

**Supporting Information**  
**for**  
**Mild and selective reduction of aldehydes utilising sodium**  
**dithionite under flow conditions**

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**Experimental part**

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## Experimental

### General methods

All solvents, chemicals, and reagents were obtained commercially and used without further purification.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) spectra were recorded on Bruker AVANCE-III-300 instrument using  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  as solvent.  $\text{CDCl}_3$  contained tetramethylsilane as an internal standard. Chemical shifts,  $\delta$ , are reported in parts per million (ppm), and splitting patterns are given as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Coupling constants,  $J$ , are expressed in hertz (Hz). In noted cases conversions were determined from NMR by comparison of integral areas of starting materials and products. Infrared spectra were run on a Bruker ALPHA Platinum ATR spectrometer. The absorptions are reported on the wavenumber ( $\text{cm}^{-1}$ ) scale, in the range 400–4000  $\text{cm}^{-1}$ . The retention factor ( $R_f$ ) values quoted are for thin-layer chromatography (TLC) on aluminium-backed Macherey-Nagel ALUGRAM Sil G/UV254 plates pre-coated with 0.25 mm silica gel 60, spots were visualised with UV light and basic  $\text{KMnO}_4$  spray reagent. Chromatographic separations were performed on Macherey-Nagel Silica gel 60 (particle size 0.063–0.200 mm). Yields refer to isolated pure products unless stated otherwise.

### General method for the reduction of aldehydes and ketones under traditional batch conditions

Benzaldehyde (1 g, 9.5 mmol, 1 equiv) was dissolved in 38 mL (1:1 IPA/  $\text{H}_2\text{O}$ ), (0.25 M). Sodium dithionite (7.5 g, 43 mmol, 4.5 equiv) and  $\text{NaHCO}_3$  (1.6 g, 19 mmol, 2 equiv) was dissolved in water (43 mL, [1 M]) and added to the aldehyde. The mixture was refluxed for 12 hours under argon. The solution was allowed to cool to room temperature and the products were extracted using  $\text{EtOAc}$  ( $3 \times 50$  mL). This was dried using  $\text{Na}_2\text{SO}_4$ , filtered and dried under vacuum with a yield of 0.95 g (92%). For entry 1.15 the compound was neutralized with 1 M HCl and extracted with  $\text{EtOAc}$  ( $3 \times 50$  mL) and washed with water ( $3 \times 50$  mL) the organic extracts were combined and dried using  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated *in vacuo* and the resulting residue purified using column chromatography. Unless specified a 3:1  $\text{EtOAc}$ /hexane eluent was used for chromatographic purification [1-3].

### General method for the reduction of aldehydes and ketones under flow conditions

A 0.165 M stock solution of aldehyde or ketone (1 equiv) was prepared by dissolution in (1:1:2 IPA/ $\text{H}_2\text{O}$ / $\text{NaHCO}_3$  [1 M]). A 0.75 M stock solution of sodium dithionite (4.5 equiv) was prepared by dissolution in (1:1:2 IPA/ $\text{H}_2\text{O}$ / $\text{NaHCO}_3$  [1 M]). The injection loops (10 mL) unless otherwise stated

were primed with the two stock solutions respectively. The solutions were then pumped continuously through a 2 mL mixing chip at ambient temperature followed by a 14 mL HT Teflon coil at 110 °C (aldehydes and ketones). Unless otherwise stated the flow rate was set to 0.25 mL·min<sup>-1</sup> (64 min residence) for aldehydes and 0.20 mL·min<sup>-1</sup> (80 min residence) for ketones. Product work-up and isolation was achieved using the approach described for the batch reductions.

#### Reduction of benzaldehyde in a sealed tube

#### General method for the selective reduction of aldehydes in the presence of ketones

A stock solution of 0.2 M concentration with respect to both the ketone and benzaldehyde was prepared by dissolution in (1:1:2 IPA/H<sub>2</sub>O/NaHCO<sub>3</sub> [1 M]). A stock solution of 0.9 M sodium dithionite (4.5 equiv) was prepared by dissolution in (1:1:2 IPA/H<sub>2</sub>O/NaHCO<sub>3</sub> [1 M]). The injection loops (10 mL) were primed with the two stock solutions respectively. The solutions were pumped continuously at a flow rate of 0.25 mL·min<sup>-1</sup> through a 2 mL mixing chip at ambient temperature followed by a 14 mL HT Teflon coil heated to 110 °C. Product isolation was not performed, and conversion was estimated from <sup>1</sup>H NMR

#### Method for scaled up reduction of benzaldehyde

A 0.165 M stock solution of benzaldehyde (A) (1 equiv) was prepared by dissolution in (1:1:2 IPA/H<sub>2</sub>O/NaHCO<sub>3</sub> [1 M]). A 0.5 M stock solution of sodium dithionite (B) (4.5 equiv) was prepared by dissolution in (1:1:2 IPA/H<sub>2</sub>O/NaHCO<sub>3</sub> [1 M]). The inlet bottles were charged with each stock solution A and B respectively. Pump A was set to 0.15 mL·min<sup>-1</sup> and pump B set to a flow rate of 0.3 mL·min<sup>-1</sup>. The solutions were pumped continuously through a T-piece at ambient temperature followed by a 29 mL coil (14 mL HT Teflon coil and 15 mL stainless steel coil) at 110 °C. The reaction was halted after 55 hours and 18 minutes. Thereafter, the flow reactor was washed with 1 M NaOH to remove any precipitate. The reaction mixture was extracted with EtOAc (5 × 100 mL). The organic extracts were combined and dried using Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the crude material obtained was purified by column chromatography 3:1 EtOAc/hexane eluent was used for chromatographic purification. to afford 6.99 g phenylmethanol in 79% yield.

**Phenylmethanol (1.1):** Colorless oil, batch yield 937 mg (92%); isolated flow yield 164 mg (92%). R<sub>f</sub> 0.78 (3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.48–7.18 (m, 5H), 4.65 (s, 2H), 2.33 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 140.80, 128.46, 127.53, 126.92, 65.12; IR ν<sub>max</sub>/cm<sup>-1</sup> 3311, 3030, 2871, 1493, 1451, 1204, 1078, 1010, 910, 734 and 693. In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR009403.PDF>.

**4-Methylbenzyl alcohol (1.2):** White solid, batch yield 82 mg (80%, reaction performed on 100 mg scale), isolated flow yield 163 mg (81%); mp 57 - 60°C; Rf 0.65 (3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.26 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 4.64 (s, 2H), 2.36 (s, 3H), 1.81 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 137.88, 137.35, 129.20, 127.08, 65.20, 21.13; IR ν<sub>max</sub>/cm<sup>-1</sup> 3345, 2917, 2856, 1675, 1608, 1573, 1513, 1443, 1412, 1343, 1280, 1207, 1177, 1115, 1010. In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR000756.PDF>.

**4-Methoxybenzyl alcohol (1.3):** Colorless oil, batch yield 907 mg (89%), isolated flow yield 166 mg (73%); Rf 0.56(3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.28 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 4.60 (m, 2H), 3.80 (s, 3H), 1.78 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.19, 133.14, 128.60, 113.94, 64.96, 55.29; IR ν<sub>max</sub>/cm<sup>-1</sup> 3423, 2936, 2837, 1608, 1509, 1460, 1299, 1240, 1171, 1028, 813 and 756. In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR001049.PDF>.

**3-Methoxybenzyl alcohol (1.4):** Colorless oil, batch yield 844 mg (83%), isolated flow yield 175 mg (77%); Rf 0.51(3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.27 (t, J = 8.1 Hz, 1H), 6.93 (d, J = 7.1 Hz, 2H), 6.84 (d, J = 9.0 Hz, 1H), 4.66 (s, 2H), 3.81 (s, 3H), 1.89 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.81, 142.52, 129.57, 119.07, 113.24, 112.22, 65.21, 55.17; IR ν<sub>max</sub>/cm<sup>-1</sup> 3333, 2937, 2837, 1592, 1487, 1258, 1153, 1033, 858, 779, 734 and 690. In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR010797.PDF>.

**4-Chlorobenzyl alcohol (1.5):** White solid, batch yield 995 mg (98%), isolated flow yield 0.165 mg (70%); mp 73-75°C; Rf 0.68 (3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.25 (m, 2H), 7.25 – 7.19 (m, 2H), 4.65 (s, 2H), 1.88 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.26, 133.35, 128.66, 128.24, 64.51; IR ν<sub>max</sub>/cm<sup>-1</sup> 3325, 2920, 2855, 1902, 1486, 1450, 1401, 1344, 1204, 1083, 1002, 828 and 647. In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR009685.PDF>.

**3-Bromobenzyl alcohol (1.6):** Colourless oil, batch yield 697 mg (69%), isolated flow yield (6 mL reaction loops) 150 mg (80%), Rf 0.79 (3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54 (s, 1H), 7.44 (dd, J = 7.5, 1.9 Hz, 1H), 7.26 (q, J = 7.5 Hz, 1H), 4.68 (s, 1H), 2.35 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 143.05, 130.63, 130.10, 129.86, 125.30, 122.63, 64.48; IR ν<sub>max</sub>/cm<sup>-1</sup> 3302, 2924, 2872, 1693, 1596, 1569, 1468, 1425, 1196, 1016, 881, 837, 774, 667. In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR002447.PDF>.

**2-Bromobenzyl alcohol (1.7):** White solid, batch yield 859 mg (85%), isolated flow yield 271 mg (88%); mp 75 - 76°C; Rf 0.84 (3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54 (d, J = 9.1 Hz,

1H), 7.48 (d,  $J$  = 6.0 Hz, 1H), 7.33 (dd,  $J$  = 7.5 Hz, 1H), 7.16 (dd,  $J$  = 7.7 Hz, 1H), 4.74 (s, 2H), 2.13 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.69, 132.57, 129.09, 128.87, 127.63, 122.54, 65.04; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3197, 2907, 2852, 1466, 1433, 1359, 1190, 1049, 1015, 741 and 660.

**Pyridin-3-ylmethanol (1.8):** Colorless oil, batch yield 937 mg (92%), isolated flow yield 144 mg (80%); Rf 0.10 (3:1 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 – 8.31 (m, 2H), 7.72 (d,  $J$  = 7.8 Hz, 1H), 7.26 (dd,  $J$  = 7.6 & 5.0 Hz, 1H), 4.68 (s, 2H), 4.40 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  147.90, 147.74, 137.15, 135.37, 123.64, 62.04; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3207, 2917, 2854, 1584, 1425, 1216, 1101, 1021, 788, 707, 635.

**Pyridin-3-ylmethanol (1.9):** White solid, batch yield 330 mg (79%), isolated flow yield (6 mL reaction loops) 108 mg (91%); mp 51 - 55°C, Rf 0.2 (3:1 EtOAc/Hexanes);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (d,  $J$  = 3.6 Hz, 2H), 7.29 (d,  $J$  = 4.9 Hz, 2H), 4.72 (s, 2H), 4.81 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.66, 148.98, 121.32, 62.72; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3116, 2904, 2855, 2818, 1603, 1561, 1455, 1414, 1296, 1225, 1094, 1053, 999, 795, 732.

**Heptanol (1.10):** Colorless oil, batch yield 657 mg (65%), isolated flow yield 136 mg (71%); Rf 0.62 (1:3 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.62 (t,  $J$  = 6.6 Hz, 2H), 1.65 – 1.48 (m, 3H), 1.38 – 1.21 (m, 8H), 0.93 – 0.81 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  63.01, 32.76, 31.79, 29.07, 25.67, 22.57, 14.03; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3320, 2924, 2857, 1460, 1376, 1054, 722. In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR010620.PDF>.

**Hexanol (1.11):** Colorless oil, batch yield 530 mg (52%), isolated flow yield 114 mg (68%); Rf 0.89 (3:1 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.63 (t,  $J$  = 6.6 Hz, 2H), 1.78 (s, 1H), 1.65 – 1.46 (m, 2H), 1.42 – 1.18 (m, 4H), 1.00 – 0.78 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  63.03, 32.73, 31.61, 25.39, 22.60, 13.99; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3340, 2926, 2860, 1460, 1377, 1187, 1050, 921 and 725. In agreement with Sigma Aldrich database

**1-(4-Chlorophenyl)ethanol (1.12):** Colorless oil, batch conversion 58%, flow conversion 11%; Rf 0.68 (3:1 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (s, 4H), 4.83 (q,  $J$  = 6.5 Hz, 1H), 2.47 (s, 1H), 1.44 (d,  $J$  = 6.5 Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  129.74, 128.89, 128.53, 126.81, 69.61, 25.24. IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3340 (C-OH); **4-chloroacetophenone:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.79 (m, 2H), 7.45 – 7.36 (m, 2H), 2.55 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.09, 144.36, 139.61, 135.36, 132.94, 26.54; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  1682(C=O). In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR001389.PDF>.

**1-(4-Methylphenyl)ethanol (1.13):** Colorless oil batch conversion 60% flow conversion 4%; Rf 0.66 (3:1 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (m, 4H), 4.85 (q,  $J$  = 6.4 Hz, 1H), 2.35 (s, 3H),

2.26 (s, 1H), 1.48 (d,  $J$  = 6.5 Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  129.26, 129.12, 128.47, 125.38, 70.14, 26.52, 25.13; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3336 (C-OH); **4-methylacetophenone**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J$  = 8.2 Hz, 1H), 7.15 (d,  $J$  = 7.9 Hz, 1H), 2.57 (s, 3H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.04, 143.93, 137.01, 134.72, 21.65, 21.11; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  1677 (C=O)

**1-(2-Hydroxyphenyl)ethanol (1.14)**: Colorless oil, batch conversion 50%, flow conversion <1%; Rf 0.37 (3:1 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 1H), 7.19 – 7.11 (m, 1H), 6.98 (dd,  $J$  = 7.4 & 1.5 Hz, 1H), 6.85 (dd,  $J$  = 7.8 & 2.4 Hz, 2H), 5.04 (q,  $J$  = 6.6 Hz, 1H), 3.30 (s, 1H), 1.56 (d,  $J$  = 6.6 Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.22, 128.77, 128.57, 126.41, 119.82, 116.90, 71.18, 23.32; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3390 (C-OH); **2-hydroxyacetophenone**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  12.26 (s, 1H), 7.71 (dd,  $J$  = 8.0, 1.6 Hz, 1H), 7.44 (ddd,  $J$  = 8.6, 7.4, 1.6 Hz, 1H), 6.95 (dd,  $J$  = 8.4, 0.8 Hz, 1H), 6.91 – 6.84 (m, 1H), 2.60 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  204.46, 162.23, 136.52, 130.72, 119.57, 118.97, 118.33, 26.48; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  1636 (C=O)

**Cyclohexanol (1.15)**: Colorless oil, batch conversion 84%, flow conversion 50%; Rf 0.46 (1:3 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.61 (dq,  $J$  = 13.1 & 4.3 Hz, 1H), 1.97 – 1.80 (m, 2H), 1.80 – 1.64 (m, 2H), 1.61 – 1.45 (m, 2H), 1.37 – 1.10 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  70.33, 35.53, 25.44, 24.11; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3326, 2926, 2853, 1449, 1359, 1293, 1260, 1230, 1137, 1065, 1025, 965, 888, 841, 786.

**3-Heptanol (1.16)**: Colorless oil, batch conversion 49%, flow conversion  $\leq$  1%; Rf 0.46 (1:3 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.52 – 3.40 (m, 1H), 1.76 (s, 1H) 1.46 – 1.33 (m, 4H), 1.33 – 1.24 (m, 4H), 0.88 (t,  $J$  = 7.5 Hz, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  73.09, 36.53, 30.02, 27.75, 22.66, 13.93, 9.74; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3490 (C-OH); **3-heptanone**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.50 – 2.21 (m, 4H), 1.50 (dt,  $J$  = 15.3 & 7.4 Hz, 2H), 1.37 – 1.09 (m, 2H), 0.99 (t,  $J$  = 7.3 Hz, 3H), 0.84 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  211.86, 42.00, 35.71, 25.92, 22.25, 13.71, 7.69; IR  $\nu_{\text{max}}/\text{cm}^{-1}$  1711 (C=O). In agreement with Sigma Aldrich database <https://www.sigmaaldrich.com/spectra/fnmr/FNMR000240.PDF>.

**1-Phenylethanol (1.17)**: Colorless oil, batch conversion 73%, flow conversion 29% (flow rate 0.2  $\text{ml} \cdot \text{min}^{-1}$ ) or 73% (flow rate 0.075  $\text{ml} \cdot \text{min}^{-1}$ ); Rf 0.80 (3:1 EtOAc/Hexanes);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.22 (m, 5H), 4.86 (q,  $J$  = 6.5 Hz, 1H), 1.48 (d,  $J$  = 6.5 Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  128.44, 128.30, 127.22, 125.28, 70.10, 25.04. IR  $\nu_{\text{max}}/\text{cm}^{-1}$  3372 (C-OH); **acetophenone**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.92 (m, 2H), 7.66 – 7.59 (m, 1H), 7.50 – 7.41 (m, 2H), 2.57 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.30, 145.80, 136.92, 133.03, 128.21, 77.43, 77.00, 76.58, 26.44. IR  $\nu_{\text{max}}/\text{cm}^{-1}$  1677

(C=O). In agreement with Sigma Aldrich database  
<https://www.sigmaaldrich.com/spectra/fnmr/FNMR011161.PDF>.

