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Supporting Information

for

Cs_2CO_3-Promoted reaction of tertiary bromopropargylic alcohols and phenols in DMF: a novel approach to α-phenoxyketones

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General information, synthetic procedures and additional optimization results, NMR spectra and characterization of synthesized compounds

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1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.1 and 100.6 MHz, respectively) in $CDCl_3$ or $(CD_3)_2CO$ using hexamethyldisiloxane as internal references at 20-25 °C.
IR spectra were measured on a Varian 3100 FT-IR Excalibur series instrument as thin films or KBr pellets. Microanalyses were performed on a Flash 2000 elemental analyzer. Melting points were determined using a Kofler micro hot stage. Mass spectra were recorded on a GCMS-QP5050A spectrometer made by Shimadzu Company. Chromatographic column parameters were as follows: SPB^{TM}-5, length 60 m, internal diameter 0.25 mm, thickness of stationary phase film 0.25 μm; injector temperature 250 °C, gas carrier – helium, flow rate 0.7 mL/min; detector temperature 250 °C; mass analyzer: quadrupole, electron ionization, electron energy: 70 eV, ion source temperature 200 °C; mass range 34-650 Da. The solvent was distilled DMF. Column chromatography was performed on silica gel 60 (230-400 mesh, particle size 0.040-0.063 mm, Merck). Bromopropargylic alcohols **1a**–**c** and chloropropargylic alcohol were prepared according to published methods [1-3]. Phenol (**2a**)**,** naphthalen-1-ol (**2b**), naphthalen-2-ol (**2c**), 4-nitrophenol (**2d**), 2-nitrophenol (**2e**), 4-methylphenol (**2f**), 4-methoxyphenol (**2g**), 4-bromophenol (**2h**), 4-allyl-2-methoxyphenol (**2i**) are commercial reagents. Commercially available starting materials were used without further purification. The structures of synthesized products have been proven by ^{1}H, ^{13}C and 2D (NOESY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC) NMR techniques, as well as IR spectra.

2. Method A. Typical procedure for preparation of phenoxyhydroxyketones 4 in DMF, 50–55 °C

To a stirred solution of Cs_2CO_3 (326 mg, 1 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 50-55 °C for 3 h, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (5.0 × 4.0 cm, gradient elution, C_6H_{14}–Et_2O, 2:1 followed by Et_2O, Me_2CO) to give 4-bromo-2-methyl-3-phenoxybut-3-en-2-ol (**3a**) (10 mg, 4%), 3-hydroxy-3-methyl-1-phenoxybutan-2-one (**4a**) (214 mg, 55%), 3-methyl-1,1-diphenoxybutan-2-one (**5a**) (30 mg, 22%) and (*Z*)-4,4-dimethyl-5-(phenoxymethylene)-1,3-dioxolan-2-one (**7**) (11 mg, 5%).

3. Method B. Typical procedure for preparation of phenoxyhydroxyketones 4 in DMF/H_2O, 50–55 °C

To a stirred solution of Cs_2CO_3 (326 mg, 1 mmol) and phenol (**2a**; 94 mg, 1 mmol) in distilled H_2O (0.5 mL) and DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 50–55 °C for 3 h. The mixture was filtered and concentrated, this gave mixture of the 3-hydroxy-3-methyl-1-phenoxybutan-2-one (**4a**) and 1,3-dihydroxy-3-methylbutan-2-one (**8a**). The mixture of the **4a** and **8a** was purified by flash column chromatography on silica gel (5.0 × 4.0 cm, gradient elution, C_6H_{14}–Et_2O, 2:1 followed by Et_2O, Me_2CO) to give products **4a** (152 mg, 78%) and **8a** (6 mg, 5%).

4. Method C. Typical procedure for preparation of phenoxyhydroxyketones 4 in DMF, 110 °C

To a stirred solution of carbonate [1 mmol (K_2CO_3, 138 mg or Cs_2CO_3, 326 mg)] and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 110 °C for 1 h. The mixture was filtered and concentrated, this gave mixture of the 4-bromo-2-methyl-3-phenoxybut-3-en-2-ol (**3a**), 3-hydroxy-3-methyl-1-phenoxybutan-2-one (**4a**) and 3-methyl-1,1-diphenoxybutan-2-one (**5a**). The mixture of the **3a**, **4a** and **5a** was purified by flash column chromatography on silica gel (5.0 × 4.0 cm, gradient elution, C_6H_{14}–Et_2O, 2:1 followed by Et_2O, Me_2CO) to give products **3a** (23 mg, 9% for K_2CO_3; 8 mg, 3% for C_2CO_3), **4a** (60 mg, 31% for K_2CO_3; 75 mg, 39% for C_2CO_3) and **5a** (28 mg, 21% for K_2CO_3; 33 mg, 24% for C_2CO_3).

5. Method D. Typical procedure for preparation of phenoxyhydroxyketones 4 in DMF, 20–25 °C

To a stirred solution of Cs_2CO_3 (326 mg, 1 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 20-25 °C for 15 h. The mixture was filtered and concentrated, this gave mixture of the 4-bromo-2-methyl-3-phenoxybut-3-en-2-ol (**3a**), 3-hydroxy-3-methyl-1-phenoxybutan-2-one (**4a**), 3-methyl-1,1-diphenoxybutan-2-one (**5a**), (*Z*)-5-(bromomethylene)-4,4-dimethyl-1,3-dioxolan-2-one (**6a**) and (*Z*)-4,4-dimethyl-5-(phenoxymethylene)-1,3-dioxolan-2-one (**7**). The mixture of the **3a**, **4a**, **5a**, **6a** and **7** was purified by flash column chromatography on silica gel (5.0 × 4.0 cm, gradient elution, C_6H_{14}–Et_2O, 2:1 followed by Et_2O, Me_2CO) to give products **3a** (10 mg, 4%), **4a** (56 mg, 29%), **5a** (21 mg, 16%) and **7** (13 mg, 6%).

6. Optimization of reaction conditions. Yields of the synthesized products.

a) Following **Method A** to a stirred solution of Cs_2CO_3 (652 mg, 2 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 50-55 °C for 3 h. After purification the desired products **4a** (85 mg, 44%) and **5a** (33 mg, 24%) were obtained.
b) Following **Method A** to a stirred solution of K_2CO_3 (138 mg, 1 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 50-55 °C for 8 h. After purification the desired products **4a** (58 mg, 30%), **5a** (13 mg, 10%) and **7** (20 mg, 9%) were obtained.
c) Following **Method A** to a stirred solution of $CsHCO_3$ (194 mg, 1 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 50-55 °C for 9 h. After purification the desired products **4a** (35 mg, 18%), **6a** (56 mg, 27%) and **7** (33 mg, 15%) were obtained.
d) Following **Method C** to a stirred solution of Cs_2CO_3 (652 mg, 2 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 110 °C for 1 h. After purification the desired products **3a** (23 mg, 9%), **4a** (49 mg, 25%) and **5a** (12 mg, 9%) were obtained.
e) Following **Method C** to a stirred solution of $CsHCO_3$ (194 mg, 1 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 110 °C for 1 h. After purification the desired products **4a** (12 mg, 6%), **5a** (11 mg, 8%) and **6a** (74 mg, 36%) were obtained.
f) Following **Method C** to a stirred solution of $KHCO_3$ (194 mg, 1 mmol) and phenol (**2a**; 94 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added

dropwise. The reaction mixture was stirred at 110 °C for 1 h. After purification the desired products **4a** (15 mg, 8%), **5a** (7 mg, 5%) and **6a** (59 mg, 29%) were obtained.
g) To a stirred solution of $CsHCO_3$ (194 mg, 1 mmol) in DMF (5 mL) 4-bromo-2-methylbut-3-yn-2-ol (**1a**; 196 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at 110 °C for 1 h. The mixture was filtered and concentrated, this gave (*Z*)-5-(bromomethylene)-4,4-dimethyl-1,3-dioxolan-2-one (**6a**). The product **6a** was purified by flash column chromatography on silica gel (5.0 × 4.0 cm, gradient elution, C_6H_{14}–Et_2O, 2:1 followed by Et_2O, Me_2CO) to give the desired product **6a** (65 mg, 31%).

7. Characterization data for all products

4-Bromo-2-methyl-3-phenoxybut-3-en-2-ol (3a)
Yield 10 mg, 4% (Method A). White solid; mp 68-70 °C.
IR (KBr): 3115, 3057, 2994, 2972, 2928, 2864, 1633, 1592, 1489, 1457, 1422, 1360, 1291, 1260, 1214, 1202, 1177, 1163, 1129, 1077, 1022, 970, 900, 775, 754, 746, 735, 688, 647, 546, 498 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.28-7.26 (m, 2 H, Ph), 6.99-6.97 (m, 3 H, Ph), 6.32 (s, 1 H, CH), 1.93 (s, 1 H, OH), 1.43 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 159.0 (CH*C*O), 156.0, 130.0, 122.2, 115.7 (Ph), 93.8 (CH), 73.9 (C–OH), 28.3 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 258 (22) $[M+1]^+$, 256 (23), 241 (10), 162 (11), 161 (14), 119 (29), 118 (14), 95 (11), 94 (82), 91 (44), 90 (12), 81 (11), 77 (74), 66 (15), 65 (32), 59 (100), 51 (38), 43 (96), 41 (16), 39 (40).
Anal. Calcd for $C_{11}H_{13}BrO_2$ (257.13): C, 51.38; H, 5.10; Br, 31.08. Found: C, 51.37; H, 5.12; Br, 31.05.

3-Hydroxy-3-methyl-1-phenoxybutan-2-one (4a)
Yield 107 mg, 55% (Method A); Yield 152 mg, 78% (Method B). White solid; mp 66-67 °C.
IR (KBr): 3066, 2979, 2922, 2876, 1727, 1597, 1496, 1414, 1357, 1295, 1250, 1185, 1142, 1040, 966, 880, 840, 754, 690, 611, 554, 505, 425 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.32-7.25 (m, 2 H, Ph), 7.00-6.96 (m, 1 H, Ph), 6.92-6.86 (m, 2 H, Ph), 4.97 (s, 2 H, CH_2), 3.15 (s, 1 H, OH), 1.46 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.2 (C=O), 157.8, 130.0, 121.9, 114.7 (Ph), 76.6 (C–OH), 69.2 (CH_2), 26.9 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 194 (11) $[M^+]$, 152 (10), 151 (96), 133 (60), 107 (21), 105 (35), 95 (24), 94 (77), 79 (17), 77 (49), 66 (11), 65 (16), 57 (55), 51 (23), 43 (100), 39 (15).
Anal. Calcd for $C_{11}H_{14}O_3$ (194.23): C, 68.02; H, 7.27. Found: C, 68.00; H, 7.30.

3-Hydroxy-3-methyl-1-(naphthalen-1-yloxy)butan-2-one (4b)
Yield 137 mg, 56% (Method A); Yield 198 mg, 81% (Method B). Brown solid; mp 87-90 °C.
IR (KBr): 3056, 2976, 2922, 2870, 1721, 1629, 1579, 1507, 1464, 1400, 1355, 1277, 1231, 1183, 1143, 1056, 1017, 962, 869, 769, 712, 591, 569, 543, 521, 492 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.34-8.32 (m, 1 H, Naphthyl), 7.80-7.78 (m, 1 H, Naphthyl), 7.53-7.42 (m, 3 H, Naphthyl), 7.31 (t, *J* = 8.0 Hz, 1 H, Naphthyl), 6.66 (d, *J* = 7.6 Hz, 1 H, Naphthyl), 5.13 (s, 2 H, CH_2), 3.19 (s, 1 H, OH), 1.50 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 208.9 (C=O), 153.7, 134.7, 127.6, 126.7, 125.7, 125.5, 122.1, 121.6, 105.2 (Naphthyl), 76.6 (C–OH), 69.5 (CH_2), 27.0 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 185 (45) $[M – Me_2COH]^+$, 158 (95), 157 (17), 144 (100), 130 (15), 129 (13), 127 (71), 125 (50), 115 (43), 114 (16), 79 (11), 75 (16), 65 (24), 64 (27), 59 (81), 57 (17), 55 (25), 51 (19), 41 (23).
Anal. Calcd for $C_{15}H_{16}O_3$ (244.29): C, 73.75; H, 6.60. Found: C, 73.71; H, 6.58.

3-Hydroxy-3-methyl-1-(naphthalen-2-yloxy)butan-2-one (4c)
Yield 132 mg, 54% (Method A); Yield 177 mg, 73% (Method B). White solid; mp 131-133 °C.
IR (KBr): 3057, 2979, 2933, 2911, 1816, 1727, 1630, 1600, 1510, 1470, 1440, 1412, 1391, 1359, 1261, 1220, 1183, 1146, 1097, 1037, 968, 842, 816, 742, 584, 476 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ =7.76 (d, *J* = 8.6 Hz, 2 H, Naphthyl), 7.69 (d, *J* = 8.1 Hz, 1 H, Naphthyl), 7.45-7.33 (m, 2 H, Naphthyl), 7.27-7.19 (m, 1 H, Naphthyl), 7.06-7.05 (m, 1 H, Naphthyl), 5.08 (s, 2 H, CH_2), 3.08 (s, 1 H, OH), 1.51 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 208.8 (C=O), 155.8, 134.3, 129.9, 129.5, 127.8, 126.9, 126.7, 124.3, 118.6, 107.3 (Naphthyl), 76.7 (C–OH), 69.3 (CH_2), 27.0 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 244 (26) [M^+], 201 (35), 183 (37), 157 (11), 145 (15), 144 (100), 143 (19), 129 (12), 127 (31), 116 (17), 115 (87), 43 (72).
Anal. Calcd for $C_{15}H_{16}O_3$ (244.29): C, 73.75; H, 6.60. Found: C, 73.73; H, 6.62.

3-Hydroxy-3-methyl-1-(4-nitrophenoxy)butan-2-one (**4d**)
Yield 156 mg, 65% (Method A); Yield 221 mg, 92% (Method B). Colorless crystals; mp 68-71 °C.
IR (KBr): 3083, 2979, 2936, 2897, 1731, 1593, 1507, 1465, 1338, 1271, 1240, 1187, 1109, 1030, 961, 850, 751, 690, 635, 574, 532, 505, 470 cm^{-1}.
^1H NMR [400.1 MHz, $(CD_3)_2CO$]: δ = 8.23-8.13 (m, 2 H, Ph), 7.10-6.99 (m, 2 H, Ph), 5.43 (s, 2 H, CH_2), 4.66 (s, 1 H, OH), 1.38 [s, 6 H, $(CH_3)_2$].
^{13}C NMR [100.6 MHz, $(CD_3)_2CO$]: δ = 209.1 (C=O), 164.3, 142.2, 126.2, 115.4 (Ph), 77.1 (C–OH), 69.9 (CH_2), 26.8 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 152 (77) [M – $(COC(OH)Me_2)]^+$, 76 (11), 59 (100), 43 (10).
Anal. Calcd for $C_{11}H_{13}NO_5$ (239.23): C, 55.23; H, 5.48; N, 5.86. Found: C, 55.25; H, 5.45; N, 5.87.

3-Hydroxy-3-methyl-1-(2-nitrophenoxy)butan-2-one (4e)
Yield 114 mg, 48% (Method A); Yield 78 mg, 33% (Method B). Yellow oil.
IR (film): 3085, 2980, 2932, 2876, 1734, 1606, 1526, 1487, 1426, 1355, 1287, 1240, 1137, 1087, 1024, 964, 858, 774, 746, 700, 664, 557, 518 cm^{-1}.
^1H NMR [400.1 MHz, $(CD_3)_2CO$]: δ = 7.84-7.78 (m, 1 H, Ph), 7.57-7.52 (m, 1 H, Ph) 7.13-7.05 (m, 2 H, Ph), 5.44 (s, 2 H, CH_2), 4.68 (s, 1 H, OH), 1.36 [s, 6 H, $(CH_3)_2$].
^{13}C NMR [100.6 MHz, $(CD_3)_2CO$]: δ = 208.9 (C=O), 151.7, 141.0, 134.1, 125.4, 121.3, 115.4 (Ph), 77.0 (C–OH), 70.4 (CH_2), 26.7 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 123 (42) [M – $(Me_2C(OH)COCH_2O)]^+$, 93 (12), 77 (12), 59 (100), 43 (12), 41 (15), 39 (14).
Anal. Calcd for $C_{11}H_{13}NO_5$ (239.23): C, 55.23; H, 5.48; N, 5.86. Found: C, 55.20; H, 5.47; N, 5.89.

3-Hydroxy-3-methyl-1-(*p*-tolyloxy)butan-2-one (4f)
Yield 65 mg, 31% (Method A); Yield 139 mg, 67% (Method B). Colorless crystals; mp 86-88 °C.
IR (KBr): 2987, 2975, 2929, 2902, 2871, 1729, 1613, 1588, 1512, 1465, 1424, 1356, 1292, 1247, 1181, 1143, 1107, 1039, 968, 814, 581, 498 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 8.0 Hz, 2 H, Ph), 6.78 (d, *J* = 8.0 Hz, 2 H, Ph), 4.93 (s, 2 H, CH_2), 3.01 (s, 1 H, OH), 2.27 (s, 3 H, CH_3), 1.45 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.3 (C=O), 155.8, 131.3, 130.1, 114.6 (Ph) , 76.5 (C–OH), 69.5 (CH_2), 26.9 [$(CH_3)_2$], 20.5 (CH_3).
MS (EI): *m/z* (%) = 208 (13) [M^+], 150 (18), 122 (66), 121 (31), 109 (10), 108 (79), 107 (32), 92 (16), 91 (44), 77 (19), 65 (30), 60 (10), 59 (100), 43 (24), 41 (17), 39 (15).
Anal. Calcd for $C_{12}H_{16}O_3$ (208.26): C, 69.21; H, 7.74. Found: C, 69.19; H, 7.76.

3-Hydroxy-1-(4-methoxyphenoxy)-3-methylbutan-2-one (4g)
Yield 80 mg, 36% (Method A); Yield 118 mg, 53% (Method B). Colorless crystals; mp 98-102 °C.
IR (KBr): 3072, 3049, 3000, 2972, 2934, 2909, 2842, 1725, 1630, 1510, 1469, 1449, 1414, 1373, 1358, 1348, 1291, 1237, 1183, 1138, 1112, 1040, 965, 827, 795, 721, 584, 549, 529 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 6.86-6.80 (m, 4 H, Ph), 4.91 (s, 2 H, CH_2), 3.75 (s, 3 H, OCH_3), 3.14 (s, 1 H, OH), 1.45 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.4 (C=O), 154.7, 152.0, 116.0, 114.8 (Ph), 76.5 (C–OH), 70.3 (CH_2), 55.8 (OCH_3), 26.9 [$(CH_3)_2$].
Anal. Calcd for $C_{12}H_{16}O_4$ (224.26): C, 64.27; H, 7.19. Found: C, 64.30; H, 7.18.

1-(4-Bromophenoxy)-3-hydroxy-3-methylbutan-2-one (4h)
Yield 136 mg, 50% (Method A); Yield 213 mg, 78% (Method B). White solid; mp 95-98 °C.
IR (KBr): 3019, 2978, 2935, 2851, 1732, 1639, 1594, 1511, 1464, 1421, 1367, 1264, 1216, 1146, 1127, 1104, 1033, 1000, 962, 919, 851, 756, 668 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.39-7.34 (m, 2 H, Ph), 6.78-6.74 (m, 2 H, Ph), 4.97 (s, 2 H, CH_2), 2.99 (s, 1 H, OH), 1.45 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 208.7 (C=O), 157.0, 132.5, 116.6, 114.1 (Ph), 76.7 (C–OH), 69.2 (CH_2), 27.0 [$(CH_3)_2$].
Anal. Calcd for $C_{11}H_{13}BrO_3$ (273.13): C, 48.37; H, 4.80; Br, 29.26. Found: C, 48.36; H, 4.76; Br, 29.29.

