Electronic Supplementary Material (ESI) for New Journal of Chemistry.

SUPPLEMENTARY INFORMATION

A Metal free approach to highly functionalized 3-substituted-3-arylbenzofuran-2(3*H*)-ones

Bhaskar B. Dhotare,[a] Sahil Kumar,[a] Amey Wadawale,[b] Sandip K. Nayak,[a] Mukesh Kumar[c,d] and Dibakar Goswami[a,d]*

[a]Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India, PIN-400085.

[b]Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India, PIN-400085

[c]Radiation Biology & Health Sciences Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India, PIN-400085.

[d]Homi Bhabha National Institute, Anushaktinagar, Mumbai, India, PIN-400094.

*Corresponding author

Spectral data for synthesized compounds

3-(2,4-Dimethoxyphenyl)-3-phenylbenzofuran-2(3H)-one (3aa). The crude product was purified by column chromatography (silica gel, 0-15% EtOAc/hexane) to afford compound **3aa** (white solid, 152.3 mg, 88% yield). mp 108 -109 °C; IR (neat) ν_{max} 2420, 1797, 1605, 1502, 1311, 1051 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.36-7.32 (m, 4H), 7.17-7.13 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.0, Hz, 1H), 6.42-6.39 (m, 2H), 3.77 (s, 3H) 3.59 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 177.9, 160.7, 157.6, 153.5, 137.3, 130.7, 130.2, 129.2, 128.7, 128.5, 128.2, 125.8, 123.8, 123.7, 110.4, 104.7, 99.6, 57.3, 55.7, 55.4. HRMS (ESI) calcd for $C_{22}H_{19}O_4$ $(M + H)^+$ 347.1283; found 347.1278.

3-Phenyl-3-(p-tolyl)benzofuran-2(3H)-one (3ab). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3ab** (white solid; 106.6 mg, 71% yield); mp 105-106 °C; IR (neat) ν_{max} 2916, 1795, 1598, 1330, 941 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 7H), 7.21-7.19 (m, 2H), 7.18-7.13 (m, 4H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 177.0, 152.5, 140.7, 137.7, 137.6, 131.3, 129.4, 129.1, 128.7, 128.1, 127.9, 127.8, 126.1, 124.5, 111.1, 61.0, 21.0. HRMS (ESI) calcd for $C_{21}H_{20}NO_2$ $(M + NH_4)^+$ 318.1494; found 318.1488.

3-(2/5-Hydroxy-2/5-methylphenyl)-3-phenylbenzofuran-2(3H)-one (3ac). The crude product was purified by column chromatography (silica gel, 0-20% EtOAc/hexane) to afford compound **3ac** (white solid; 96.5 mg, 61% yield); mp 182-183 °C; IR (neat) ν_{max} 3341, 1762, 1302, 1083, 999 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.33 (m, 5H), 7.26-7.11 (m, 3H), 7.02-6.88 (m, 3H), 6.76-6.72 (m, 1H), 6.60 and 6.26 (two broad s, 1H), 2.34 and 2.20 (two s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 179.8, 179.4, 154.3, 152.8, 151.9, 150.7, 138.1, 138.0, 134.2, 130.4, 130.3, 130.0, 129.9, 129.8, 129.7, 1.29.5, 129.1, 128.8, 128.1, 127.7, 126.8, 126.4, 124.4, 120.6, 118.1, 118.0, 111.0, 110.6, 59.7, 59.5, 21.2, 20.6. HRMS (ESI) calcd for $C_{21}H_{17}O_3$ $(M+H)^+$ 317.1178; found 317.1172.

3-(5-Allyl-2-methoxyphenyl)-3-phenylbenzofuran-2(3H)-one (3ad). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3ad** (white solid; yield; 94.4 mg, 53% yield); mp 130-131 °C; IR (neat) ν_{max} 2975, 1799, 1280, 1180, 987 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.36-7.33 (m, 4H), 7.19-7.14 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.70 (s, 1H), 5.90-5.84 (m, 1H), 5.01-4.94 (m, 2H), 3.60 (s, 3H), 3.24 (d, *J* = 6.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 177.5, 155.0, 153.5,

137.4, 137.1, 132.3, 131.1, 130.3, 129.7, 129.1, 128.7, 128.3, 128.1, 125.8, 125.8, 123.6, 115.5, 112.2, 110.3, 57.7, 55.8, 39.3. HRMS (ESI) calcd for $C_{24}H_{21}O_3$ $(M + H)^+$ 357.1491; found 357.1485.

3-(2,4-Dimethoxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (3ba). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3ba** (white solid; 135.2 mg, 75% yield); mp 141-142 °C; IR (neat) ν_{max} 2913, 1792, 1459, 1311, 1051 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.46 (m, 2H), 7.36-7.34 (m, 3H), 7.12 (d, *J* = 8.5, Hz, 1H), 7.04 (d, *J* = 8.0, Hz, 1H), 6.86 (s, 1H), 6.75 (d, *J* = 8.0, Hz, 1H), 6.42-6.39 (m, 2H), 3.77 (s, 3H) 3.61 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3) δ = 178.1, 160.6, 157.6, 151.4, 137.4, 133.2, 130.4, 130.1, 129.2, 129.1, 128.4, 128.0, 126.2, 124.0, 110.0, 104.6, 99.6, 57.4, 55.7, 55.3, 21.2. HRMS (ESI) calcd for $C_{23}H_{21}O_4$ $(M + H)^+$ 361.1440; found 361.1424.

5-Methyl-3-phenyl-3-(p-tolyl)benzofuran-2(3H)-one (3bb). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3bb** (white solid; 116.3 mg, 74% yield); mp 149-150 °C; IR (neat) ν_{max} 2919, 1796, 1445, 1254, 1083 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5H), 7.20-7.14 (m, 5H), 7.11-7.09 (m, 2H), 2.35 and 2.36 (two s merged together, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3) δ 177.3, 150.4, 140.8, 137.8, 137.6, 134.1, 131.0, 129.5, 129.3, 128.6, 128.0, 127.9, 127.7, 126.4, 110.6, 61.1, 21.2, 21.0. HRMS (ESI) calcd for $C_{22}H_{18}NaO_2$ $(M + Na)^+$ 337.1204; found 337.1199.

3-(2-Hydroxy-5-methylphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (3bc). The crude product was purified by column chromatography (silica gel, 0-20% EtOAc/hexane) to afford compound **3bc** (white solid; 120.5 mg, 73% yield); mp 136-137 °C; IR (neat) ν_{max} 3516, 3431, 1805, 1767, 1484, 1106 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.36-7.29 (m, 5H), 7.17-7.15 (m, 1H), 7.11-7.09 (m, 1H), 7.05-7.03 (m, 1H), 6.96 (s, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.72 (s, 1H), 6.23 (s, 1H), 2.35 (s, 3H), 2.21 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3) δ = 179.7, 152.0, 150.7, 138.3, 134.1, 130.3, 130.2, 129.9, 129.7, 128.8, 128.1, 127.7, 126.8, 126.2, 118.1, 110.6, 59.7, 21.2, 20.7. HRMS (ESI) calcd for $C_{22}H_{18}NaO_3$ $(M + Na)^+$ 353.1154; found 353.1149.

3-(5-allyl-2-methoxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (3bd). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3bd** (colourless viscous oil; 129.6 mg, 70% yield); IR (neat) ν_{max} 2916, 1797, 1502, 1158, 1054 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 2H), 7.35-7.34 (m, 3H), 7.14-7.05 (m, 3H), 6.86 (s, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 1.0 Hz, 1H), 5.91-5.83 (m, 1H), 5.01-4.94 (m, 2H), 3.62 (s, 3H), 3.24 (d, *J* = 6.0 Hz, 2H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3) δ 177.8, 155.1,

151.5, 137.4, 137.3, 133.2, 132.3, 131.3, 130.1, 129.8, 129.2, 129.0, 128.3, 128.0, 126.2, 115.5, 112.3, 109.9, 57.9, 55.9, 39.3, 21.1. HRMS (ESI) calcd for $C_{25}H_{23}O_3$ $(M + H)^+$ 371.1647; found 371.1632.

3-(2/5-hydroxy-2/5-isopropylphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (***3be***). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3be** (viscous liquid; 123.6 mg, 69% yield); IR (neat) ν_{max} 3472, 2959, 1782, 1612, 1485, 1270 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.37-7.29 (m, 3H), 7.28-7.20 (m, 2H), 7.17-7.12 (m, 1H), 7.11-7.08 (m, 1H), 7.00-6.92 (two s, 1H), 6.81-6.70 (m, 3H), 6.32 and 6.38 (two broad s, 1H), 2.93-2.85 and 2.79-2.70 (two m, 1H), 2.34 and 2.19 (two s, 3H), 1.22 (dd, *J* = 5.4 Hz and 1.2 Hz, 3H), 1.13 (d, *J* = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (200 MHz, CDCl3) δ = 179.9, 179.8, 152.2, 150.9, 145.4, 141.0, 138.4, 134.1, 130.3, 130.2, 129.9, 129.8, 129.7, 128.8, 128.2, 128.1, 128.0, 127.8, 127.6, 127.4, 126.9, 126.8, 126.4, 126.3, 124.6, 118.1, 117.8, 110.7, 59.9, 59.8, 33.9, 33.3, 26.9, 24.3, 24.2, 24.0, 21.3, 20.7. Anal. Found: C, 80.35; H, 6.47. Calcd. for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19 %.

3-(2/5-(tert-butyl)-2/5-hydroxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (***3bf***) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3bf** (viscous liquid; 115.5 mg, 62% yield); IR (neat) ν_{max} 3417, 2960, 1778, 1486, 1064 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.44-7.20 (m, 7H), 7.19-6.99 (m, 3H), 6.98-6.85 (m, 1H), 6.84-6.68 (m, 1H), 2.35 and 2.20 (two s, 3H), 1.29 and 1.18 (two s, 9H); $^{13}C\{^1H\}$ NMR (200 MHz, CDCl3) δ = 180.0, 179.8, 152.2, 151.9, 150.8, 150.6, 147.8, 143.3, 138.4, 134.1, 130.3, 129.9, 129.6, 128.8, 128.1, 127.8, 127.6, 126.8, 126.5, 123.5, 118.3, 117.6, 110.7, 110.3, 60.0, 34.7, 34.2, 31.5, 31.4, 21.2, 20.7. Anal. Found: C, 80.48; H, 6.34. Calcd. for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50 %.

3-(2/5-(sec-butyl)-2/5-hydroxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (***3bg***) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3bg** (viscous liquid; 139.7 mg, 75% yield); IR (neat) ν_{max} 3457, 2962, 1780, 1612, 1476, 1280, 1140 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.28-7.23 (m, 6H), 7.20-7.07 (m, 2H), 7.06-7.01 (m, 1H), 6.96-6.89 (m, 1H), 6.82-6.76 (m, 1H), 6.75-6.69 (m, 1H), 2.64-2.53 and 2.47-2.39 (two m, 1H), 2.33 and 2.19 and 2.18 (three s, 3H), 1.62-1.50 and 1.49-1.38 (two m, 2H), 1.21 (d, *J* = 7.8 Hz) and 1.19 (d, *J* = 7.2 Hz) and 1.11 (t, *J* = 7.2 Hz) (3H), 0.82 (t, *J* = 6.6 Hz) and 0.77 (t, *J* = 7.0 Hz) (3H); $^{13}C\{^1H\}$ NMR (200 MHz, CDCl3) δ = 180.2, 179.9, 179.8, 179.7, 152.2, 150.9, 139.7, 138.5, 138.4, 134.1, 130.5, 130.4, 130.3, 130.2, 129.9, 129.8, 129.7, 128.9, 128.8, 128.4, 128.1, 127.9, 127.8, 127.6, 127.4, 126.8, 125.4, 125.1, 118.4, 118.2, 117.8, 110.8, 110.7, 60.1, 59.9, 59.7, 41.4, 41.3, 40.8, 31.5, 31.4, 31.1, 29.7, 22.0, 21.9, 21.8, 21.6, 21.3, 20.7, 12.2, 12.1. Anal. Found: C, 80.66; H, 6.23. Calcd. for $C_{25}H_{24}O_3$: C, 80.62; H, 6.50 %.

3-(2/5-(hexyloxy)-2/5-hydroxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one (***3bh***) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3bh** (viscous liquid; 147.9 mg, 71% yield); IR (neat) ν_{max} 3482, 2963, 1785, 1142 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.55-7.38 (m, 1H), 7.37-7.24 (m, 5H), 7.17-7.05 (m, 1H), 7.04-6.98 (m, 1H), 6.97-6.83 (m, 1H), 6.82-6.74 (m, 1H), 6.72-6.66 (m, 1H), 6.52 (d, *J* = 2.4 Hz) and 6.33 (d, *J* = 1.8 Hz) (1H), 3.88-3.86 and 3.79-3.74 and 3.65-3.61 (three m, 2H), 2.33 and 2.32 and 2.20 (three s, 3H), 1.78-1.71 and 1.70-1.66 (two m, 2H), 1.57-1.47 and 1.46-1.20 (two m, 6H), 0.90-0.86 (two t merged together, 3H); $^{13}C\{^{1}H\}$ NMR (200 MHz, CDCl3) δ = 179.8, 179.6, 178.0, 156.2, 151.6, 150.2, 149.2, 148.0, 138.1, 137.2, 133.3, 131.8, 130.3, 130.2, 130.0, 129.8, 129.2, 128.8, 128.5, 128.2, 127.9, 126.8, 126.5, 126.4, 118.6, 117.8, 117.3, 116.8, 116.1, 115.7, 115.3, 114.8, 114.5, 113.2, 113.1, 111.4, 110.7, 110.1, 69.3, 68.8, 68.7, 60.1, 59.6, 58.1, 31.8, 29.7, 29.4, 29.3, 29.1, 28.6, 26.0, 25.9, 22.7, 22.6, 21.2, 20.7, 14.2, 14.1. Anal. Found: C, 78.02; H, 6.64. Calcd. for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78 %.

5-methyl-3-phenyl-3-(thiophen-2-yl)benzofuran-2(3H)-one (***3bi***) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3bi** (colourless liquid; 88.8 mg, 58% yield); IR (neat) ν_{max} 3064, 2919, 1799, 1448, 1132 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.38-7.28 (m, 6H), 7.24-7.13 (m, 2H), 7.12-7.06 (m, 2H), 7.03-6.95 (m, 1H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 176.1, 150.5, 142.8, 140.4, 134.5, 131.2, 130.1, 128.8, 128.2, 127.8, 127.6, 127.4, 126.8, 126.5, 126.2, 110.8, 58.1, 21.3. Anal. Found: C, 74.32; H, 4.81; S, 10.28. Calcd. for $C_{19}H_{14}O_2S$: C, 74.49; H, 4.61; S, 10.46%.

5-Bromo-3-(2,4-dimethoxyphenyl)-3-phenylbenzofuran-2(3H)-one (3ca) The crude product was purified by column chromatography (silica gel, 0-15% EtOAc/hexane) to afford compound **3ca** (white solid; 155.2 mg, 73% yield); mp 130-132 °C; IR (neat) ν_{max} 2917, 1808, 1583, 1319, 1086 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.44 (m, 3H), 7.37-7.35 (m, 3H), 7.18 (d, *J* = 1.5 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.42-6.39 (m, 2H), 3.78 (s, 3H) 3.62 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ = 177.0, 160.9, 157.5, 152.5, 136.5, 132.8, 131.7, 130.2, 129.0, 128.8, 128.6, 128.4, 123.0, 116.2, 112.0, 104.8, 99.5, 57.5, 55.6, 55.4. HRMS (ESI) calcd for $C_{22}H_{18}BrO_4$ $(M + H)^+$ 425.0388; found 425.0383.

3-(5-Allyl-2-methoxyphenyl)-5-bromo-3-phenylbenzofuran-2(3H)-one (3cd). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **3ca** (white solid; 141.4 mg, 65% yield); mp 175-176 °C IR (neat) ν_{max} 2916, 1800, 1493, 1461, 1261, 1062 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.48-7.37 (m, 6H), 7.18 (d, *J* = 2.0, Hz, 1H), 7.12 (dd, *J* = 1.0 and 8.0 Hz, 1H), 7.07 (d, *J*

= 8.5 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.65 (d, *J* = 1.5 Hz, 1H), 5.90-5.81 (m, 1H), 5.01-4.95 (m, 2H), 3.62 (s, 3H), 3.23 (d, *J* = 6.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ = 176.7, 155.0, 152.5, 137.3, 136.4, 132.5, 131.8, 130.3, 129.7, 129.5, 129.0, 128.8, 128.5, 128.4, 116.2, 115.6, 112.1, 112.0, 57.9, 55.8, 39.3. HRMS (ESI) calcd for $C_{24}H_{20}BrO_3$ $(M + H)^+$ 435.0596; found 435.0590.

2-(5-Methyl-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)-1,3-diphenylpropane-1,3-dione (4a) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **4a** (white solid; 189.7 mg, 85% yield); mp 211-212 °C; IR (neat) ν_{max} 3014, 2339, 1784, 1657, 1485, 1228 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (t, *J* = 6.5, Hz, 4H), 7.50-7.44 (m, 5H), 7.31-7.27 (m, 4H), 7.19-7.09 (m, 4H), 7.05-7.03 (m, 1H), 6.50 (s, 1H), 2.44 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 194.6, 194.2, 177.1, 151.6, 136.5, 135.4, 135.2, 133.5, 133.4, 133.2, 129.7, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.6, 126.6, 110.3, 63.5, 55.2, 21.5. HRMS (ESI) calcd for $C_{30}H_{22}NaO_4$ $(M + Na)^+$ 469.1416; found 469.1410.

2-(5-Bromo-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)-1,3-diphenylpropane-1,3-dione (4b). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **4b** (white solid; 219.9 mg, 86% yield); mp 212-213 °C; IR (neat) ν_{max} 3100, 1791, 1594, 1461, 1182 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.5 Hz, 1H), 7.69 (dd, *J* = 1.5 and 6.0 Hz, 4H), 7.54 (dd, *J* = 1.5 and 8.5 Hz, 1H), 7.49-7.46 (m, 4H), 7.32-7.26 (m, 4H), 7.17-7.07 (m, 4H), 6.44 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 194.5, 193.9, 176.1, 152.7, 136.2, 135.1, 134.0, 133.7, 132.2, 130.5, 129.3, 128.9, 128.7, 128.6, 128.4, 127.5, 116.4, 112.3, 63.6, 55.2. HRMS (ESI) calcd for $C_{29}H_{19}BrKO_4$ $(M + K)^+$ 549.0104; found 549.0098 .

ethyl 2-(5-methyl-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)-3-oxobutanoate (4c) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **4c** (colourless liquid; 126.9 mg, 72% yield); IR (neat) ν_{max} 2978, 1803, 1703, 1484, 1134 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.16-7.08 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 4.14-4.05 (m, 1H), 4.04-3.99 (m, 1H), 2.69 (s, 3H), 2.21 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H) ; $^{13}C\{^{1}H\}$ NMR (75 MHz, CDCl3) δ 174.8, 163.3, 156.7, 152.8, 145.4, 144.2, 133.9, 131.5, 129.7, 129.6, 128.9, 127.6, 123.5. 122.9, 122.2, 110.5, 62.9, 60.5, 20.9, 13.6, 12.7. Anal. Found: C, 71.73; H, 5.48. Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72 %.

diethyl 2-(5-methyl-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)malonate (4d) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **4d** (colourless liquid; 130.0 mg, 68% yield); IR (neat) ν_{max} 3012, 1854, 1768, 1164 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.36-7.31 (m, 2H), 7.30-7.24 (m, 5H), 7.22-7.18 (m, 1H), 7.07-7.03 (m, 1H), 5.30 (broad s, 0.3 H), 4.86 (s, 1H), 4.04 (q, *J* = 7.5 Hz, 2H), 3.95-3.88 (m, 2H), 2.42 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, CDCl3) δ 176.7, 166.5, 166.3, 151.9, 136.1, 134.0, 130.3, 128.7, 128.3, 127.1, 126.2, 110.3, 62.2, 61.6, 59.3, 55.4, 29.7, 22.7, 21.4, 14.1, 13.7, 13.3. Anal. Found: C, 69.08; H, 5.94. Calcd. for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80 %.

2-((5-Methyl-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-yl)thio)acetic acid (5a). The crude product was purified by column chromatography (silica gel, 0-40% EtOAc/hexane) to afford compound **5a** (colourless oil; 114.7 mg, 73% yield); IR (neat) νmax 3020, 2915, 1793, 1698, 1484, 1064 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.44-7.39 (m, 2H), 7.38-7.33 (m, 1H), 7.19-7.14 (m, 2H), 7.07-7.03 (m, 1H), 3.44 (d, *J* = 15.5 Hz, 1H), 3.34 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 174.8, 174.3, 150.1, 134.8, 130.9, 129.1, 128.9, 127.4, 127.3, 125.8, 110.9, 56.3, 32.8, 21.1. Anal. Found: C, 65.11; H, 4.22; S, 10.26. Calcd. for $C_{17}H_{14}O_4S$: C, 64.95; H, 4.49; S, 10.20 %.

3-((tert-Butylthio)oxy)-5-methyl-3-phenylbenzofuran-2(3H)-one (5b). The crude product was purified by column chromatography (silica gel, 0-5% EtOAc/hexane) to afford compound **5b** (colourless oil; 93.7 mg, 60% yield); IR (neat) ν_{max} 2961, 1799, 1484, 1254, 1083 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.69-7.66 (m, 2H), 7.38-7.27 (m, 4H), 7.20-7.15 (m, 1H), 7.08-7.03 (m, 1H), 2.41 (s, 3H), 1.15 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 176.6, 149.9, 136.7, 134.1, 130.3, 128.7, 128.6, 128.4, 127.5, 127.4, 110.8, 56.9, 48.6, 31.5, 21.2. HRMS (ESI) calcd for $C_{19}H_{24}NO_2S$ $(M + NH_4)^+$ 330.1528; found 330.1522.

5-Methyl-3-((4-nitrobenzyl)-oxy)-3-phenylbenzofuran-2(3H)-one (5c). The crude product was purified by column chromatography (silica gel, 0-20% EtOAc/hexane) to afford compound **5c** (white solid; 135.1 mg, 72% yield); mp 82-83 °C; IR (neat) ν_{max} 2916, 1818, 1599, 1333, 1137 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.47-7.43 (m, 2H), 7.42-7.36 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.18-7.13 (m, 2H), 4.55 (dd, *J* = 12.0 and 12.0 Hz, 2H), 2.38, (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 174.2, 151.9, 147.5, 144.4, 137.1, 135.2, 132.1, 129.3, 128.8, 128.0, 126.3, 126.3, 125.7, 123.6, 111.4, 83.2, 67.0, 21.2. HRMS (ESI) calcd for $C_{22}H_{18}NO_5$ $(M + H)^+$ 376.1185; found 376.1179.

5-Methyl-3-phenyl-3-(prop-2-yn-1-yloxy)benzofuran-2(3H)-one (5d). The crude product was purified by column chromatography (silica gel, 0-20% EtOAc/hexane) to afford compound **5d** (colourless oil; 90.4 mg, 65% yield); IR (neat) ν_{max} 3293, 1812, 1485, 1224, 1066 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.39-7.34 (m, 3H), 7.28-7.23 (m, 1H), 7.17-7.14 (m, 1H), 7.11-7.07 (m, 1H), 4.17 (d, *J* = 2.5 Hz, 2H), 2.45 (t, 2.5 Hz, 1H), 2.38 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 174.0, 151.9, 137.1, 134.9, 132.0, 129.1, 128.7, 126.6, 126.3, 125.3, 111.3, 82.4, 78.3, 75.6, 54.4, 21.1. Anal. Found: C, 77.78; H, 5.32. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07 %.

3-Methoxy-5-methyl-3-phenylbenzofuran-2(3H)-one (5e). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **5e** (colourless oil; 85.1 mg, 67% yield); IR (neat) ν_{max} 2928, 1812, 1484, 1223, 1065 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 7.37-7.35 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.12-7.09 (m, 2H), 3.31 (s, 3H), 2.38 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 174.6, 152.1, 137.7, 134.9, 131.7, 129.0, 128.6, 126.3, 125.9, 111.1, 83.4, 53.7, 21.2. HRMS (ESI) calcd for $C_{16}H_{14}NaO_3$ $(M + Na)^+$ 277.0841; found 277.0835.

3-Ethoxy-5-methyl-3-phenylbenzofuran-2(3H)-one (5f). The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **5f** (white solid; 84.5 mg, 63% yield); mp 122-123 °C; IR (neat) ν_{max} 2921, 1799, 1483, 1168, 1069 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.42-7.32 (m, 5H), 7.25-7.22 (m, 1H), 7.11-7.07 (m, 2H), 3.47-3.37 (m, 2H), 2.37 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 174.9, 151.9, 138.0, 134.7, 131.5, 128.9, 128.6, 126.6, 126.3, 126.2, 110.1, 82.8, 61.9, 21.2, 15.3. Anal. Found: C, 75.81; H, 5.78. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01 %.

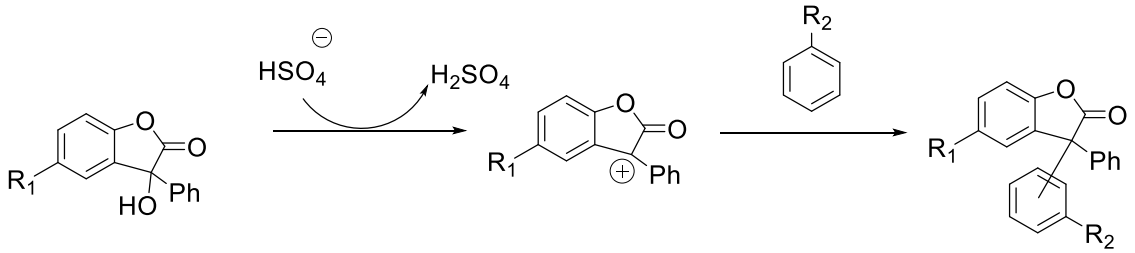
3-((5-chloropentyl)oxy)-5-methyl-3-phenylbenzofuran-2(3H)-one (***5g***) The crude product was purified by column chromatography (silica gel, 0-10% EtOAc/hexane) to afford compound **5g** (colourless liquid; 122.4 mg, 71% yield); IR (neat) ν_{max} 3020, 2869, 1811, 1619, 1134 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46-7.30 (m, 5H), 7.29-7.19 (m, 1H), 7.13-7.05 (m, 2H), 3.63-3.47 (m, 2H), 3.45-3.22 (m, 2H), 2.38 (s, 3H), 1.89-1.46 (m, 6H); $^{13}C\{^{1}H\}$ NMR (75 MHz, CDCl3) δ = 174.8, 151.9, 138.0, 134.8, 131.6, 128.9, 128.6, 126.4, 126.2, 111.1, 82.8, 65.7, 44.9, 32.2, 28.9, 23.4, 21.2. Anal. Found: C, 69.49; H, 5.85. Calcd. for $C_{20}H_{21}ClO_3$: C, 69.66; H, 6.14 %.

Methyl 2-hydroxy-2-(2-hydroxy-5-methylphenyl)-2-phenylacetate (6a). The crude residue which was purified by column chromatography (silica gel, 0-20% EtOAc/hexane) to afford pure **6a** (colourless oil ; 93.9 mg, 69% yield); IR (neat) ν_{max} 3100, 1797, 1585, 1484, 1118 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (broad s, 1H), 7.42-7.38 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.66 (s, 1H), 4.57 (broad s, 1H),

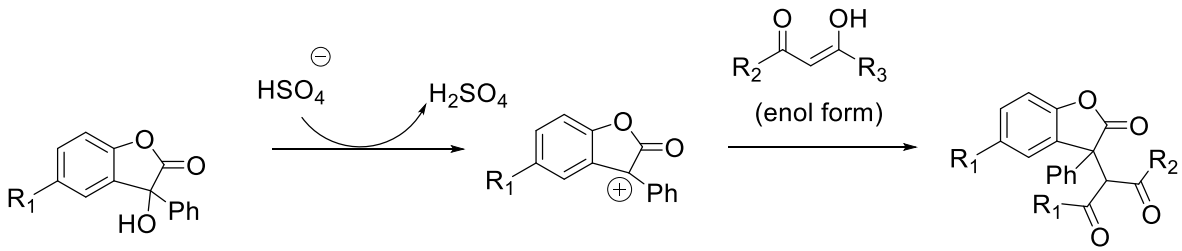
3.88 (s, 3H), 2.21 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 174.2, 153.3, 139.8, 130.6, 128.8, 128.7, 128.6, 128.3, 126.9, 125.5, 117.6, 82.0, 53.7, 20.6. Anal. Found: C, 70.69; H, 5.68. Calcd. for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92 %.

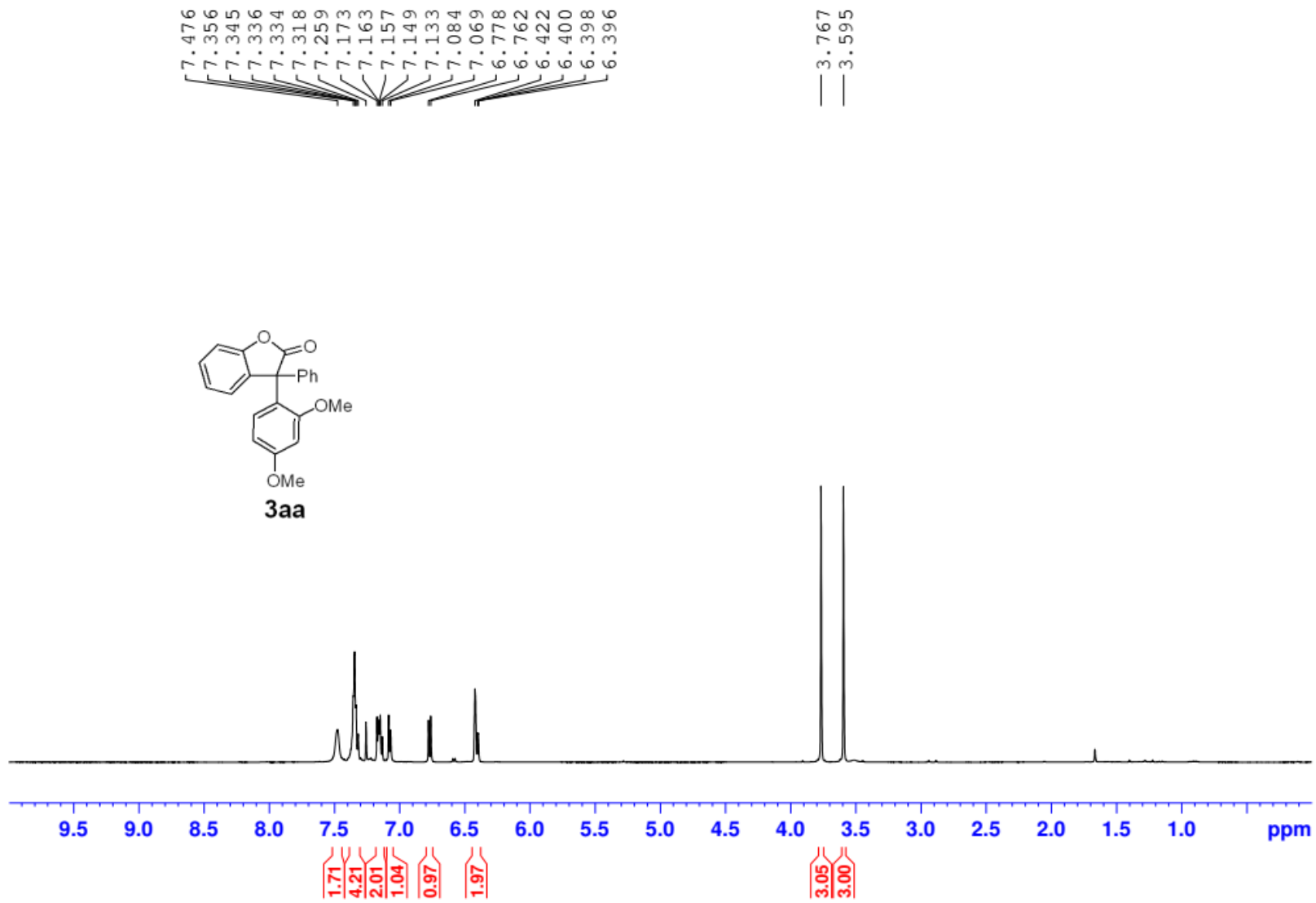
Ethyl 2-hydroxy-2-(2-hydroxy-5-methylphenyl)-2-phenylacetate (6b). The crude residue which was purified by column chromatography (silica gel, 0-20% EtOAc/hexane) to afford pure **6b** (colourless oil ; 93.0 mg, 65% yield); IR (neat) ν_{max} 3381, 1726, 1494, 1221, 1058 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.77 (broad s, 1H), 7.45-7.37 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 4.66 (s, 1H), 4.39-4.35 (m, 2H), 2.21 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 173.5, 153.4, 140.0, 130.5, 128.7, 128.6, 128.4, 128.3, 126.9, 125.4, 117.6, 81.9, 63.2, 20.6, 14.0. Anal. Found: C, 71.53; H, 6.13. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34 %.

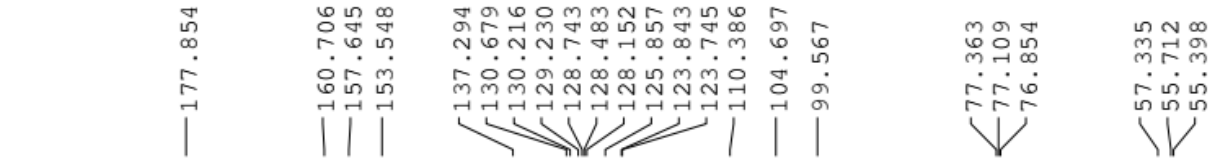
Possible reaction mechanism for dehydrative Friedel Crafts reaction.

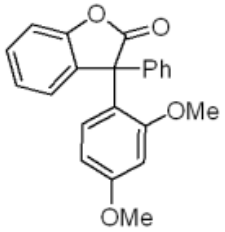


Possible reaction mechanism with 1,3-diketones.

