

Supporting Information

Transfer hydrogenation of carbonyl derivatives catalyzed by an inexpensive phosphine-free manganese pre-catalyst.

Antoine Bruneau-Voisine,^a Ding Wang,^a Vincent Dorcet,^b Thierry Roisnel,^b Christophe Darcel,^a Jean-Baptiste Sortais^{a,c,*}.

^a Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Team Organometallics: Materials and Catalysis, 263 avenue du Général Leclerc, 35046, 35046 Rennes Cedex, France.

^b Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Centre de Diffractométrie X, 263 avenue du Général Leclerc, 35046, 35046 Rennes Cedex, France.

^c Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05, France.

Table of Contents

General Information.....	3
Synthesis of Manganese Complexes	4
Complex 1	4
Complex 2	4
Complex 3	5
Complex 5	5
General procedure for transfer hydrogenation reactions	6
Representative procedure for transfer hydrogenation reaction of acetophenone a1 (0.5 mmol scale).....	6
Representative procedure for transfer hydrogenation reaction of propiophenone a2 (2 mmol scale).....	6
Comparison of catalytic activities of 1 and 2	7
Characterization of the hydrogenated products.....	7
X-ray data for complex 1	16
X-Ray data for complex 2	17
X-Ray data for complex 3	18
X-Ray data for complex 5	20
¹ H, and ¹³ C{ ¹ H} NMR data for manganese complexes 1-3, 5	22
¹ H, and ¹³ C{ ¹ H} NMR data for the products of catalysis	26
Typical ¹ H NMR of crude mixture after reaction	56
References.....	58

General Information

All reactions were carried out with oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon or in an argon-filled glove-box. Toluene, THF, diethyl ether (Et₂O), and CH₂Cl₂ were dried over Braun MB-SPS-800 solvent purification system and degassed by thaw-freeze cycles. Technical grade petroleum ether and diethyl ether were used for chromatography column. Analytical TLC was performed on Merck 60F₂₅₄ silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 μm, 60 Å). All reagents were obtained from commercial sources and liquid reagents were dried on 4 Å molecular sieves and degassed prior to use.

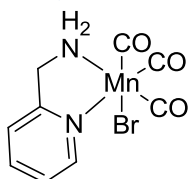
2-[(dimethylamino)methyl]pyridine¹ and complex **4**² were prepared according to reported procedures.

¹H, ¹³C and ³¹P NMR spectra were recorded in CDCl₃, C₆D₆, C₇D₈, (CD₃)CO at 298 K unless otherwise stated, on Bruker, AVANCE 400 and AVANCE 300 spectrometers at 400 and 300 MHz, respectively. ¹H and ¹³C NMR spectra were calibrated using the residual solvent signal as internal standard (¹H: CDCl₃ 7.26 ppm, C₆D₆ 7.16 ppm, C₇H₈ 2.08 ppm, DMSO-*d*₆ 2.50 ppm (CD₃)CO 2.05 ppm ¹³C: CDCl₃, central peak is 77.16 ppm, C₆D₆, central peak is 128.1 ppm, C₇D₈, central peak is 20.4 ppm, DMSO-*d*₆, central peak is 39.5 ppm, (CD₃)CO central peak is 29.84 ppm). ³¹P NMR spectra were calibrated against an external H₃PO₄ standard. Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet, and br. for broad).

IR spectra were measured with a Shimadzu IR-Affinity 1 instrument. HR-MS spectra and microanalysis were carried out by the corresponding facilities at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest), University of Rennes 1.

Synthesis of Manganese Complexes

Complex 1



To a solution of 2-(aminomethyl)pyridine (0.73 mmol, 79 mg, 75 μ L) in toluene was added 1 equivalent of manganese pentacarbonyl bromide (0.73 mmol, 200 mg). After stirring at 110 $^{\circ}$ C during 4 h, the toluene was evaporated under reduced pressure to afford a yellow solid. This solid was washed two times with pentane to give complex **1**, as a yellow powder (227 mg, 95% yield). Suitable single crystals for X-Ray diffraction studies were obtained by evaporation of a saturated solution of the complex in diethyl ether.

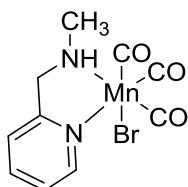
^1H NMR (400 MHz, Acetone- d_6) δ 9.00 (br. d, J = 5.0 Hz, 1H), 7.92 (br. t, J = 6.1 Hz, 1H), 7.56 (br. d, J = 5.5 Hz, 1H), 7.49 (br. t, J = 5.5 Hz, 1H), 5.06 (br. s, 1H, NH), 4.67 (d, J = 14 Hz, 1H, CH₂), 4.37 (d, J = 14 Hz, 1H, CH₂), 3.59 (br. s, 1H, NH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Acetone- d_6) δ 223.2 (br., CO), 162.3 (C_q), 153.7(CH_{py}), 139.0(CH_{py}), 124.9(CH_{py}), 121.9(CH_{py}), 51.5 (CH₂).

Anal.Calc (%). for (C₉H₈BrMnN₂O₃): C, 33.06; H, 2.47; N, 8.57. Found: C, 32.67; H, 2.62; N, 8.60.

IR (ν , cm⁻¹, CH₂Cl₂): 2029, 1936, 1911.

Complex 2



According to the same procedure, starting for 2-[(methylamino)methyl]pyridine(0.73 mmol, 89 mg, 90 μ L), complex **2** was obtained as an yellow solid (231 mg, 93% yield).

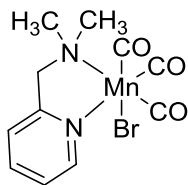
^1H NMR (400 MHz, Acetone- d_6) δ 8.96 (d, J = 5.0 Hz, 1H), 7.97 (t, J = 7.0 Hz, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.56 – 7.42 (t, J = 5.5 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H, CH₂), 4.24 – 4.13 (m, 1H, CH₂), 4.10 (br. s, 1H, NH), 3.03 (d, J = 4.4 Hz, 3H, CH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Acetone- d_6) δ 161.0 (C_q), 154.4 (CH_{py}), 139.4 (CH_{py}), 125.5 (CH_{py}), 122.3 (CH_{py}), 61.9 (CH₂), 43.9 (CH₃). (CO signals were not detected)

Anal.Calc (%). for (C₁₀H₁₀BrMnN₂O₃): C, 35.22; H, 2.96; N, 8.21; Found: C, 35.49; H, 3.08; N, 8.32.

IR (ν , cm⁻¹, CH₂Cl₂): 2029, 1936, 1911.

Complex 3



According to the same procedure, starting for 2-[(dimethylamino)methyl]pyridine (0.37 mmol, 50 mg), complex **3** was obtained as a yellow solid (120 mg, 93% yield).

^1H NMR (400 MHz, Acetone- d_6) δ 9.01 (s, 1H), 7.97 (s, 1H), 7.55 (s, 2H), 4.77 (s, 1H), 3.69 (s, 1H), 3.03 (s, 3H), 2.85 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Acetone- d_6) δ 223.1 (br., CO), 161.4 (Cq), 153.6 (CH_{py}), 139.8 (CH_{py}), 125.1 (CH_{py}), 123.9 (CH_{py}), 69.0 (CH_2), 56.0 (CH_3), 52.5 (CH_3).

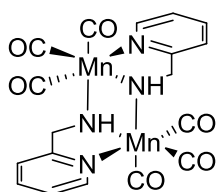
Anal. Calc (%) for ($\text{C}_{11}\text{H}_{12}\text{BrMnN}_2\text{O}_3$): C, 37.21; H, 3.41; N, 7.89; Found: C, 36.42; H, 3.85; N, 7.53.

HR MS (ESI): m/z [M^+Na] $^+$ calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3^{79}\text{BrNaMn}$, 376.93039 found 376.9306 (0 ppm); m/z [M^+K] $^+$ calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3^{79}\text{BrKMn}$, 392.90433 found 392.9041 (1 ppm)

IR (ν , cm^{-1} , CH_2Cl_2): 2027, 1936, 1909.

Complex 5

To a solution of **1** (0.3 mmol, 100 mg) in a mixture of THF (3.4 mL) : Et₂O (6.7 mL) was added *t*-BuOK (0.3 mmol, 34 mg). After stirring at room temperature overnight, solvent were removed and the brown solid was washed with pentane (2 x 5 mL) and then with cold acetone (2 x 7 mL) to give pure **5** (31 mg, 0.063 mmol, 42% yield). **5** has a low solubility in most common organic solvent (methanol, acetone, toluene, dichloromethane and DMSO...) which hampers the acquisition of $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum.



5

^1H NMR (400 MHz, Toluene- d_8) δ 8.63 (d, J = 4.9 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 6.61 (t, J = 6.2 Hz, 1H), 4.19 (d, J = 16.3 Hz, 1H), 3.89 (dd, J = 16.3, 5.2 Hz, 1H), -1.02 (s, 1H). Note : one aromatic CH is overlapping with toluene- d_8 signal

^1H NMR (400 MHz, Acetone- d_6) δ 9.26 (d, J = 5.2 Hz, 1H), 8.00 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 6.4 Hz, 1H), 4.62 (d, J = 16.6 Hz, 1H), 4.37 (dd, J = 16.6, 5.3 Hz, 1H), 0.18 (d, J = 2.8 Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$

NMR (101 MHz, Acetone- d_6) δ 168.6, 153.5, 138.8, 124.7, 123.2, 67.3.

IR (ν , cm^{-1} , CH_2Cl_2): 1990, 1892.

General procedure for transfer hydrogenation reactions

Stock solutions of manganese precatalyst (0.005 mol.L^{-1}) and base (0.005 mol.L^{-1}) in degassed 2-propanol were first prepared in two Schlenk tubes. Then to a solution of ketone (0.5 mmol or 2 mmol) in 2-propanol (final concentration 0.25 mol.L^{-1}) was added the stock solution of pre-catalyst, followed, in this order, by the stock solution of base. The reaction mixture was stirred for 20 minutes at $80 \text{ }^\circ\text{C}$ or 16 hours at $30 \text{ }^\circ\text{C}$ in an oil bath. The solution was then filtered through a small pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the conversion was determined by ^1H NMR. The crude residue was then purified by column chromatography (SiO_2 , mixture of petroleum ether/ethyl acetate or diethyl ether as eluent).