1-(4-Allyl-2-methoxyphenoxy)-3-hydroxy-3-methylbutan-2-one (4i)
Yield 89 mg, 34% (Method A); Yield 145 mg, 55% (Method B). Colorless crystals; mp 61-63 °C.
IR (KBr): 3019, 2978, 2935, 2919, 2851, 1732, 1639, 1594, 1511, 1464, 1421, 1367, 1264, 1216, 1146, 1127, 1104, 1033, 1000, 962, 919, 756, 668 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 6.74-6.66 (m, 3 H, Ph), 5.98-5.88 (m, 1 H, CH_2CH), 5.09-5.03 (m, 2 H, $=CH_2$), 4.94 (s, 2 H, CH_2), 3.85 (s, 3 H, OCH_3), 3.52 (s, 1 H, OH), 3.32 (d, *J* = 6.8 Hz, 1 H, CH_2CH), 1.44 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.2 (C=O), 149.7, 145.6 (Ph), 137.4 ($CH=CH_2$), 134.8, 120.6 (Ph), 115.9 ($=CH_2$), 114.9, 112.6 (Ph), 71.6 (C–OH), 55.9 (CH_2), 39.9 (OCH_3), 26.7 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 264 (5) [M^+], 178 (27), 164 (40), 163 (18), 147 (13), 115 (13), 103 (10), 91 (15), 77 (13), 59 (100), 43 (18), 41 (21), 39 (12).
Anal. Calcd for $C_{15}H_{20}O_4$ (264.32): C, 68.16; H, 7.63. Found: C, 68.15; H, 7.66.

1-(1-Hydroxycyclohexyl)-2-phenoxyethan-1-one (**4j**)
Yield 141 mg, 60% (Method A); Yield 140 mg, 60% (Method B). Colorless crystallizing substance.
IR (KBr): 3064, 2933, 2857, 1731, 1710, 1600, 1497, 1446, 1433, 1409, 1387, 1351, 1306, 1291, 1247, 1228, 1200, 1175, 1153, 1130, 1084, 1038, 984, 928, 883, 862, 842, 828, 751, 689, 580, 555, 533, 507, 437 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.28-7.24 (m, 2 H, Ph), 6.98-6.94 (m, 1 H, Ph), 6.89-6.86 (m, 2 H, Ph), 5.00 (s, 2 H, CH_2), 2.94 (s, 1 H, OH), 1.83-1.58 [m, 9 H, $(CH_2)_5$], 1.33-1.23 [m, 1 H, $(CH_2)_5$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.3 (C=O), 157.9, 129.6, 121.7, 114.7 (Ph), 78.3 (C–OH), 69.4 (CH_2), 34.1, 25.1, 20.8 [$(CH_2)_5$].
MS (EI): *m/z* (%) = 234 (29) [M^+], 141 (10), 112 (18), 108 (47), 107 (39), 99 (29), 97 (12), 95 (24), 94 (100), 81 (28), 79 (20), 77 (38), 70 (12), 69 (13), 65 (13), 55 (44), 51 (10), 43 (60), 42 (10), 41 (22), 39 (18).

Anal. Calcd for $C_{14}H_{18}O_3$ (234.30): C, 71.77; H, 7.74. Found: C, 71.80; H, 7.69.

1-(1-Hydroxycyclohexyl)-2-(4-nitrophenoxy)ethan-1-one (**4k**)
Yield 217 mg, 78% (Method B). Colorless crystals; mp 110-114 °C.
IR (KBr): 3114, 2934, 2856, 1716, 1590, 1512, 1450, 1415, 1340, 1274, 1228, 1182, 1111, 1061, 990, 846, 751, 688, 637, 518 cm^{-1}.
^1H NMR [400.1 MHz, $(CD_3)_2CO$]: δ = 8.19-8.15 (m, 2 H, Ph), 7.05-7.01 (m, 2 H, Ph), 5.42 (s, 2 H, CH_2), 4.53 (s, 1 H, OH), 1.74-1.52 [m, 9 H, $(CH_2)_5$], 1.32-1.23 [m, 1 H, $(CH_2)_5$].
^{13}C NMR [100.6 MHz, $(CD_3)_2CO$]: δ = 209.5 (C=O), 164.4 (C*i*), 142.3 (C*p*), 126.2, 115.5 (Ph), 78.7 (C–OH), 70.2 (CH_2), 34.2, 25.8, 21.3 [$(CH_2)_5$].
MS (EI): *m/z* (%) = 279 (4) [M^+], 167 (14), 150 (12), 149 (43), 125 (12), 123 (13), 113 (11), 109 (20), 99 (74), 98 (17), 95 (24), 94 (12), 93 (26), 85 (21), 83 (49), 82 (19), 81 (31), 80 (11), 71 (53), 70 (29), 69 (48), 65 (43), 64 (10), 57 (100), 56 (19), 55 (58), 45 (13), 44 (15), 43 (45), 41 (34), 39 (23).
Anal. Calcd for $C_{14}H_{17}NO_5$ (279.29): C, 60.21; H, 6.14; N, 5.02. Found: C, 60.33; H, 6.12; N, 5.00.

3-Hydroxy-3,4,4-trimethyl-1-phenoxypentan-2-one (4l)
Yield 80 mg, 34% (Method A); Yield 46 mg, 39% (Method B, conversion of **1b** was 50%). Colorless crystals; mp 91-94 °C.
IR (KBr): 2983, 2959, 2908, 2875, 1721, 1600, 1587, 1497, 1446, 1415, 1394, 1364, 1337, 1292, 1247, 1222, 1163, 1140, 1100, 1033, 1006, 975, 912, 884, 850, 756, 719, 691, 623, 557, 509, 477, 450 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.32-7.19 (m, 2 H, Ph), 7.00-6.85 (m, 3 H, Ph), 5.07-4.94 (m, 2 H, CH_2), 2.36 (s, 1 H, OH), 1.37 (s, 3 H, CH_3), 1.01 [s, 9 H, $(CH_3)_3$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 209.5 (C=O), 158.2, 129.6, 121.6, 115.0 (Ph), 83.8 (C–OH), 71.6 (CH_2), 38.0 [*C*-$(CH_3)_3$], 25.3 [$(CH_3)_3$], 21.7 (CH_3).
MS (EI): *m/z* (%) = 236 (2) [M^+], 194 (17), 136 (32), 108 (57), 107 (14), 102 (14), 101 (100), 95 (11), 94 (88), 85 (13), 83 (86), 77 (42), 59 (12), 57 (34), 55 (44), 51 (15), 43 (65), 41 (42), 39 (18).
Anal. Calcd for $C_{14}H_{20}O_3$ (236.31): C, 71.16; H, 8.53. Found: C, 71.12; H, 8.55.

3-Methyl-1,1-diphenoxybutan-2-one (5a)
Yield 30 mg, 22 % (Method A). Pale yellow oil.
IR (film): 3066, 3042, 2975, 2932, 2874, 1815, 1731, 1595, 1492, 1469, 1383, 1367, 1329, 1289, 1240, 1203, 1172, 1103, 1031, 991, 894, 857, 834, 754, 692, 612, 506 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 7.34-7.20 (m, 5 H, Ph), 7.12-6.93 (2m, 5 H, Ph), 5.85 [s, 1 H, C*H*-$(OPh)_2$], 3.34-3.24 [m, 1 H, C*H*-$(CH_3)_2$], 1.16 [d, *J* = 6.8 Hz, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.5 (C=O) , 156.0, 129.8, 123.3, 117.3 (Ph), 100.2 [*C*H-$(OPh)_2$], 35.8 [*C*H-$(CH_3)_2$], 18.7 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 200 (42) [M – $(Me_2CHCO)]^+$, 199 (100), 171 (11), 153 (52), 152 (17), 107 (18), 105 (10), 95 (13), 94 (16), 93 (13), 78 (13), 77 (80), 65 (16), 55 (32), 51 (35), 43 (37), 41 (19), 39 (26).
Anal. Calcd for $C_{17}H_{18}O_3$ (270.33): C, 75.53; H, 6.71. Found: C, 75.55; H, 6.70.

3-Methyl-1,1-bis(naphthalen-1-yloxy)butan-2-one (5b)
Purity 88%, yield 10 mg, 5% (Method A). Pale yellow oil.
IR (film): 3056, 2973, 2928, 2873, 2852, 1820, 1730, 1630, 1596, 1579, 1507, 1463, 1396, 1317, 1263, 1234, 1175, 1156, 1122, 1087, 1059, 1018, 985, 894, 792, 771, 740, 569 cm^{-1}.
^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.26-8.24 (m, 2 H, Naphthyl), 7.81-7.79 (m, 2 H, Naphthyl), 7.53-7.47 (m, 6 H, Naphthyl), 7.25-7.23 (m, 2 H, Naphthyl), 6.94-6.92 (m, 2 H, Naphthyl), 6.26 [s, 1 H, C*H*-$(ONaphthyl)_2$], 3.55-3.44 [m, 1 H, C*H*-$(CH_3)_2$], 1.26 [d, *J* = 6.9 Hz, 6 H, $(CH_3)_2$].

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.4 (C=O) , 151.8, 134.8, 127.7, 126.8, 126.0, 125.9, 125.7, 122.9, 122.0, 109.1 (Naphthyl), 100.7 [*C*H-(ONaphthyl)$_2$], 35.8 [*C*H-(CH$_3$)$_2$], 18.9 [(CH$_3$)$_2$].
MS (EI): *m/z* (%) = 370 (2) [M$^+$], 369 (10), 300 (21), 299 (81), 186 (12), 155 (13), 129 (16), 127 (33), 126 (17), 125 (17), 115 (100), 69 (13), 51 (10), 43 (95), 41 (12).
Anal. Calcd for $C_{25}H_{22}O_3$ (370.45): C, 81.06; H, 5.99. Found: C, 81.08; H, 5.96.

3-Methyl-1,1-bis(naphthalen-2-yloxy)butan-2-one (5c)
Purity 87%, yield 25 mg, 12% (Method A). Pale yellow oil.
IR (film): 3058, 3029, 2973, 2931, 2874, 2853, 1821, 1730, 1631, 1599, 1510, 1466, 1444, 1386, 1359, 1249, 1210, 1164, 1120, 1099, 1043, 1006, 962, 914, 845, 811, 748, 623, 474 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.78-7.76 (m, 4 H, Naphthyl), 7.68-7.66 (m, 2 H, Naphthyl), 7.44-7.32 (m, 6 H, Naphthyl), 7.25-7.22 (m, 2 H, Naphthyl), 6.13 [s, 1 H, C*H*-(ONaphthyl)$_2$], 3.42-3.35 [m, 1 H, C*H*-(CH$_3$)$_2$], 1.21 [d, *J* = 6.8 Hz, 6 H, (CH$_3$)$_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.5 (C=O) , 153.7, 134.2, 130.2, 130.0, 127.8, 127.3, 126.7, 124.8, 119.1, 111.7 (Naphthyl), 100.3 [*C*H-(ONaphthyl)$_2$], 35.9 [*C*H-(CH$_3$)$_2$], 18.8 [(CH$_3$)$_2$].
MS (EI): *m/z* (%) = 370 (9) [M$^+$], 300 (29), 299 (100), 157 (32), 144 (16), 143 (29), 128 (14), 127 (73), 126 (17), 115 (39), 71 (12), 55 (11), 43 (27).
Anal. Calcd for $C_{25}H_{22}O_3$ (370.45): C, 81.06; H, 5.99. Found: C, 81.03; H, 5.98.

3-Methyl-1,1-bis(*p*-tolyloxy)butan-2-one (5d)
Yield 24 mg, 16% (Method A). Pale yellow oil.
IR (film): 3032, 2973, 2925, 2873, 1730, 1611, 1589, 1508, 1466, 1382, 1364, 1320, 1285, 1241, 1203, 1175, 1144, 1105, 1043, 1006, 933, 896, 864, 817, 753, 720, 660, 510 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.04 (d, *J* = 8.5 Hz, 4 H, Ph), 6.85 (d, *J* = 8.5 Hz, 4 H, Ph), 5.74 [s, 1 H, C*H*-(OPh)$_2$], 3.32-3.23 [m, 1 H, C*H*-(CH$_3$)$_2$], 2.26 [s, 6 H, Ph-(C*H*$_3$)$_2$], 1.15 [d, *J* = 6.8 Hz, 6 H, CH-(C*H*$_3$)$_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.7 (C=O) , 153.9, 130.2, 129.8, 117.2 (Ph), 100.8 [*C*H-(OPh)$_2$], 35.7 [*C*H-(CH$_3$)$_2$], 20.7 [Ph-(*C*H$_3$)$_2$], 18.7 [CH-(*C*H$_3$)$_2$].
MS (EI): *m/z* (%) = 298 (2) [M$^+$], 228 (40), 227 (100), 199 (12), 166 (25), 121 (28), 119 (12), 109 (18), 108 (14), 107 (55), 91 (67), 79 (14), 77 (18), 65 (50), 55 (28), 43 (23), 41 (13), 39 (14).
Anal. Calcd for $C_{19}H_{22}O_3$ (298.38): C, 76.48; H, 7.43. Found: C, 76.47; H, 7.40.

1,1-Bis(4-methoxyphenoxy)-3-methylbutan-2-one (5e)
Yield 32 mg, 19 % (Method A). Pale yellow oil.
IR (film): 3047, 2997, 2972, 2934, 2875, 2836, 1821, 1729, 1679, 1639, 1609, 1593, 1505, 1465, 1443, 1384, 1295, 1233, 1197, 1126, 1103, 1036, 1005, 946, 896, 829, 799, 768, 718, 661, 643, 523 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.92-6.89 (m, 4 H, Ph), 6.80-6.77 (2m, 4 H, Ph), 5.63 [s, 1 H, C*H*-(OPh)$_2$], 3.74 [s, 6 H, (OCH$_3$)$_2$], 3.29-3.23 [m, 1 H, C*H*-(CH$_3$)$_2$], 1.15 [d, *J* = 6.8 Hz, 6 H, (CH$_3$)$_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.8 (C=O) , 155.7, 150.0, 119.0, 114.8 (Ph), 102.2 [*C*H-(OPh)$_2$], 55.7 [(OCH$_3$)$_2$], 35.8 [*C*H-(CH$_3$)$_2$], 18.7 [(CH$_3$)$_2$].
Anal. Calcd for $C_{19}H_{22}O_5$ (330.38): C, 69.07; H, 6.71. Found: C, 69.07; H, 6.73.

1,1-Bis(4-bromophenoxy)-3-methylbutan-2-one (5f)
Yield 51 mg, 24 % (Method A). Pale yellow oil.
IR (film): 3095, 3070, 2974, 2931, 2874, 1733, 1642, 1584, 1485, 1403, 1383, 1366, 1321, 1278, 1241, 1203, 1172, 1102, 1068, 1047, 1006, 938, 897, 824, 684, 671, 504 cm^{-1}.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.39-7.36 (m, 4 H, Ph), 6.87-6.84 (2m, 4 H, Ph), 5.76 [s, 1 H, C*H*-$(OPh)_2$], 3.26-3.19 [m, 1 H, C*H*-$(CH_3)_2$], 1.15 [d, *J* = 6.8 Hz, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 206.6 (C=O) , 154.8, 132.8, 121.4, 119.1, 116.1 (Ph), 100.0 [*C*H-$(OPh)_2$], 36.0 [*C*H-$(CH_3)_2$], 18.6 [$(CH_3)_2$].
Anal. Calcd for $C_{17}H_{16}Br_2O_3$ (428.12): C, 47.69; H, 3.77; Br, 37.33. Found: C, 47.71; H, 3.74; Br, 37.33.

1,1-Bis(4-allyl-2-methoxyphenoxy)-3-methylbutan-2-one (5g)
Yield 45 mg, 22 % (Method A). Pale yellow oil.
IR (film): 3079, 3060, 3014, 2975, 2937, 2915, 2876, 2839, 1818, 1729, 1639, 1593, 1509, 1465, 1419, 1384, 1368, 1311, 1268, 1216, 1207, 1152, 1125, 1097, 1036, 995, 917, 851, 812, 756, 668 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.90-6.88 (m, 2 H, Ph), 6.67-6.65 (m, 2 H, Ph), 6.62-6.59 (m, 2 H, Ph), 5.95-5.85 [m, 2 H, $(=CH)_2$], 5.69 [s, 1 H, C*H*-$(OPh)_2$], 5.07-5.00 [m, 4 H, $(=CH_2)_2$], 3.72 [s, 6 H, $(OCH_3)_2$], 3.44-3.37 [m, 1 H, C*H*-$(CH_3)_2$], 3.30-3.28 [m, 4 H, $(CH_2)_2$], 1.20 [d, *J* = 6.8 Hz, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.3 (C=O) , 150.7, 143.7 (Ph), 137.4 [$(CH=CH_2)_2$], 120.7, 120.6 (Ph), 115.9 [$(=CH_2)_2$], 112.9 (Ph), 103.2 [*C*H-$(OPh)_2$], 55.8 [$(OCH_3)_2$], 39.9 [$(CH_2)_2$], 35.4 [*C*H-$(CH_3)_2$], 18.7 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 339 (100) $[M - (Me_2CHCO)]^+$, 163 (20), 162 (17), 161 (15), 131 (11), 115 (27), 105 (11), 104 (19), 103 (22), 91 (31), 78 (13), 77 (17), 55 (23), 43 (34), 41 (29), 39 (10).
Anal. Calcd for $C_{25}H_{30}O_5$ (410.51): C, 73.15; H, 7.37. Found: C, 73.17; H, 7.34.

(Z)-5-(Bromomethylene)-4-(*tert*-butyl)-4-methyl-1,3-dioxolan-2-one (6b)
Yield 13 mg, 5% (Method A). Pale yellow oil.
IR (film): 3105, 2973, 2919, 2878, 1831, 1739, 1678, 1595, 1490, 1400, 1381, 1371, 1303, 1263, 1228, 1202, 1132, 1105, 1052, 1021, 995, 937, 890, 758, 691 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.39 (s, 1 H, CH), 1.57 (s, 3 H, CH_3), 1.02 [s, 9 H, $(CH_3)_3$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 153.1 (*C*=CH), 150.3 (C=O), 93.1 (*C*–CH_3), 79.7 (C=*C*H), 38.4 [*C*–$(CH_3)_3$], 24.2 [$(CH_3)_3$], 21.4 (CH_3).
MS (EI): *m/z* (%) = 193 (2) $[M-(CH_3)_3]^+$, 125 (11), 85 (10), 84 (100), 69 (98), 67 (15), 57 (88), 56 (12), 55 (15), 53 (11), 43 (44), 41 (75), 39 (27).
Anal. Calcd for $C_{19}H_{13}BrO_3$ (249.10): C, 43.40; H, 5.26; Br, 32.08. Found: C, 43.37; H, 5.29; Br, 32.06.

(*Z*)-4,4-Dimethyl-5-(phenoxymethylene)-1,3-dioxolan-2-one (7)
Yield 11 mg, 5% (Method A). White crystals; mp 112-114 °C.
IR (KBr): 3048, 2983, 2937, 2870, 1802, 1737, 1679, 1593, 1492, 1363, 1228, 1153, 1127, 1069, 1025, 840, 758, 687, 614, 508 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.37-7.29 (m, 2 H, Ph), 7.08 (t, *J* = 7.4 Hz, 1 H, Ph), 7.03-6.97 (m, 2 H, Ph), 6.04 (s, 1 H, CH), 1.66 [s, 6 H, $(CH_3)_2$].
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 157.0 (C_{ipso}), 150.8 (C=O), 140.6 (*C*=CH), 129.9, 123.5, 116.1 (Ph), 119.5 (C=*C*H), 83.3 [*C*$(CH_3)_2$], 28.2 [$(CH_3)_2$].
MS (EI): *m/z* (%) = 220 (2) $[M^+]$, 129 (14), 97 (18), 94 (22), 87 (10), 85 (19), 84 (21), 83 (32), 82 (16), 81 (33), 77 (14), 73 (62), 71 (34), 70 (22), 69 (84), 68 (20), 67 (24), 61 (19), 60 (49), 57 (63), 56 (22), 55 (78), 51 (12), 45 (21), 44 (19), 43 (100), 42 (22), 41 (94), 39 (24).
Anal. Calcd for $C_{12}H_{12}O_4$ (220.22): C, 65.45; H, 5.49. Found: C, 65.41; H, 5.52.