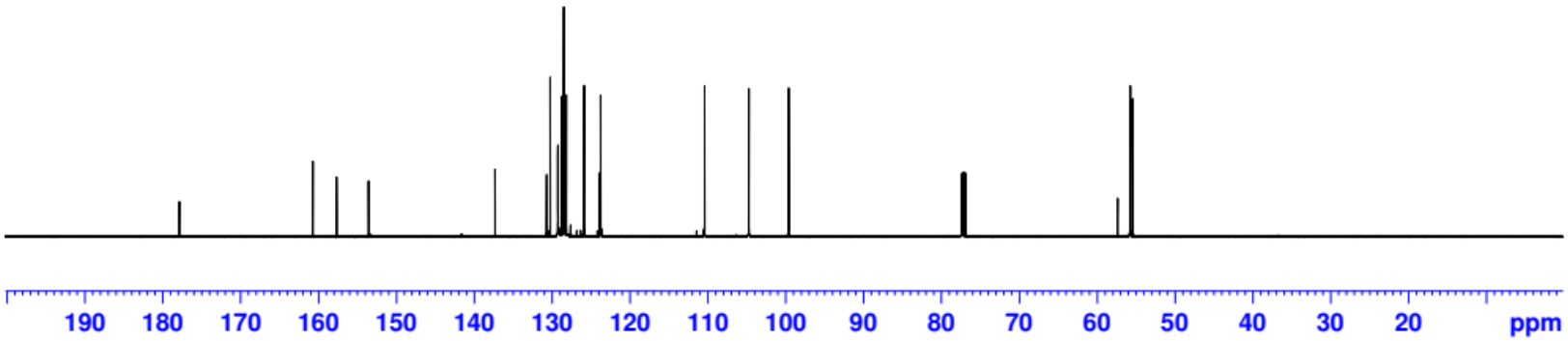


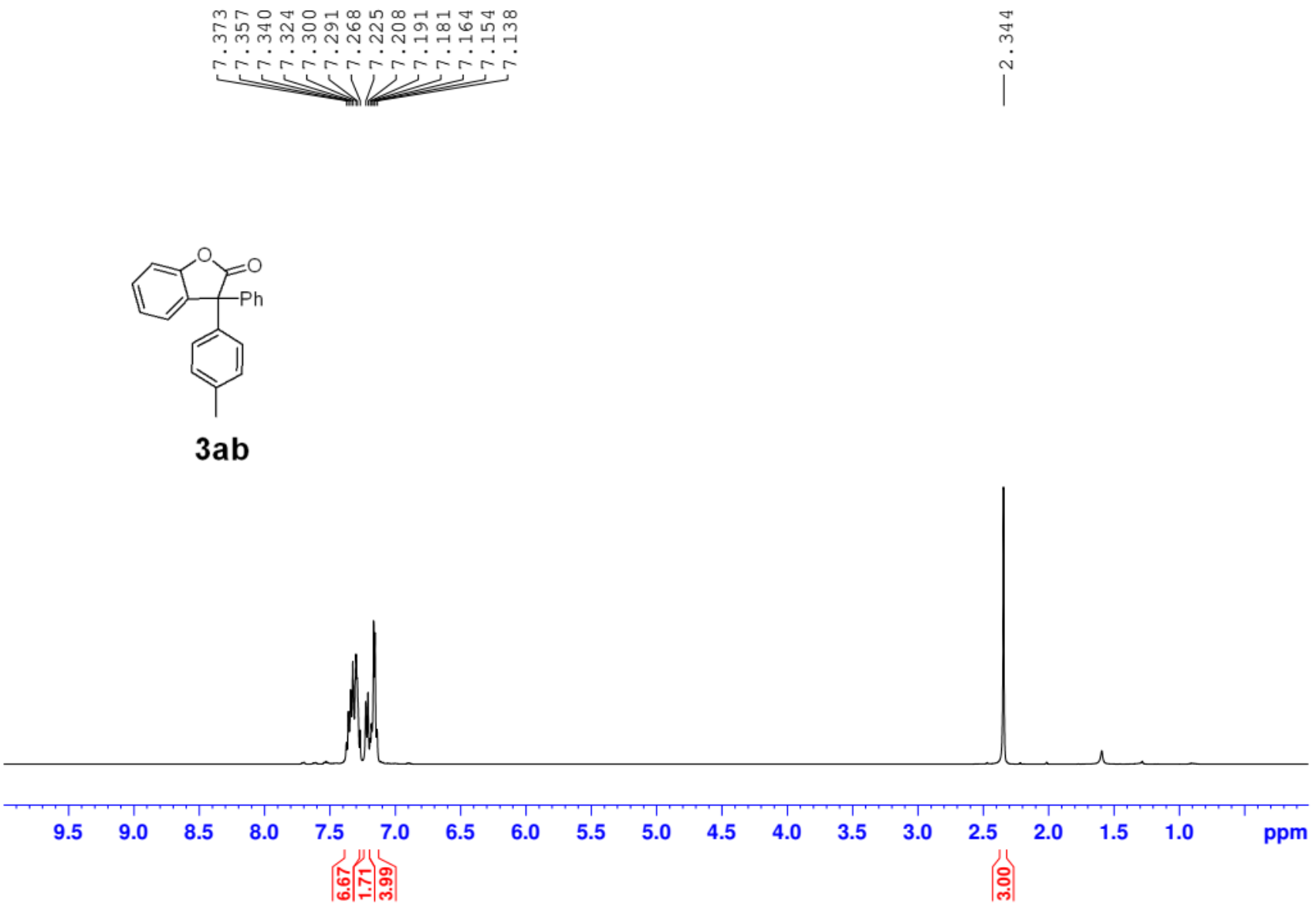

7.476
7.356
7.345
7.336
7.334
7.318
7.259
7.173
7.163
7.157
7.149
7.133
7.084
7.069
6.778
6.762
6.422
6.400
6.398
6.396
3.767
3.595
O
O
Ph
OMe
OMe
3aa
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.71
4.21
2.01
1.04
0.97
1.97
3.05
3.00


177.854
160.706
157.645
153.548
137.294
130.679
130.216
129.230
128.743
128.483
128.152
125.857
123.843
123.745
110.386
104.697
99.567
77.363
77.109
76.854
57.335
55.712
55.398

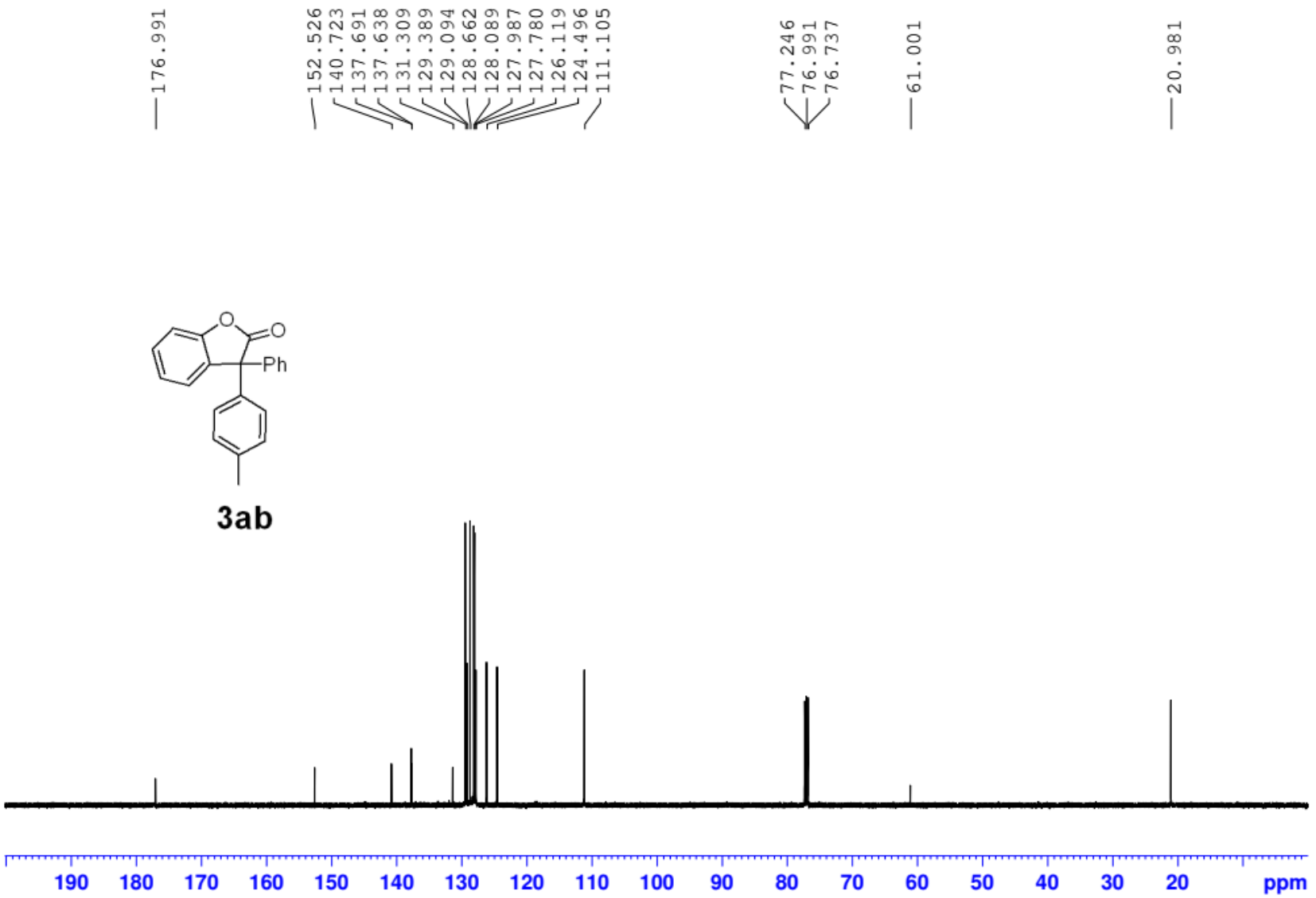

O
O
Ph
OMe
OMe

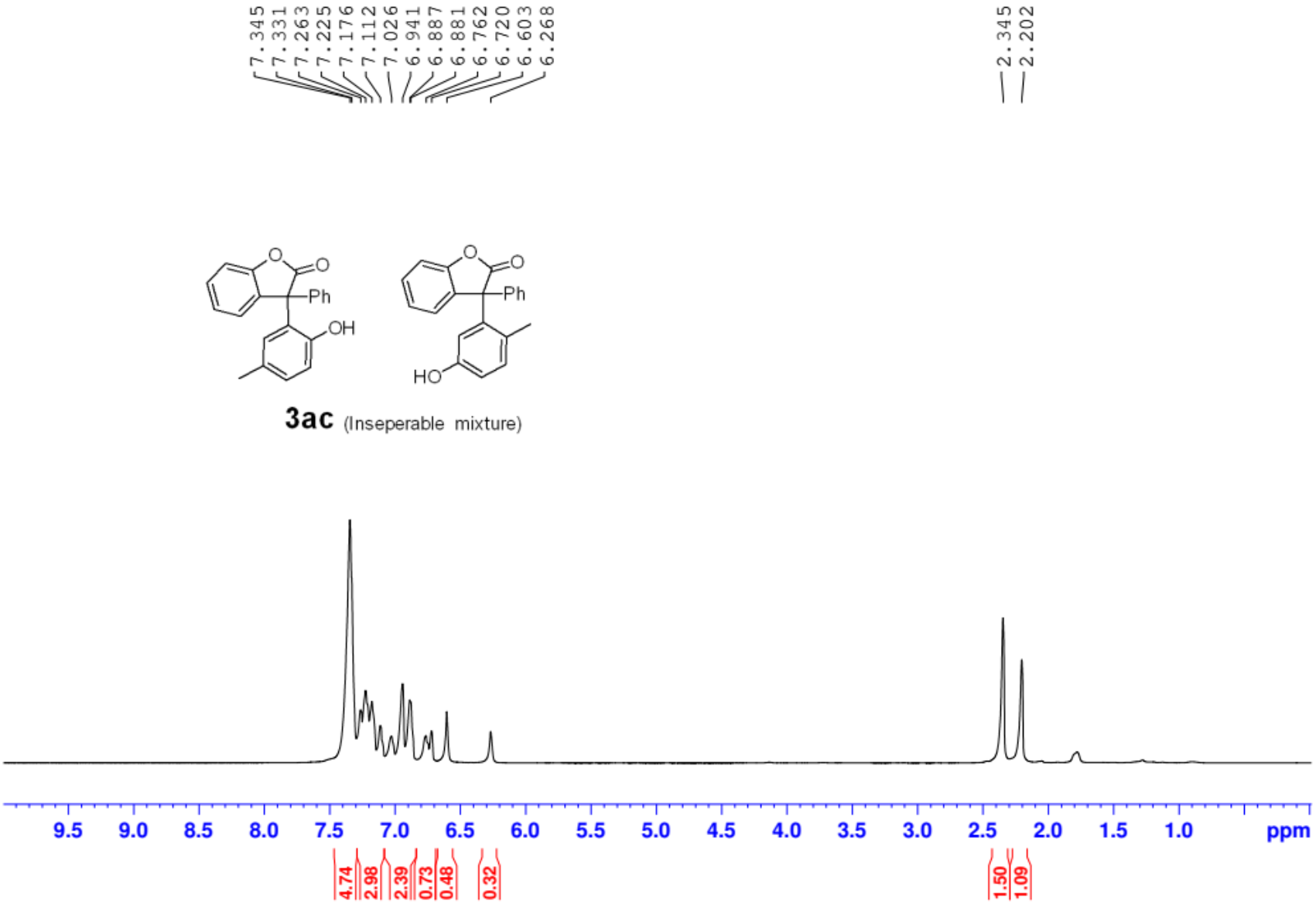
3aa


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

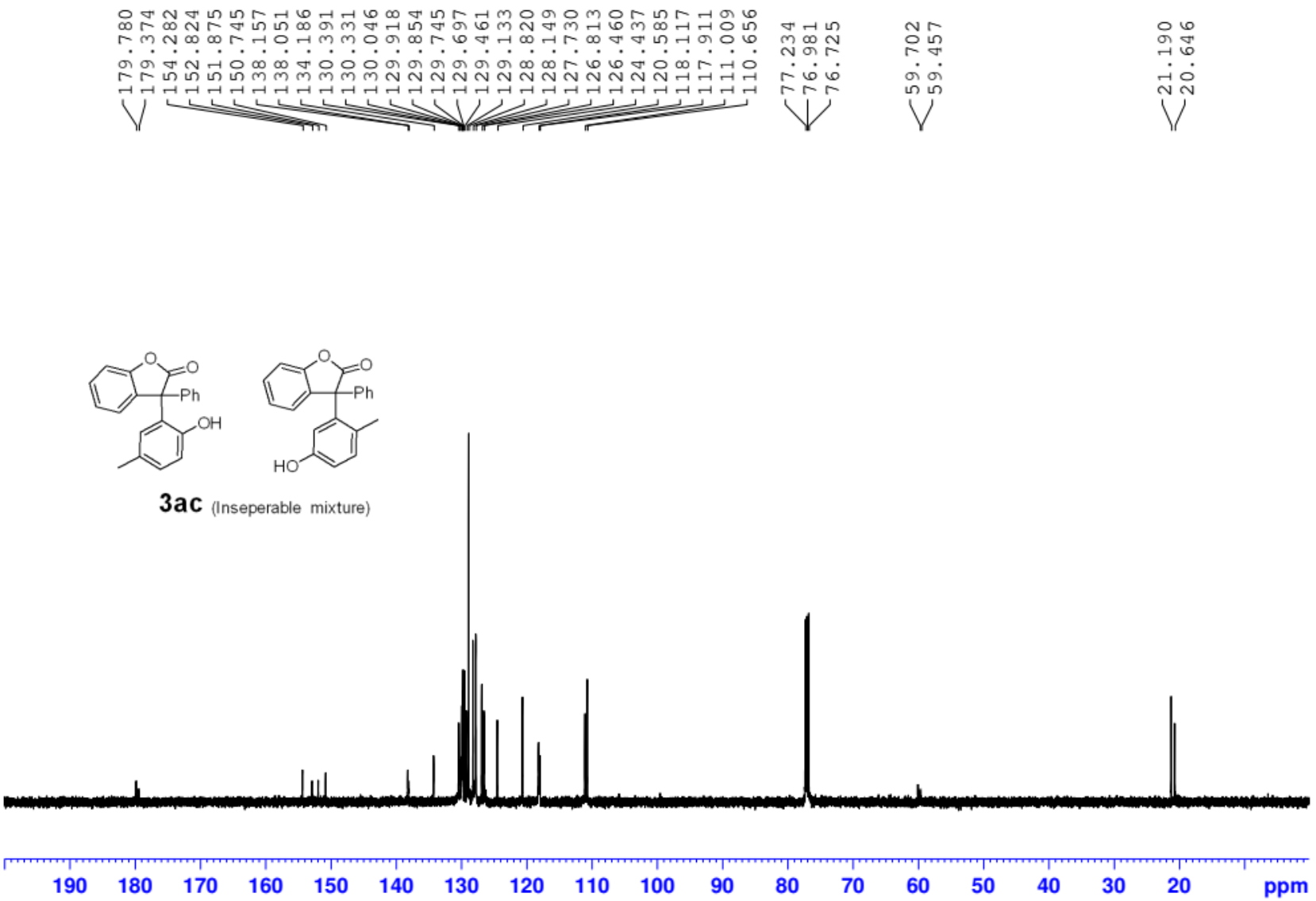

7.373
7.357
7.340
7.324
7.300
7.291
7.268
7.225
7.208
7.191
7.181
7.164
7.154
7.138
2.344
O
O
Ph
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
6.67
1.71
3.99
3.00

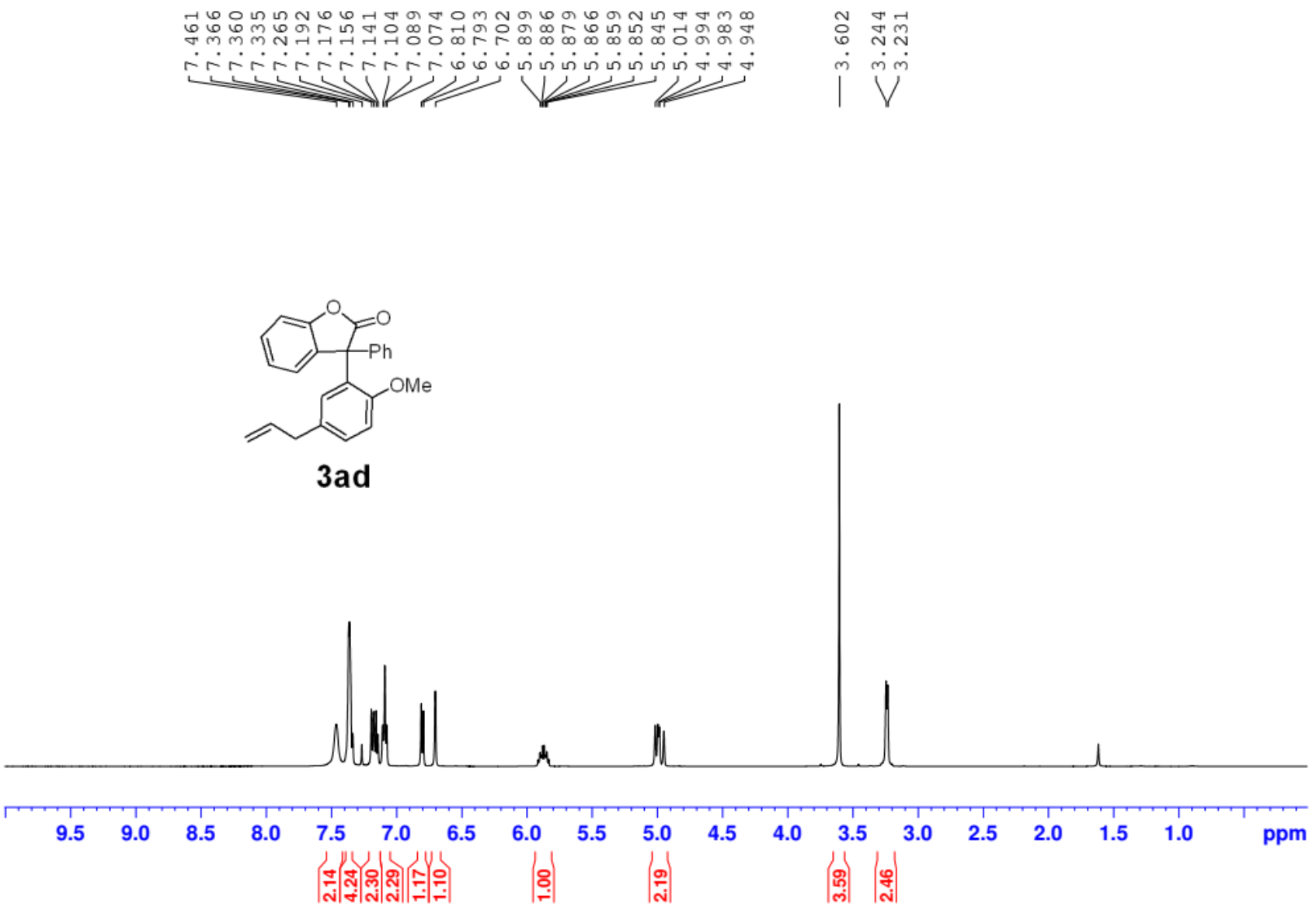
3ab


176.991
152.526
140.723
137.691
137.638
131.309
129.389
129.094
128.662
128.089
127.987
127.780
126.119
124.496
111.105
77.246
76.991
76.737
61.001
20.981
O
O
Ph
3ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

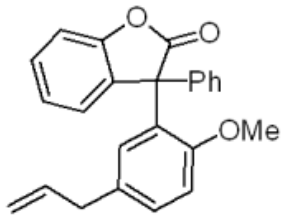


3ac (Inseperable mixture)

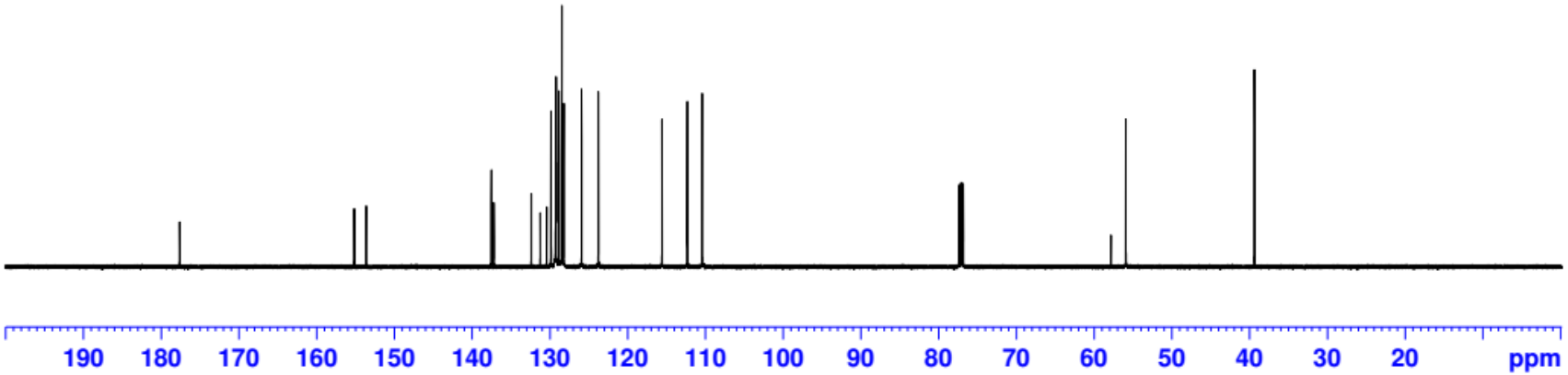

179.780
179.374
154.282
152.824
151.875
150.745
138.157
138.051
134.186
130.391
130.331
130.046
129.918
129.854
129.745
129.697
129.461
129.133
128.820
128.149
127.730
126.813
126.460
124.437
120.585
118.117
117.911
111.009
110.656
77.234
76.981
76.725
59.702
59.457
21.190
20.646
Ph
OH
Ph
HO
3ac (Inseperable mixture)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

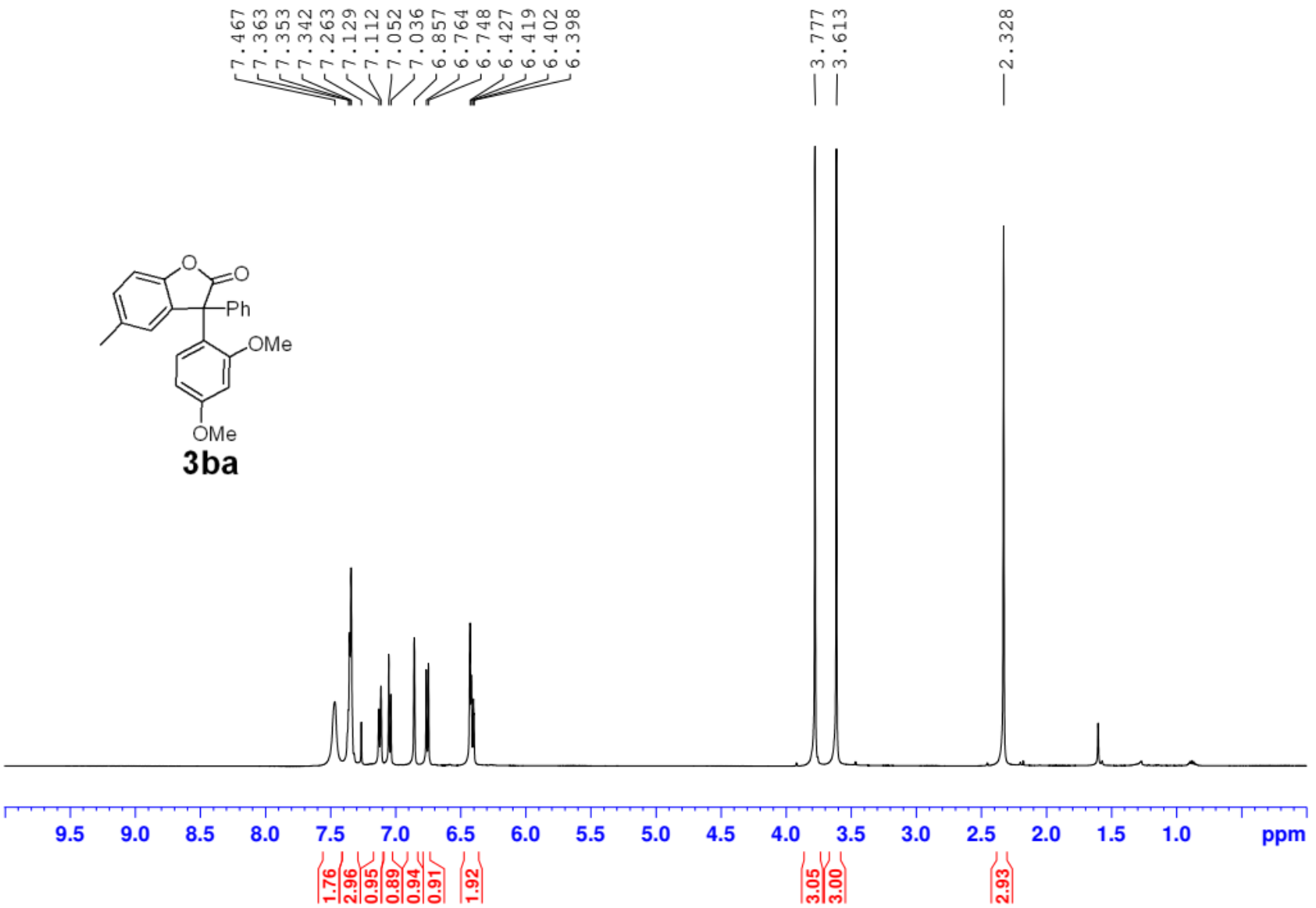

7.461
7.366
7.360
7.335
7.265
7.192
7.176
7.156
7.141
7.104
7.089
7.074
6.810
6.793
6.702
5.899
5.886
5.879
5.866
5.859
5.852
5.845
5.014
4.994
4.983
4.948
3.602
3.244
3.231
O
O
Ph
OMe
3ad
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.14
4.24
2.30
2.29
1.17
1.10
1.00
2.19
3.59
2.46

177.518
155.072
153.541
137.433
137.118
132.296
131.143
130.315
129.754
129.159
129.103
128.740
128.365
128.119
125.829
123.666
115.485
112.222
110.320
77.244
76.990
76.735
57.728
55.811
39.270

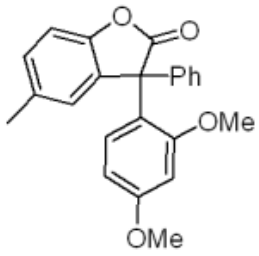


3ad

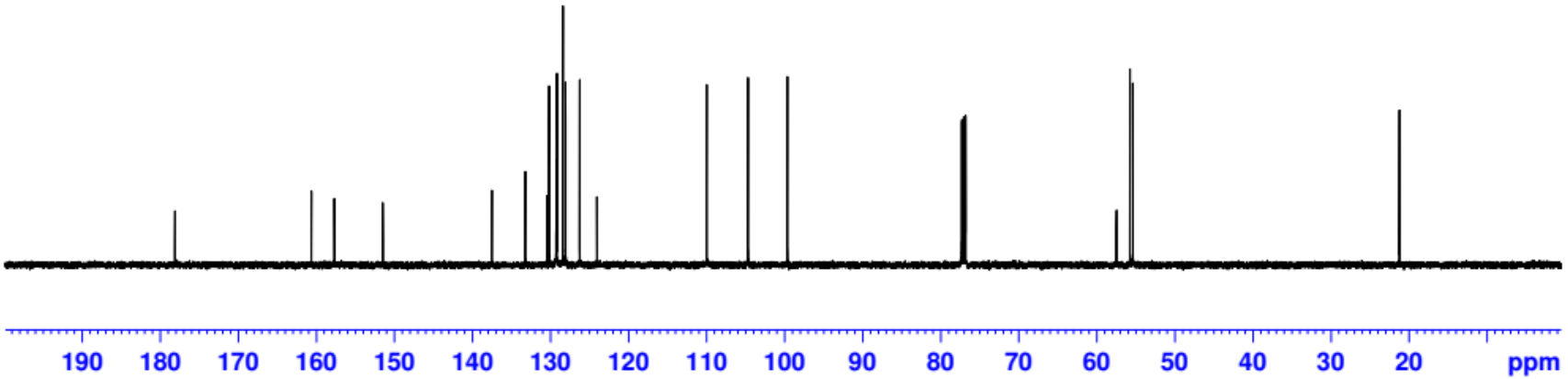


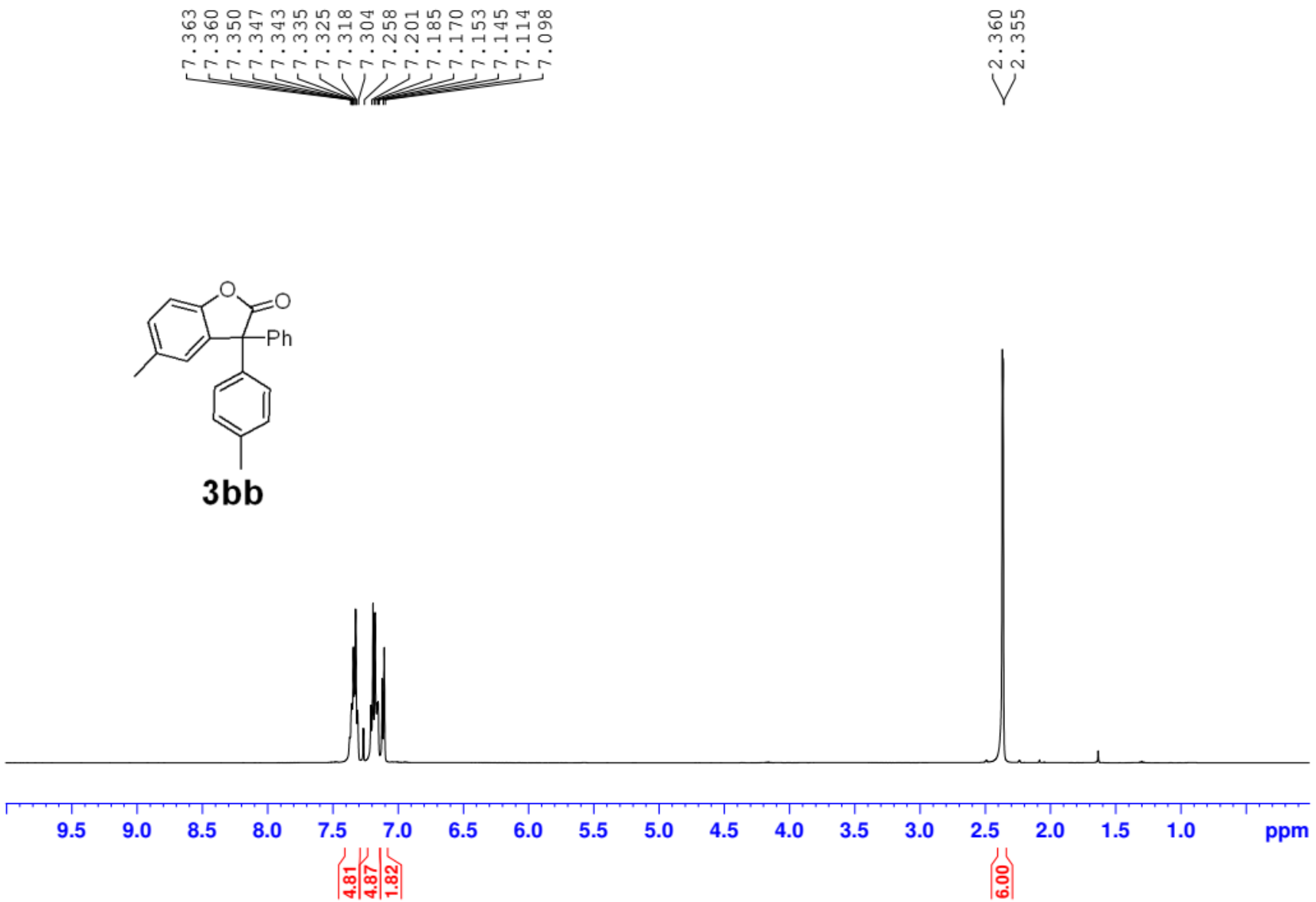

7.467
7.363
7.353
7.342
7.263
7.129
7.112
7.052
7.036
6.857
6.764
6.748
6.427
6.419
6.402
6.398
3.777
3.613
2.328
O
O
Ph
OMe
OMe
3ba
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.76
2.96
0.95
0.89
0.94
0.91
1.92
3.05
3.00
2.93

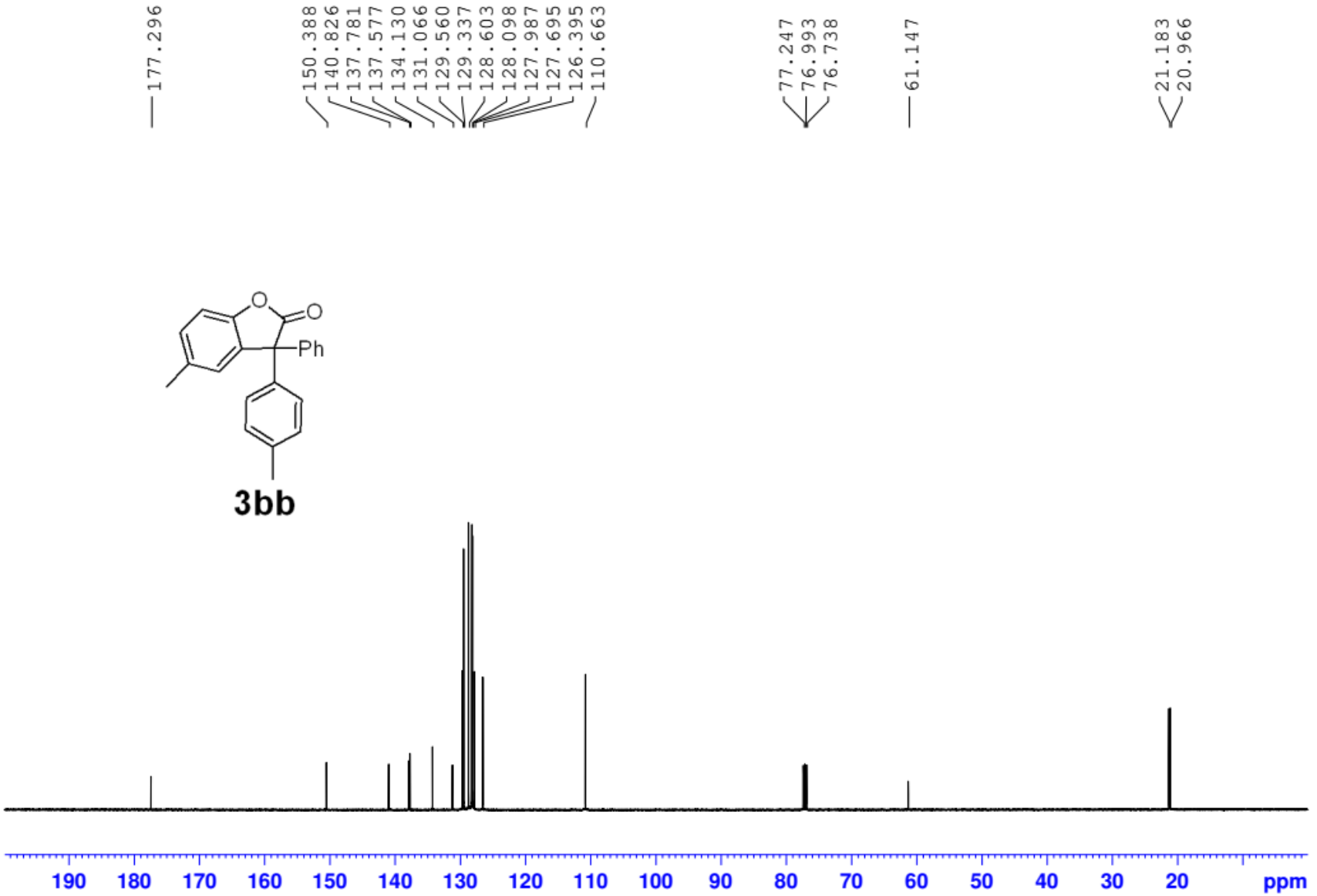
178.070
160.577
157.645
151.420
137.448
133.174
130.371
130.134
129.202
129.104
128.353
128.002
126.207
123.992
109.922
104.631
99.584
77.246
76.992
76.738
57.421
55.694
55.324
21.164

