Supporting Information:

β-Hydroxy Ketones Prepared by Regioselective Hydroacylation

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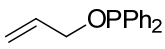
1. General Considerations

Commercial reagents were purchased from Sigma Aldrich, Strem or Alfa Aesar and used without further purification. Reactions were monitored using thin-layer chromatography (TLC) on EMD Silica Gel 60 F254 plates. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300, Varian Mercury 400, VRX-S (Unity) 400, or Bruker AV-III 400 spectrometer. ^1H NMR spectra were internally referenced to the residual solvent signal or TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI). Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 1000 FT-IR Systems and are reported in terms of frequency of absorption (cm^{-1}). Melting point ranges were determined on a Fisher-Johns Melting Point Apparatus. Column chromatography was performed with Silicycle Silia-P Flash Silica Gel, using either glass columns or a Biotage SP-1 system. All salts were purchased from Aldrich and used without purification. Solvents were purchased from Caledon and were purified according to standard procedures. Solvents used in hydroacylations were degassed by three freeze-pump-thaw cycles before being taken into a glove box

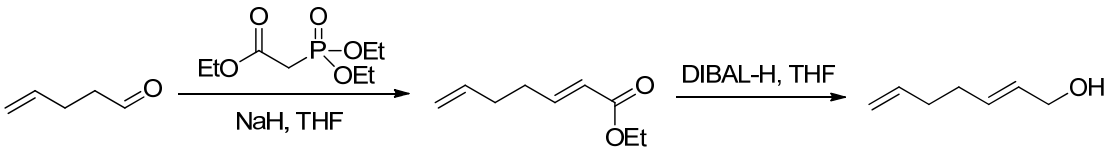
2. Preparation of Substrates

allyldiphenylphosphinite:



Allyl alcohol (0.395 mL, 6.8 mmol) was added dropwise to a vigorously stirring solution of triethylamine (0.688 g, 6.8 mmol) and chlorodiphenylphopshine (1.500 g, 6.8 mmol) in toluene (15 mL). A white precipitate formed immediately. The solution was stirred for two hours, and then transferred to a round bottom flask via cannula filtration. The remaining precipitate was washed with 2x15 mL toluene and the washings were transferred to the round bottom flask in the same manner. The solvent was removed under reduced pressure. The residual oil was passed through a short plug of neutral alumina to yield the pure product as a colourless oil. 78% yield. The title compound was confirmed

by ^{1}H NMR comparison to literature values.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (ddt, J = 9.7, 5.2, 1.7 Hz, 2H), 4.89-4.95 (m, 1H), 5.12-5.20 (m, 1H), 5.70-5.80 (m, 1H), 6.97-7.10 (m, 6H), 7.53-7.60 (m, 4H).



1,5-heptadien-7-ol: Triethylphosphonoacetate (1.190 mL, 6 mmol) was added to a vigourously stirring solution of NaH (0.240 g, 6 mmol) in anhydrous THF at 0°C. After 15 minutes, 4-pentenal (0.592 mL, 6 mmol) was added dropwise and the reaction was stirred for 30 minutes at 0°C, and then 30 minutes at room temperature. The solution was diluted with diethyl ether and washed sequentially with a saturated $Na_2CO_{3(aq)}$ solution, water, and brine. The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo to yield the desired ester as a clear colourless oil (0.8836 g, 96%) which was used in the next step without further purification. The crude ester was dissolved in THF and the solution was cooled to -10°C. DIBAL-H (1.0 M in hexanes, 12.61 mL, 12.61 mmol) was added dropwise. The solution was stirred for two hours while gradually warming to 10°C. The solution was diluted with diethyl ether and quenched by the addition of methanol followed by 1M HCl solution. The solution was washed sequentially with water and brine. The organic layer was separated and dried over $MgSO_4$, and the solvent was removed in vacuo. The residual oil was purified via flash chromatography (4:1 Hx:EtOAc mixture) to afford the desired allylic alcohol as a clear colourless oil (0.3511 g, 57%). ^{1}H NMR (300 MHz): δ 2.08-2.23 (m, 4H), 4.05-4.13 (m, 2H), 4.91-5.08 (m, 2H), 5.61-5.89 (m, 3H), ^{13}C NMR (75 MHz) δ 31.55, 33.27, 63.76, 114.87, 120.41, 132.45, 138.07. HRMS (ESI+): calculated for $[C_7H_{16}O_1N_1]^+$ $[M+NH_4]^+$ 130.12319, found 130.12308.

[1] P. W. Clark, J. L. S. Curtis, P. E. Garrou, G. E. Hartwell, *Can. J. Chem.* **1974**, *52*, 1714-1720.

4. Rh-catalyzed Intermolecular Olefin Hydroacylation

4i) Standard Procedures

Standard Procedure A: Rh-catalyzed Olefin Hydroacylation with Liquid Aldehydes

In a glovebox, $[Rh(COD)Cl]_2$ (0.01 mmol, 2.5 mol %) and sodium acetate (0.08 mmol, 20 mol %) were weighed into a vial. 1.0 mL of degassed dichloroethane was added. Methyl diphenylphosphinite (0.01 mmol, 25 mol %), aldehyde (0.4 mmol, 1.0 equiv.) and the alcohol (0.6 mmol, 1.5 equiv.) were added via syringe. The vial was charged with a stir bar, sealed with a Teflon-lined screw-cap, and heated at 67 °C for the indicated period of time. The product was isolated by Si gel or thin layer chromatography. Some reactions were performed with 0.2 mmol of the aldehyde. In these cases, the amounts of the other reaction components were adjusted to maintain the ratios given in the standard procedure.

Standard Procedure B: Rh-catalyzed Olefin Hydroacylation with Solid Aldehydes

In a glovebox, $[Rh(COD)Cl]_2$ (0.01 mmol, 2.5 mol %) and sodium acetate (0.08 mmol, 20 mol %), and the aldehyde (0.4 mmol, 1.0 equiv.) were weighed into a vial. 1.0 mL of degassed dichloroethane was added. Methyl diphenylphosphinite (0.01 mmol, 25 mol %) and the alcohol (0.6 mmol, 1.5 equiv.) were added via syringe. The vial was charged with a stir bar, sealed with a Teflon-lined screw-cap and heated at 67 °C for the indicated period of time. The product was isolated by Si gel or thin layer chromatography. Specified reactions were performed with 0.2 mmol of the aldehyde. In these cases, the amounts of the other reaction components were adjusted to maintain the ratios given in the standard procedure.

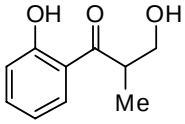
4ii) Hydroacylation of Allylic Alcohol with Wilkinson's Complex

In a glovebox, $RhCl(PPh_3)_3$ (18.5 mg, 0.02 mmol) and sodium acetate (3.3 mg, 0.04 mmol) were weighed into a vial. 1.0 mL of degassed dichloroethane was added. Allyl alcohol (17.4 mg, 0.3 mmol) and salicylaldehyde (24.4 mg, 0.2 mmol) were added via syringe. The vial was charged with a stir bar, sealed with a Teflon-lined screw-cap and heated at 70 °C for the 3 hours. The reaction was then cooled to room temperature and the solvent was removed in vacuo. ^1H NMR analysis of the crude material with 1,3,5-trimethoxybenzene as the internal standard showed that reaction reached 32% conversion

with 28% yield of the decarbonylation product, and 4% yield of the linear product with a 16:1 linear to branched ratio.

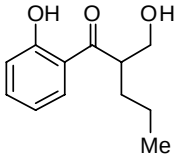
4iii) Substrate Scope

2-(2-hydroxybenzoyl)propan-1-ol (Table 1, entry 1)



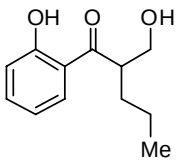
The title compound was prepared from salicylaldehyde (0.4 mmol) and allyl alcohol according to Standard Procedure A (3 h reaction time) with the exception that $[Rh(COD)Cl]_2$ (0.02 mmol, 9.9 mg) and Ph_2POMe (0.24 mmol, 51.9 mg) were used and the temperature was set to 70°C. Purification via silica gel column chromatography (gradient 15:1 → 7:3 hexanes:ethyl acetate) afforded the title compound as a light yellow oil (47.5 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (d, J = 7.0 Hz, 3H), 3.69-3.79 (m, 1H), 3.82 (dd, J = 11.0, 4.3 Hz, 1H), 3.98 (dd, J = 11.0, 4.0 Hz, 1H), 6.93 (t, 7.7 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 15.0, 42.5, 64.43, 118.6, 118.9, 119.1, 130.1, 136.8, 163.2, 210.0. HRMS (ESI+), calculated for $[C_{10}H_{12}O_3]^+$ $[M+H]^+$ 180.0786, found 180.0787.