Representative procedure for transfer hydrogenation reaction of acetophenone **a1** (0.5 mmol scale)

To a solution of acetophenone **a1** (58 μL , 0.5 mmol) in 2-propanol (1mL) was added the stock solution of pre-catalyst (0.5 mL, 0.005 mol.L^{-1}) followed, in this order, by the stock solution of tBuOK (0.5 mL, 0.005 mol.L^{-1}). The reaction mixture was stirred for 20 minutes at $80 \text{ }^\circ\text{C}$ in an oil bath. The solution was then filtered through a small pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the conversion was determined by ^1H NMR. The crude residue was then purified by column chromatography (SiO_2 , mixture of petroleum ether/ethyl acetate or diethyl ether as eluent), giving the corresponding alcohol **b1** as a colorless oil (57mg, 93%).

Representative procedure for transfer hydrogenation reaction of propiophenone **a2** (2 mmol scale)

To a solution of propiophenone **a2** (266 μL , 2 mmol) in 2-propanol (8 mL, 0.25 mol L^{-1}) was added pre-catalyst **1** (3.3 mg, 0.01 mmol, 0.5 mol %), followed, in this order, by tBuOK (2.2 mg, 0.02 mmol, 1 mol %). The reaction mixture was stirred for 16 hours at $30 \text{ }^\circ\text{C}$ in an oil bath. The solution was then filtered through a small pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the conversion was determined by ^1H NMR. The crude residue was then purified by column chromatography (SiO_2 , mixture of petroleum ether/ethyl acetate or diethyl ether as eluent), giving the corresponding alcohol **b2** as a colorless oil (229 mg, 84 %).

Comparison of catalytic activities of 1 and 2

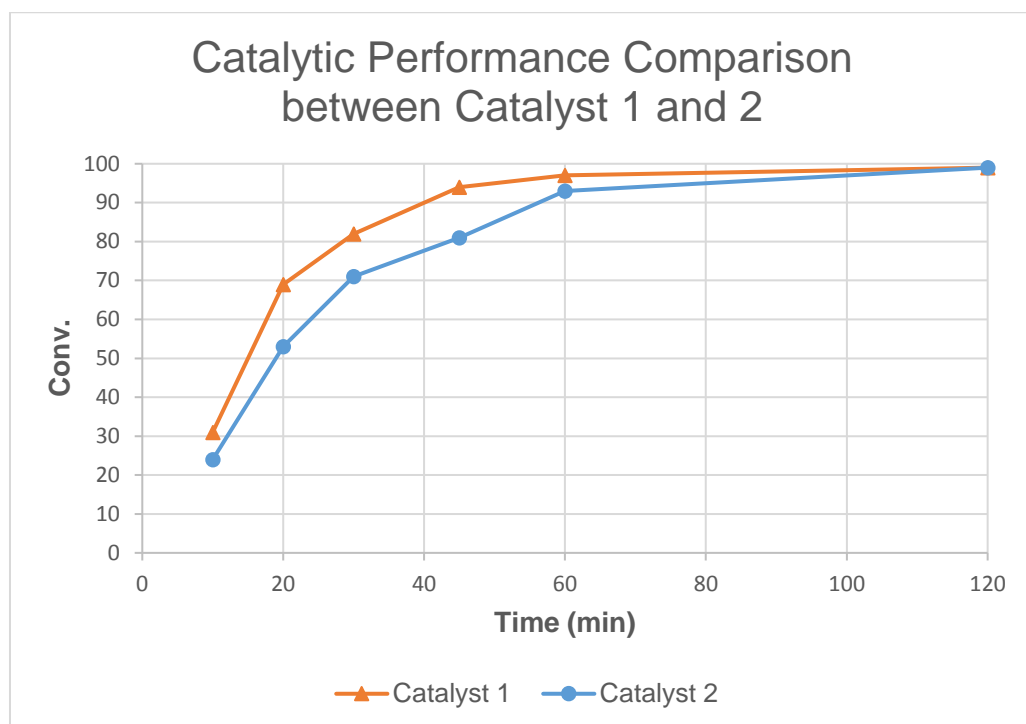
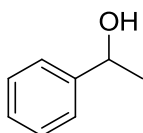


Figure S1: Kinetic of reduction of acetophenone performed at 60 °C by **1** and **2** (0.5 mmol, 0.5 mol% catalyst, 1 mol% tBuOK, iPrOH (2 mL))

Characterization of the hydrogenated products

1-Phenylethanol (**b1**)³

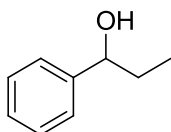


According to general procedure, acetophenone **a1** (58 μ L, 0.5 mmol) gave the title compound **b1** as a colorless oil (57mg, 93%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 5H), 4.89 (q, $J=6.4$, 1H), 2.35 (s, 1H), 1.51 (d, $J=6.5$, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 145.9, 128.5, 127.5, 125.5, 70.4, 25.2.

1-Phenylpropan-1-ol (**b2**)⁴

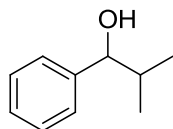


According to general procedure, propiophenone **a2** (266 μ L, 2 mmol) gave the title compound **b2** as a colorless oil (229 mg, 84 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.40-7.34 (m, 4H), 7.33 – 7.26 (m, 1H), 4.61 (t, J = 6.6 Hz, 1H), 2.08 (s, 1H), 1.96 – 1.55 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 144.7, 128.5, 127.6, 126.1, 76.1, 32.0, 10.2.

2-Methyl-1-phenylpropan-1-ol (**b3**)³

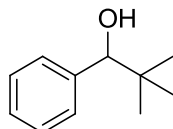


According to general procedure, isobutyrophenone **a3** (75 μL , 0.5 mmol) gave the title compound **b3** as a light yellow oil (71 mg, 95%).

^1H NMR (300 MHz, Chloroform-*d*) δ 7.31 (m, 5H), 4.36 (d, J = 6.4 Hz, 1H), 1.97 (oct., J = 6.8 Hz, 1H), 1.87 (s, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 143.8, 128.3, 127.5, 126.7, 80.2, 35.4, 19.1, 18.4.

2,2-Dimethyl-1-phenylpropan-1-ol (**b4**)⁵

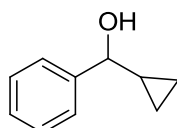


According to general procedure, 2,2-dimethyl-1-phenylpropan-1-one **a4** (336 μL , 2 mmol) gave the title compound **b4** as a colorless oil (326 mg, 99 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.67-7.03 (m, 5H), 4.42 (s, 1H), 2.04 (s, 1H), 0.96 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 142.3, 127.7, 127.6, 127.3, 82.5, 35.7, 26.0.

Cyclopropylphenylmethanol (**b5**)

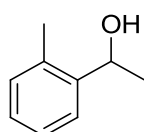


According to general procedure, cyclopropyl phenyl ketone **a5** (69 μL , 0.5mmol) gave the title compound **b5** as a colorless oil (45 mg, 62 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.43 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 4.05 (d, J = 8.3 Hz, 1H), 2.00 (s, 1H), 1.29-1.21 (m, 1H), 0.70-0.64 (m, 1H), 0.63 – 0.55 (m, 1H), 0.54 – 0.47 (m, 1H), 0.45 – 0.36 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 143.9, 128.5, 127.7, 126.1, 78.7, 19.3, 3.7, 2.9.

1-(2-Methylphenyl)ethanol (**b6**)⁶

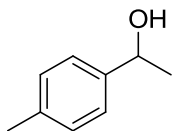


According to general procedure, 2-methylacetophenone **a6** (66 μ L, 0.5 mmol) gave the title compound **b6** as a yellow oil (60 mg, 88%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, J = 7.4 Hz, 1H), 7.30-7.13 (m, 3H), 5.11 (q, J = 5.7 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 1H), 1.47 (d, J = 6.2 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 143.9, 134.3, 130.4, 127.2, 126.4, 124.6, 66.8, 24.0, 19.0.

1-(4-Methylphenyl)ethanol (**b7**)³

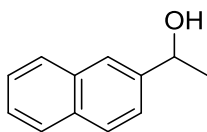


According to general procedure, 4-methylacetophenone **a7** (67 μ L, 0.5 mmol) gave the title compound **b7** as a colorless oil (59 mg, 87%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 4.88 (q, J = 6.5 Hz, 1H), 2.38 (s, 3H), 2.07 (s, 1H), 1.51 (d, J = 6.5 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ = 143.0, 137.2, 129.2, 125.5, 70.3, 25.2, 21.2.

1-(2-Naphthyl)ethanol (**b8**)⁷

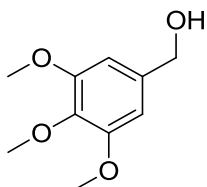


According to general procedure, 1-(naphthalen-2-yl)ethanone **a8** (340 mg, 2 mmol) gave the title compound **b8** as a white solid (307 mg, 89%).

^1H NMR (400 MHz, CDCl_3) δ 8.27-7.71 (m, 4H), 7.55-7.45 (m, 3H), 5.01 (q, J = 6.4 Hz, 1H), 2.70 (s, 1H), 1.58 (d, J = 6.5 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 143.3, 133.3, 132.9, 128.3, 128.0, 127.7, 126.1, 125.8, 123.9, 123.8, 70.4, 25.1.

