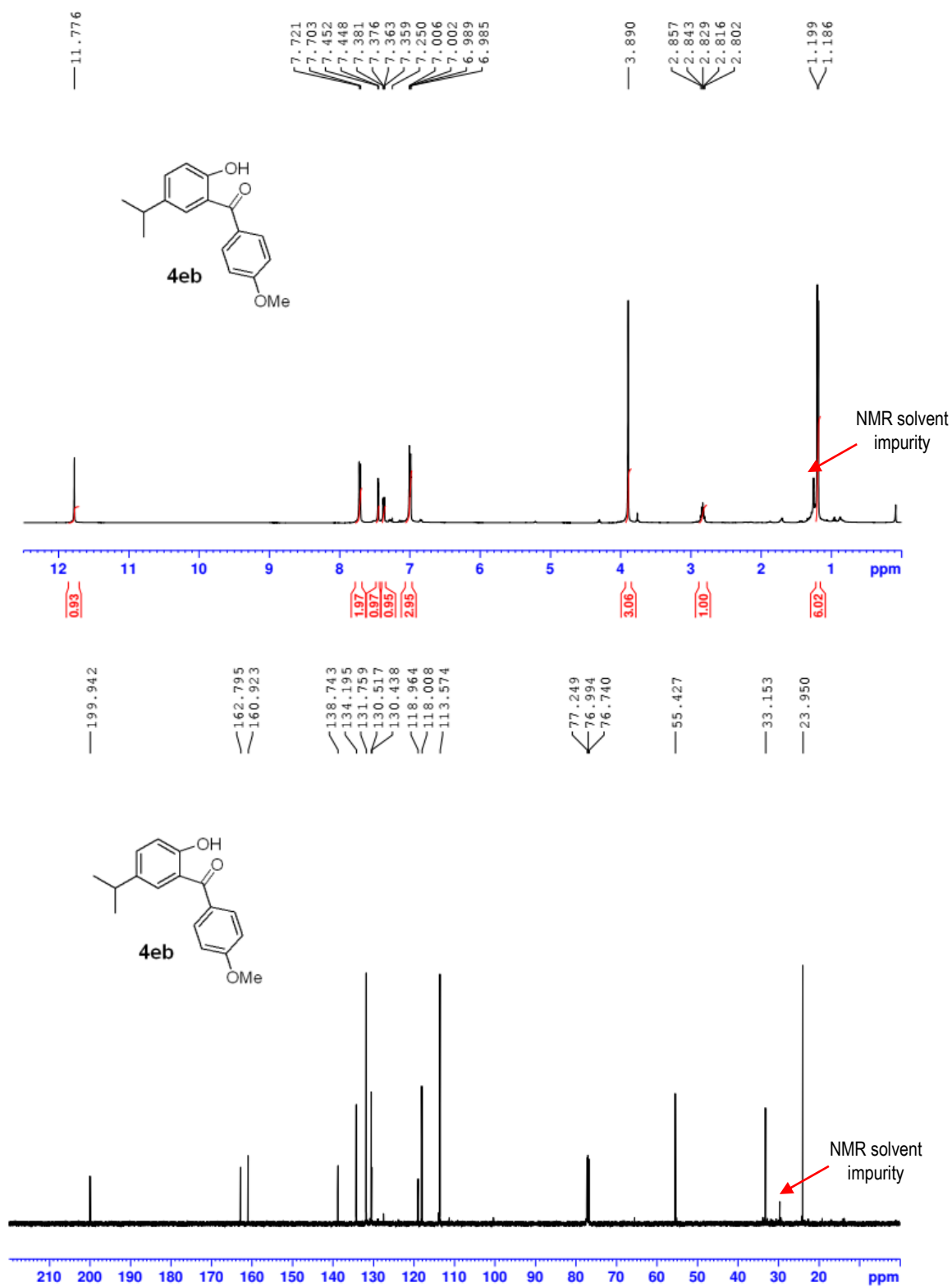


Figure S19. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4eb**.

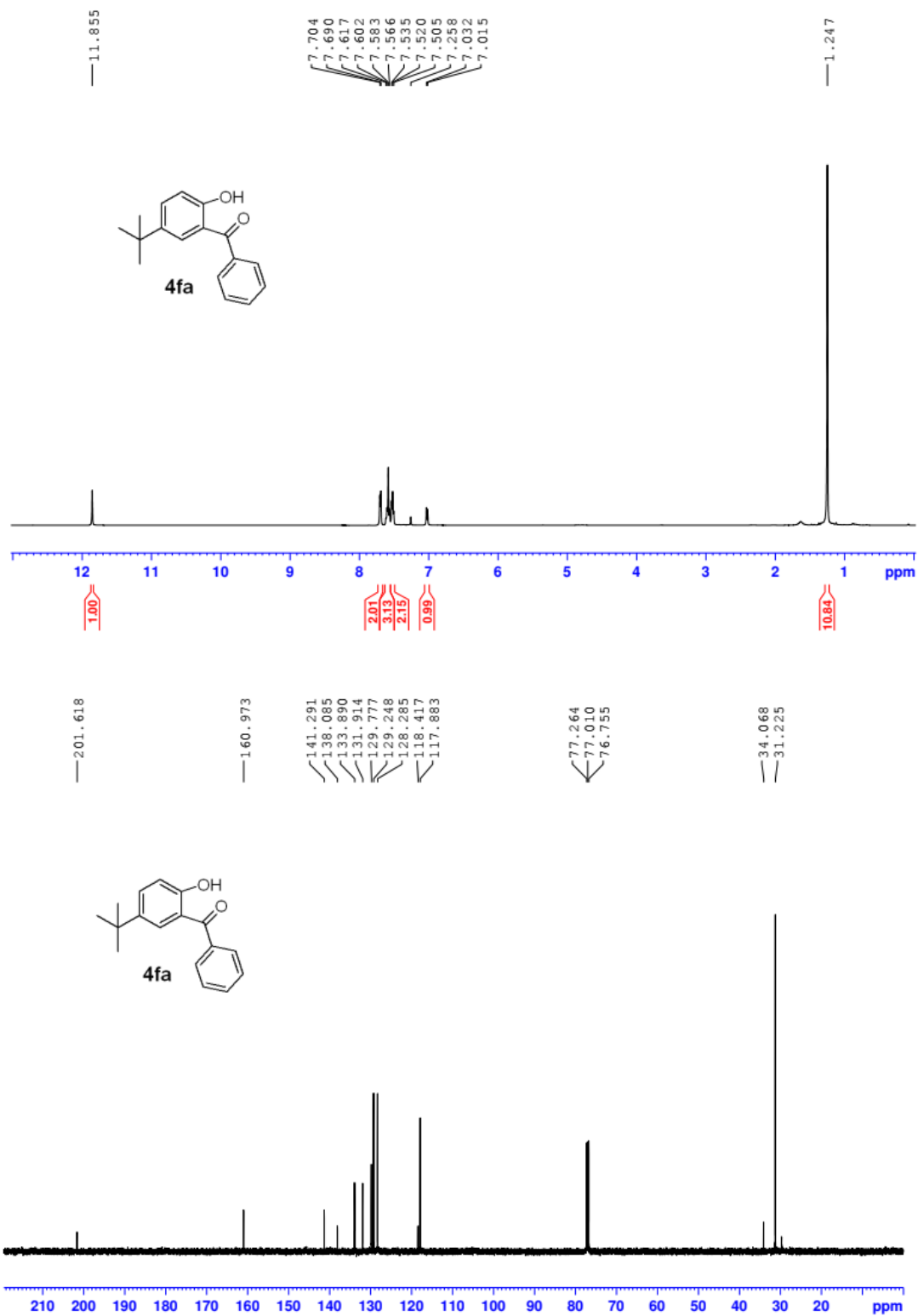


Figure S20. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4fa**.



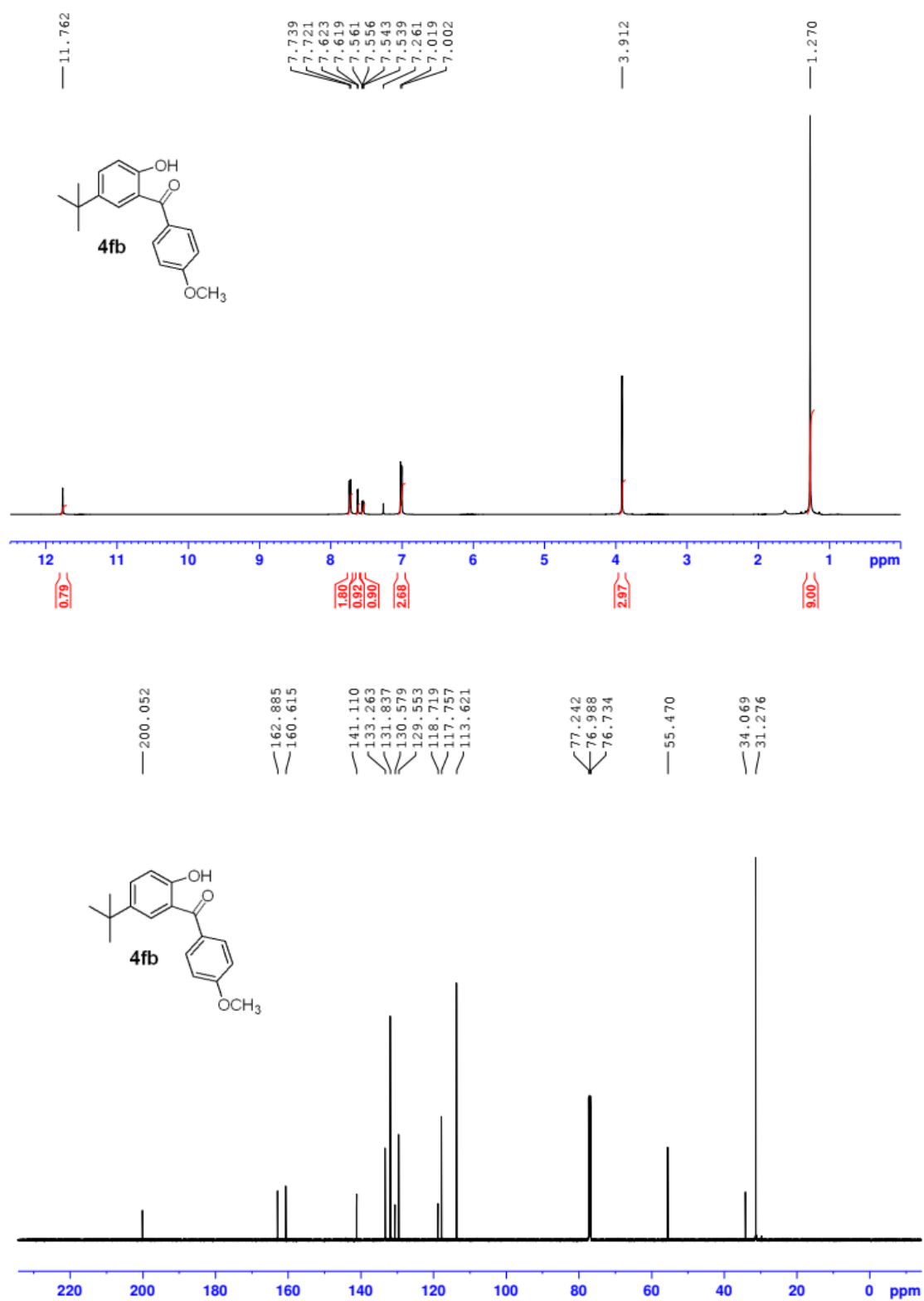
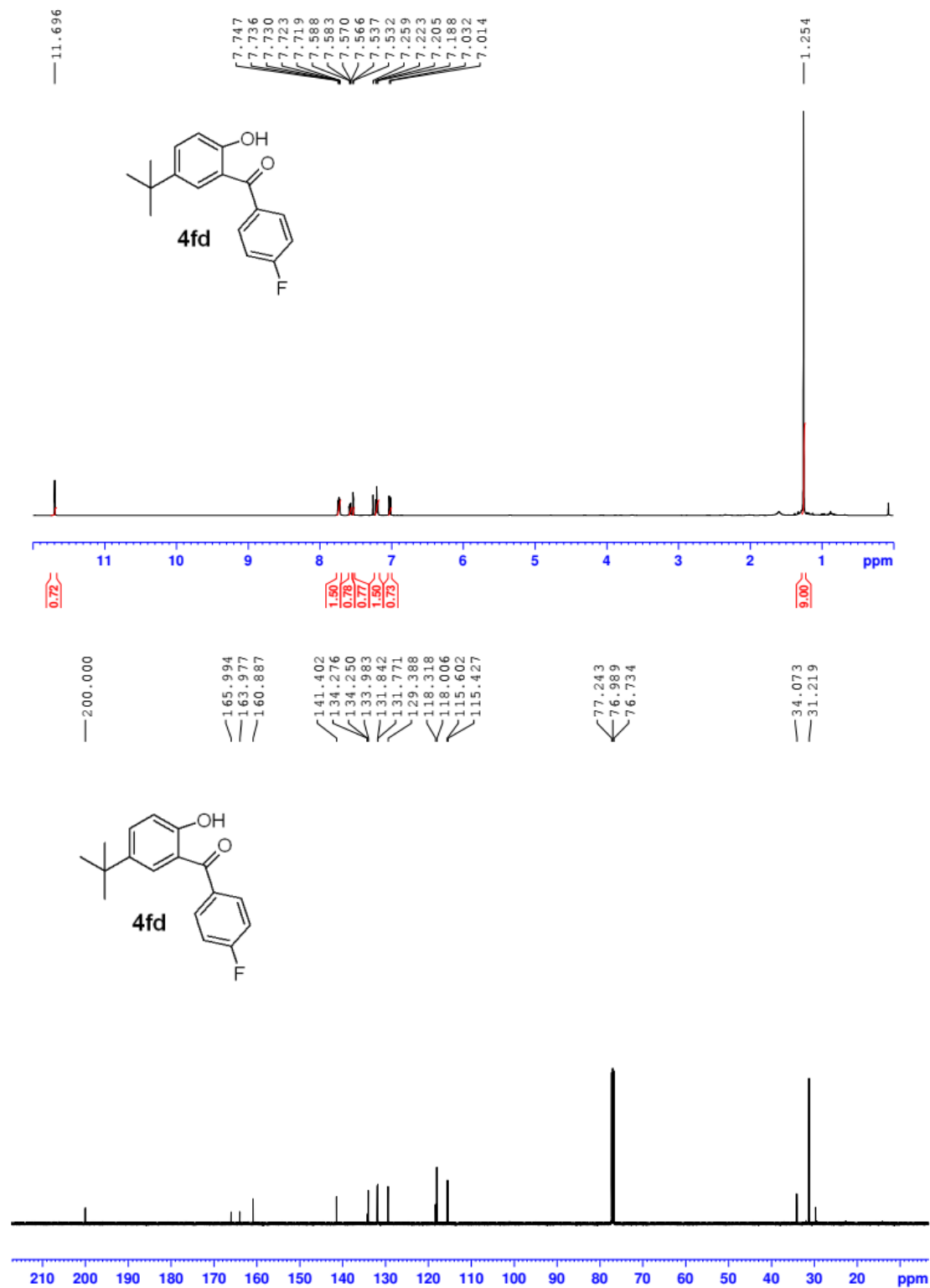


Figure S21. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of 4fb.