Analyzing data for **6a** [4] and **8a**,**b** [5] were published in literature.

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8. Rearrangement of the synthesized phenoxyhydroxyketones 4a,f

The mixture of 3-hydroxy-3-methyl-1-phenoxybutan-2-one (**4a**, 97 mg, 0.5 mmol) or 3-hydroxy-3-methyl-1-(p-tolyloxy)butan-2-one (**4f**, 104 mg, 0.5 mmol) and neutral aluminum oxide (900 mg, 8.5 mmol) was stirred at ~150 ℃ for 3 h. The resulting products were washed off aluminum oxide with acetone to give 3-hydroxy-3-methyl-4-phenoxybutan-2-one (**9a**) (58 mg, 60%) or 3-hydroxy-3-methyl-4-(p-tolyloxy)butan-2-one (**9b**) (57 mg, 55%).

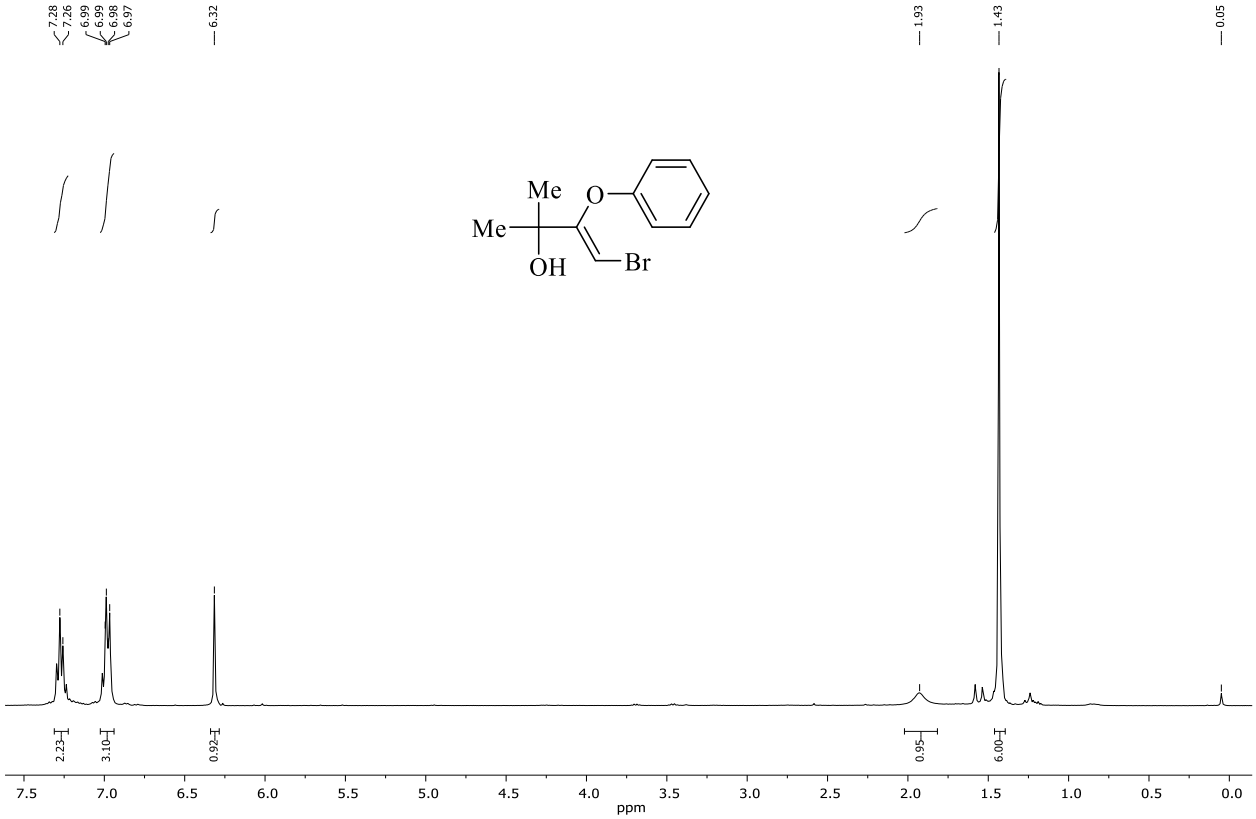
9. Characterization data for 9a, 9b

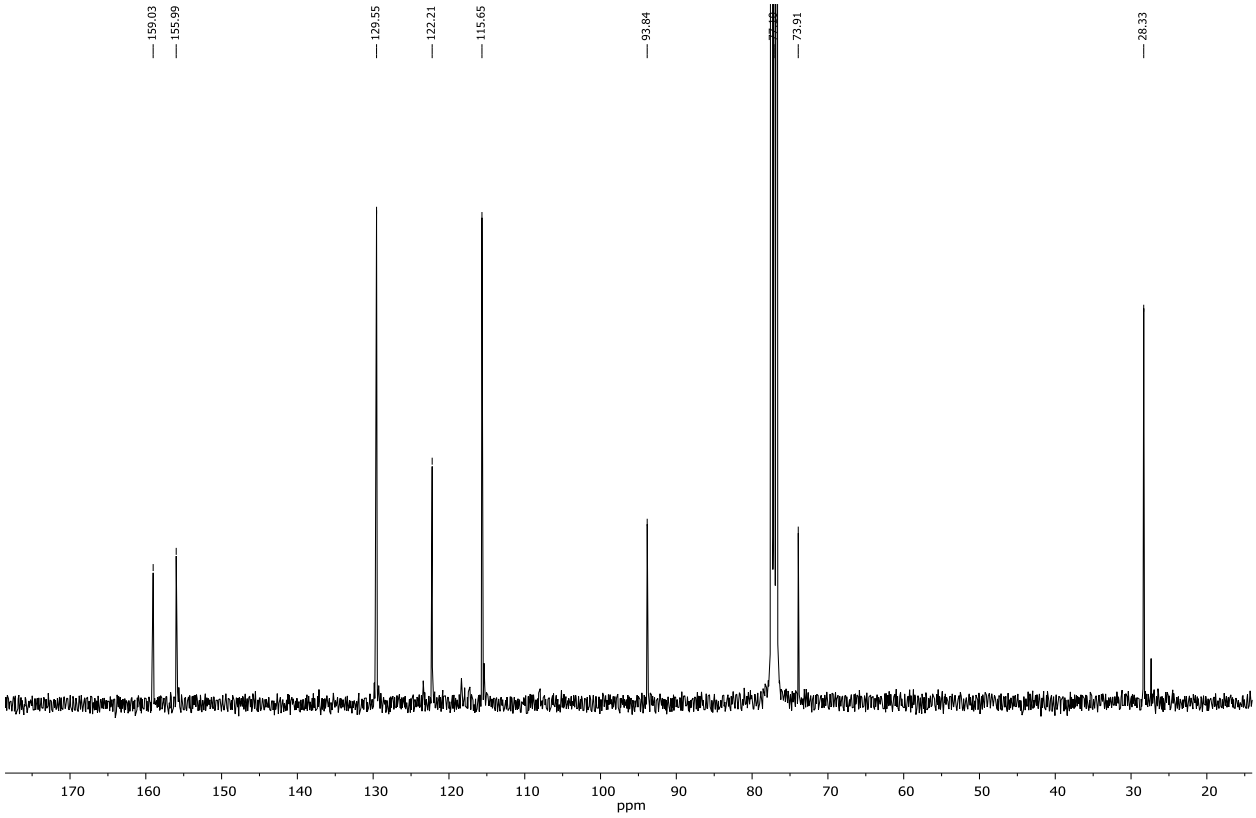
3-Hydroxy-3-methyl-4-phenoxybutan-2-one (9a)
Yield 58 mg, 60%. Yellow oil.
IR (KBr): 3063, 3040, 2978, 2928, 2873, 1716, 1599, 1495, 1459, 1417, 1382, 1355, 1292, 1243, 1189, 1172, 1153, 1133, 1095, 1078, 1047, 994, 965, 887, 817, 755, 692, 640, 611, 596, 569, 550, 510 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.38-7.23 (m, 2 H, Ph), 6.97-6.93 (m, 1 H, Ph), 6.87-6.84 (m, 2 H, Ph), 4.17-4.14 (m, 1 H, CH_2), 3.99-3.96 (m, 2 H, OH, CH_2), 2.29 (s, 3 H, CH_3CO), 1.41 (s, 3 H, C*H*$_3$COH).
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 210.4 (C=O), 158.2, 129.6, 121.5, 114.6 (Ph), 78.4 (C–OH), 73.0 (CH_2), 24.7 (*C*H_3CO), 21.8 (*C*H_3COH).
Anal. Calcd for $C_{11}H_{14}O_3$ (194.23): C, 68.02; H, 7.27. Found: C, 68.05; H, 7.25.

3-Hydroxy-3-methyl-4-(*p*-tolyloxy)butan-2-one (9b)
Yield 57 mg, 55%. Yellow oil.
IR (KBr): 3061, 3031, 2979, 2926, 2902, 2870, 1716, 1614, 1587, 1512, 1460, 1419, 1381, 1355, 1291, 1243, 1176, 1134, 1110, 1048, 965, 943, 900, 844, 817, 757, 696, 629, 594, 549, 512 cm^{-1}.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.07-7.03 (m, 2 H, Ph), 6.79-6.74 (m, 2 H, Ph), 4.14-4.11 (m, 1 H, CH_2), 3.99-3.93 (m, 2 H, OH, CH_2), 2.28 (s, 3 H, CH_3CO), 2.25 (s, 3 H, C*H*$_3$Ph), 1.40 (s, 3 H, C*H*$_3$COH).
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 210.5 (C=O), 156.2, 130.8, 130.0, 114.6 (Ph), 78.4 (C–OH), 73.3 (CH_2), 24.7 (*C*H_3CO), 21.8 (*C*H_3Ph), 20.5 (*C*H_3COH).
Anal. Calcd for $C_{12}H_{16}O_3$ (208.26): C, 69.21; H, 7.74. Found: C, 69.22; H, 7.75.

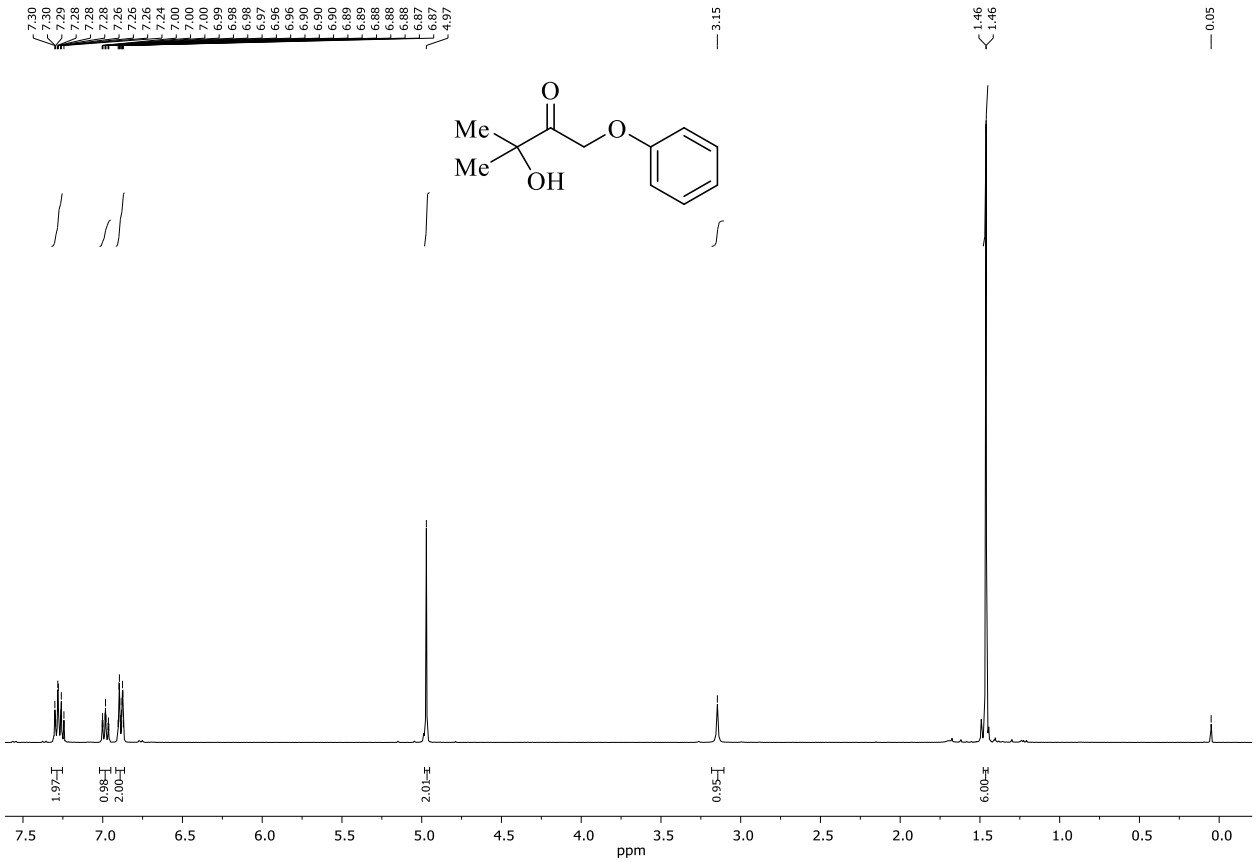
10. ^{1}H and ^{13}C spectra of the synthesized products

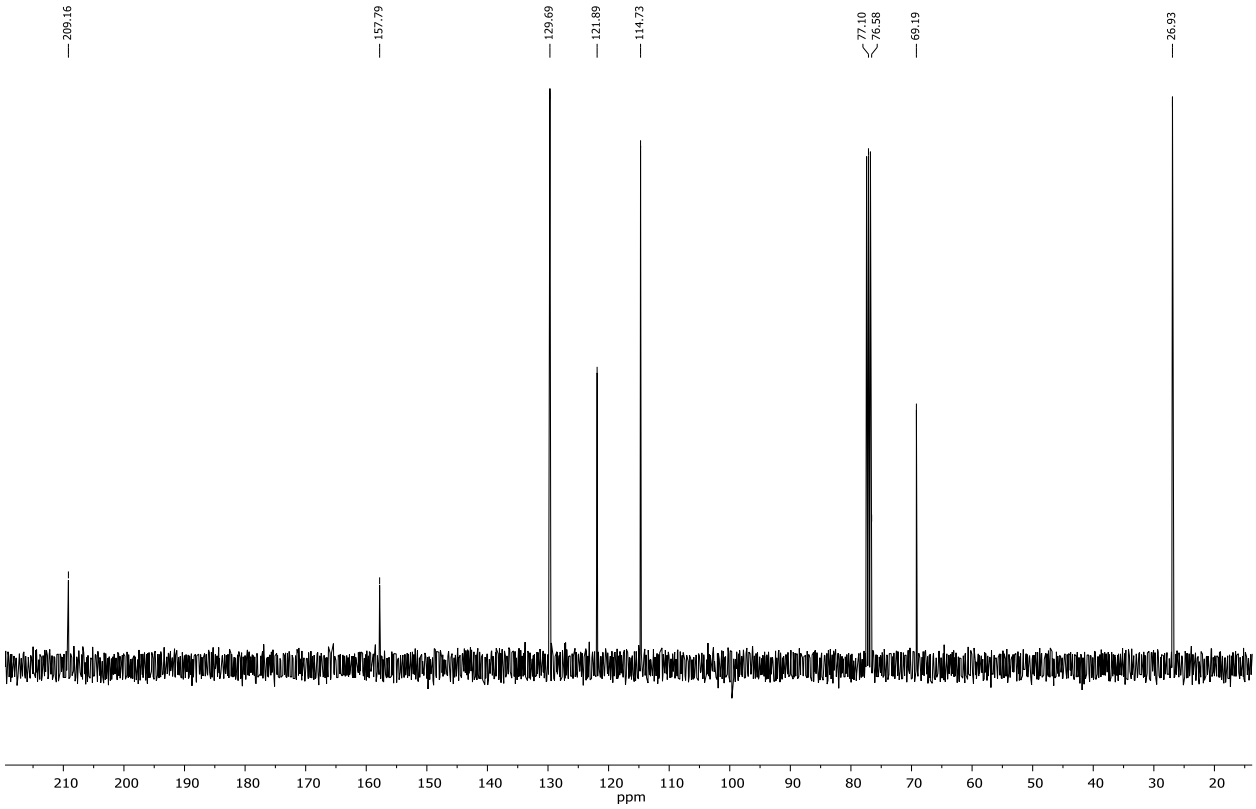
4-Bromo-2-methyl-3-phenoxybut-3-en-2-ol (3a)