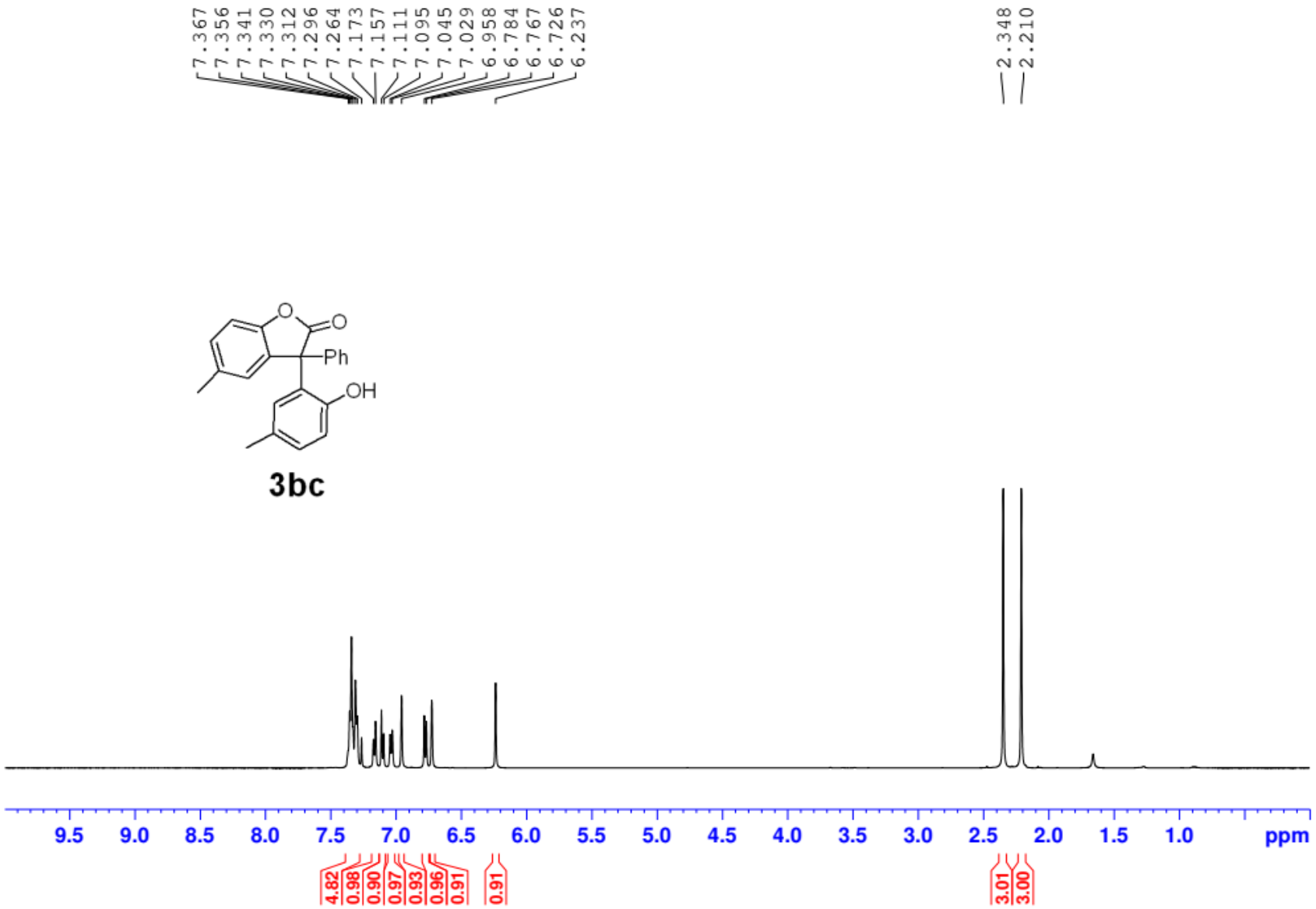


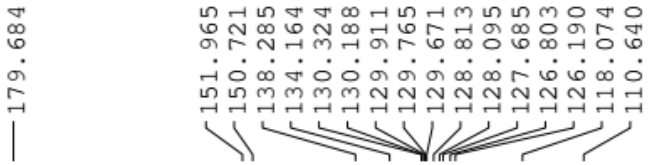
3ba

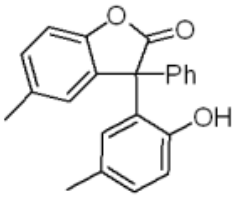



7.363
7.360
7.350
7.347
7.343
7.335
7.325
7.318
7.304
7.258
7.201
7.185
7.170
7.153
7.145
7.114
7.098
2.360
2.355
O
O
Ph
3bb
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.81
4.87
1.82
6.00

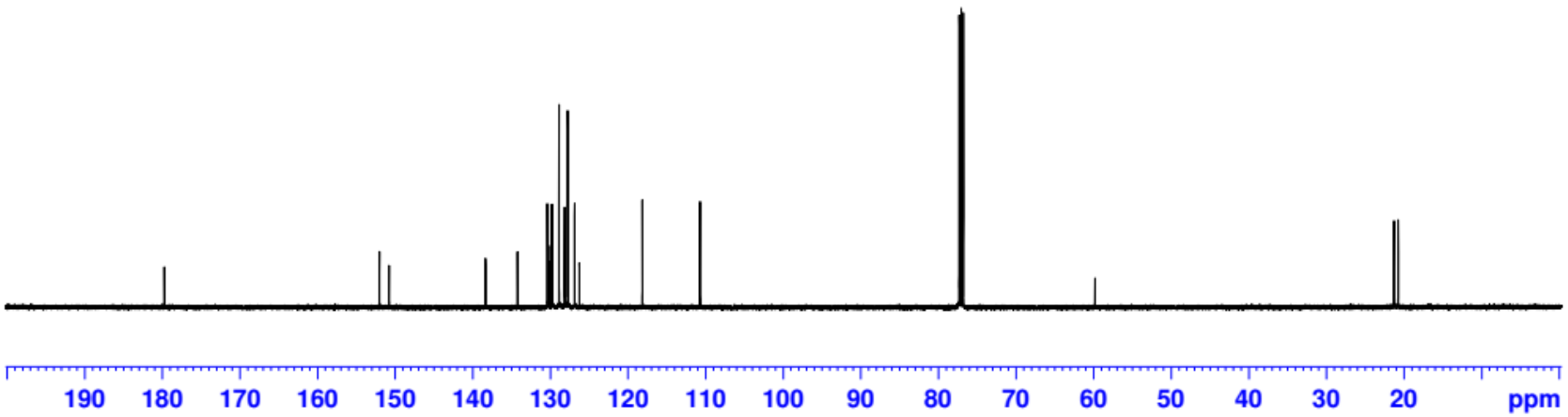

177.296
150.388
140.826
137.781
137.577
134.130
131.066
129.560
129.337
128.603
128.098
127.987
127.695
126.395
110.663
77.247
76.993
76.738
61.147
21.183
20.966
O
O
Ph
3bb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

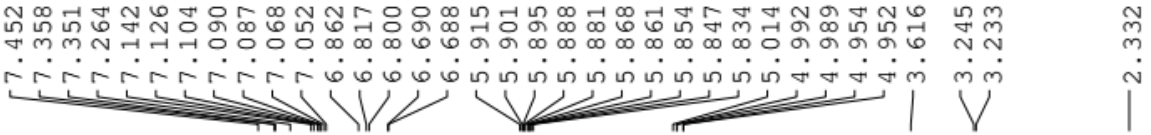

7.367
7.356
7.341
7.330
7.312
7.296
7.264
7.173
7.157
7.111
7.095
7.045
7.029
6.958
6.784
6.767
6.726
6.237
2.348
2.210
O
O
Ph
OH
3bc
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.82
0.98
0.90
0.97
0.93
0.96
0.91
0.91
3.01
3.00

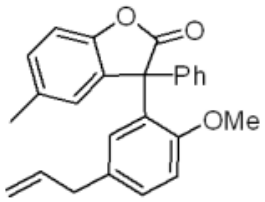

179.684
151.965
150.721
138.285
134.164
130.324
130.188
129.911
129.765
129.671
128.813
128.095
127.685
126.803
126.190
118.074
110.640
77.230
76.976
76.722
59.726
21.206
20.668


O
O
Ph
OH

3bc

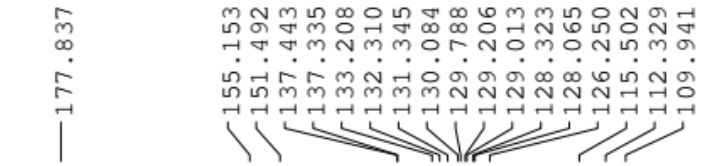

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

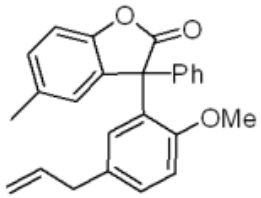

7.452
7.358
7.351
7.264
7.142
7.126
7.104
7.090
7.087
7.068
7.052
6.862
6.817
6.800
6.690
6.688
5.915
5.901
5.895
5.888
5.881
5.868
5.861
5.854
5.847
5.834
5.014
4.992
4.989
4.954
4.952
3.616
3.245
3.233
2.332


O
O
Ph
OMe

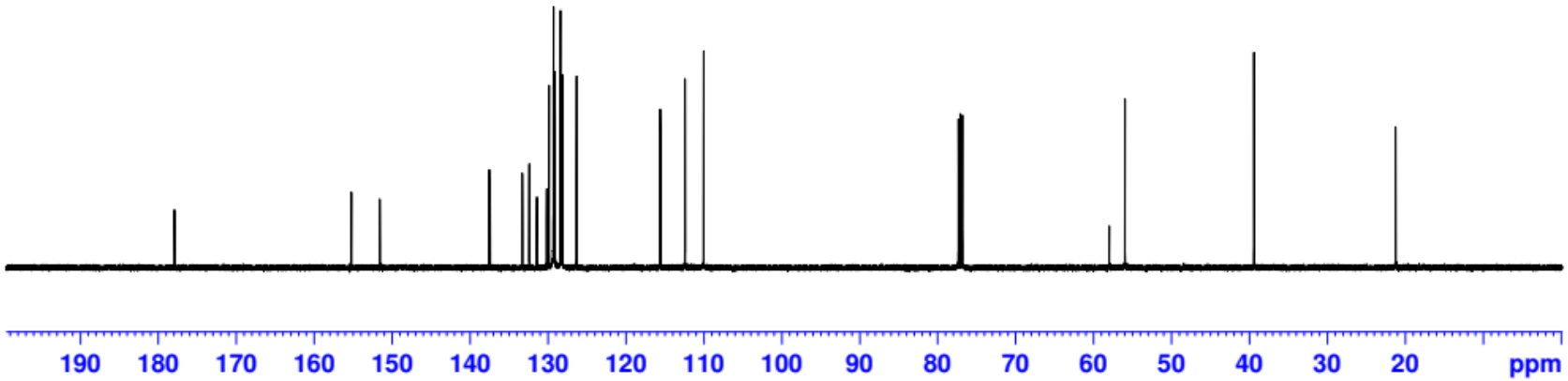
3bd

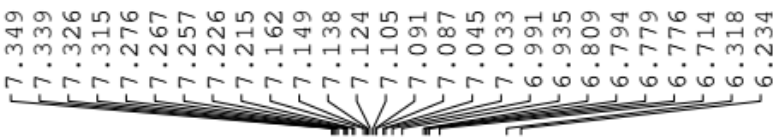
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.67
3.01
2.93
0.96
1.00
0.96
0.84
1.85
3.00
1.94
3.01

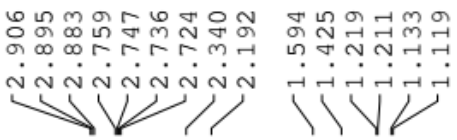

177.837
155.153
151.492
137.443
137.335
133.208
132.310
131.345
130.084
129.788
129.206
129.013
128.323
128.065
126.250
115.502
112.329
109.941
77.243
76.989
76.734
57.906
55.883
39.312
21.152

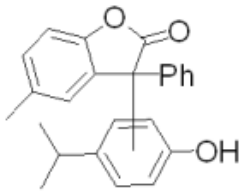

O
O
Ph
OMe

3bd

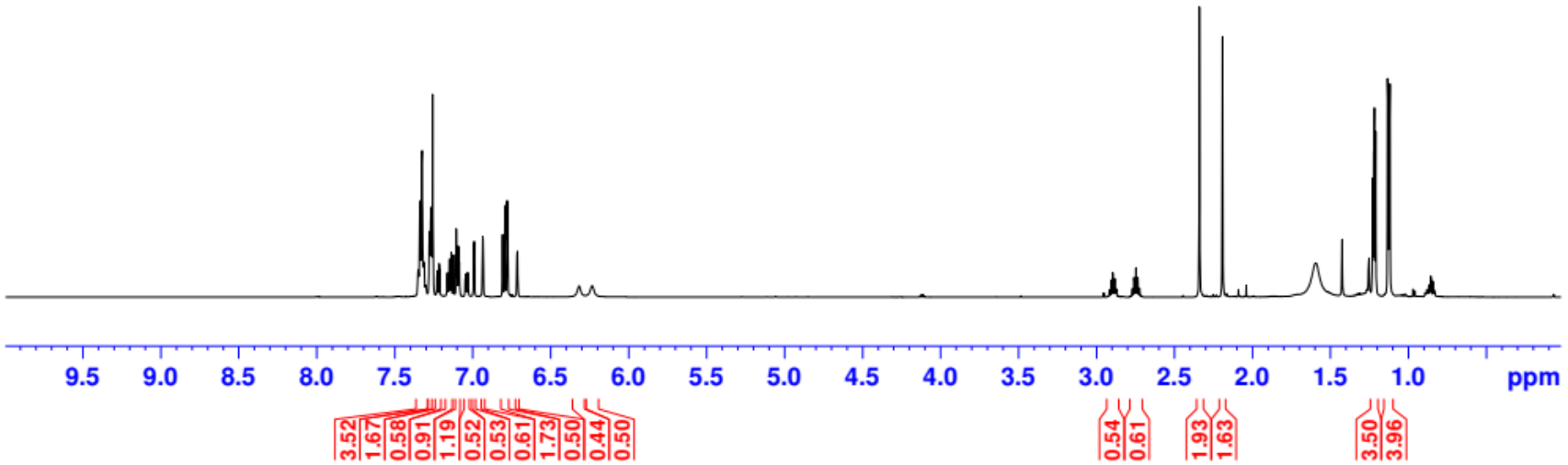

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

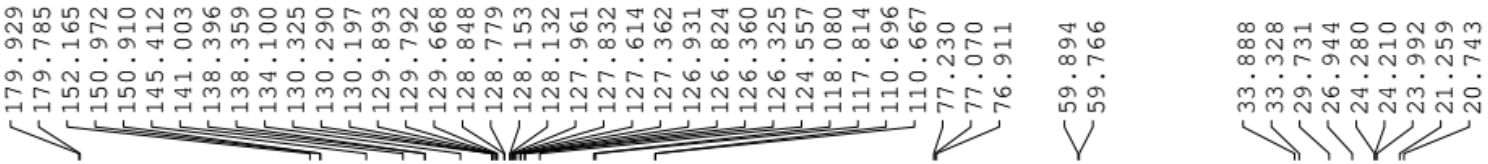

7.349
7.339
7.326
7.315
7.276
7.267
7.257
7.226
7.215
7.162
7.149
7.138
7.124
7.105
7.091
7.087
7.045
7.033
6.991
6.935
6.809
6.794
6.779
6.776
6.714
6.318
6.234

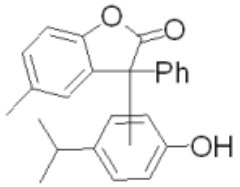

2.906
2.895
2.883
2.759
2.747
2.736
2.724
2.340
2.192
1.594
1.425
1.219
1.211
1.133
1.119


O
O
Ph
OH

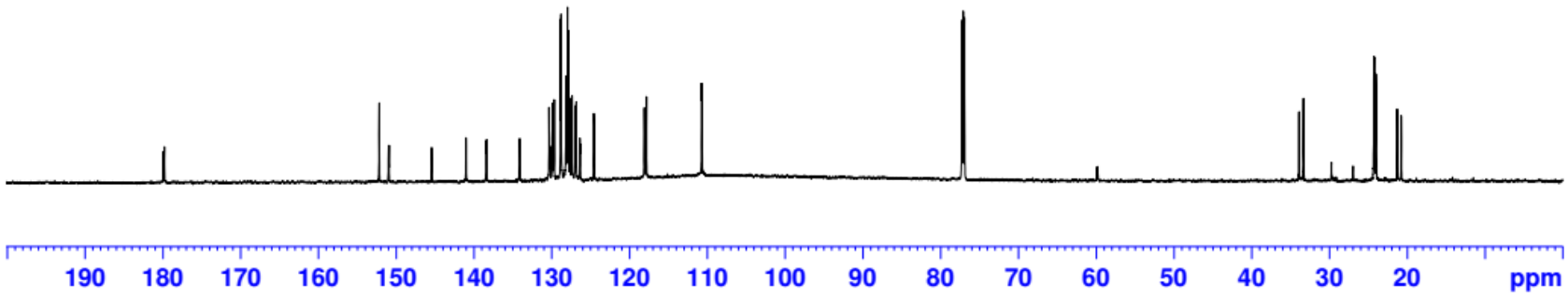
3be

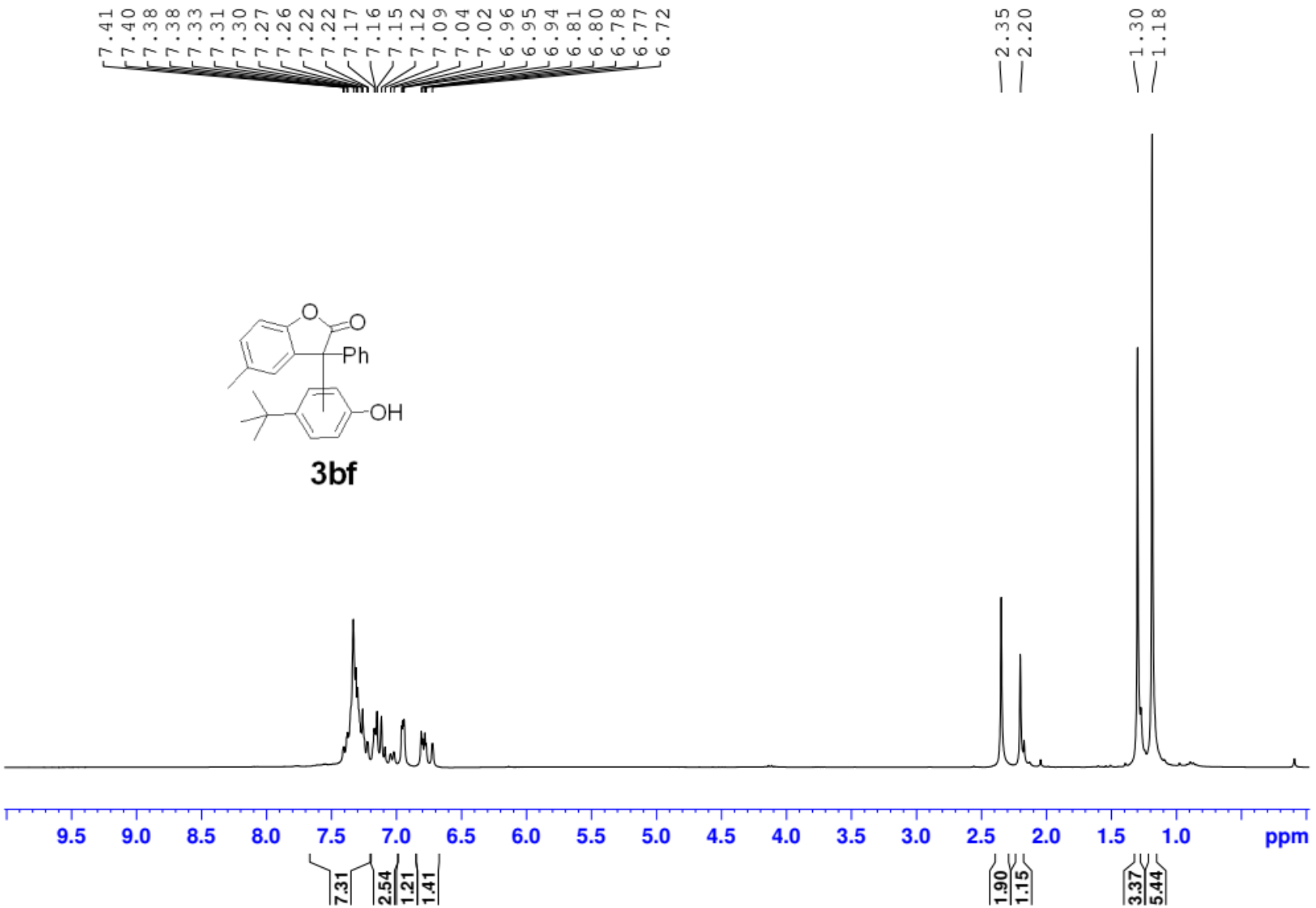

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.52
1.67
0.58
0.91
1.19
0.52
0.53
0.61
1.73
0.50
0.44
0.50
0.54
0.61
1.93
1.63
3.50
3.96

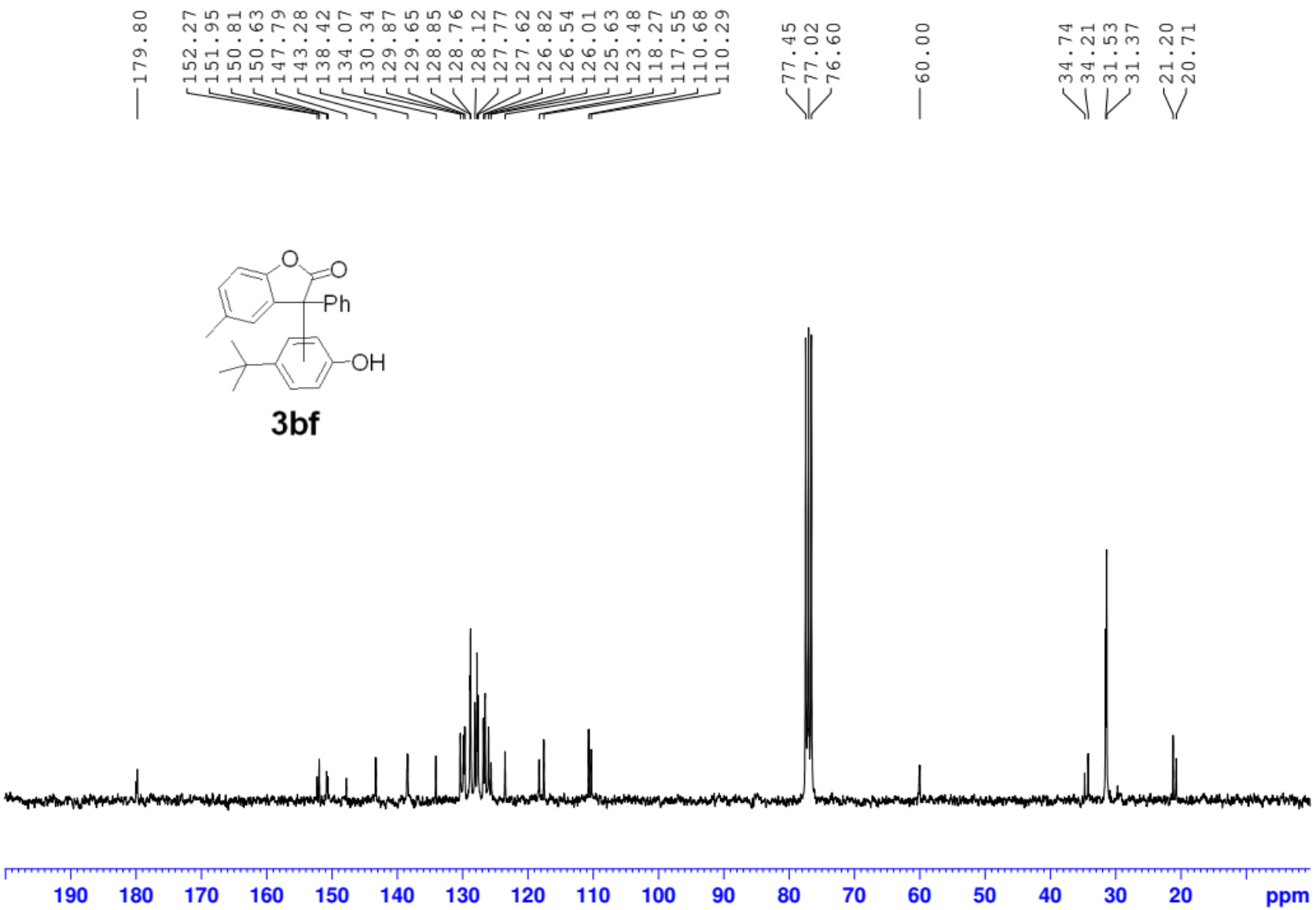

179.929
179.785
152.165
150.972
150.910
145.412
141.003
138.396
138.359
134.100
130.325
130.290
130.197
129.893
129.792
129.668
128.848
128.779
128.153
128.132
127.961
127.832
127.614
127.362
126.931
126.824
126.360
126.325
124.557
118.080
117.814
110.696
110.667
77.230
77.070
76.911
59.894
59.766
33.888
33.328
29.731
26.944
24.280
24.210
23.992
21.259
20.743

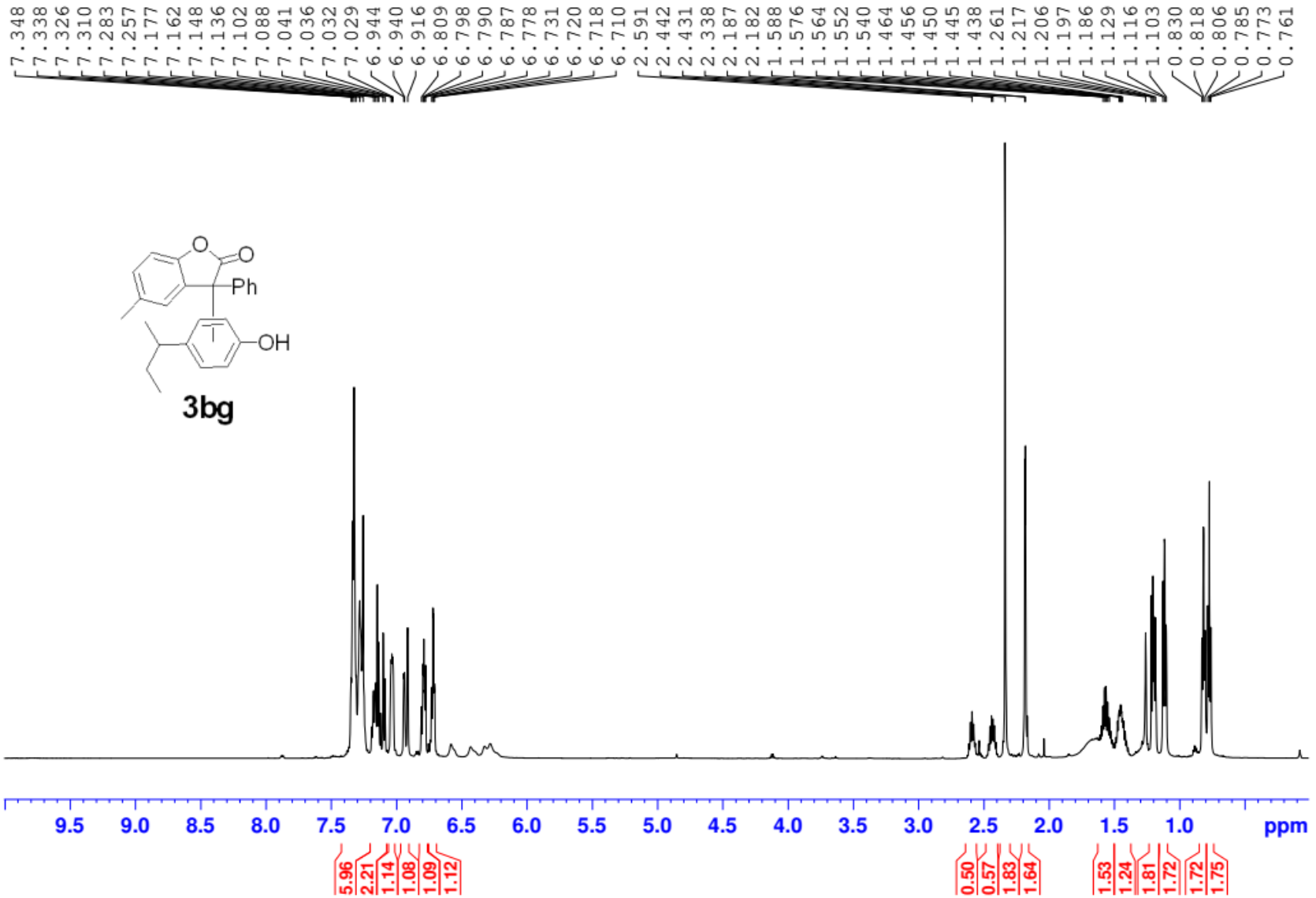

O
O
Ph
OH

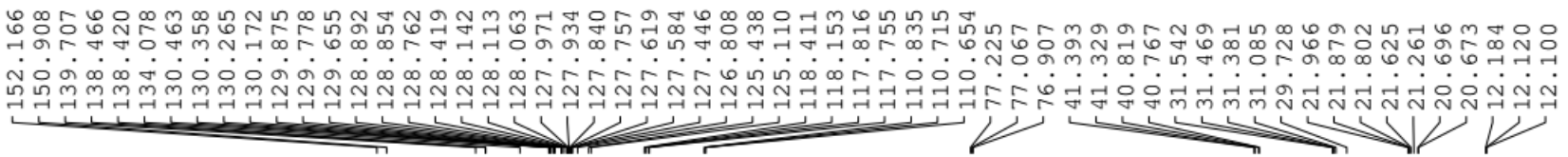
3be

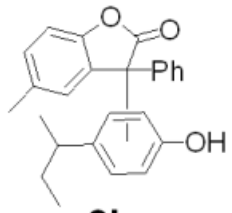

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.41
7.40
7.38
7.38
7.33
7.31
7.30
7.27
7.26
7.22
7.22
7.17
7.16
7.15
7.12
7.09
7.04
7.02
6.96
6.95
6.94
6.81
6.80
6.78
6.77
6.72
2.35
2.20
1.30
1.18
O
O
Ph
OH
3bf
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
7.31
2.54
1.21
1.41
1.90
1.15
3.37
5.44

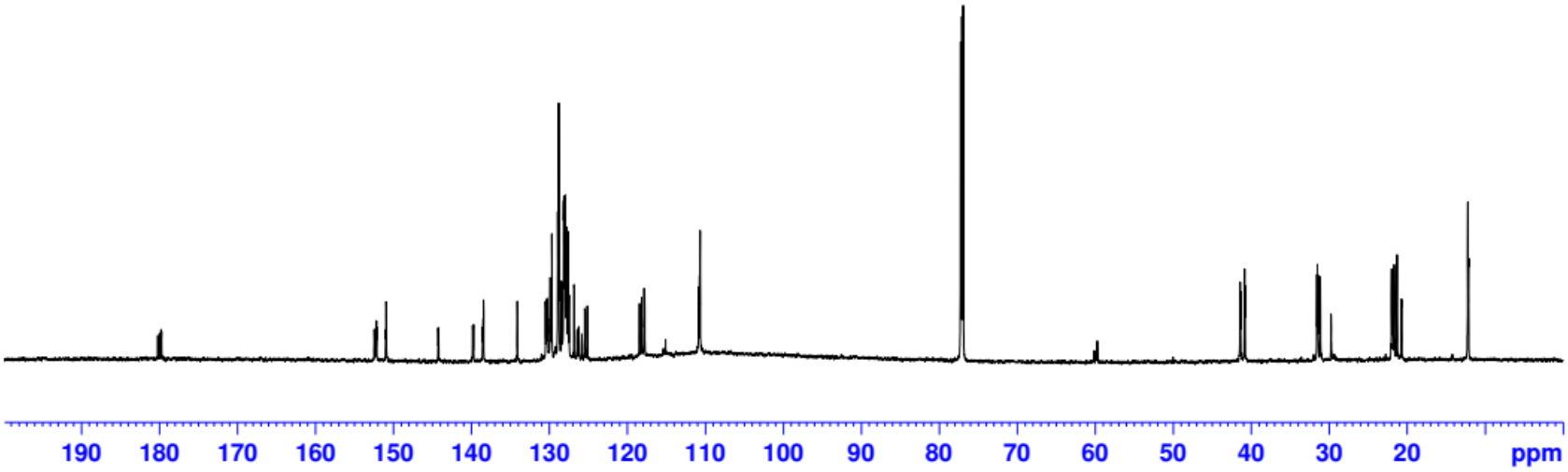

179.80
152.27
151.95
150.81
150.63
147.79
143.28
138.42
134.07
130.34
129.87
129.65
128.85
128.76
128.12
127.77
127.62
126.82
126.54
126.01
125.63
123.48
118.27
117.55
110.68
110.29
77.45
77.02
76.60
60.00
34.74
34.21
31.53
31.37
21.20
20.71
O
O
Ph
OH
3bf
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

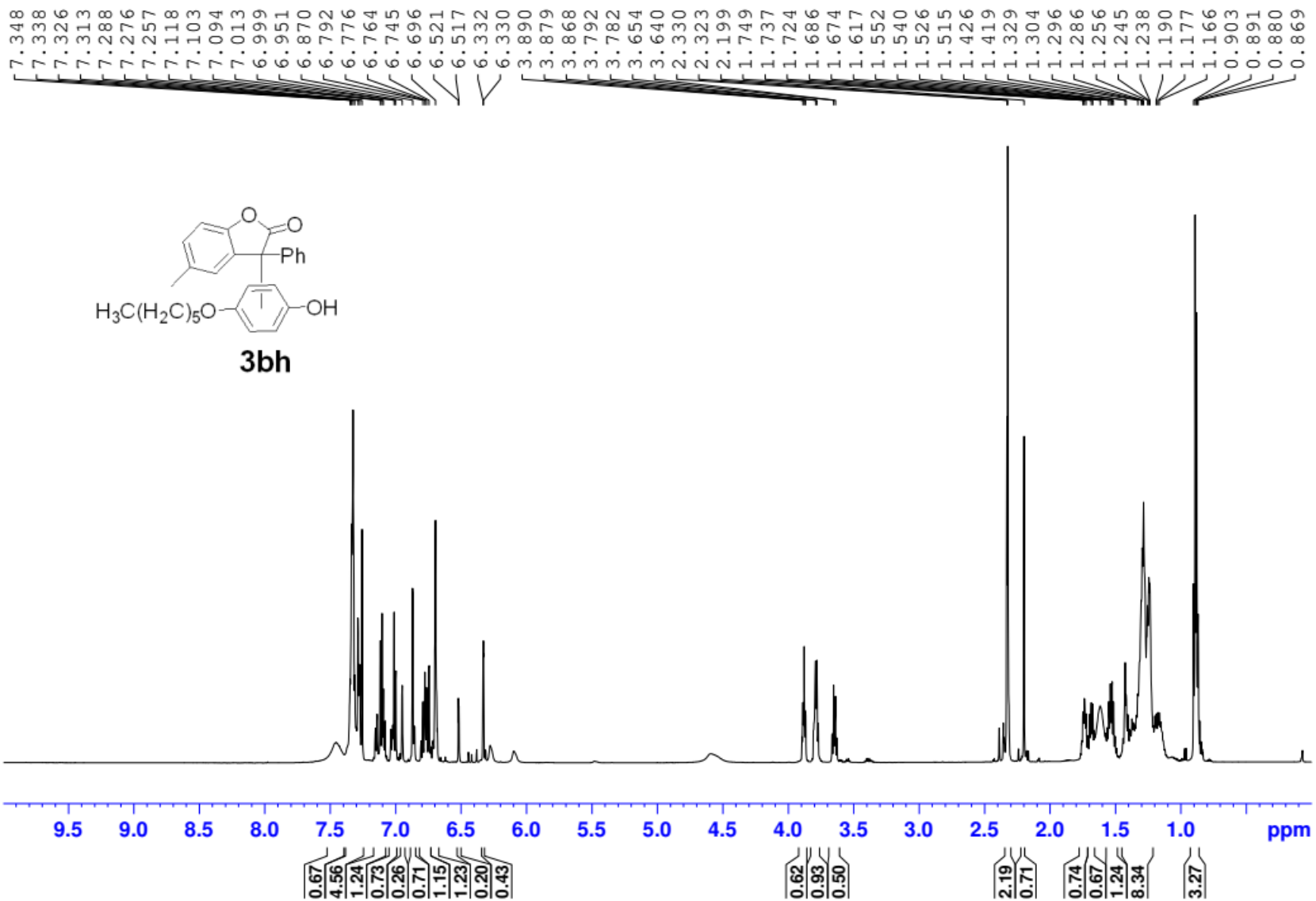

7.348
7.338
7.326
7.310
7.283
7.257
7.177
7.162
7.148
7.136
7.102
7.088
7.041
7.036
7.032
7.029
6.944
6.940
6.916
6.809
6.798
6.790
6.787
6.778
6.731
6.720
6.718
6.710
2.591
2.442
2.431
2.338
2.187
2.182
1.588
1.576
1.564
1.552
1.540
1.464
1.456
1.450
1.445
1.438
1.261
1.217
1.206
1.197
1.186
1.129
1.116
1.103
0.830
0.818
0.806
0.785
0.773
0.761
O
O
Ph
OH
3bg
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.96
2.21
1.14
1.08
1.09
1.12
0.50
0.57
1.83
1.64
1.53
1.24
1.81
1.72
1.72
1.75