**methyl 3-(hydroxymethyl)benzoate (3.8):** Colourless oil, flow conversion 85 %; Rf 0.65 (3:1 EtOAc/Hexanes); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ7.99 (s, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 4.80 (s, 2H), 2.64 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ198.15, 141.38, 137.39, 131.57, 128.85, 127.62, 126.63, 77.45, 77.02, 76.60, 64.82, 26.72; IR ν<sub>max</sub>/cm<sup>-1</sup> 3392 (C-OH), 1675 (C=O)

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$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of reduced aldehydes:

Phenylmethanol

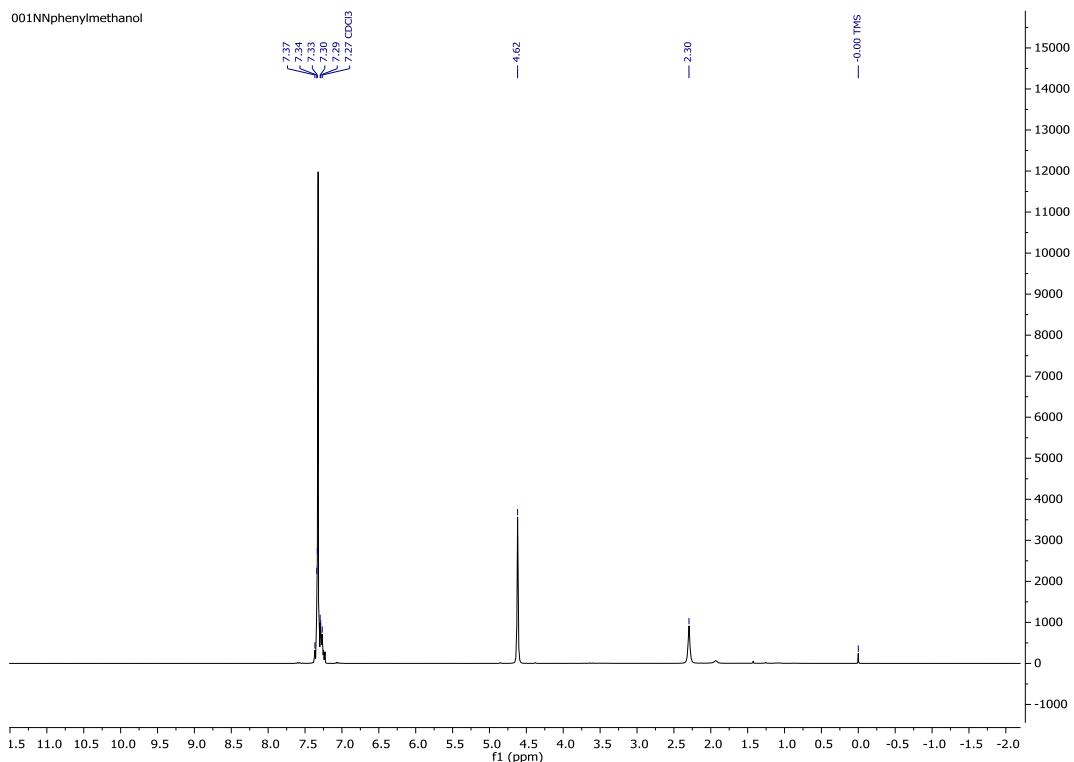


Figure S1:  $^1\text{H}$  NMR spectrum of phenylmethanol.

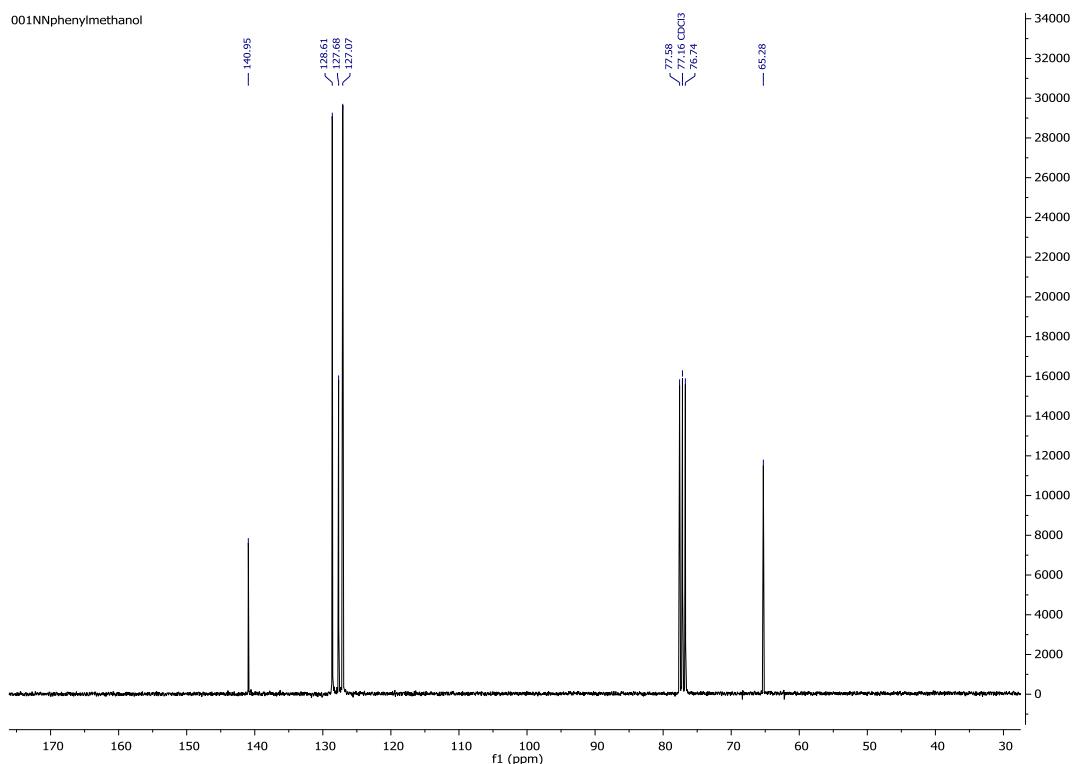


Figure S2:  $^{13}\text{C}$  NMR spectrum of phenylmethanol.

(4-Methylphenyl)methanol

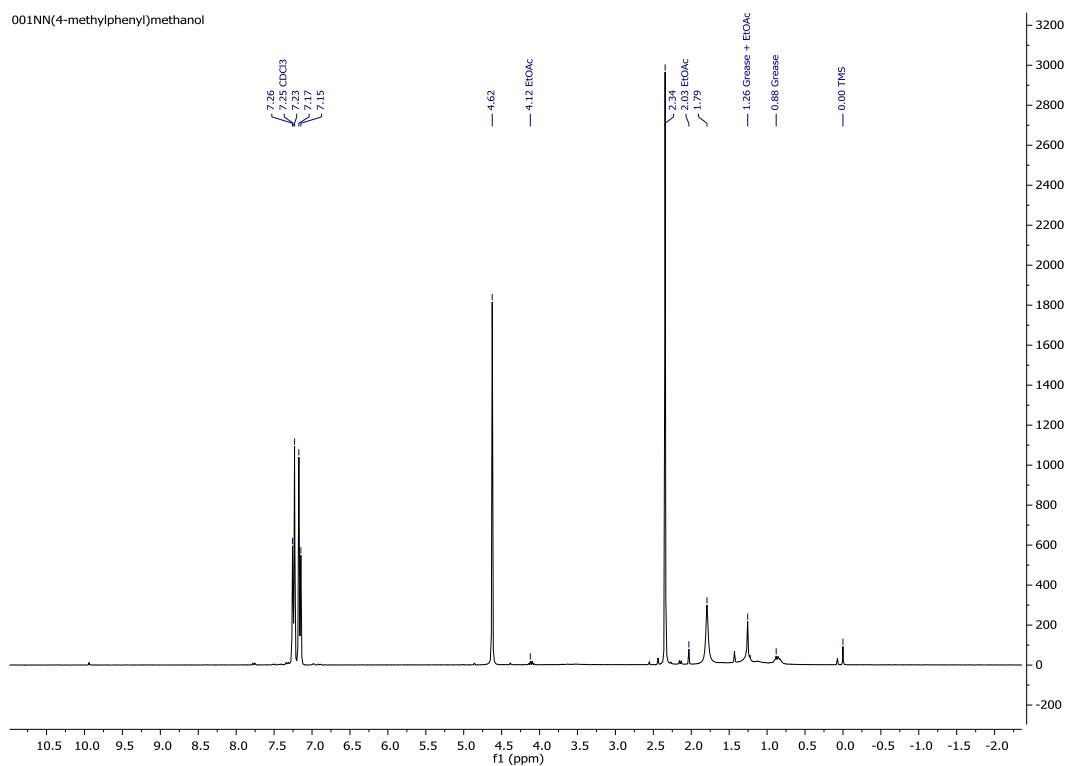


Figure S3:  $^1\text{H}$  NMR spectrum of (4-methylphenyl)methanol.

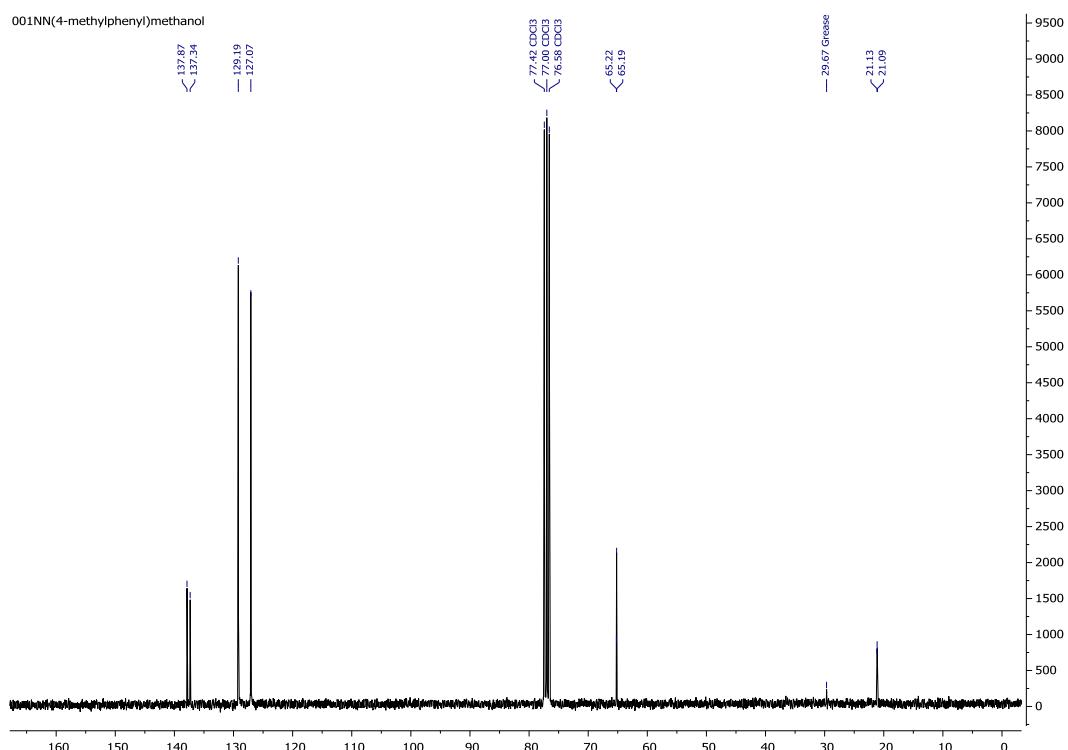


Figure S4:  $^{13}\text{C}$  NMR spectrum of (4-methylphenyl)methanol.

(4-Methoxyphenyl)methanol

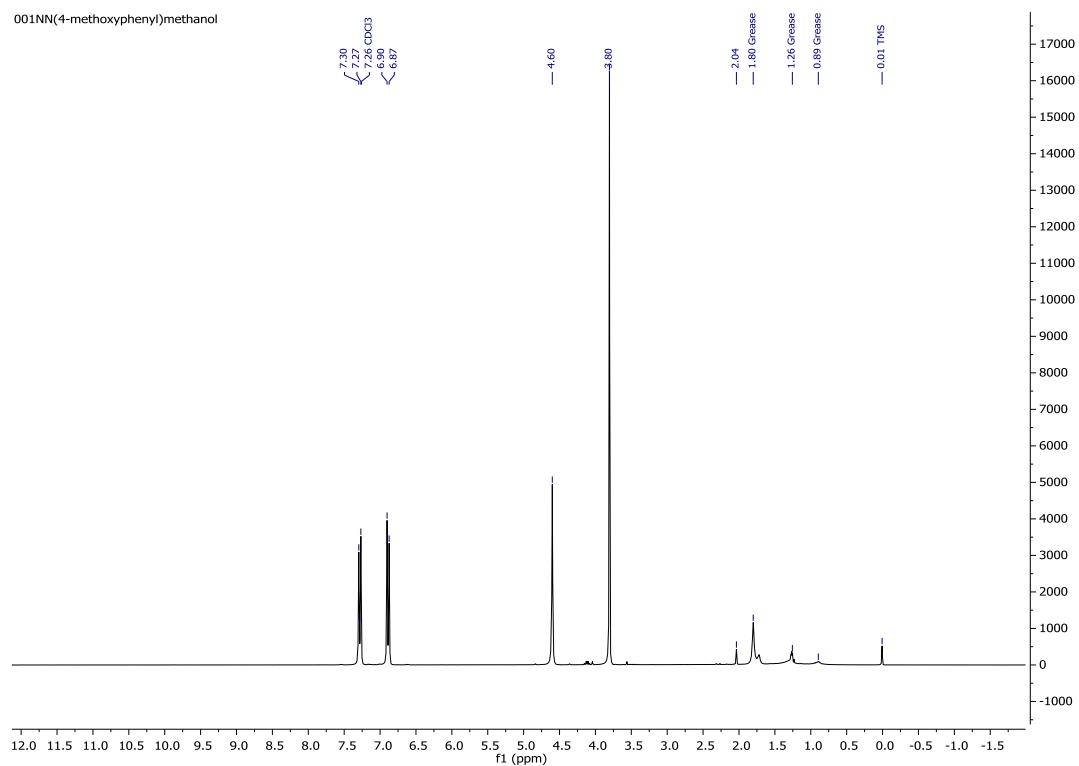


Figure S5: <sup>1</sup>H NMR spectrum of (4-methoxyphenyl)methanol.

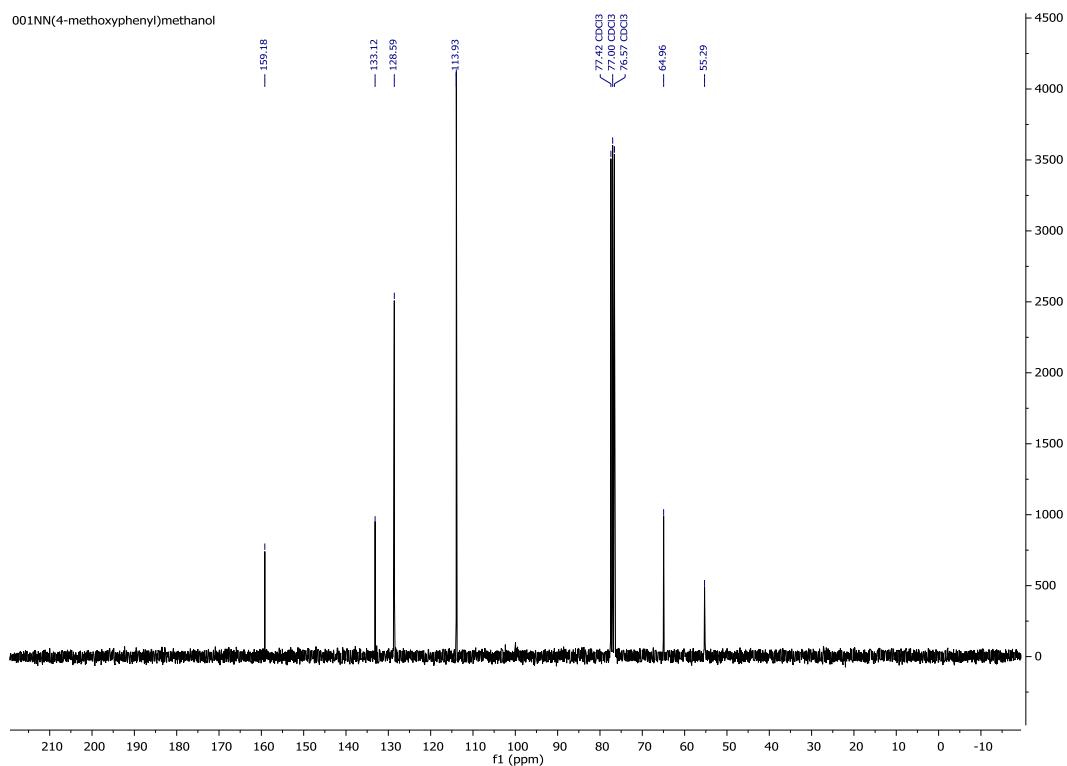


Figure S4: <sup>13</sup>C NMR spectrum of (4-methoxyphenyl)methanol.