(3,4,5-Trimethoxyphenyl)-methanol (**b10**)⁶

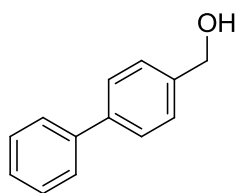


According to general procedure, 3,4,5-trimethoxybenzaldehyde **a10** (98 mg, 0.5 mmol) gave the title compound **b10** as a brown oil (97 mg, 99 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 6.57 (s, 2H), 4.60 (s, 2H), 3.83 (s, 9H), 2.14 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 153.4, 137.3, 136.8, 103.9, 65.5, 60.9, 56.2.

[1,1'-Biphenyl]-4-yl-methanol (**b11**)⁸

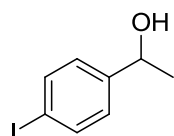


According to general procedure, 1,1'-biphenyl-4-carboxaldehyde **a11** (91 mg, 0.5 mmol) gave the title compound **b11** as a white solid (85 mg, 92 %). Note: the alcohol is contaminated with c.a. 5% of (*E*)-4-([1,1'-biphenyl]-4-yl)but-3-en-2-one resulting from the aldol condensation of the aldehyde with acetone.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.7 Hz, 4H), 7.50 – 7.37 (m, 4H), 7.36 (t, *J* = 7.1 Hz, 1H), 4.75 (s, 2H), 1.77 (s, 1H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ = 140.9, 140.8, 140.0, 128.9, 127.6, 127.4, 127.2, 65.3.

1-(4-Iodophenyl)ethanol (**b12**)⁴

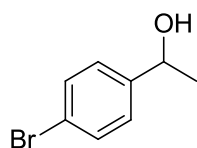


According to general procedure, 4-iodoacetophenone **a12** (246 mg, 1 mmol) gave the title compound **b12** as a brown oil after one week at 30 °C (244 mg, 99 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.84 (q, *J* = 6.6 Hz, 1H), 1.96 (s, 1H), 1.46 (d, *J* = 6.2 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 145.6, 137.6, 127.5, 92.8, 70.0, 25.3..

1-(4-Bromophenyl)ethanol (**b13**)⁶

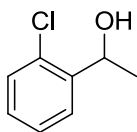


According to general procedure for 30°C, 4-bromoacetophenone **a13** (398 mg, 2 mmol) gave the title compound **b13** as a colorless oil (352 mg, 87%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 4.85 (q, *J* = 6.4 Hz, 1H), 1.74 (s, 1H), 1.45 (d, *J* = 6.4 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 144.8, 131.5, 127.2, 121.1, 69.7, 25.2.

1-(2-Chlorophenyl)ethanol (**b14**)⁹

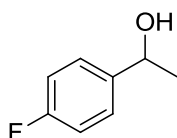


According to general procedure, 2-chloroacetophenone **a14** (260 μ L, 2 mmol) gave the title compound **b14** as a colorless oil (341 mg, 99 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.34-7.25 (m, 2H), 7.18 (t, *J* = 8.2 Hz, 1H), 5.27 (q, *J* = 6.4 Hz, 1H), 2.26 (s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 143.2, 131.7, 129.5, 128.5, 127.3, 126.5, 67.0, 23.6.

1-(4-Fluorophenyl)ethanol (**b15**)³



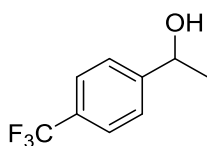
According to general procedure, 4-fluoroacetophenone **a15** (61 μ L, 0.5 mmol) gave the title compound **b15** as a light-rose oil (70 mg, 85 %).

¹H NMR (400 MHz, CDCl₃) δ 7.32-7.27 (m, 2H), 7.03-6.97 (m, 2H), 4.82 (q, *J* = 6.4 Hz, 1H), 2.51 (s, 1H), 1.43 (d, *J* = 6.5 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -115.44.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 162.1 (d, *J* = 245 Hz), 141.6 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.4 Hz), 69.7, 25.3.

1-(4-Trifluoromethylphenyl)ethanol (**b16**)¹⁰



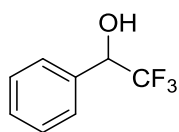
According to general procedure, 4-trifluoromethylacetophenone **a16** (412 μ L, 2 mmol) gave the title compound **b16** as a colorless oil (365 mg, 96 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 4.97 (q, *J* = 6.5 Hz, 1H), 1.94 (s, 1H), 1.51 (d, *J* = 6.5 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -62.48.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 149.8, 129.7 (q, *J* = 32.3 Hz), 125.7, 125.5 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.9 Hz), 69.9, 25.4.

2,2,2-Trifluoro-1-phenylethanol (**b17**)⁴



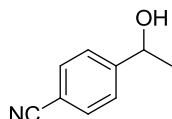
According to general procedure, 2,2,2-trifluoroacetophenone **a17** (70 μ L, 0.5 mmol) gave the title compound **b17** as a colorless oil (51 mg, 58 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.36 (m, 5H), 5.03 (qd, *J* = 6.6, 2.9 Hz, 1H), 2.60 (d, *J* = 3.3 Hz, 1H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 129.7, 128.8, 127.6, 123.0, δ 73.0 (q, *J* = 32.0 Hz). Note: the quartet for carbon of CF₃ was not observed due to low intensity.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -78.37 (d, *J* = 6.7 Hz).

4-(1-Hydroxyethyl)benzonitrile (**b18**)¹¹

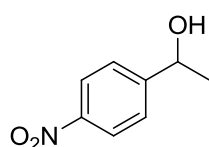


According to general procedure, 4-acetylbenzonitrile **a18** (290 mg, 2 mmol) gave the title compound **b18** as a brown oil (230 mg, 78 %).

¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 4.95 (q, *J* = 6.5 Hz, 1H), 2.23 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ 151.3, 132.4, 126.2, 119.0, 111.1, 69.7, 25.5.

1-(4-Nitrophenyl)ethanol (**b19**)¹²

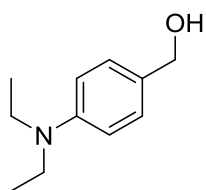


According to general procedure, 4-nitroacetophenone **a19** (330 mg, 2 mmol) gave the title compound **b19** as a white solid (333 mg, 99%).

¹H NMR (400 MHz, Chloroform-*d*) 8.16 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 5.00 (q, *J* = 6.6 Hz, 1H), 2.38 (s, 1H), 1.50 (d, *J* = 6.4 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*) δ = 153.3, 147.2, 126.2, 123.8, 69.6, 25.6.

(4-(Diethylamino)phenyl)methanol (b21) ¹²

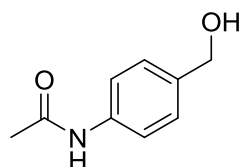


According to general procedure, 4-(diethylamino)benzaldehyde **a21** (89 mg, 0.5 mmol) gave the title compound **b21** as a yellow oil (74 mg, 83 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.55 (s, 2H), 3.36 (q, *J* = 7.0 Hz, 4H), 1.66 (s, 1H), 1.17 (t, *J* = 7.1 Hz, 6H).

¹³C {¹H} NMR (101 MHz, Chloroform-*d*) δ 147.6, 129.1, 127.8, 111.9, 65.5, 44.5, 12.6.

N-(4-(hydroxymethyl)phenyl)acetamide (b23) ¹³

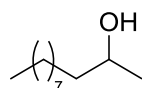


According to general procedure, *N*-(4-formylphenyl)acetamide **a23** (81 mg, 0.5 mmol) gave the title compound **b23** as a white solid (73 mg, 90%).

¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.33 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.54 (d, *J* = 5.8 Hz, 2H), 3.15 (t, *J* = 5.9 Hz, 1H), 2.07 (s, 3H). Note: c.a. 5% of the product of aldol condensation with acetone is present in the product.

¹³C {¹H} NMR (101 MHz, Acetone-*d*₆) δ 168.9, 139.2, 138.1, 127.9, 119.8, 64.4, 24.2.

Undecan-2-ol (b25) ³

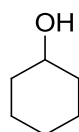


According to general procedure, undecan-2-one **a25** (103 μL, 0.5 mmol) gave the title compound **b25** as a colorless oil (80 mg, 93 %).

¹H NMR (400 MHz, CDCl₃) δ 3.77 (m, 1H), 1.51 – 1.2 (m, 20H), 0.87 (t, *J* = 6.7 Hz, 3H).

¹³C {¹H} NMR (101 MHz, Chloroform-*d*) δ 68.3, 39.5, 32.0, 29.79, 29.77, 29.70, 29.5, 25.9, 23.6, 22.8, 14.2.

Cyclohexanol (b26)

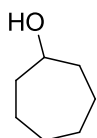


According to general procedure, cyclohexanone **a26** (52 μ L, 0.5 mmol) gave the title compound **b26** as a colorless oil (49 mg, 99 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 3.60-3.57 (m, 1H), 1.92-1.66 (m, 5H), 1.54-1.51 (m, 1H), 1.31 – 1.06 (m, 5H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 70.4, 35.6, 25.6, 24.3.

Cycloheptanol (**b27**)³

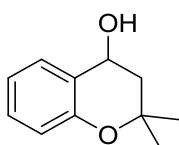


According to general procedure, cycloheptanone **a27** (236 μ L, 2 mmol) gave the title compound **b27** as a colorless oil (215 mg, 94 %).

^1H NMR (400 MHz, CDCl_3) δ 3.85-3.79 (m, 1H), 1.92-1.86 (m, 2H), 1.69-1.47 (m, 9H), 1.43 – 1.28 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 72.9, 37.7, 28.2, 22.7.