2-(2-hydroxybenzoyl)pentan-1-ol (Table 1, entry 2)



The title compound was prepared from salicylaldehyde (0.4 mmol), and *c*is-2-penten-1-ol according to Standard Procedure **A** (3 h reaction time). Purification via Si gel chromatography (15:1 → 7:3 hexanes:ethyl acetate) afforded the product as a yellow oil (73.3 mg, 88 %). ^{1}H NMR (400MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.30-1.49 (m, 2H), 1.59-1.77 (m, 2H), 2.11 (br s, 1H), 3.67 (dddd, *J* = 7.0, 7.0, 7.0, 4.0 Hz, 1H), 3.85 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.97 (dd, *J* = 11.0, 7.1 Hz, 1H), 6.92 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.00 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.49 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.80 (dd, *J* = 8.1,1.6 Hz, 1H), 12.39 (br s, 0.9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3, 20.8, 31.9, 47.7, 63.2, 118.9, 119.2, 119.4, 130.3, 136.9, 163.2, 210.4; HRMS (ESI+) Calcd. for $[C_{12}H_{17}O_3]^+$ $[M+H]^+$ 209.11777, found 209.11824.

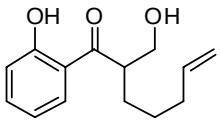
2-(2-hydroxybenzoyl)pentan-1-ol (Table 1, entry 3)



The title compound was prepared from salicylaldehyde (0.4 mmol) and *trans*-2-penten-1-ol according to Standard Procedure **A** (3 h reaction time). Purification via Si gel chromatography (gradient 15:1 → 7:3 hexanes:ethyl acetate) afforded the product as a

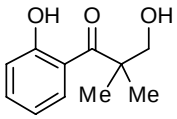
yellow oil (71.0 mg, 85%). The title compound was confirmed by ^{1}H NMR comparison to product **5ab**.

2-(2-hydroxybenzoyl)-6-hepten-1-ol (Table 1, entry 4)



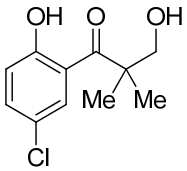
The title compound was prepared from salicylaldehyde (0.4 mmol) and 1,5-heptadiene-7-ol according to Standard Procedure **A** (3 h reaction time). Purification via Si gel chromatography (gradient 15:1 → 7:3 hexanes:ethyl acetate) afforded the product as a yellow oil (88.2 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35-1.55 (m, 2H), 1.59-1.83 (m, 2H), 2.06 (q, 7.2 Hz, 2H), 2.31 (br s, 1H), 3.62-3.71 (m, 1H), 3.83 (dd, J = 11.0, 4.0, 1H), 3.96 (dd, J = 11.1, 7.3 Hz, 1H), 4.91-5.03 (m, 2H), 5.69-5.81 (m, 1H), 6.92 (t, J = 7.4, 1H), 7.00 (d, J = 7.0 Hz, 1H), 7.49 (t, 7.9 Hz, 1H), 7.80 (d, J = 7.9, 1H), 12.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.77, 29.24, 33.90, 47.90, 63.33, 115.31, 118.98, 119.29, 119.62, 130.44, 137.01, 138.19, 163.26, 210.27. HRMS (ESI+), calculated for $[C_{14}H_{19}O_3]^+$ $[M+H]^+$ 235.13342, found 235.13306.

2-(2-hydroxybenzoyl)-2-methylpropan-1-ol (Table 1, entry 6)



The title compound was prepared from salicylaldehyde (0.4 mmol) and 2-methylallyl alcohol according to Standard Procedure **A** (3 h reaction time). Purification via Si gel chromatography (35% diethyl ether in hexanes) afforded the product as a yellow oil (69.5 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 6H), 2.53 (t, *J* = 7.3 Hz, 1H), 3.69 (d, *J* = 7.2 Hz, 2H), 6.87 (ddd, *J* = 8.3, 7.2, 1.3 Hz , 1H), 7.02 (dd, *J* = 8.5, 1.2 Hz , 1H), 7.45 (ddd, *J* = 8.6, 7.2, 1.6 Hz , 1H), 8.00 (dd, *J* = 8.3, 1.6 Hz , 1H), 12.43 (br s, 0.9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.8, 49.4, 71.5, 117.7, 118.2, 119.6, 130.8, 136.1, 163.9, 212.8; HRMS (ESI+) Calcd. for $[C_{11}H_{15}O_3]^+$ $[M+H]^+$ 195.10212, found 195.10242.

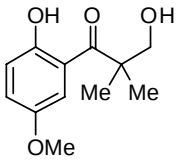
2-(2-hydroxy-5-chlorobenzoyl)-2-methylpropan-1-ol (Table 2, entry 2)



The title compound was prepared from 5-chlorosalicylaldehyde (0.2 mmol) and 2-methylallyl alcohol according to Standard Procedure **A** (5 h reaction time) except that NaOAc (0.01 mmol, 0.8 mg) was used. Purification via thin layer chromatography (gradient 15:1 → 7:3 hexanes:ethyl acetate) afforded the product as a yellow oil (33.5 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (s, 6H), 3.70 (s, 2H), 6.97 (d, J = 8.9 Hz, 1H), 7.39 (dd, J = 8.9, 2.6 Hz, 1H), 7.93 (d, J = 2.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.76, 49.74, 71.28, 118.46,

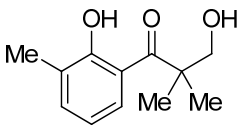
121.21, 123.06, 129.99, 136.03, 162.29, 211.95. HRMS (ESI), calculated for $[C_{11}H_{14}ClO_3]^+$ $[M+H]^+$ 229.06315, found 229.06263.

3-hydroxy-1-(2-hydroxy-5-methoxyphenyl)-2,2-dimethylpropan-1-one (Table 2, entry 3)



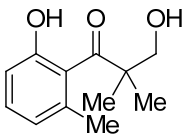
The title compound was prepared from 2-hydroxy-5-methoxybenzaldehyde (0.2 mmol)and 2-methylallyl alcohol according to Standard Procedure **A** (4h reaction time). Purification was performed via preparative thin layer chromatography (3:2 hexanes:ethyl acetate). The Si gel was extracted via sonication with ethyl acetate (2 extractions), to give the product as a yellow oil (33.8 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 6H), 2.56 (t, *J* = 7.1 Hz, 1H), 3.69 (d, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 6.97 (d, *J* = 9.1 Hz, 1H), 7.11 (dd, *J* = 9.1, 3.0 Hz , 1H), 7.45 (d, *J* = 3.0 Hz , 1H), 11.95 (br s, 0.9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.7, 49.3, 56.1, 71.5, 114.2, 117.2, 120.2, 123.8, 151.0, 158.2, 212.3; HRMS (ESI+) Calcd. for $[C_{12}H_{17}O_4]^+$ $[M+H]^+$ 225.11268, found 225.11295.

2-(2-hydroxy-3-methylbenzoyl)-2-methylpropan-1-ol (Table 2, entry 4)



The title compound was prepared from 3-methylsalicylaldehyde (0.4 mmol) and 2-methylallyl alcohol according to Standard Procedure **A** (5 h reaction time). Purification via Si gel chromatography (gradient 15:1 → 7:3 hexanes:ethyl acetate) afforded the product as a yellow oil (66.5 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (s, 6H), 2.26 (s, 3H), 2.66 (br s, 1H), 3.68 (s, 2H), 6.77 (t, J = 7.9 Hz, 1H), 7.32 (d, J = 7.1 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 12.77 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.13, 23.96, 49.48, 71.66, 117.01, 117.59, 128.53, 128.65, 136.89, 162.57, 213.20. MS: calculated for $[C_{12}H_{17}O_3]^+$ $[M+H]^+$ 209.11777; found 209.11798.

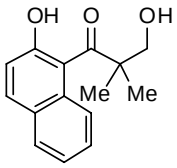
2-(2-hydroxy-6-methylbenzoyl)-2-methylpropan-1-ol (Table 2, entry 5)



The title compound was prepared from 6-methylsalicylaldehyde (0.4 mmol) and 2-methylallyl alcohol according to Standard Procedure **A** (5 h reaction time). Purification via Si gel chromatography (gradient 15:1 → 7:3 hexanes:ethyl acetate) afforded the product as a yellow oil (65.0 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50 (s, 6H), 2.25 (s, 3H), 2.73 (br s, 1H), 3.67 (s, 2H), 6.76 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.84 (d, 8.2 Hz, 1H), 12.77 (s,

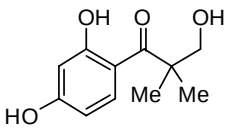
1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.13, 23.95, 49.49, 71.62, 116.02, 117.60, 128.53, 128.63, 136.56, 162.56, 213.18. HRMS (ESI), calculated for $[C_{12}H_{17}O_3]^+$ 209.11777, found 209.11682.