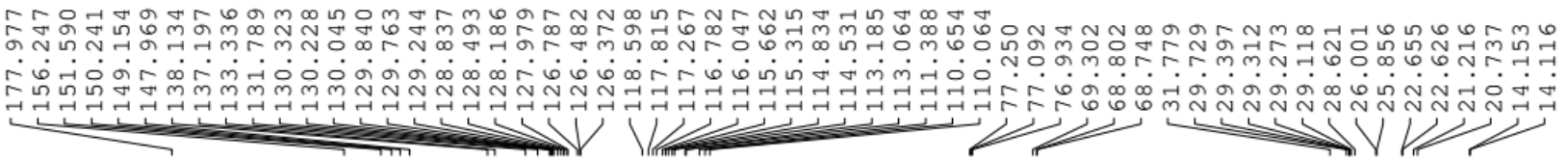

152.166
150.908
139.707
138.466
138.420
134.078
130.463
130.358
130.265
130.172
129.875
129.778
129.655
128.892
128.854
128.762
128.419
128.142
128.113
128.063
127.971
127.934
127.840
127.757
127.619
127.584
127.446
126.808
125.438
125.110
118.411
118.153
117.816
117.755
110.835
110.715
110.654
77.225
77.067
76.907
41.393
41.329
40.819
40.767
31.542
31.469
31.381
31.085
29.728
21.966
21.879
21.802
21.625
21.261
20.696
20.673
12.184
12.120
12.100

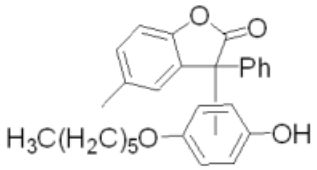

O
O
Ph
OH

3bg

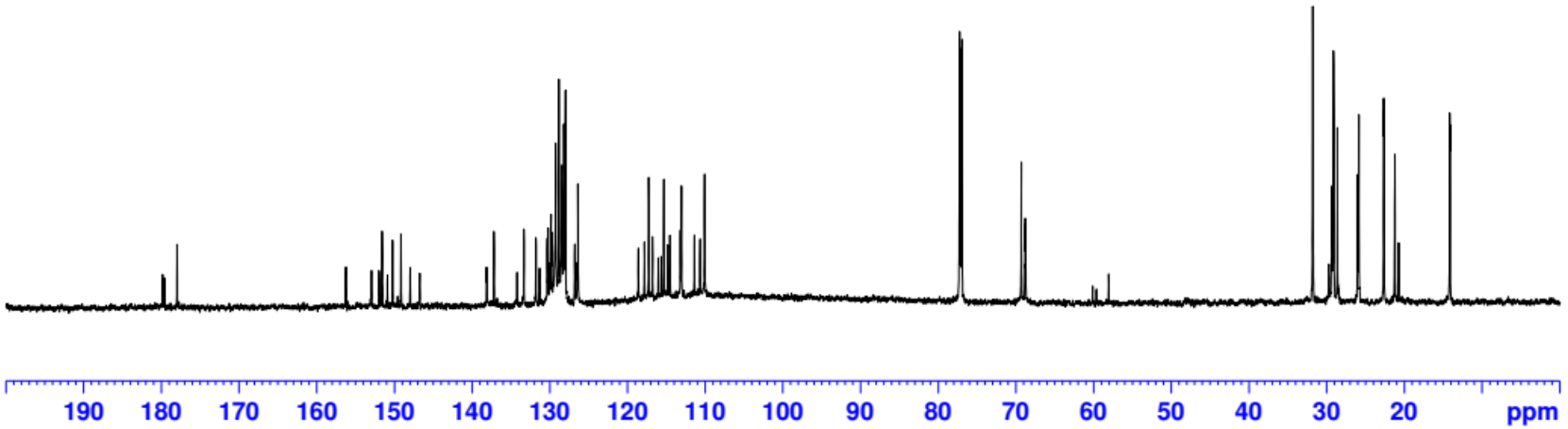

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

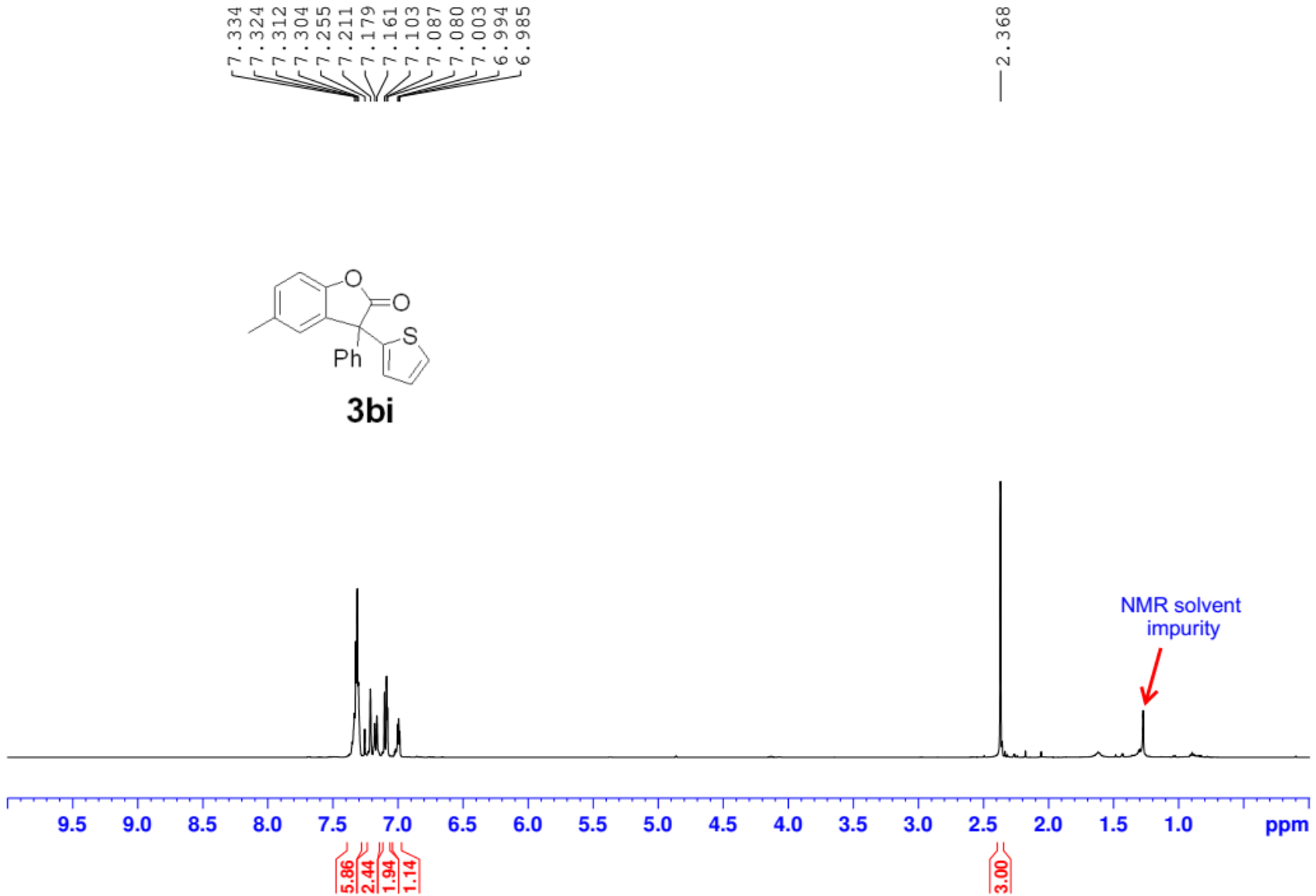

7.348
7.338
7.326
7.313
7.288
7.276
7.257
7.118
7.103
7.094
7.013
6.999
6.951
6.870
6.792
6.776
6.764
6.745
6.696
6.521
6.517
6.332
6.330
3.890
3.879
3.868
3.792
3.782
3.654
3.640
2.330
2.323
2.199
1.749
1.737
1.724
1.686
1.674
1.617
1.552
1.540
1.526
1.515
1.426
1.419
1.329
1.304
1.296
1.286
1.256
1.245
1.238
1.190
1.177
1.166
0.903
0.891
0.880
0.869
O
O
Ph
H3C(H2C)5O
OH
3bh
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.67
4.56
1.24
0.73
0.26
0.71
1.15
1.23
0.20
0.43
0.62
0.93
0.50
2.19
0.71
0.74
0.67
1.24
8.34
3.27

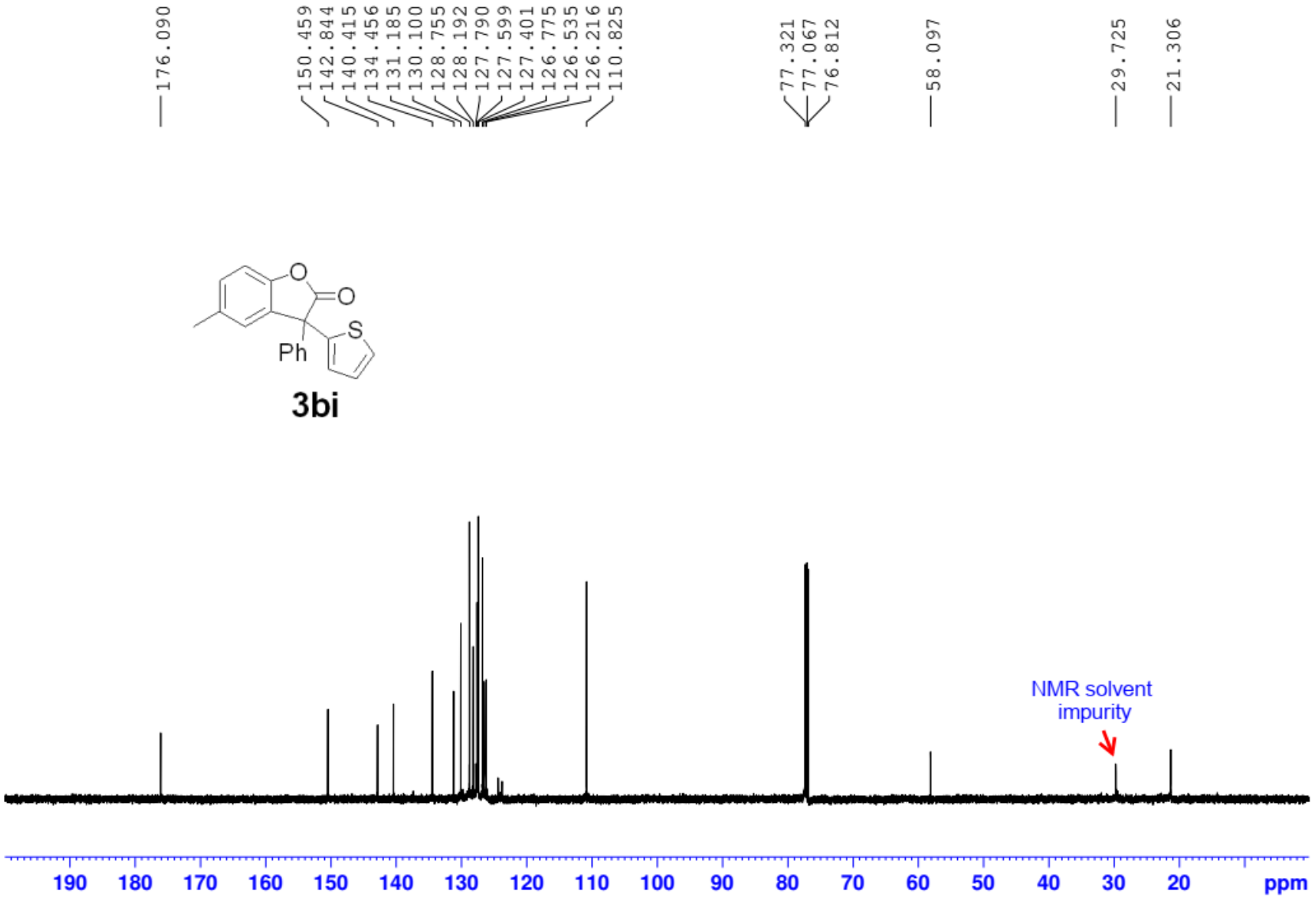

177.977
156.247
151.590
150.241
149.154
147.969
138.134
137.197
133.336
131.789
130.323
130.228
130.045
129.840
129.763
129.244
128.837
128.493
128.186
127.979
126.787
126.482
126.372
118.598
117.815
117.267
116.782
116.047
115.662
115.315
114.834
114.531
113.185
113.064
111.388
110.654
110.064
77.250
77.092
76.934
69.302
68.802
68.748
31.779
29.729
29.397
29.312
29.273
29.118
28.621
26.001
25.856
22.655
22.626
21.216
20.737
14.153
14.116


O
O
Ph
H3C(H2C)5O
OH

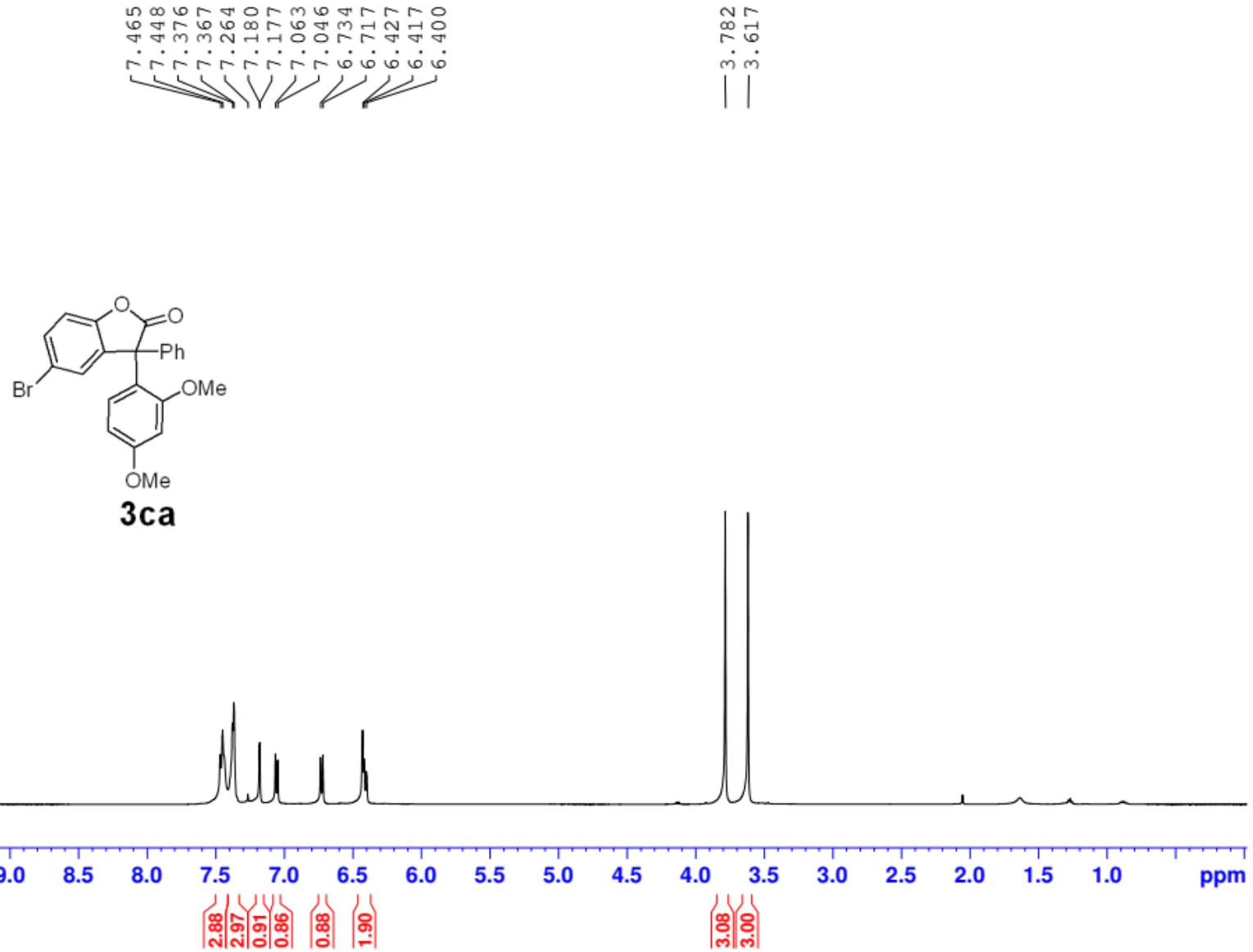
3bh

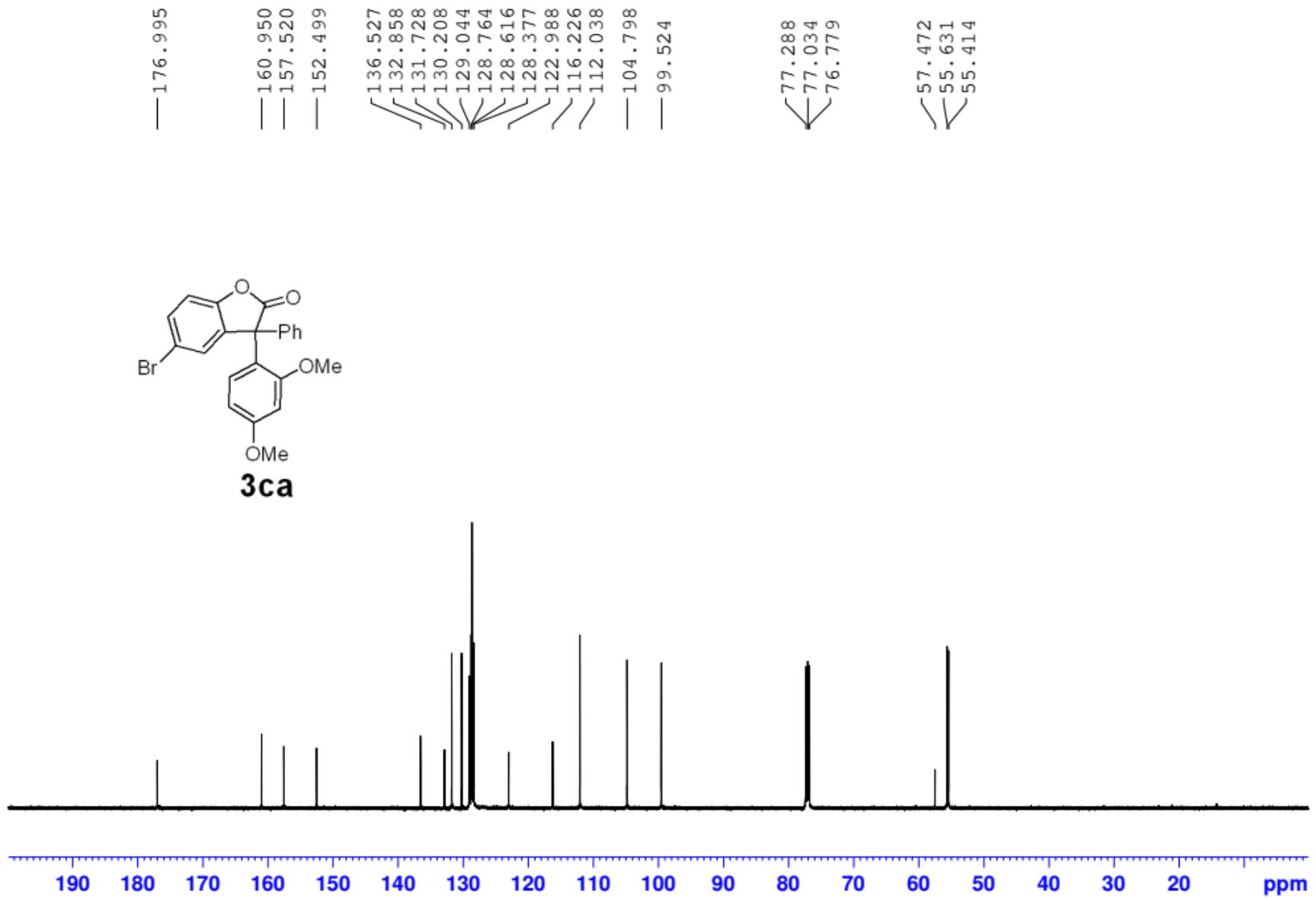

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

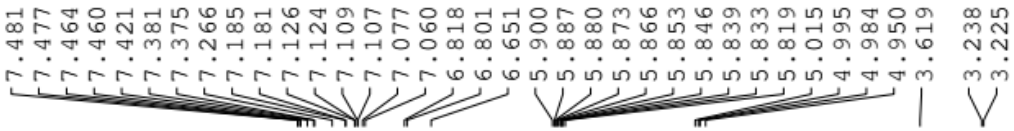

7.334
7.324
7.312
7.304
7.255
7.211
7.179
7.161
7.103
7.087
7.080
7.003
6.994
6.985
2.368
O
O
S
Ph
3bi
NMR solvent impurity
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.86
2.44
1.94
1.14
3.00

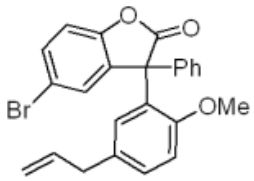

176.090
150.459
142.844
140.415
134.456
131.185
130.100
128.755
128.192
127.790
127.599
127.401
126.775
126.535
126.216
110.825
77.321
77.067
76.812
58.097
29.725
21.306
O
O
S
Ph
NMR solvent
impurity
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

3bi

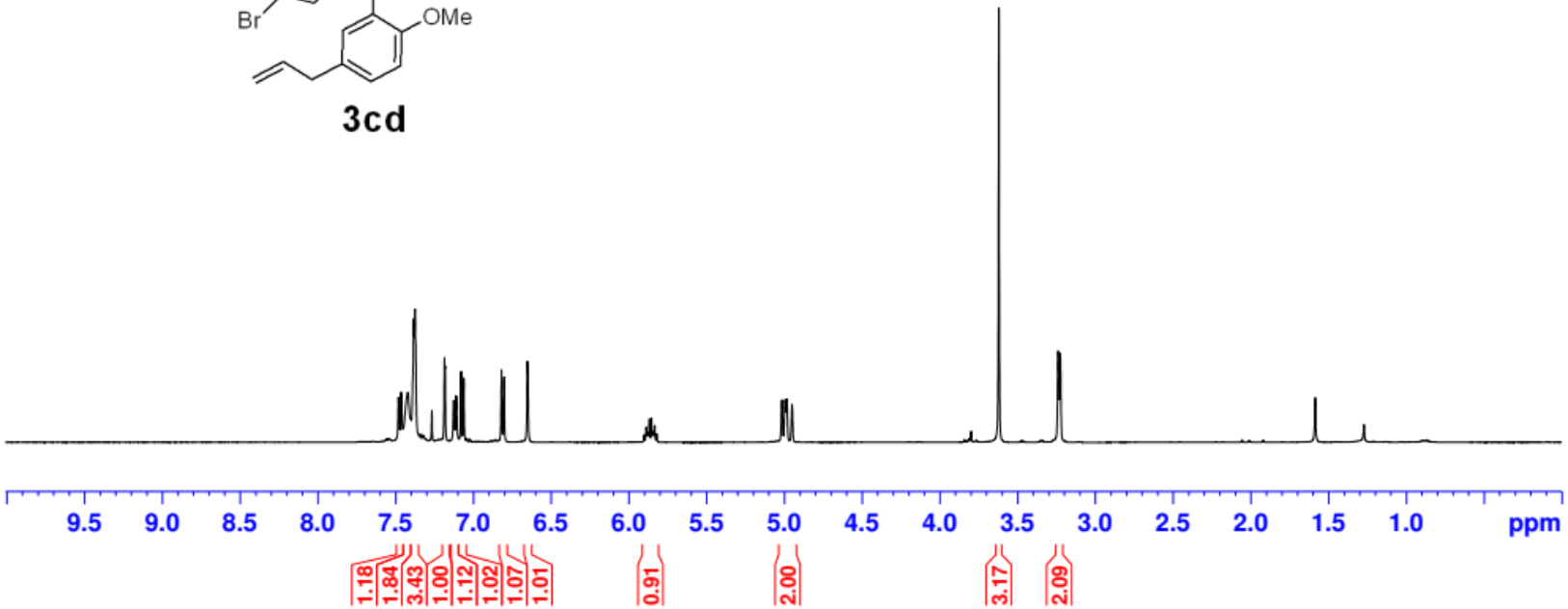

7.465
7.448
7.376
7.367
7.264
7.180
7.177
7.063
7.046
6.734
6.717
6.427
6.417
6.400
3.782
3.617
O
O
Ph
Br
OMe
OMe
3ca
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.88
2.97
0.91
0.86
0.88
1.90
3.08
3.00

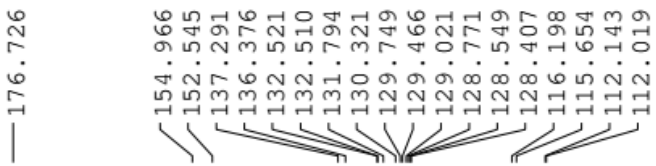

176.995
160.950
157.520
152.499
136.527
132.858
131.728
130.208
129.044
128.764
128.616
128.377
122.988
116.226
112.038
104.798
99.524
77.288
77.034
76.779
57.472
55.631
55.414
O
O
Ph
Br
OMe
OMe
3ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

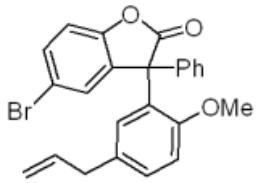

7.481
7.477
7.464
7.460
7.421
7.381
7.375
7.266
7.185
7.181
7.126
7.124
7.109
7.107
7.077
7.060
6.818
6.801
6.651
5.900
5.887
5.880
5.873
5.866
5.853
5.846
5.839
5.833
5.819
5.015
4.995
4.984
4.950
3.619
3.238
3.225


O
O
Ph
Br
OMe

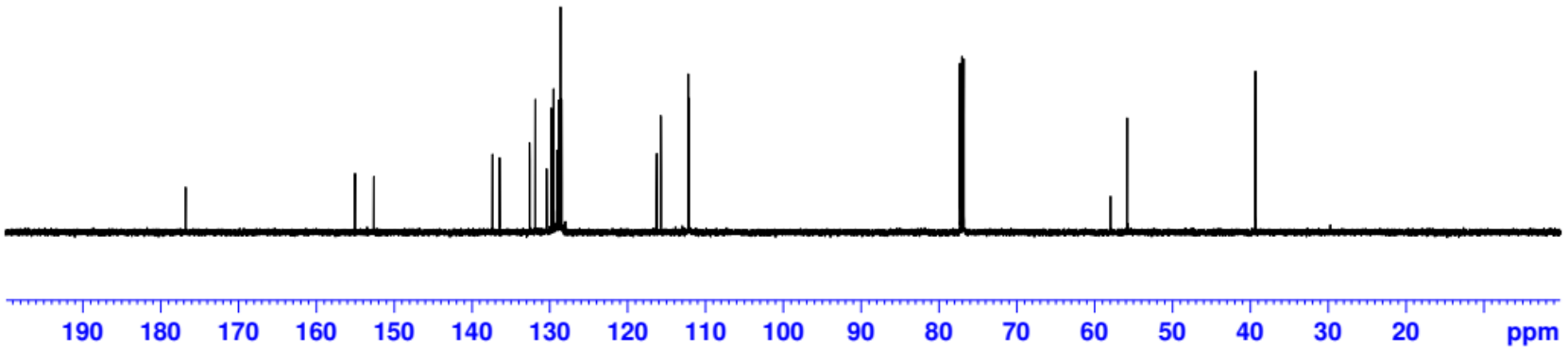
3cd

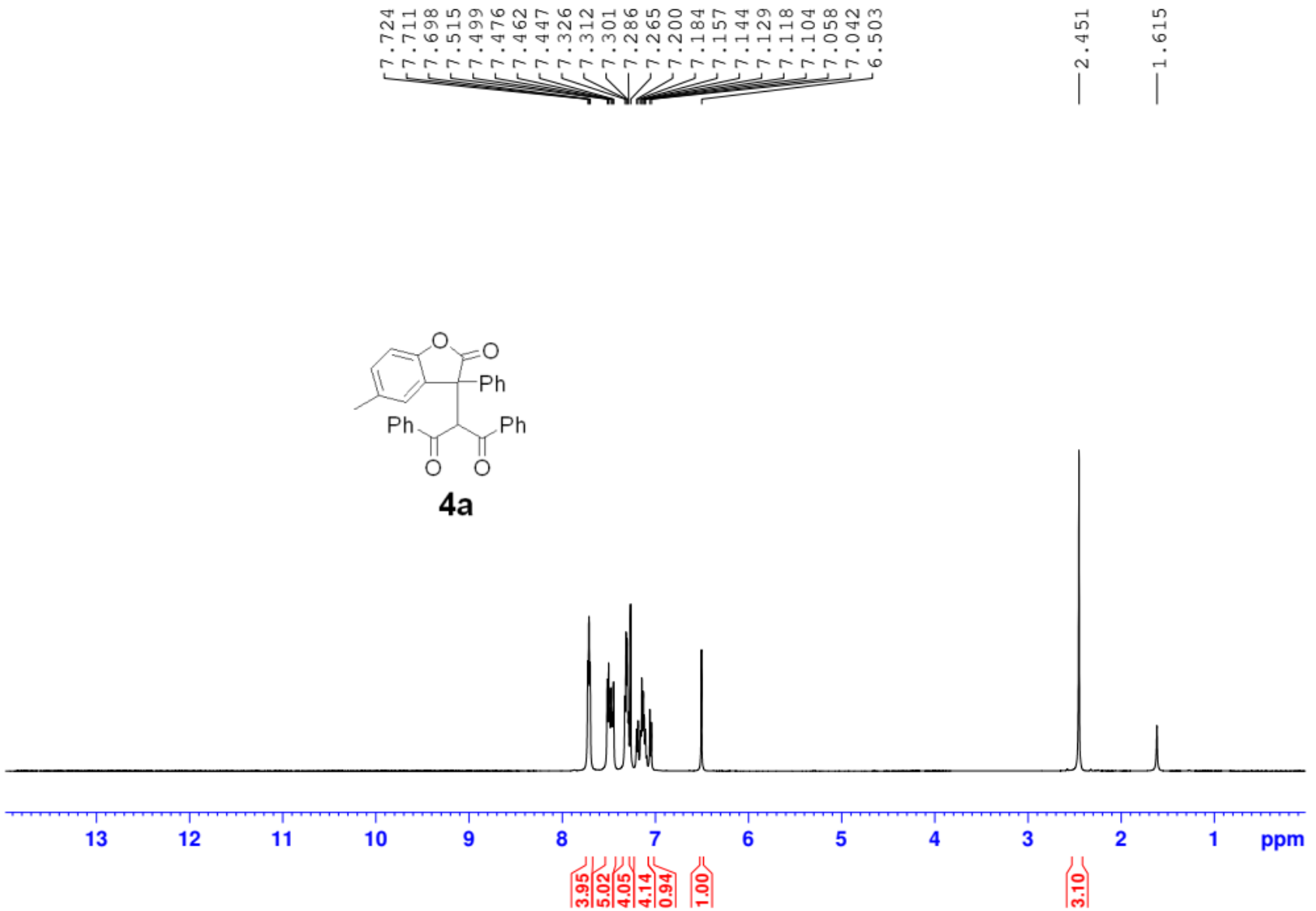

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.18
1.84
3.43
1.00
1.12
1.02
1.07
1.01
0.91
2.00
3.17
2.09


176.726
154.966
152.545
137.291
136.376
132.521
132.510
131.794
130.321
129.749
129.466
129.021
128.771
128.549
128.407
116.198
115.654
112.143
112.019
77.245
76.991
76.736
57.900
55.752
39.276