### (3-Methoxyphenyl)methanol

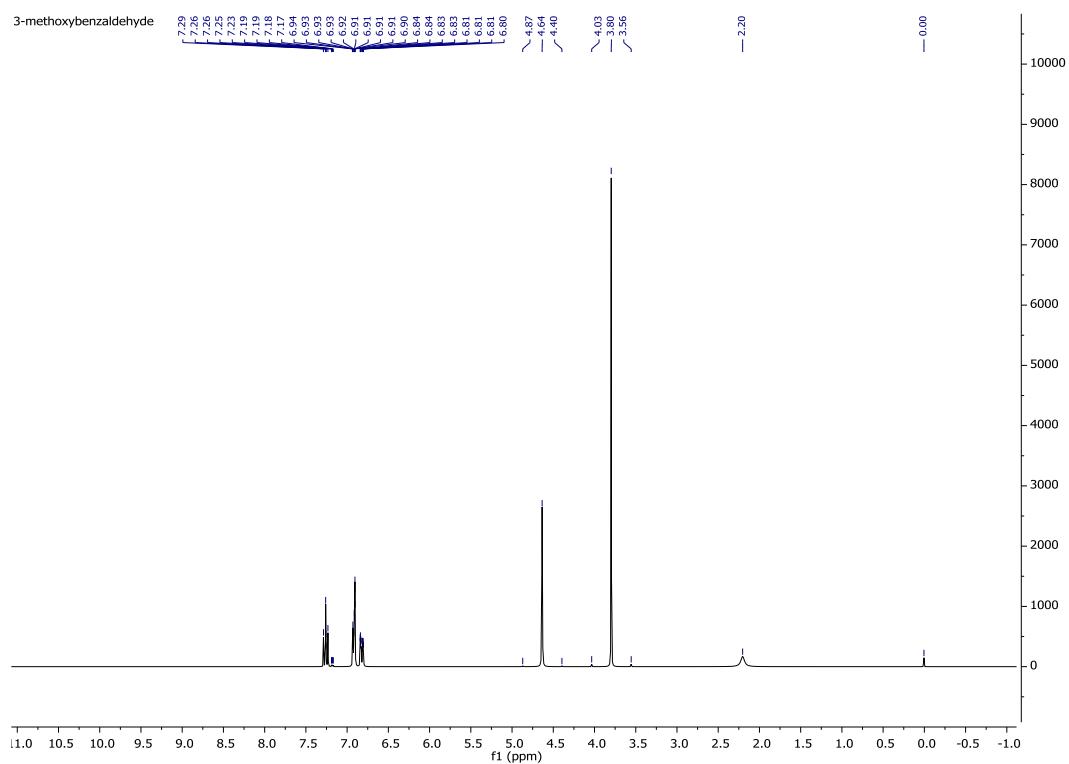


Figure S5:  $^1\text{H}$  NMR spectrum of (3-methoxyphenyl)methanol.

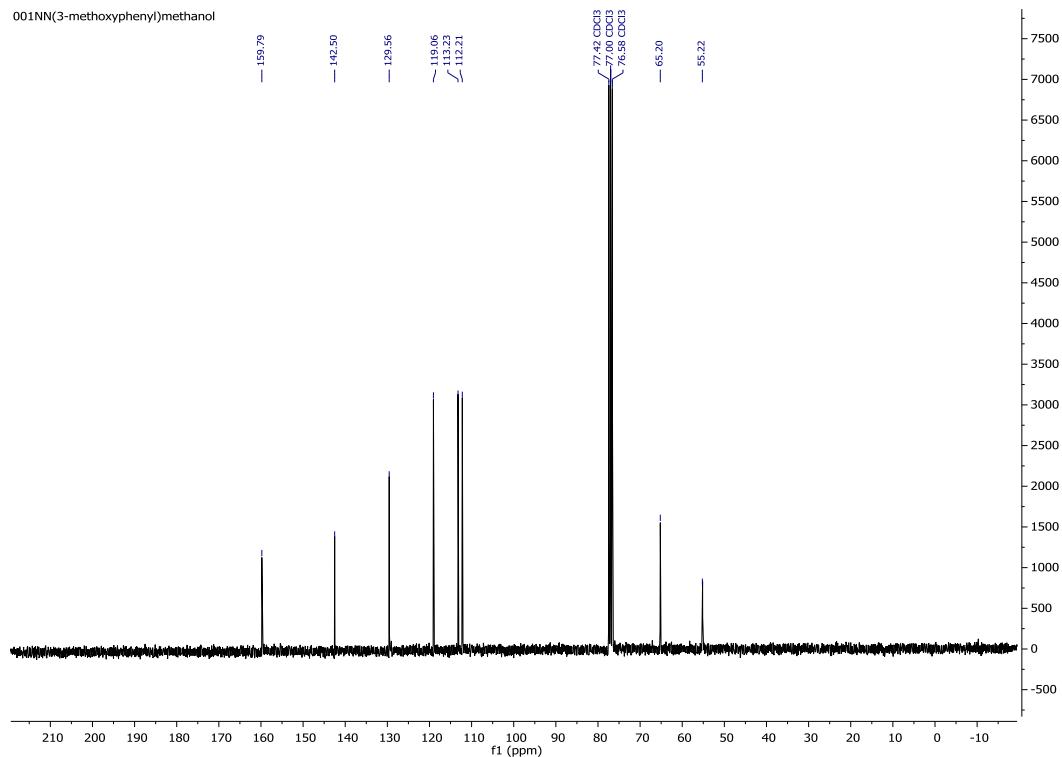


Figure S6:  $^{13}\text{C}$  NMR spectrum of (3-methoxyphenyl)methanol.

(4-Chlorophenyl)methanol

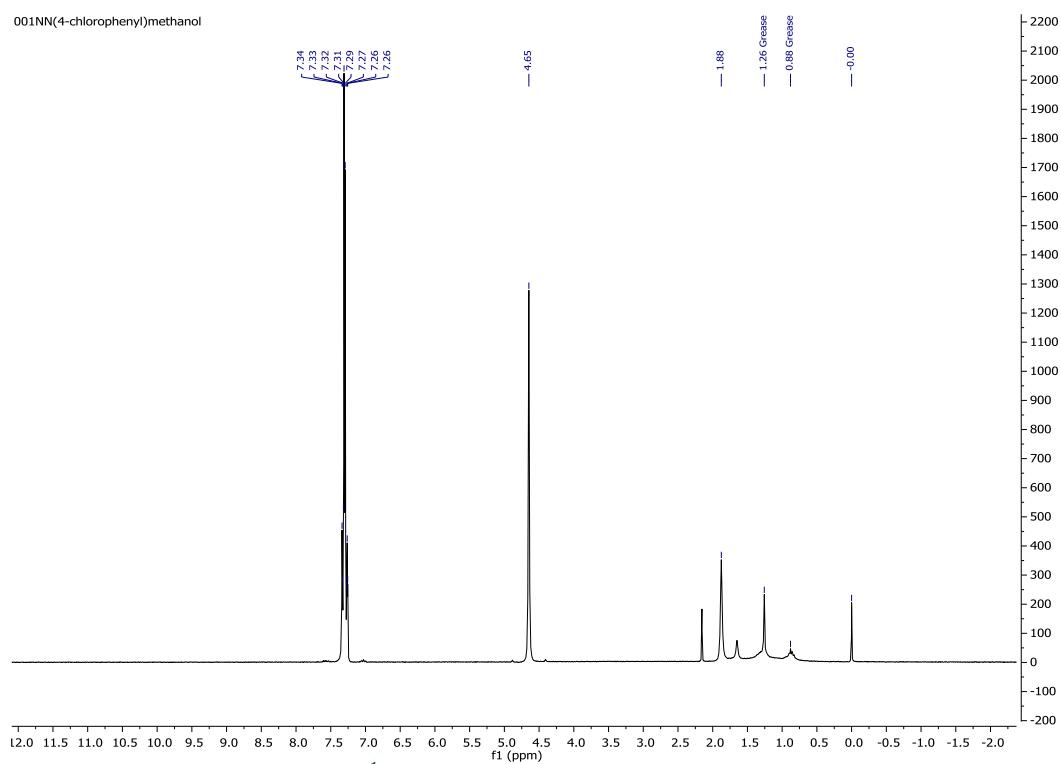


Figure S7:  $^1\text{H}$  NMR spectrum of (4-chlorophenyl)methanol.

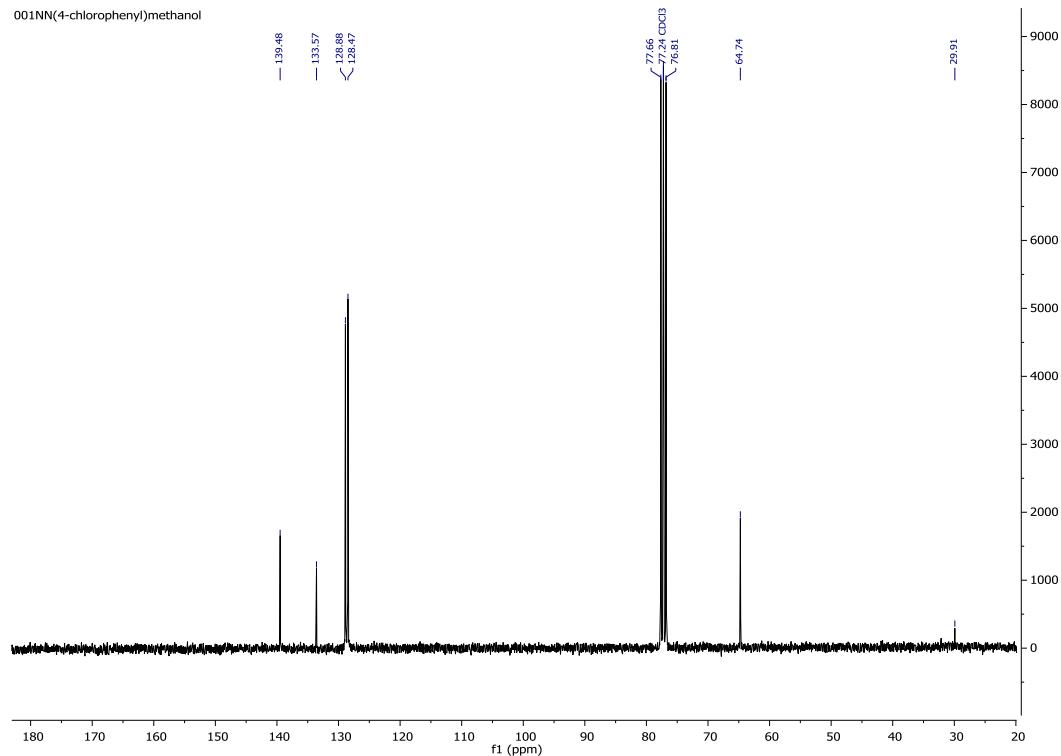


Figure S8:  $^{13}\text{C}$  NMR spectrum of (4-chlorophenyl)methanol.

(3-Bromophenyl)methanol

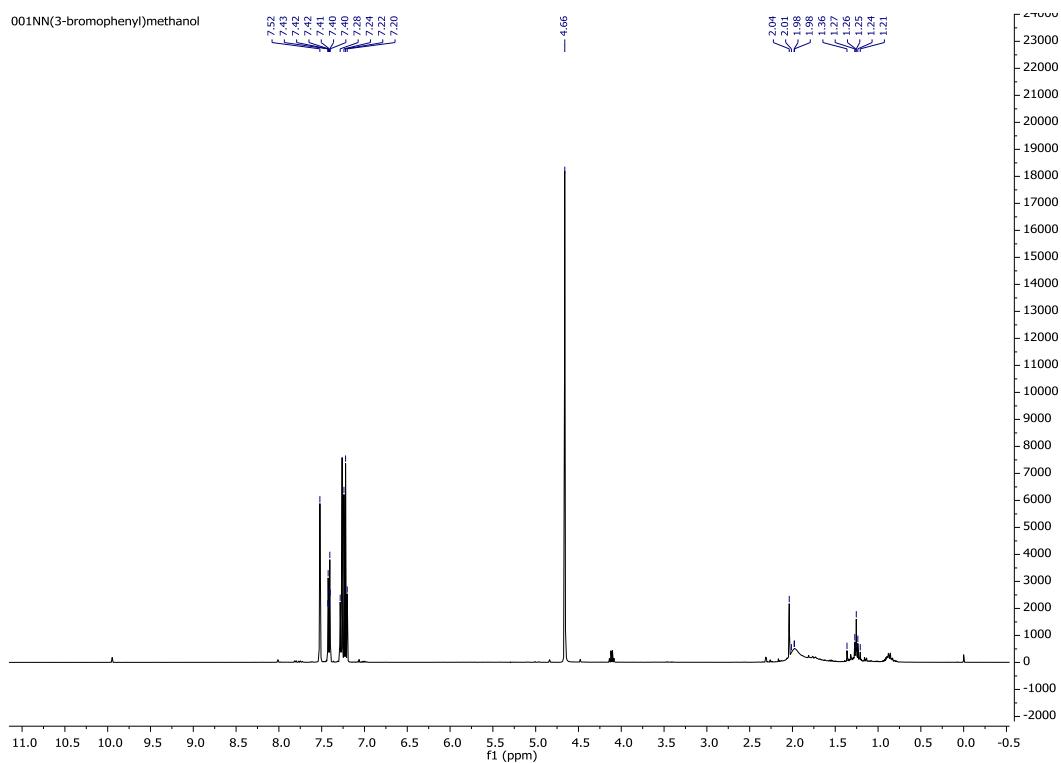


Figure S9:  $^1\text{H}$  NMR spectrum of (3-bromophenyl)methanol.

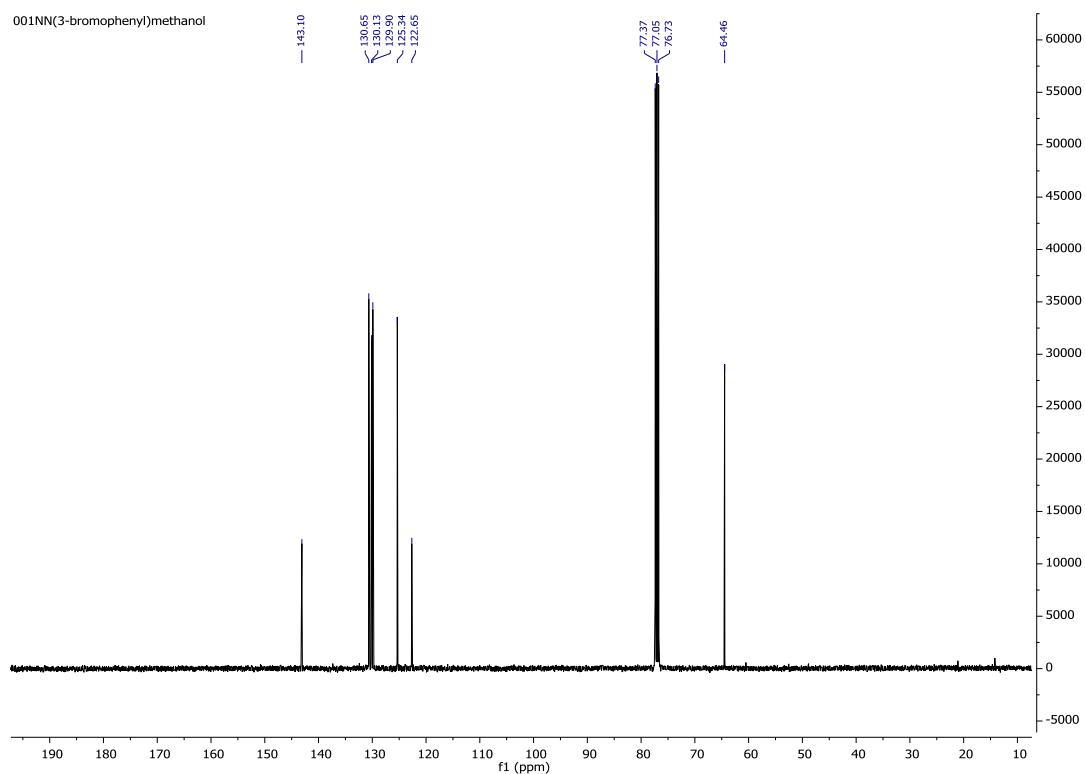


Figure S10:  $^{13}\text{C}$  NMR spectrum of (3-bromophenyl)methanol.