3-hydroxy-1-(2-hydroxynaphthalen-1-yl)-2,2-dimethylpropan-1-one (Table 2, entry 6)



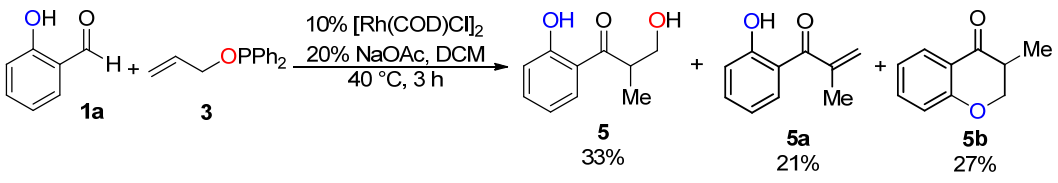
The title compound was prepared from 2-hydroxy-1-naphthaldehyde (0.2 mmol) and 2-methylallyl alcohol according to Standard Procedure **B** (16 h reaction time). Purification was performed via preparative thin layer chromatography (hexanes:ethyl acetate). The Si gel was extracted via sonication with tetrahydrofuran (2 extractions), to give the product as a white solid (39.0 mg, 80 %, MP 153-154 °C). ^{1}H NMR (400 MHz, DMSO-D_6) δ 1.16 (s, 6H), 3.60 (s, 2H), 4.98 (bs, 0.9H), 7.16 (d, J = 8.9 Hz, 1H), 7.29 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.38 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.55 (d, J = 8.4 Hz , 1H), 7.78-7.81 (m, 2H), 10.05 (br s, 1H); ^{13}C NMR (101 MHz, DMSO-D_6) δ 21.9, 50.3, 68.6, 118.0, 122.2, 122.9, 123.8, 126.5, 127.5, 127.9, 129.8, 131.0, 150.2, 214.7; HRMS (ESI+) Calcd. for $[C_{15}H_{17}O_3]^+$ $[M+H]^+$ 245.11777, found 245.11800.

1-(2,4-dihydroxyphenyl)-3-hydroxy-2,2-dimethylpropan-1-one (Table 2, entry 7)



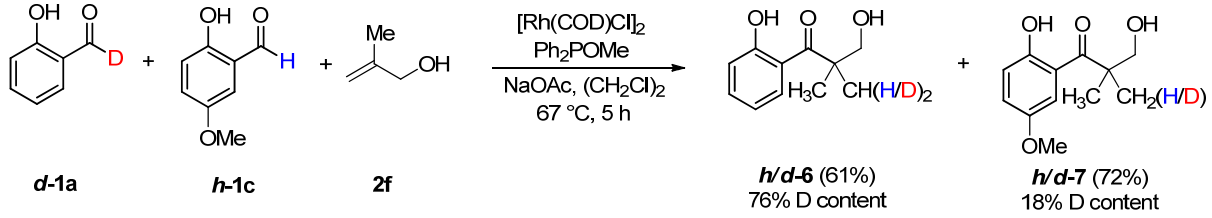
The title compound was prepared from 2,4-dihydroxybenzaldehyde (0.2 mmol) and 2-methylallyl alcohol using tetrahydrofuran as solvent according to Standard Procedure **B** (4 h reaction time). Purification was performed via preparative thin layer chromatography (3:2 hexanes:tetrahydrofuran). The Si gel was extracted via sonication with tetrahydrofuran (2 extractions). The isolated product was washed twice with chloroform and concentrated to give a white solid (34.5 mg, 82 %, MP 140-142 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.25 (s, 6H), 3.66 (s, 2H), 4.84 (br s, 0.9H), 6.25 (d, J = 2.4 Hz, 1H), 6.32 (dd, J = 8.9, 2.5 Hz, 1H), 7.80 (d, J = 8.9 Hz , 1H), 10.35 (br s, 0.9H), 12.51 (br s, 0.7H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 23.5, 49.7, 69.1, 102.9, 107.0, 112.8, 132.2, 162.9, 163.7, 209.7; HRMS (ESI+) Calcd. for $[C_{11}H_{15}O_4]^+$ $[M+H]^+$ 211.09703, found 211.09674.

4iv) Stoichiometric Reactions



In a glovebox, $[Rh(COD)Cl]_2$ (9.9 mg, 0.02 mmol) and sodium acetate (3.3 mg, 0.04 mmol) were weighed into a vial. 0.500 mL of degassed 1,2-dichloroethane was added. Allyl diphenylphosphinite (73.0 mg, 0.3 mmol) and salicylaldehyde (24.0 mg, 0.2 mmol) were added via syringe. The vial was charged with a stir bar, sealed with a Teflon-lined screw-cap, and heated at 40 °C for 2 hours. The products were isolated by Si gel chromatography (gradient 15:1 → 7:3 hexanes:ethyl acetate). **5** was obtained as a light yellow oil (33%, 11.9 mg). (see Section 4iii for characterization). **5a** was obtained as a white solid (21%, 6.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08-2.12 (m, 3H), 5.43-5.45 (m, 1H), 5.73-5.75 (m, 1H), 6.89 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 11.90 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 19.5, 118.4, 118.6, 123.1, 132.8, 136.3, 142.7, 144.2, 163.1, 203.5; HRMS (ESI+) Calcd. for $[C_{10}H_{11}O2]^+$ $[M+H]^+$ 163.07590, found 163.07571. **5b** was obtained as light yellow liquid (27%, 8.7 mg), which was confirmed by comparison to the literature ^{1}H NMR values.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, J = 6.9, 3H), 2.82-2.93 (m, 1H), 4.17 (t, J = 11.0 Hz, 1H), 4.51 (dd, J = 11.3 Hz, 5.3 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 7.02 (t, J = 7.9 Hz, 1H), 7.44-7.51 (m, 1H), 7.91 (d, 7.9 Hz, 1H).

4v) Deuterium Labelling Studies



***d*-1a** ***h*-1c** **2f** ***h*/*d*-6** (61%) 76% D content ***h*/*d*-7** (72%) 18% D content

In a glovebox, $[Rh(COD)Cl]_2$ (3.0 mg, 6.17 µmol) and sodium acetate (2.0 mg, 24.7 µmol) were weighed into a vial. 0.300 mL of degassed 1,2-dichloroethane was added. Methyl diphenylphosphinite (13.3 mg, 61.7 µmol), d_1-salicylaldehyde (prepared according to a literature procedure, see Ref 2.) (7.6 mg, 61.7 µmol), 5-methoxysalicylaldehyde (9.4 mg, 61.7 µmol) and 2-methyl-2-propen-1-ol (8.9 mg, 123.5 µmol) were added via syringe. The vial was charged with a stir bar, sealed with a Teflon-lined screw-cap, and heated at 67 °C for 5 hours. The products were isolated by thin layer chromatography (4:1 hexanes:ethyl acetate, 3 elutions). ***h*/*d*-6** was obtained as a colourless liquid (7.4 mg, 61%) and ***h*/*d*-7** was obtained as a yellow liquid (10.0 mg, 71%). The isolated products were analyzed using DART-

[2] Hirano, K.; Biju, A.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 14190–14191

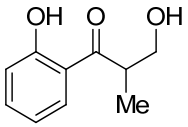
TOF-MS. Table 1 shows the intensities of the relevant peaks. From these values, the ratios of the various isotopologues were calculated. For product ***h/d*-6**, the ratio of non-deuterated:monodeuterated:dideuterated was 24:66:10. For product ***h/d*-7**, the ratio of non-deuterated:monodeuterated:dideuterated was 82:18:0. The reaction was repeated in the absence of alkene and no deuterium incorporation into **1c** was observed by GC-MS.