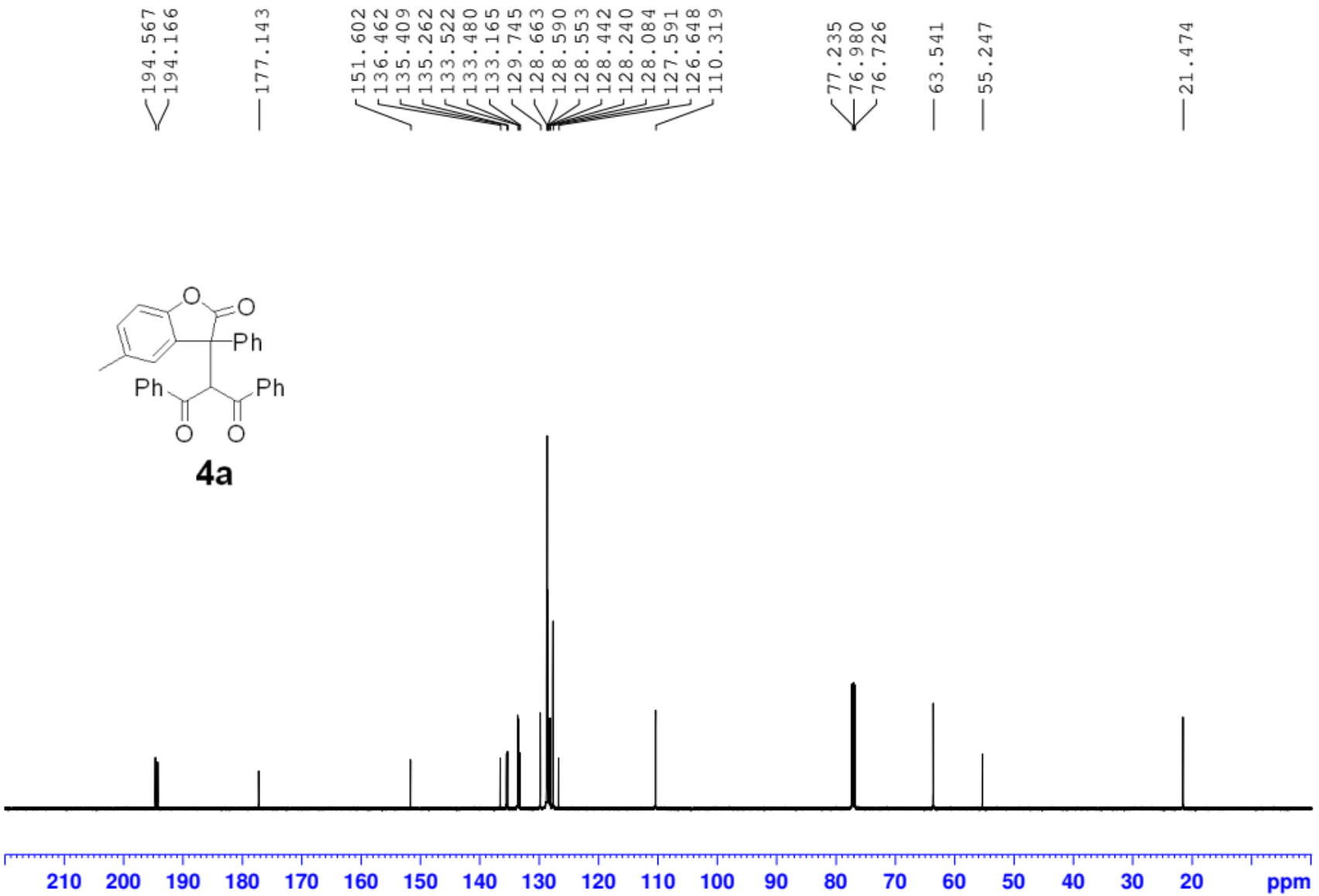

O
O
Ph
Br
OMe

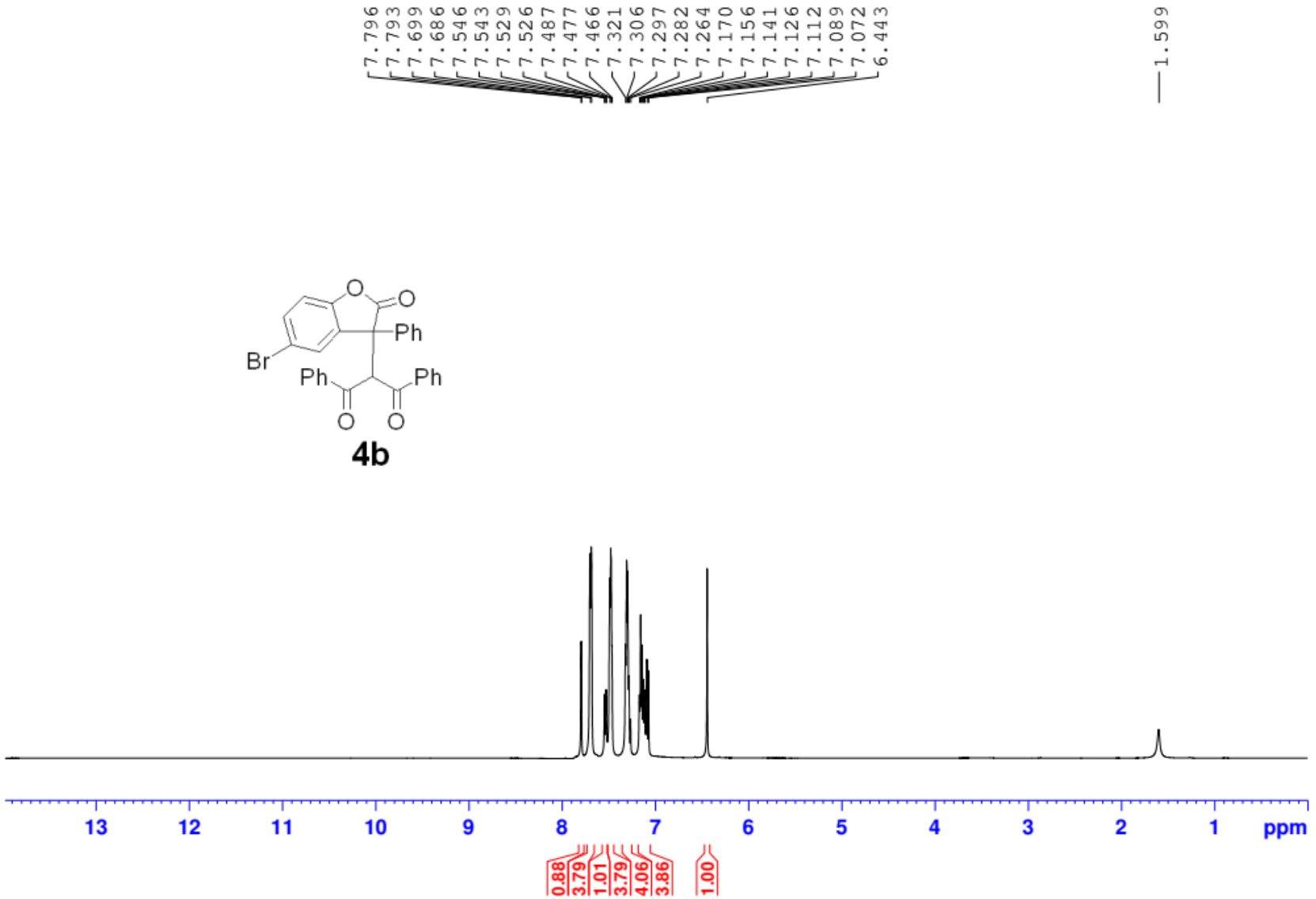
3cd


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.724
7.711
7.698
7.515
7.499
7.476
7.462
7.447
7.326
7.312
7.301
7.286
7.265
7.200
7.184
7.157
7.144
7.129
7.118
7.104
7.058
7.042
6.503
2.451
1.615
O
O
Ph
Ph
Ph
O
O
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
3.95
5.02
4.05
4.14
0.94
1.00
3.10

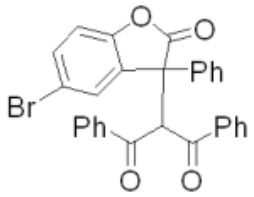
4a


194.567
194.166
177.143
151.602
136.462
135.409
135.262
133.522
133.480
133.165
129.745
128.663
128.590
128.553
128.442
128.240
128.084
127.591
126.648
110.319
77.235
76.980
76.726
63.541
55.247
21.474
O
O
Ph
Ph
Ph
O
O
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

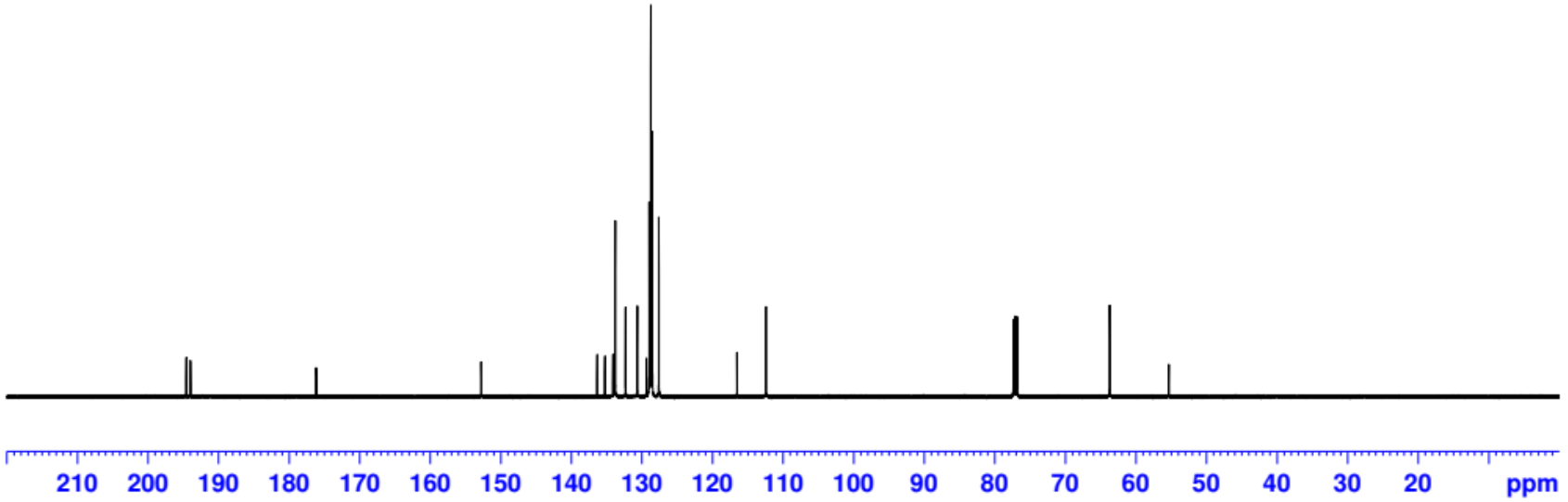

7.796
7.793
7.699
7.686
7.546
7.543
7.529
7.526
7.487
7.477
7.466
7.321
7.306
7.297
7.282
7.264
7.170
7.156
7.141
7.126
7.112
7.089
7.072
6.443
1.599
O
O
Ph
Br
Ph
Ph
O
O
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.88
3.79
1.01
3.79
4.06
3.86
1.00

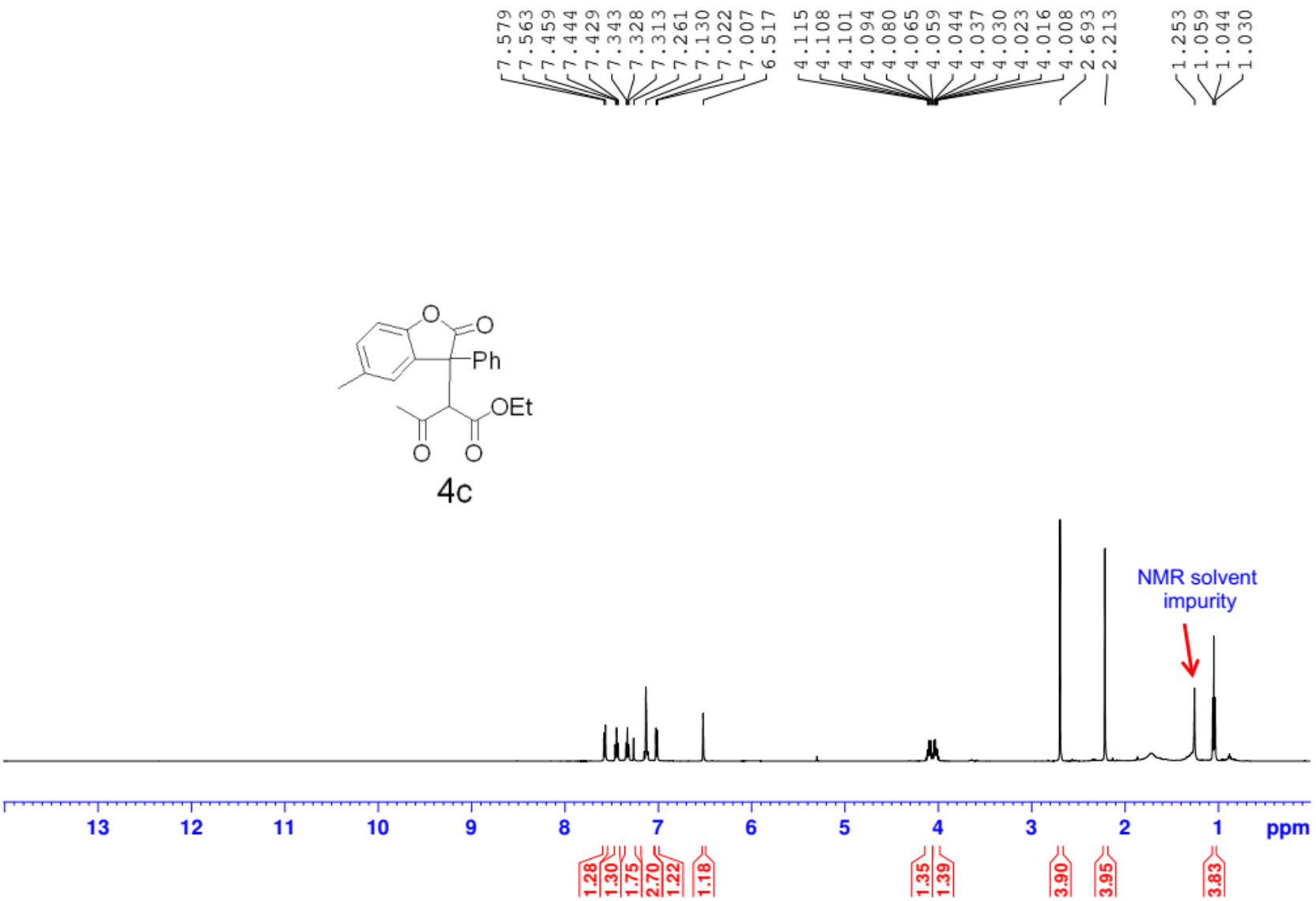
4b

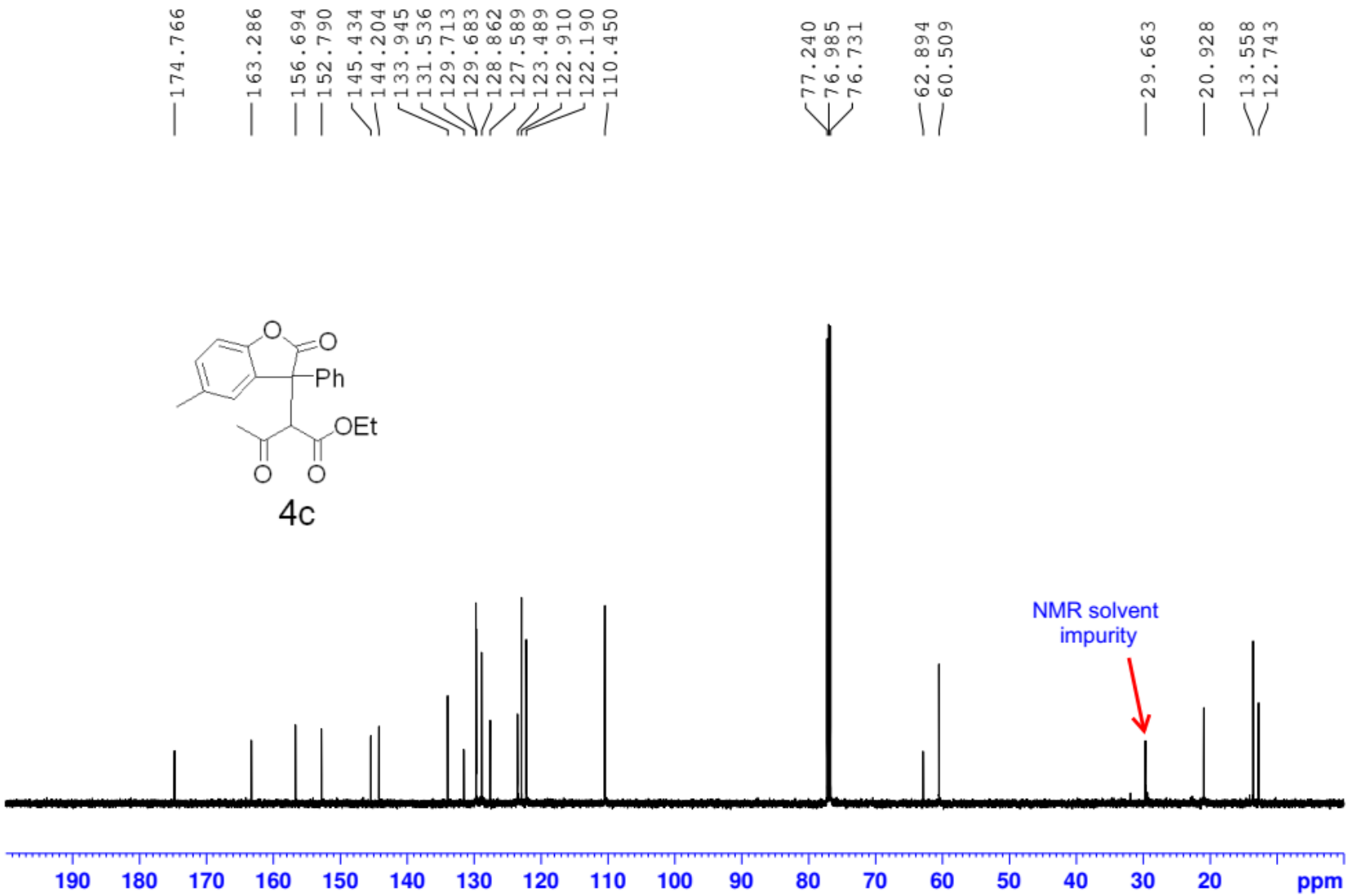
194.484
193.890
176.075
152.685
136.255
135.154
134.010
133.697
132.227
130.565
129.267
128.876
128.676
128.649
128.430
127.518
116.434
112.335
77.237
76.983
76.728
63.604
55.240

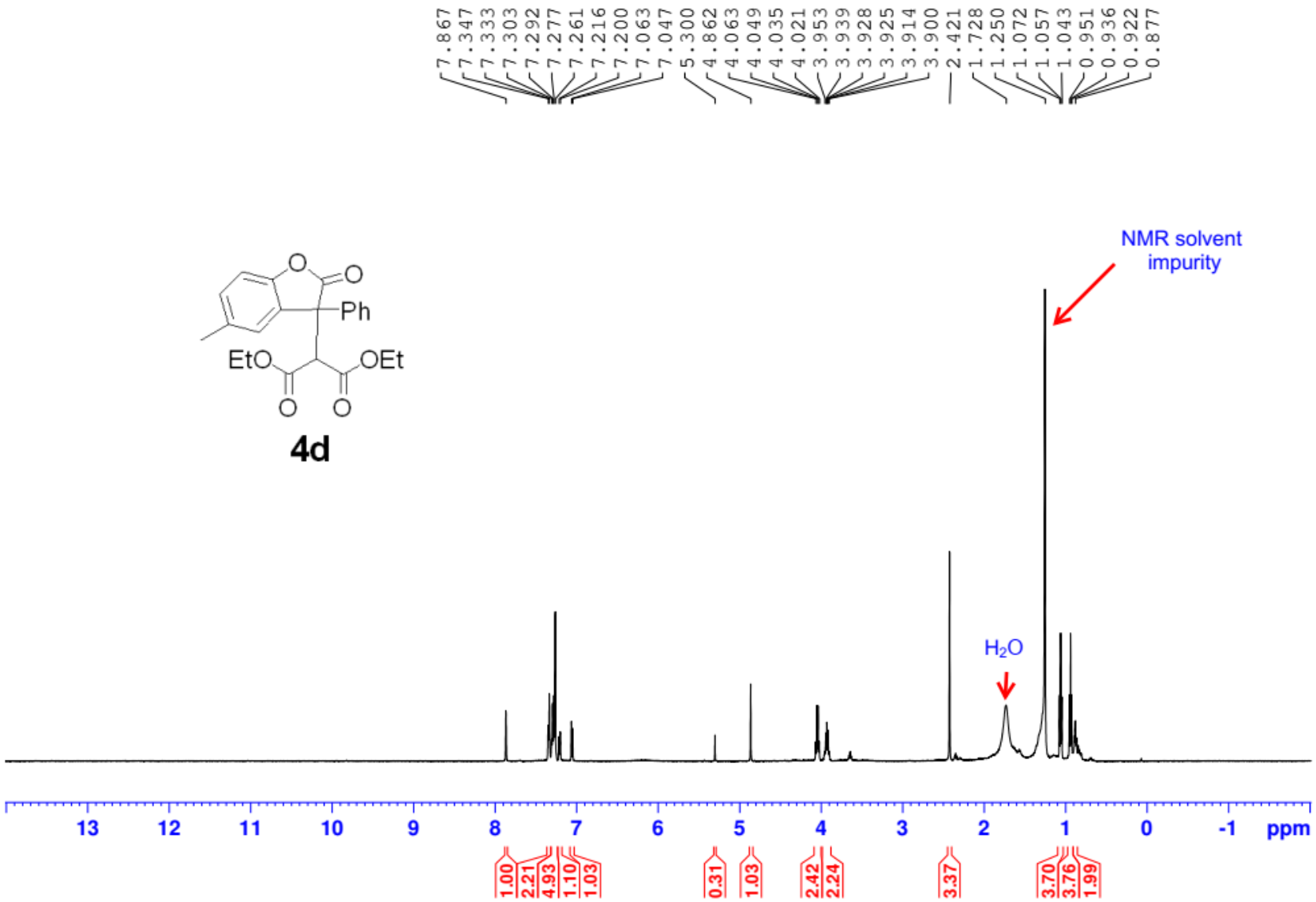


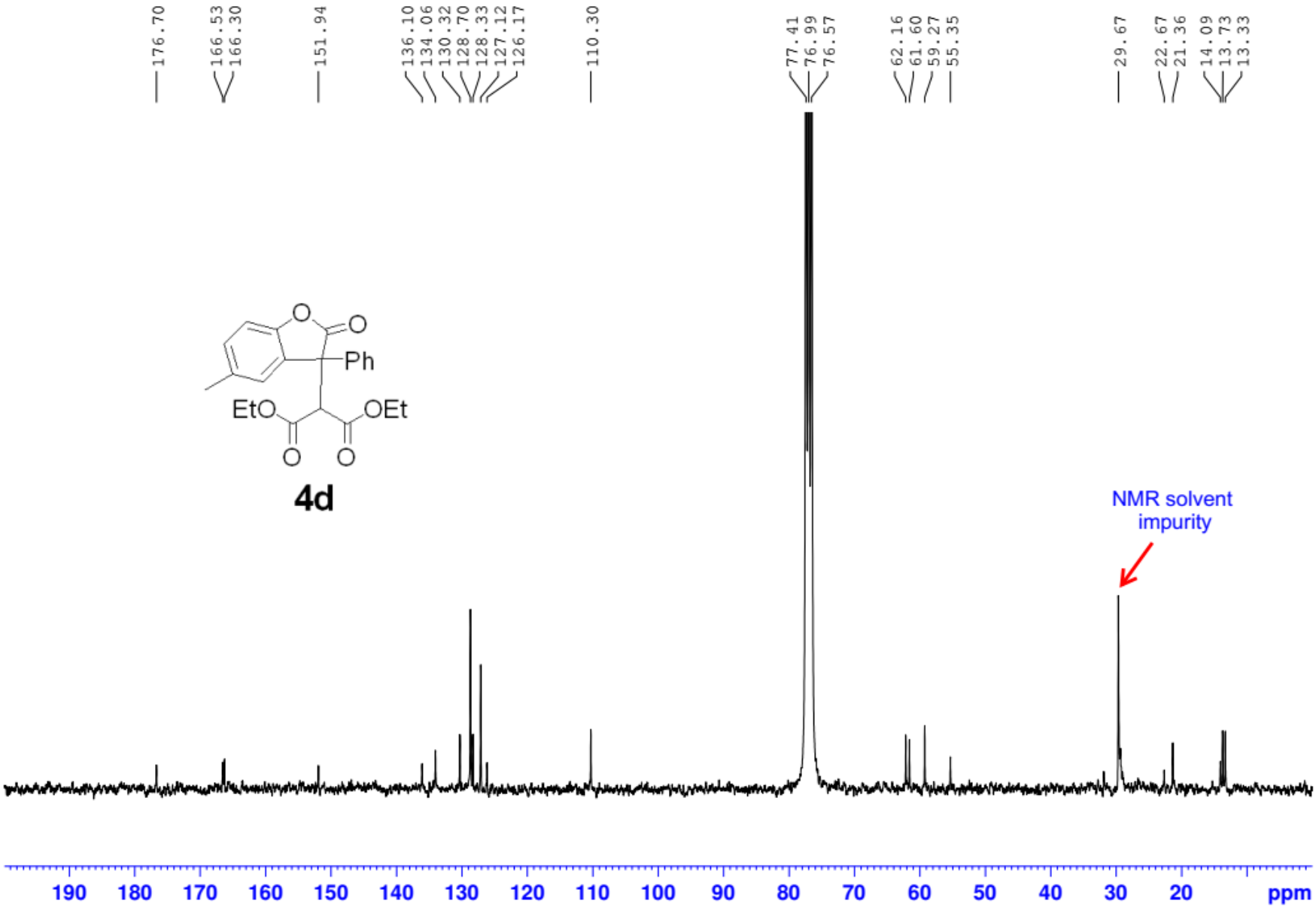
4b

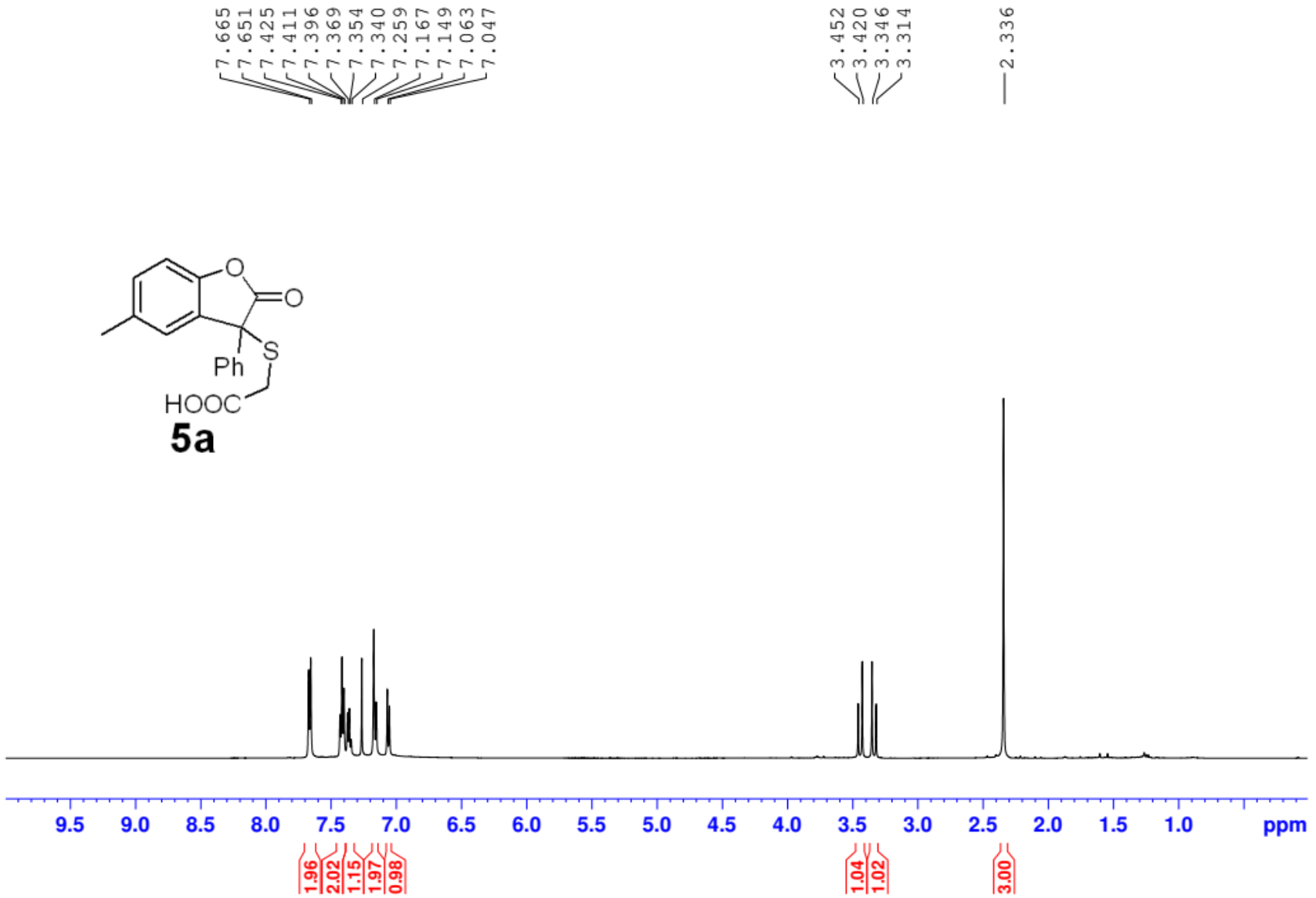


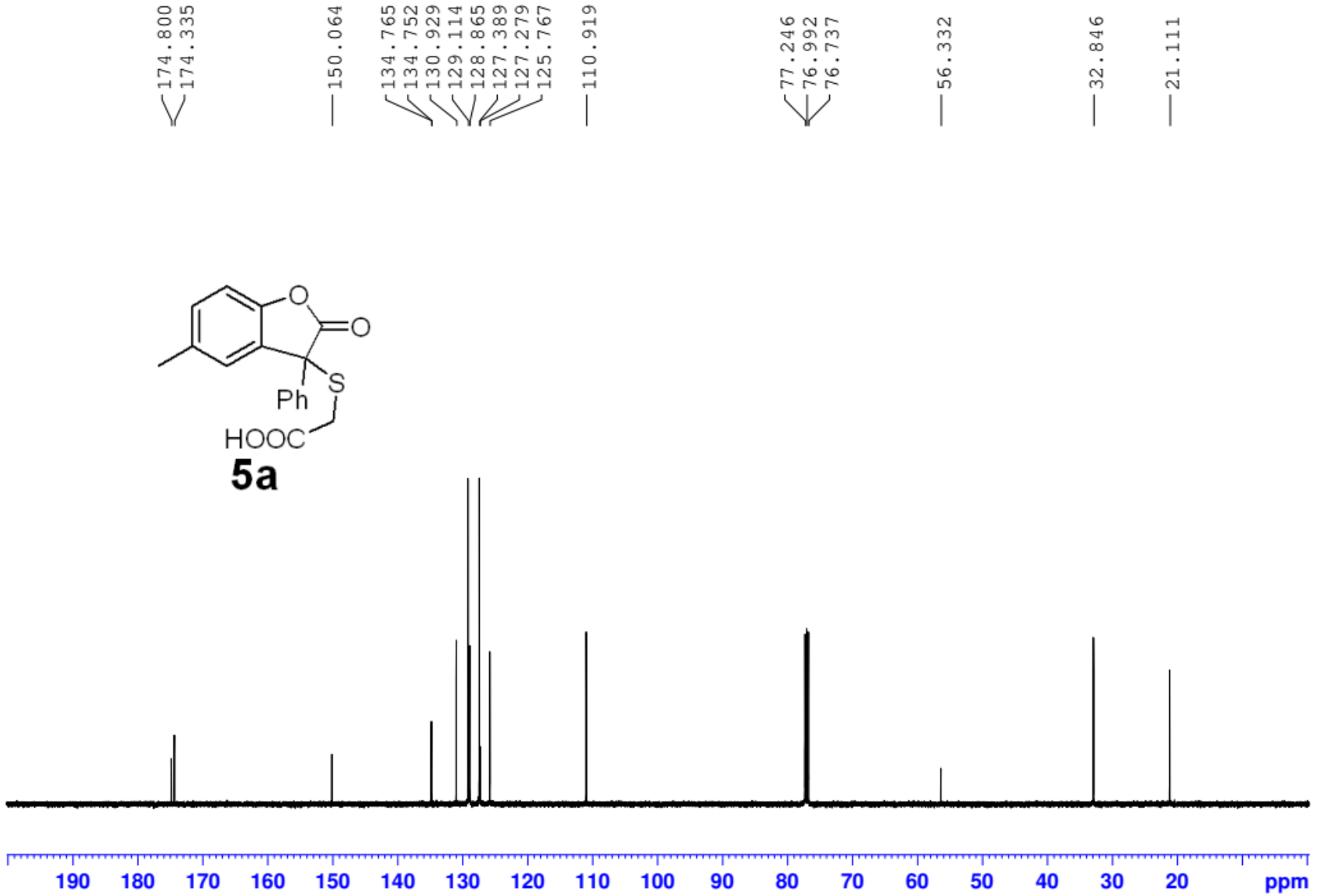

7.579
7.563
7.459
7.444
7.429
7.343
7.328
7.313
7.261
7.130
7.022
7.007
6.517
4.115
4.108
4.101
4.094
4.080
4.065
4.059
4.044
4.037
4.030
4.023
4.016
4.008
2.693
2.213
1.253
1.059
1.044
1.030
O
O
Ph
OEt
O
O
4c
NMR solvent impurity
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.28
1.30
1.75
2.70
1.22
1.18
1.35
1.39
3.90
3.95
3.83

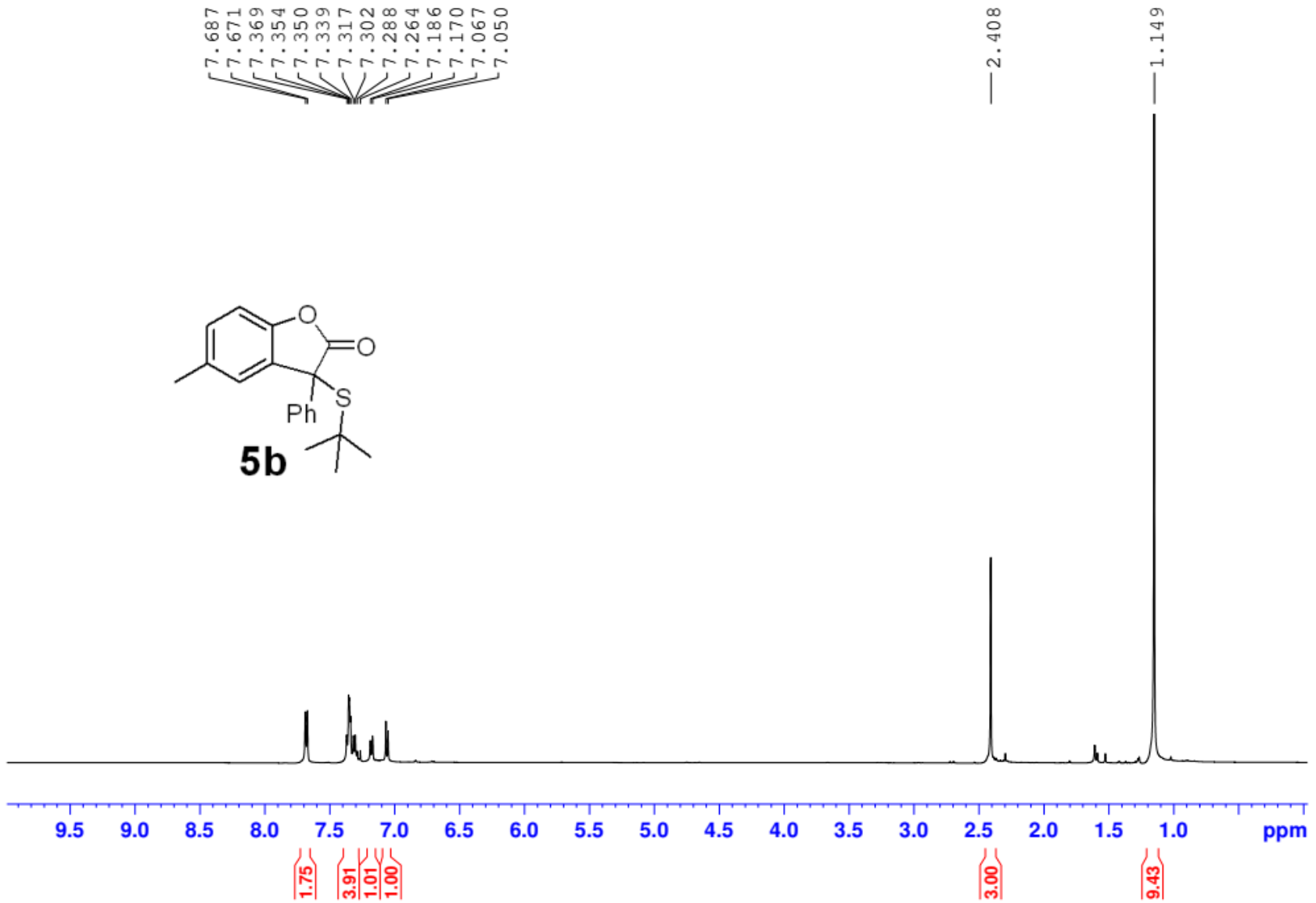

174.766
163.286
156.694
152.790
145.434
144.204
133.945
131.536
129.713
129.683
128.862
127.589
123.489
122.910
122.190
110.450
77.240
76.985
76.731
62.894
60.509
29.663
20.928
13.558
12.743
O
O
Ph
OEt
O
O
4c
NMR solvent
impurity
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