(2-Bromophenyl)methanol

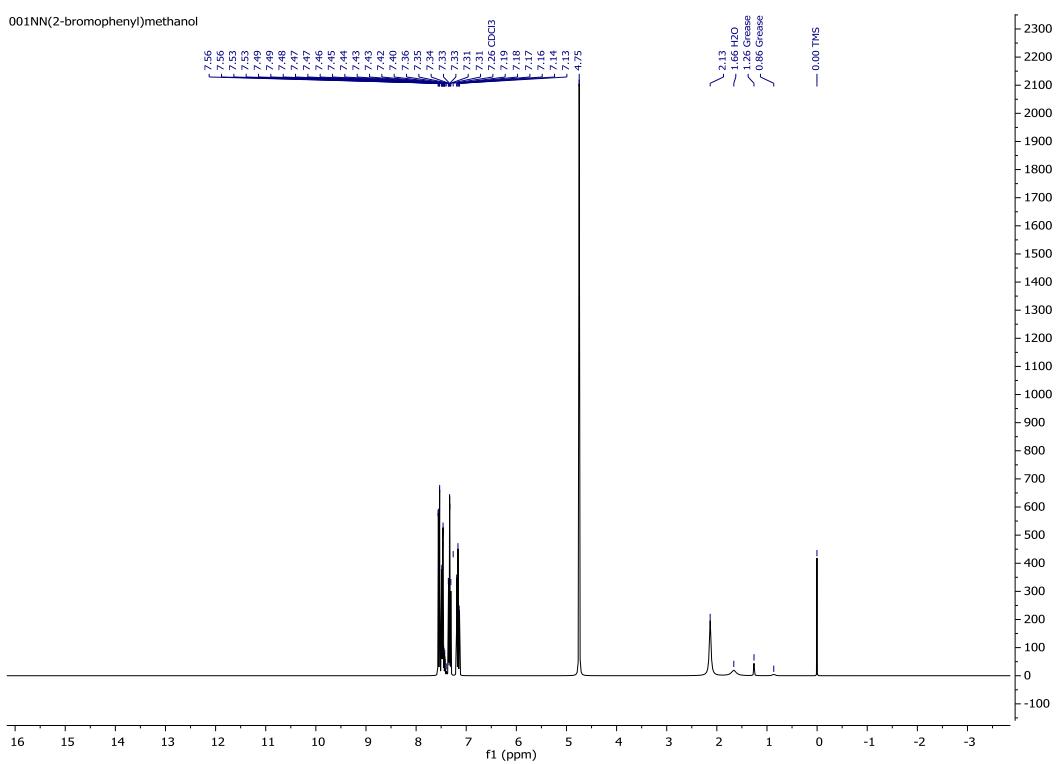


Figure S12:  $^1\text{H}$  NMR spectrum of (2-bromophenyl)methanol.

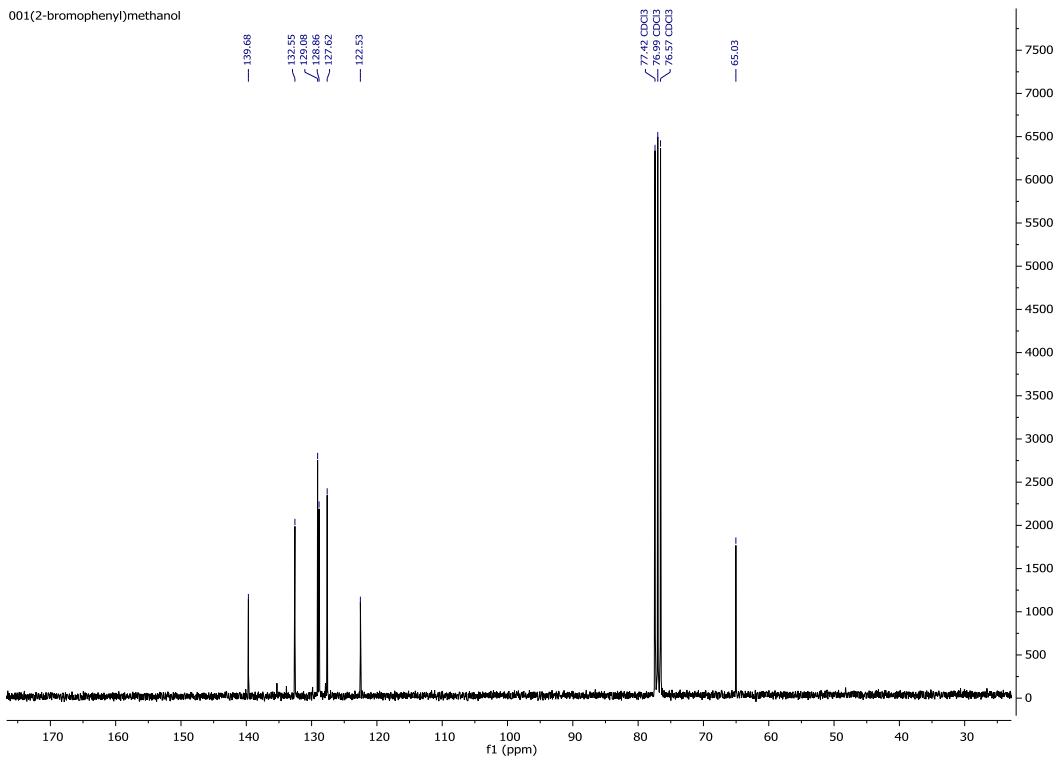


Figure S11:  $^{13}\text{C}$  NMR spectrum of (2-bromophenyl)methanol.

Pyridin-3-ylmethanol

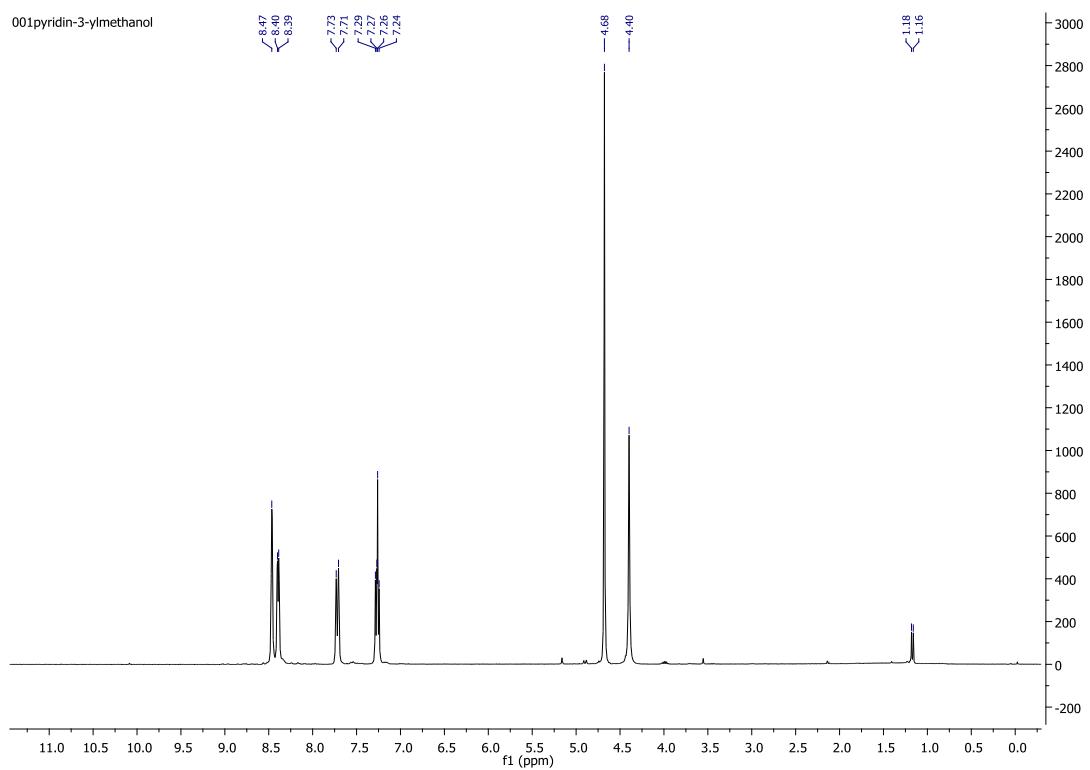


Figure S13:  $^1\text{H}$  NMR spectrum of pyridin-3-ylmethanol.

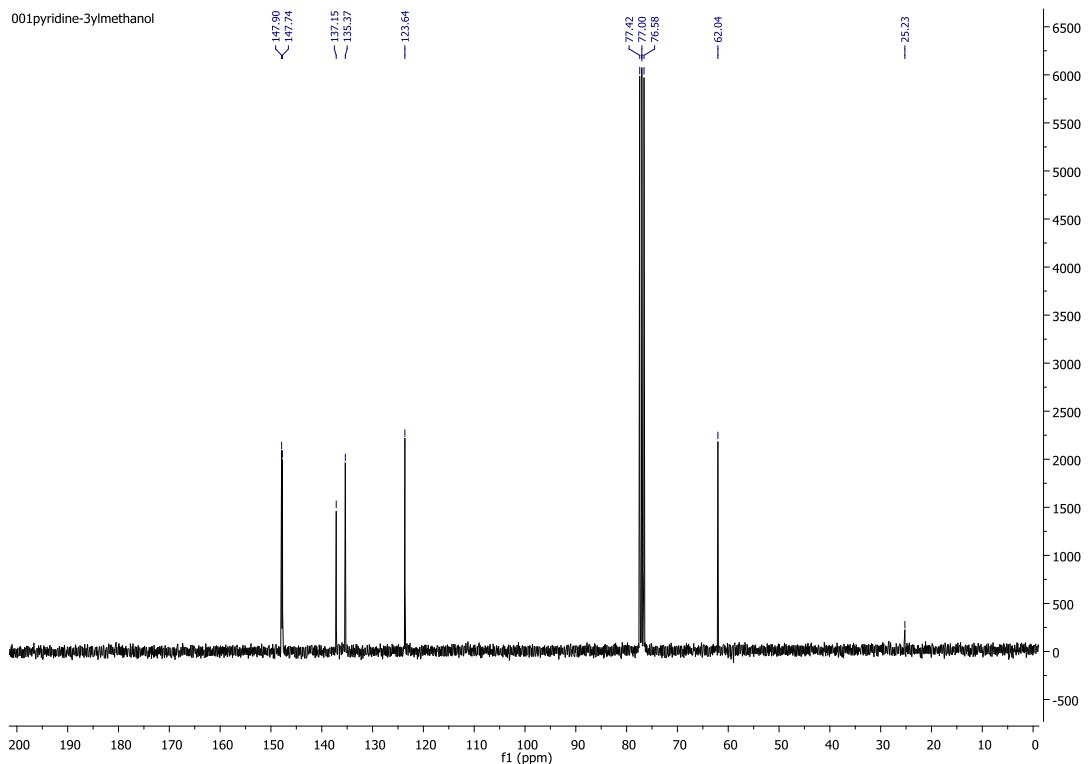
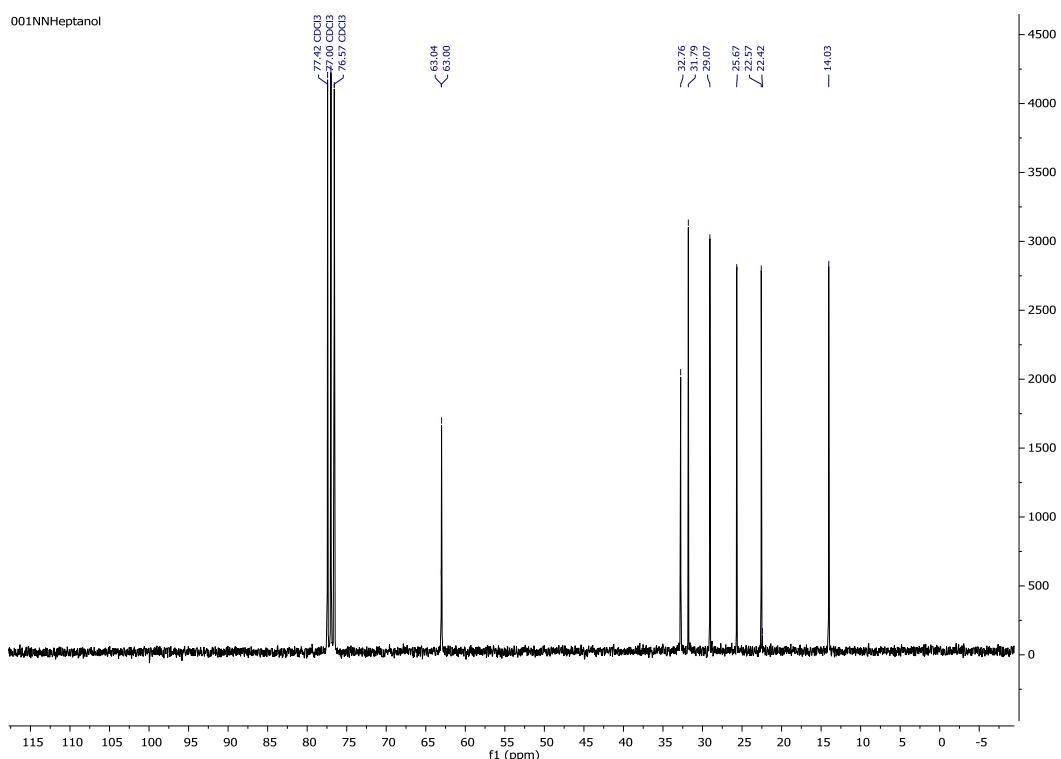
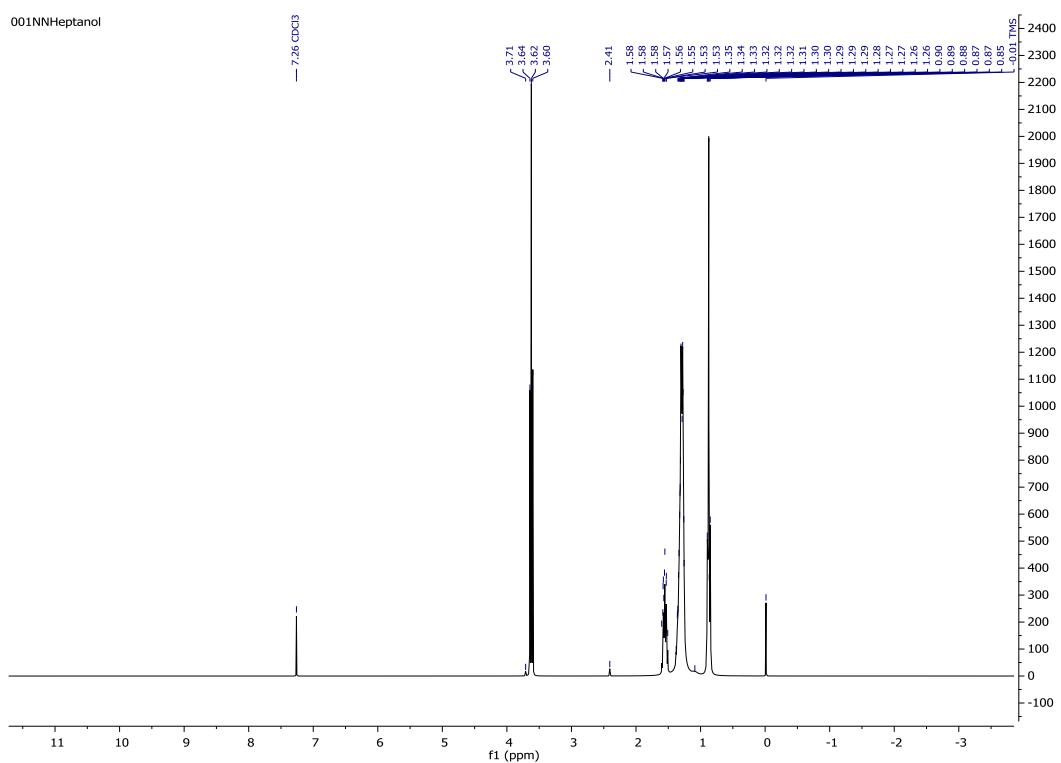


Figure S14:  $^{13}\text{C}$  NMR spectrum of pyridine-3-ylmethanol.

## Heptanol



## Hexanol

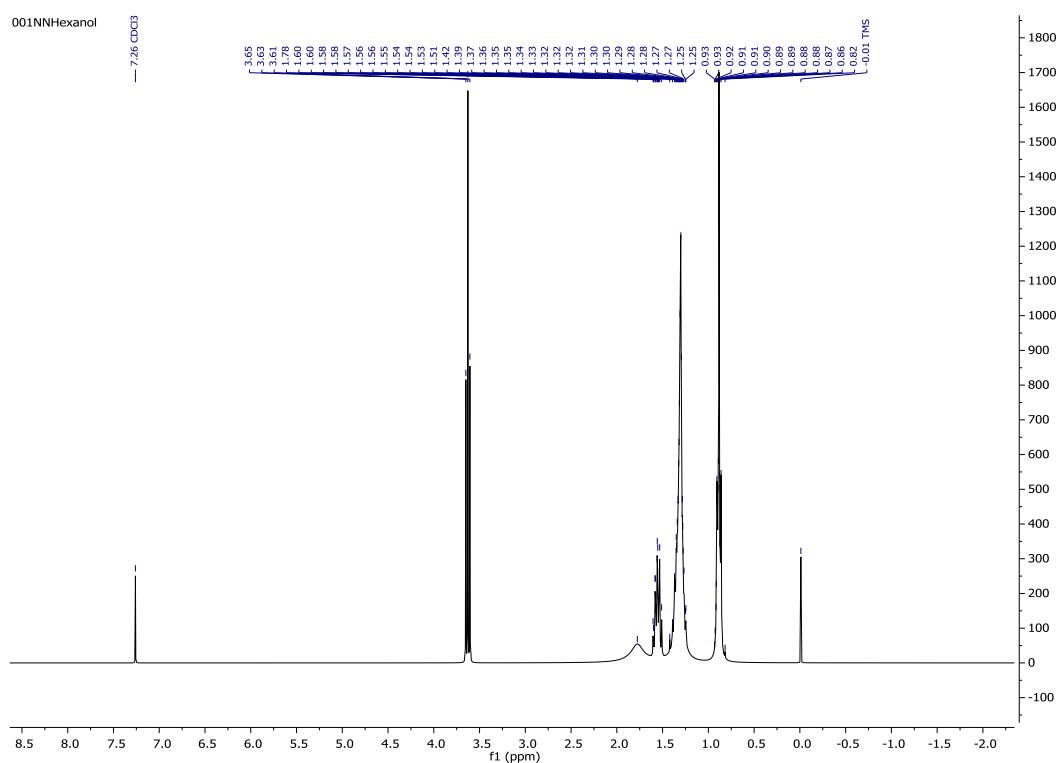


Figure S18:  $^1\text{H}$  NMR spectrum of hexanol.