2,2-Dimethylchroman-4-ol (**b28**)

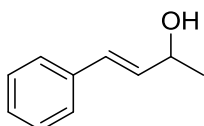


According to general procedure, 2,2-dimethylchroman-4-one **a28** (88 mg, 0.5 mmol) gave the title compound **b28** as a colorless oil (88 mg, 99%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, $J = 7.5$ Hz, 1H), 7.22 – 7.13 (m, 1H), 6.93 (td, $J = 7.4, 1.2$ Hz, 1H), 6.79 (dd, $J = 8.2, 1.2$ Hz, 1H), 4.85 (q, $J = 7.3$ Hz, 1H), 2.18 (dd, $J = 13.4, 6.1$ Hz, 1H), 1.87 (dd, $J = 13.4, 8.7$ Hz, 1H), 1.74 (d, $J = 7.4$ Hz, 1H), 1.45 (s, 3H), 1.32 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 153.3, 129.4, 127.7, 124.5, 120.4, 117.4, 75.4, 63.9, 42.9, 29.0, 26.1

4-Phenylbut-3-en-2-ol (**b30**)¹⁰

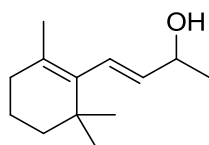


According to general procedure, 4-phenylbut-3-en-2-one **a30** (412 μ L, 2 mmol) gave the title compound **b30** as a yellow oil (258 mg, 87 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, $J = 7.4$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.29 (d, $J = 7.9$ Hz, 1H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.31 (dd, $J = 15.9, 6.4$ Hz, 1H), 4.54 (quint., $J = 6.3$ Hz, 1H), 1.62 (s, 1H), 1.42 (d, $J = 6.4$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ = 136.8, 133.7, 129.5, 128.7, 127.8, 126.6, 69.1, 23.6.

4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-3-en-2-ol (beta-ionol) (**b31**)¹⁰

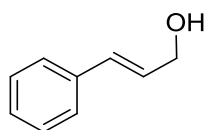


According to general procedure, beta-ionone **a31** (103 μL , 2 mmol) gave the title compound **b31** as a colorless oil (88 mg, 90 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 6.03 (d, J = 15.9 Hz, 1H), 5.47 (dd, J = 15.9, 6.7 Hz, 1H), 4.34 (quint., J = 6.4, 1H), 1.96 (t, J = 6.0 Hz, 2H), 1.71 (br. s, 1H), 1.65 (s, 3H), 1.62 – 1.51 (m, 2H), 1.48 – 1.38 (m, 2H), 1.30 (d, J = 6.3 Hz, 3H), 0.97 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 137.8, 136.78, 128.9, 127.6, 69.6, 39.5, 34.0, 32.8, 28.8, 28.8, 23.7, 21.4, 19.3.

Cinnamylalcohol (**b32**)¹⁰

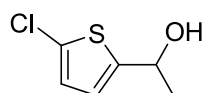


According to general procedure, cinnamyl ketone **a32** (63 μL , 0.5 mmol) gave the title compound **b32** as a colorless oil (54 mg, 80 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.39 (m, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.28-7.24 (m, 1H), 6.63 (d, J = 15.9 Hz, 1H), 6.38 (dt, J = 15.9, 5.7 Hz, 1H), 4.33 (dd, J = 5.7, 1.5 Hz, 1H), 2.06 (br. s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.8, 131.2, 128.7, 128.6, 127.8, 126.6, 63.8.

1-(5-Chlorothiophen-2-yl)ethanol (**b33**)⁴



According to general procedure, 1-(5-chlorothiophen-2-yl)ethanone **a33** (80 mg, 0.5 mmol) gave the title compound **b33** as a brown oil (78 mg, 96 %).

^1H NMR (400 MHz, Chloroform-*d*) δ 6.75 (d, J = 3.8 Hz, 1H), 6.71 (d, J = 3.8 Hz, 1H), 4.99 (q, J = 6.4 Hz, 1H), 2.24 (s, 1H), 1.55 (d, J = 6.4 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*) δ 148.7, 129.1, 125.7, 122.5, 66.5, 25.1.

CCDC 1545746-1545749 contain the supplementary crystallographic data for complexes **1**, **2**, **3** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

X-ray data for complex 1

X-ray diffraction data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a PHOTON 100 CMOS detector, using multilayers monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150 (2) \text{ K}$. The structure was solved by dual-space algorithm using the *SHELXT* program,¹⁴ and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).¹⁵ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 3811 unique intensities and 192 parameters converged at $\omega R(F^2) = 0.0733$ ($R(F) = 0.0353$) for 3004 observed reflections with $I > 2\sigma(I)$.

Table S1. Crystal data and structure refinement for complex **1**.

Empirical formula	C ₁₃ H ₁₈ Br Mn N ₂ O ₄
Formula weight	401.14
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 2 ₁ /c
Unit cell dimensions	a = 9.8700(9) Å, alpha = 90 ° b = 10.2436(10) Å, beta = 95.410(4) ° c = 16.5179(15) Å, gamma = 90 °
Volume	1662.6(3) Å ³
Z, Calculated density	4, 1.603 (g.cm ⁻³)
Absorption coefficient	3.212 mm ⁻¹
F(000)	808
Crystal size	0.550 x 0.450 x 0.090 mm
Crystal color	orange
Theta range for data collection	3.050 to 27.484 °
h_min, h_max	-12, 12
k_min, k_max	-13, 13
l_min, l_max	-21, 21
Reflections collected / unique	19509 / 3811 [R(int) = 0.0827]
Reflections [$I > 2\sigma(I)$]	3004
Completeness to theta_max	0.998
Absorption correction type	multi-scan
Max. and min. transmission	0.749, 0.412
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3811 / 0 / 192
Goodness-of-fit	1.042
Final R indices [$I > 2\sigma(I)$]	$R1^a = 0.0353$, $wR2^b = 0.0733$
R indices (all data)	$R1^a = 0.0539$, $wR2^b = 0.0790$
Largest diff. peak and hole	0.624 and -0.433 e.Å ⁻³

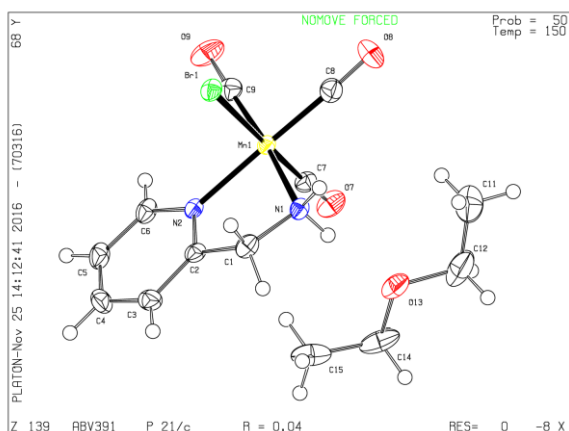
$$R_{int} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum [F_o^2]}$$

$$S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$$

$${}^aR1 = \sum | |F_o| - |F_c| | / \sum |F_o|$$

$${}^bWR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

$$w = 1 / [\sigma(F_o^2) + aP^2 + bP] \text{ where } P = [2F_c^2 + \text{MAX}(F_o^2, 0)] / 3$$



X-Ray data for complex 2

X-ray diffraction data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a PHOTON 100 CMOS detector, using multilayers monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150 \text{ K}$. The structure was solved by dual-space algorithm using the *SHELXT* program,¹⁴ and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).¹⁵ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except nitrogen linked hydrogen atom that was introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on F^2 with 2522 unique intensities and 159 parameters converged at $\omega R(F^2) = 0.1038$ ($R(F) = 0.0398$) for 2400 observed reflections with $I > 2\sigma(I)$.

Table S2. Crystal data and structure refinement for complex 2.

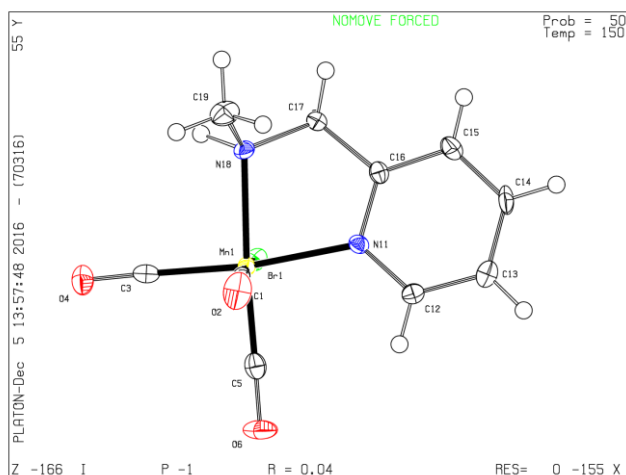
Empirical formula	C ₁₀ H ₁₀ Br Mn N ₂ O ₃
Formula weight	341.05
Temperature	150 K
Wavelength	0.71073 \AA
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 6.7610(15) \AA , alpha = 78.215(8) $^\circ$ b = 7.2814(16) \AA , beta = 85.488(8) $^\circ$ c = 13.336(3) \AA , gamma = 72.757(7) $^\circ$
Volume	613.7(2) \AA^3
Z, Calculated density	2, 1.846 (g.cm ⁻³)
Absorption coefficient	4.327 mm ⁻¹
F(000)	336
Crystal size	0.330 x 0.250 x 0.160 mm
Crystal color	yellow
Theta range for data collection	2.984 to 27.523 $^\circ$

h_min, h_max	-8, 8
k_min, k_max	-9, 9
l_min, l_max	0, 17
Reflections collected / unique	2522 / 2522
Reflections [$I > 2\sigma(I)$]	2400
Completeness to theta_max	0.917
Absorption correction type	multi-scan
Max. and min. transmission	0.500 , 0.371
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2522 / 0 / 159
Goodness-of-fit	1.059
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0398, wR2 = 0.1038
R indices (all data)	R1 = 0.0449, wR2 = 0.1066
Largest diff. peak and hole	0.769 and -0.957 e.Å ⁻³

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

$$w = 1 / [\sigma(F_o^2) + aP^2 + bP] \text{ where } P = [2F_c^2 + \text{MAX}(F_o^2, 0)] / 3$$



X-Ray data for complex 3

(X-ray diffraction data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a PHOTON 100 CMOS detector, using multilayers monochromated Mo-Ka radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150 (2) \text{ K}$. The structure was solved by dual-space algorithm using the *SHELXT* program,¹⁴ and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).¹⁵ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 3113 unique intensities and 165 parameters converged at $\omega R(F^2) = 0.0589$ ($R(F) = 0.0230$) for 2805 observed reflections with $I > 2\sigma(I)$.