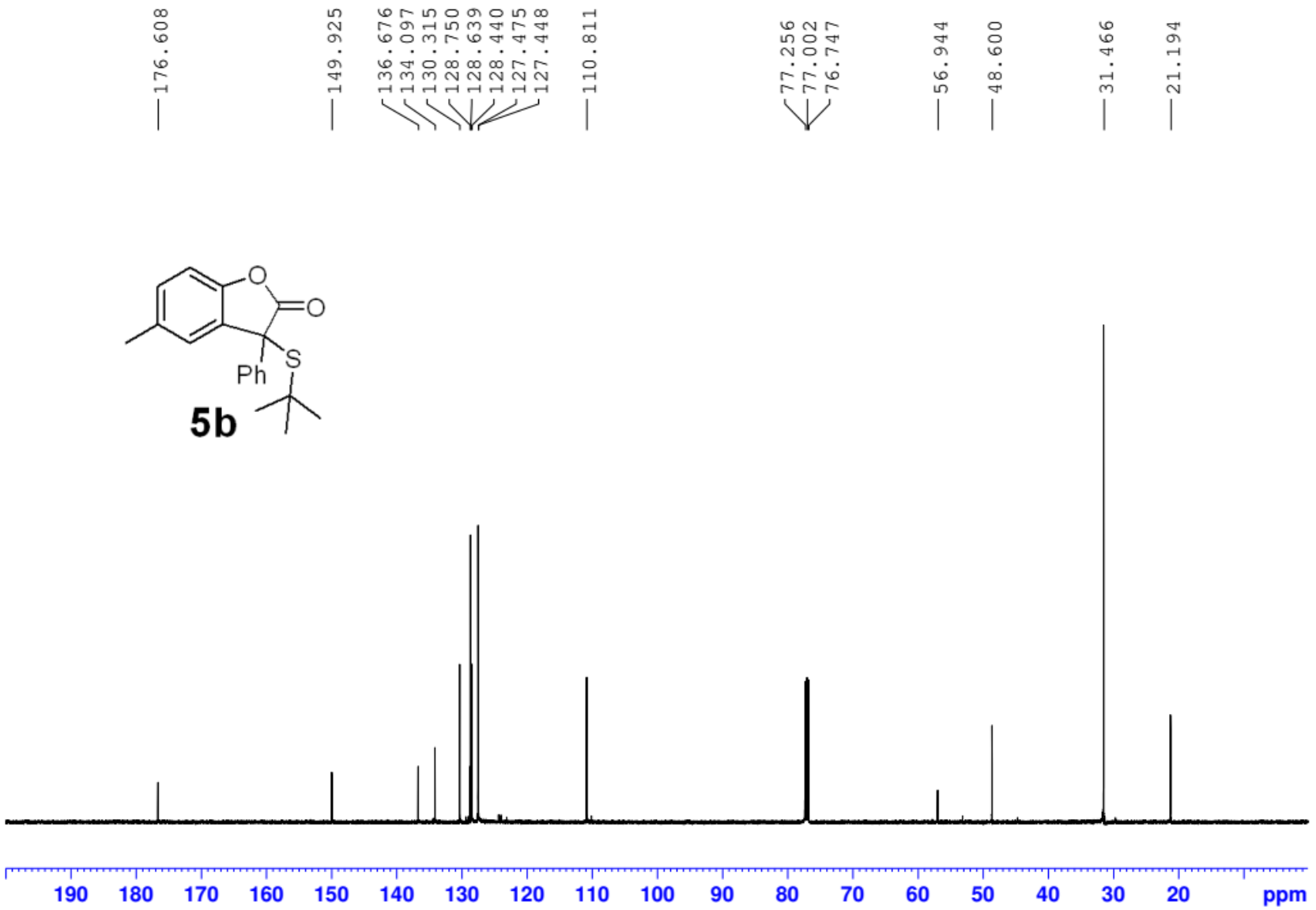

7.867
7.347
7.333
7.303
7.292
7.277
7.261
7.216
7.200
7.063
7.047
5.300
4.862
4.063
4.049
4.035
4.021
3.953
3.939
3.928
3.925
3.914
3.900
2.421
1.728
1.250
1.072
1.057
1.043
0.951
0.936
0.922
0.877
O
O
Ph
EtO
OEt
O
O
4d
NMR solvent impurity
H2O
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
2.21
4.93
1.10
1.03
0.31
1.03
2.42
2.24
3.37
3.70
3.76
1.99

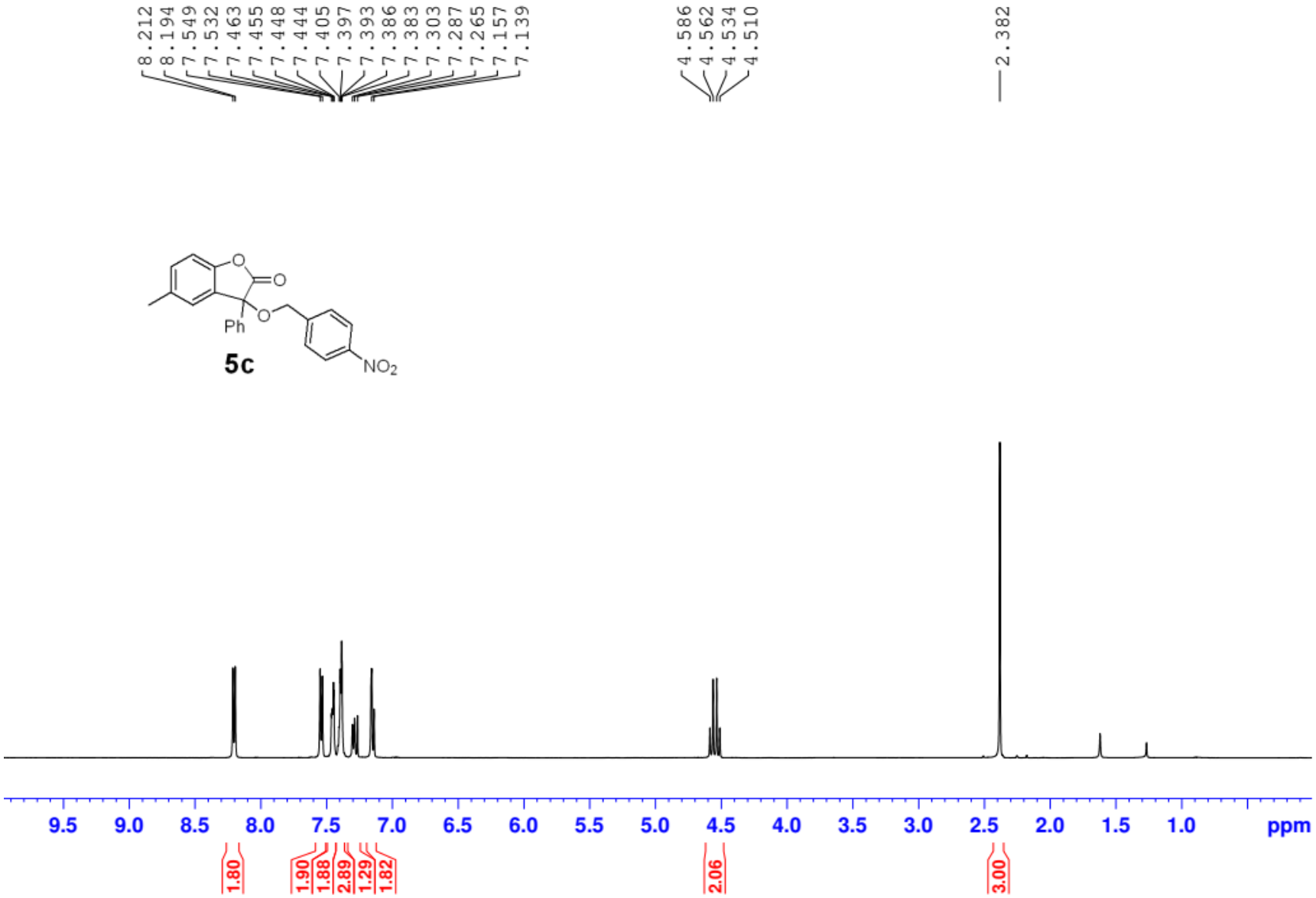

176.70
166.53
166.30
151.94
136.10
134.06
130.32
128.70
128.33
127.12
126.17
110.30
77.41
76.99
76.57
62.16
61.60
59.27
55.35
29.67
22.67
21.36
14.09
13.73
13.33
O
O
Ph
EtO
OEt
O
O
4d
NMR solvent
impurity
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.665
7.651
7.425
7.411
7.396
7.369
7.354
7.340
7.259
7.167
7.149
7.063
7.047
3.452
3.420
3.346
3.314
2.336
O
O
Ph
S
HOOC
5a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.96
2.02
1.15
1.97
0.98
1.04
1.02
3.00

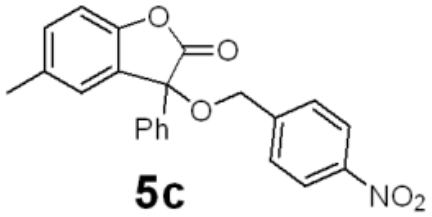

174.800
174.335
150.064
134.765
134.752
130.929
129.114
128.865
127.389
127.279
125.767
110.919
77.246
76.992
76.737
56.332
32.846
21.111
O
O
S
Ph
HOOC
5a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.687
7.671
7.369
7.354
7.350
7.339
7.317
7.302
7.288
7.264
7.186
7.170
7.067
7.050
2.408
1.149
O
O
S
Ph
5b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.75
3.91
1.01
1.00
3.00
9.43

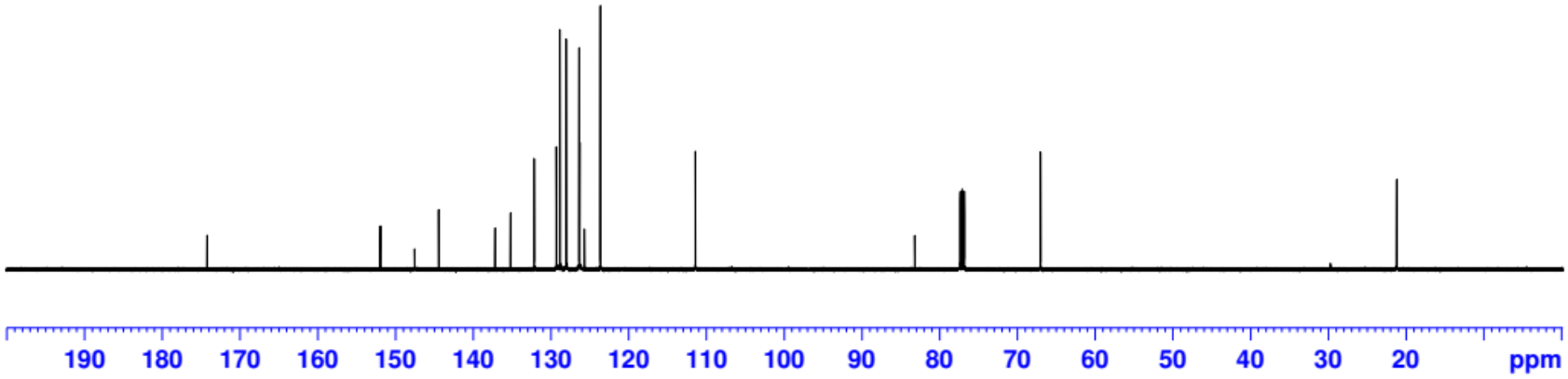

176.608
149.925
136.676
134.097
130.315
128.750
128.639
128.440
127.475
127.448
110.811
77.256
77.002
76.747
56.944
48.600
31.466
21.194
O
O
Ph
S
5b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

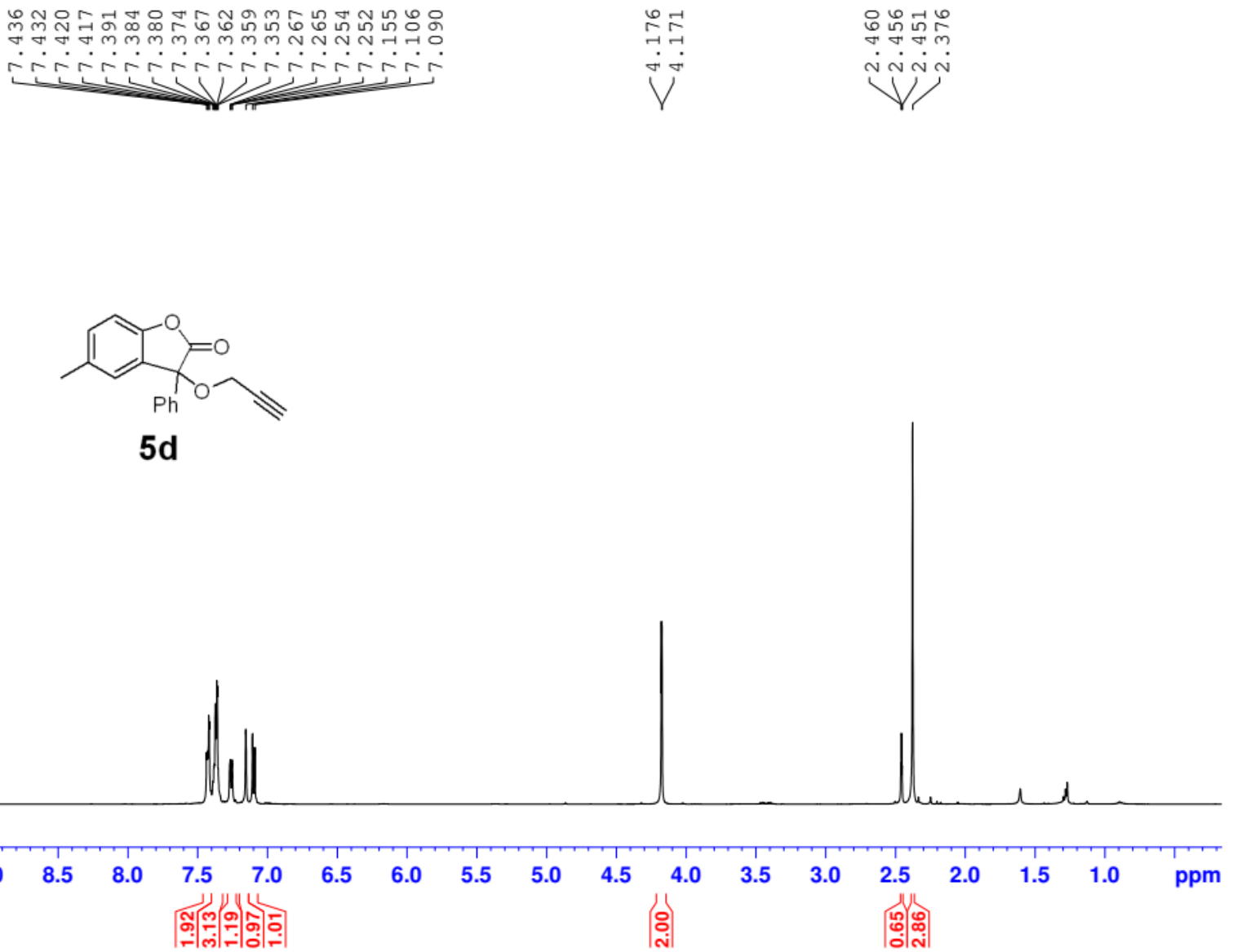

8.212
8.194
7.549
7.532
7.463
7.455
7.448
7.444
7.405
7.397
7.393
7.386
7.383
7.303
7.287
7.265
7.157
7.139
4.586
4.562
4.534
4.510
2.382
O
O
O
Ph
NO2
5c
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.80
1.90
1.88
2.89
1.29
1.82
2.06
3.00

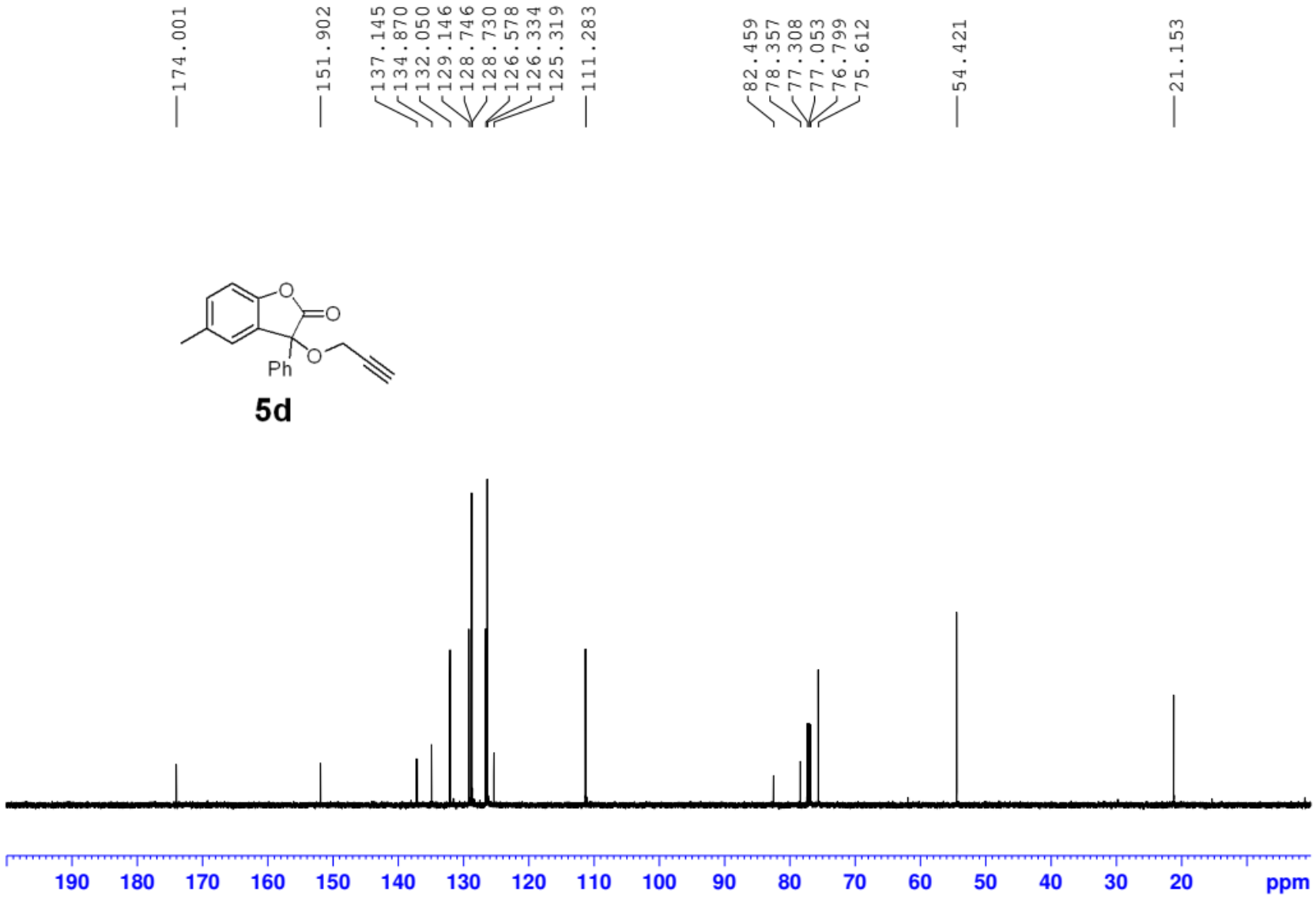
174.207
151.919
147.526
144.410
137.143
135.174
132.149
129.280
128.825
128.020
126.349
126.286
125.681
123.619
111.406
83.166
77.319
77.064
76.810
67.013
21.174

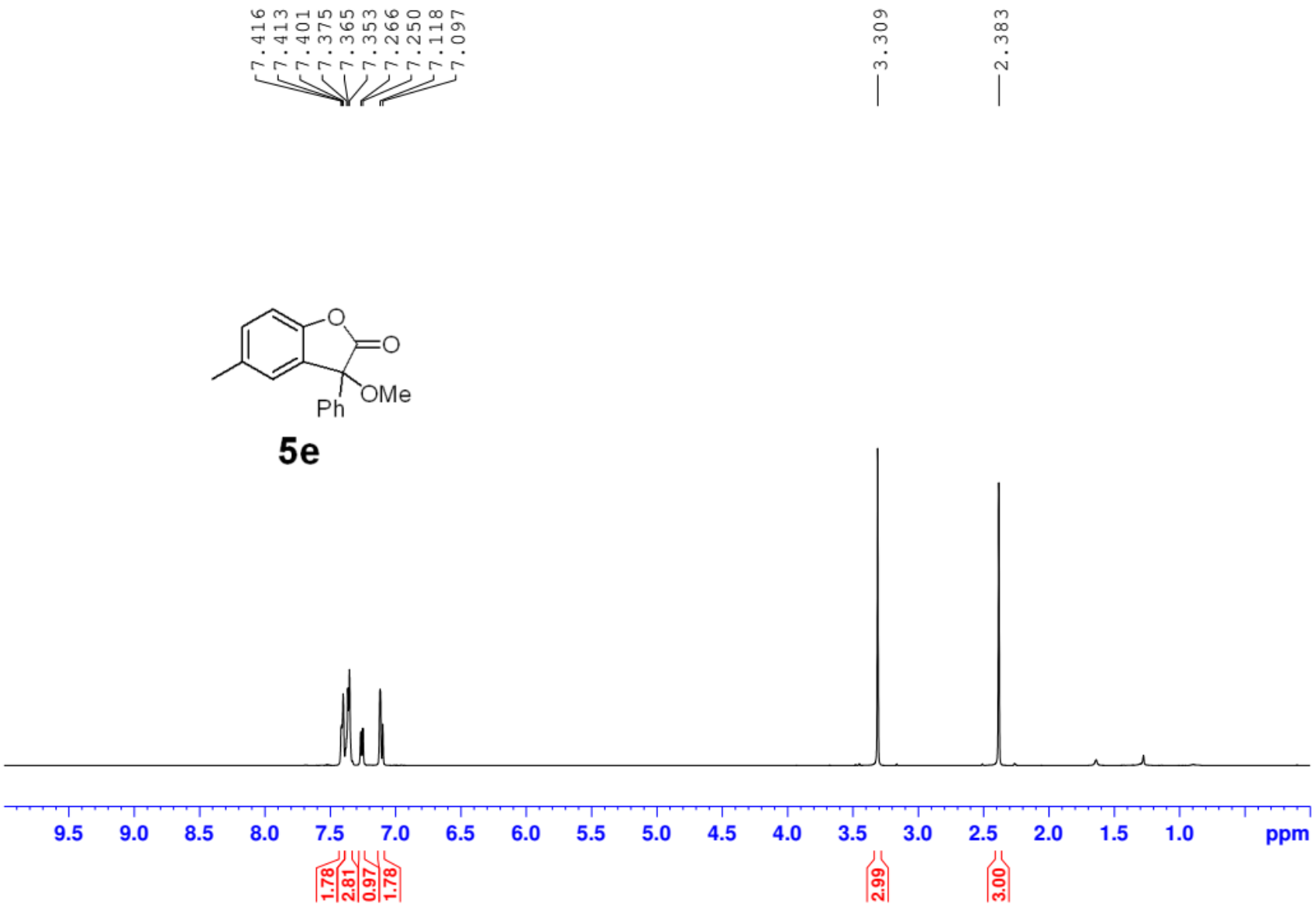


5c



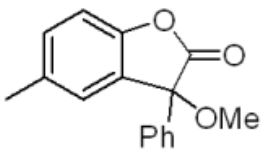

7.436
7.432
7.420
7.417
7.391
7.384
7.380
7.374
7.367
7.362
7.359
7.353
7.267
7.265
7.254
7.252
7.155
7.106
7.090
4.176
4.171
2.460
2.456
2.451
2.376
O
O
O
Ph
5d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.92
3.13
1.19
0.97
1.01
2.00
0.65
2.86


174.001
151.902
137.145
134.870
132.050
129.146
128.746
128.730
126.578
126.334
125.319
111.283
82.459
78.357
77.308
77.053
76.799
75.612
54.421
21.153
O
O
O
Ph
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

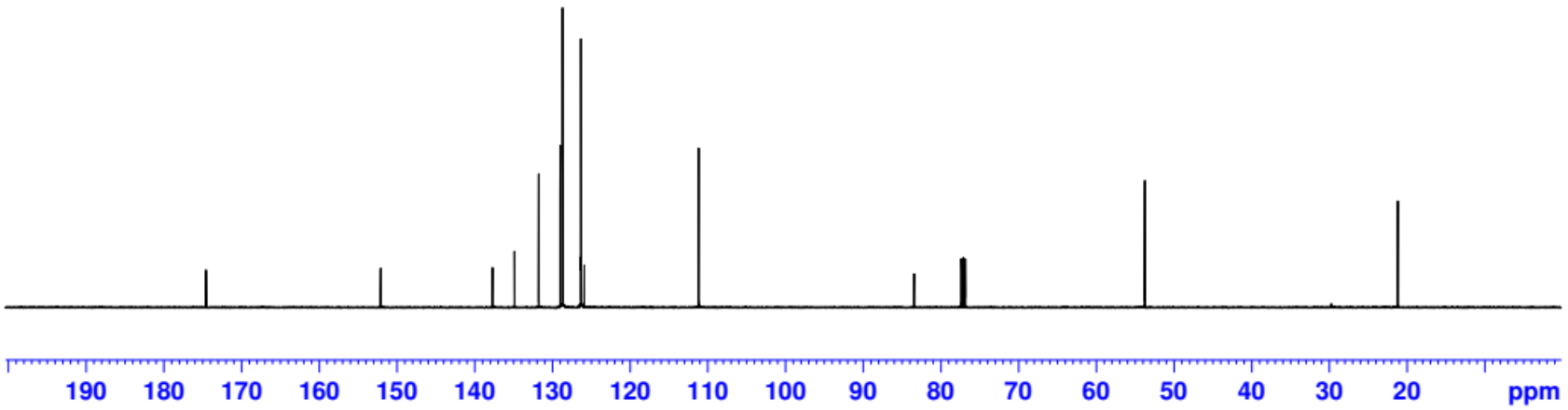

7.416
7.413
7.401
7.375
7.365
7.353
7.266
7.250
7.118
7.097
3.309
2.383
O
O
OMe
Ph
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.78
2.81
0.97
1.78
2.99
3.00

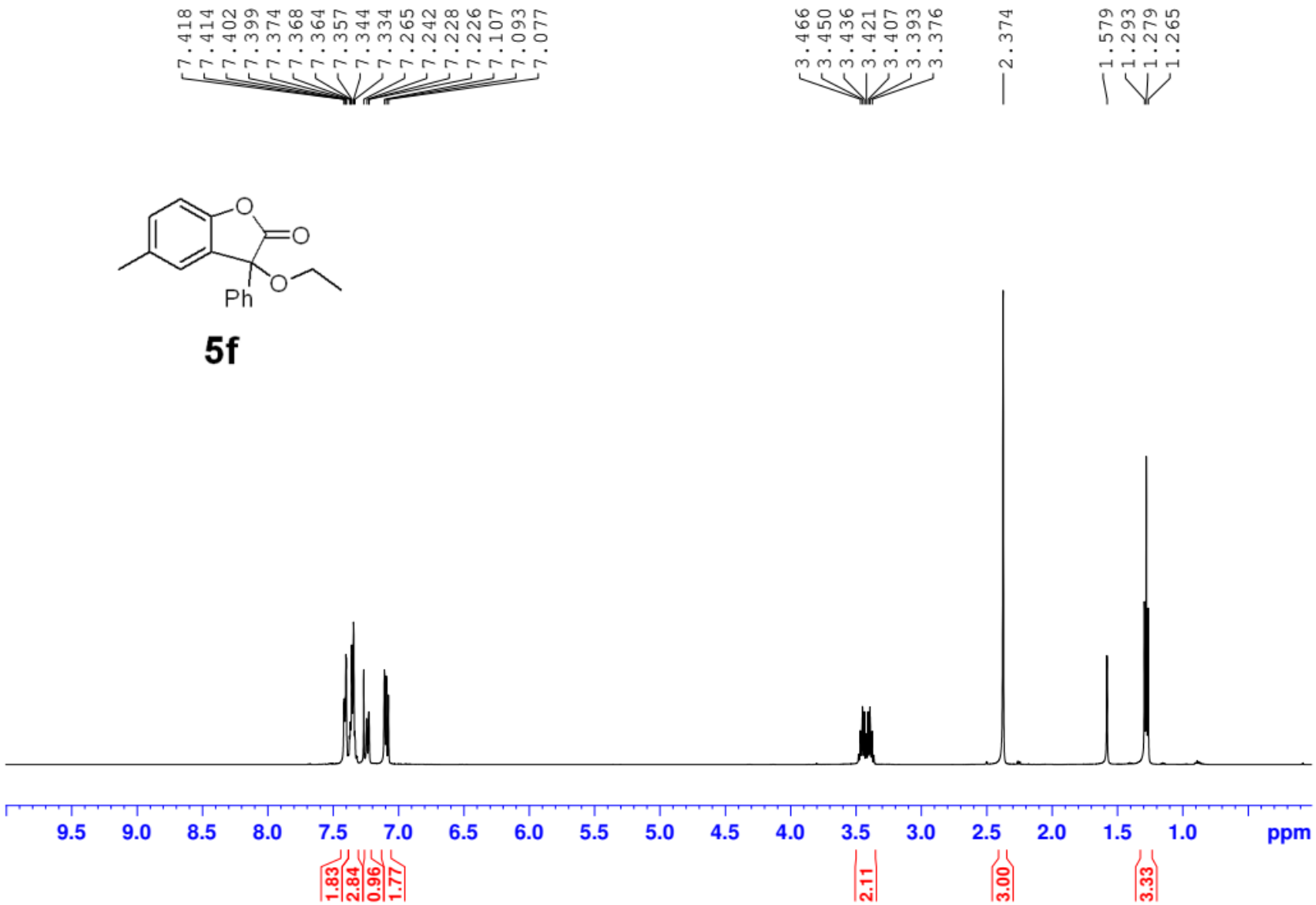
5e

174.549
152.073
137.665
134.857
131.733
128.965
128.649
126.317
126.295
125.864
111.140
83.420
77.334
77.079
76.825
53.722
21.162

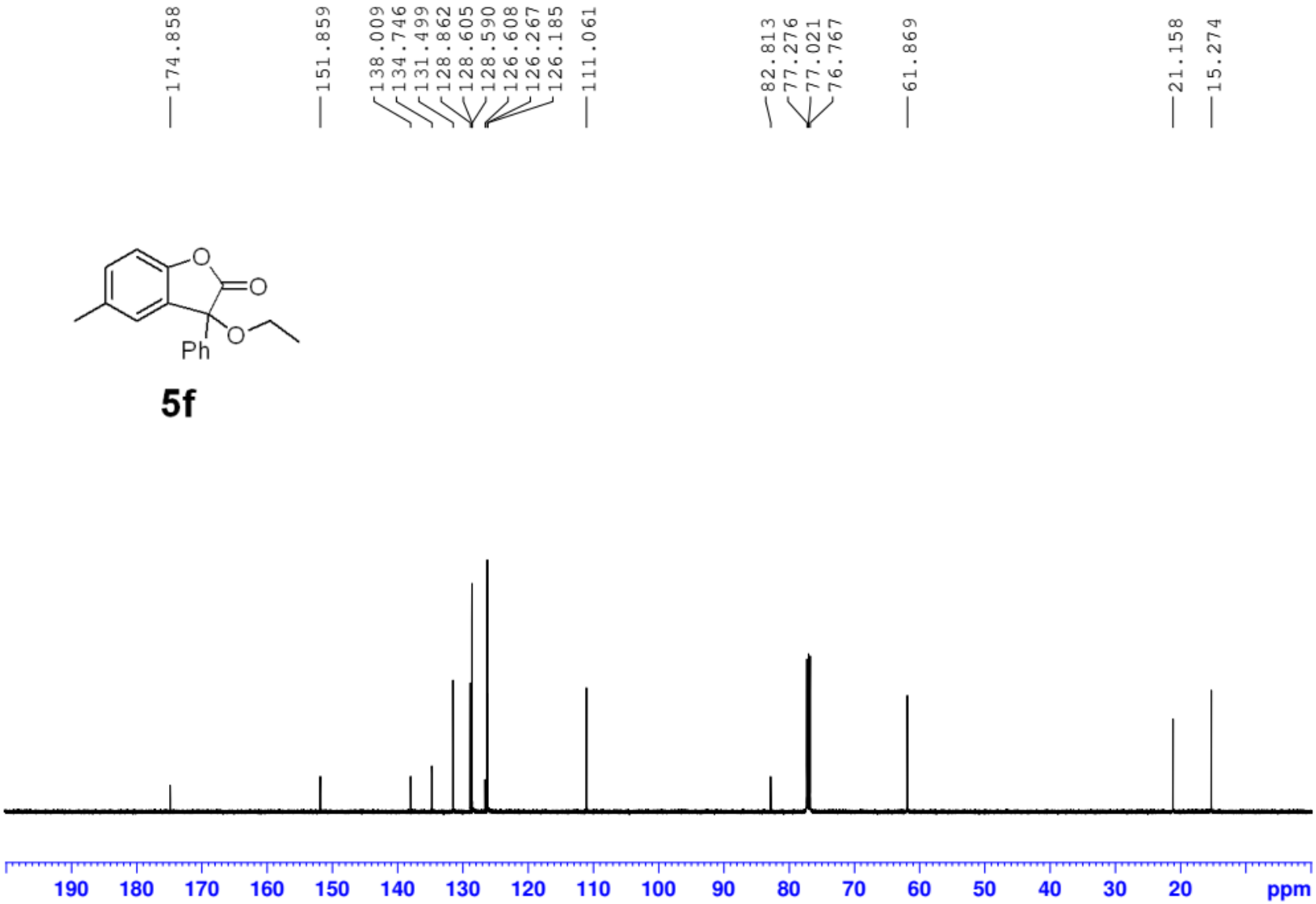


5e

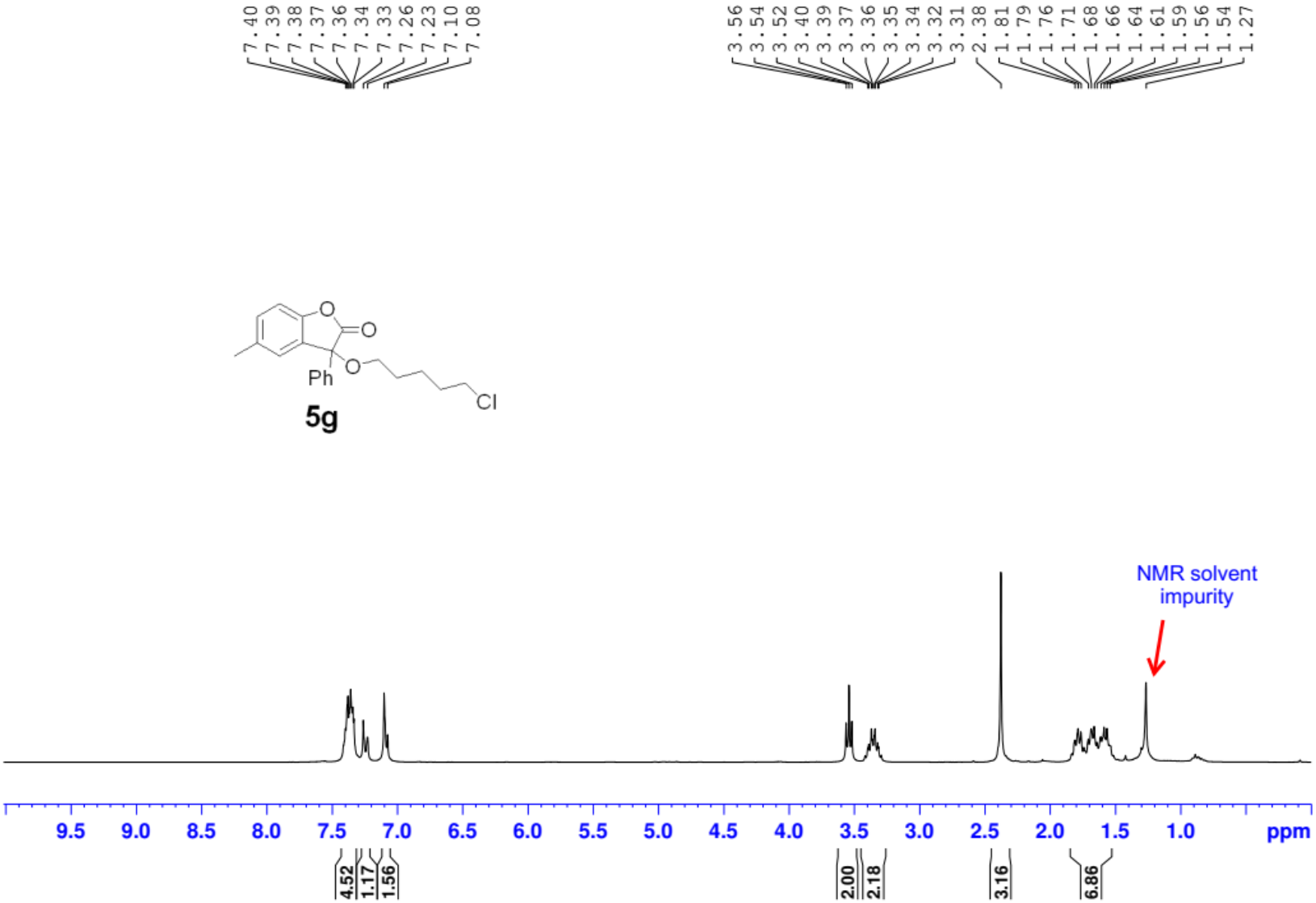


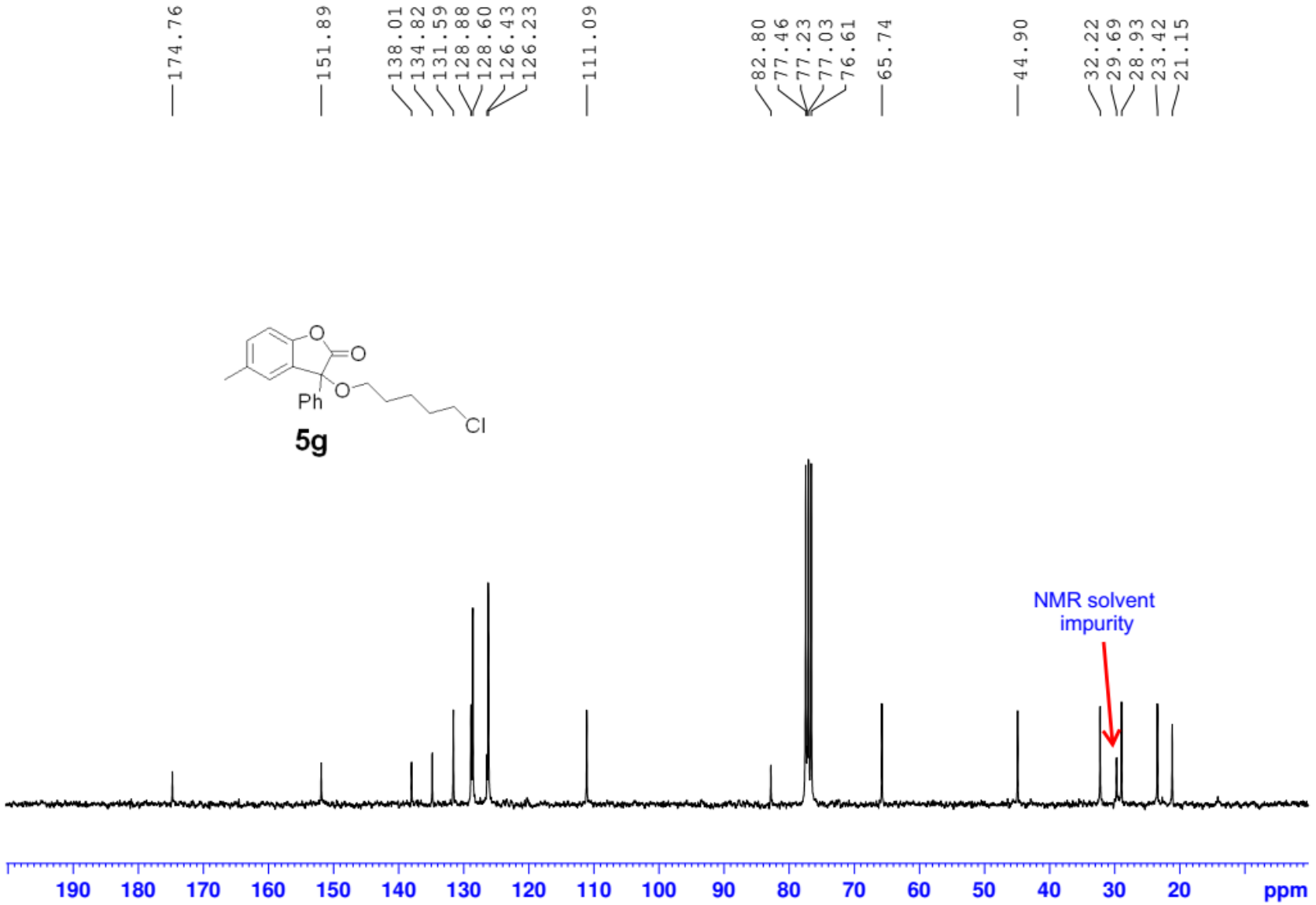

7.418
7.414
7.402
7.399
7.374
7.368
7.364
7.357
7.344
7.334
7.265
7.242
7.228
7.226
7.107
7.093
7.077
3.466
3.450
3.436
3.421
3.407
3.393
3.376
2.374
1.579
1.293
1.279
1.265
O
O
O
Ph
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.83
2.84
0.96
1.77
2.11
3.00
3.33