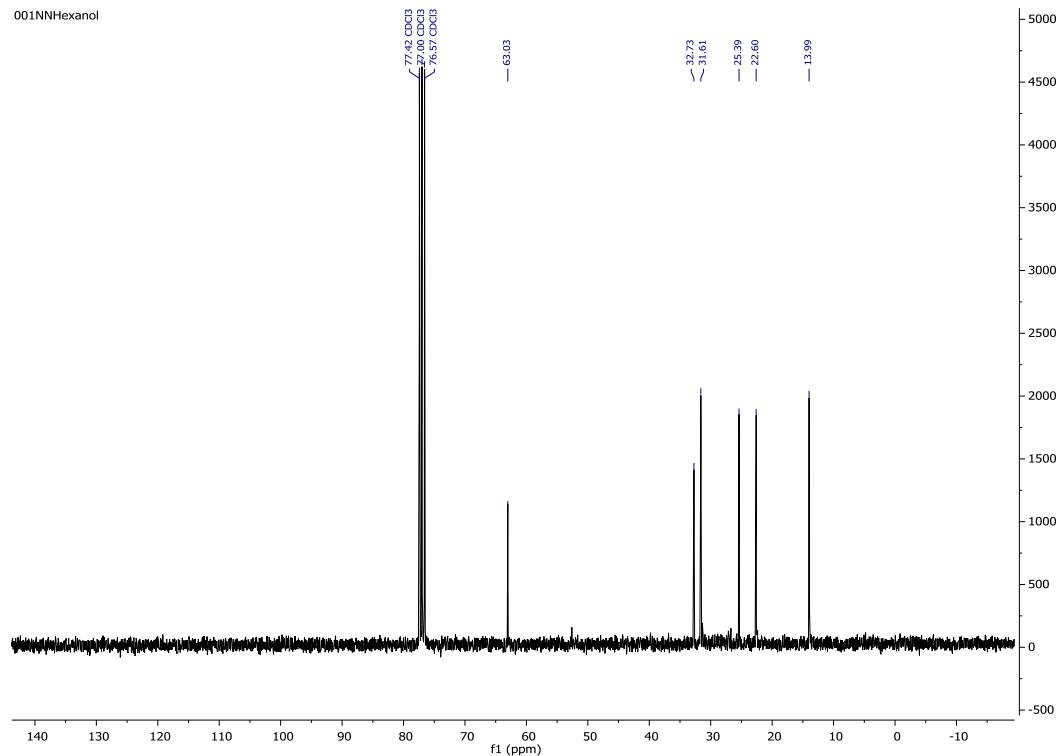


Figure S17:  $^{13}\text{C}$  NMR spectrum of heptanol.

<sup>1</sup>H and <sup>13</sup>C NMR for reduced ketones in batch:

### 1-(4-Chlorophenyl)ethanol and 4-chloroacetophenone mixture

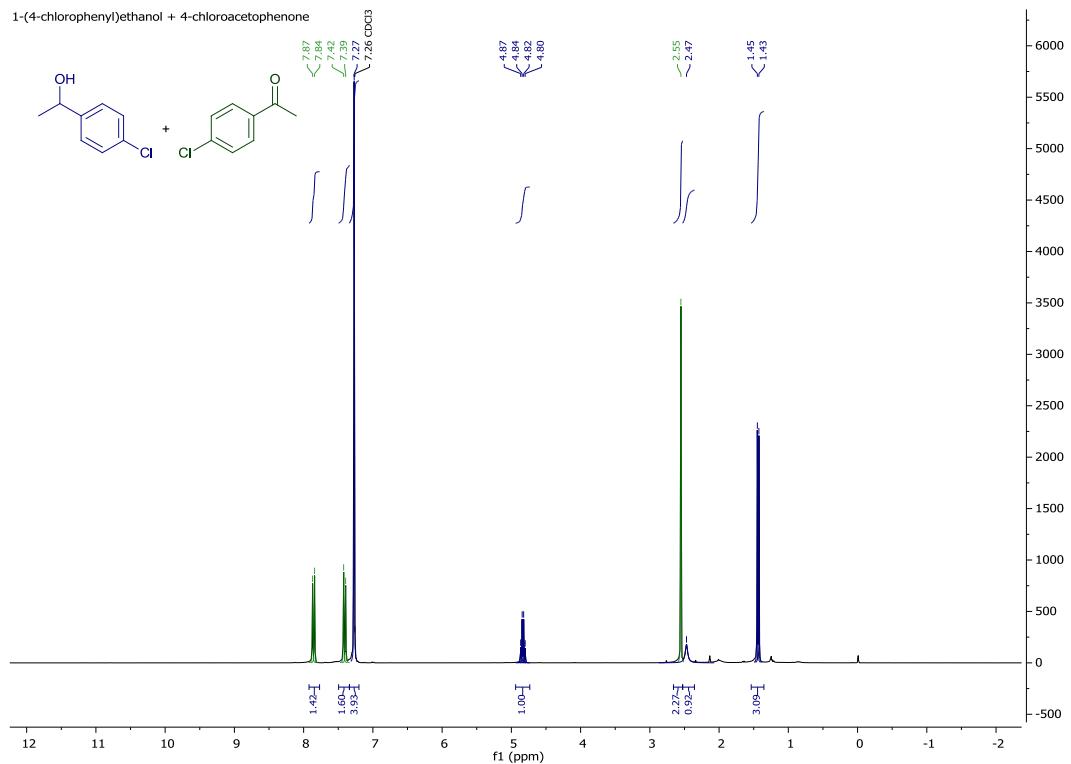


Figure S19: <sup>1</sup>H NMR spectrum of 1-(4-chlorophenyl)ethanol and 4-chloroacetophenone.

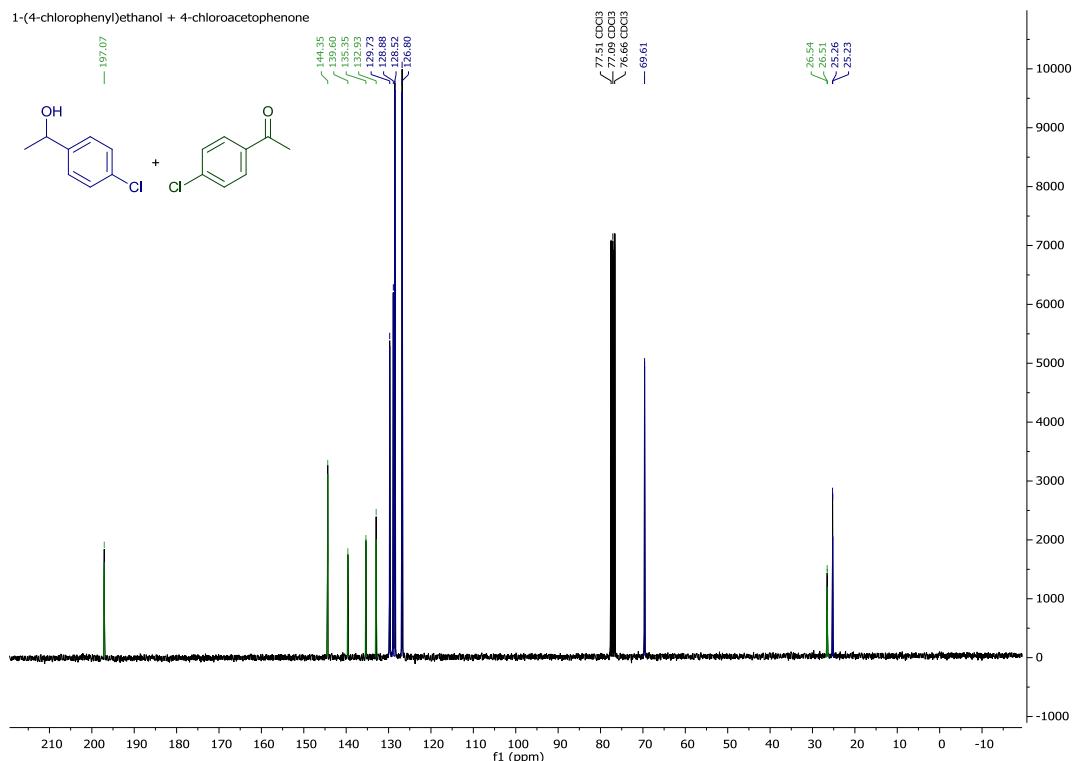


Figure S20: <sup>13</sup>C NMR spectrum of 1-(4-chlorophenyl)ethanol and 4-chloroacetophenone.

### 1-(*p*-Tolylethanol) and 4-methylacetophenone mixture

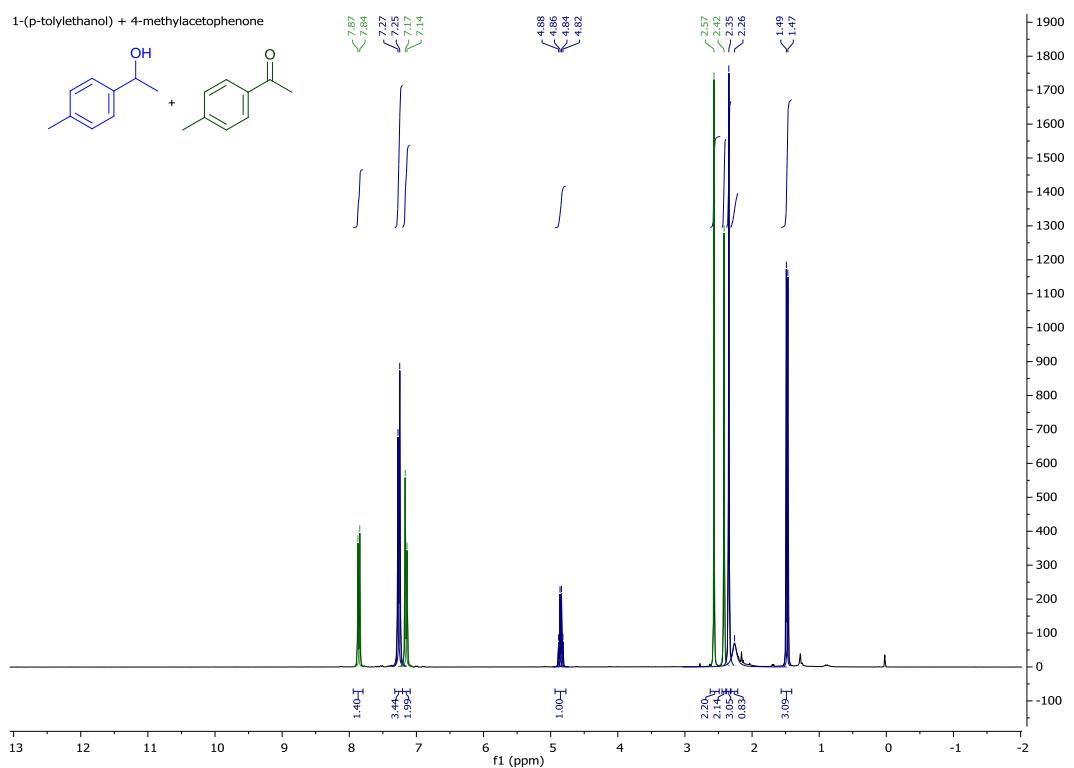


Figure S22:  $^1\text{H}$  NMR spectrum of 1-(4-methylphenyl) ethanol and 4-methylacetophenone.

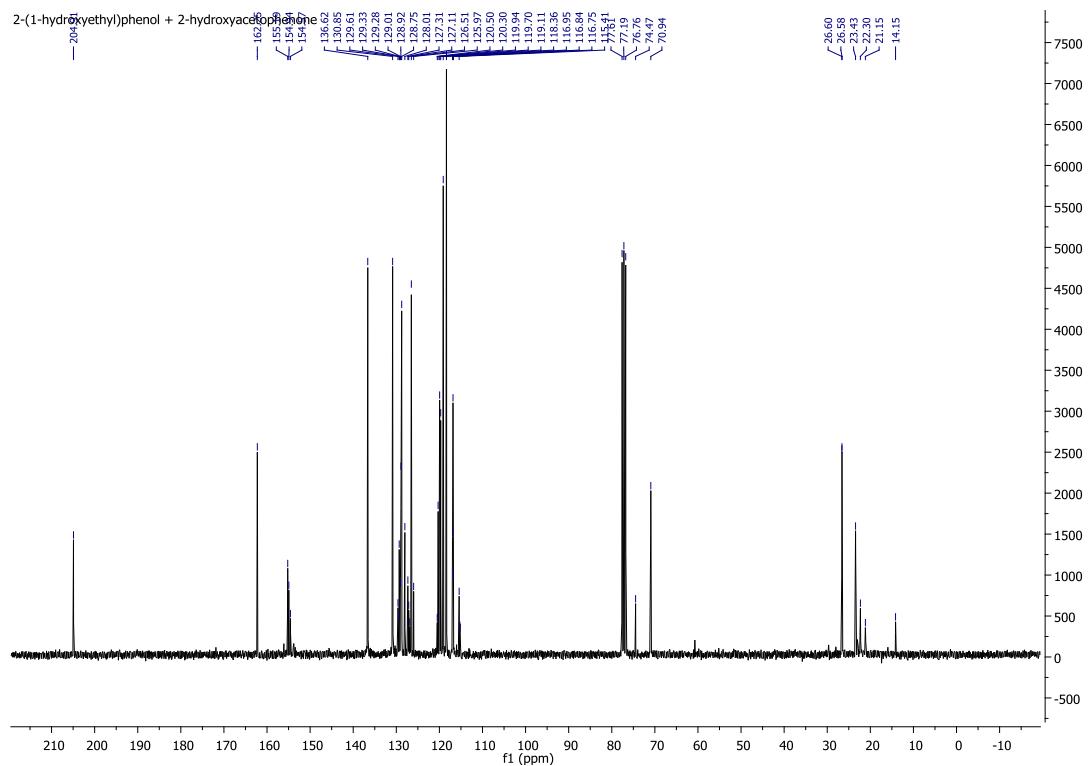


Figure S21:  $^{13}\text{C}$  NMR spectrum of 1-(4-methylphenyl) ethanol and 4-methylacetophenone

## 2-(1-Hydroxyethyl)phenol and 2-hydroxyacetophenone mixture

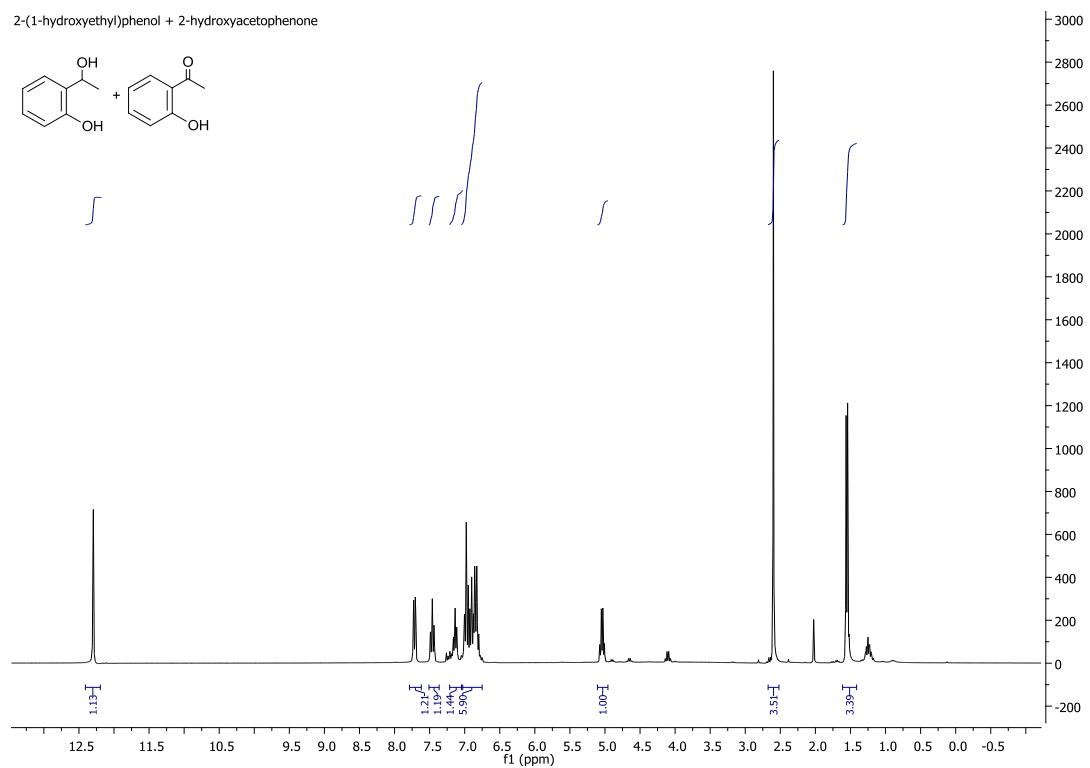


Figure S23:  $^1\text{H}$  NMR spectrum of 1-(2-hydroxyphenyl)ethanol and 2-hydroxyacetophenone.