Table S3. Crystal data and structure refinement for complex 3.

Empirical formula	C ₁₁ H ₁₂ Br Mn N ₂ O ₃
Formula weight	355.08
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 2 ₁ /c
Unit cell dimensions	a = 13.6291(7) Å, alpha = 90 ° b = 7.5001(3) Å, beta = 113.980(2) ° c = 14.5567(7) Å, gamma = 90 °
Volume	1359.55(11) Å ³
Z, Calculated density	4, 1.735 (g.cm ⁻³)
Absorption coefficient	3.910 mm ⁻¹
F(000)	704
Crystal size	0.350 x 0.110 x 0.070 mm
Crystal color	yellow
Theta range for data collection	3.063 to 27.482 °
h_min, h_max	-17, 17
k_min, k_max	-8, 9
l_min, l_max	-18, 18
Reflections collected / unique	19651 / 3113 [R(int) = 0.0352]
Reflections [I > 2sigma(I)]	2805
Completeness to theta_max	0.999
Absorption correction type	multi-scan
Max. and min. transmission	0.761 , 0.577
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3113 / 0 / 165
Goodness-of-fit	0.711
Final R indices [I > 2sigma(I)]	R1 ^a = 0.0230, wR2 ^b = 0.0589
R indices (all data)	R1 ^a = 0.0279, wR2 ^b = 0.0642
Largest diff. peak and hole	0.449 and -0.508

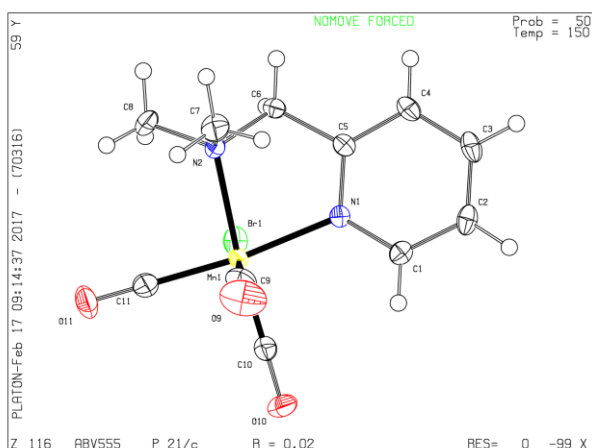
$$R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum [F_o^2]$$

$$S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$$

$${}^a R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$$

$${}^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

$$w = 1 / [\sigma(F_o^2) + aP^2 + bP] \text{ where } P = [2F_c^2 + \text{MAX}(F_o^2, 0)] / 3$$



X-Ray data for complex 5

X-ray diffraction data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a PHOTON 100 CMOS detector, using multilayers monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150 (2) \text{ K}$. The structure was solved by dual-space algorithm using the *SHELXT* program,¹⁴ and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).¹⁵ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except nitrogen linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on F^2 with 2189 unique intensities and 139 parameters converged at $\omega R(F^2) = 0.0982$ ($R(F) = 0.0262$) for 2132 observed reflections with $I > 2\sigma(I)$.

Table S4. Crystal data and structure refinement for complex 5.

Empirical formula	C ₁₈ H ₁₄ Mn ₂ N ₄ O ₆
Formula weight	492.21
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 7.2912(9) Å, alpha = 106.422(3)° b = 8.1947(10) Å, beta = 100.106(4)° c = 9.5912(11) Å, gamma = 113.184(3)°
Volume	477.83(10) Å ³
Z, Calculated density	1, 1.711 (g.cm ⁻³)
Absorption coefficient	1.366 mm ⁻¹
F(000)	248
Crystal size	0.590 x 0.260 x 0.210 mm
Crystal color	yellow
Theta range for data collection	2.935 to 27.484°
h _{min} , h _{max}	-9, 9
k _{min} , k _{max}	-10, 10
l _{min} , l _{max}	-12, 12
Reflections collected / unique	9005 / 2189 [R(int) = 0.0265]

Reflections [$I > 2\sigma(I)$]	2132
Completeness to θ_{max}	0.998
Absorption correction type	multi-scan
Max. and min. transmission	0.751 , 0.621
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2189 / 0 / 139
Goodness-of-fit	1.373
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0262, wR2 = 0.0982
R indices (all data)	R1 = 0.0280, wR2 = 0.1075
Largest diff. peak and hole	0.648 and -0.696 $e.\text{\AA}^{-3}$

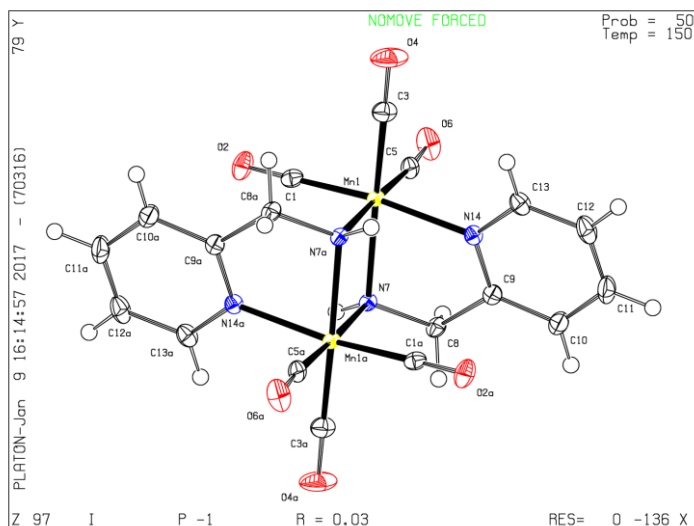
$$R_{int} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum [F_o^2]}$$

$$S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$$

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

$$w = 1 / [\sigma(F_o^2) + aP^2 + bP] \text{ where } P = [2F_c^2 + \text{MAX}(F_o^2, 0)] / 3$$



^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR data for manganese complexes 1-3, 5

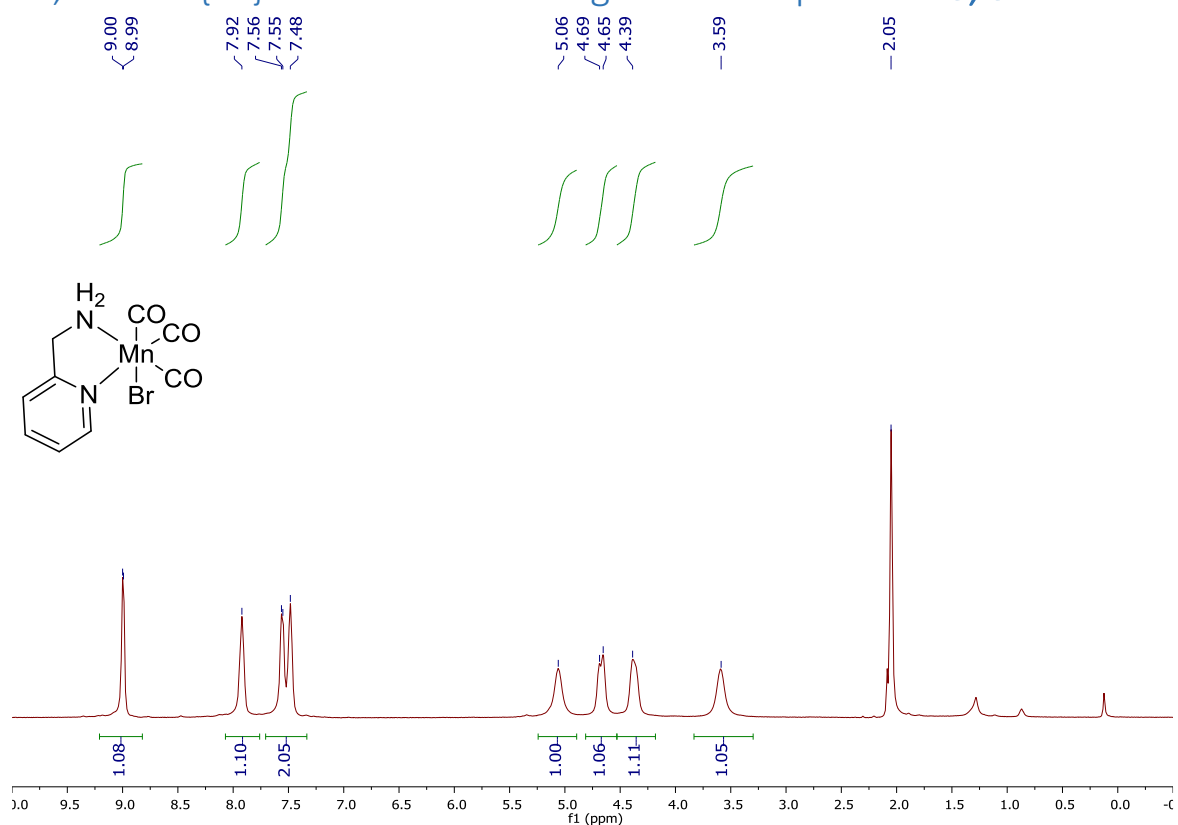


Figure S2: ^1H NMR spectrum of manganese complex 1 in $(\text{CD}_3)_2\text{CO}$ (400 MHz).