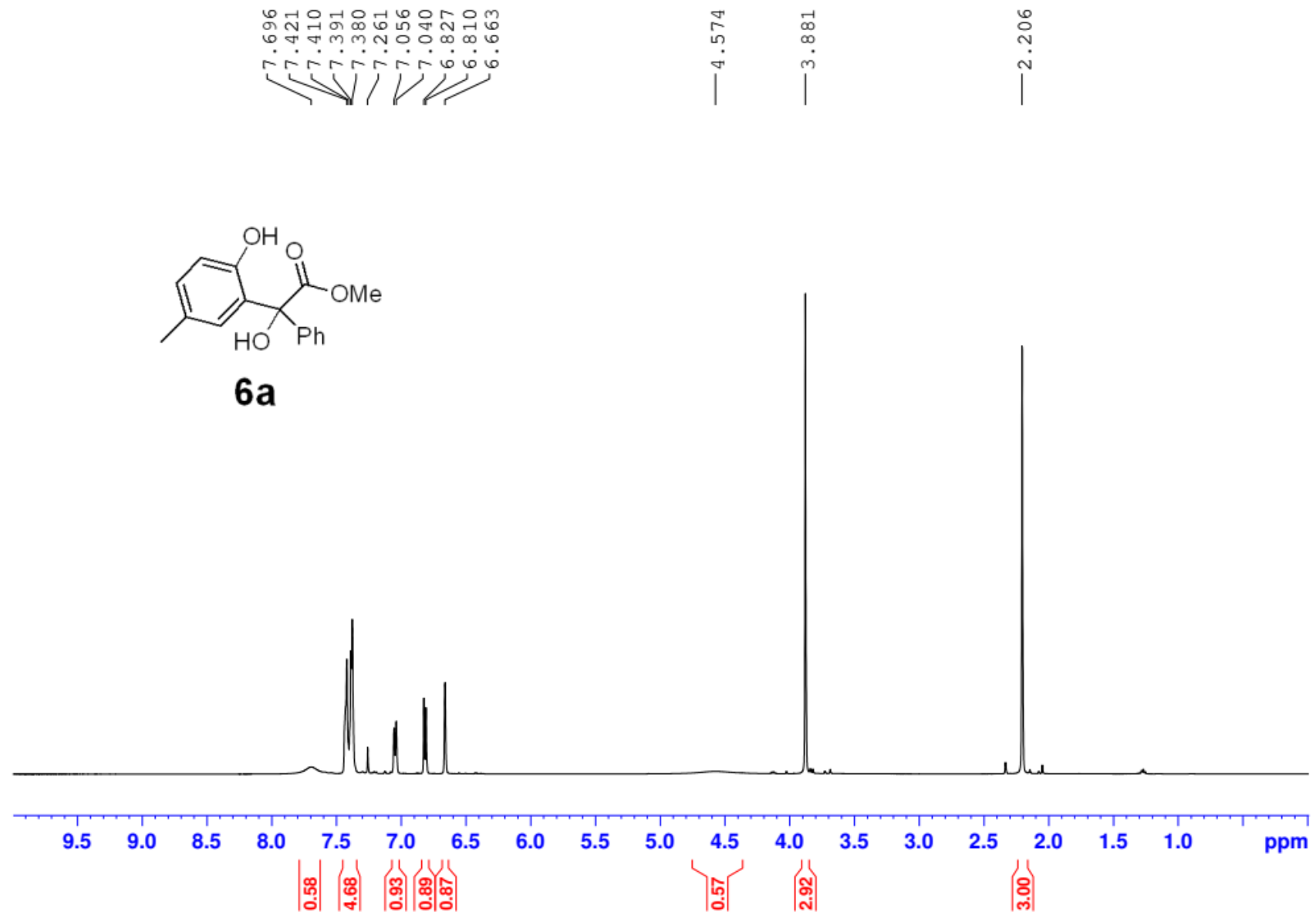
5f

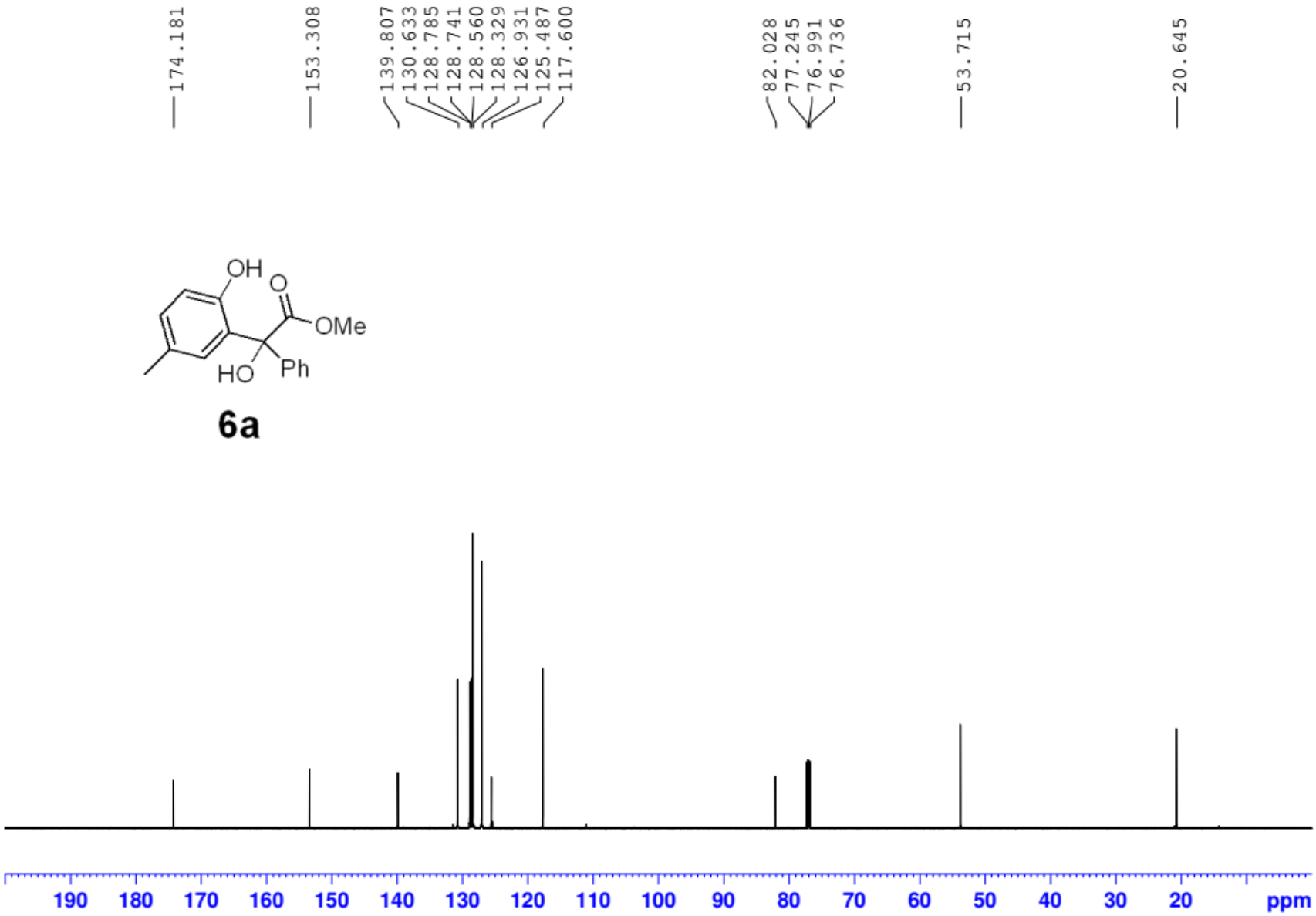

174.858
151.859
138.009
134.746
131.499
128.862
128.605
128.590
126.608
126.267
126.185
111.061
82.813
77.276
77.021
76.767
61.869
21.158
15.274
O
O
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

5f

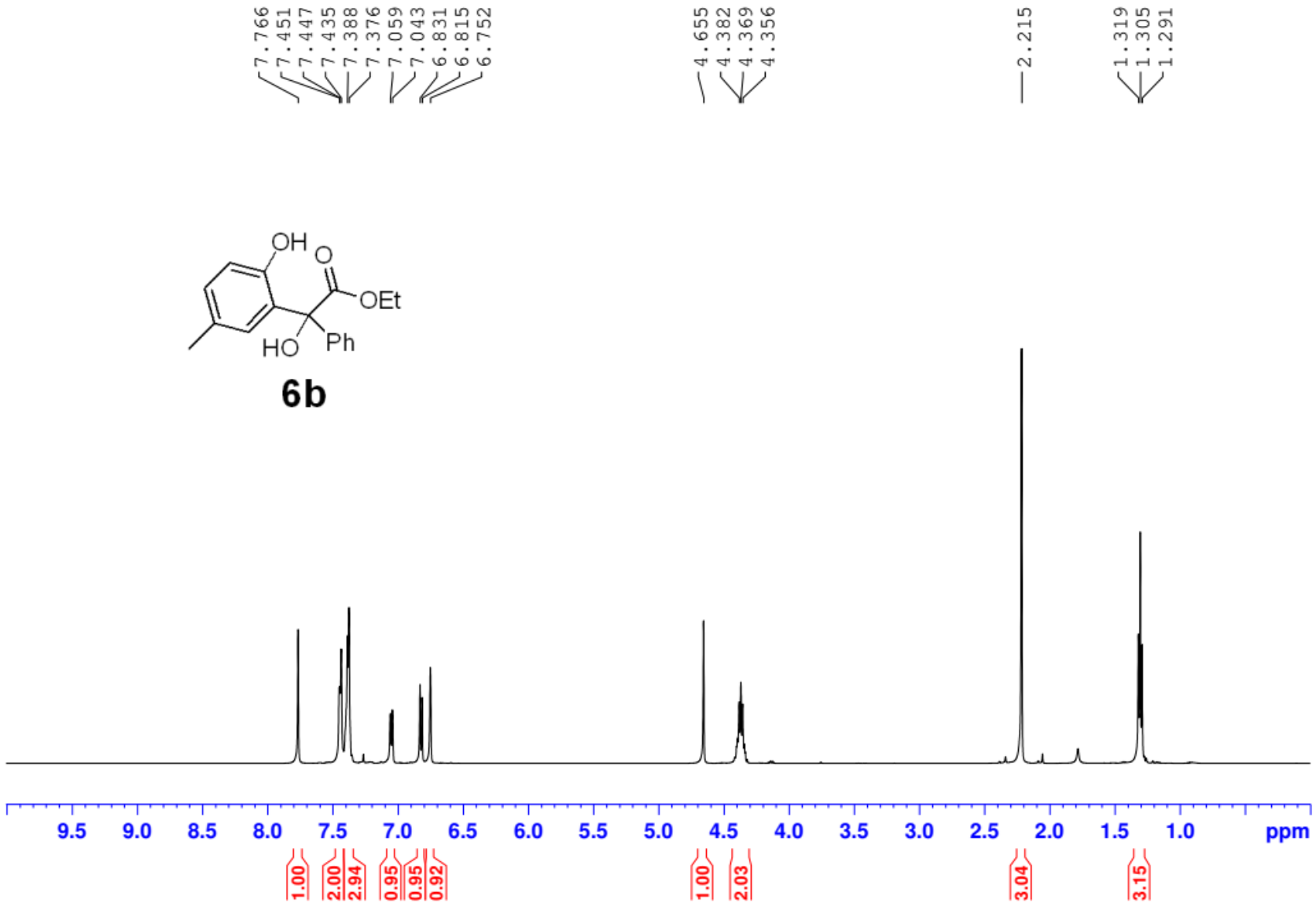

7.40
7.39
7.38
7.37
7.36
7.34
7.33
7.26
7.23
7.10
7.08
3.56
3.54
3.52
3.40
3.39
3.37
3.36
3.35
3.34
3.32
3.31
2.38
1.81
1.79
1.76
1.71
1.68
1.66
1.64
1.61
1.59
1.56
1.54
1.27
O
O
O
Ph
Cl
5g
NMR solvent
impurity
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.52
1.17
1.56
2.00
2.18
3.16
6.86

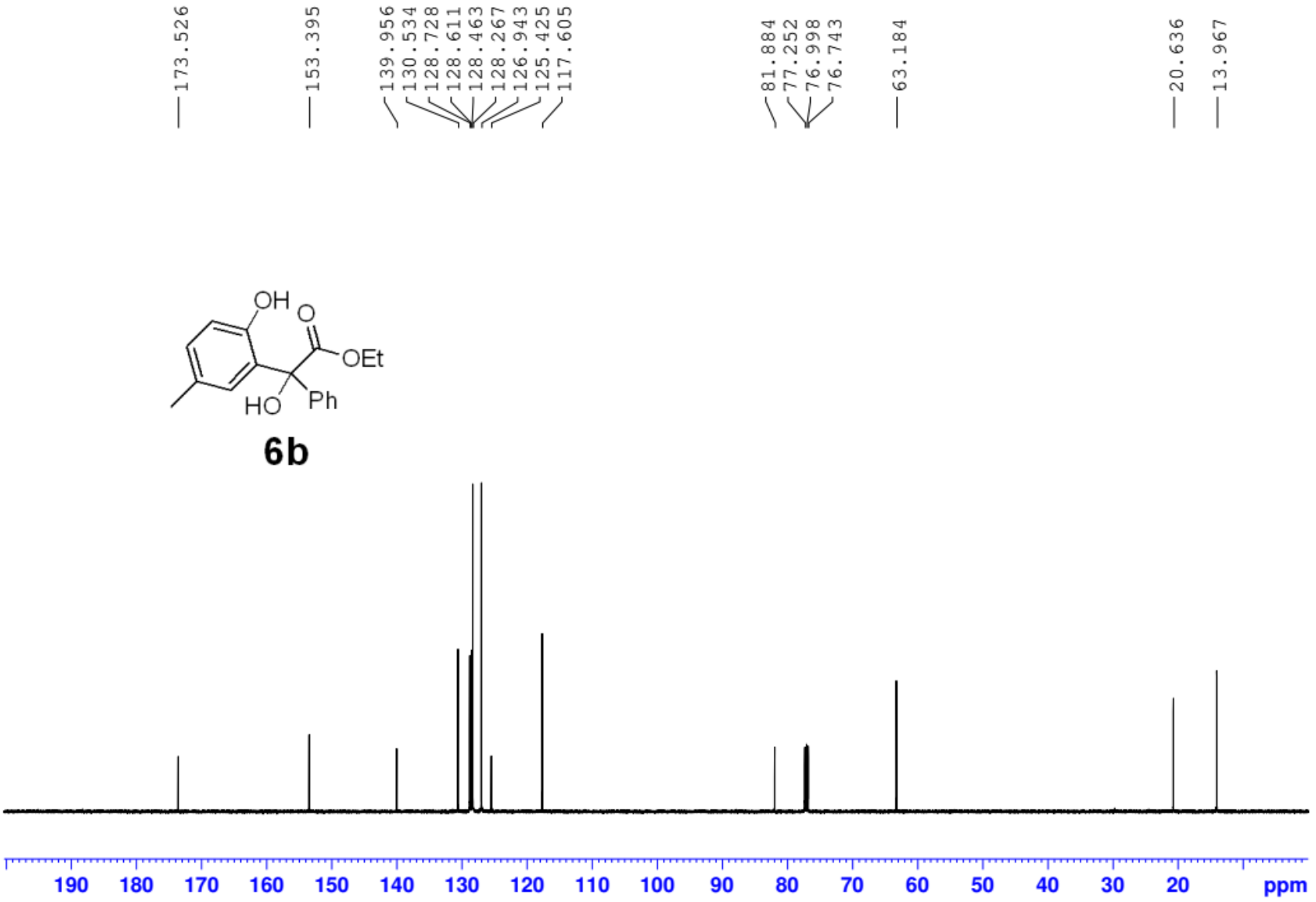

174.76
151.89
138.01
134.82
131.59
128.88
128.60
126.43
126.23
111.09
82.80
77.46
77.23
77.03
76.61
65.74
44.90
32.22
29.69
28.93
23.42
21.15
O
O
O
Ph
Cl
5g
NMR solvent impurity
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.696
7.421
7.410
7.391
7.380
7.261
7.056
7.040
6.827
6.810
6.663
4.574
3.881
2.206
OH
O
OMe
HO
Ph
6a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.58
4.68
0.93
0.89
0.87
0.57
2.92
3.00


174.181
153.308
139.807
130.633
128.785
128.741
128.560
128.329
126.931
125.487
117.600
82.028
77.245
76.991
76.736
53.715
20.645
OH
O
OMe
HO
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

6a


7.766
7.451
7.447
7.435
7.388
7.376
7.059
7.043
6.831
6.815
6.752
4.655
4.382
4.369
4.356
2.215
1.319
1.305
1.291
OH
O
OEt
HO
Ph
6b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.00
2.94
0.95
0.95
0.92
1.00
2.03
3.04
3.15


173.526
153.395
139.956
130.534
128.728
128.611
128.463
128.267
126.943
125.425
117.605
81.884
77.252
76.998
76.743
63.184
20.636
13.967
OH
O
OEt
HO
Ph
6b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

Crystallographic data

X-ray data were collected either on an Agilent Supernova system equipped with a microfocus Cu source (λ = 1.54184 Å) and a Titan CCD detector, or on a XtaLAB Synergy, Dualflex, HyPix four-circle diffractometer with a micro-focus sealed X-ray tube using mirror as monochromator and a HyPix detector. All data were integrated and a multi-scan absorption correction was applied using CrysAlis PRO.[1,2]The structure were solved by iterative methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2017/1.[2,3]All non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms were refined isotropically on calculated positions using a riding model. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. ORTEP was employed for the final data presentation and structure plots.[4]

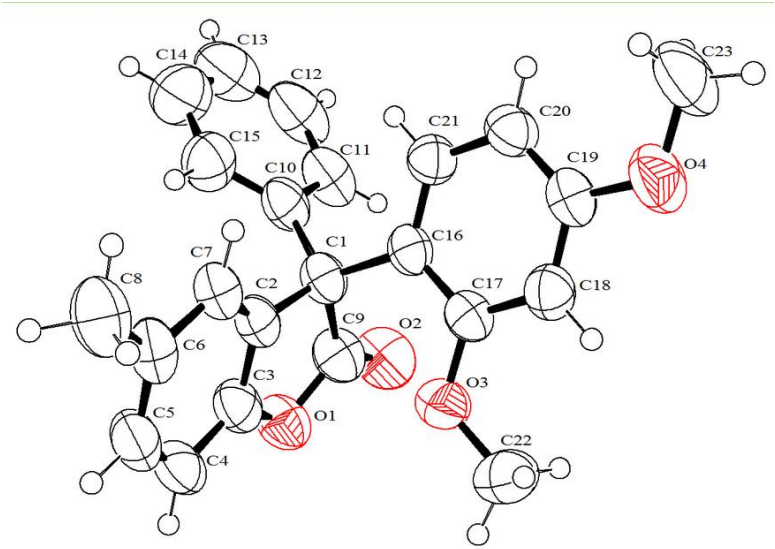


Fig. 1. Crystal structure of **3ba (CCDC 2174827)**

Table 1. Crystal data and structure refinement for **3ba (CCDC 2174827)**

Properties	**values**	**Properties**	**values**
Empirical formula	$C_{23}H_{20}O_4$	$F(000)$	1520
Formula weight	360.39	Crystal size [mm^3]	0.200×0.150×0.100
Temperature [K]	298(2)	Crystal colour	Colourless
Crystal system	monoclinic	Crystal shape	block
Space group (number)	$P2/c$ (15)	Radiation	Cu K_α (λ=1.54184 Å)
a [Å]	18.5957(3)	2Θ range [°]	9.26 to 153.80 (0.79 Å)
b [Å]	11.1708(2)	Index ranges	$-22 \leq h \leq 23$
			$-13 \leq k \leq 12$
			$-22 \leq l \leq 23$
c [Å]	18.5559(3)	Reflections collected	26647
α [Å]	90	Independent reflections	3922
			R_{int} = 0.0637
			R_{sigma} = 0.0299
β [Å]	97.671(2)	Completeness to θ = 67.684°	99.7 %
γ [Å]	90	Data / Restraints / Parameters	3922/0/248
Volume [$Å^3$]	3820.10(11)	Goodness-of-fit on F^2	1.198
Z	8	Final R indexes	R_1 = 0.0466
		[$I \geq 2\sigma(I)$]	wR_2 = 0.1385
ρ_{calc} [g/cm^3]	1.253	Final R indexes	R_1 = 0.0907
		[all data]	wR_2 = 0.1909
μ [mm^{-1}]	0.690	Largest peak/hole [$eÅ^3$]	0.41/-0.34
		Extinction coefficient	0.00053(13)

Table 2. Bond lengths and angles for shelx [**3ba (CCDC 2174827)]**

Atom–Atom-Atom	Length [Å]Angle [°]	Atom–Atom-Atom	Length [Å]Angle [°]
C1–C2	1.514(2)	C3–C2–C1	108.80(15)
C1–C16	1.532(2)	C7–C2–C1	131.50(16)
C1–C10	1.537(3)	C2–C3–C4	122.70(19)
C1–C9	1.556(3)	C2–C3–O1	112.47(16)
C2–C3	1.377(3)	C4–C3–O1	124.78(18)
C2–C7	1.381(3)	C3–C4–C5	116.66(19)
C3–C4	1.380(3)	C4–C5–C6	122.63(17)
C3–O1	1.393(2)	C5–C6–C7	118.55(19)
C4–C5	1.388(3)	C5–C6–C8	121.15(19)
C5–C6	1.388(3)	C7–C6–C8	120.3(2)
C6–C7	1.397(2)	C2–C7–C6	119.83(18)
C6–C8	1.505(3)	O2–C9–O1	120.95(19)
C9–O2	1.191(2)	O2–C9–C1	129.22(19)
C9–O1	1.378(2)	O1–C9–C1	109.74(15)
C10–C15	1.388(3)	C15–C10–C11	118.1(2)
C10–C11	1.393(3)	C15–C10–C1	121.70(17)
C11–C12	1.377(4)	C11–C10–C1	120.14(19)
C12–C13	1.380(5)	C12–C11–C10	120.4(3)
C13–C14	1.370(4)	C11–C12–C13	120.8(2)
C14–C15	1.381(3)	C14–C13–C12	119.2(2)
C16–C21	1.381(2)	C13–C14–C15	120.5(3)
C16–C17	1.398(2)	C14–C15–C10	120.9(2)
C17–O3	1.363(2)	C21–C16–C17	117.59(15)
C17–C18	1.382(2)	C21–C16–C1	122.37(15)
C18–C19	1.386(3)	C17–C16–C1	119.79(15)
C19–O4	1.367(2)	O3–C17–C18	123.47(16)
C19–C20	1.373(3)	O3–C17–C16	115.44(15)
C20–C21	1.392(2)	C18–C17–C16	121.07(16)
C22–O3	1.423(3)	C17–C18–C19	119.71(17)
C23–O4	1.417(3)	O4–C19–C20	124.83(17)
C2–C1–C16	110.23(13)	O4–C19–C18	114.59(17)
C2–C1–C10	114.13(14)	C20–C19–C18	120.58(16)
C16–C1–C10	111.70(14)	C19–C20–C21	118.89(16)
C2–C1–C9	100.11(14)	C16–C21–C20	122.15(16)
C16–C1–C9	112.46(14)	C9–O1–C3	108.22(15)
C10–C1–C9	107.68(14)	C17–O3–C22	117.87(16)
C3–C2–C7	119.59(16)	C19–O4–C23	117.61(18)

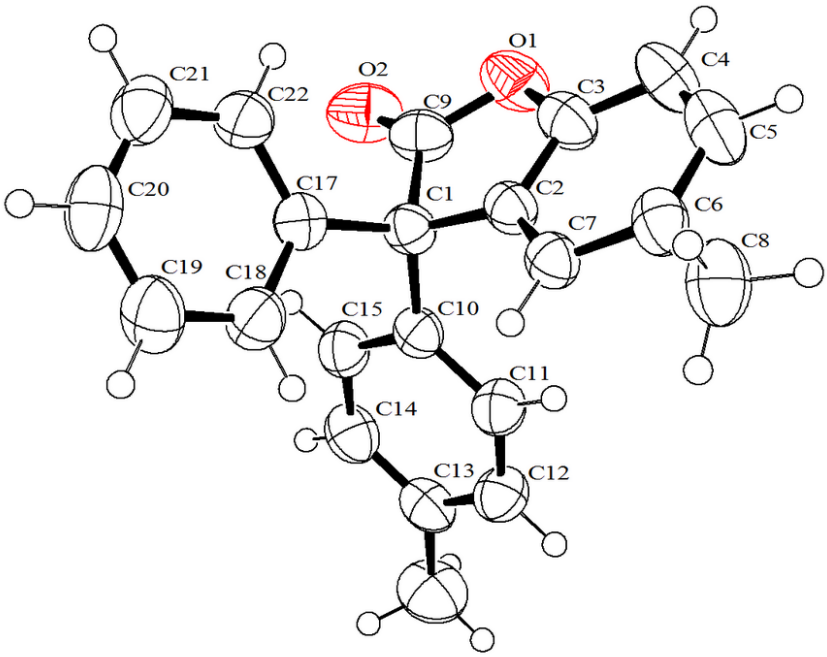


Fig. 2. Crystal structure of **3bb (CCDC 2174812)**

Table 3. Crystal data and structure refinement for **3bb (CCDC 2174812)**

Properties	**values**	**Properties**	**values**
Empirical formula	$C_{22}H_{18}O_2$	$F(000)$	664
Formula weight	314.36	Crystal size [mm^3]	0.010×0.010×0.010
Temperature [K]	298(2)	Crystal colour	colourless
Crystal system	monoclinic	Crystal shape	block
Space group (number)	$P2_1/c$ (14)	Radiation	Mo K_α (λ=0.71073 Å)
a [Å]	13.0664(8)	2Θ range [°]	4.05 to 62.31 (0.69 Å)
b [Å]	8.5960(6)	Index ranges	-18 ≤ h ≤ 17 -12 ≤ k ≤ 12 -21 ≤ l ≤ 21
c [Å]	14.8892(9)	Reflections collected	71229
α [Å]	90	Independent reflections	4903 R_{int} = 0.0942 R_{sigma} = 0.0374
β [Å]	92.737(5)	Completeness to θ = 25.242°	100.0 %
γ [Å]	90	Data / Restraints / Parameters	4903/0/219
Volume [Å^3]	1670.43(19)	Goodness-of-fit on F^2	1.128
Z	4	Final R indexes [I≥2σ(I)]	R_1 = 0.0670 wR_2 = 0.2046
ρ_{calc} [g/cm^3]	1.250	Final R indexes [all data]	R_1 = 0.1189 wR_2 = 0.2890
μ [mm^{-1}]	0.079	Largest peak/hole [eÅ^3]	0.32/-0.31

Table 4. Atomic coordinates and Ueq [Å2] for shelx. [**3bb (CCDC 2174812)]**

Atom	***x***	***y***	***z***	U_{eq}
C1	0.26448(13)	0.6220(2)	0.50327(12)	0.0417(4)
C2	0.30657(14)	0.6287(2)	0.59951(12)	0.0426(4)
C3	0.24222(17)	0.7177(3)	0.64755(15)	0.0542(5)
C4	0.2590(2)	0.7465(4)	0.73788(17)	0.0722(7)
H4	0.214241	0.807226	0.769605	0.087
C5	0.3452(2)	0.6812(3)	0.77919(16)	0.0671(7)
H5	0.358532	0.699121	0.840236	0.081
C6	0.41298(17)	0.5898(2)	0.73330(13)	0.0510(5)
C7	0.39144(14)	0.5621(2)	0.64208(12)	0.0426(4)
H7	0.434396	0.498708	0.610064	0.051
C8	0.5054(2)	0.5221(3)	0.78091(16)	0.0671(7)
H8A	0.526026	0.587158	0.830982	0.101
H8B	0.560092	0.515753	0.740243	0.101
H8C	0.489668	0.419883	0.802188	0.101
C9	0.16310(16)	0.7116(3)	0.51149(15)	0.0523(5)
C10	0.32809(14)	0.7136(2)	0.43756(12)	0.0411(4)
C11	0.42163(16)	0.7781(2)	0.46212(14)	0.0493(5)
H11	0.448271	0.766712	0.520791	0.059
C12	0.47664(17)	0.8600(3)	0.40016(15)	0.0532(5)
H12	0.540342	0.901060	0.417744	0.064
C13	0.43869(18)	0.8818(2)	0.31306(14)	0.0523(5)
C14	0.34509(19)	0.8180(3)	0.28913(14)	0.0568(5)
H14	0.317852	0.832152	0.230858	0.068
C15	0.29034(17)	0.7334(3)	0.34920(14)	0.0513(5)
H15	0.227860	0.689362	0.330627	0.062
C16	0.4978(3)	0.9729(4)	0.2463(2)	0.0787(8)
H16A	0.502743	0.913250	0.192145	0.118
H16B	0.565381	0.994381	0.271433	0.118
H16C	0.463068	1.069053	0.232736	0.118
C17	0.24581(14)	0.4544(2)	0.47383(12)	0.0431(4)
C18	0.32409(16)	0.3721(3)	0.43670(16)	0.0547(5)
H18	0.385283	0.422026	0.425365	0.066
C19	0.3123(2)	0.2160(3)	0.41623(19)	0.0663(7)
H19	0.365819	0.161600	0.391831	0.080
C20	0.2219(2)	0.1405(3)	0.43165(17)	0.0656(7)
H20	0.214063	0.035624	0.417683	0.079
C21	0.1435(2)	0.2217(3)	0.46781(17)	0.0635(6)
H21	0.082003	0.171899	0.478085	0.076
C22	0.15548(17)	0.3768(3)	0.48900(14)	0.0529(5)
H22	0.101886	0.430315	0.513958	0.064
O1	0.15776(13)	0.7713(2)	0.59603(12)	0.0664(5)
O2	0.09668(12)	0.7340(2)	0.45617(13)	0.0704(5)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 5. Bond lengths and angles for shelx [**3bb (CCDC 2174812)]**

Atom–Atom-Atom	Length [Å]Angle [°]	Atom–Atom-Atom	Length [Å]Angle [°]	Atom–Atom-Atom	Length [Å]Angle [°]
C1–C2	1.511(3)	C20–C21	1.370(4)	C15–C10–C1	119.18(17)
C1–C17	1.522(3)	C20–H20	0.9300	C10–C11–C12	120.63(19)
C1–C10	1.532(3)	C21–C22	1.377(3)	C10–C11–H11	119.7
C1–C9	1.542(3)	C21–H21	0.9300	C12–C11–H11	119.7
C2–C3	1.364(3)	C22–H22	0.9300	C13–C12–C11	121.3(2)
C2–C7	1.376(3)	C2–C1–C17	110.82(14)	C13–C12–H12	119.3
C3–C4	1.375(3)	C2–C1–C10	113.70(15)	C11–C12–H12	119.3
C3–O1	1.392(3)	C17–C1–C10	112.78(15)	C14–C13–C12	117.78(19)
C4–C5	1.376(4)	C2–C1–C9	100.41(15)	C14–C13–C16	121.0(2)
C4–H4	0.9300	C17–C1–C9	111.65(16)	C12–C13–C16	121.2(2)
C5–C6	1.388(3)	C10–C1–C9	106.75(15)	C13–C14–C15	121.7(2)
C5–H5	0.9300	C3–C2–C7	119.69(18)	C13–C14–H14	119.1
C6–C7	1.394(3)	C3–C2–C1	108.25(17)	C15–C14–H14	119.1
C6–C8	1.489(3)	C7–C2–C1	132.05(16)	C14–C15–C10	120.4(2)
C7–H7	0.9300	C2–C3–C4	122.7(2)	C14–C15–H15	119.8
C8–H8A	0.9600	C2–C3–O1	112.90(19)	C10–C15–H15	119.8
C8–H8B	0.9600	C4–C3–O1	124.4(2)	C13–C16–H16A	109.5
C8–H8C	0.9600	C3–C4–C5	116.9(2)	C13–C16–H16B	109.5
C9–O2	1.183(3)	C3–C4–H4	121.5	H16A–C16–H16B	109.5
C9–O1	1.364(3)	C5–C4–H4	121.5	C13–C16–H16C	109.5
C10–C11	1.376(3)	C4–C5–C6	122.6(2)	H16A–C16–H16C	109.5
C10–C15	1.393(3)	C4–C5–H5	118.7	H16B–C16–H16C	109.5
C11–C12	1.388(3)	C6–C5–H5	118.7	C18–C17–C22	118.2(2)
C11–H11	0.9300	C5–C6–C7	118.2(2)	C18–C17–C1	119.25(17)
C12–C13	1.379(3)	C5–C6–C8	120.6(2)	C22–C17–C1	122.38(18)
C12–H12	0.9300	C7–C6–C8	121.2(2)	C17–C18–C19	120.5(2)
C13–C14	1.372(3)	C2–C7–C6	119.89(18)	C17–C18–H18	119.7
C13–C16	1.507(3)	C2–C7–H7	120.1	C19–C18–H18	119.7
C14–C15	1.379(3)	C6–C7–H7	120.1	C20–C19–C18	120.6(2)
C14–H14	0.9300	C6–C8–H8A	109.5	C20–C19–H19	119.7
C15–H15	0.9300	C6–C8–H8B	109.5	C18–C19–H19	119.7
C16–H16A	0.9600	H8A–C8–H8B	109.5	C21–C20–C19	119.2(2)
C16–H16B	0.9600	C6–C8–H8C	109.5	C21–C20–H20	120.4
C16–H16C	0.9600	H8A–C8–H8C	109.5	C19–C20–H20	120.4
C17–C18	1.381(3)	H8B–C8–H8C	109.5	C20–C21–C22	120.3(2)
C17–C22	1.384(3)	O2–C9–O1	120.8(2)	C20–C21–H21	119.9
C18–C19	1.383(3)	O2–C9–C1	129.1(2)	C22–C21–H21	119.9
C18–H18	0.9300	O1–C9–C1	110.07(18)	C21–C22–C17	121.2(2)
C19–C20	1.376(4)	C11–C10–C15	118.15(18)	C21–C22–H22	119.4
C19–H19	0.9300	C11–C10–C1	122.67(17)	C17–C22–H22	119.4
				C9–O1–C3	108.03(16)

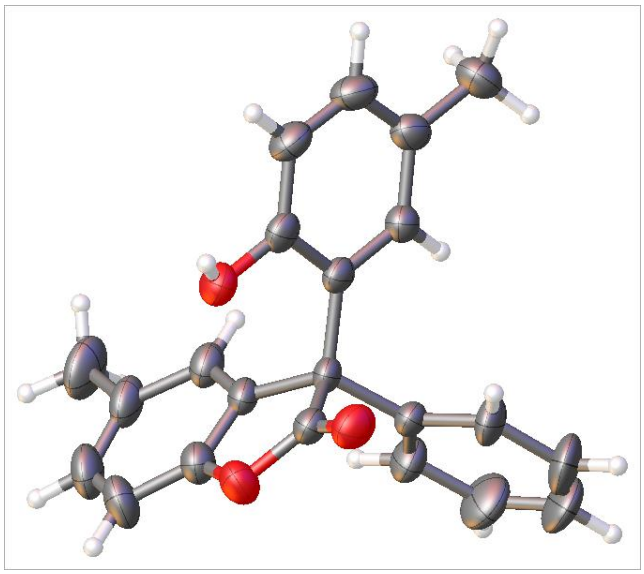


Fig. 3. Crystal structure of **3bc (CCDC 2174811);** Crystal Data for $C_{22}H_{18}O_3$ (*M* =330.36 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 15.5619(6) Å, *b* = 12.6968(9) Å, *c* = 17.5458(8) Å, *V* = 3466.8(3) Å^3, *Z* = 8, *T* = 293 K, μ(CuKα) = 0.670 mm^{-1}, *Dcalc* = 1.266 g/cm^3, 7752 reflections measured (10.082° ≤ 2Θ ≤ 146.718°), 3372 unique (R_{int} = 0.1569, R_{sigma} = 0.1077) which were used in all calculations. The final R_1 was 0.1250 (I > 2σ(I)) and wR_2 was 0.3596 (all data).