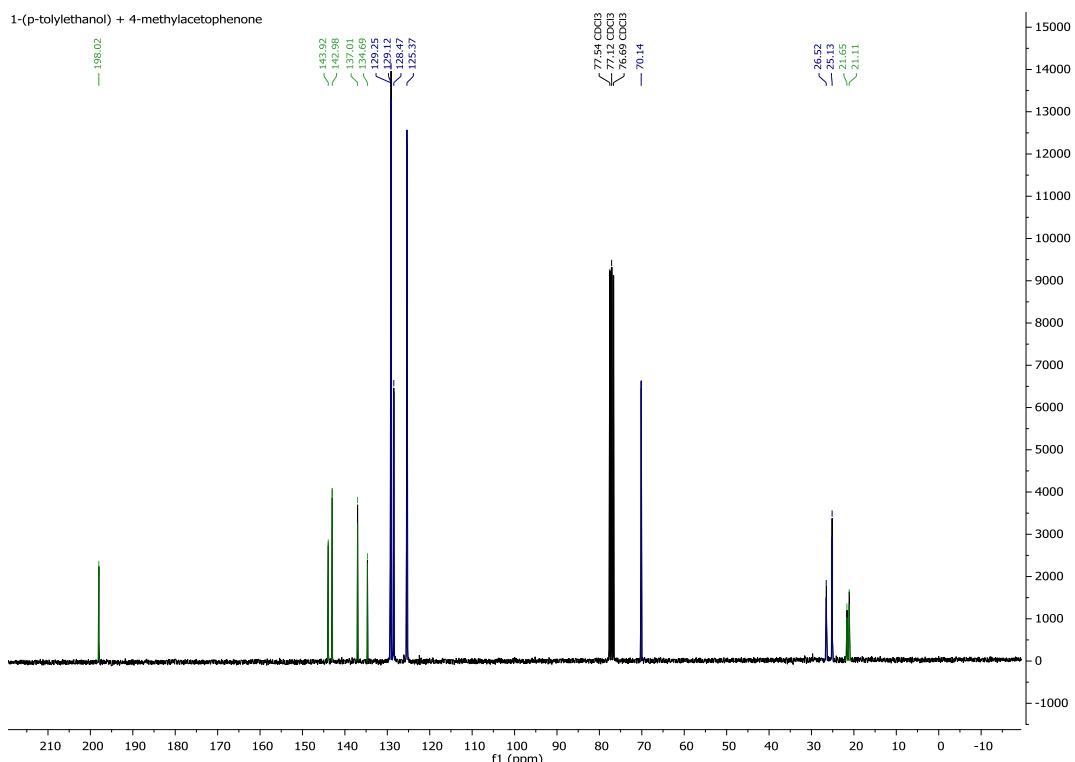


Figure S24:  $^{13}\text{C}$  NMR spectrum of 1-(2-hydroxyphenyl)ethanol and 2-hydroxyacetophenone.

## Cyclohexanol

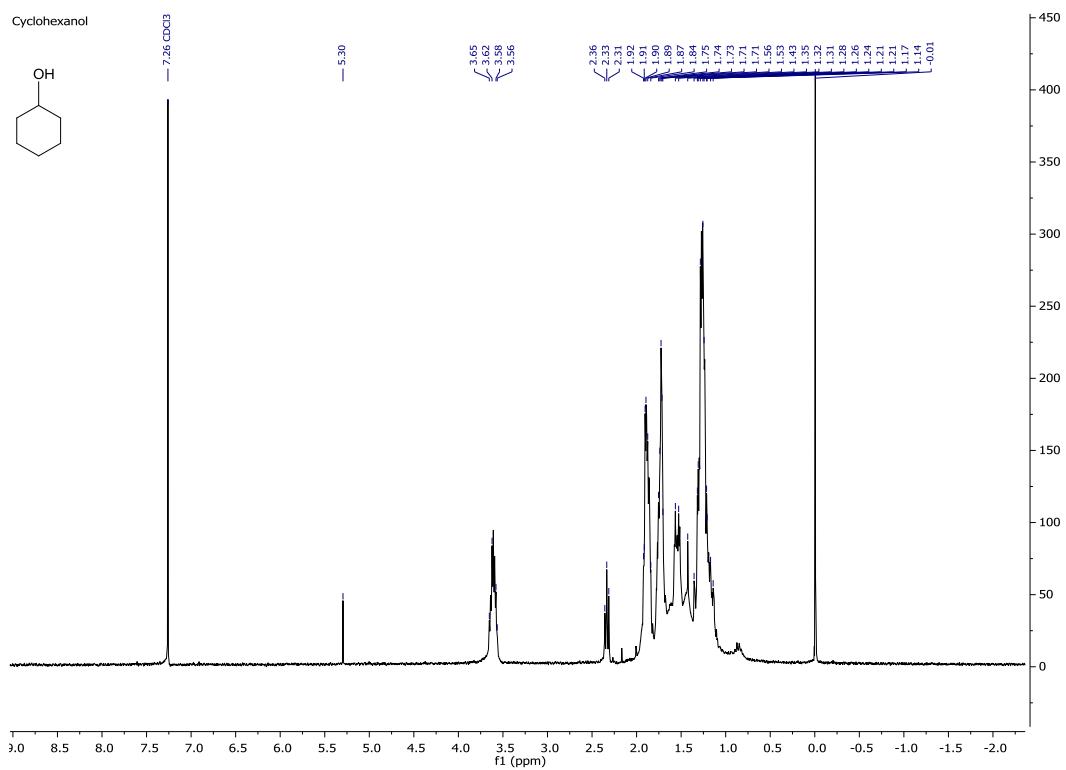


Figure S26:  $^1\text{H}$  NMR spectrum of cyclohexanol.

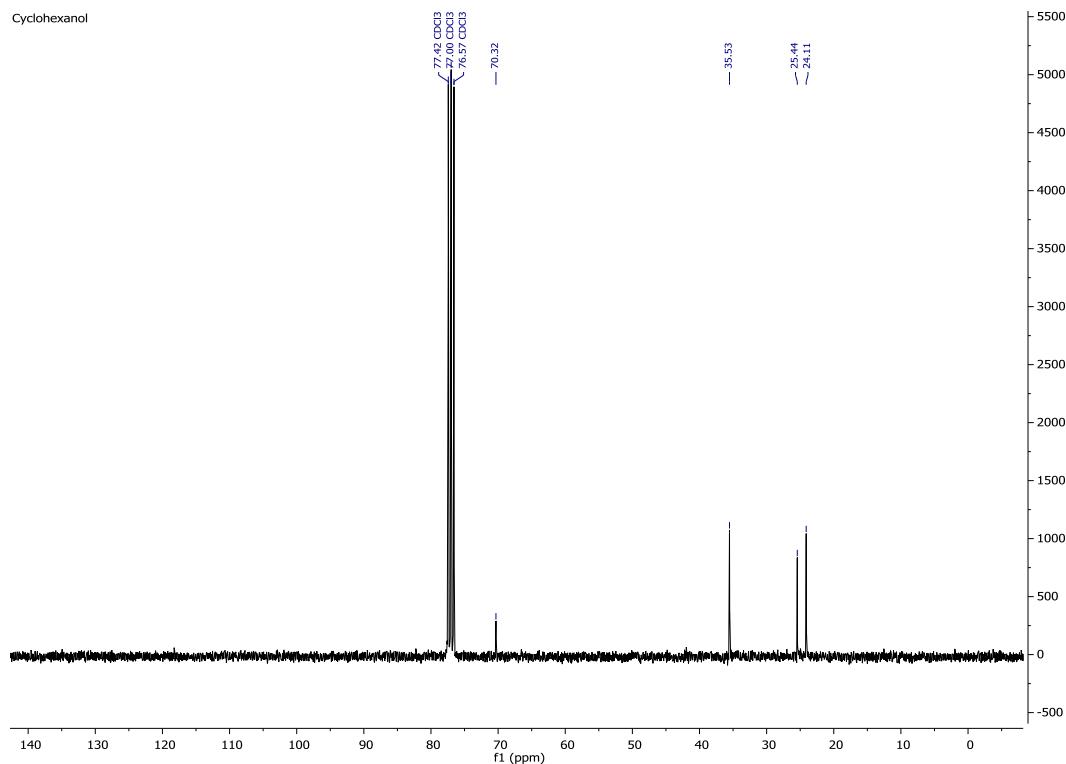


Figure S25:  $^{13}\text{C}$  NMR spectrum of cyclohexanol.

### 3-Heptanol and 3-heptanone mixture

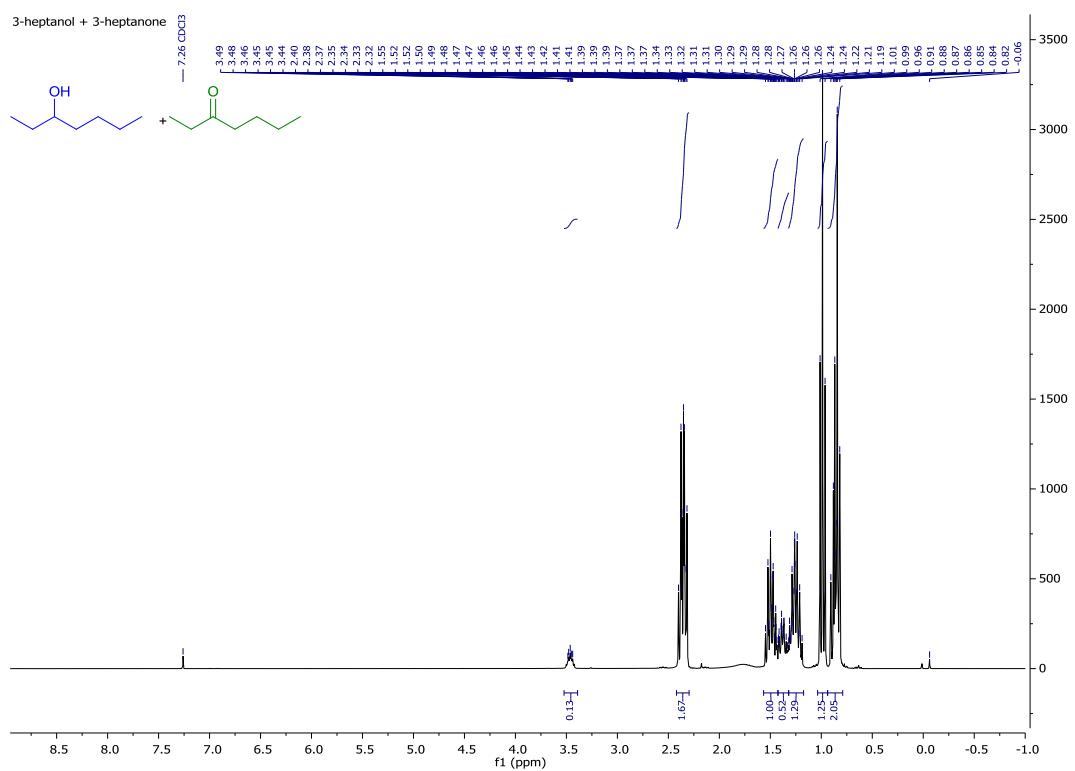


Figure S27:  $^1\text{H}$  NMR spectrum of 3-hetanol and 3-heptanone.

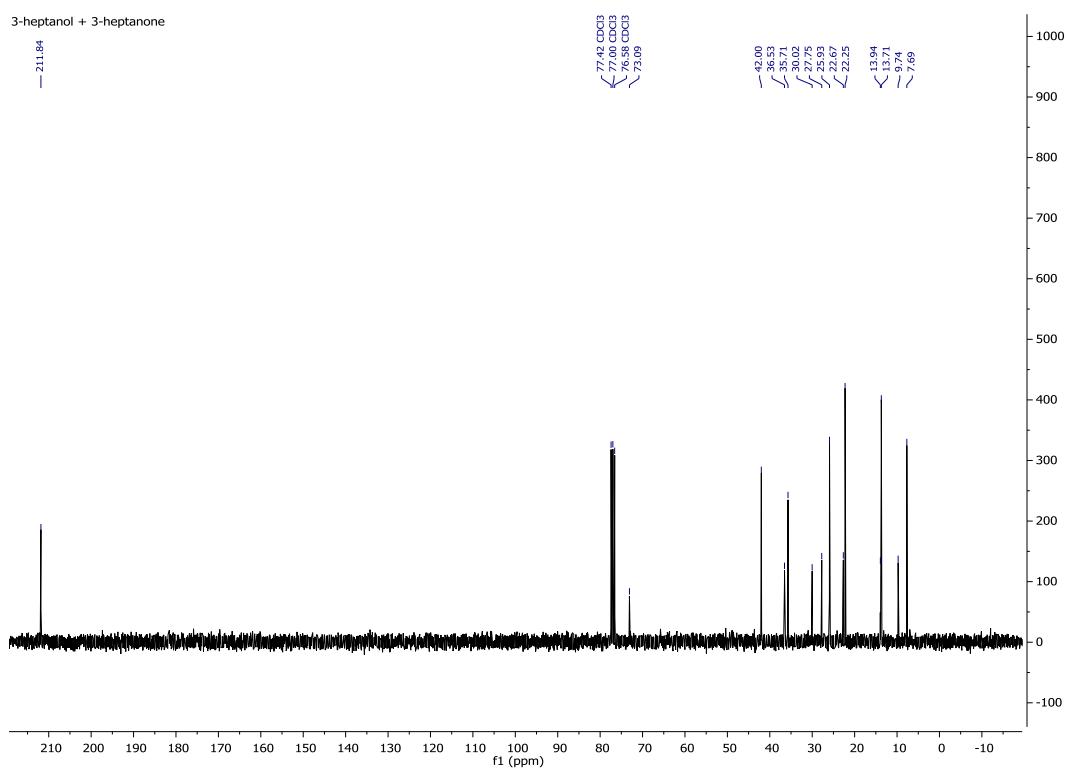


Figure S30:  $^{13}\text{C}$  NMR spectrum of 3-hetanol and 3-heptanone.

### 1-Phenylethanol and acetophenone mixture

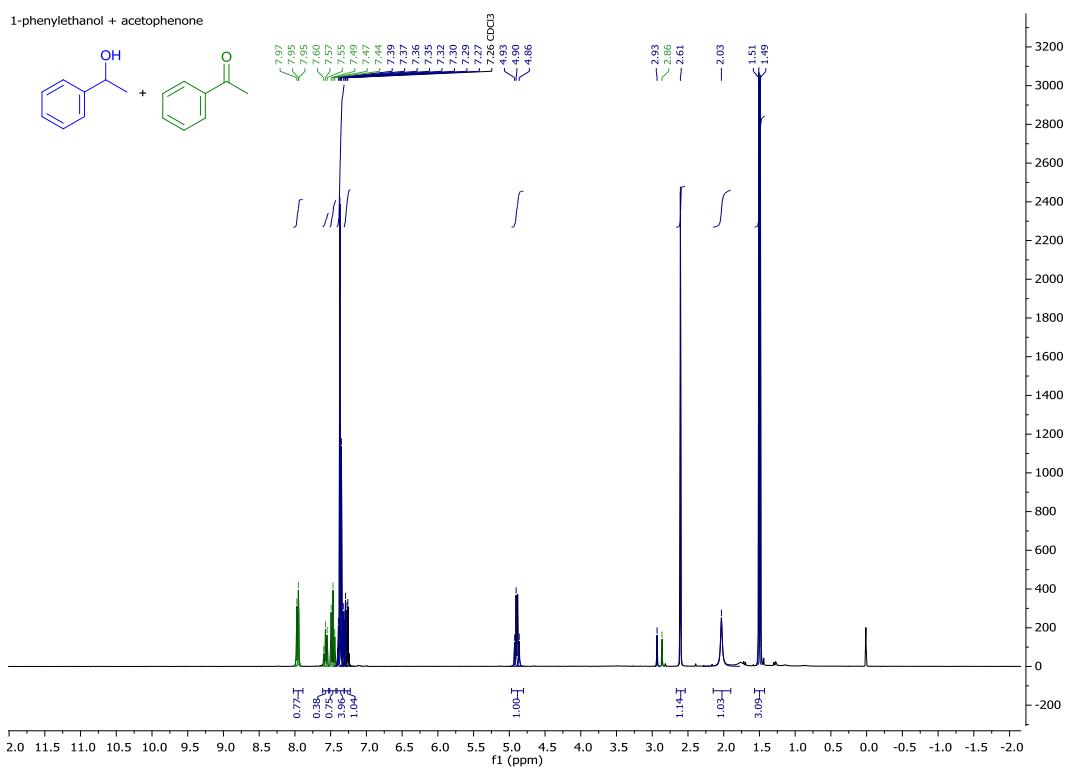


Figure S28:  $^1\text{H}$  NMR spectrum for 1-phenylethanol and acetophenone.