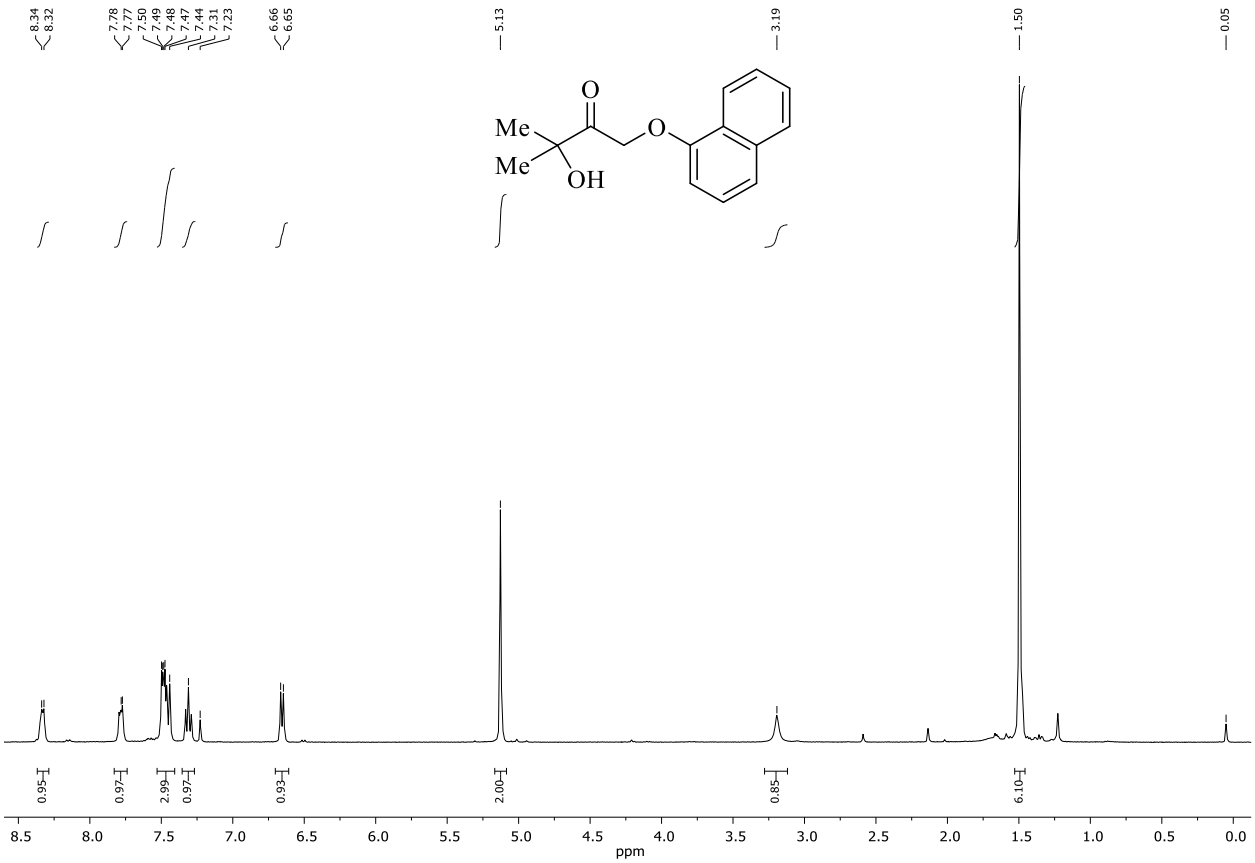


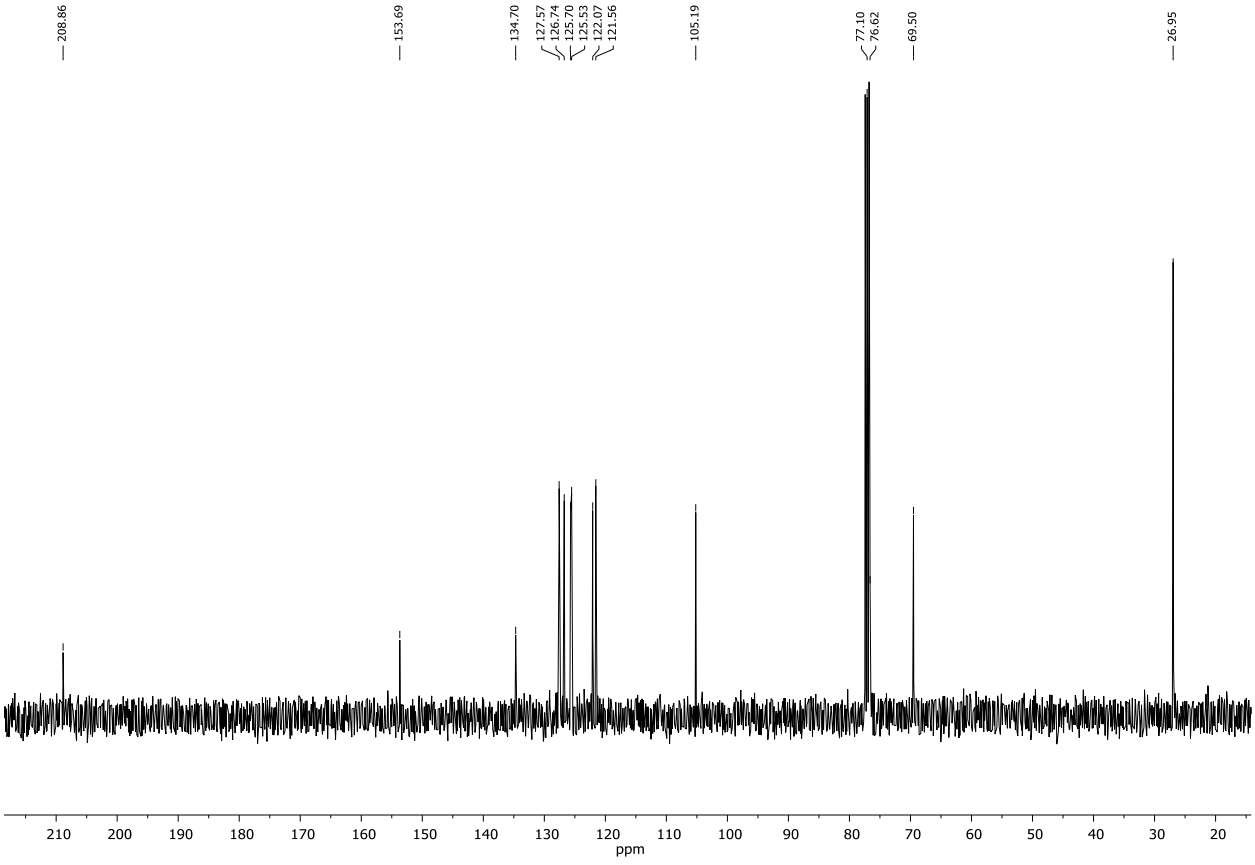
3-Hydroxy-3-methyl-1-phenoxybutan-2-one (4a)



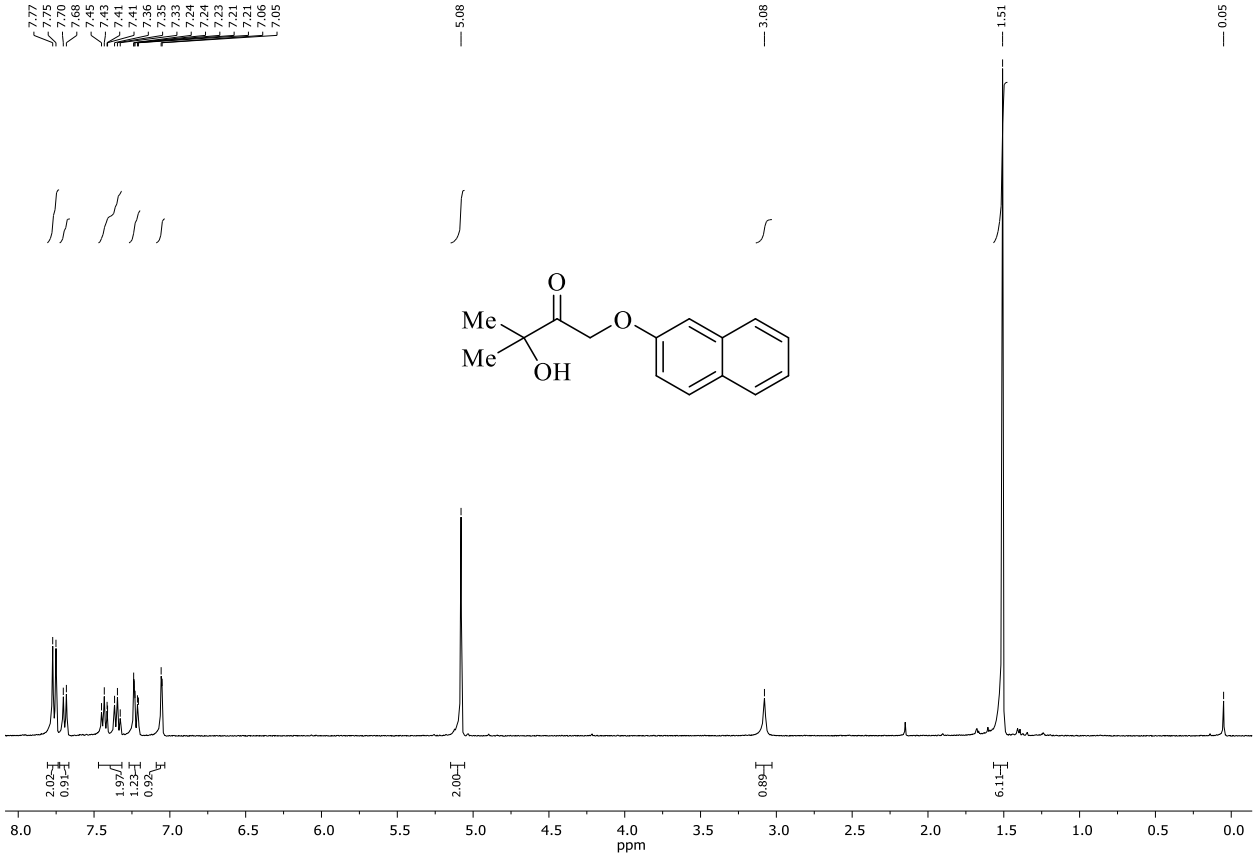


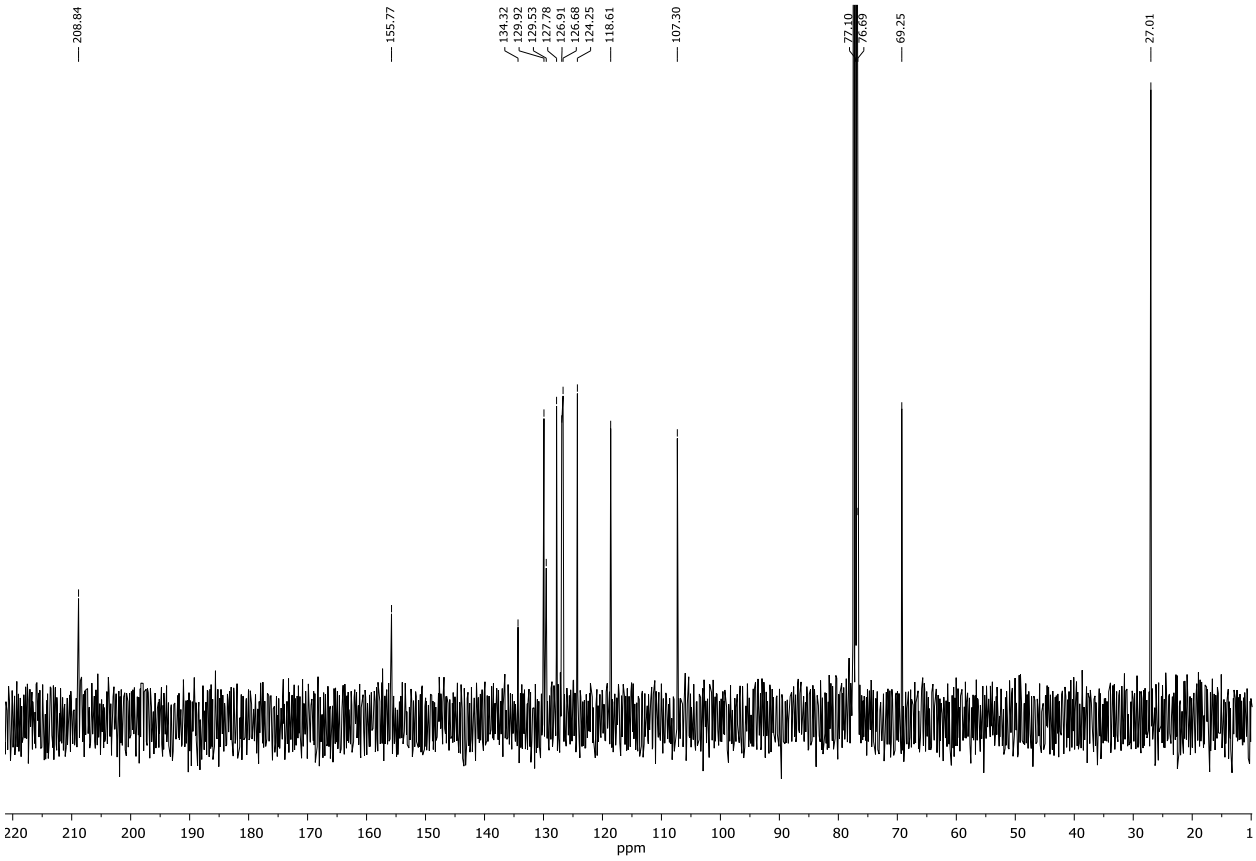
3-Hydroxy-3-methyl-1-(naphthalen-1-yloxy)butan-2-one (4b)



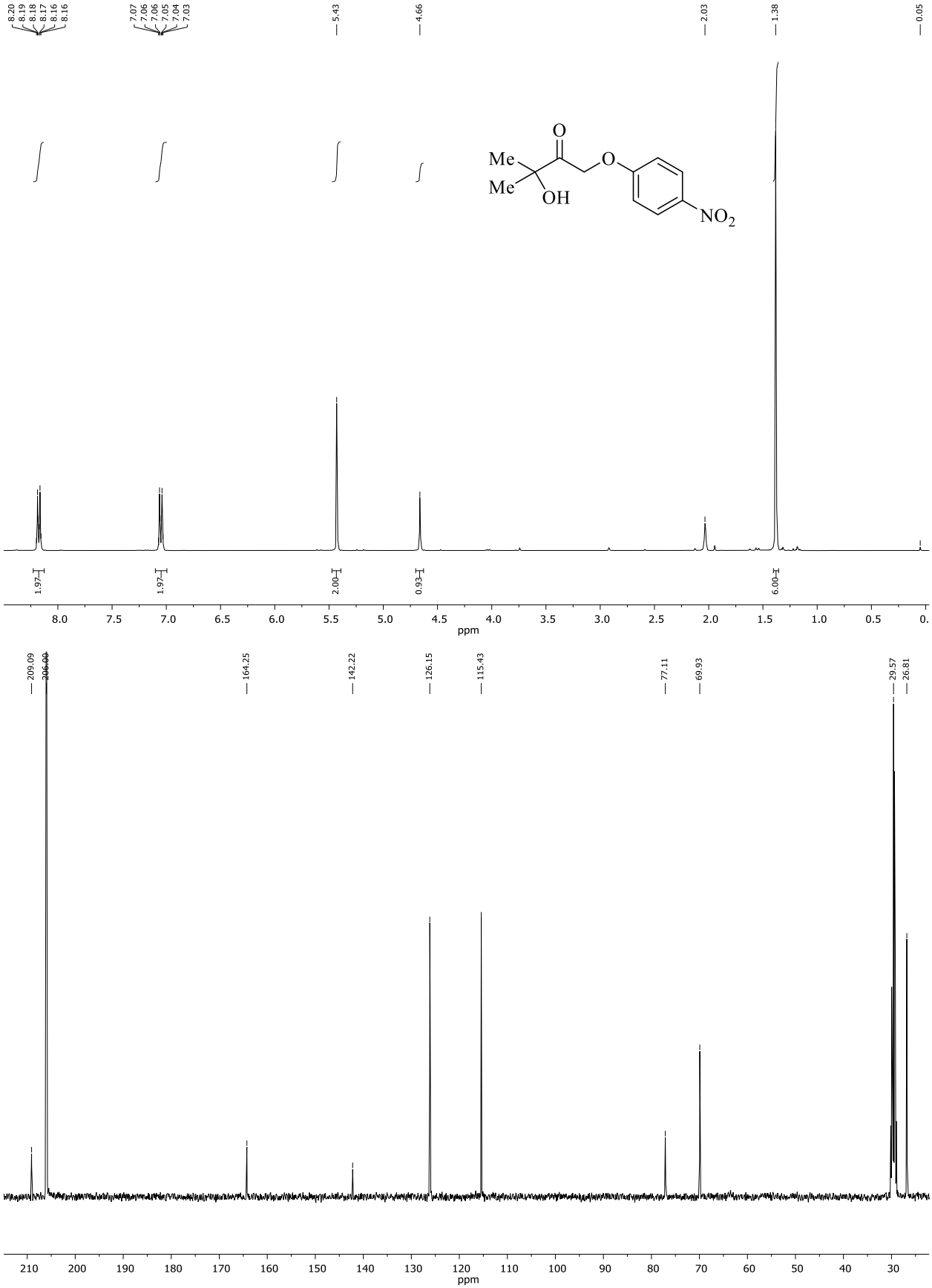


3-Hydroxy-3-methyl-1-(naphthalen-2-yloxy)butan-2-one (4c)





3-Hydroxy-3-methyl-1-(4-nitrophenoxy)butan-2-one (4d)