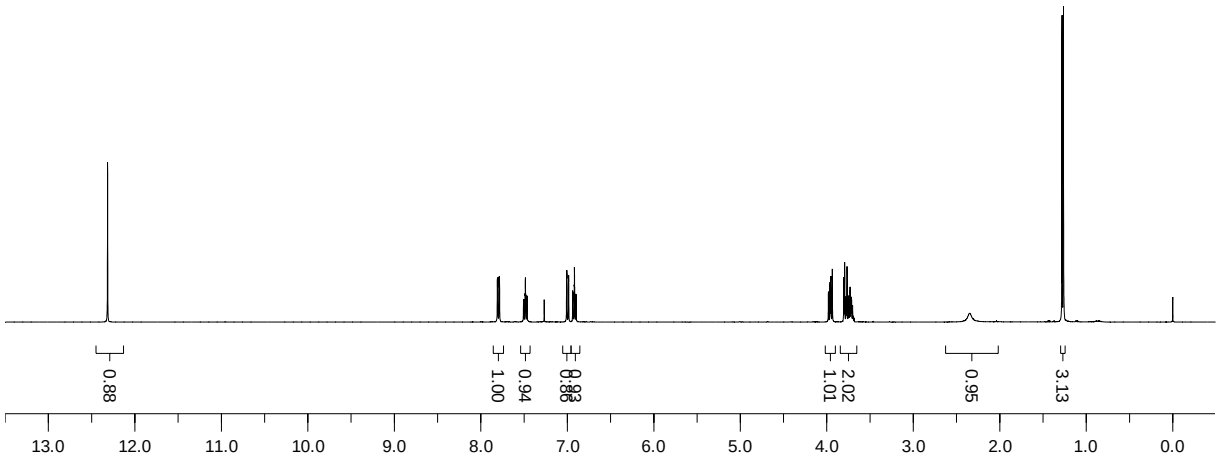
Table 1: Isotope ratios for the isolated products.

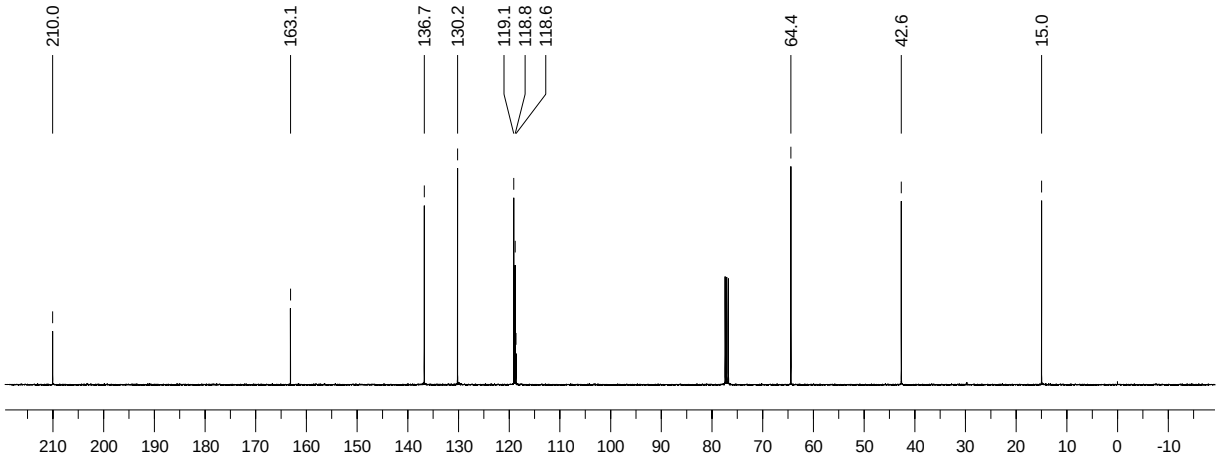
***h/d*-6**		***h/d*-7**	
m/z	**Area**	**m/z**	**Area**
195.1	9177.33	225.1	35571.52
196.1	26512.67	226.1	11014.6
197.1	7123.50		

5. ^{1}H and ^{13}C NMR Spectra of New Compounds

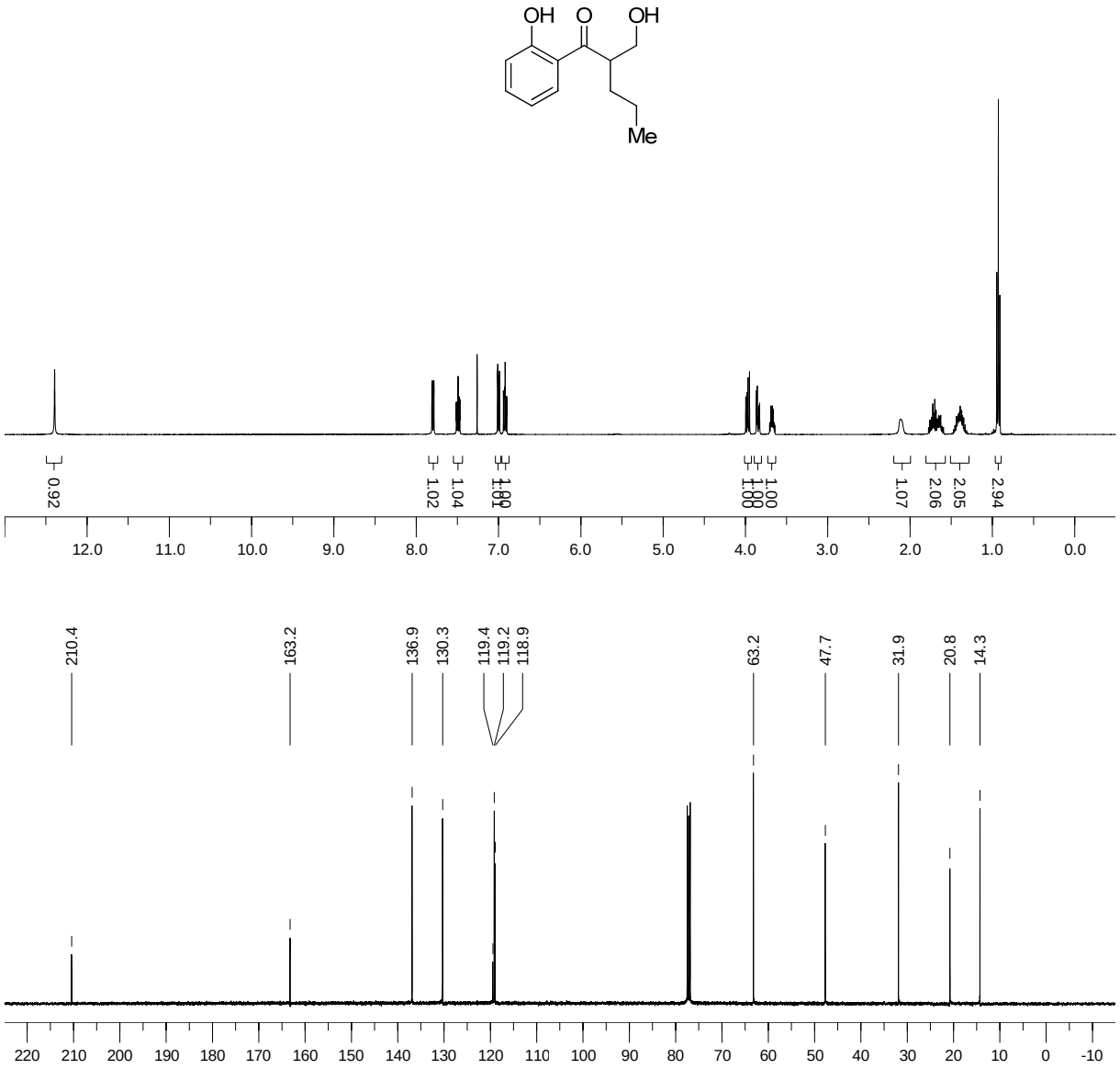
2-(2-hydroxybenzoyl)propan-1-ol (Table 1, entry 1)