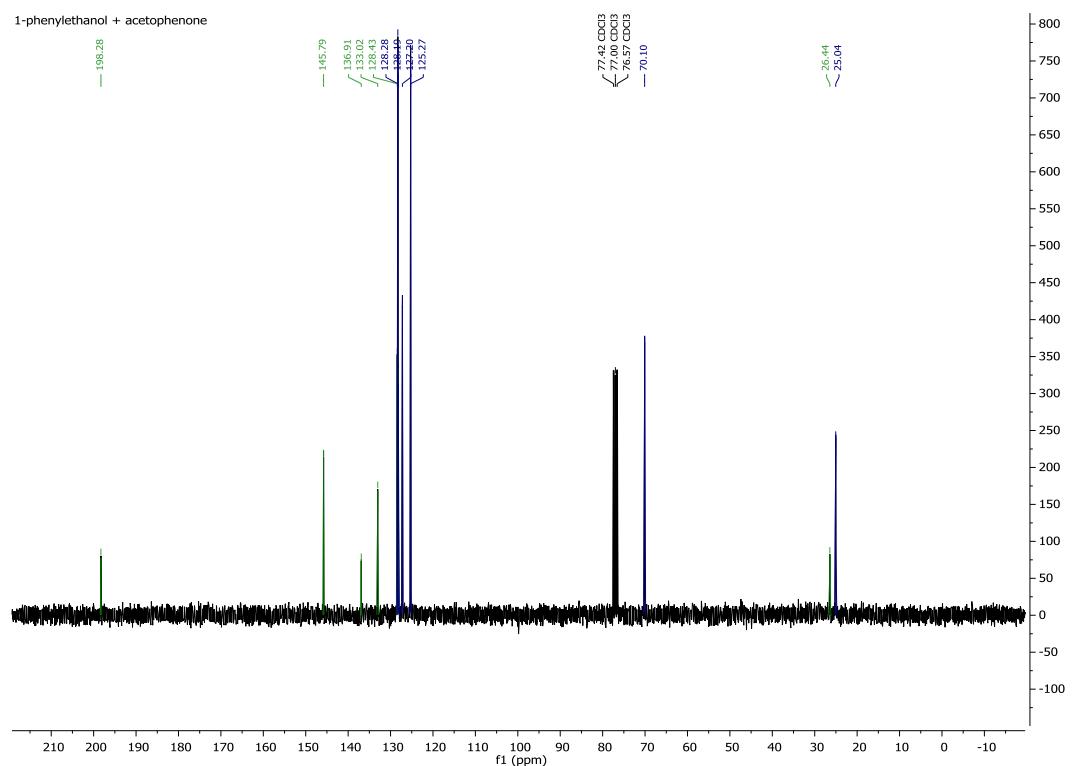


Figure S29:  $^{13}\text{C}$  NMR spectrum of 1-phenylethanol and acetophenone.

<sup>1</sup>H NMR for reduced ketones in flow:

1-(4-Chlorophenyl)ethanol and 4-chloroacetophenone mixture

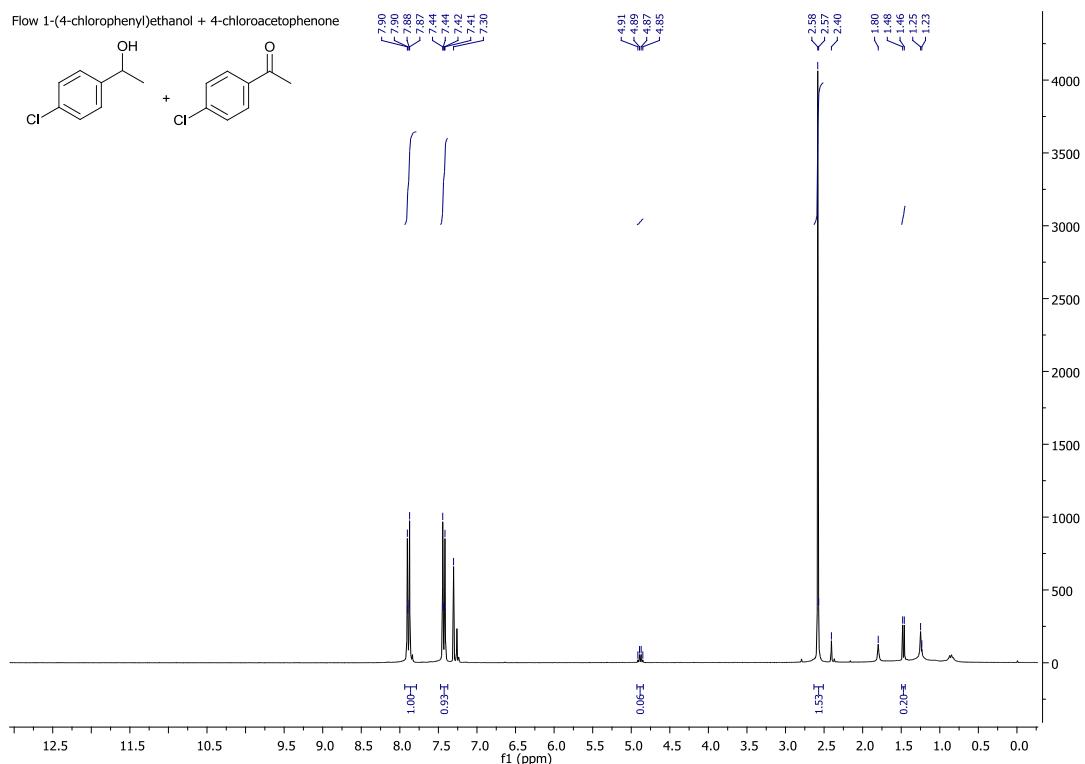


Figure S30: <sup>1</sup>H NMR spectrum of 1-phenylacetophenone and acetophenone.

1-(4-Methylphenyl)ethanol and 4-methylacetophenone mixture

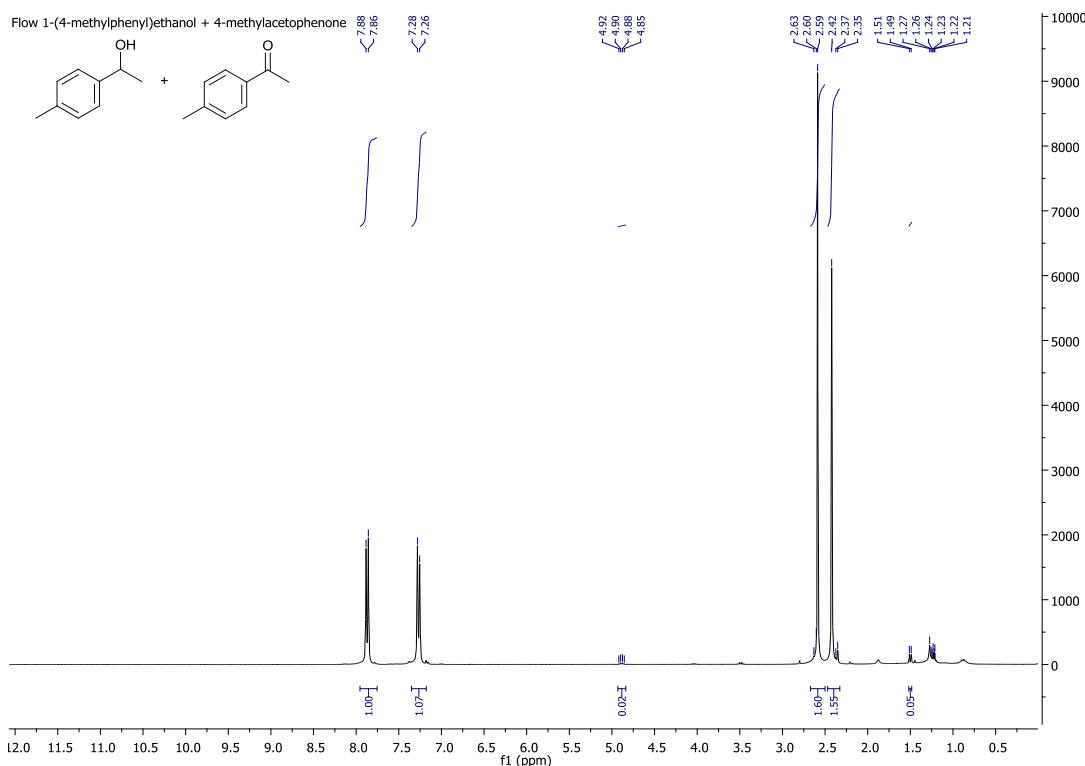


Figure S31: <sup>1</sup>H NMR spectrum of 1-(4-methylphenyl)ethanol and 4-methylacetophenone.

### 1-(2-Hydroxyphenyl)ethanol and 2-hydroxyacetophenone mixture

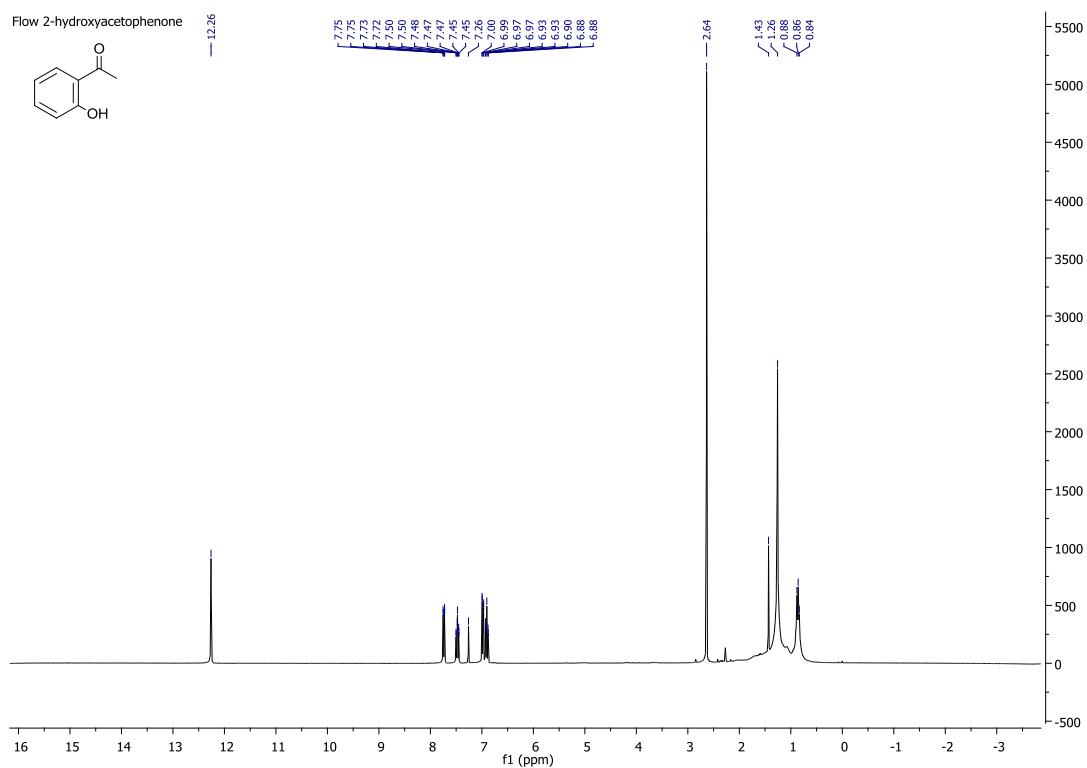


Figure S32:  $^1\text{H}$  NMR spectrum of 1-(2-hydroxyphenyl)ethanol and 2-hydroxyacetophenone mixture.

### Cyclohexanol and cyclohexanone mixture

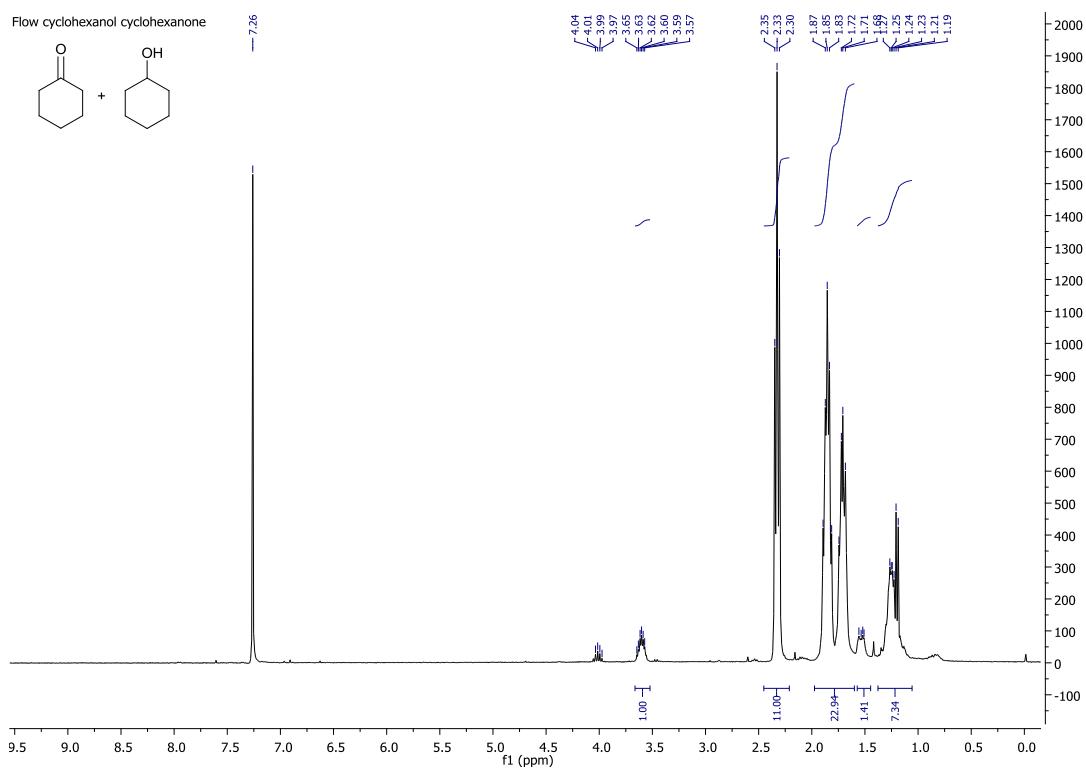


Figure S33:  $^1\text{H}$  NMR spectrum of cyclohexanol and cyclohexanone.

### 3-Heptanone (no 3-heptanol formation)

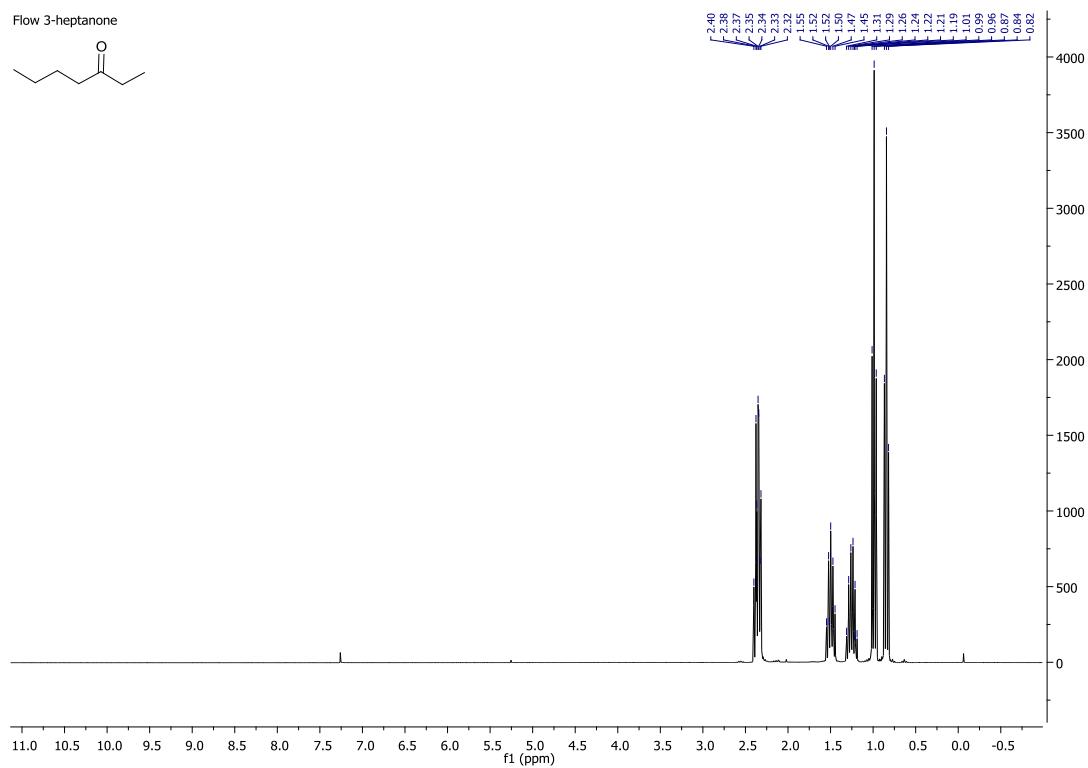


Figure S34:  $^1\text{H}$  NMR spectrum of 3-heptanone.