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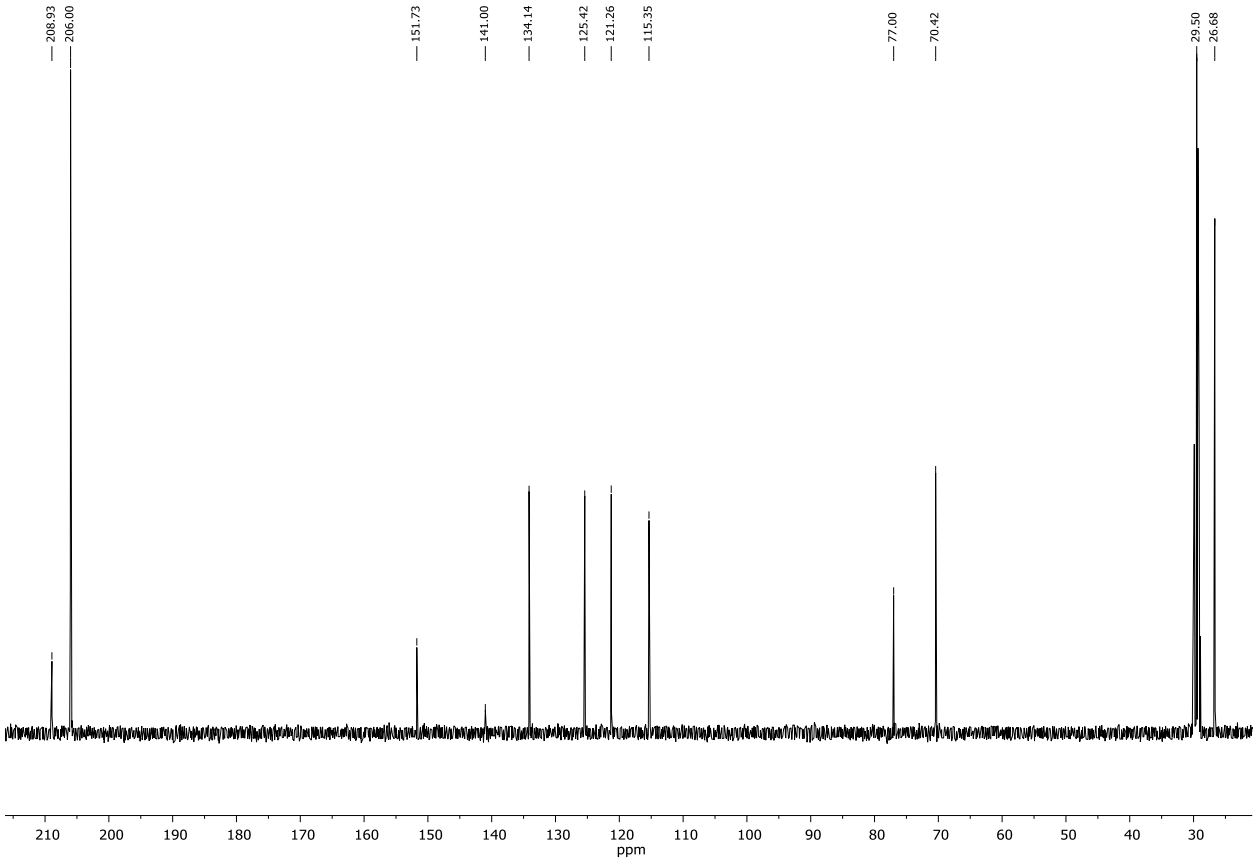
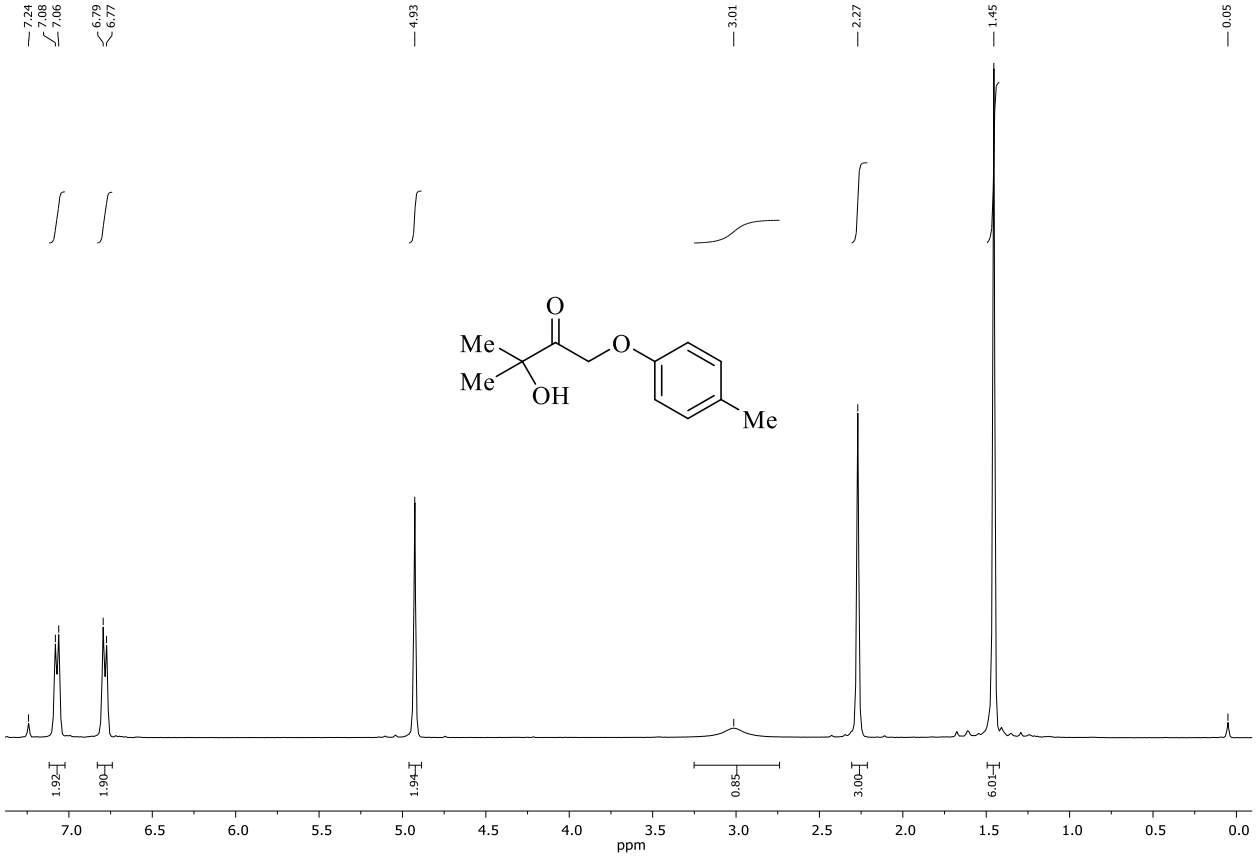
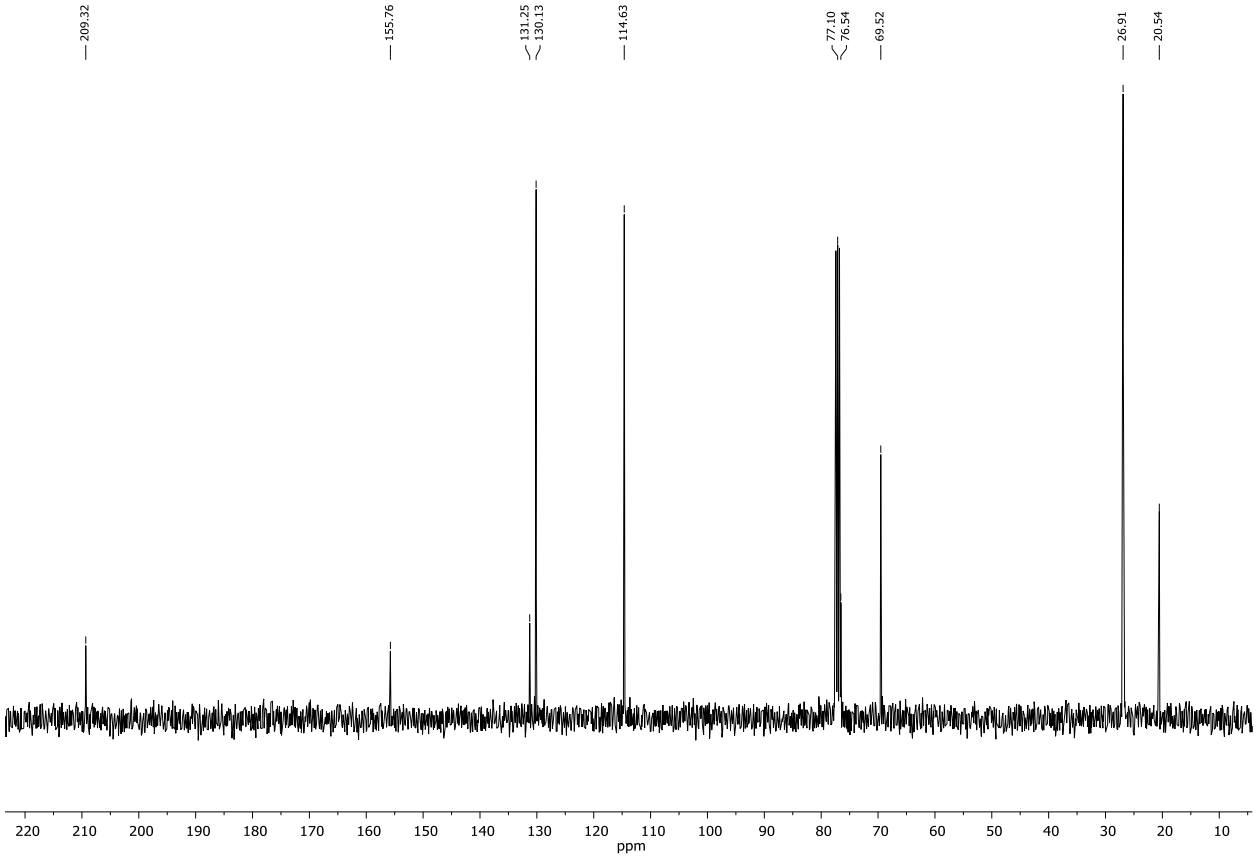
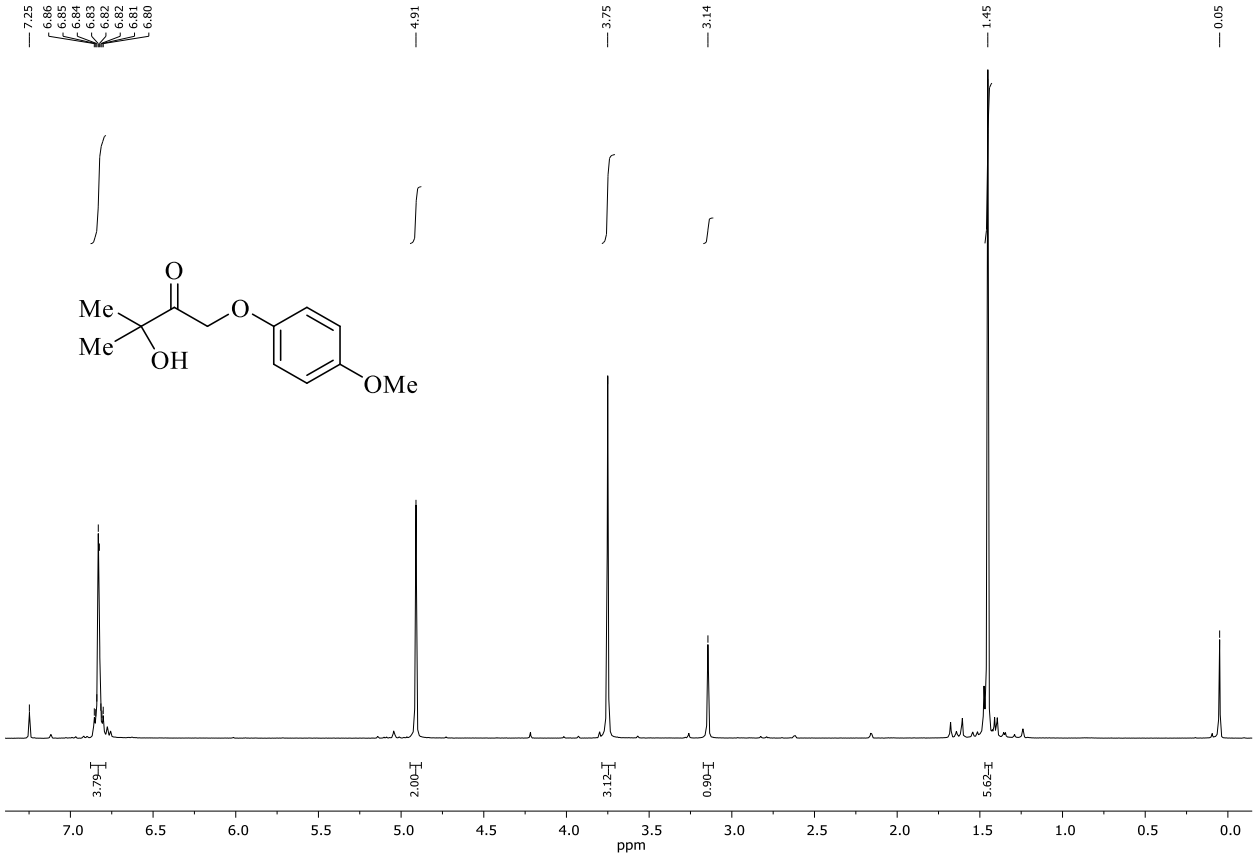


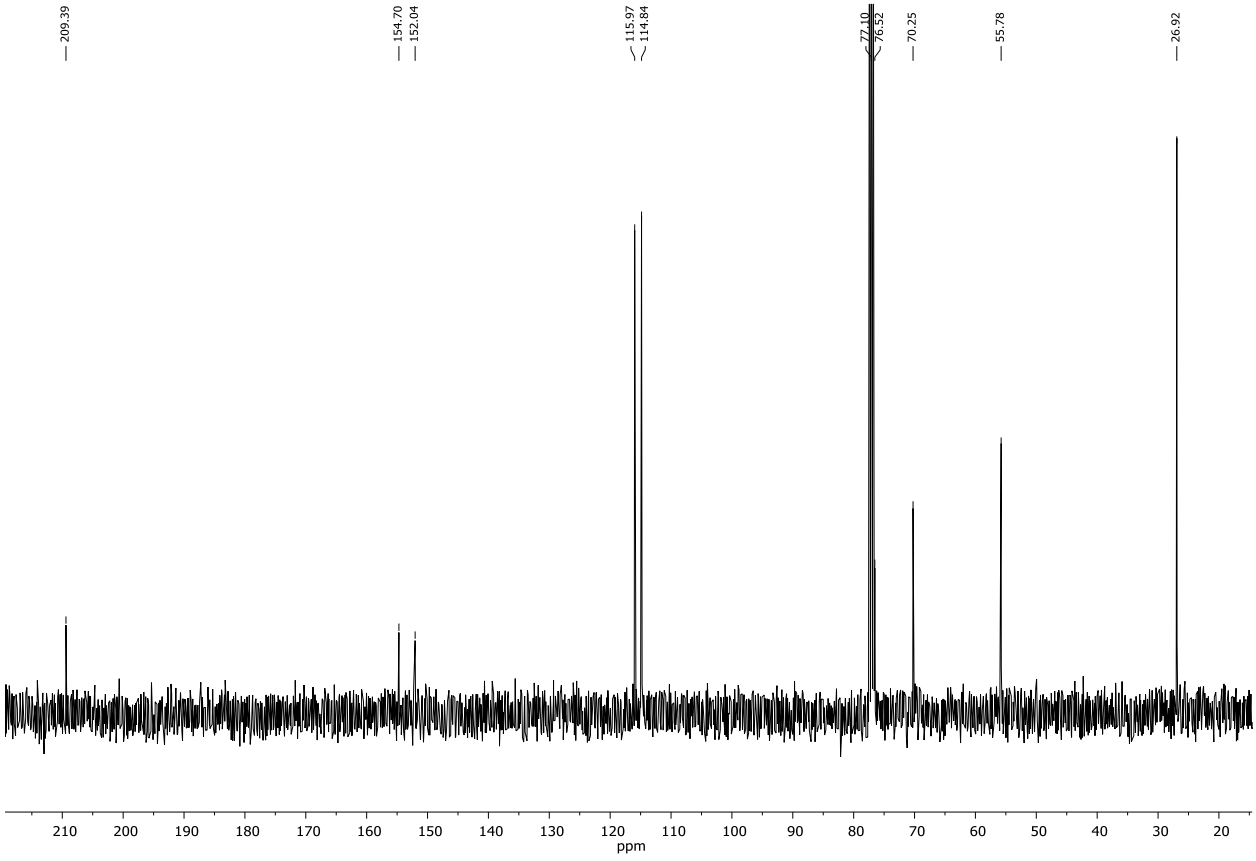
3-Hydroxy-3-methyl-1-(*p*-tolyloxy)butan-2-one (4f)



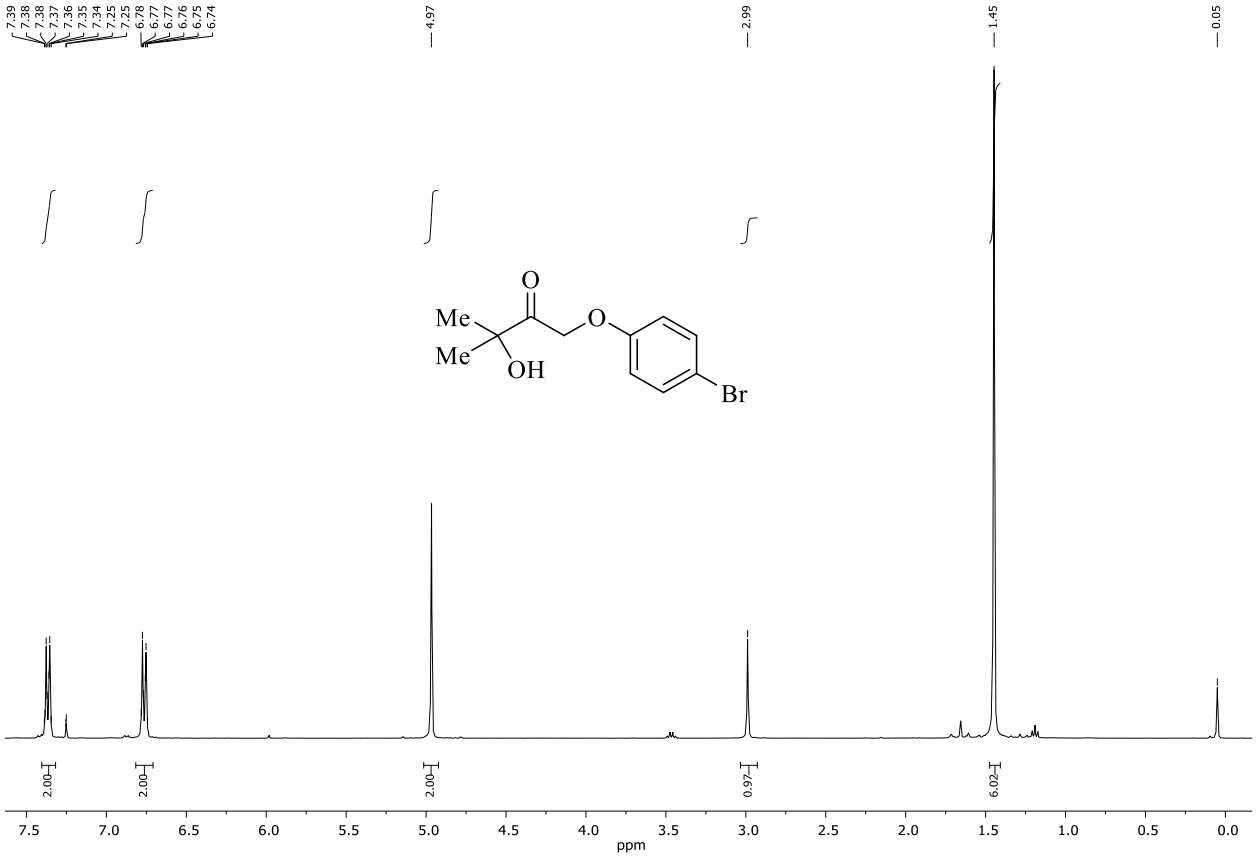


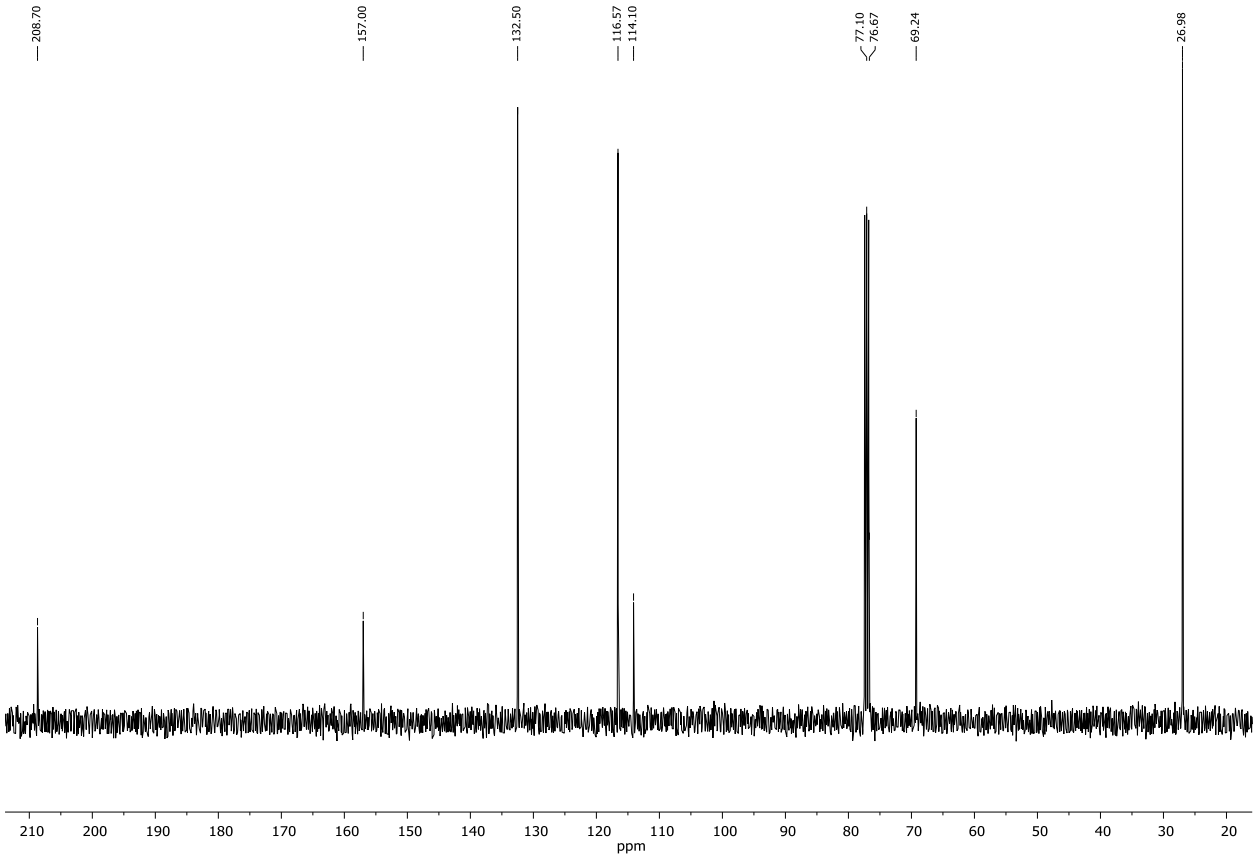
3-Hydroxy-1-(4-methoxyphenoxy)-3-methylbutan-2-one (4g)