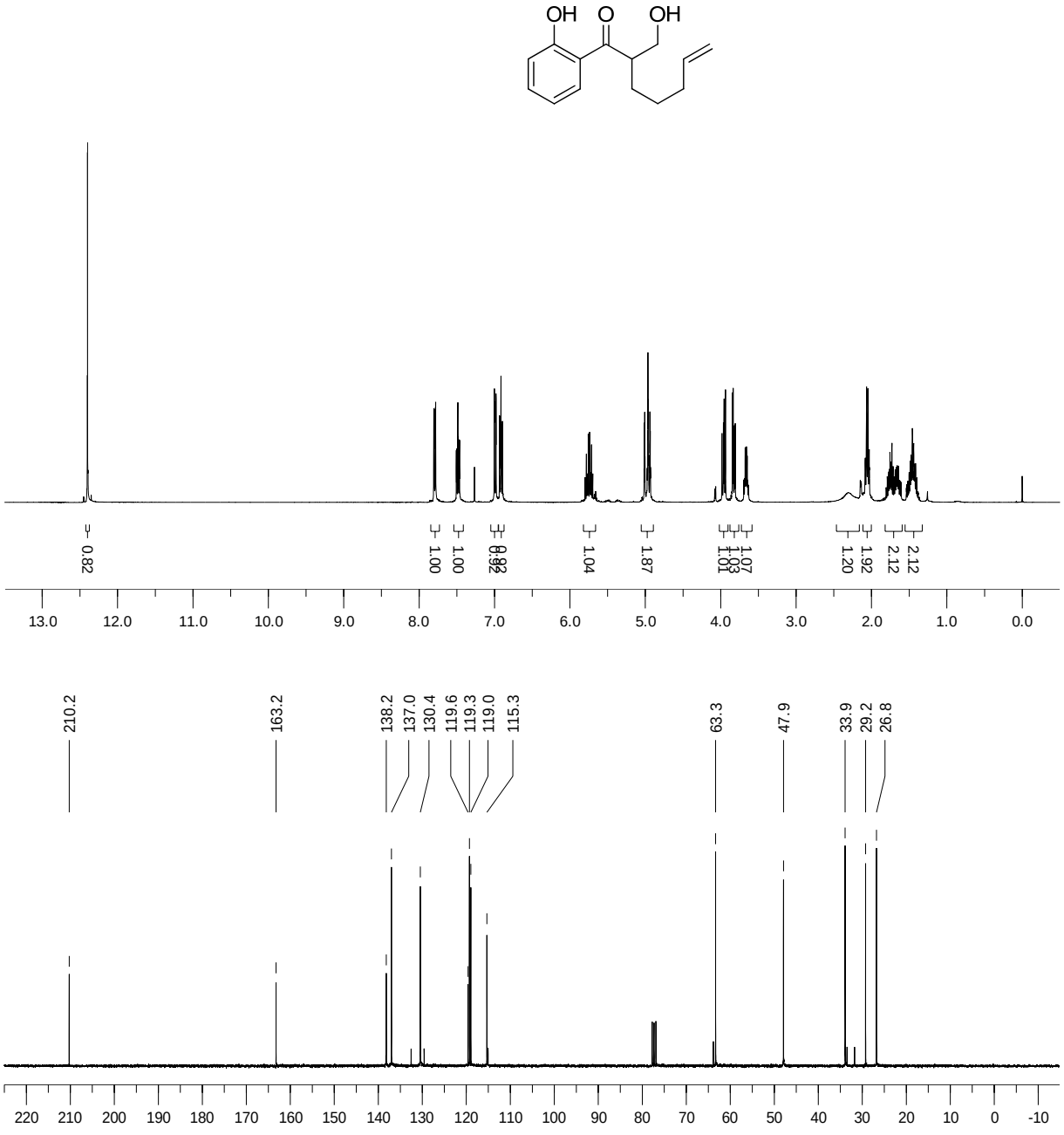




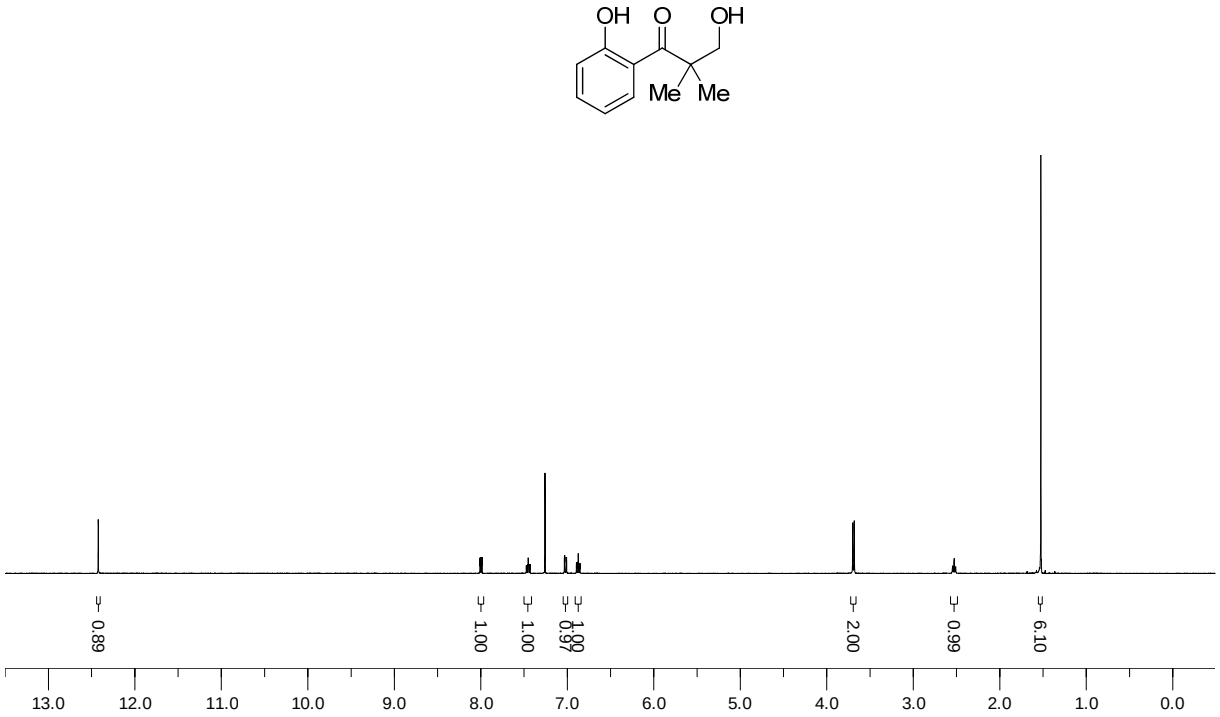
2-(2-hydroxybenzoyl)pentan-1-ol (Table 1, entry 2/3)

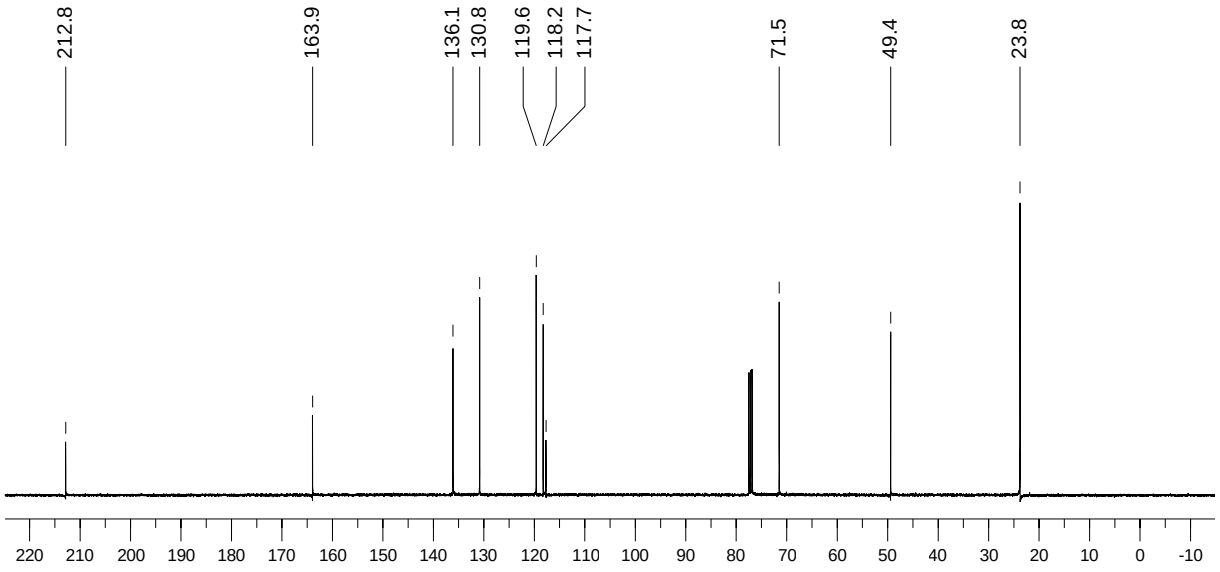


2-(2-hydroxybenzoyl)-6-hepten-1-ol (Table 1, entry 4)