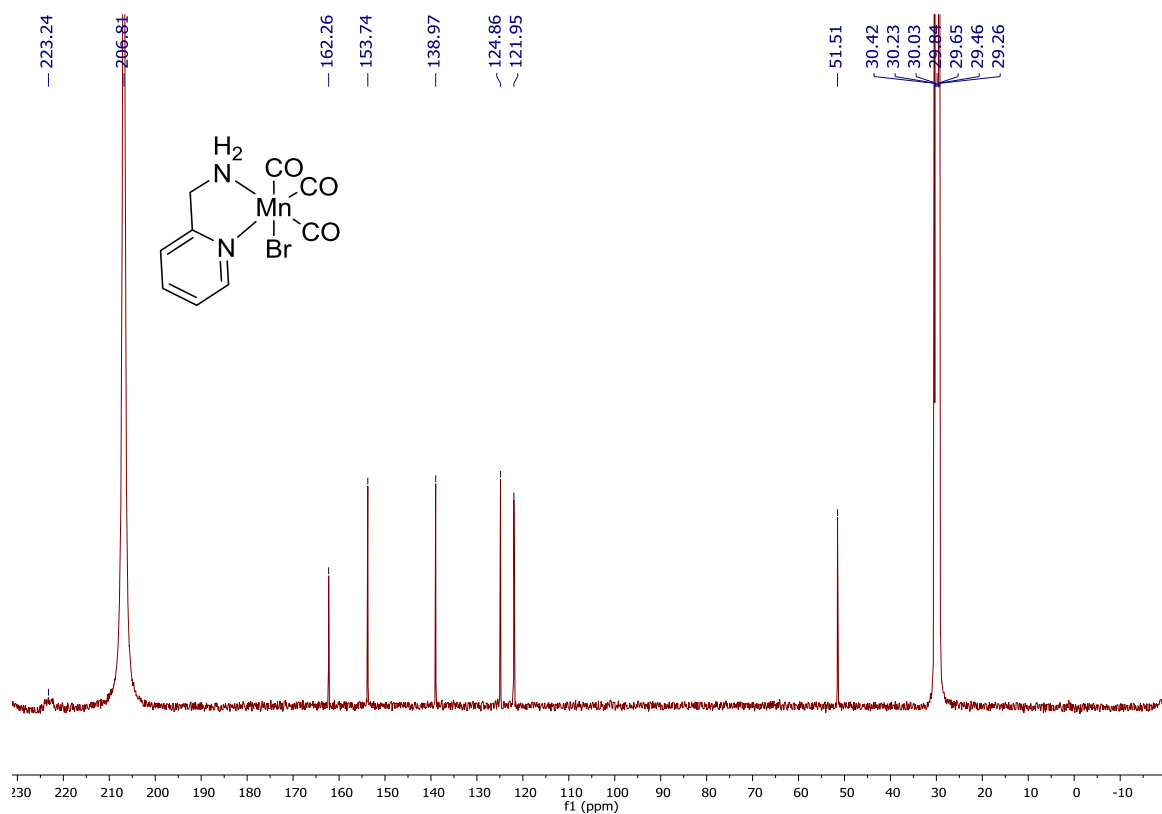


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of manganese complex 1 in $(\text{CD}_3)_2\text{CO}$ (101 MHz).

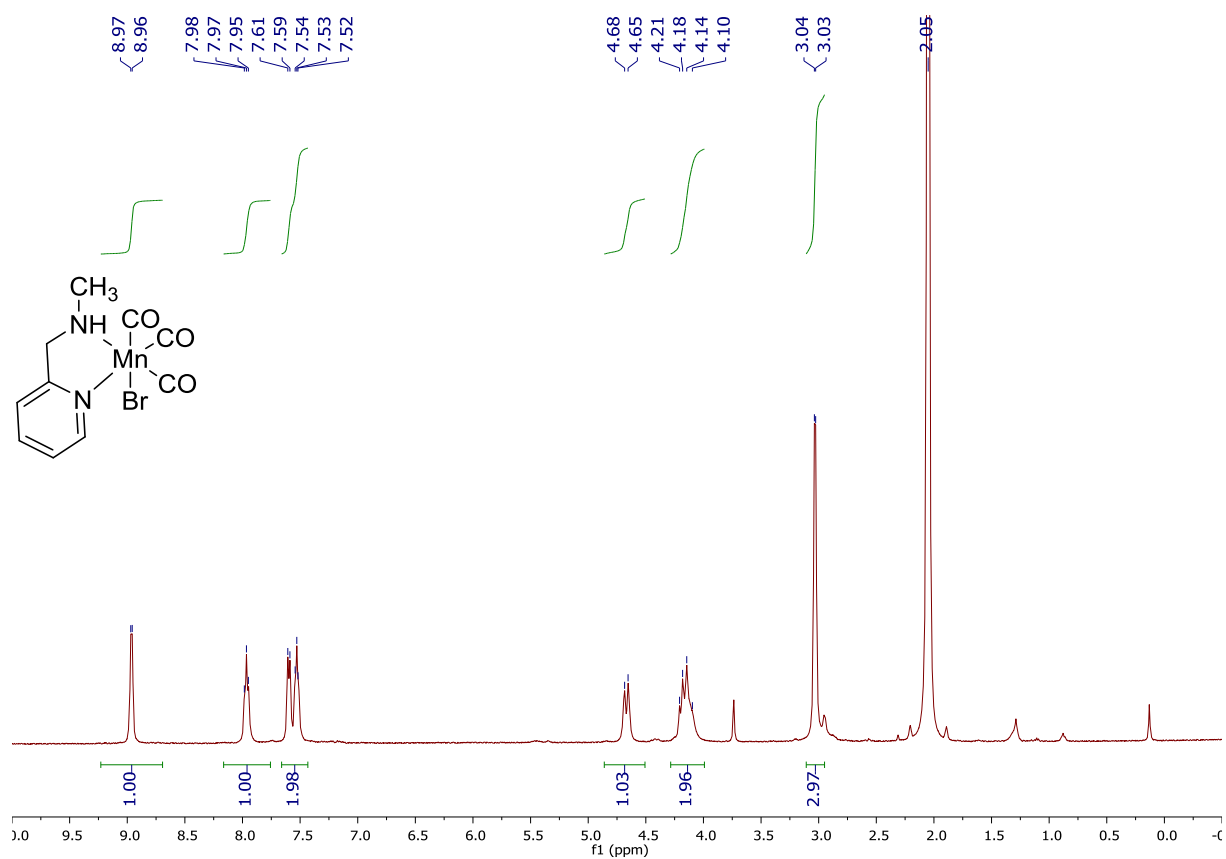


Figure S4: ^1H NMR spectrum of manganese complex **2** in $(\text{CD}_3)_2\text{CO}$ (400 MHz).

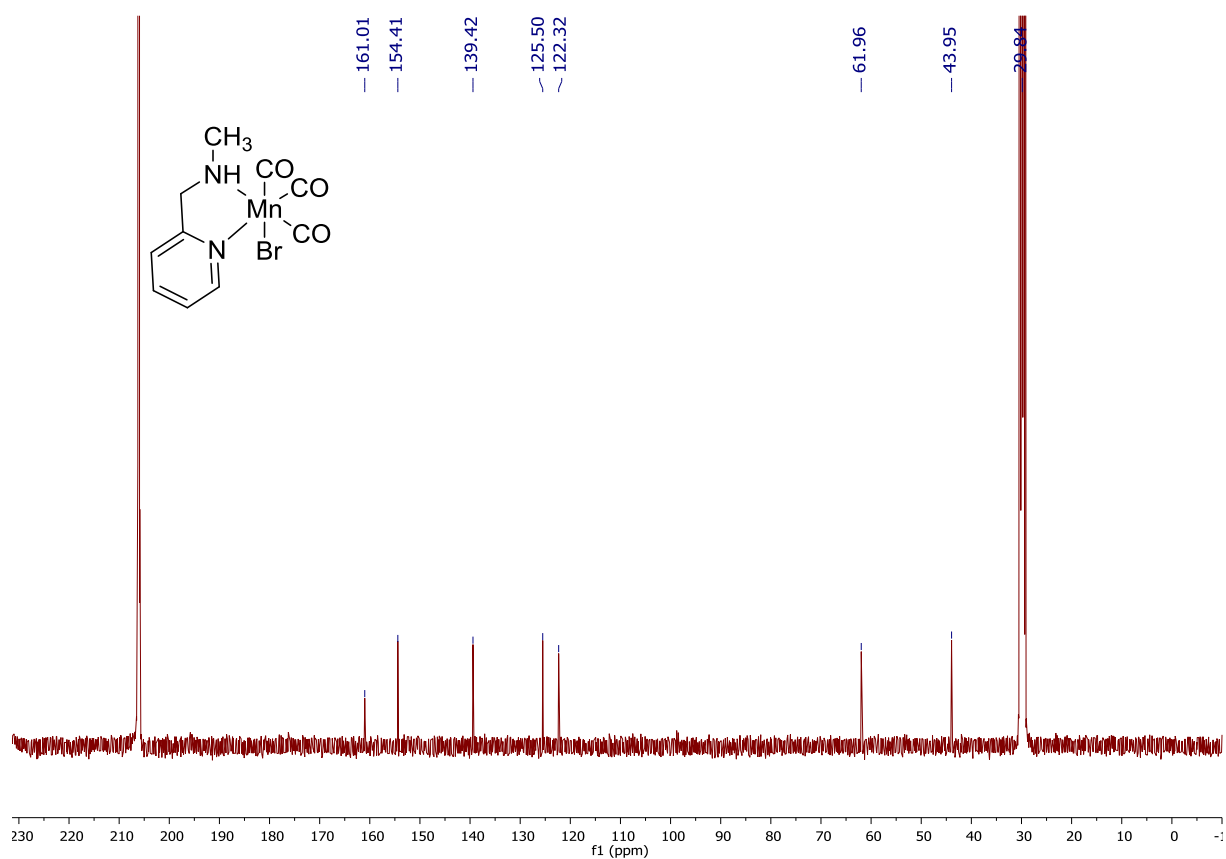


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of manganese complex **2** in $(\text{CD}_3)_2\text{CO}$ (101 MHz).