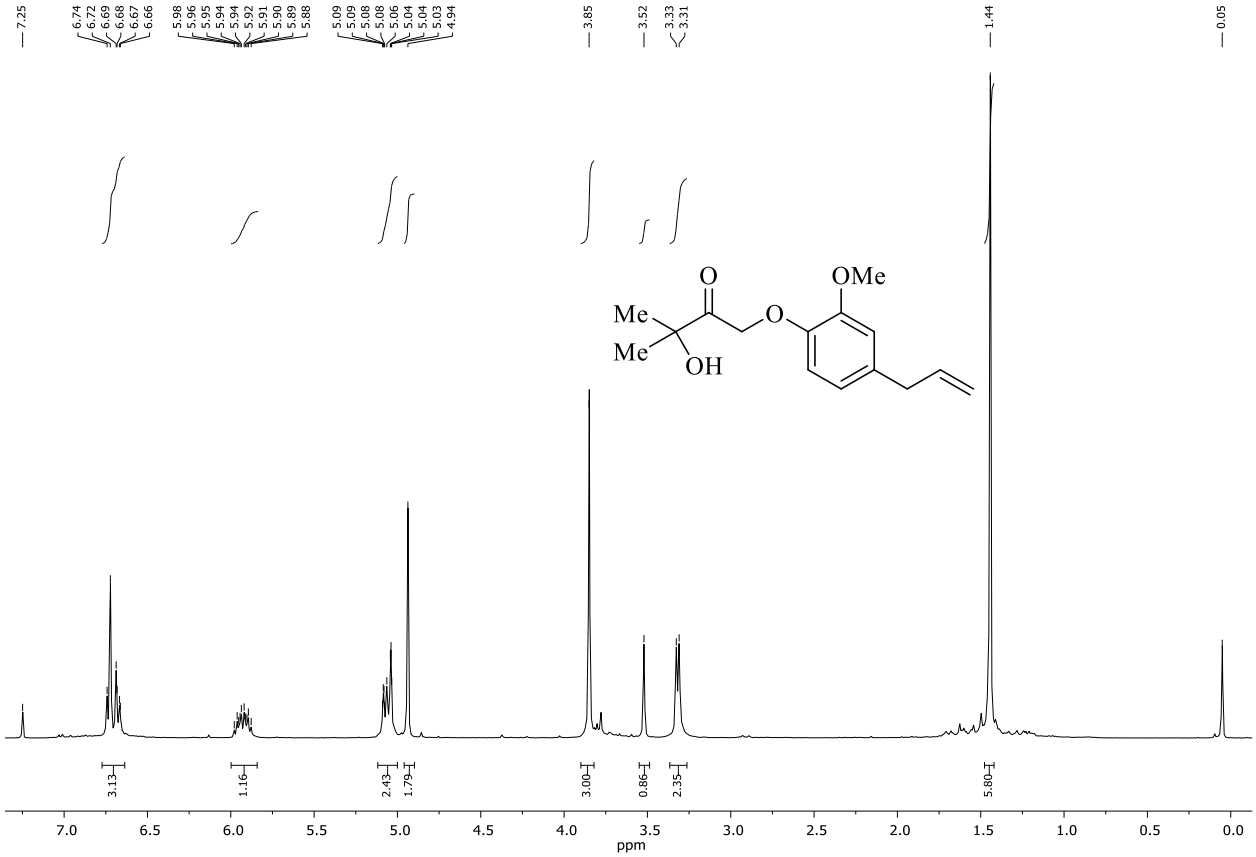


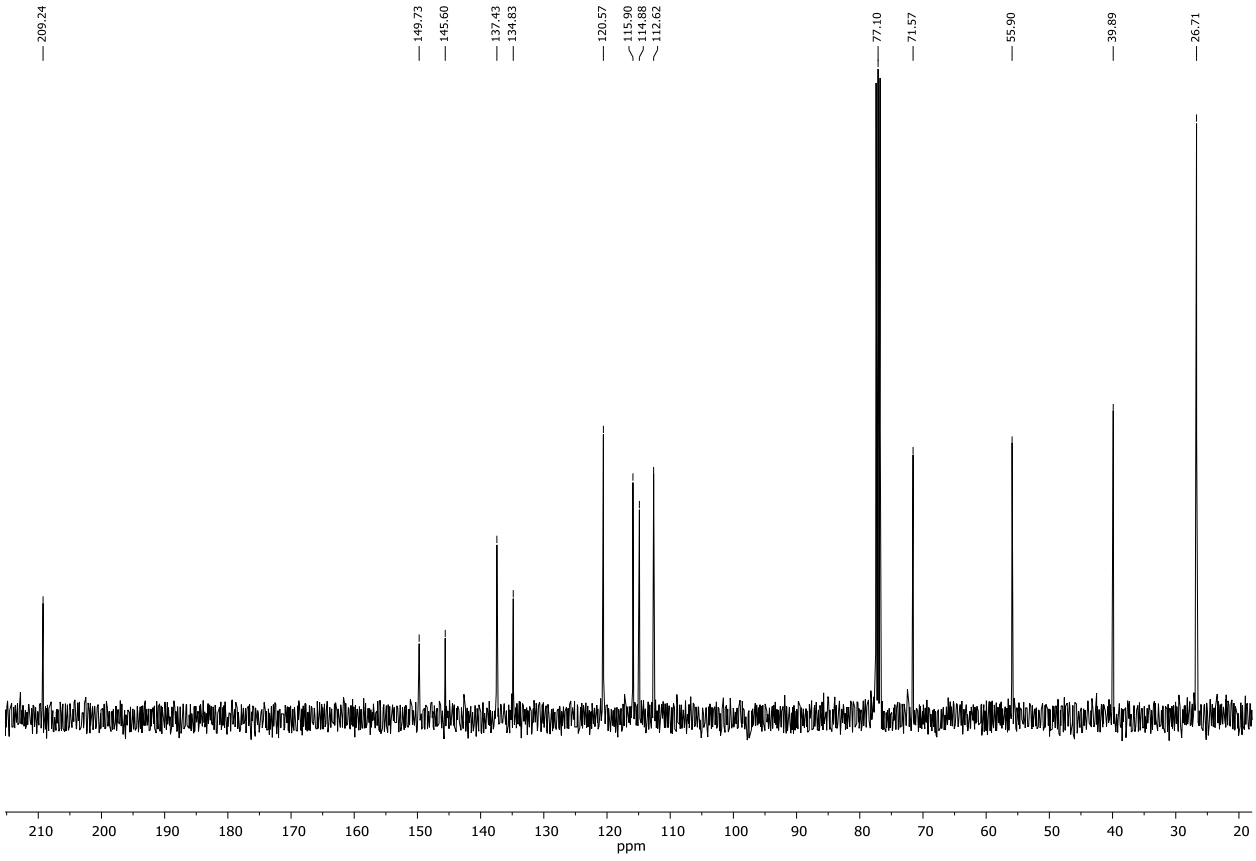
1-(4-Bromophenoxy)-3-hydroxy-3-methylbutan-2-one (4h)



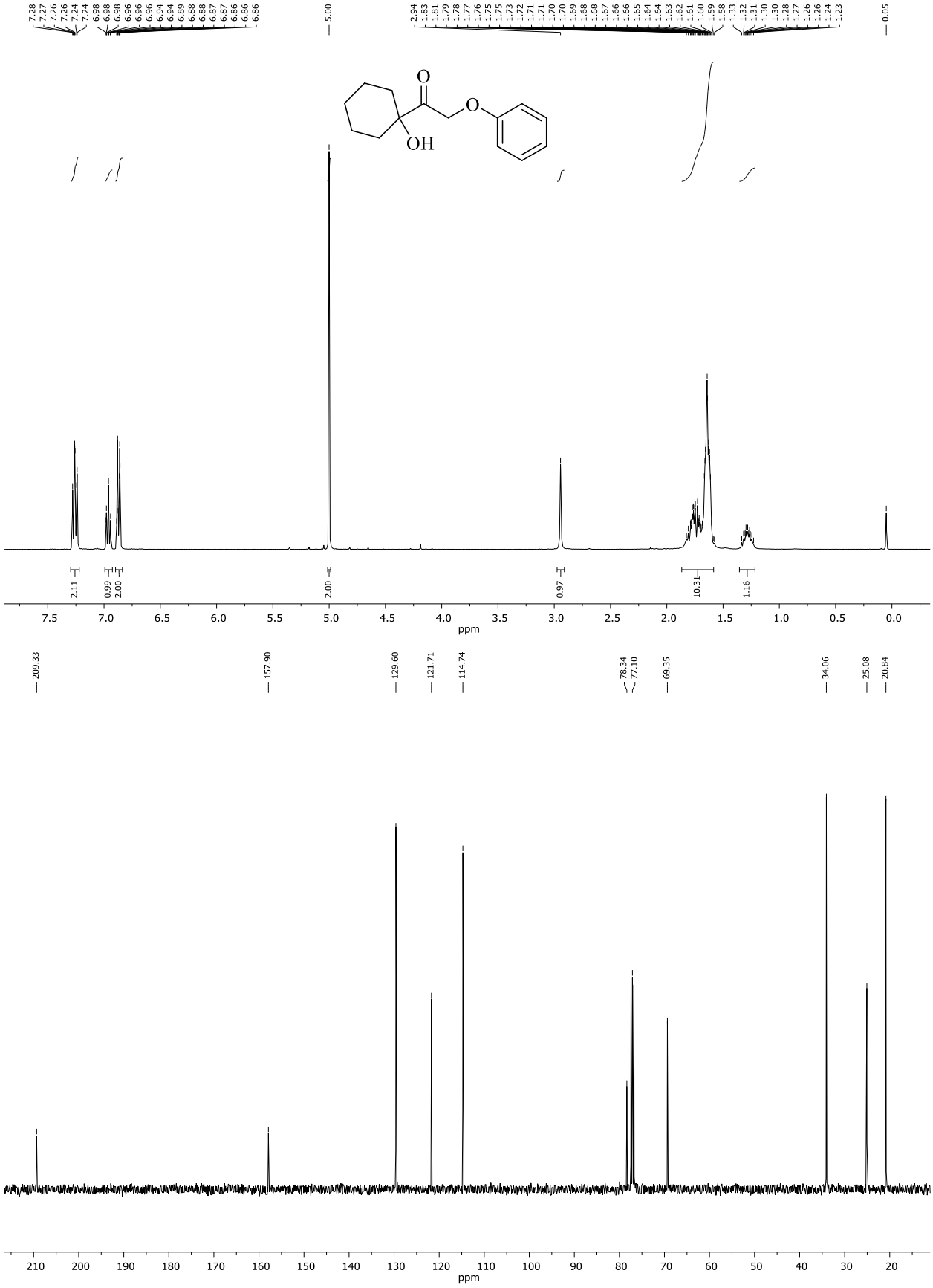


1-(4-Allyl-2-methoxyphenoxy)-3-hydroxy-3-methylbutan-2-one (4i)

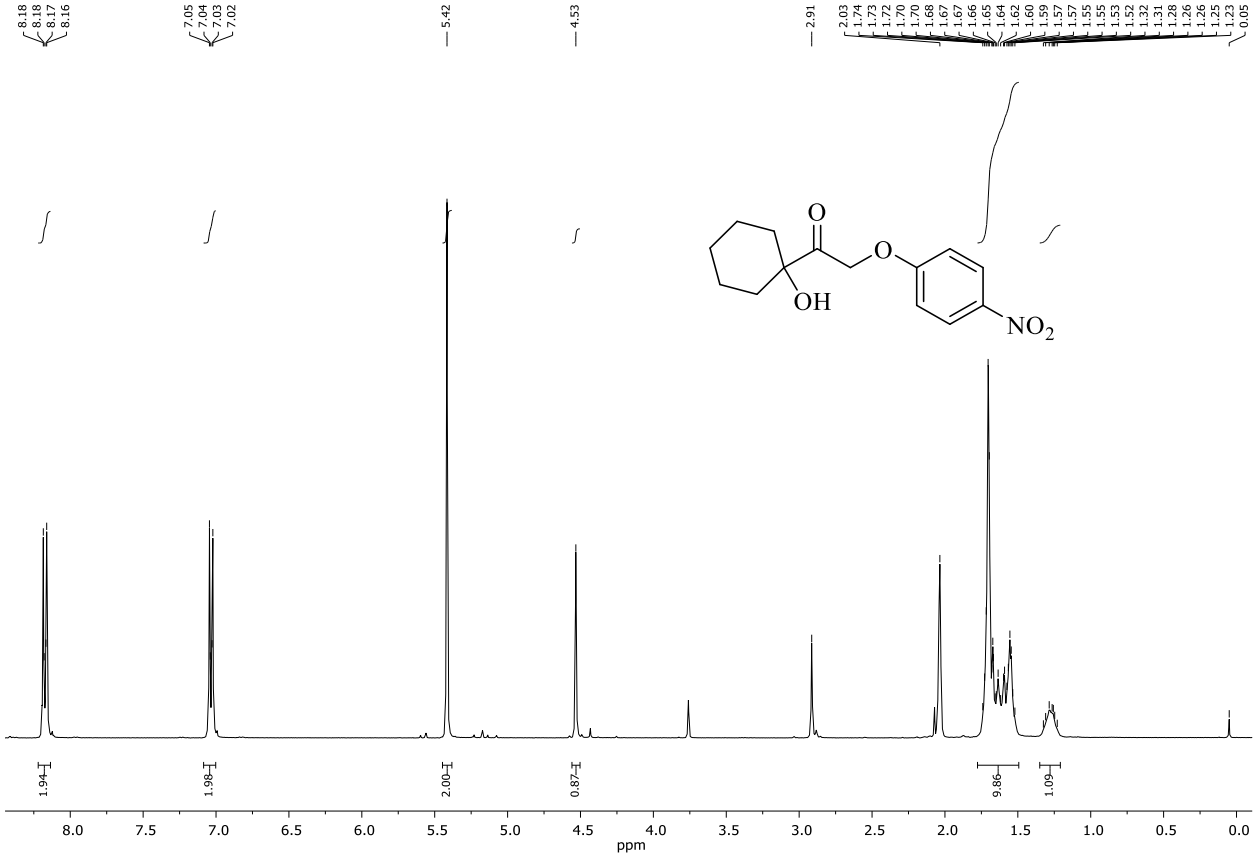


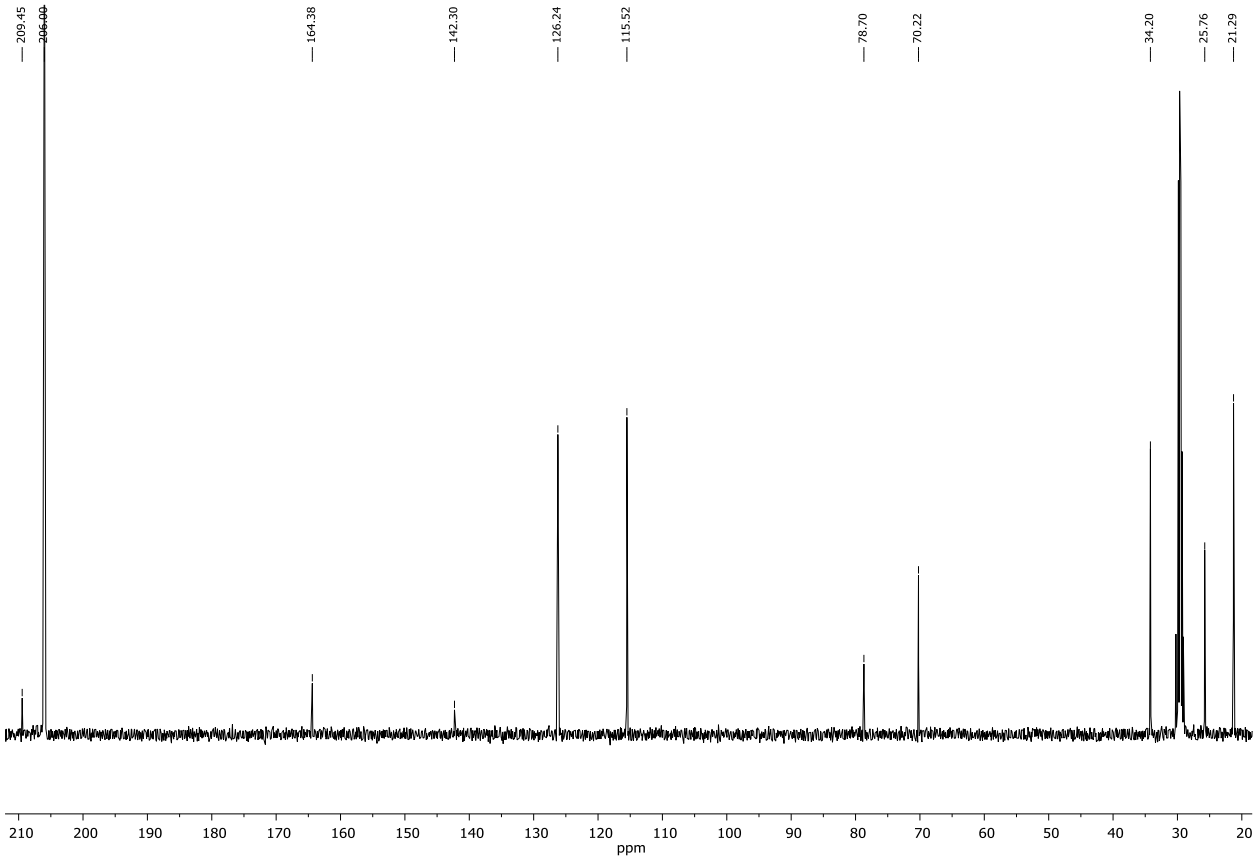


1-(1-Hydroxycyclohexyl)-2-phenoxyethan-1-one (4j)

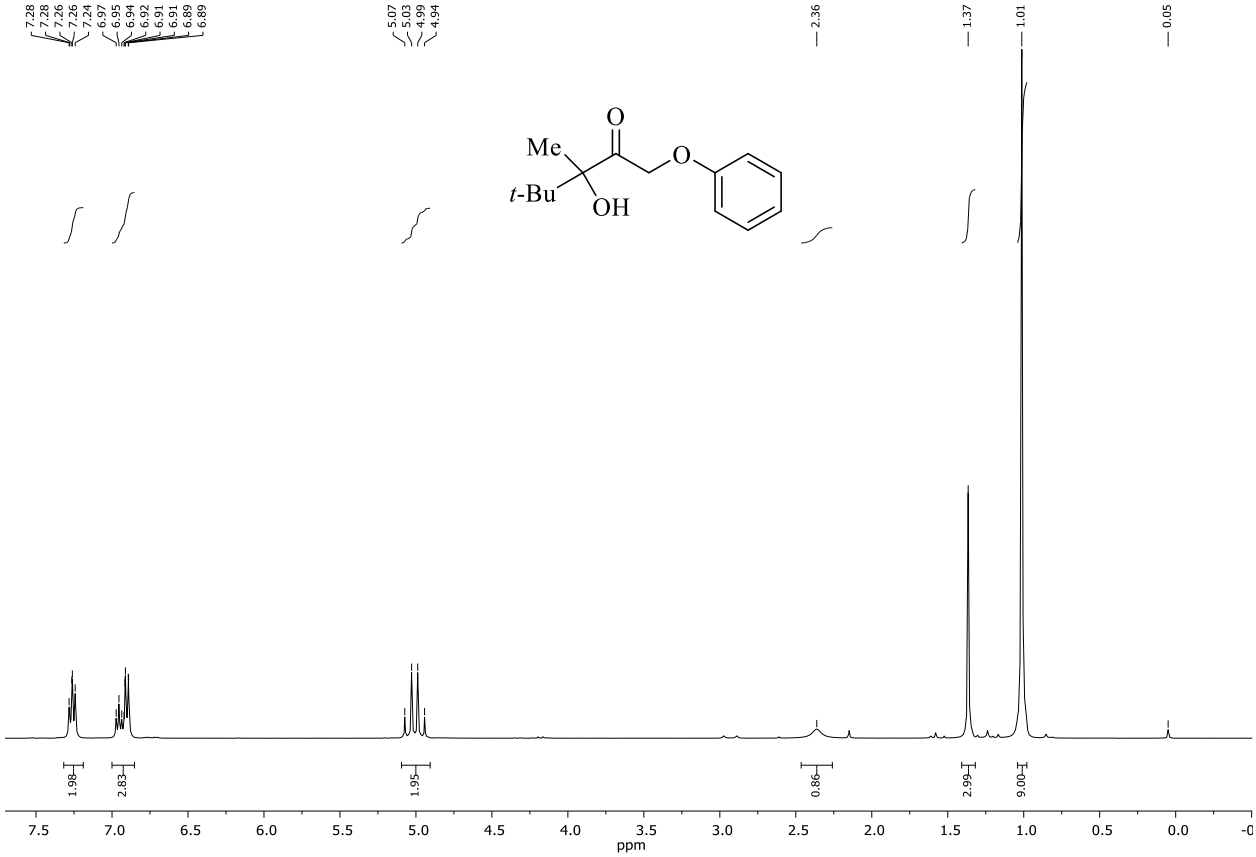


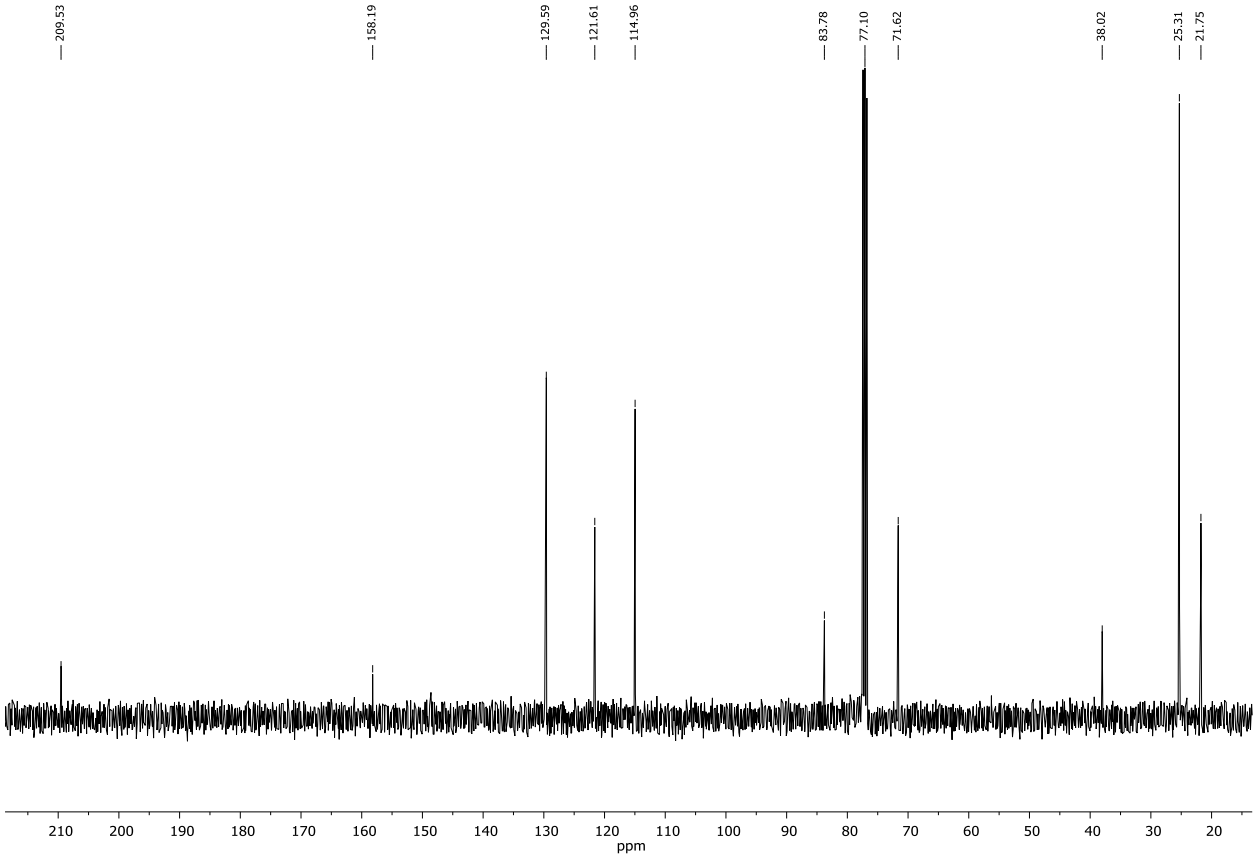
1-(1-Hydroxycyclohexyl)-2-(4-nitrophenoxy)ethan-1-one (4k)