**Figure S22.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4fd**.

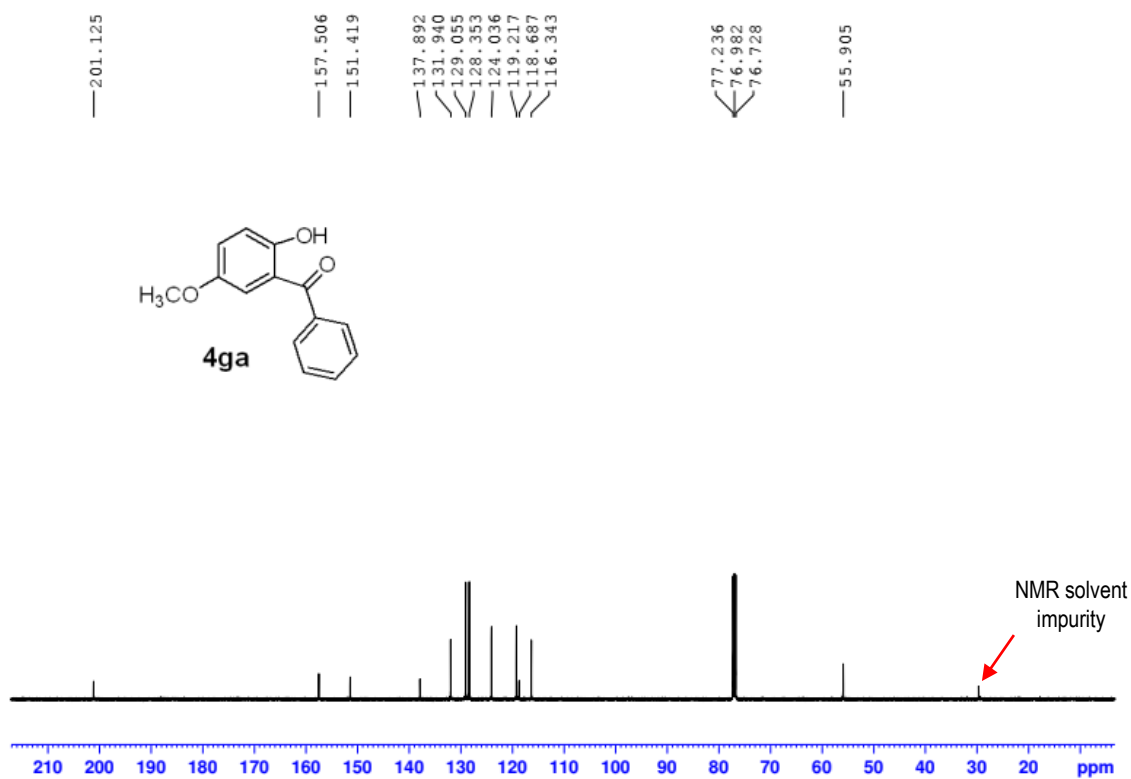
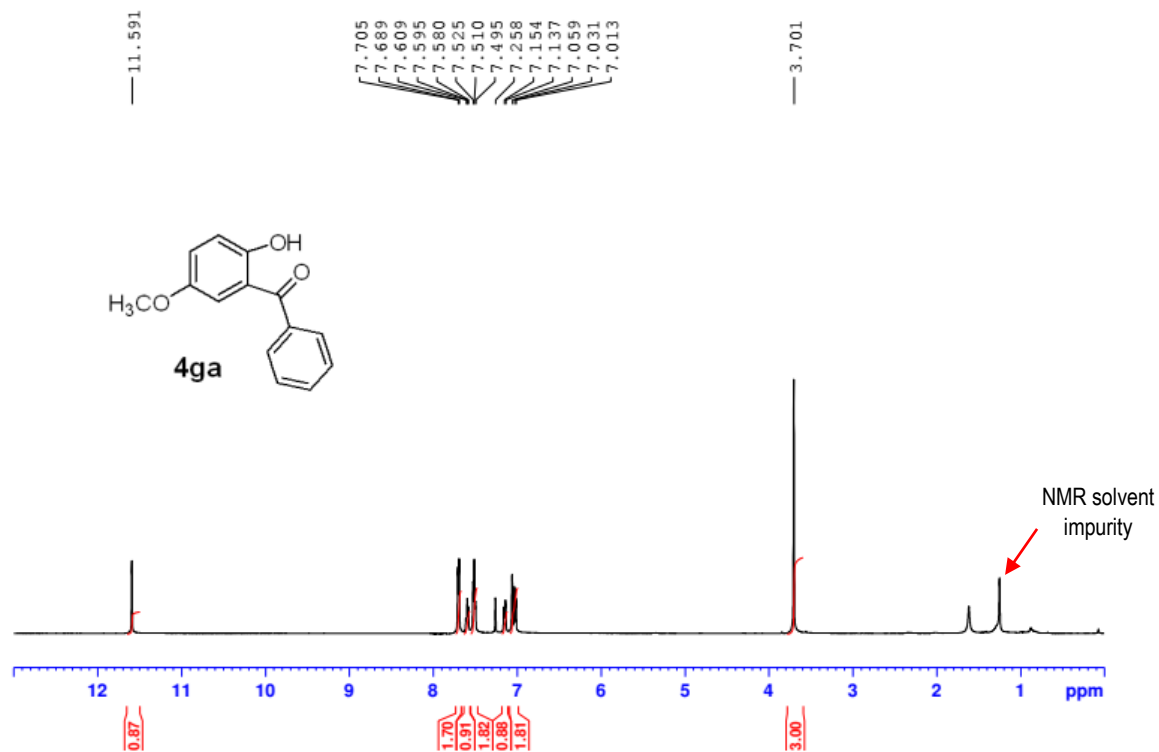


Figure S23.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **4ga**.

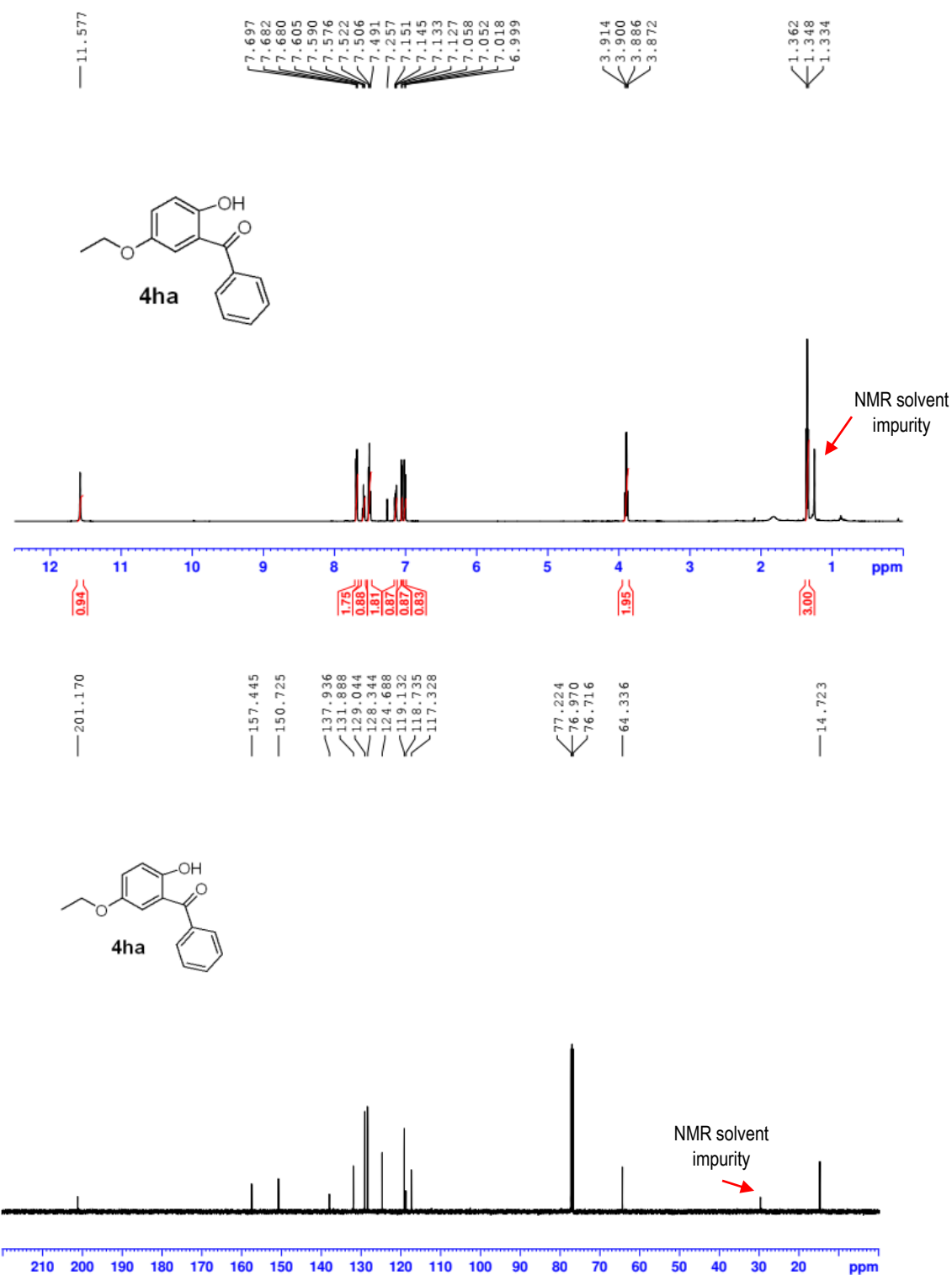


Figure S24. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4ha**.

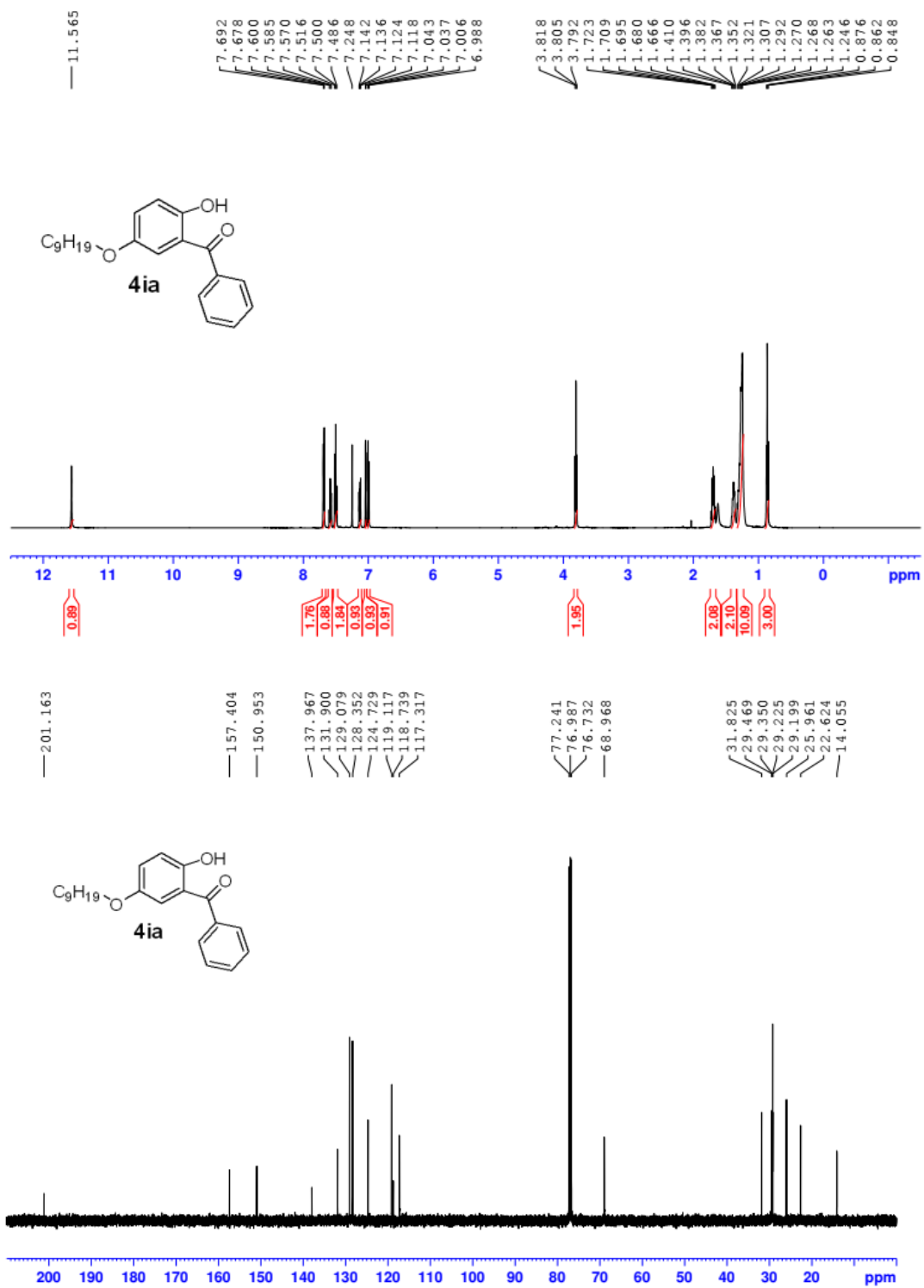


Figure S25. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4ia**.