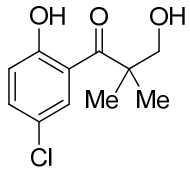


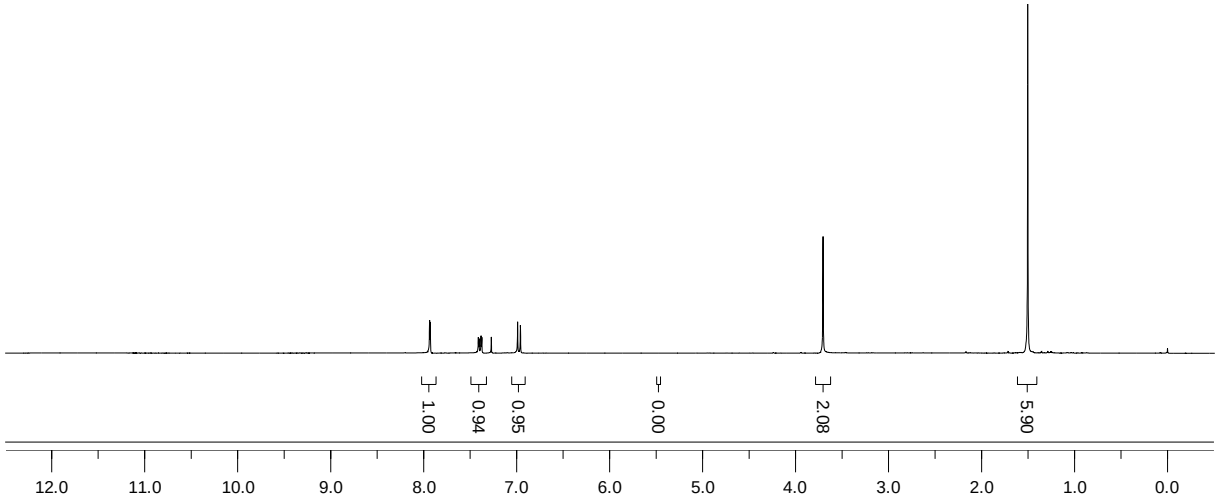
2-(2-hydroxybenzoyl)-2-methylpropan-1-ol (Table 1, entry 6)

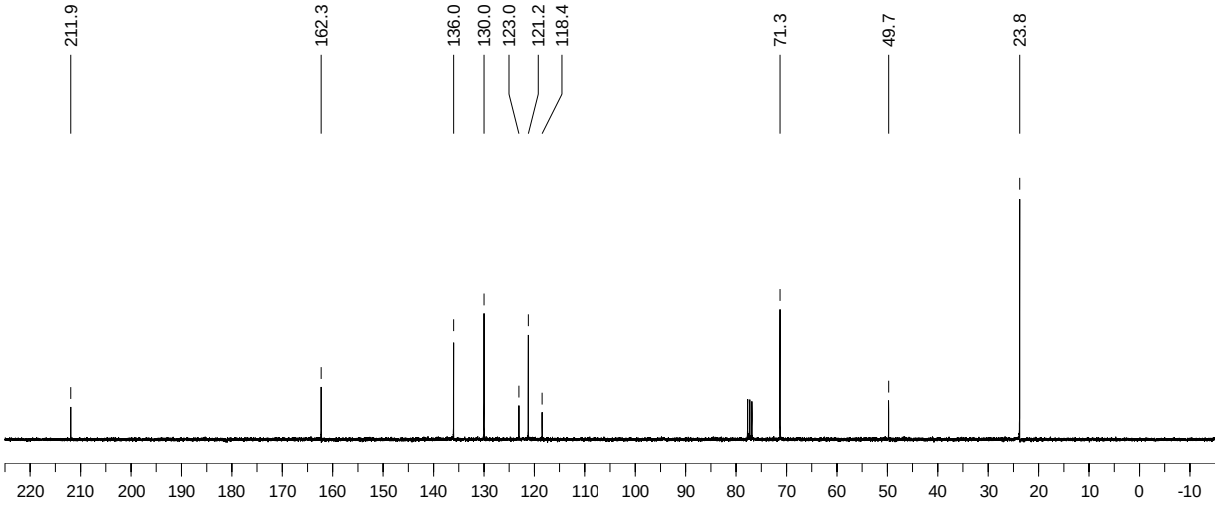




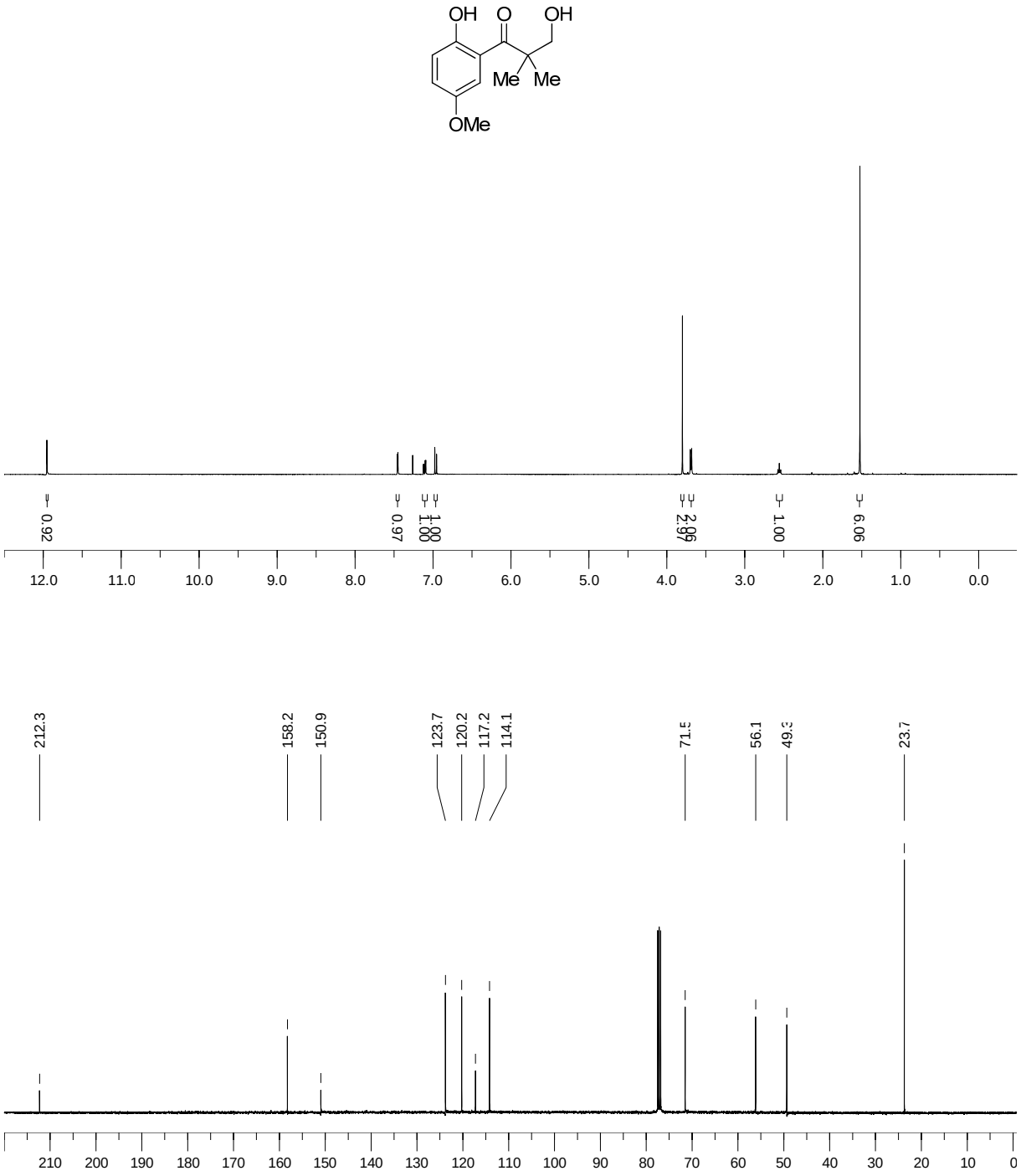
2-(2-hydroxy-5-chlorobenzoyl)-2-methylpropan-1-ol (Table 2, entry 2)