### 1-Phenylethanol and acetophenone mixture

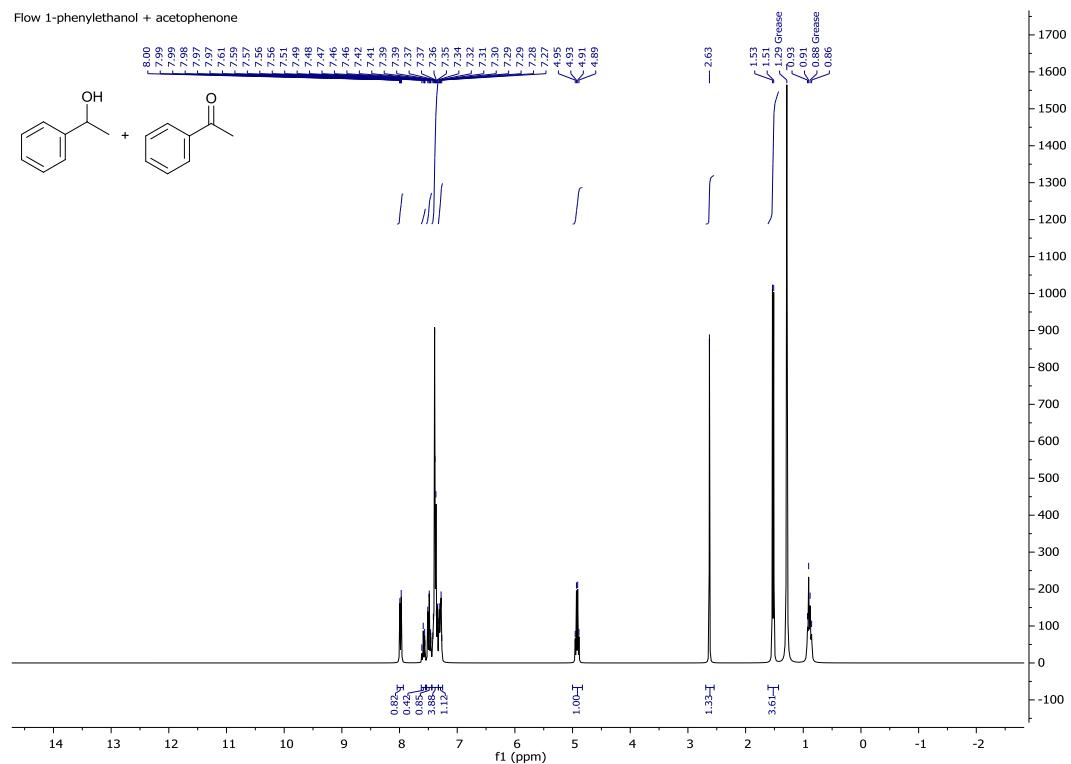


Figure S35:  $^1\text{H}$  NMR spectrum of 1-phenylacetophenone and acetophenone.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of reduced benzaldehyde in the presence of a ketone:  
Benzaldehyde and acetophenone mixture

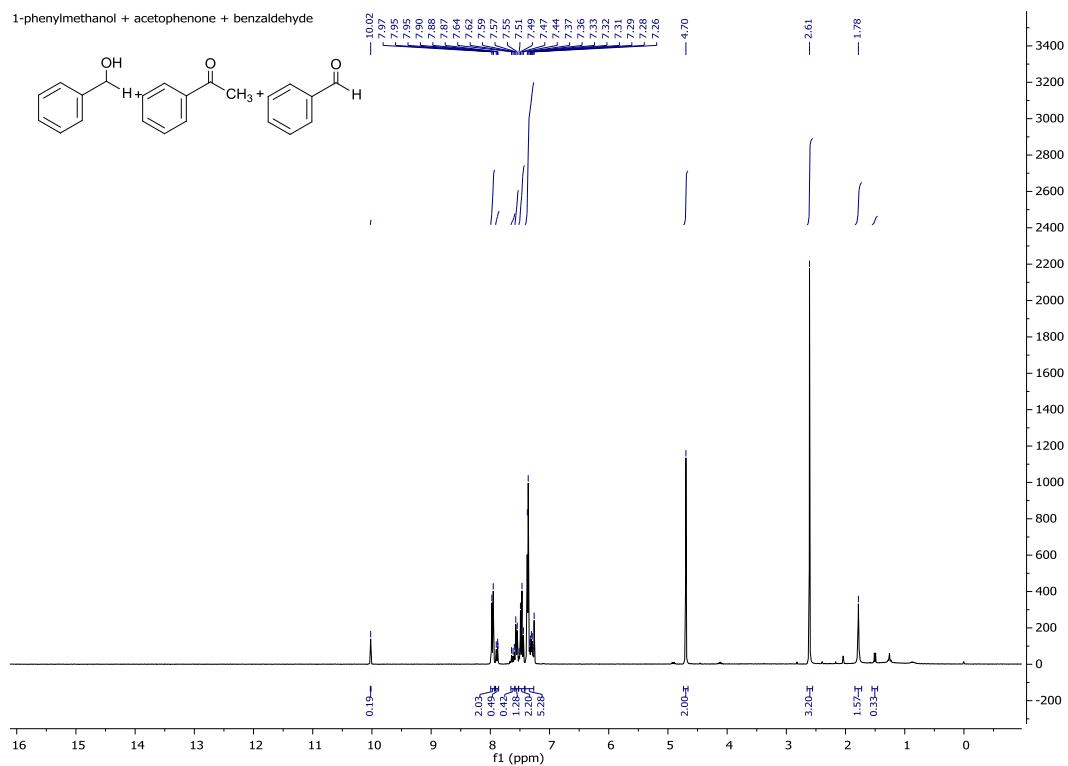


Figure S36:  $^1\text{H}$  NMR spectrum of benzaldehyde, acetophenone and phenylmethanol mixture.

### Benzaldehyde and 3-heptanone mixture

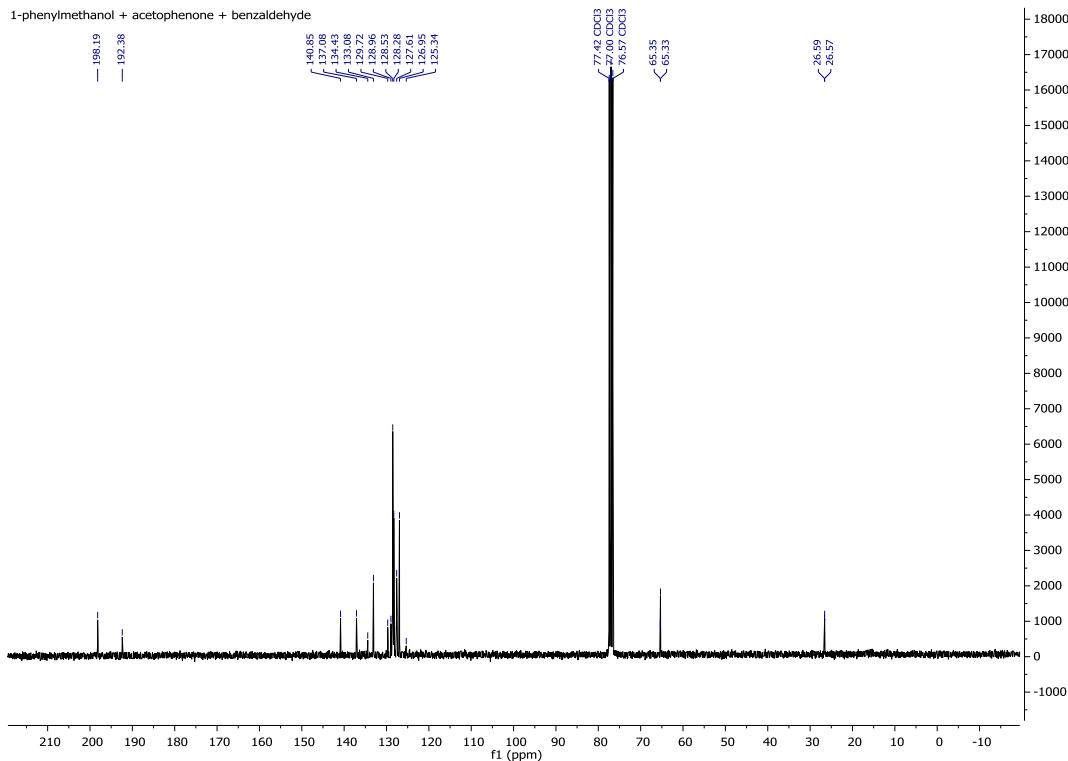


Figure S37:  $^{13}\text{C}$  NMR spectrum of benzaldehyde, acetophenone and phenylmethanol mixture.

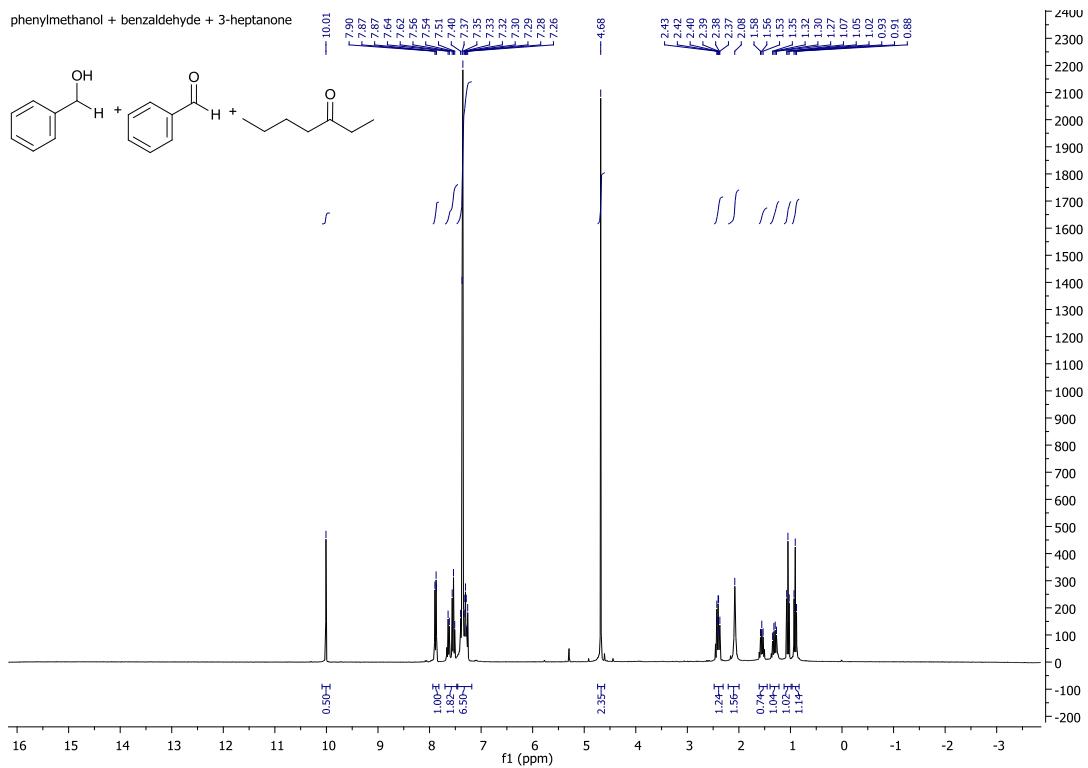


Figure S38:  $^1\text{H}$  NMR spectrum of benzaldehyde, 3-heptanone and phenylmethanol mixture.

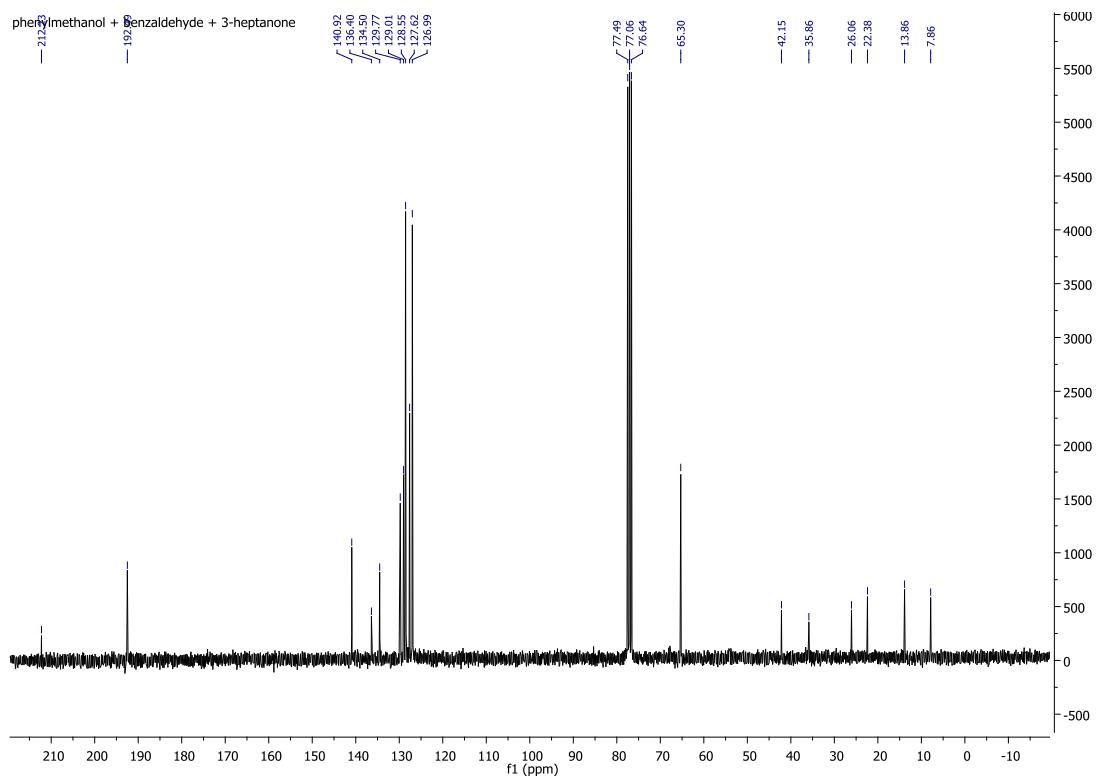


Figure S39:  $^{13}\text{C}$  NMR spectrum of benzaldehyde, 3-heptanone and phenylmethanol mixture.

### 3-Acetylbenzaldehyde and 1-(3-(hydroxymethyl)phenyl)ethenone mixture

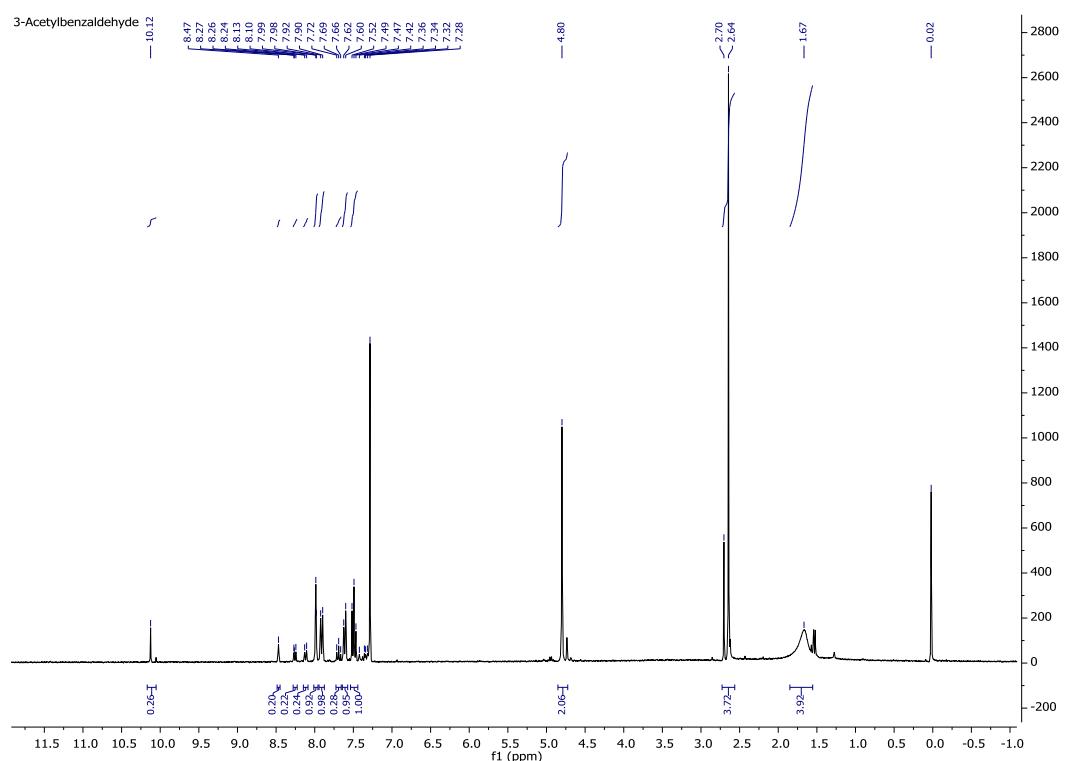


Figure S43:  $^1\text{H}$  NMR spectrum of 3-Acetylbenzaldehyde and 1-(3-(hydroxymethyl)phenyl)ethenone mixture