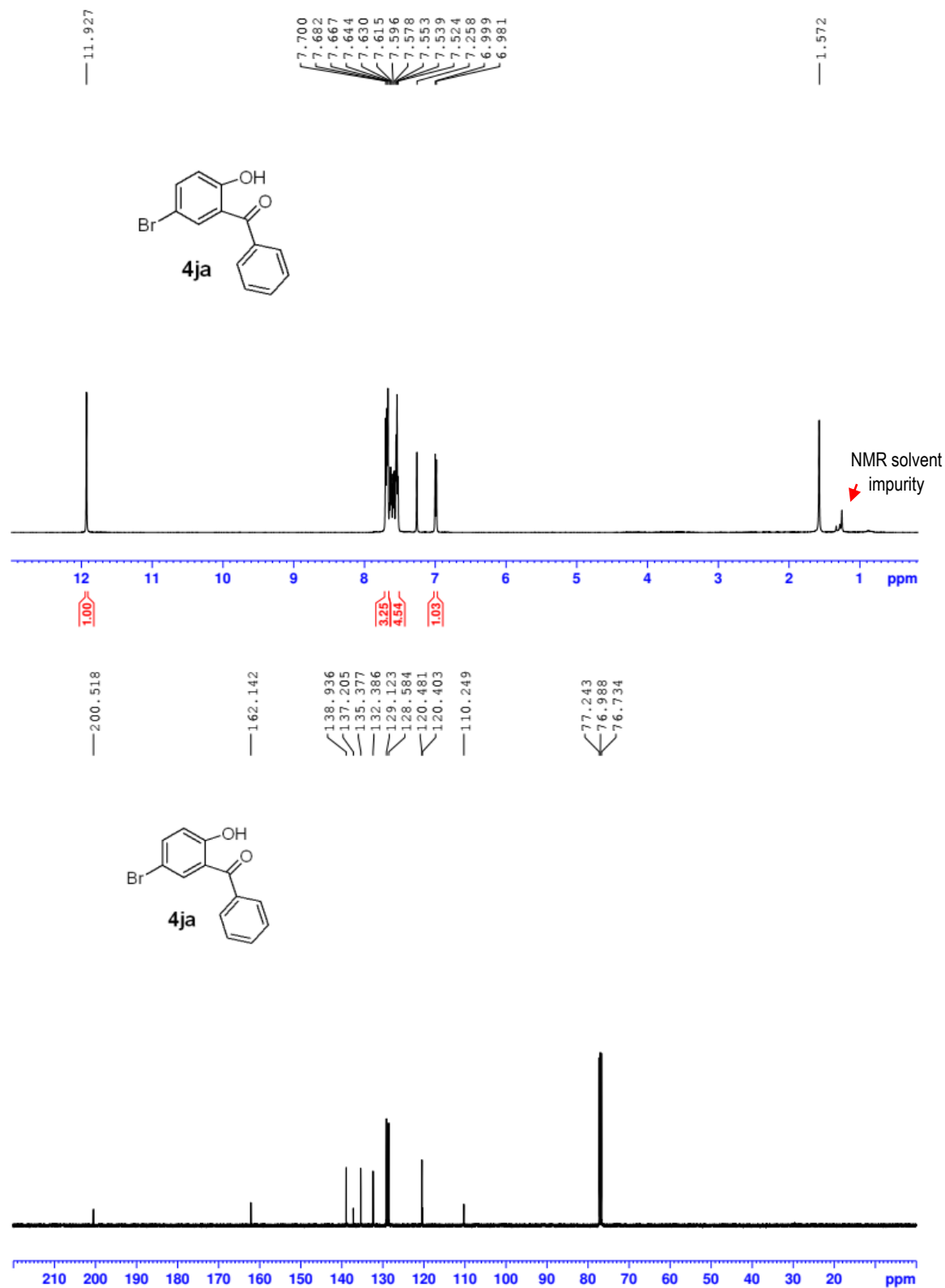


Figure S26. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4ja**.

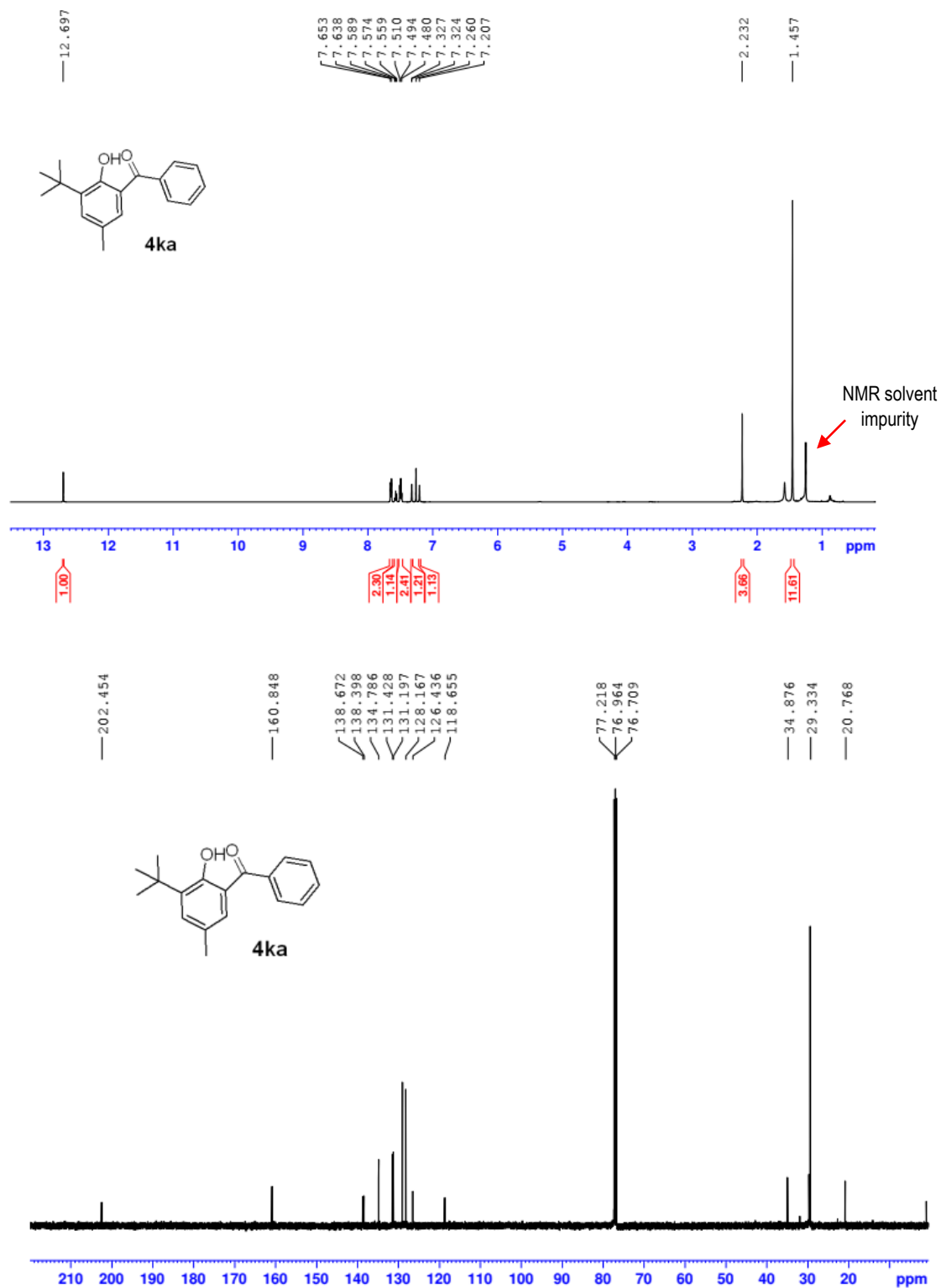


Figure S27.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **4ka**.

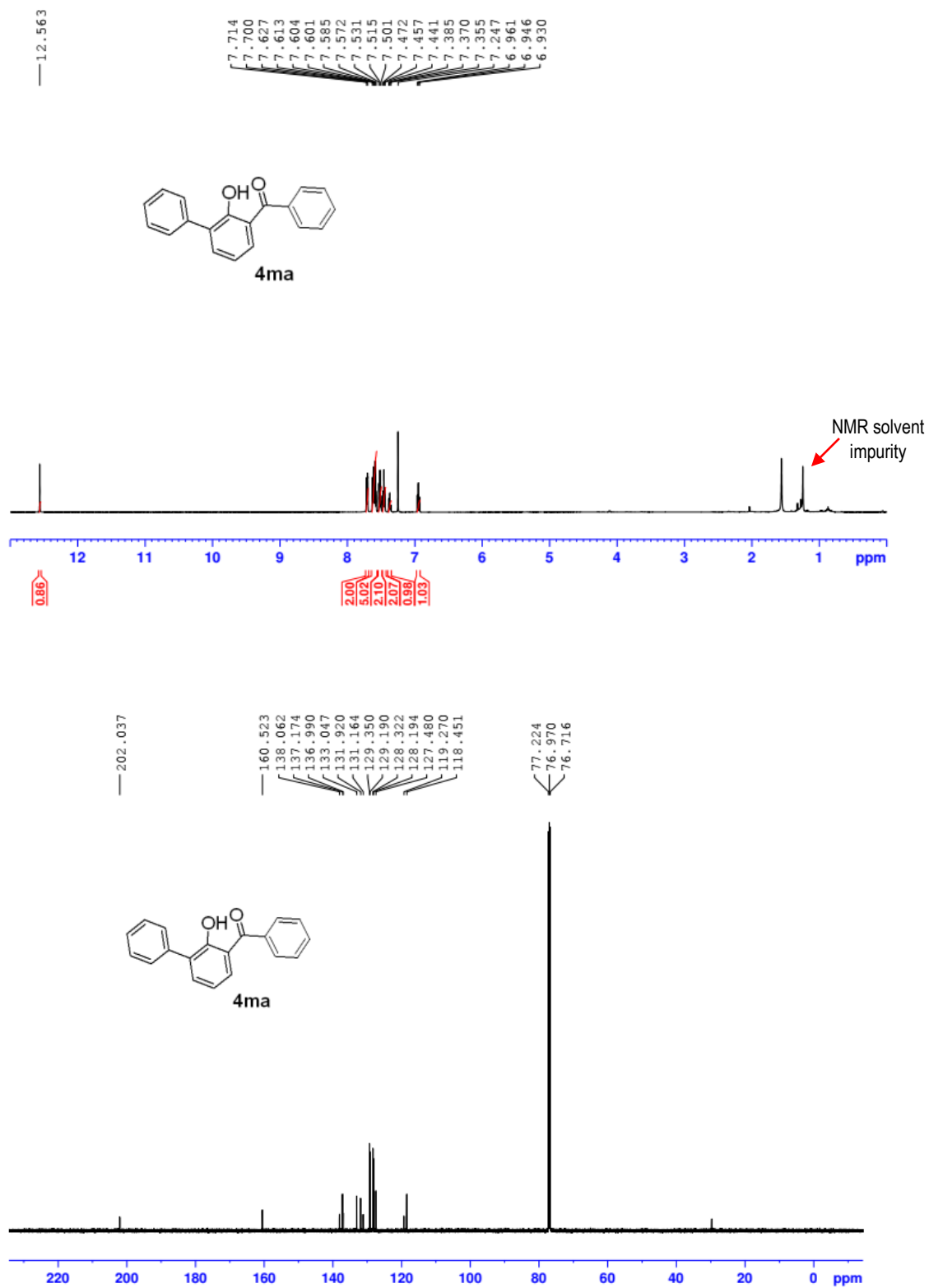


Figure S28. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of **4ma**.