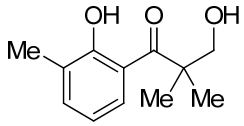


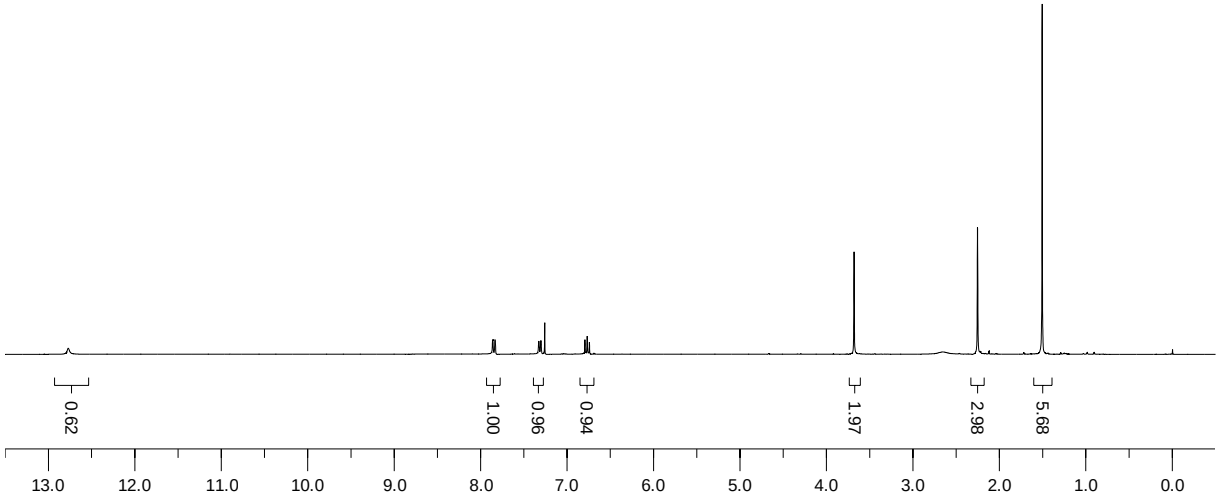


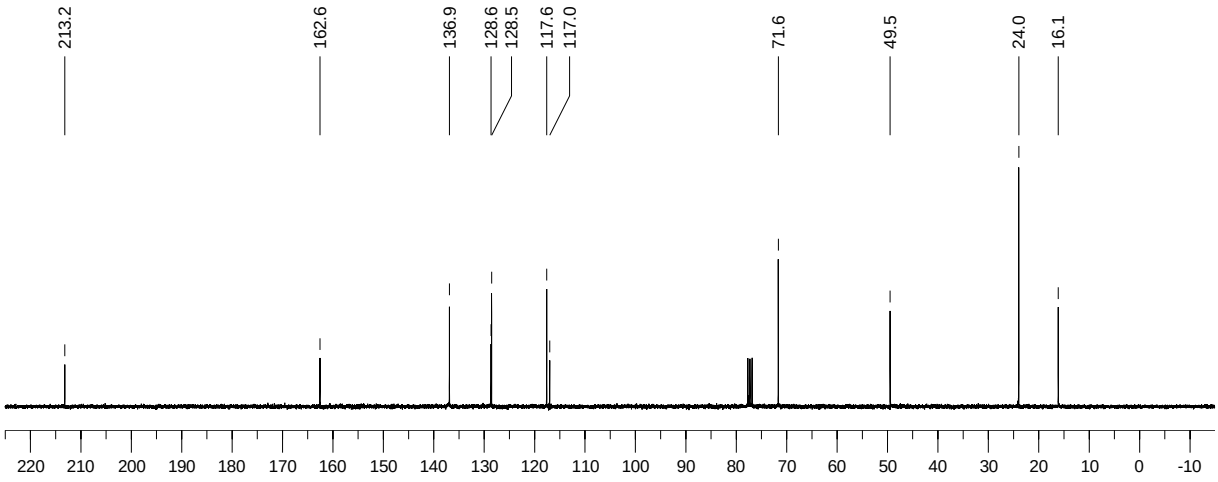
3-hydroxy-1-(2-hydroxy-5-methoxyphenyl)-2,2-dimethylpropan-1-one (Table 2, entry 3)



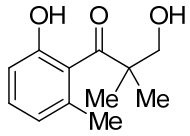
2-(2-hydroxy-3-methylbenzoyl)-2-methylpropan-1-ol (Table 2, entry 4)