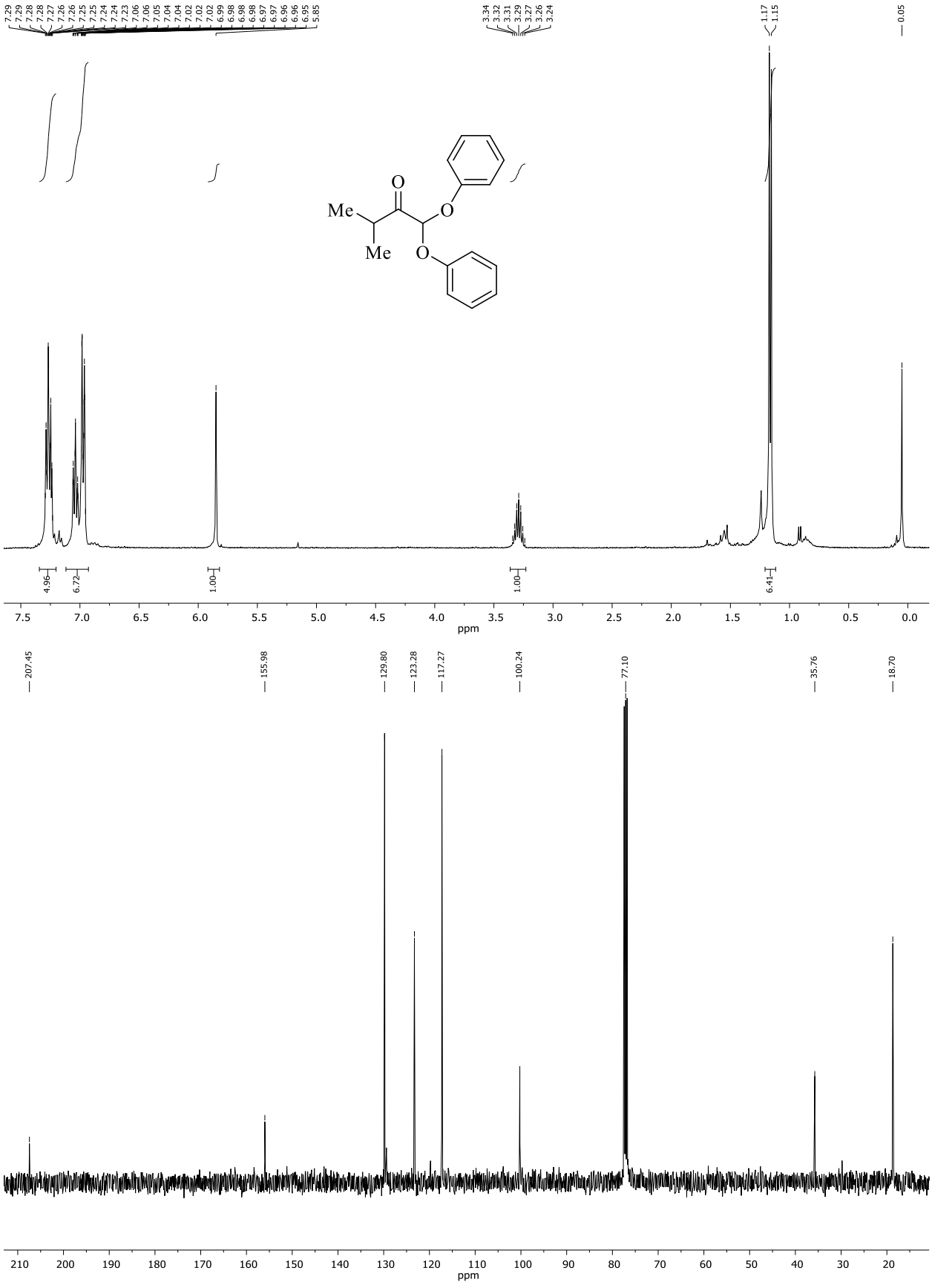


3-Hydroxy-3,4,4-trimethyl-1-phenoxypentan-2-one (4l)

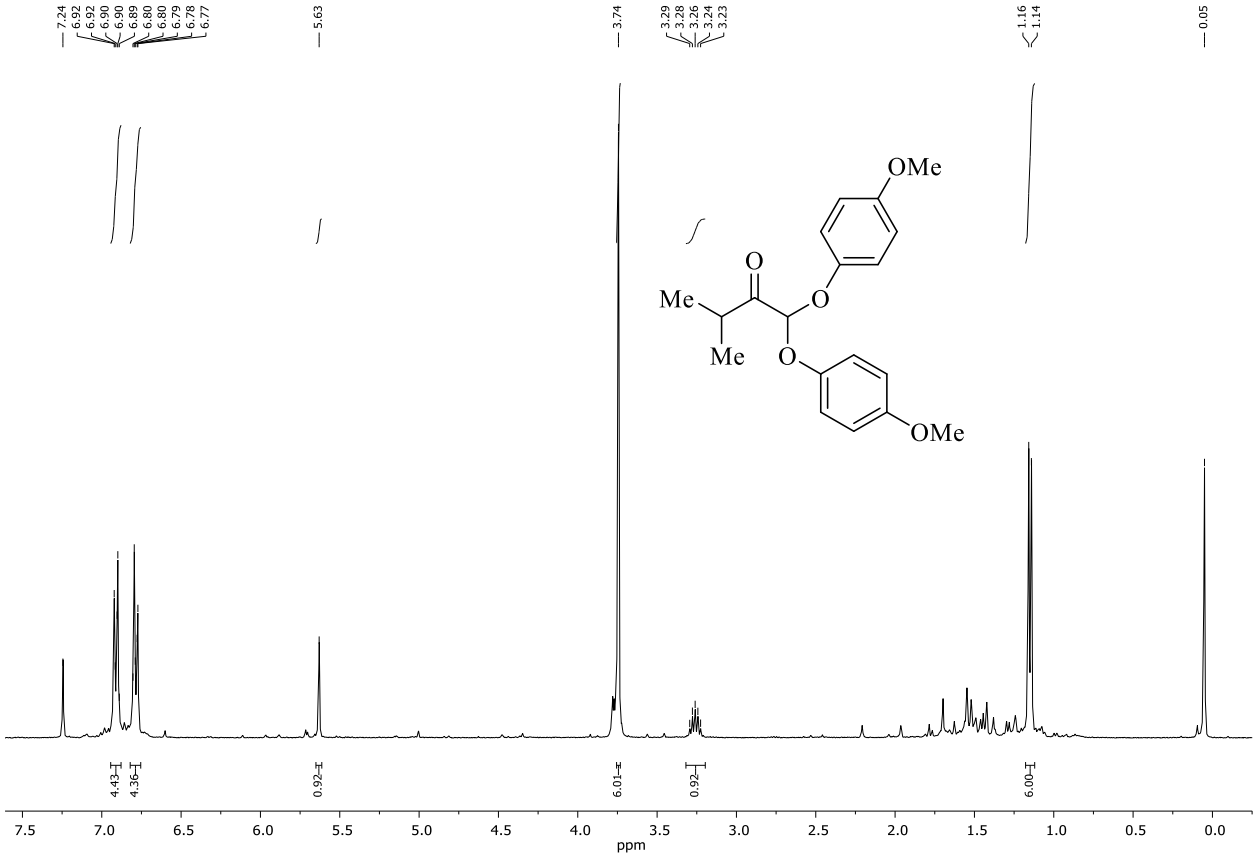


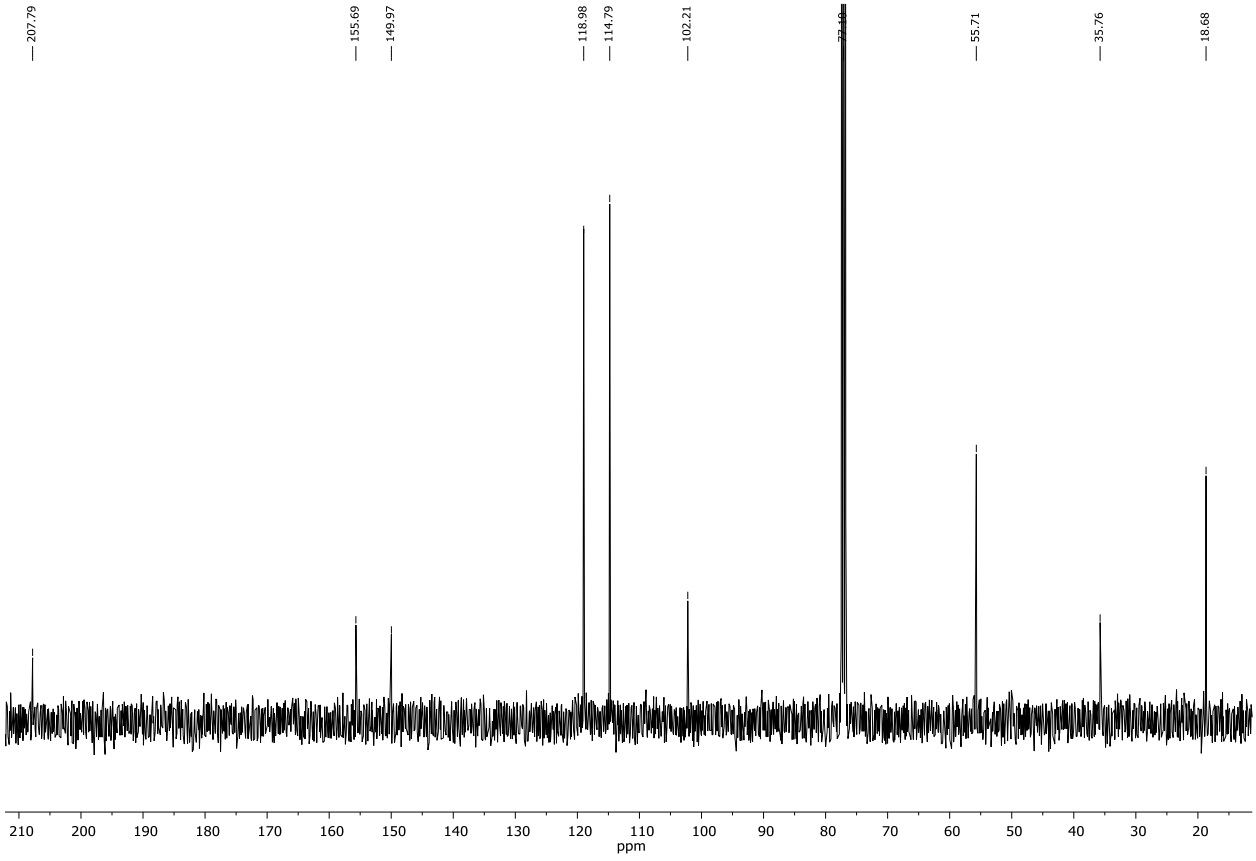


3-Methyl-1,1-diphenoxybutan-2-one (5a)

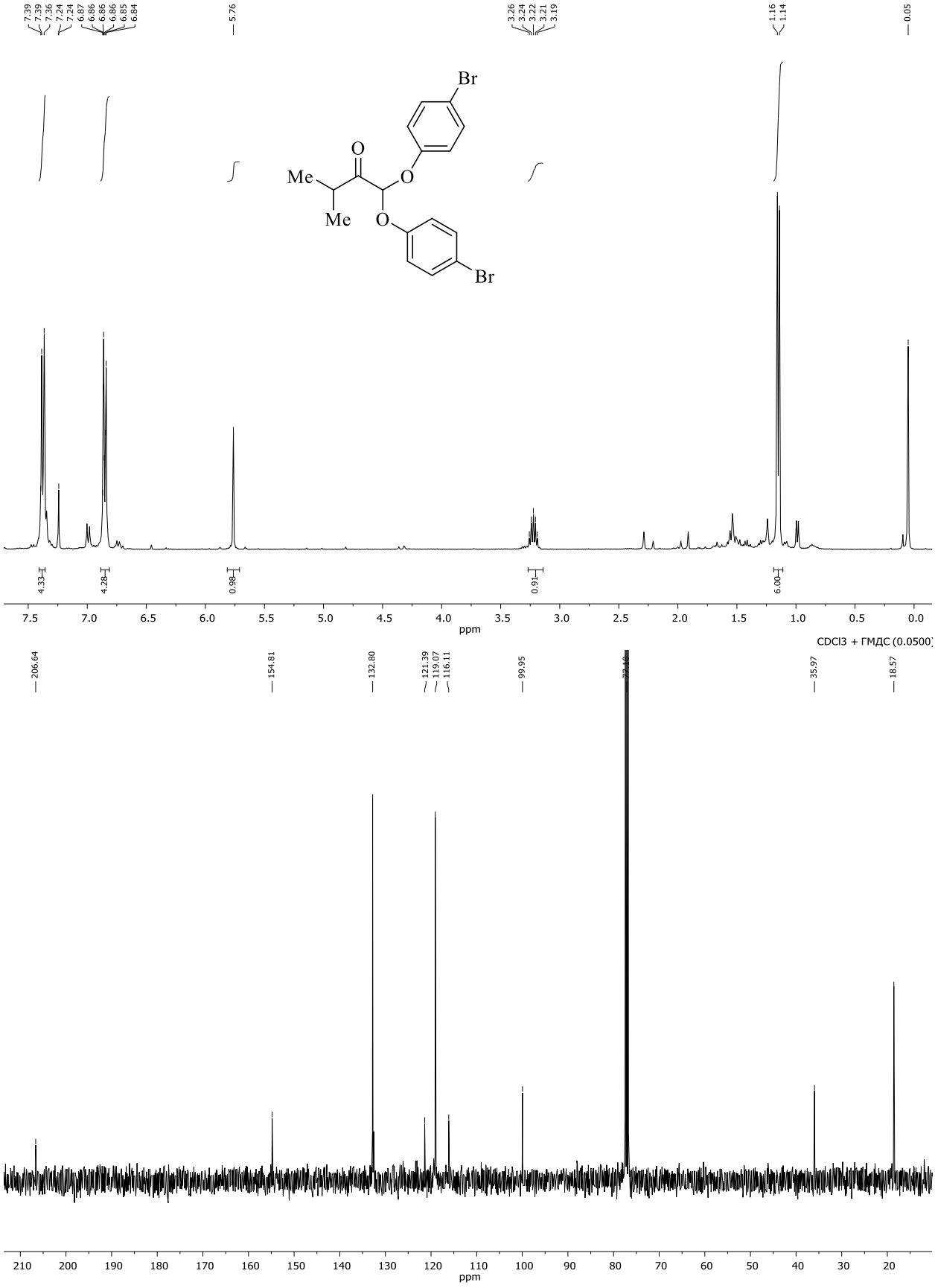


1,1-Bis(4-methoxyphenoxy)-3-methylbutan-2-one (5e)