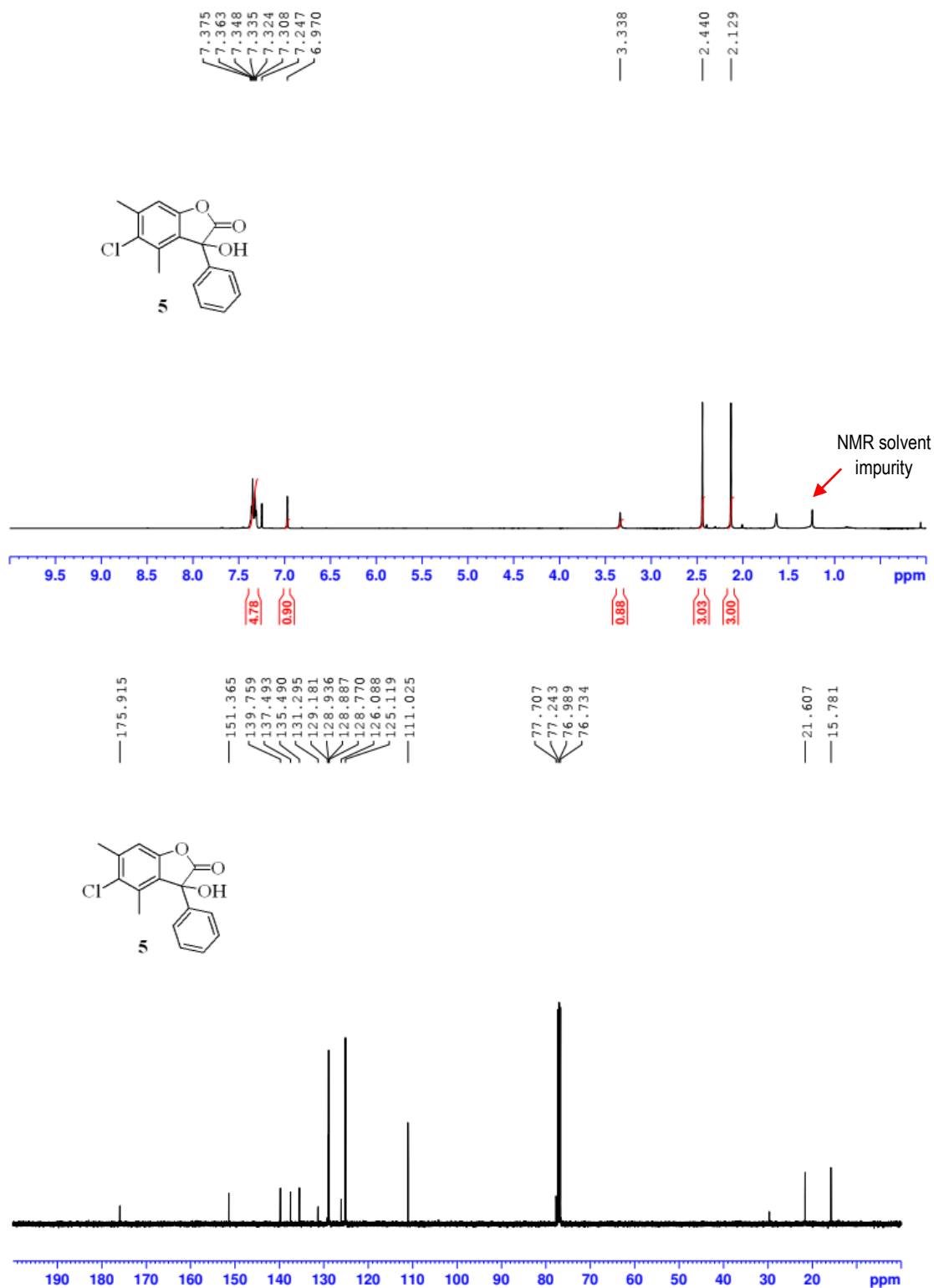


Figure S29.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **5**.

## Single crystal XRD data for compound **4ja** (CCDC no. 2348642)

### checkCIF/PLATON report

Structure factors have been supplied for datablock(s) bod-bd-cs-23-10

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.    CIF dictionary    Interpreting this report

### Datablock: bod-bd-cs-23-10

Bond precision:    C-C = 0.0033 Å    Wavelength=1.54184

Cell:                a=15.9403(3)        b=5.8978(1)        c=12.1235(2)  
                      alpha=90        beta=106.196(2)        gamma=90  
Temperature:        298 K

|                        | Calculated   | Reported     |
|------------------------|--------------|--------------|
| Volume                 | 1094.53(4)   | 1094.53(3)   |
| Space group            | P 21/c       | P 1 21/c 1   |
| Hall group             | -P 2ybc      | -P 2ybc      |
| Moiety formula         | C13 H9 Br O2 | C13 H9 Br O2 |
| Sum formula            | C13 H9 Br O2 | C13 H9 Br O2 |
| Mr                     | 277.10       | 277.11       |
| Dx, g cm <sup>-3</sup> | 1.682        | 1.682        |
| Z                      | 4            | 4            |
| Mu (mm <sup>-1</sup> ) | 4.964        | 4.964        |
| F000                   | 552.0        | 552.0        |
| F000'                  | 550.59       |              |
| h,k,lmax               | 20,7,15      | 19,7,15      |
| Nref                   | 2317         | 2238         |
| Tmin,Tmax              | 0.639,0.609  | 0.668,1.000  |
| Tmin'                  | 0.580        |              |

Correction method= # Reported T Limits: Tmin=0.668 Tmax=1.000  
AbsCorr = MULTI-SCAN

Data completeness= 0.966    Theta(max)= 77.081

R(reflections)= 0.0308( 2018)    wR2(reflections)=  
S = 1.136    Npar= 146    0.1053( 2238)

The following ALERTS were generated. Each ALERT has the format  
test-name\_ALERT\_alert-type\_alert-level.  
Click on the hyperlinks for more details of the test.

 **Alert level C**  
PLAT911\_ALERT\_3\_C Missing FCF Refl Between Thmin & STh/L= 0.600    2 Report  
0 7 2, -17 0 10,

 **Alert level G**  
PLAT007\_ALERT\_5\_G Number of Unrefined Donor-H Atoms ..... 1 Report  
H1  
PLAT912\_ALERT\_4\_G Missing # of FCF Reflections Above STh/L= 0.600    75 Note  
PLAT969\_ALERT\_5\_G The 'Henn et al.' R-Factor-gap value ..... 3.98 Note  
Predicted wR2: Based on SigI\*\*2 2.65 or SHELX Weight 9.59  
PLAT978\_ALERT\_2\_G Number C-C Bonds with Positive Residual Density. 3 Info

0 ALERT level A = Most likely a serious problem - resolve or explain  
0 ALERT level B = A potentially serious problem, consider carefully  
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight  
4 ALERT level G = General information/check it is not something unexpected  
  
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data  
1 ALERT type 2 Indicator that the structure model may be wrong or deficient  
1 ALERT type 3 Indicator that the structure quality may be low  
1 ALERT type 4 Improvement, methodology, query or suggestion  
2 ALERT type 5 Informative message, check

Database bod-bd-cs-23-10 - allpost plot

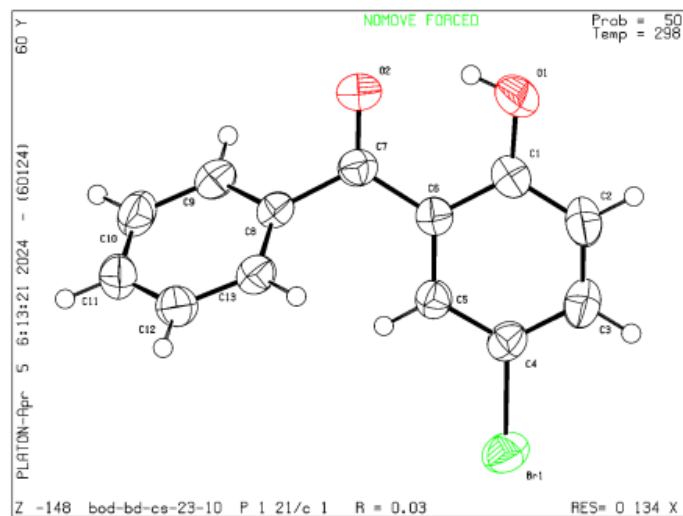


Table S2. Crystal data and structure refinement for **4ja** (CCDC no. 2348642)

|                                                      |                                                                                |
|------------------------------------------------------|--------------------------------------------------------------------------------|
| CCDC number                                          |                                                                                |
| Empirical formula                                    | C <sub>13</sub> H <sub>9</sub> BrO <sub>2</sub>                                |
| Formula weight                                       | 277.11                                                                         |
| Temperature [K]                                      | 298                                                                            |
| Crystal system                                       | monoclinic                                                                     |
| Space group (number)                                 | <i>P</i> 2 <sub>1</sub> / <i>c</i> (14)                                        |
| <i>a</i> [Å]                                         | 15.9403(3)                                                                     |
| <i>b</i> [Å]                                         | 5.89780(10)                                                                    |
| <i>c</i> [Å]                                         | 12.1235(2)                                                                     |
| $\alpha$ [°]                                         | 90                                                                             |
| $\beta$ [°]                                          | 106.196(2)                                                                     |
| $\gamma$ [°]                                         | 90                                                                             |
| Volume [Å <sup>3</sup> ]                             | 1094.53(3)                                                                     |
| <i>Z</i>                                             | 4                                                                              |
| $\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]            | 1.682                                                                          |
| $\mu$ [mm <sup>-1</sup> ]                            | 4.964                                                                          |
| <i>F</i> (000)                                       | 552                                                                            |
| Crystal size [mm <sup>3</sup> ]                      | 0.1×0.1×0.1                                                                    |
| Crystal colour                                       | colourless                                                                     |
| Crystal shape                                        | block                                                                          |
| Radiation                                            | Cu <i>K</i> $\alpha$ ( $\lambda$ =1.54184 Å)                                   |
| 2 $\theta$ range [°]                                 | 5.77 to 154.16 (0.79 Å)                                                        |
| Index ranges                                         | -19 ≤ <i>h</i> ≤ 19<br>-7 ≤ <i>k</i> ≤ 7<br>-14 ≤ <i>l</i> ≤ 15                |
| Reflections collected                                | 12336                                                                          |
| Independent reflections                              | 2238<br><i>R</i> <sub>int</sub> = 0.0590<br><i>R</i> <sub>sigma</sub> = 0.0297 |
| Completeness to $\theta$ = 67.684°                   | 99.9 %                                                                         |
| Data / Restraints / Parameters                       | 2238/0/146                                                                     |
| Goodness-of-fit on <i>F</i> <sup>2</sup>             | 1.136                                                                          |
| Final <i>R</i> indexes [I ≥ 2 $\sigma$ ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0308<br><i>wR</i> <sub>2</sub> = 0.0838              |
| Final <i>R</i> indexes [all data]                    | <i>R</i> <sub>1</sub> = 0.0554<br><i>wR</i> <sub>2</sub> = 0.1053              |
| Largest peak/hole [eÅ <sup>-3</sup> ]                | 0.63/-1.35                                                                     |

Table S3. Bond lengths and angles for **4ja** (CCDC no. 2348642)

| Atom–Atom<br>Atom–Atom | Length<br>[Å] Angle [°] |
|------------------------|-------------------------|
| Br1–C4                 | 1.897(3)                |
| O1–H1                  | 0.8200                  |
| O1–C1                  | 1.344(3)                |
| C1–C2                  | 1.385(4)                |
| C1–C6                  | 1.413(3)                |
| O2–C7                  | 1.231(3)                |
| C2–C3                  | 1.374(4)                |
| C3–C4                  | 1.388(4)                |
| C4–C5                  | 1.377(3)                |
| C5–C6                  | 1.398(3)                |
| C6–C7                  | 1.472(3)                |
| C7–C8                  | 1.496(3)                |
| C8–C9                  | 1.389(3)                |
| C8–C13                 | 1.390(4)                |
| C9–C10                 | 1.387(4)                |
| C10–C11                | 1.377(4)                |
| C11–C12                | 1.377(4)                |
| C12–C13                | 1.383(4)                |
| C1–O1–H1               | 109.5                   |
| O1–C1–C2               | 117.8(2)                |
| O1–C1–C6               | 122.5(2)                |
| C2–C1–C6               | 119.7(2)                |
| C3–C2–C1               | 120.8(2)                |
| C2–C3–C4               | 119.4(2)                |
| C3–C4–Br1              | 119.60(19)              |
| C5–C4–Br1              | 119.08(18)              |
| C5–C4–C3               | 121.3(2)                |
| C4–C5–C6               | 119.6(2)                |
| C1–C6–C7               | 119.2(2)                |
| C5–C6–C1               | 119.1(2)                |
| C5–C6–C7               | 121.6(2)                |
| O2–C7–C6               | 121.4(2)                |
| O2–C7–C8               | 118.1(2)                |
| C6–C7–C8               | 120.4(2)                |
| C9–C8–C7               | 118.1(2)                |
| C9–C8–C13              | 119.8(2)                |
| C13–C8–C7              | 122.0(2)                |
| C10–C9–C8              | 119.9(2)                |
| C11–C10–C9             | 119.9(3)                |
| C10–C11–C12            | 120.5(3)                |
| C11–C12–C13            | 120.2(3)                |
| C12–C13–C8             | 119.7(2)                |

Table S4. Torsion angles for **4ja** (CCDC no. 2348642).

| Atom-Atom-Atom-<br>Atom | Torsion Angle [°] |
|-------------------------|-------------------|
| Br1-C4-C5-C6            | -177.32(17)       |
| O1-C1-C2-C3             | -176.8(3)         |
| O1-C1-C6-C5             | 176.2(2)          |
| O1-C1-C6-C7             | -0.2(4)           |
| C1-C2-C3-C4             | 0.0(4)            |
| C1-C6-C7-O2             | 9.4(4)            |
| C1-C6-C7-C8             | -170.9(2)         |
| O2-C7-C8-C9             | 48.7(3)           |
| O2-C7-C8-C13            | -127.0(3)         |
| C2-C1-C6-C5             | -3.6(4)           |
| C2-C1-C6-C7             | -180.0(2)         |
| C2-C3-C4-Br1            | 176.7(2)          |
| C2-C3-C4-C5             | -2.5(4)           |
| C3-C4-C5-C6             | 2.0(4)            |
| C4-C5-C6-C1             | 1.1(3)            |
| C4-C5-C6-C7             | 177.4(2)          |
| C5-C6-C7-O2             | -166.9(2)         |
| C5-C6-C7-C8             | 12.8(3)           |
| C6-C1-C2-C3             | 3.1(4)            |
| C6-C7-C8-C9             | -131.0(2)         |
| C6-C7-C8-C13            | 53.2(3)           |
| C7-C8-C9-C10            | -176.6(2)         |
| C7-C8-C13-C12           | 174.0(2)          |
| C8-C9-C10-C11           | 2.1(4)            |
| C9-C8-C13-C12           | -1.8(4)           |
| C9-C10-C11-C12          | -1.1(4)           |
| C10-C11-C12-C13         | -1.4(4)           |
| C11-C12-C13-C8          | 2.8(4)            |
| C13-C8-C9-C10           | -0.7(4)           |

Single crystal XRD data for compound **4fb** (CCDC no. 2348641)

**checkCIF/PLATON report**

Structure factors have been supplied for datablock(s) shelx

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No syntax errors found.      CIF dictionary      Interpreting this report

**Datablock: shelx**

---

Bond precision:    C-C = 0.0081 Å                      Wavelength=1.54184

Cell:                      a=13.9577(3)              b=13.9083(3)              c=33.1018(8)  
                                alpha=90                      beta=100.790(2)              gamma=90

Temperature:              298 K

|                        | Calculated   | Reported     |
|------------------------|--------------|--------------|
| Volume                 | 6312.4(2)    | 6312.4(2)    |
| Space group            | C c          | C c          |
| Hall group             | C -2yc       | C -2yc       |
| Moiety formula         | C18 H20 O3   | ?            |
| Sum formula            | C18 H20 O3   | C18 H20 O3   |
| Mr                     | 284.34       | 284.34       |
| Dx, g cm <sup>-3</sup> | 1.197        | 1.197        |
| Z                      | 16           | 16           |
| Mu (mm <sup>-1</sup> ) | 0.645        | 0.645        |
| F000                   | 2432.0       | 2432.0       |
| F000'                  | 2439.30      |              |
| h, k, lmax             | 17, 17, 42   | 17, 17, 41   |
| Nref                   | 13828[ 6918] | 11098        |
| Tmin, Tmax             | 0.940, 0.994 | 0.633, 1.000 |
| Tmin'                  | 0.938        |              |

Correction method= # Reported T Limits: Tmin=0.633 Tmax=1.000  
AbsCorr = MULTI-SCAN

Data completeness= 1.60/0.80                      Theta(max)= 80.243

|                               |                                  |
|-------------------------------|----------------------------------|
| R(reflections)= 0.0748( 8167) | wR2(reflections)= 0.2966( 11098) |
| S = 1.188                     | Npar= 874                        |

The following ALERTS were generated. Each ALERT has the format  
**test-name\_ALERT\_alert-type\_alert-level.**  
Click on the hyperlinks for more details of the test.