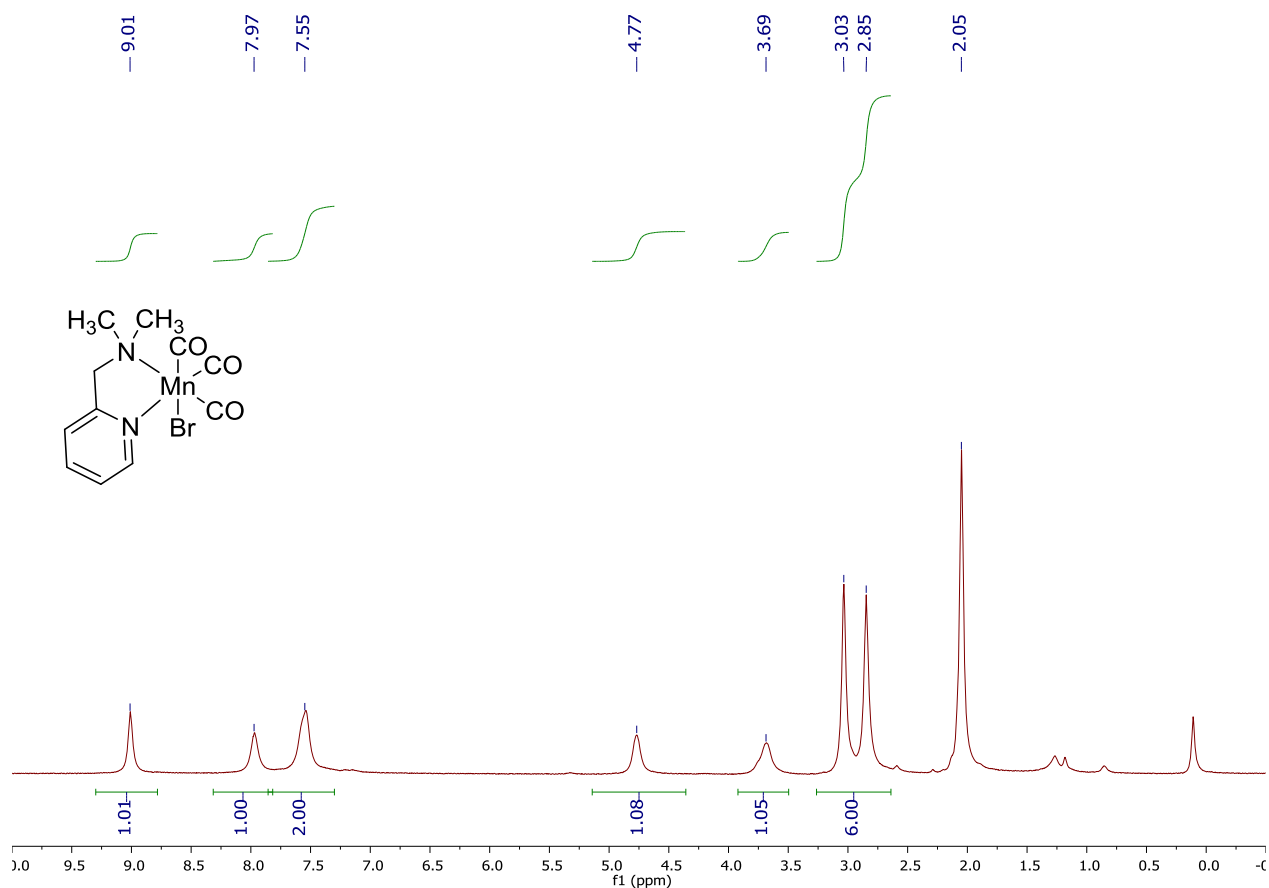


Figure S6: ^1H NMR spectrum of manganese complex **3** in $(\text{CD}_3)_2\text{CO}$ (400 MHz).

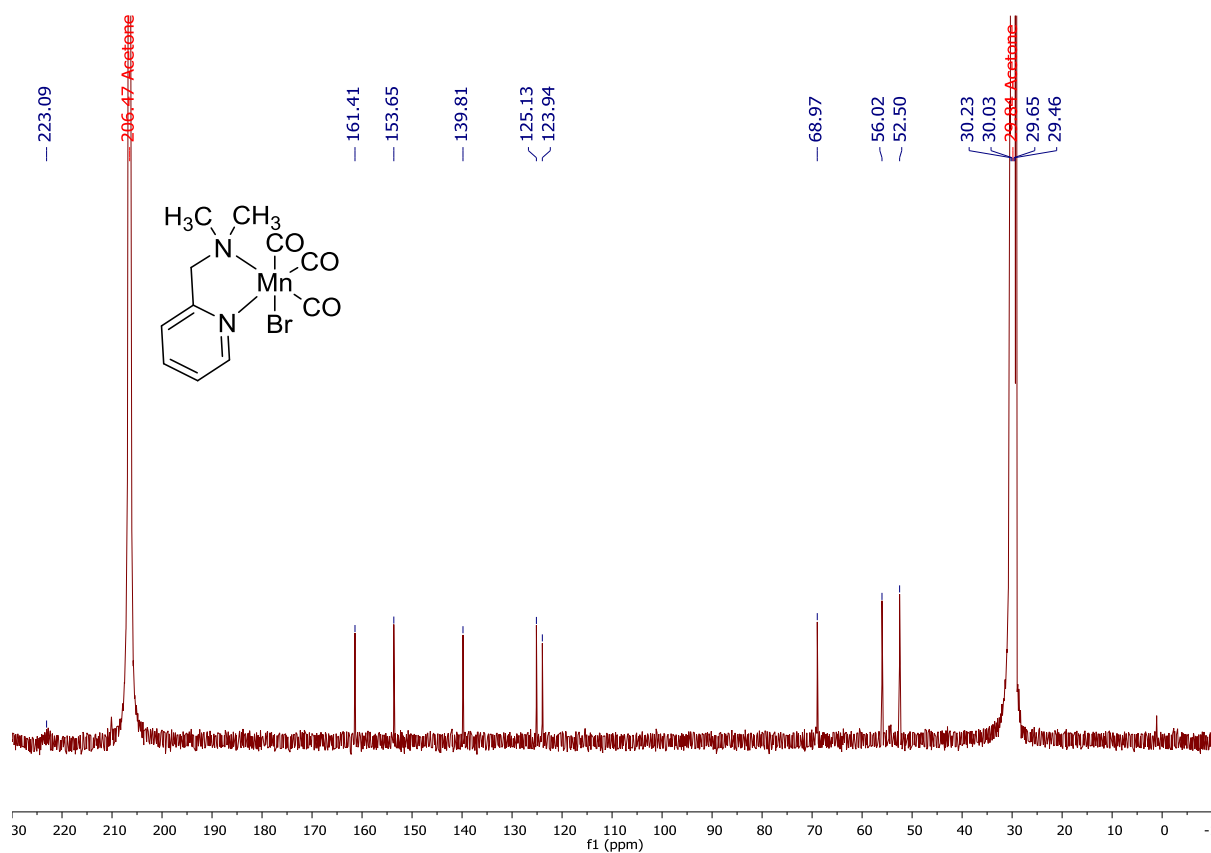
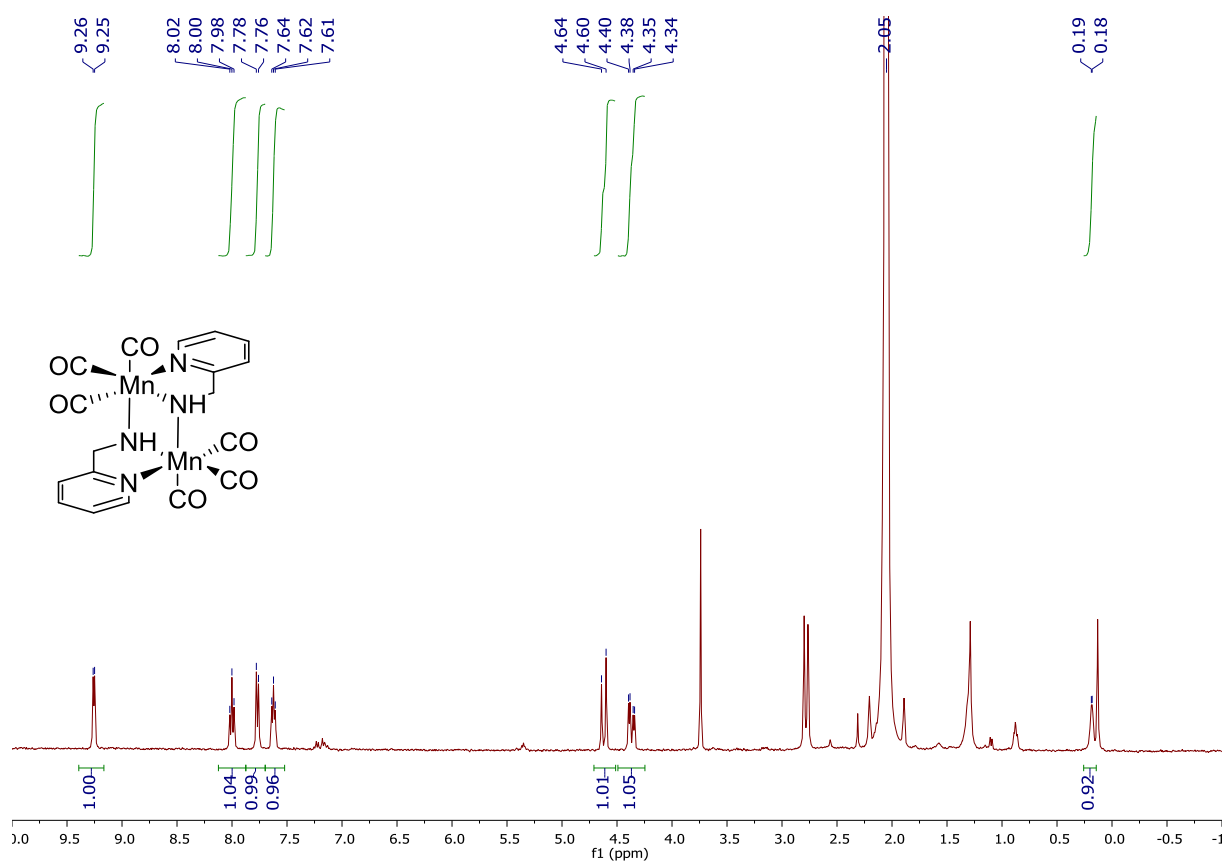
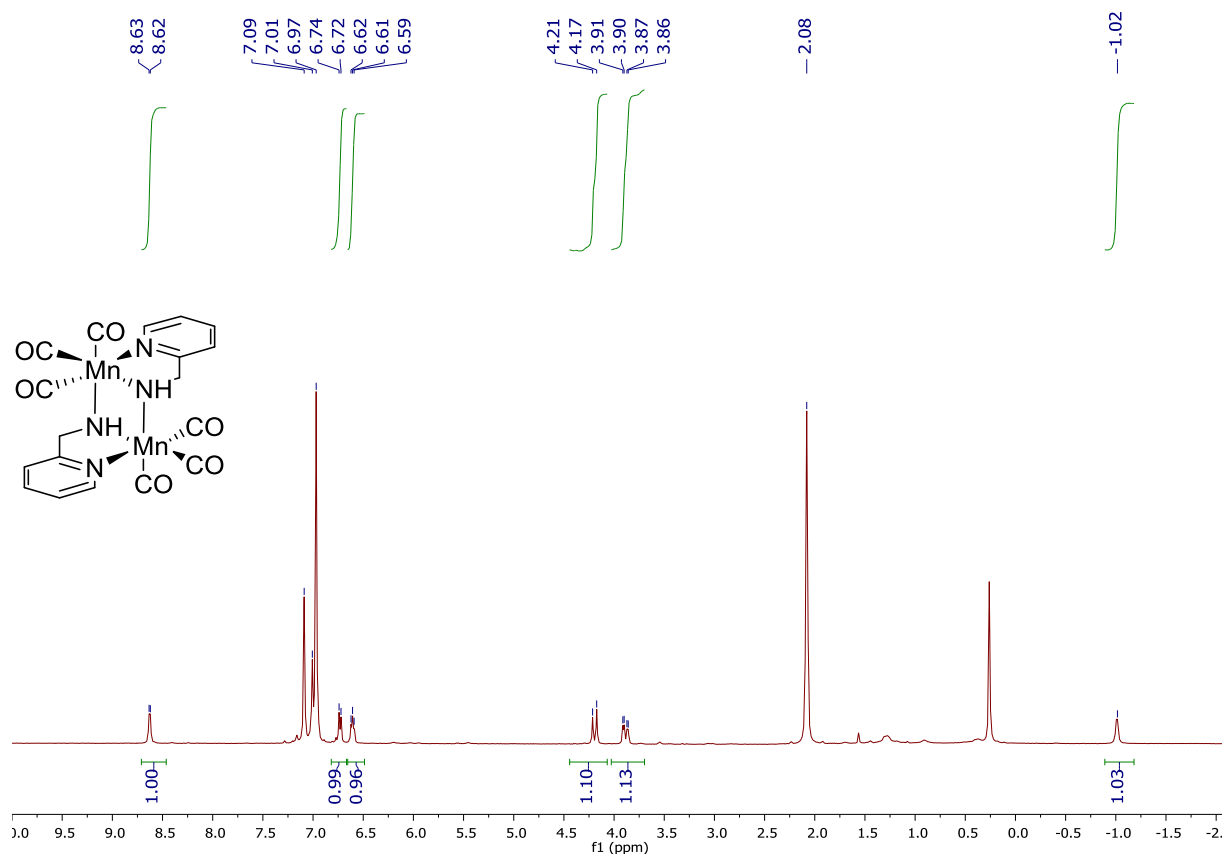