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C3(H3A), C4(H4), C7(H7), C11(H11), C12(H12), C13(H13), C14(H14), C15(H15),
 C17(H17), C20(H20), C21(H21)
2.b Idealised Me refined as rotating group:
 C1(H1A,H1B,H1C), C19(H19A,H19B,H19C)
2.c Idealised tetrahedral OH refined as rotating group:
 O3(H3)
```

Table 6. Crystal data and structure refinement for **3bc (CCDC 2174811)**

Properties	values	Properties	values
Identification code	BD-25-19_1	ρ_{calc}g/cm^3	1.266
Empirical formula	$C_{22}H_{18}O_3$	μ/mm^{-1}	0.670
Formula weight	330.36	F(000)	1392.0
Temperature/K	293	Crystal size/mm^3	0.761 × 0.455 × 0.133
Crystal system	orthorhombic	Radiation	CuKα (λ = 1.54184)
Space group	Pbca	2Θ range for data collection/°	10.082 to 146.718
a/Å	15.5619(6)	Index ranges	-18 ≤ h ≤ 15, -15 ≤ k ≤ 14, -21 ≤ l ≤ 12

b/Å	12.6968(9)	Reflections collected	7752
c/Å	17.5458(8)	Independent reflections	3372 [R_{int} = 0.1569, R_{sigma} = 0.1077]
α/°	90	Data/restraints/parameters	3372/0/229
β/°	90	Goodness-of-fit on F^2	1.122
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.1250, wR_2 = 0.2978
Volume/$Å^3$	3466.8(3)	Final R indexes [all data]	R_1 = 0.1724, wR_2 = 0.3596
Z	8	Largest diff. peak/hole / e $Å^{-3}$	0.55/-0.53

Table 7. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3bc (CCDC 2174811).**

Atom	***x***	***y***	***z***	**U(eq)**
O1	5369(2)	1484(3)	6465.3(18)	52.9(9)
O2	4157(2)	982(3)	5895.9(19)	52.7(9)
O3	5615(2)	986(3)	4782.9(18)	50.6(8)
C1	7741(3)	4647(6)	5669(4)	79.6(18)
C2	7109(3)	3830(5)	5909(3)	57.8(13)
C3	7286(3)	3156(5)	6518(4)	68.6(16)
C4	6738(3)	2358(5)	6734(3)	66.2(15)
C5	5982(3)	2266(4)	6345(3)	50.1(11)
C6	5746(2)	2953(4)	5760(2)	40.6(9)
C7	6311(3)	3715(4)	5539(3)	48.1(10)
C8	4855(2)	2659(3)	5509(2)	37.0(9)
C9	4738(2)	1599(4)	5937(2)	43.5(10)
C10	4158(2)	3382(4)	5842(2)	42.5(10)
C11	4367(3)	4311(5)	6209(3)	58.2(13)
C12	3718(4)	4927(6)	6521(4)	84(2)
C13	2882(4)	4659(7)	6490(4)	93(2)
C14	2668(3)	3732(7)	6122(5)	86(2)
C15	3293(3)	3093(5)	5795(3)	60.7(14)
C16	4784(2)	2517(4)	4651(2)	37.8(9)
C17	4360(2)	3245(4)	4181(2)	43.2(10)
C18	4320(3)	3131(4)	3396(2)	48.6(11)
C19	3867(4)	3922(5)	2901(3)	62.5(14)
C20	4702(3)	2230(4)	3080(2)	53.7(12)
C21	5126(3)	1504(4)	3526(2)	52.2(11)
C22	5174(2)	1654(4)	4310(2)	43.4(10)

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Table 8. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3bc (CCDC 2174811).** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	39.8(15)	73(2)	45.9(15)	10.2(15)	-7.1(13)	3.0(15)
O2	39.7(15)	68(2)	51.1(17)	-2.4(15)	7.3(13)	-7.1(14)
O3	40.3(15)	65(2)	46.8(16)	-2.6(15)	3.1(13)	13.9(14)
C1	30(2)	109(5)	100(5)	-14(4)	10(3)	-13(3)
C2	24.1(18)	83(3)	67(3)	-16(3)	1.9(18)	1(2)
C3	29(2)	104(4)	74(3)	-7(3)	-12(2)	10(2)
C4	37(2)	95(4)	67(3)	9(3)	-17(2)	11(2)
C5	31.1(19)	75(3)	44(2)	-1(2)	-2.9(17)	7(2)
C6	24.3(17)	62(2)	35.0(17)	-5.5(17)	1.0(14)	8.4(16)
C7	27.9(17)	66(3)	50(2)	-8(2)	3.0(17)	3.5(18)
C8	20.3(15)	57(2)	33.5(17)	-1.3(16)	2.2(13)	6.1(15)
C9	27.7(17)	69(3)	34.0(17)	-1.3(18)	3.8(15)	6.8(18)
C10	26.2(18)	70(3)	31.0(16)	1.1(19)	3.8(14)	7.9(17)
C11	38(2)	84(3)	53(2)	-14(2)	4.0(19)	17(2)
C12	69(4)	103(5)	79(4)	-29(4)	14(3)	30(3)
C13	58(3)	142(6)	80(4)	-16(4)	21(3)	48(4)
C14	30(2)	134(6)	95(4)	-1(5)	15(3)	26(3)
C15	22.4(19)	97(4)	63(3)	-6(3)	5.9(18)	9(2)
C16	21.5(15)	59(2)	33.1(17)	-3.1(17)	3.7(13)	-1.3(15)
C17	29.5(17)	64(3)	35.9(18)	-0.1(18)	0.0(15)	5.1(17)
C18	36(2)	75(3)	34.1(19)	4.7(19)	0.7(16)	-3(2)
C19	55(3)	92(4)	40(2)	11(2)	-7(2)	8(3)
C20	51(2)	78(3)	32.7(18)	-6(2)	7.1(18)	-4(2)
C21	45(2)	70(3)	41(2)	-10(2)	10.0(18)	7(2)
C22	24.6(17)	64(3)	42(2)	-0.6(19)	7.4(15)	-1.9(16)

Table 9. Bond Lengths for **3bc (CCDC 2174811).**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C5	1.393(6)	C8	C16	1.521(5)
O1	C9	1.358(5)	C10	C11	1.383(8)
O2	C9	1.198(5)	C10	C15	1.399(6)
O3	C22	1.371(5)	C11	C12	1.390(7)
C1	C2	1.491(8)	C12	C13	1.345(11)
C2	C3	1.395(9)	C13	C14	1.384(11)
C2	C7	1.410(6)	C14	C15	1.391(7)
C3	C4	1.378(8)	C16	C17	1.404(6)
C4	C5	1.365(6)	C16	C22	1.387(6)
C5	C6	1.396(6)	C17	C18	1.386(6)
C6	C7	1.363(6)	C18	C19	1.504(7)
C6	C8	1.502(5)	C18	C20	1.404(7)
C8	C9	1.552(6)	C20	C21	1.378(7)
C8	C10	1.536(5)	C21	C22	1.390(6)

Table 10. Bond Angles for **3bc (CCDC 2174811).**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O1	C5	108.4(3)	O2	C9	C8	128.8(4)
C3	C2	C1	120.8(5)	C11	C10	C8	121.4(4)
C3	C2	C7	117.6(5)	C11	C10	C15	118.6(4)
C7	C2	C1	121.6(6)	C15	C10	C8	120.1(4)
C4	C3	C2	122.7(4)	C10	C11	C12	119.5(5)
C5	C4	C3	117.3(5)	C13	C12	C11	123.0(7)
O1	C5	C6	112.1(4)	C12	C13	C14	117.8(5)
C4	C5	O1	125.2(5)	C13	C14	C15	121.3(5)
C4	C5	C6	122.7(5)	C14	C15	C10	119.7(6)
C5	C6	C8	107.6(4)	C17	C16	C8	122.5(4)
C7	C6	C5	118.9(4)	C22	C16	C8	119.3(4)
C7	C6	C8	133.4(4)	C22	C16	C17	118.2(4)
C6	C7	C2	120.7(5)	C18	C17	C16	122.4(4)
C6	C8	C9	100.5(3)	C17	C18	C19	121.7(4)
C6	C8	C10	113.1(3)	C17	C18	C20	117.3(4)
C6	C8	C16	112.8(3)	C20	C18	C19	121.0(4)
C10	C8	C9	104.6(3)	C21	C20	C18	121.6(4)
C16	C8	C9	111.5(3)	C20	C21	C22	119.7(4)
C16	C8	C10	113.4(3)	O3	C22	C16	116.5(4)
O1	C9	C8	109.8(4)	O3	C22	C21	122.7(4)
O2	C9	O1	121.1(4)	C16	C22	C21	120.8(4)

Table 11. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3bc (CCDC 2174811).**

Atom	*x*	*y*	*z*	U(eq)
H3	5607	389	4604	76
H1A	7828	4606	5128	119
H1B	8278	4529	5926	119
H1C	7526	5332	5799	119
H3A	7794	3250	6788	82
H4	6877	1901	7129	79
H7	6167	4163	5139	58
H11	4938	4523	6246	70
H12	3868	5552	6763	101
H13	2462	5083	6709	112
H14	2094	3533	6092	104
H15	3136	2476	5545	73
H17	4096	3825	4404	52
H19A	3410	4245	3184	94
H19B	3635	3574	2461	94
H19C	4268	4453	2741	94
H20	4668	2120	2557	64
H21	5380	916	3304	63

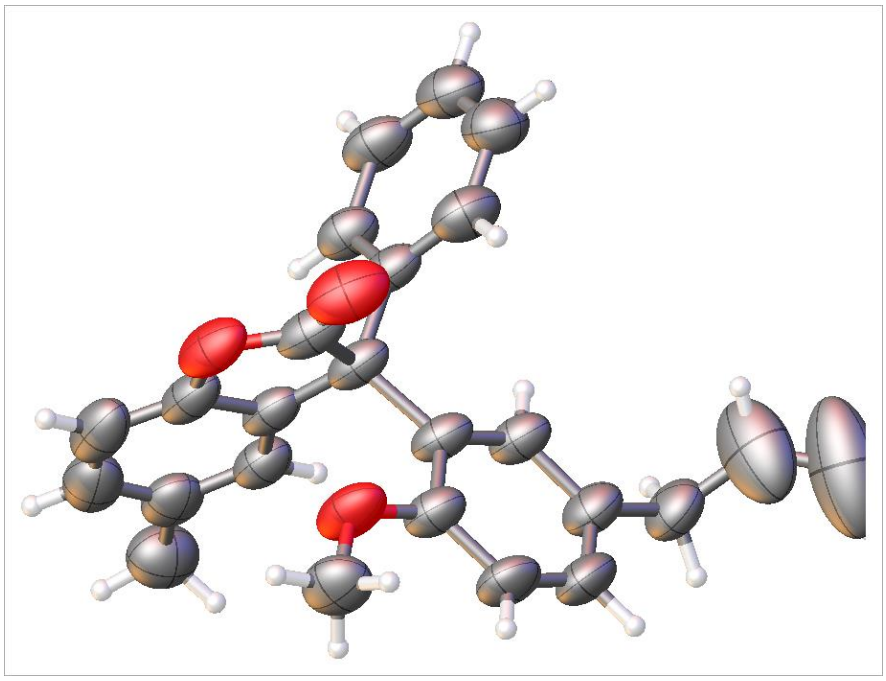


Fig. 4. Crystal structure of **3bd (CCDC 2174815);** Crystal Data for $C_{25}H_{22}O_3$ (*M* =370.42 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 13.3483(3) Å, *b* = 14.7869(4) Å, *c* = 20.1111(10) Å, *V* = 3969.5(2) $Å^3$, *Z* = 8, *T* = 293 K, μ(CuKα) = 0.640 mm^{-1}, *Dcalc* = 1.240 g/cm^3, 10136 reflections measured (9.952° ≤ 2Θ ≤ 146.456°), 3869 unique (R_{int} = 0.0579, R_{sigma} = 0.0456) which were used in all calculations. The final R_1 was 0.0723 (I > 2σ(I)) and wR_2 was 0.2462 (all data).

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C23(H23A,H23B)
2.b Aromatic/amide H refined with riding coordinates:
 C3(H3), C4(H4), C7(H7), C11(H11), C12(H12), C13(H13), C14(H14), C15(H15),
 C17(H17), C19(H19), C20(H20), C24(H24)
2.c X=CH2 refined with riding coordinates:
 C25(H25A,H25B)
2.d Idealised Me refined as rotating group:
 C1(H1A,H1B,H1C), C22(H22A,H22B,H22C)
```

Table 12. Crystal data and structure refinement for **3bd (CCDC 2174815)**

Properties	**values**	**Properties**	**values**
Identification code	BD-20-18_1	$\rho_{calc}g/cm^3$	1.240
Empirical formula	$C_{25}H_{22}O_3$	μ/mm^{-1}	0.640
Formula weight	370.42	F(000)	1568.0
Temperature/K	293	Crystal size/mm^3	1.0 × 0.2 × 0.07
Crystal system	orthorhombic	Radiation	CuKα (λ = 1.54184)

Space group	Pbca	2Θ range for data collection/°	9.952 to 146.456
a/Å	13.3483(3)	Index ranges	$-16 \leq h \leq 14$, $-17 \leq k \leq 17$, $-17 \leq l \leq 24$
b/Å	14.7869(4)	Reflections collected	10136
c/Å	20.1111(10)	Independent reflections	3869 [R_{int} = 0.0579, R_{sigma} = 0.0456]
α/°	90	Data/restraints/parameters	3869/0/255
β/°	90	Goodness-of-fit on F^2	1.069
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0723, wR_2 = 0.1973
Volume/Å^3	3969.5(2)	Final R indexes [all data]	R_1 = 0.1042, wR_2 = 0.2462
Z	8	Largest diff. peak/hole / e Å^{-3}	0.21/-0.33

Table 13. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3bd (CCDC 2174815).**

Atom	***x***	***y***	***z***	**U(eq)**
O1	2322.6(11)	5017.9(12)	7329.9(13)	77.1(7)
O2	2435.9(15)	5155.5(14)	6232.0(14)	92.9(8)
O3	2666.0(13)	6949.1(11)	6939.8(13)	79.7(7)
C1	5097(3)	5932(2)	9331(2)	95(1)
C2	4342(2)	5668.9(16)	8816.8(18)	73.3(8)
C3	3396(2)	5359.1(18)	8988(2)	83.9(10)
C4	2681(2)	5114.7(19)	8521(2)	85.1(10)
C5	2946.5(17)	5198.3(14)	7868.1(18)	68.4(8)
C6	3889.2(15)	5482.8(13)	7670.9(16)	59.6(7)
C7	4584.8(18)	5722.9(15)	8145.5(16)	63.2(7)
C8	3931.8(15)	5479.5(14)	6922.5(16)	59.4(7)
C9	2823.6(19)	5235.6(15)	6758.6(19)	70.5(9)
C10	4556.1(16)	4700.8(14)	6630.5(16)	59.0(7)
C11	4597(2)	4577.5(18)	5946.4(19)	78.7(9)
C12	5131(2)	3863(2)	5671(2)	84.9(9)
C13	5627(2)	3265.0(18)	6076(2)	78.4(9)
C14	5594(2)	3378.2(17)	6747(2)	76.3(9)
C15	5065.9(15)	4097.2(16)	7028.3(17)	62.9(7)
C16	4252.6(16)	6406.5(14)	6653.8(15)	59.0(7)
C17	5232.8(16)	6562.4(15)	6456.0(16)	62.8(7)
C18	5569.1(19)	7412.1(16)	6265.6(16)	67.6(8)
C19	4886(2)	8111.4(16)	6268.6(17)	73.0(8)
C20	3906(2)	7985.1(15)	6470.9(17)	71.0(8)
C21	3593.0(18)	7137.3(15)	6683.0(16)	62.9(7)
C22	1953(2)	7652(2)	6996(2)	84.6(10)
C23	6654(2)	7562.0(19)	6076(2)	79.1(9)
C24	6869(3)	7403(5)	5389(3)	152(2)
C25	7270(4)	7855(7)	4952(4)	209(4)

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Table 14. Anisotropic Displacement Parameters ($Å^2×10^3$) for **3bd (CCDC 2174815).** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	42.7(8)	55.6(9)	133(2)	6.1(10)	-2.6(10)	-7.1(7)
O2	64.7(11)	73.9(12)	140(2)	-1.4(13)	-36.3(14)	-4.1(9)
O3	55.7(9)	46.6(9)	137(2)	8.3(10)	2.7(11)	7.5(7)
C1	107(2)	82(2)	96(3)	2.1(18)	-11(2)	8.6(18)
C2	75.6(15)	45.4(12)	99(3)	6.3(13)	8.0(17)	11.6(11)
C3	84.5(18)	60.7(15)	107(3)	8.0(16)	26(2)	17.1(14)
C4	62.1(14)	60.5(15)	133(3)	16.7(18)	29.3(19)	7.3(12)
C5	49.3(11)	40.5(11)	115(3)	7.5(13)	10.9(15)	-0.2(9)
C6	45.8(10)	35.5(9)	98(2)	5.3(11)	2.8(12)	0.1(8)
C7	55.1(11)	42.7(11)	92(2)	6.3(12)	0.8(13)	-0.7(9)
C8	42.6(9)	38.1(10)	97(2)	7.1(11)	-8.3(12)	-3.0(8)
C9	48.4(11)	44.0(11)	119(3)	2.9(14)	-13.9(16)	-1.6(9)
C10	45.1(9)	39.2(10)	93(2)	3.8(12)	-6.1(12)	-6.0(8)
C11	82.5(17)	53.6(14)	100(3)	4.2(15)	-12.5(18)	-0.5(12)
C12	88.4(18)	67.2(16)	99(3)	-10.3(17)	2.3(19)	-5.6(15)
C13	63.9(14)	55.4(14)	116(3)	-9.2(16)	3.1(18)	-2.7(11)
C14	59.0(12)	50.0(13)	120(3)	5.9(16)	-6.6(16)	7.5(10)
C15	48.4(10)	48.5(11)	92(2)	4.4(13)	-5.6(12)	1.9(9)
C16	50.2(10)	37.8(10)	89(2)	3.3(11)	-11.8(12)	-2.9(8)
C17	50.9(10)	42.9(11)	95(2)	3.0(12)	-6.3(13)	-2.1(9)
C18	63.0(13)	49.9(12)	90(2)	3.0(12)	-4.7(13)	-13.4(10)
C19	83.7(16)	41.5(12)	94(2)	7.5(12)	-0.3(16)	-11.5(11)
C20	75.8(15)	39.2(11)	98(2)	5.9(12)	-3.5(16)	5.6(10)
C21	54.4(11)	41.9(10)	93(2)	3.1(12)	-5.8(13)	-1.4(9)
C22	68.4(14)	66.8(16)	118(3)	-1.4(17)	3.8(17)	18.1(13)
C23	69.7(14)	65.0(15)	103(3)	8.1(16)	5.4(17)	-19.0(12)
C24	69.7(19)	261(7)	126(4)	-21(5)	5(3)	-22(3)
C25	86(3)	415(13)	126(5)	53(6)	7(3)	-2(5)

Table 15. Bond Lengths for **3bd (CCDC 2174815).**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C5	1.391(4)	C10	C11	1.389(4)
O1	C9	1.368(4)	C10	C15	1.378(4)
O2	C9	1.185(4)	C11	C12	1.389(4)
O3	C21	1.369(3)	C12	C13	1.372(5)
O3	C22	1.414(3)	C13	C14	1.361(5)
C1	C2	1.495(5)	C14	C15	1.395(4)
C2	C3	1.387(4)	C16	C17	1.387(3)
C2	C7	1.391(4)	C16	C21	1.395(3)
C3	C4	1.388(5)	C17	C18	1.388(3)
C4	C5	1.365(5)	C18	C19	1.378(4)
C5	C6	1.385(3)	C18	C23	1.515(4)
C6	C7	1.378(4)	C19	C20	1.383(4)
C6	C8	1.506(4)	C20	C21	1.388(3)
C8	C9	1.558(3)	C23	C24	1.429(7)
C8	C10	1.538(3)	C24	C25	1.227(8)
C8	C16	1.534(3)			

Table 16. Bond Angles for **3bd (CCDC 2174815).**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O1	C5	108.4(2)	C11	C10	C8	119.8(2)
C21	O3	C22	119.3(2)	C15	C10	C8	122.1(3)
C3	C2	C1	121.8(3)	C15	C10	C11	118.1(2)
C3	C2	C7	118.2(3)	C10	C11	C12	121.0(3)
C7	C2	C1	120.0(3)	C13	C12	C11	120.1(3)
C2	C3	C4	122.9(4)	C14	C13	C12	119.5(3)
C5	C4	C3	116.7(3)	C13	C14	C15	120.8(3)
C4	C5	O1	125.1(2)	C10	C15	C14	120.5(3)
C4	C5	C6	122.6(3)	C17	C16	C8	120.85(19)
C6	C5	O1	112.3(3)	C17	C16	C21	118.6(2)
C5	C6	C8	108.6(2)	C21	C16	C8	120.1(2)
C7	C6	C5	119.5(3)	C16	C17	C18	122.3(2)
C7	C6	C8	131.9(2)	C17	C18	C23	120.8(2)
C6	C7	C2	120.0(2)	C19	C18	C17	117.6(2)
C6	C8	C9	100.2(2)	C19	C18	C23	121.6(2)
C6	C8	C10	113.9(2)	C18	C19	C20	121.7(2)
C6	C8	C16	111.1(2)	C19	C20	C21	119.8(2)
C10	C8	C9	105.10(19)	O3	C21	C16	115.38(19)
C16	C8	C9	113.41(19)	O3	C21	C20	124.8(2)
C16	C8	C10	112.5(2)	C20	C21	C16	119.8(2)
O1	C9	C8	109.9(3)	C24	C23	C18	114.3(3)
O2	C9	O1	120.9(2)	C25	C24	C23	133.6(8)
O2	C9	C8	128.8(3)				

Table 17. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3bd (CCDC 2174815).**

Atom	*x*	*y*	*z*	U(eq)
H1A	5597	5469	9366	143
H1B	4769	6006	9753	143
H1C	5408	6492	9205	143
H3	3234	5313	9437	101
H4	2052	4904	8646	102
H7	5217	5921	8017	76
H11	4262	4979	5668	94
H12	5153	3791	5212	102
H13	5984	2786	5893	94
H14	5927	2971	7022	92
H15	5058	4170	7488	76
H17	5681	6081	6451	75
H19	5090	8683	6131	88
H20	3458	8467	6465	85
H22A	1810	7893	6563	127
H22B	2215	8122	7275	127
H22C	1348	7417	7189	127
H23A	6836	8180	6183	95
H23B	7071	7166	6343	95
H24	6660	6837	5243	183
H25A	7505	8433	5048	251
H25B	7338	7621	4526	251

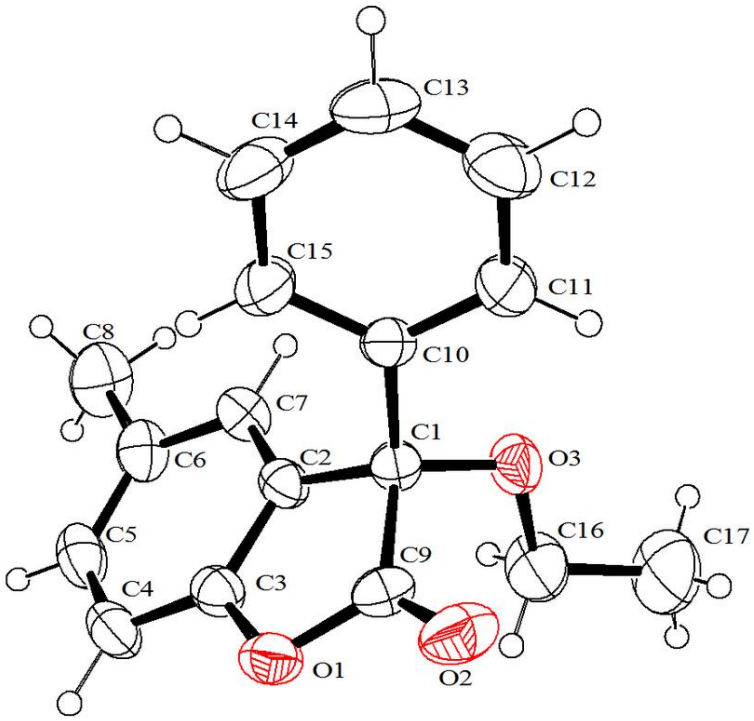


Fig. 5. Crystal structure of **5f (CCDC 2174816)**

Table 18. Crystal data and structure refinement for **5f (CCDC 2174816)**

Properties	values	Properties	values
CCDC number	2174816	$F(000)$	568
Empirical formula	$C_{17}H_{16}O_3$	Crystal size [mm^3]	0.200×0.150×0.100
Formula weight	268.30	Crystal colour	colourless
Temperature [K]	298(2)	Crystal shape	block
Crystal system	monoclinic	Radiation	Cu K_α (λ=1.54184 Å)
Space group (number)	$P2_1/c$ (14)	2Θ range [°]	10.21 to 154.20 (0.79 Å)
a [Å]	8.60280(10)	Index ranges	-10 ≤ h ≤ 9 -12 ≤ k ≤ 12 -20 ≤ l ≤ 21
b [Å]	10.12580(10)	Reflections collected	17553
c [Å]	17.0368(3)	Independent reflections	3016 R_{int} = 0.0384 R_{sigma} = 0.0247
α [Å]	90	Completeness to θ = 67.684°	99.7 %
β [Å]	100.558(2)	Data / Restraints / Parameters	3016/0/184
γ [Å]	90	Goodness-of-fit on F^2	1.137
Volume [Å^3]	1458.95(4)	Final R indexes [I≥2σ(I)]	R_1 = 0.0448 wR_2 = 0.1300
Z	4	Final R indexes [all data]	R_1 = 0.0613 wR_2 = 0.1509
ρ_{calc} [g/cm^3]	1.221	Largest peak/hole [eÅ^3]	0.27/-0.20
μ [mm^{-1}]	0.672	Extinction coefficient	0.0046(7)

Table 19. Atomic coordinates and U_{eq} [Å^2] for **5f (CCDC 2174816)**

Atom	***x***	***y***	***z***	U_{eq}
C1	0.67849(16)	0.41381(13)	0.62805(8)	0.0438(3)
C2	0.70199(15)	0.29480(13)	0.57869(8)	0.0438(3)
C3	0.82093(16)	0.21825(14)	0.62090(9)	0.0479(3)
C4	0.8698(2)	0.10152(15)	0.59249(11)	0.0609(4)
H4	0.950611	0.051392	0.621895	0.073
C5	0.7924(2)	0.06257(15)	0.51792(11)	0.0629(4)
H5	0.823698	-0.015384	0.496506	0.075
C6	0.6692(2)	0.13504(16)	0.47323(9)	0.0576(4)
C7	0.62471(18)	0.25359(15)	0.50468(8)	0.0516(4)
H7	0.543653	0.304316	0.475919	0.062
C8	0.5830(3)	0.0852(2)	0.39355(12)	0.0852(6)
H8A	0.537528	0.158465	0.361600	0.128
H8B	0.500579	0.025632	0.401744	0.128
H8C	0.655935	0.039766	0.366629	0.128
C9	0.81075(16)	0.39079(15)	0.70234(9)	0.0507(4)
C10	0.52058(15)	0.41707(13)	0.65657(8)	0.0438(3)
C11	0.4615(2)	0.53546(16)	0.67802(10)	0.0589(4)
H11	0.515758	0.613587	0.673070	0.071
C12	0.3209(2)	0.5379(2)	0.70703(12)	0.0758(5)
H12	0.280285	0.618333	0.720275	0.091
C13	0.2415(2)	0.4240(2)	0.71640(12)	0.0749(6)
H13	0.148302	0.426633	0.736710	0.090
C14	0.2998(2)	0.3058(2)	0.69573(12)	0.0753(5)
H14	0.246052	0.227882	0.701911	0.090
C15	0.43912(19)	0.30193(17)	0.66556(11)	0.0612(4)
H15	0.477915	0.221414	0.651293	0.073
C16	0.8442(3)	0.5538(2)	0.56401(15)	0.0825(6)
H16A	0.838537	0.505497	0.514391	0.099
H16B	0.931529	0.518611	0.602494	0.099
C17	0.8703(4)	0.6931(2)	0.5508(2)	0.1203(10)
H17A	0.783990	0.727295	0.512366	0.181
H17B	0.967181	0.703821	0.531022	0.181
H17C	0.877167	0.740281	0.600159	0.181
O1	0.88507(12)	0.27284(11)	0.69552(6)	0.0558(3)
O2	0.84904(14)	0.46016(14)	0.75863(8)	0.0725(4)
O3	0.69938(13)	0.53767(10)	0.59328(7)	0.0570(3)

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 20. Bond lengths and angles for **5f (CCDC 2174816).**

Atom–Atom-Atom	Length [Å]Angle [°]	Atom–Atom-Atom	Length [Å]Angle [°]
C1–O3	1.4125(16)	C10–C1–C9	107.78(11)
C1–C2	1.5042(18)	C3–C2–C7	119.69(13)
C1–C10	1.5246(18)	C3–C2–C1	108.80(12)
C1–C9	1.5567(19)	C7–C2–C1	131.49(12)
C2–C3	1.3768(19)	C4–C3–C2	123.16(15)
C2–C7	1.378(2)	C4–C3–O1	124.34(13)
C3–C4	1.372(2)	C2–C3–O1	112.50(13)
C3–O1	1.4033(18)	C3–C4–C5	116.36(14)
C4–C5	1.379(3)	C4–C5–C6	122.85(14)
C5–C6	1.395(2)	C5–C6–C7	118.49(15)
C6–C7	1.396(2)	C5–C6–C8	120.92(16)
C6–C8	1.510(3)	C7–C6–C8	120.57(16)
C9–O2	1.1856(18)	C2–C7–C6	119.43(14)
C9–O1	1.3696(19)	O2–C9–O1	121.36(14)
C10–C11	1.377(2)	O2–C9–C1	128.48(15)
C10–C15	1.383(2)	O1–C9–C1	110.16(12)
C11–C12	1.388(2)	C11–C10–C15	119.04(14)
C12–C13	1.365(3)	C11–C10–C1	119.79(12)
C13–C14	1.368(3)	C15–C10–C1	121.07(12)
C14–C15	1.388(2)	C10–C11–C12	119.86(16)
C16–O3	1.433(2)	C13–C12–C11	120.92(17)
C16–C17	1.453(3)	C12–C13–C14	119.61(16)
O3–C1–C2	115.88(11)	C13–C14–C15	120.12(17)
O3–C1–C10	107.68(10)	C10–C15–C14	120.44(16)
C2–C1–C10	114.48(11)	O3–C16–C17	109.50(18)
O3–C1–C9	110.10(11)	C9–O1–C3	107.95(11)
C2–C1–C9	100.46(11)	C1–O3–C16	115.61(12)

References.

[1] Rigaku Oxford Diffraction , CrysAlisPro Software System, Version 1.171, Rigaku Corporation, Oxford, UK, (2015).

[2] G. M. Sheldrick, *Acta Cryst.***2015**, *A71*, 3–8, doi:10.1107/S2053273314026370.

[3] G. M. Sheldrick, *Acta Cryst.***2015**, *C71*, 3–8, doi:10.1107/S2053229614024218.

[4] L. J. Farrugia, WinGX and ORTEP for Windows: an update. J. Appl. Cryst. 45, 849-854(2012).