#### Alert level A

SHFSU01\_ALERT\_2\_A The absolute value of parameter shift to su ratio > 0.20  
Absolute value of the parameter shift to su ratio given 0.541  
Additional refinement cycles may be required.

**Author Response:** May be due to rotational disorder in t-but groups and the oscillating H-atom on hydroxyl group in para paostion to it The refinement did not converge even after multiple L.S. cycles.

PLAT080\_ALERT\_2\_A Maximum Shift/Error ..... 0.54 Why ?

**Author Response:** May be due to rotational disorder in t-but groups and the oscillating H-atom on hydroxyl group in para paostion to it The refinement did not converge even after multiple L.S. cycles.

#### Alert level C

STRVA01\_ALERT\_4\_C Flack parameter is too small  
From the CIF: \_refine\_ls\_abs\_structure\_Flack -0.300  
From the CIF: \_refine\_ls\_abs\_structure\_Flack\_su 0.400  
PLAT084\_ALERT\_3\_C High wR2 Value (i.e. > 0.25) ..... 0.30 Report  
PLAT213\_ALERT\_2\_C Atom C15B has ADP max/min Ratio ..... 3.4 prolat  
PLAT213\_ALERT\_2\_C Atom C51A has ADP max/min Ratio ..... 3.6 prolat  
PLAT213\_ALERT\_2\_C Atom C53B has ADP max/min Ratio ..... 3.4 prolat  
PLAT220\_ALERT\_2\_C NonSolvent Resd 3 C Ueq(max)/Ueq(min) Range 3.3 Ratio  
PLAT242\_ALERT\_2\_C Low 'MainMol' Ueq as Compared to Neighbors of C14 Check  
PLAT242\_ALERT\_2\_C Low 'MainMol' Ueq as Compared to Neighbors of C32 Check  
PLAT242\_ALERT\_2\_C Low 'MainMol' Ueq as Compared to Neighbors of C50 Check  
PLAT242\_ALERT\_2\_C Low 'MainMol' Ueq as Compared to Neighbors of C68 Check  
PLAT340\_ALERT\_3\_C Low Bond Precision on C-C Bonds ..... 0.00815 Ang.  
PLAT911\_ALERT\_3\_C Missing FCF Refl Between Thmin & STh/L= 0.600 2 Report  
-16 0 6, 9 3 19,  
PLAT927\_ALERT\_1\_C Reported and Calculated wR2 Differ by ..... -0.0025 Check

#### Alert level G

PLAT002\_ALERT\_2\_G Number of Distance or Angle Restraints on AtSite 28 Note  
PLAT003\_ALERT\_2\_G Number of Uiso or Uij Restrained non-H Atoms ... 68 Report  
PLAT007\_ALERT\_5\_G Number of Unrefined Donor-H Atoms ..... 4 Report  
H3A H6A H9 H12  
PLAT032\_ALERT\_4\_G Std. Uncertainty on Flack Parameter Value High . 0.400 Report  
PLAT172\_ALERT\_4\_G The CIF-Embedded .res File Contains DFIX Records 16 Report  
PLAT177\_ALERT\_4\_G The CIF-Embedded .res File Contains DELU Records 12 Report  
PLAT178\_ALERT\_4\_G The CIF-Embedded .res File Contains SIMU Records 12 Report  
PLAT301\_ALERT\_3\_G Main Residue Disorder ..... (Resd 1) 14% Note  
PLAT301\_ALERT\_3\_G Main Residue Disorder ..... (Resd 2) 14% Note

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PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 3) 14% Note
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 4) 14% Note
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H11 ..H16D . 2.03 Ang.
x,y,z = 1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H29 ..H33A . 1.97 Ang.
x,y,z = 1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H31 ..H34A . 2.05 Ang.
x,y,z = 1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H47 ..H51C . 1.97 Ang.
x,y,z = 1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H49 ..H53A . 2.14 Ang.
x,y,z = 1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H49 ..H53E . 2.01 Ang.
x,y,z = 1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H65 ..H69B . 2.04 Ang.
x,y,z = 1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn H67 ..H70F . 2.12 Ang.
x,y,z = 1_555 Check
PLAT721_ALERT_1_G Bond Calc 0.97000, Rep 0.96000 Dev... 0.01 Ang.
C17B -H17D 1_555 1_555 ..... # 47 Check
PLAT721_ALERT_1_G Bond Calc 0.97000, Rep 0.96000 Dev... 0.01 Ang.
C51B -H51D 1_555 1_555 ..... # 147 Check
PLAT722_ALERT_1_G Angle Calc 111.00, Rep 109.50 Dev... 1.50 Degree
H15D -C15B -H15E 1_555 1_555 1_555 # 72 Check
PLAT722_ALERT_1_G Angle Calc 109.00, Rep 110.10 Dev... 1.10 Degree
C14 -C15B -H15F 1_555 1_555 1_555 # 73 Check
PLAT722_ALERT_1_G Angle Calc 109.00, Rep 110.10 Dev... 1.10 Degree
C14 -C16B -H16D 1_555 1_555 1_555 # 76 Check
PLAT722_ALERT_1_G Angle Calc 110.00, Rep 108.90 Dev... 1.10 Degree
C14 -C16B -H16E 1_555 1_555 1_555 # 77 Check
PLAT722_ALERT_1_G Angle Calc 108.00, Rep 109.10 Dev... 1.10 Degree
C14 -C17B -H17D 1_555 1_555 1_555 # 82 Check
PLAT722_ALERT_1_G Angle Calc 111.00, Rep 109.50 Dev... 1.50 Degree
H17E -C17B -H17F 1_555 1_555 1_555 # 87 Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 656 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT899_ALERT_4_G SHELXL2018 is Deprecated and Succeeded by SHELXL 2019/3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 294 Note
PLAT915_ALERT_3_G No Flack x Check Done: Low Friedel Pair Coverage 65 %
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by . 0.37 Check
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File 70 Note
6 -2 -2, 8 2 0, 9 -1-27, -7 7 26, 11 -7 -2, 9 -9-14,
10 2 17, 7 -3 -2, 10 4 17, 11 7 8, 10 4 15, 9 -3-27,
9 1 20, 10 6 12, 1 1 32, 9 -9-15, 8 -10-13, 8 -8-21,
1 1 31, 9 -9-16, 8 2-27, 10 6 11, 9 1-27, 9 3-26,
9 9-15, 10 2 18, 9 3-27, 9 3 20, 8 4-27, 10 2-27,
9 9-14, 8 4-26, 11 7 -3, 11 7 -4, 11 5 10, 8 10-15,
3 11 16, 8 10-16, 11 7 1, 7 1 25, 11 7 -1, -9 3-19,
11 7 4, 9 7-22, 11 7 7, 9 3 19, 10 2-26, 9 3-25,
7 1 24, 9 7-20,
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ..... 4.50 Note
Predicted wR2: Based on SigI**2 6.59 or SHELX Weight 26.04
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 0 Info

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2 ALERT level A = Most likely a serious problem - resolve or explain  
0 ALERT level B = A potentially serious problem, consider carefully



13 ALERT level C = Check. Ensure it is not caused by an omission or oversight  
36 ALERT level G = General information/check it is not something unexpected

10 ALERT type 1 CIF construction/syntax error, inconsistent or missing data  
23 ALERT type 2 Indicator that the structure model may be wrong or deficient  
9 ALERT type 3 Indicator that the structure quality may be low  
7 ALERT type 4 Improvement, methodology, query or suggestion  
2 ALERT type 5 Informative message, check

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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special\_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

#### **Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that **full publication checks** are run on the final version of your CIF prior to submission.

#### **Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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PLATON version of 06/01/2024; check.def file version of 05/01/2024

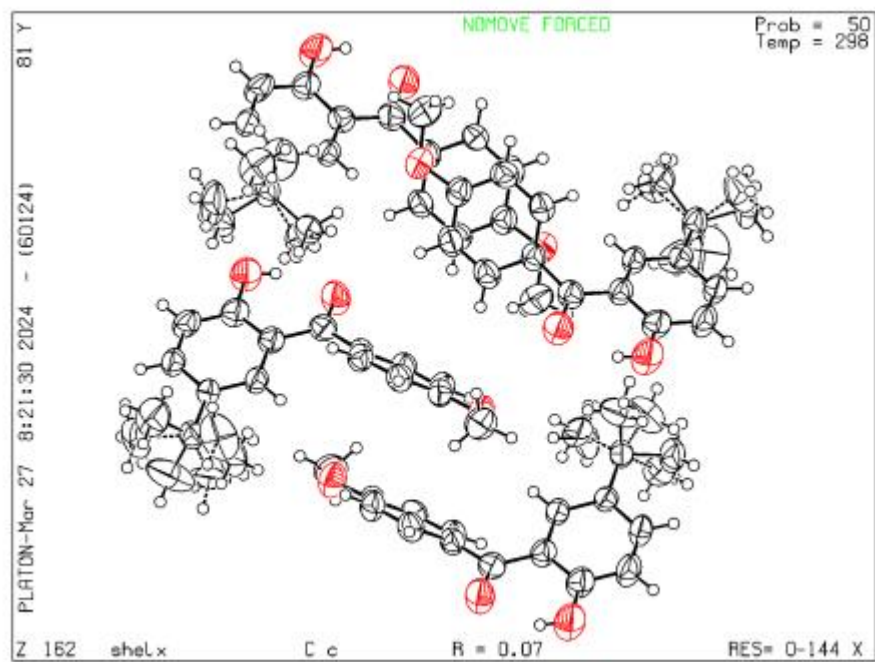


Table S5. Crystal data and structure refinement for shelx (**4fb** : CCDC no. 2348641)

|                                                                 |                                                                                 |
|-----------------------------------------------------------------|---------------------------------------------------------------------------------|
| CCDC number                                                     |                                                                                 |
| Empirical formula                                               | C <sub>18</sub> H <sub>20</sub> O <sub>3</sub>                                  |
| Formula weight                                                  | 284.34                                                                          |
| Temperature [K]                                                 | 298(2)                                                                          |
| Crystal system                                                  | monoclinic                                                                      |
| Space group (number)                                            | Cc (9)                                                                          |
| <i>a</i> [Å]                                                    | 13.9577(3)                                                                      |
| <i>b</i> [Å]                                                    | 13.9083(3)                                                                      |
| <i>c</i> [Å]                                                    | 33.1018(8)                                                                      |
| $\alpha$ [°]                                                    | 90                                                                              |
| $\beta$ [°]                                                     | 100.790(2)                                                                      |
| $\gamma$ [°]                                                    | 90                                                                              |
| Volume [Å <sup>3</sup> ]                                        | 6312.4(2)                                                                       |
| <i>Z</i>                                                        | 16                                                                              |
| $\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]                       | 1.197                                                                           |
| $\mu$ [mm <sup>-1</sup> ]                                       | 0.645                                                                           |
| <i>F</i> (000)                                                  | 2432                                                                            |
| Crystal size [mm <sup>3</sup> ]                                 | 0.100×0.080×0.010                                                               |
| Crystal colour                                                  | colourless                                                                      |
| Crystal shape                                                   | block                                                                           |
| Radiation                                                       | Cu K $\alpha$ ( $\lambda$ =1.54184 Å)                                           |
| 2 $\theta$ range [°]                                            | 5.44 to 160.49 (0.78 Å)                                                         |
| Index ranges                                                    | -17 ≤ <i>h</i> ≤ 15<br>-17 ≤ <i>k</i> ≤ 17<br>-41 ≤ <i>l</i> ≤ 41               |
| Reflections collected                                           | 44813                                                                           |
| Independent reflections                                         | 11098<br><i>R</i> <sub>int</sub> = 0.0907<br><i>R</i> <sub>sigma</sub> = 0.0618 |
| Completeness to $\theta$ = 67.684°                              | 100.0 %                                                                         |
| Data / Restraints / Parameters                                  | 11098/656/874                                                                   |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                        | 1.188                                                                           |
| Final <i>R</i> indexes<br>[ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0748<br><i>wR</i> <sub>2</sub> = 0.2099               |
| Final <i>R</i> indexes<br>[all data]                            | <i>R</i> <sub>1</sub> = 0.1240<br><i>wR</i> <sub>2</sub> = 0.2966               |
| Largest peak/hole [eÅ <sup>-3</sup> ]                           | 0.57/-0.37                                                                      |
| Flack X parameter                                               | -0.3(4)                                                                         |