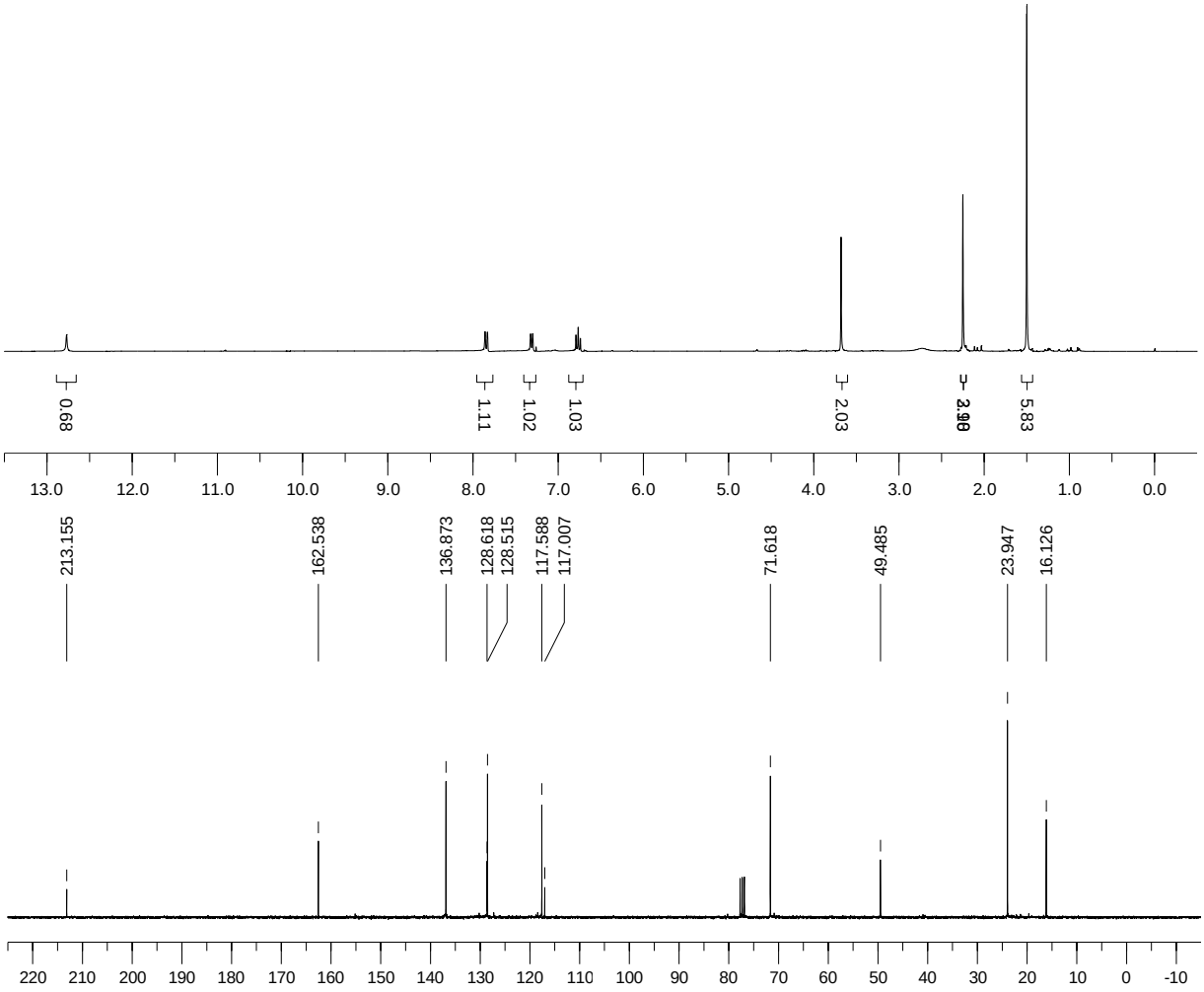




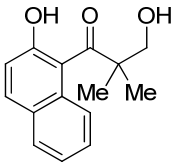


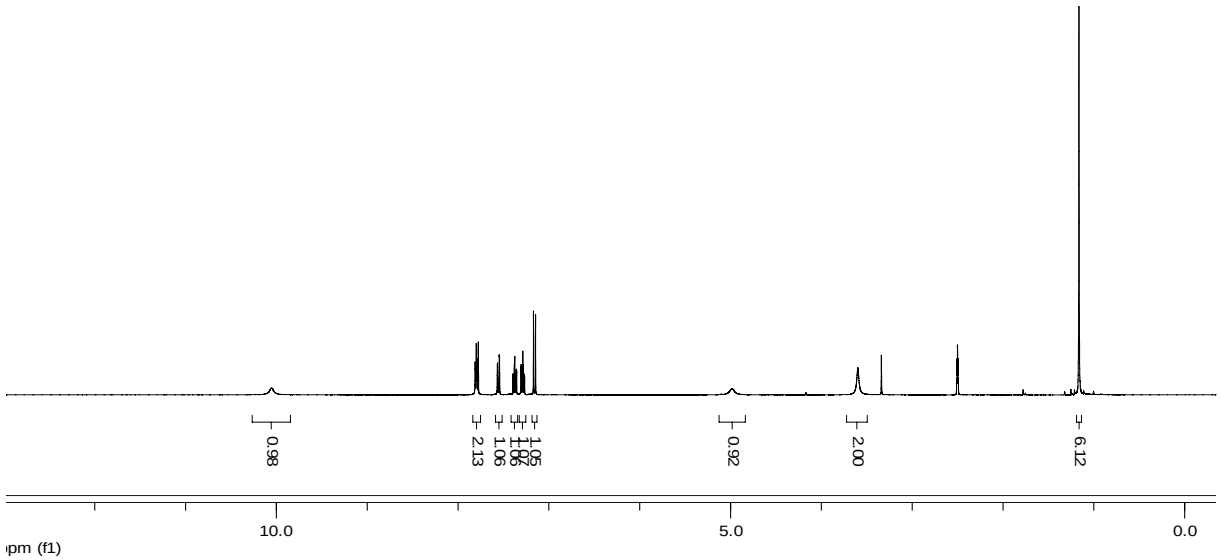
2-(2-hydroxy-6-methylbenzoyl)-2-methylpropan-1-ol (Table 2, entry 5)

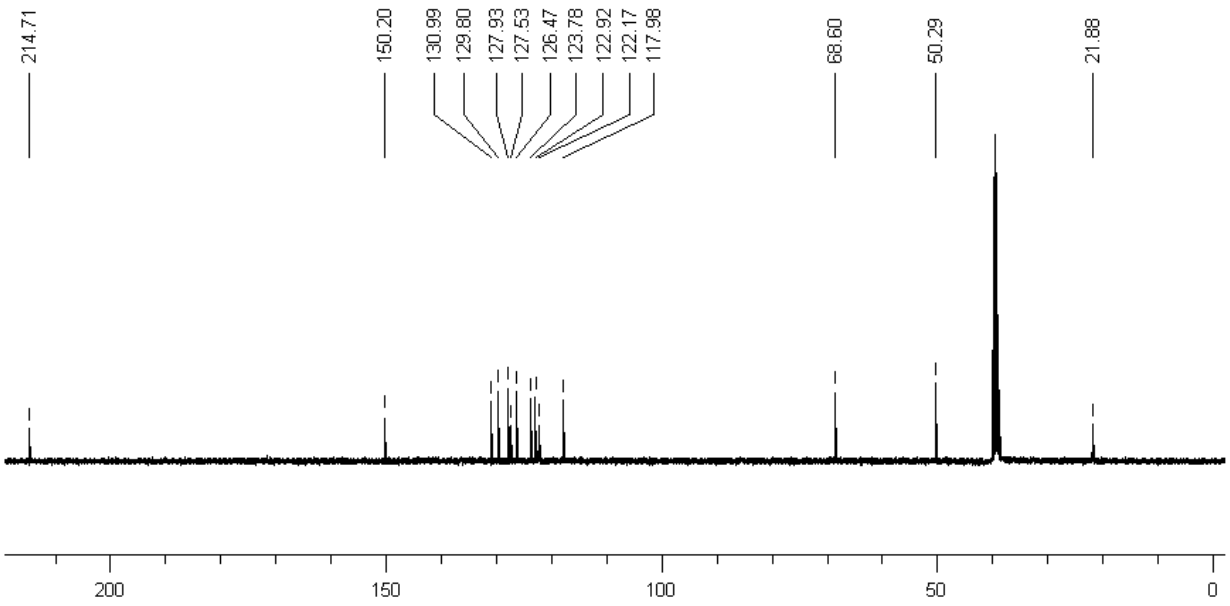




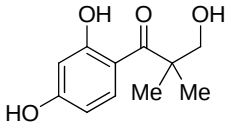
3-hydroxy-1-(2-hydroxynaphthalen-1-yl)-2,2-dimethylpropan-1-one (Table 2, entry 6)

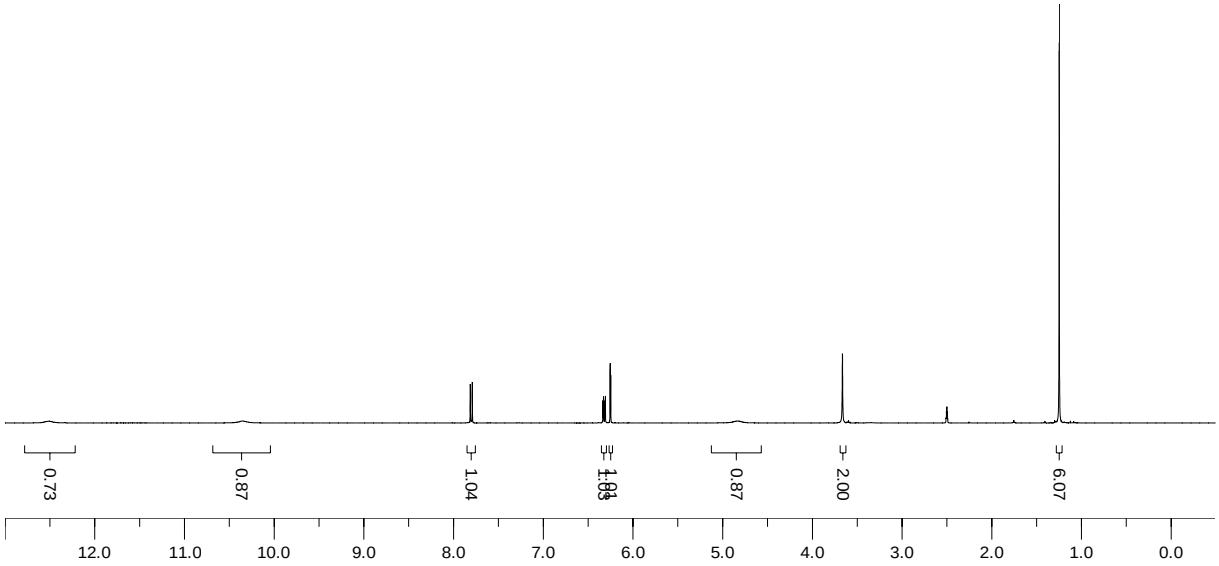


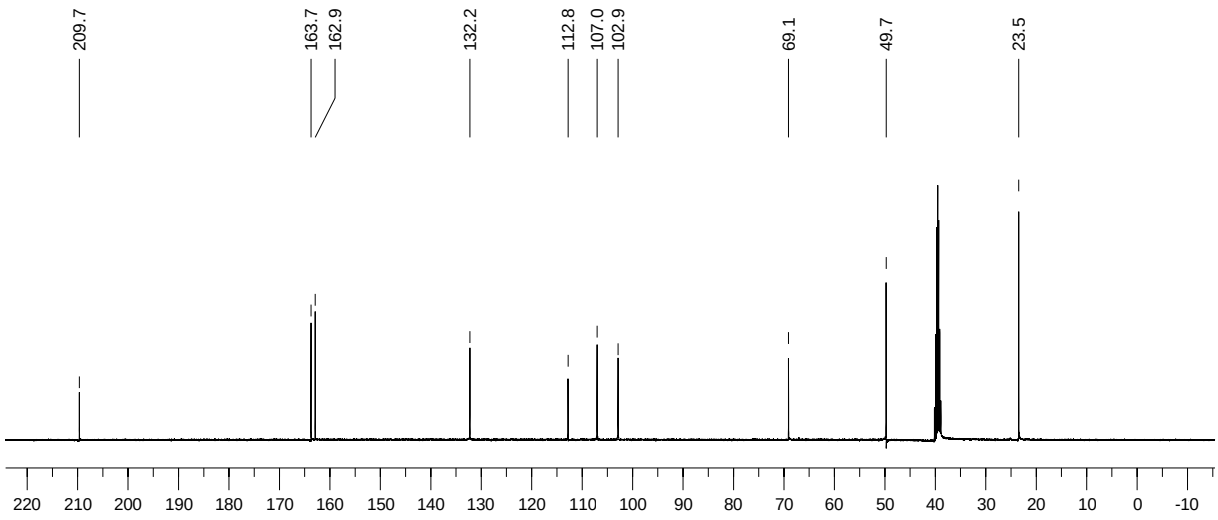




1-(2,4-dihydroxyphenyl)-3-hydroxy-2,2-dimethylpropan-1-one (Table 2, entry 7)







2-(2-hydroxybenzoyl)propene (5a):