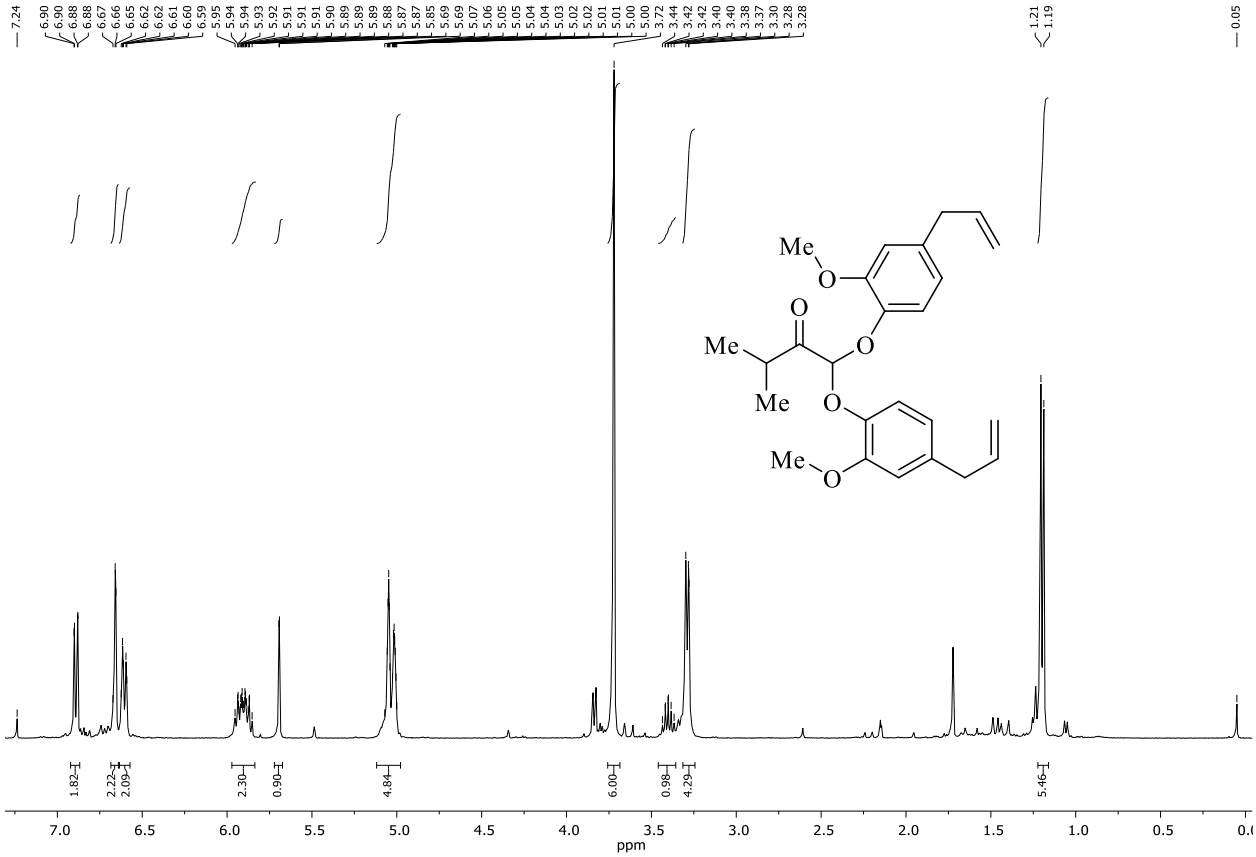


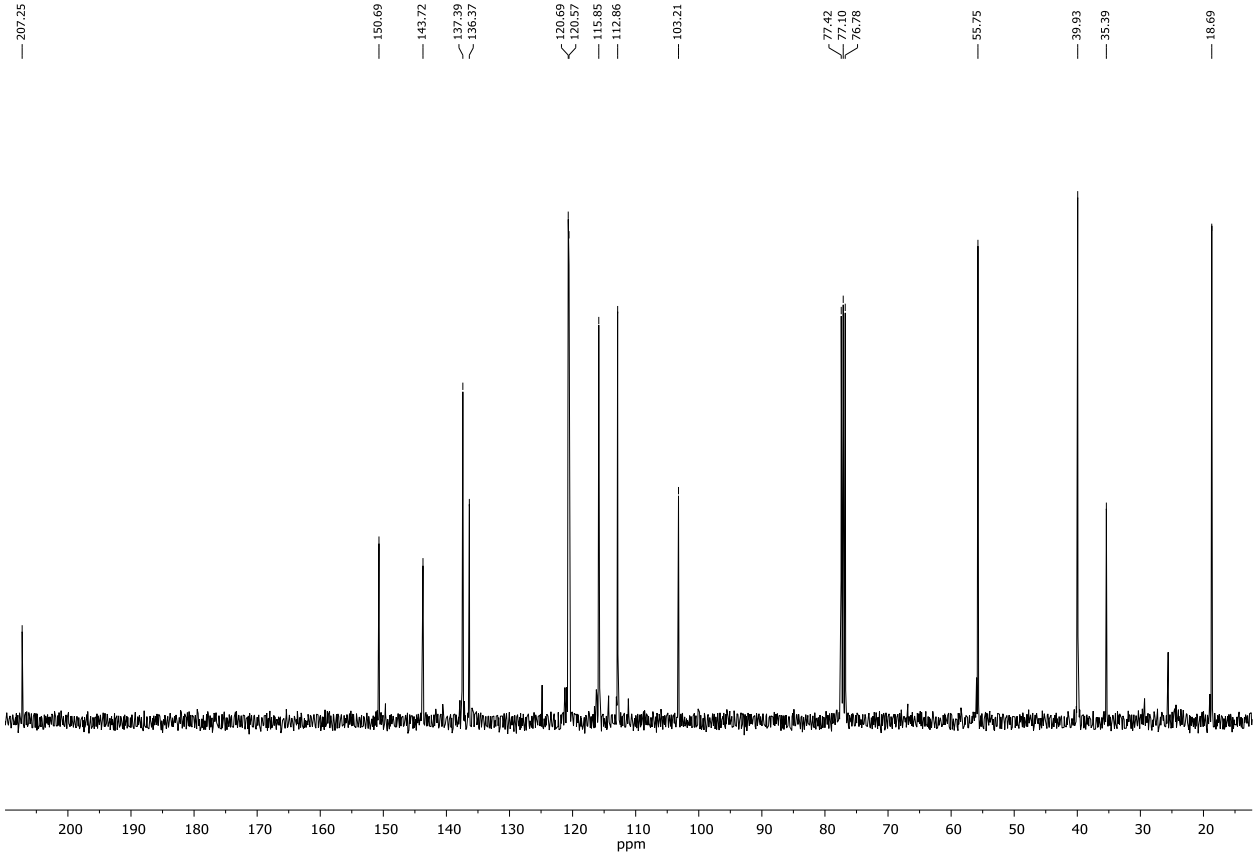


1,1-Bis(4-bromophenoxy)-3-methylbutan-2-one (5f)

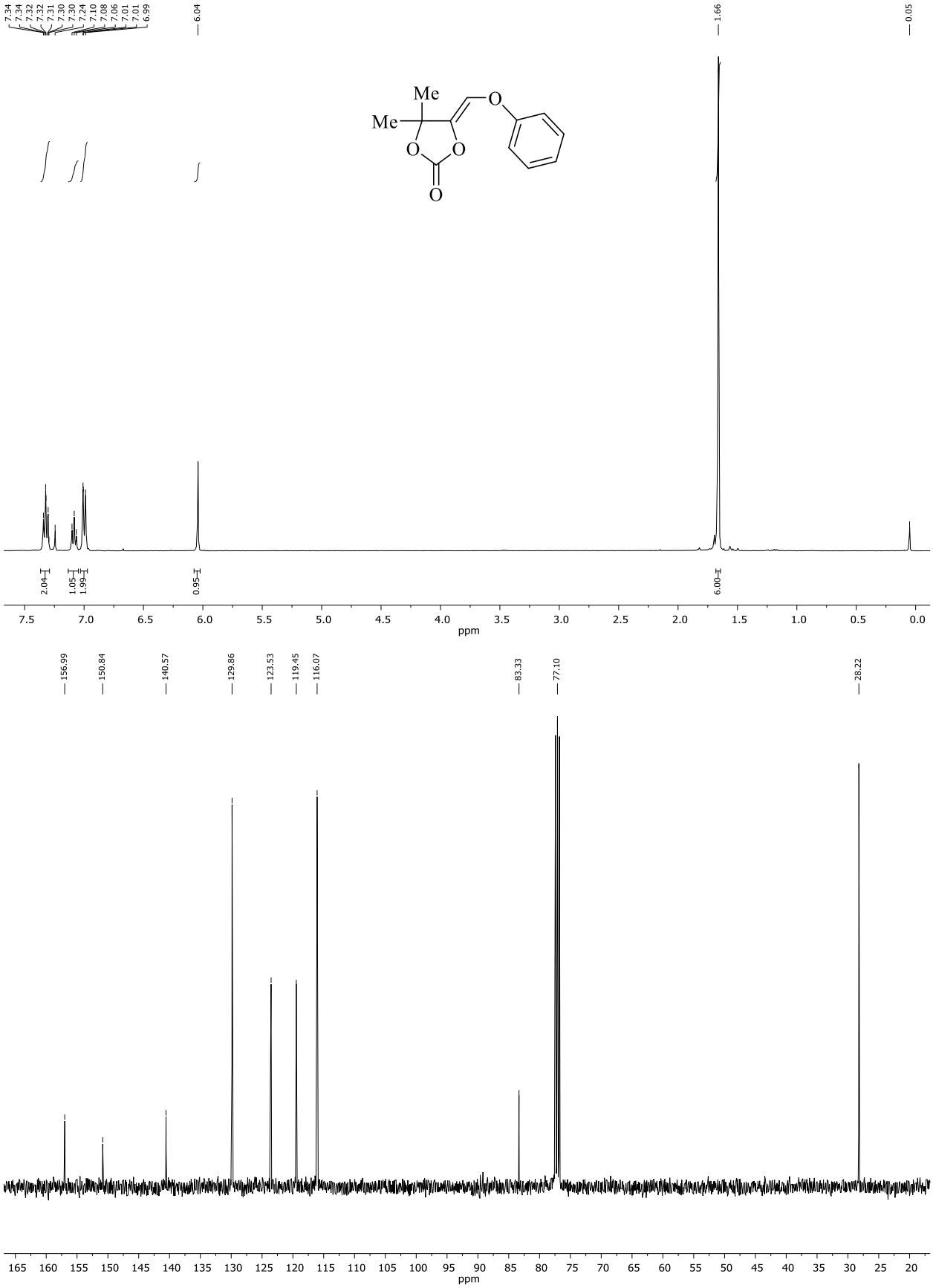


1,1-Bis(4-allyl-2-methoxyphenoxy)-3-methylbutan-2-one (5g)

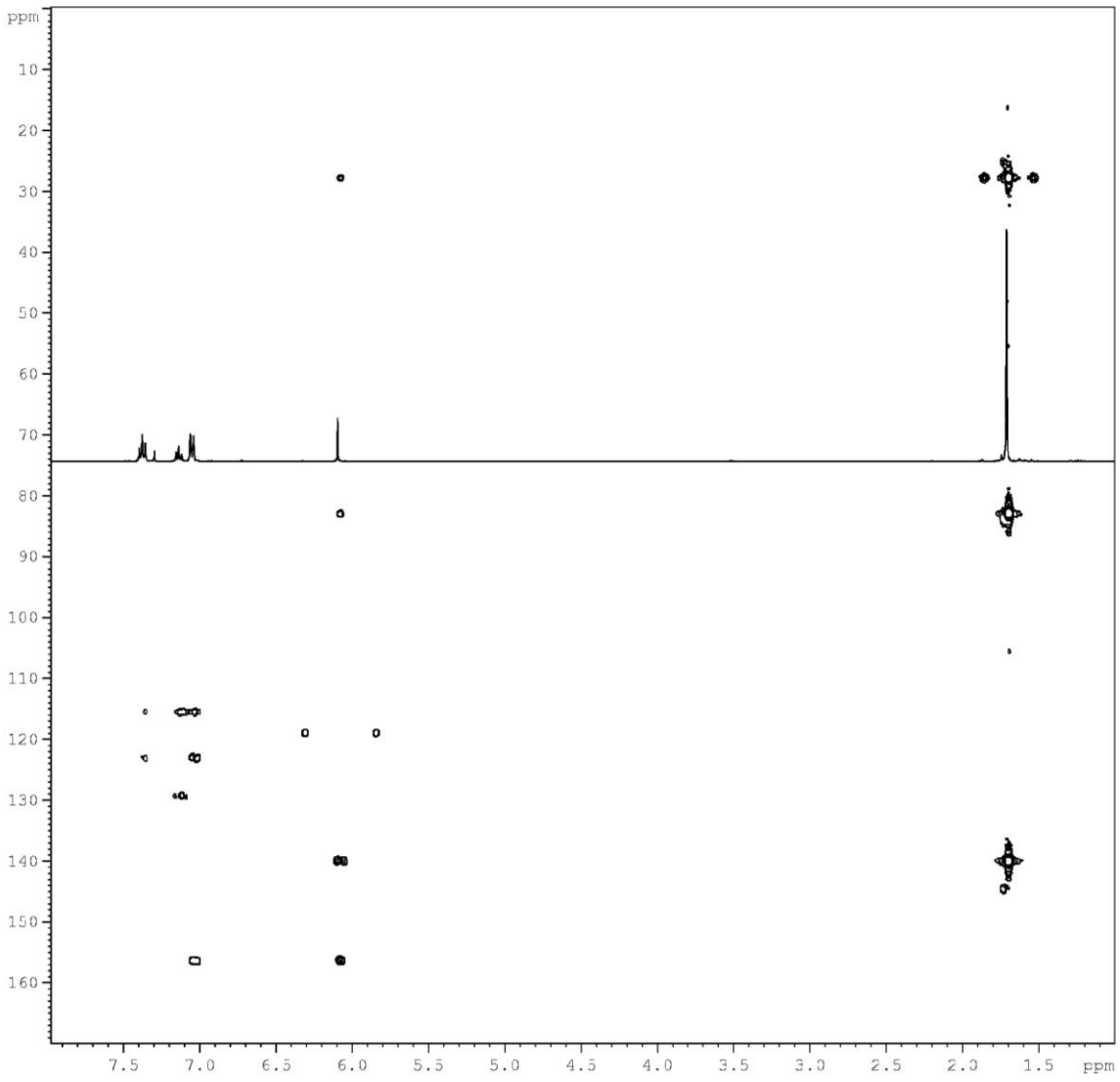




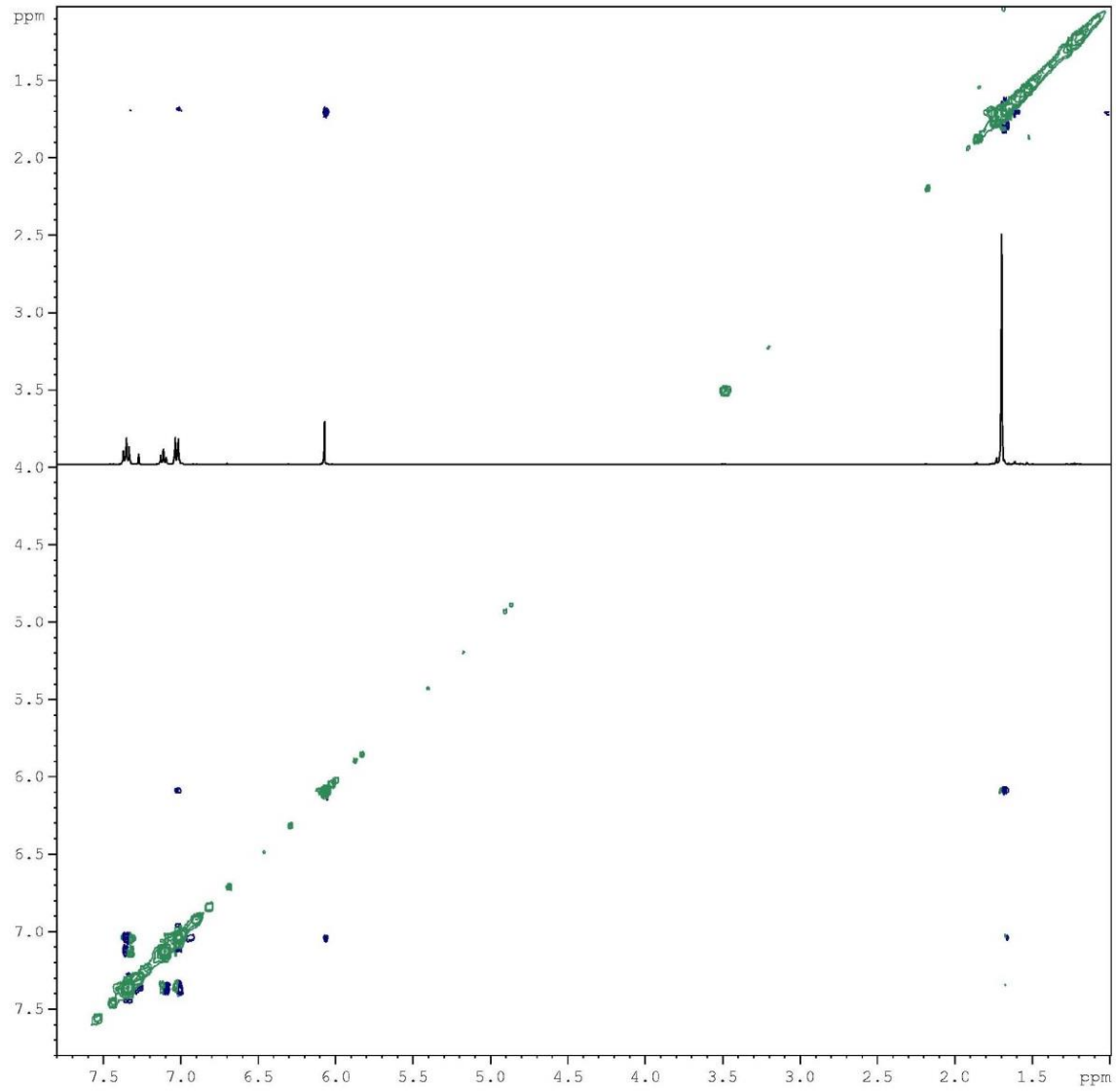
(Z)-4,4-Dimethyl-5-(phenoxymethylene)-1,3-dioxolan-2-one (7)



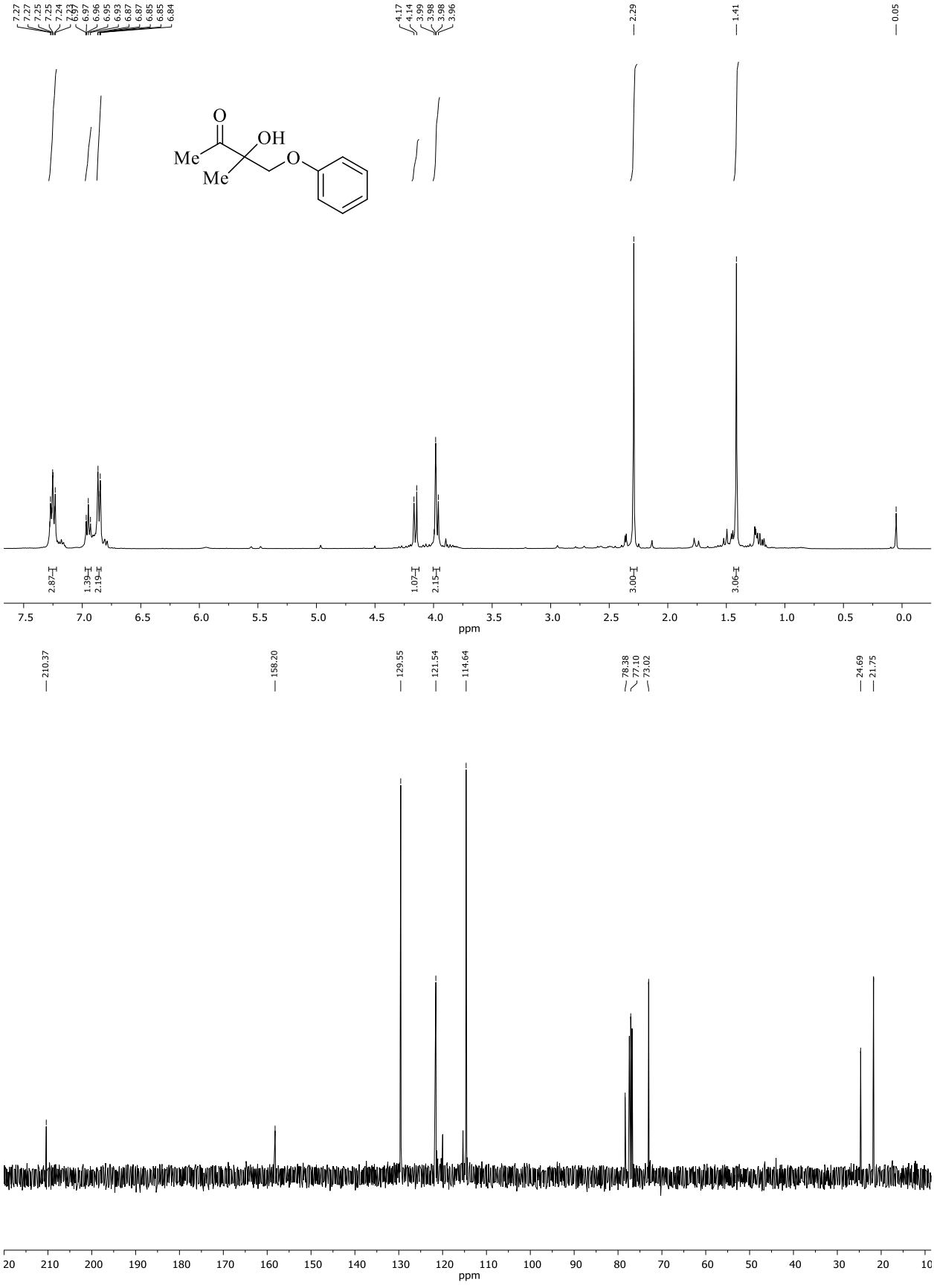
2D ^{1}H-^{13}C HMBC Spectrum of 7 ($CDCl_3$)



2D NOESY Spectrum of 7 ($CDCl_3$)



3-Hydroxy-3-methyl-4-phenoxybutan-2-one (9a)



3-Hydroxy-3-methyl-4-(*p*-tolyloxy)butan-2-one (9b)