Table S6. Bond lengths and angles for shelx (**4fb** : **CCDC no. 2348641**)

| Atom-Atom      | Length [Å] | —             | —         | —             | —         | —             | —         |
|----------------|------------|---------------|-----------|---------------|-----------|---------------|-----------|
| C1-C2          | 1.384(9)   | C19-C20       | 1.380(9)  | C37-C38       | 1.384(9)  | C55-C56       | 1.388(9)  |
| C1-C6          | 1.381(8)   | C19-C24       | 1.392(8)  | C37-C42       | 1.384(8)  | C55-C60       | 1.391(8)  |
| C1-O1          | 1.372(6)   | C19-O4        | 1.360(6)  | C37-O7        | 1.372(7)  | C55-O10       | 1.351(7)  |
| C2-C3          | 1.368(8)   | C20-C21       | 1.380(8)  | C38-C39       | 1.369(9)  | C56-C57       | 1.370(8)  |
| C3-C4          | 1.418(7)   | C21-C22       | 1.409(8)  | C39-C40       | 1.400(8)  | C57-C58       | 1.407(8)  |
| C4-C5          | 1.379(8)   | C22-C23       | 1.369(8)  | C40-C41       | 1.381(8)  | C58-C59       | 1.380(8)  |
| C4-C7          | 1.489(7)   | C22-C25       | 1.496(7)  | C40-C43       | 1.498(7)  | C58-C61       | 1.484(7)  |
| C5-C6          | 1.397(7)   | C23-C24       | 1.391(8)  | C41-C42       | 1.385(8)  | C59-C60       | 1.387(8)  |
| C7-C8          | 1.475(7)   | C25-C26       | 1.468(8)  | C43-C44       | 1.470(7)  | C61-C62       | 1.486(8)  |
| C7-O2          | 1.239(7)   | C25-O5        | 1.235(7)  | C43-O8        | 1.232(7)  | C61-O11       | 1.238(7)  |
| C8-C13         | 1.399(7)   | C26-C27       | 1.418(7)  | C44-C45       | 1.418(7)  | C62-C63       | 1.414(7)  |
| C8-C9          | 1.421(7)   | C26-C31       | 1.399(7)  | C44-C49       | 1.399(7)  | C62-C67       | 1.398(7)  |
| C9-C10         | 1.376(9)   | C27-C28       | 1.391(9)  | C45-C46       | 1.408(9)  | C63-C64       | 1.377(9)  |
| C9-O3          | 1.343(7)   | C27-O6        | 1.343(8)  | C45-O9        | 1.333(7)  | C63-O12       | 1.351(7)  |
| C10-C11        | 1.369(9)   | C28-C29       | 1.345(9)  | C46-C47       | 1.353(9)  | C64-C65       | 1.388(9)  |
| C11-C12        | 1.408(7)   | C29-C30       | 1.406(7)  | C47-C48       | 1.408(8)  | C65-C66       | 1.402(7)  |
| C12-C13        | 1.379(7)   | C30-C31       | 1.390(7)  | C48-C49       | 1.380(7)  | C66-C67       | 1.385(7)  |
| C12-C14        | 1.528(8)   | C30-C32       | 1.526(8)  | C48-C50       | 1.521(8)  | C66-C68       | 1.518(7)  |
| C14-C15A       | 1.529(10)  | C32-C33A      | 1.487(14) | C50-C51A      | 1.495(15) | C68-C69A      | 1.524(19) |
| C14-C15B       | 1.51(2)    | C32-C33B      | 1.582(17) | C50-C51B      | 1.558(19) | C68-C69B      | 1.561(11) |
| C14-C16A       | 1.557(11)  | C32-C34A      | 1.515(15) | C50-C52A      | 1.572(17) | C68-C70A      | 1.55(2)   |
| C14-C16B       | 1.53(2)    | C32-C34B      | 1.526(13) | C50-C52B      | 1.54(2)   | C68-C70B      | 1.542(12) |
| C14-C17A       | 1.520(11)  | C32-C35A      | 1.614(16) | C50-C53A      | 1.527(15) | C68-C71A      | 1.60(2)   |
| C14-C17B       | 1.58(2)    | C32-C35B      | 1.524(17) | C50-C53B      | 1.545(17) | C68-C71B      | 1.522(12) |
| C18-O1         | 1.412(9)   | C36-O4        | 1.429(10) | C54-O7        | 1.418(9)  | C72-O10       | 1.414(9)  |
| O3-H3A         | 0.8201     | O6-H6A        | 0.8200    | O9-H9         | 0.8200    | O12-H12       | 0.8201    |
|                |            |               |           |               |           |               |           |
| Atom-Atom-Atom | Angle [°]  | —             | —         | —             | —         | —             | —         |
| C6-C1-C2       | 120.6(5)   | O4-C19-C20    | 115.5(5)  | O7-C37-C38    | 114.8(5)  | O10-C55-C56   | 115.3(5)  |
| O1-C1-C2       | 114.4(5)   | C20-C19-C24   | 119.7(5)  | C38-C37-C42   | 120.2(5)  | C56-C55-C60   | 119.3(5)  |
| O1-C1-C6       | 125.0(5)   | O4-C19-C24    | 124.7(5)  | O7-C37-C42    | 125.1(5)  | O10-C55-C60   | 125.3(5)  |
| C3-C2-C1       | 120.3(5)   | C21-C20-C19   | 120.9(5)  | C39-C38-C37   | 120.2(5)  | C57-C56-C55   | 121.0(5)  |
| C2-C3-C4       | 120.4(5)   | C20-C21-C22   | 119.5(5)  | C38-C39-C40   | 120.3(6)  | C56-C57-C58   | 120.1(5)  |
| C5-C4-C3       | 118.3(5)   | C23-C22-C21   | 119.2(5)  | C41-C40-C39   | 119.0(5)  | C59-C58-C57   | 118.8(5)  |
|                |            |               |           |               |           |               |           |
| C3-C4-C7       | 117.0(5)   | C21-C22-C25   | 116.5(5)  | C39-C40-C43   | 117.0(5)  | C57-C58-C61   | 117.1(5)  |
| C5-C4-C7       | 124.6(5)   | C23-C22-C25   | 124.2(5)  | C41-C40-C43   | 123.8(5)  | C59-C58-C61   | 124.0(5)  |
| C4-C5-C6       | 121.4(5)   | C22-C23-C24   | 121.4(5)  | C40-C41-C42   | 120.7(5)  | C58-C59-C60   | 121.1(5)  |
| C1-C6-C5       | 119.0(5)   | C19-C24-C23   | 119.2(5)  | C41-C42-C37   | 119.5(5)  | C59-C60-C55   | 119.7(5)  |
| C8-C7-C4       | 121.0(4)   | C26-C25-C22   | 121.3(4)  | C44-C43-C40   | 121.1(4)  | O11-C61-C58   | 118.1(5)  |
| O2-C7-C4       | 117.7(5)   | O5-C25-C22    | 117.5(5)  | O8-C43-C40    | 118.0(5)  | C58-C61-C62   | 121.2(4)  |
| O2-C7-C8       | 121.2(5)   | O5-C25-C26    | 121.1(5)  | O8-C43-C44    | 120.9(5)  | O11-C61-C62   | 120.6(5)  |
| C13-C8-C7      | 122.3(5)   | C27-C26-C25   | 119.4(5)  | C45-C44-C43   | 119.0(5)  | C63-C62-C61   | 119.2(5)  |
| C9-C8-C7       | 119.2(5)   | C31-C26-C25   | 122.2(4)  | C49-C44-C43   | 122.6(4)  | C67-C62-C61   | 122.1(5)  |
| C13-C8-C9      | 118.4(5)   | C31-C26-C27   | 118.4(5)  | C49-C44-C45   | 118.2(5)  | C67-C62-C63   | 118.7(5)  |
| O3-C9-C10      | 118.7(5)   | C28-C27-C26   | 118.6(5)  | C46-C45-C44   | 118.4(5)  | C64-C63-C62   | 119.3(5)  |
| C10-C9-C8      | 119.1(5)   | O6-C27-C26    | 122.3(6)  | O9-C45-C44    | 123.1(5)  | O12-C63-C62   | 122.4(5)  |
| O3-C9-C8       | 122.2(5)   | O6-C27-C28    | 119.0(5)  | O9-C45-C46    | 118.5(5)  | O12-C63-C64   | 118.3(5)  |
| C11-C10-C9     | 120.9(5)   | C29-C28-C27   | 121.1(5)  | C47-C46-C45   | 120.8(5)  | C63-C64-C65   | 120.7(5)  |
| C10-C11-C12    | 121.9(5)   | C28-C29-C30   | 123.0(6)  | C46-C47-C48   | 122.7(5)  | C64-C65-C66   | 121.5(5)  |
| C13-C12-C11    | 116.9(5)   | C31-C30-C29   | 116.0(5)  | C49-C48-C47   | 116.2(5)  | C67-C66-C65   | 117.2(5)  |
| C11-C12-C14    | 120.1(5)   | C29-C30-C32   | 121.3(5)  | C47-C48-C50   | 120.4(5)  | C65-C66-C68   | 119.9(5)  |
| C13-C12-C14    | 123.0(5)   | C31-C30-C32   | 122.7(5)  | C49-C48-C50   | 123.3(5)  | C67-C66-C68   | 122.9(5)  |
| C12-C13-C8     | 122.6(5)   | C30-C31-C26   | 122.8(5)  | C48-C49-C44   | 123.6(5)  | C66-C67-C62   | 122.6(5)  |
| C15B-C14-C12   | 111(2)     | C33A-C32-C30  | 113.9(9)  | C51A-C50-C48  | 109.6(10) | C66-C68-C69A  | 112.9(17) |
| C17A-C14-C12   | 111.1(7)   | C34A-C32-C30  | 114.1(10) | C48-C50-C51B  | 111.7(14) | C66-C68-C69B  | 110.2(6)  |
| C12-C14-C15A   | 112.3(5)   | C34B-C32-C30  | 110.0(9)  | C52B-C50-C51B | 109.4(18) | C70B-C68-C69B | 107.5(8)  |
| C17A-C14-C15A  | 107.8(8)   | C35B-C32-C30  | 114.2(12) | C53B-C50-C51B | 105.9(14) | C71B-C68-C69B | 108.5(8)  |
| C12-C14-C16A   | 108.6(6)   | C30-C32-C33B  | 106.7(8)  | C48-C50-C52A  | 105.2(11) | C66-C68-C70A  | 118.8(17) |
| C15A-C14-C16A  | 106.9(7)   | C34B-C32-C33B | 107.4(12) | C51A-C50-C52A | 110.8(14) | C69A-C68-C70A | 110.8(17) |
| C17A-C14-C16A  | 110.1(9)   | C35B-C32-C33B | 108.1(11) | C53A-C50-C52A | 106.9(11) | C66-C68-C70B  | 110.7(7)  |
| C12-C14-C16B   | 112.3(19)  | C33A-C32-C34A | 112.5(12) | C48-C50-C52B  | 111(2)    | C71B-C68-C70B | 108.4(9)  |
| C15B-C14-C16B  | 114.0(19)  | C35B-C32-C34B | 110.1(13) | C48-C50-C53A  | 114.3(9)  | C66-C68-C71A  | 98.9(19)  |
| C12-C14-C17B   | 98.8(19)   | C30-C32-C35A  | 101.8(10) | C51A-C50-C53A | 109.9(11) | C69A-C68-C71A | 107.7(15) |
| C15B-C14-C17B  | 111(2)     | C33A-C32-C35A | 106.3(11) | C48-C50-C53B  | 107.8(12) | C70A-C68-C71A | 106.2(18) |
| C16B-C14-C17B  | 109(2)     | C34A-C32-C35A | 107.1(11) | C52B-C50-C53B | 110.6(17) | C66-C68-C71B  | 111.4(9)  |
| C1-O1-C18      | 118.5(5)   | C19-O4-C36    | 119.7(6)  | C37-O7-C54    | 119.3(5)  | C55-O10-C72   | 118.8(5)  |

Table S7. Hydrogen bonds for shelx (**4fb** : CCDC no. 2348641)

| D-H...A [Å]   | d(D-H) [Å] | d(H...A) [Å] | d(D...A) [Å] | <(DHA) [°] |
|---------------|------------|--------------|--------------|------------|
| O3-H3A...O2   | 0.82       | 1.85         | 2.574(6)     | 146.1      |
| O6-H6A...O5   | 0.82       | 1.86         | 2.580(7)     | 145.7      |
| O9-H9...O8    | 0.82       | 1.86         | 2.575(7)     | 145.5      |
| O12-H12...O11 | 0.82       | 1.86         | 2.565(7)     | 143.1      |
| O3-H3A...O2   | 0.82       | 1.85         | 2.574(6)     | 146.1      |
| O6-H6A...O5   | 0.82       | 1.86         | 2.580(7)     | 145.7      |
| O9-H9...O8    | 0.82       | 1.86         | 2.575(7)     | 145.5      |
| O12-H12...O11 | 0.82       | 1.86         | 2.565(7)     | 143.1      |

Table S8. Torsion angles for shelx (**4fb** : CCDC no. 2348641)

|                  |            | Torsion Angle [°] |            |                  |            |                  |            |
|------------------|------------|-------------------|------------|------------------|------------|------------------|------------|
| C1-C2-C3-C4      | -0.6(9)    | C37-C38-C39-C40   | -4.0(10)   | C19-C20-C21-C22  | 2.9(9)     | C55-C56-C57-C58  | 0.7(9)     |
| C2-C3-C4-C5      | 0.0(8)     | C38-C39-C40-C41   | 2.7(9)     | C20-C21-C22-C23  | -1.1(9)    | C56-C57-C58-C59  | -0.2(9)    |
| C2-C3-C4-C7      | 177.3(5)   | C38-C39-C40-C43   | 178.6(6)   | C20-C21-C22-C25  | -178.3(5)  | C56-C57-C58-C61  | -177.0(6)  |
| C2-C1-C6-C5      | 1.0(8)     | C38-C37-C42-C41   | 0.1(9)     | C20-C19-C24-C23  | 0.6(8)     | C56-C55-C60-C59  | -1.8(9)    |
| C2-C1-O1-C18     | -176.0(6)  | C38-C37-O7-C54    | -176.9(6)  | C20-C19-O4-C36   | 176.5(6)   | C56-C55-O10-C72  | 175.6(6)   |
| C3-C4-C5-C6      | 1.1(8)     | C39-C40-C41-C42   | 0.0(8)     | C21-C22-C23-C24  | -0.9(9)    | C57-C58-C59-C60  | -1.3(8)    |
| C3-C4-C7-O2      | -42.2(8)   | C39-C40-C43-O8    | -42.4(8)   | C21-C22-C25-O5   | 42.7(8)    | C57-C58-C61-O11  | 43.0(8)    |
| C3-C4-C7-C8      | 136.3(6)   | C39-C40-C43-C44   | 136.6(6)   | C21-C22-C25-C26  | -136.7(6)  | C57-C58-C61-C62  | -134.2(6)  |
| C4-C5-C6-C1      | -1.6(9)    | C40-C41-C42-C37   | -1.4(9)    | C22-C23-C24-C19  | 1.2(9)     | C58-C59-C60-C55  | 2.3(9)     |
| C4-C7-C8-C13     | -11.8(9)   | C40-C43-C44-C49   | -12.7(9)   | C22-C25-C26-C31  | 13.3(9)    | C58-C61-C62-C67  | 8.7(9)     |
| C4-C7-C8-C9      | 172.5(6)   | C40-C43-C44-C45   | 171.5(6)   | C22-C25-C26-C27  | -168.9(6)  | C58-C61-C62-C63  | -173.9(5)  |
| C5-C4-C7-O2      | 134.8(7)   | C41-C40-C43-O8    | 133.4(6)   | C23-C22-C25-O5   | -134.3(7)  | C59-C58-C61-O11  | -133.6(7)  |
| C5-C4-C7-C8      | -46.6(8)   | C41-C40-C43-C44   | -47.7(8)   | C23-C22-C25-C26  | 46.2(9)    | C59-C58-C61-C62  | 49.1(8)    |
| C6-C1-C2-C3      | 0.1(9)     | C42-C37-C38-C39   | 2.6(9)     | C24-C19-C20-C21  | -2.6(9)    | C60-C55-C56-C57  | 0.3(9)     |
| C6-C1-O1-C18     | 4.1(9)     | C42-C37-O7-C54    | 3.2(10)    | C24-C19-O4-C36   | -2.9(9)    | C60-C55-O10-C72  | -5.2(10)   |
| C7-C4-C5-C6      | -176.0(5)  | C43-C40-C41-C42   | -175.6(5)  | C25-C22-C23-C24  | 176.1(5)   | C61-C58-C59-C60  | 175.3(5)   |
| C7-C8-C9-O3      | -1.9(10)   | C43-C44-C45-O9    | -1.4(10)   | C25-C26-C27-O6   | 0.2(11)    | C61-C62-C63-O12  | 0.0(10)    |
| C7-C8-C9-C10     | -179.1(6)  | C43-C44-C45-C46   | 179.5(6)   | C25-C26-C27-C28  | 179.7(7)   | C61-C62-C63-C64  | 179.4(6)   |
| C7-C8-C13-C12    | 179.4(6)   | C43-C44-C49-C48   | -179.4(6)  | C25-C26-C31-C30  | 179.3(6)   | C61-C62-C67-C66  | 179.9(5)   |
| C8-C9-C10-C11    | -2.9(10)   | C44-C45-C46-C47   | -2.0(11)   | C26-C27-C28-C29  | 1.6(13)    | C62-C63-C64-C65  | 1.5(11)    |
| C9-C10-C11-C12   | 0.4(10)    | C45-C46-C47-C48   | 0.3(11)    | C27-C28-C29-C30  | 0.1(12)    | C63-C64-C65-C66  | 0.8(10)    |
| C9-C8-C13-C12    | -4.8(9)    | C45-C44-C49-C48   | -3.6(9)    | C27-C26-C31-C30  | 1.5(10)    | C63-C62-C67-C66  | 2.5(9)     |
| C10-C11-C12-C13  | 0.0(9)     | C46-C47-C48-C49   | -0.2(10)   | C28-C29-C30-C31  | -1.1(10)   | C64-C65-C66-C67  | -1.5(9)    |
| C10-C11-C12-C14  | -178.6(6)  | C46-C47-C48-C50   | -177.7(6)  | C28-C29-C30-C32  | 178.2(7)   | C64-C65-C66-C68  | 178.8(6)   |
| C11-C12-C13-C8   | 2.3(9)     | C47-C48-C49-C44   | 1.9(9)     | C29-C30-C31-C26  | 0.2(9)     | C65-C66-C67-C62  | -0.2(9)    |
| C11-C12-C14-C15B | -134(3)    | C47-C48-C50-C51A  | -33.3(17)  | C29-C30-C32-C33A | 20.7(19)   | C65-C66-C68-C71B | -68.9(11)  |
| C11-C12-C14-C17A | 69.1(11)   | C47-C48-C50-C53A  | -157.2(12) | C29-C30-C32-C34A | 151.7(13)  | C65-C66-C68-C69A | 24(3)      |
| C11-C12-C14-C15A | -170.1(8)  | C47-C48-C50-C52B  | 68(2)      | C29-C30-C32-C35B | -66.3(17)  | C65-C66-C68-C70B | 170.4(9)   |
| C11-C12-C14-C16B | -5(3)      | C47-C48-C50-C53B  | -170.2(18) | C29-C30-C32-C34B | 169.3(15)  | C65-C66-C68-C70A | 156(2)     |
| C11-C12-C14-C16A | -52.1(9)   | C47-C48-C50-C51B  | -54(2)     | C29-C30-C32-C33B | 53.1(15)   | C65-C66-C68-C69B | 51.6(11)   |
| C11-C12-C14-C17B | 109(3)     | C47-C48-C50-C52A  | 85.9(16)   | C29-C30-C32-C35A | -93.3(13)  | C65-C66-C68-C71A | -89(2)     |
| C13-C8-C9-O3     | -177.8(7)  | C49-C44-C45-O9    | -177.4(7)  | C31-C26-C27-O6   | 178.1(7)   | C67-C62-C63-O12  | 177.4(7)   |
| C13-C8-C9-C10    | 5.0(9)     | C49-C44-C45-C46   | 3.5(10)    | C31-C26-C27-C28  | -2.4(11)   | C67-C62-C63-C64  | -3.1(9)    |
| C13-C12-C14-C15B | 47(3)      | C49-C48-C50-C51A  | 149.3(17)  | C31-C30-C32-C33A | -160.1(18) | C67-C66-C68-C71B | 111.4(11)  |
| C13-C12-C14-C17A | -109.5(11) | C49-C48-C50-C53A  | 25.4(14)   | C31-C30-C32-C34A | -29.1(14)  | C67-C66-C68-C69A | -156(3)    |
| C13-C12-C14-C15A | 11.4(10)   | C49-C48-C50-C52B  | -109(2)    | C31-C30-C32-C35B | 112.9(17)  | C67-C66-C68-C70B | -9.2(11)   |
| C13-C12-C14-C16B | 176(3)     | C49-C48-C50-C53B  | 12(2)      | C31-C30-C32-C34B | -11.5(16)  | C67-C66-C68-C70A | -23(2)     |
| C13-C12-C14-C16A | 129.4(9)   | C49-C48-C50-C51B  | 128(2)     | C31-C30-C32-C33B | -127.7(14) | C67-C66-C68-C69B | -128.1(11) |
| C13-C12-C14-C17B | -69(3)     | C49-C48-C50-C52A  | -91.5(16)  | C31-C30-C32-C35A | 85.9(13)   | C67-C66-C68-C71A | 91(2)      |
| C14-C12-C13-C8   | -179.1(5)  | C50-C48-C49-C44   | 179.4(6)   | C32-C30-C31-C26  | -179.0(6)  | C68-C66-C67-C62  | 179.5(5)   |
| O1-C1-C2-C3      | -179.9(6)  | O7-C37-C38-C39    | -177.3(6)  | O4-C19-C20-C21   | 178.0(6)   | O10-C55-C56-C57  | 179.6(6)   |
| O1-C1-C6-C5      | -179.0(5)  | O7-C37-C42-C41    | -180.0(6)  | O4-C19-C24-C23   | 179.9(5)   | O10-C55-C60-C59  | 179.0(6)   |
| O2-C7-C8-C13     | 166.7(6)   | O8-C43-C44-C49    | 166.2(6)   | O5-C25-C26-C31   | -166.1(7)  | O11-C61-C62-C67  | -168.4(6)  |
| O2-C7-C8-C9      | -9.0(10)   | O8-C43-C44-C45    | -9.6(10)   | O5-C25-C26-C27   | 11.7(10)   | O11-C61-C62-C63  | 8.9(9)     |
| O3-C9-C10-C11    | 179.8(7)   | O9-C45-C46-C47    | 178.9(8)   | O6-C27-C28-C29   | -178.8(8)  | O12-C63-C64-C65  | -179.0(7)  |

## Single crystal XRD data for compound **4ma** (CCDC no. 2348646)

### checkCIF/PLATON report

Structure factors have been supplied for datablock(s) bod-bd-23-88

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.      CIF dictionary      Interpreting this report

### Datablock: bod-bd-23-88

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Bond precision:    C-C = 0.0040 Å                      Wavelength=1.54184

Cell:                      a=14.6923 (3)              b=13.0967 (2)              c=7.5634 (2)  
                                alpha=90              beta=102.745 (2)              gamma=90

Temperature:              298 K

|                        | Calculated   | Reported     |
|------------------------|--------------|--------------|
| Volume                 | 1419.50 (5)  | 1419.50 (5)  |
| Space group            | P 21/c       | P 21/c 1     |
| Hall group             | -P 2ybc      | -P 2ybc      |
| Moiety formula         | C19 H14 O2   | C19 H14 O2   |
| Sum formula            | C19 H14 O2   | C19 H14 O2   |
| Mr                     | 274.30       | 274.30       |
| Dx, g cm <sup>-3</sup> | 1.283        | 1.284        |
| Z                      | 4            | 4            |
| Mu (mm <sup>-1</sup> ) | 0.655        | 0.655        |
| F000                   | 576.0        | 576.0        |
| F000'                  | 577.70       |              |
| h, k, lmax             | 18, 16, 9    | 18, 16, 9    |
| Nref                   | 3005         | 2956         |
| Tmin, Tmax             | 0.949, 0.974 | 0.760, 1.000 |
| Tmin'                  | 0.949        |              |

Correction method= # Reported T Limits: Tmin=0.760 Tmax=1.000  
AbsCorr = MULTI-SCAN

Data completeness= 0.984                      Theta(max)= 77.188

R(reflections)= 0.0693 ( 2195)                      wR2(reflections)=  
S = 1.226                      Npar= 191                      0.2829 ( 2956)

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The following ALERTS were generated. Each ALERT has the format  
**test-name\_ALERT\_alert-type\_alert-level**.  
Click on the hyperlinks for more details of the test.

---

 **Alert level C**  
PLAT084\_ALERT\_3\_C High wR2 Value (i.e. > 0.25) ..... 0.28 Report

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 **Alert level G**  
PLAT007\_ALERT\_5\_G Number of Unrefined Donor-H Atoms ..... 1 Report  
H2  
PLAT072\_ALERT\_2\_G SHELXL First Parameter in WGHT Unusually Large 0.16 Report  
PLAT912\_ALERT\_4\_G Missing # of FCF Reflections Above STh/L= 0.600 48 Note  
PLAT969\_ALERT\_5\_G The 'Henn et al.' R-Factor-gap value ..... 9.71 Note  
Predicted wR2: Based on SigI\*\*2 2.91 or SHELX Weight 23.86  
PLAT978\_ALERT\_2\_G Number C-C Bonds with Positive Residual Density. 0 Info  
PLAT992\_ALERT\_5\_G Repd & Actual \_reflms\_number\_gt Values Differ by 3 Check

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0 **ALERT level A** = Most likely a serious problem - resolve or explain  
0 **ALERT level B** = A potentially serious problem, consider carefully  
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight  
6 **ALERT level G** = General information/check it is not something unexpected

0 **ALERT type 1** CIF construction/syntax error, inconsistent or missing data  
2 **ALERT type 2** Indicator that the structure model may be wrong or deficient  
1 **ALERT type 3** Indicator that the structure quality may be low  
1 **ALERT type 4** Improvement, methodology, query or suggestion  
3 **ALERT type 5** Informative message, check

---

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special\_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

#### Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that [full publication checks](#) are run on the final version of your CIF prior to submission.

#### Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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PLATON version of 06/01/2024; check.def file version of 05/01/2024

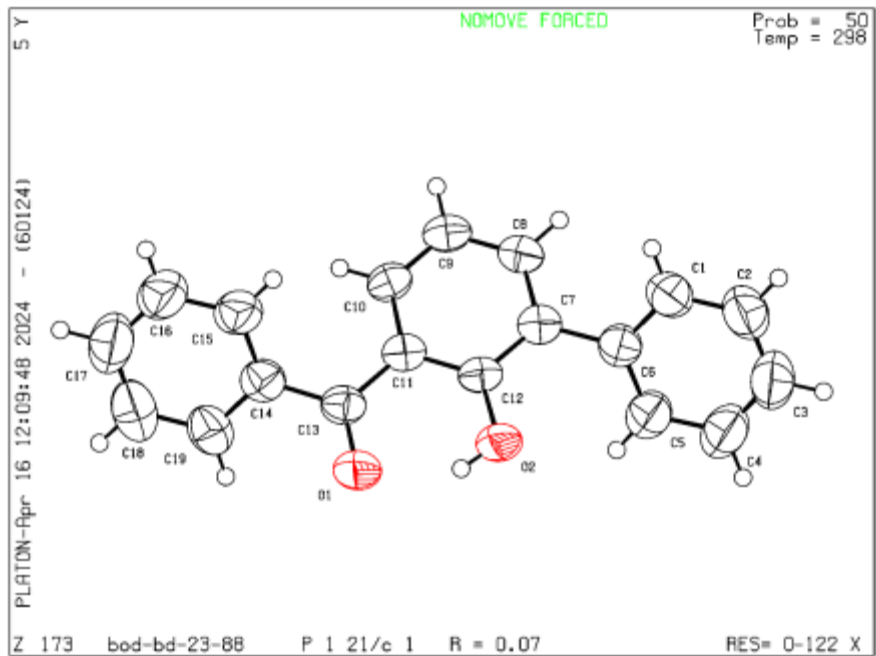




Table S9. Crystal data and structure refinement for **4ma (CCDC no. 2348646)**

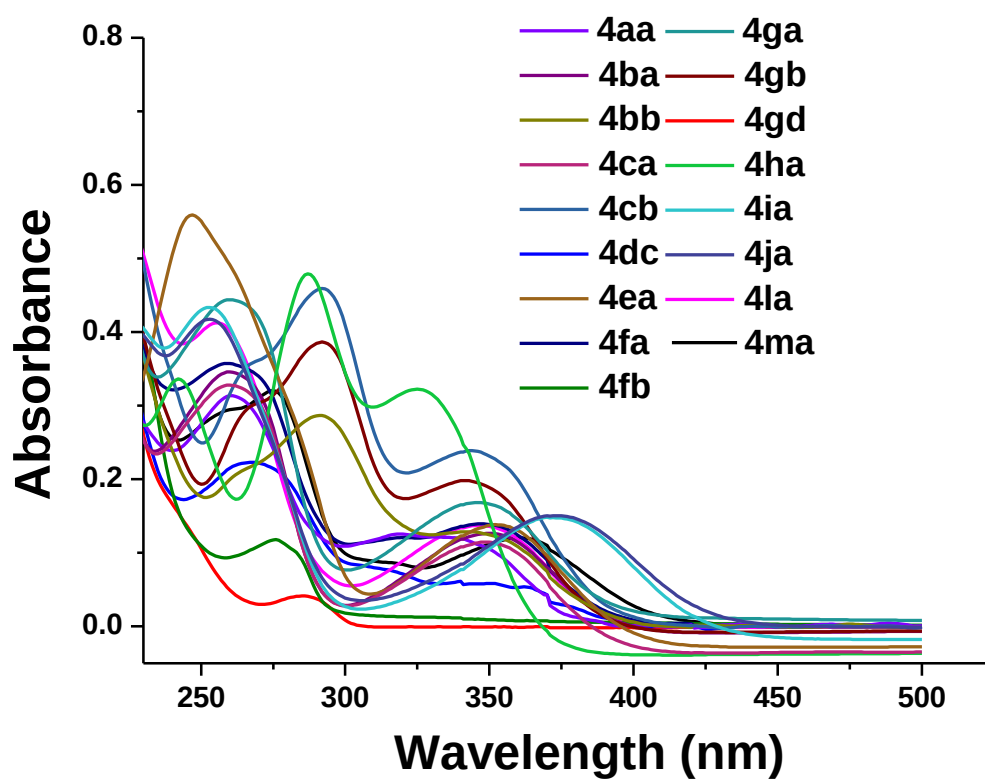
|                                            |                                                                                |
|--------------------------------------------|--------------------------------------------------------------------------------|
| Empirical formula                          | C <sub>19</sub> H <sub>14</sub> O <sub>2</sub>                                 |
| Formula weight                             | 274.30                                                                         |
| Temperature [K]                            | 298                                                                            |
| Crystal system                             | monoclinic                                                                     |
| Space group (number)                       | <i>P</i> 2 <sub>1</sub> /c (14)                                                |
| <i>a</i> [Å]                               | 14.6923(3)                                                                     |
| <i>b</i> [Å]                               | 13.0967(2)                                                                     |
| <i>c</i> [Å]                               | 7.5634(2)                                                                      |
| $\alpha$ [°]                               | 90                                                                             |
| $\beta$ [°]                                | 102.745(2)                                                                     |
| $\gamma$ [°]                               | 90                                                                             |
| Volume [Å <sup>3</sup> ]                   | 1419.50(5)                                                                     |
| <i>Z</i>                                   | 4                                                                              |
| $\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]  | 1.284                                                                          |
| $\mu$ [mm <sup>-1</sup> ]                  | 0.655                                                                          |
| <i>F</i> (000)                             | 576                                                                            |
| Crystal size [mm <sup>3</sup> ]            | 0.08×0.08×0.04                                                                 |
| Crystal colour                             | colourless                                                                     |
| Crystal shape                              | plate                                                                          |
| Radiation                                  | Cu <i>K</i> $\alpha$ ( $\lambda$ =1.54184 Å)                                   |
| 2 $\theta$ range [°]                       | 6.17 to 154.38 (0.79 Å)                                                        |
| Index ranges                               | -18 ≤ <i>h</i> ≤ 18<br>-16 ≤ <i>k</i> ≤ 16<br>-9 ≤ <i>l</i> ≤ 8                |
| Reflections collected                      | 43973                                                                          |
| Independent reflections                    | 2956<br><i>R</i> <sub>int</sub> = 0.0683<br><i>R</i> <sub>sigma</sub> = 0.0237 |
| Completeness to<br>$\theta = 67.684^\circ$ | 100.0 %                                                                        |
| Data / Restraints /                        | 2956/0/191                                                                     |
| Parameters                                 |                                                                                |
| Goodness-of-fit on <i>F</i> <sup>2</sup>   | 1.226                                                                          |
| Final <i>R</i> indexes                     | <i>R</i> <sub>1</sub> = 0.0693                                                 |
| [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]      | <i>wR</i> <sub>2</sub> = 0.2098                                                |
| Final <i>R</i> indexes                     | <i>R</i> <sub>1</sub> = 0.1012                                                 |
| [all data]                                 | <i>wR</i> <sub>2</sub> = 0.2829                                                |
| Largest peak/hole [eÅ <sup>-3</sup> ]      | 0.26/-0.26                                                                     |

Table S10. Bond lengths and angles for **4ma (CCDC no. 2348646)**

| Atom–Atom | Length<br>[Å] | Atom–Atom   | Angle [°]  |
|-----------|---------------|-------------|------------|
| O2–H2     | 0.8200        | C12–O2–H2   | 109.5      |
| O2–C12    | 1.342(2)      | C2–C1–C6    | 120.5(3)   |
| O1–C13    | 1.229(3)      | C3–C2–C1    | 120.3(3)   |
| C1–C2     | 1.391(4)      | C2–C3–C4    | 120.0(3)   |
| C1–C6     | 1.391(4)      | C3–C4–C5    | 120.6(3)   |
| C2–C3     | 1.361(6)      | C4–C5–C6    | 120.6(3)   |
| C3–C4     | 1.369(5)      | C1–C6–C5    | 118.0(2)   |
| C4–C5     | 1.381(4)      | C1–C6–C7    | 119.9(2)   |
| C5–C6     | 1.391(4)      | C5–C6–C7    | 122.0(2)   |
| C6–C7     | 1.487(3)      | C8–C7–C6    | 120.4(2)   |
| C7–C8     | 1.388(3)      | C8–C7–C12   | 118.0(2)   |
| C7–C12    | 1.408(3)      | C12–C7–C6   | 121.7(2)   |
| C8–C9     | 1.380(3)      | C9–C8–C7    | 122.4(2)   |
| C9–C10    | 1.373(3)      | C10–C9–C8   | 119.4(2)   |
| C10–C11   | 1.399(3)      | C9–C10–C11  | 121.1(2)   |
| C11–C12   | 1.418(3)      | C10–C11–C12 | 118.6(2)   |
| C11–C13   | 1.474(3)      | C10–C11–C13 | 122.2(2)   |
| C13–C14   | 1.489(3)      | C12–C11–C13 | 119.12(19) |
| C14–C15   | 1.394(4)      | O2–C12–C7   | 117.4(2)   |
| C14–C19   | 1.388(4)      | O2–C12–C11  | 122.27(19) |
| C15–C16   | 1.378(4)      | C7–C12–C11  | 120.26(19) |
| C16–C17   | 1.375(6)      | O1–C13–C11  | 121.0(2)   |
| C17–C18   | 1.374(6)      | O1–C13–C14  | 118.2(2)   |
| C18–C19   | 1.387(4)      | C11–C13–C14 | 120.8(2)   |
|           |               | C15–C14–C13 | 123.0(2)   |
|           |               | C19–C14–C13 | 117.5(2)   |
|           |               | C19–C14–C15 | 119.4(3)   |
|           |               | C16–C15–C14 | 119.7(3)   |
|           |               | C17–C16–C15 | 120.4(3)   |
|           |               | C18–C17–C16 | 120.5(3)   |
|           |               | C17–C18–C19 | 119.7(3)   |
|           |               | C18–C19–C14 | 120.2(3)   |

Table S11. Torsion angles for **4ma (CCDC no. 2348646)**

| Atom-Atom-Atom-Atom | Torsion Angle [°] |
|---------------------|-------------------|
| O1-C13-C14-C15      | 133.9(3)          |
| O1-C13-C14-C19      | -42.6(3)          |
| C1-C2-C3-C4         | -0.5(6)           |
| C1-C6-C7-C8         | 45.0(3)           |
| C1-C6-C7-C12        | -135.8(2)         |
| C2-C1-C6-C5         | 0.6(4)            |
| C2-C1-C6-C7         | -177.4(3)         |
| C2-C3-C4-C5         | 0.5(6)            |
| C3-C4-C5-C6         | 0.0(5)            |
| C4-C5-C6-C1         | -0.5(4)           |
| C4-C5-C6-C7         | 177.4(3)          |
| C5-C6-C7-C8         | -132.9(3)         |
| C5-C6-C7-C12        | 46.3(3)           |
| C6-C1-C2-C3         | -0.1(5)           |
| C6-C7-C8-C9         | 177.3(2)          |
| C6-C7-C12-O2        | 0.9(3)            |
| C6-C7-C12-C11       | 179.11(18)        |
| C7-C8-C9-C10        | 2.6(3)            |
| C8-C7-C12-O2        | -179.89(19)       |
| C8-C7-C12-C11       | -1.7(3)           |
| C8-C9-C10-C11       | 0.4(3)            |
| C9-C10-C11-C12      | -3.9(3)           |
| C9-C10-C11-C13      | 178.2(2)          |
| C10-C11-C12-O2      | -177.39(19)       |
| C10-C11-C12-C7      | 4.5(3)            |
| C10-C11-C13-O1      | 170.1(2)          |
| C10-C11-C13-C14     | -9.6(3)           |
| C11-C13-C14-C15     | -46.4(3)          |
| C11-C13-C14-C19     | 137.1(2)          |
| C12-C7-C8-C9        | -1.9(3)           |
| C12-C11-C13-O1      | -7.9(3)           |
| C12-C11-C13-C14     | 172.46(18)        |
| C13-C11-C12-O2      | 0.6(3)            |
| C13-C11-C12-C7      | -177.44(18)       |
| C13-C14-C15-C16     | -178.0(3)         |
| C13-C14-C19-C18     | 179.9(3)          |
| C14-C15-C16-C17     | -0.8(5)           |
| C15-C14-C19-C18     | 3.2(4)            |
| C15-C16-C17-C18     | 1.4(6)            |
| C16-C17-C18-C19     | 0.2(6)            |
| C17-C18-C19-C14     | -2.6(5)           |
| C19-C14-C15-C16     | -1.5(4)           |



**Figure S30.** UV–vis absorption spectra of synthesized compounds **4aa–ma** from 225–500 nm.

Table S12. Optical properties of the compounds **4aa–ma**.

| No.        | $\lambda_{\max}$ (nm) | $\epsilon$<br>(mol <sup>-1</sup> cm <sup>-1</sup> L) | $\lambda_c$ (nm) | Broad spectrum | UVA/UV<br>B | SPF   |
|------------|-----------------------|------------------------------------------------------|------------------|----------------|-------------|-------|
| <b>4aa</b> | 261<br>334            | 7856<br>3051                                         | 387              | Y              | 0.91        | 10.45 |
| <b>4ba</b> | 259<br>350            | 8663<br>3168                                         | 374              | Y              | 1.73        | 7.69  |
| <b>4bb</b> | 292<br>352            | 7188<br>3140                                         | 386              | Y              | 0.76        | 9.59  |
| <b>4ca</b> | 260<br>350            | 8205<br>2858                                         | 384              | Y              | 1.11        | 7.60  |
| <b>4cb</b> | 291<br>345            | 11495<br>6050                                        | 380              | Y              | 0.64        | 10.55 |
| <b>4dc</b> | 269                   | 5615                                                 | 387              | Y              | 0.88        | 7.76  |
| <b>4ea</b> | 264<br>352            | 8908<br>3463                                         | 388              | Y              | 0.95        | 6.66  |
| <b>4eb</b> | 292<br>243            | 10190<br>5233                                        | 365              | Y              | 1.17        | 10.79 |
| <b>4fa</b> | 261<br>347            | 11063<br>4180                                        | 373              | Y              | 1.25        | 7.70  |
| <b>4fb</b> | 292<br>342            | 9650<br>4940                                         | 364              | Y              | 0.42        | 11.02 |
| <b>4fd</b> | 286                   | 1050                                                 | 343              | N              | 0.08        | 1.97  |
| <b>4ga</b> | 287<br>326            | 11968<br>8033                                        | 350              | Y              | 0.38        | 8.95  |
| <b>4ha</b> | 253<br>372            | 10828<br>3790                                        | 390              | Y              | 2.44        | 4.90  |
| <b>4ia</b> | 253<br>373            | 10450<br>3808                                        | 390              | Y              | 1.47        | 3.78  |
| <b>4ja</b> | 256<br>347            | 10298<br>3433                                        | 374              | Y              | 1.24        | 7.37  |
| <b>4ka</b> | 275<br>362            | 7998<br>3035                                         | 386              | Y              | 0.95        | 4.32  |
| <b>4ma</b> | 275<br>362            | 8077<br>3000                                         | 385              | Y              | 1.07        | 8.07  |



**Figure S31.** Picture of the reaction set-up for the synthesis of **4aa-4ma**.

## References

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