Figure S7: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of manganese complex **3** in $(\text{CD}_3)_2\text{CO}$ (101 MHz).



^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR data for the products of catalysis

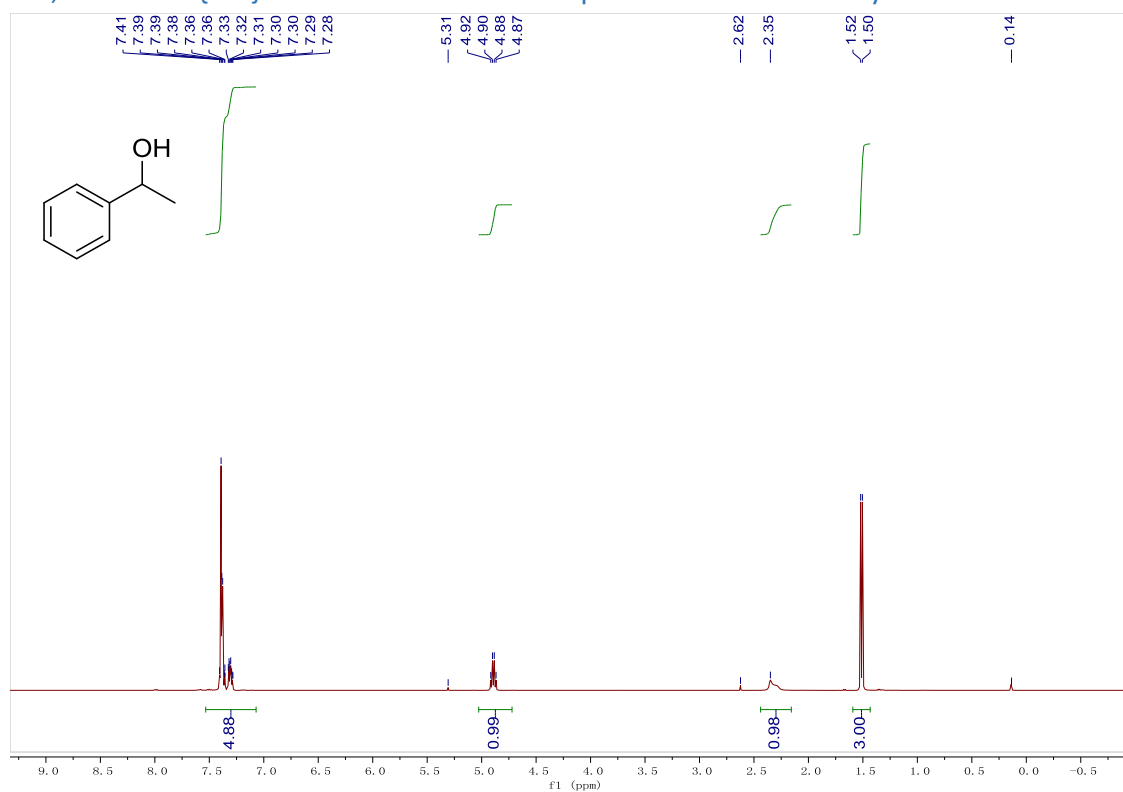


Figure S10: ^1H NMR spectrum of **1-Phenylethanol b1** in CDCl_3 recorded at 400MHz.

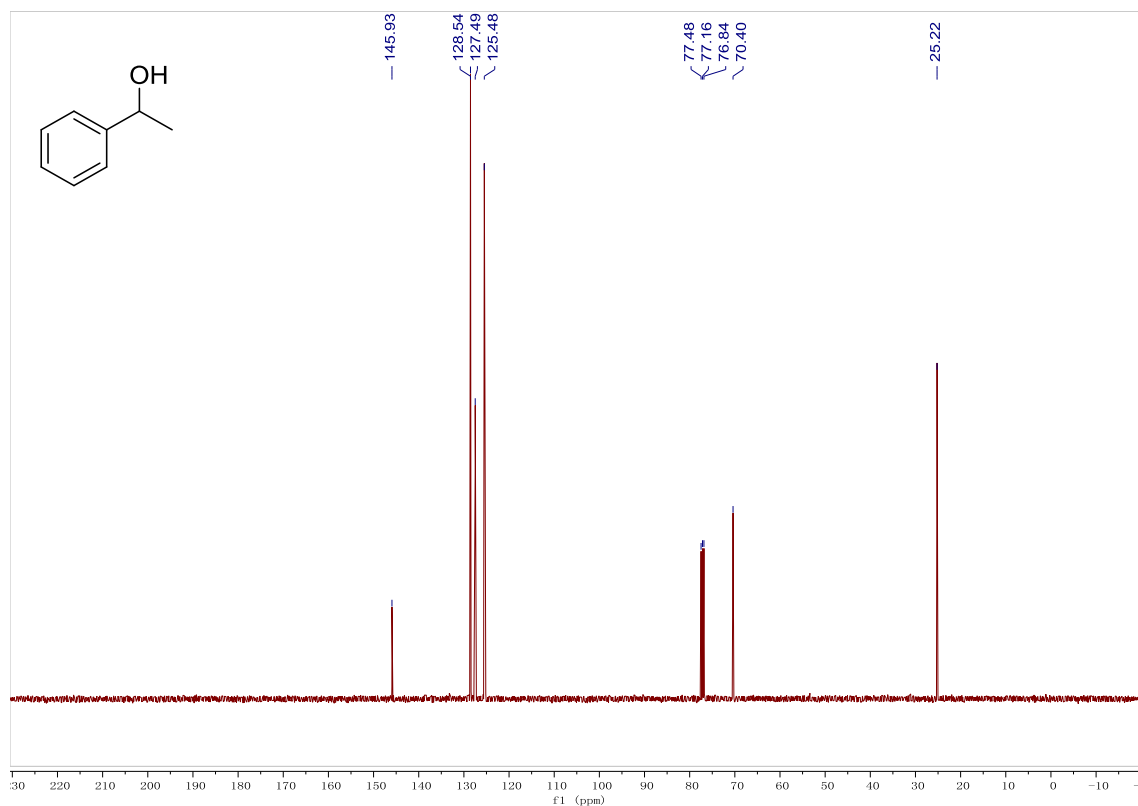


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1-Phenylethanol b1** in CDCl_3 recorded at 101 MHz.

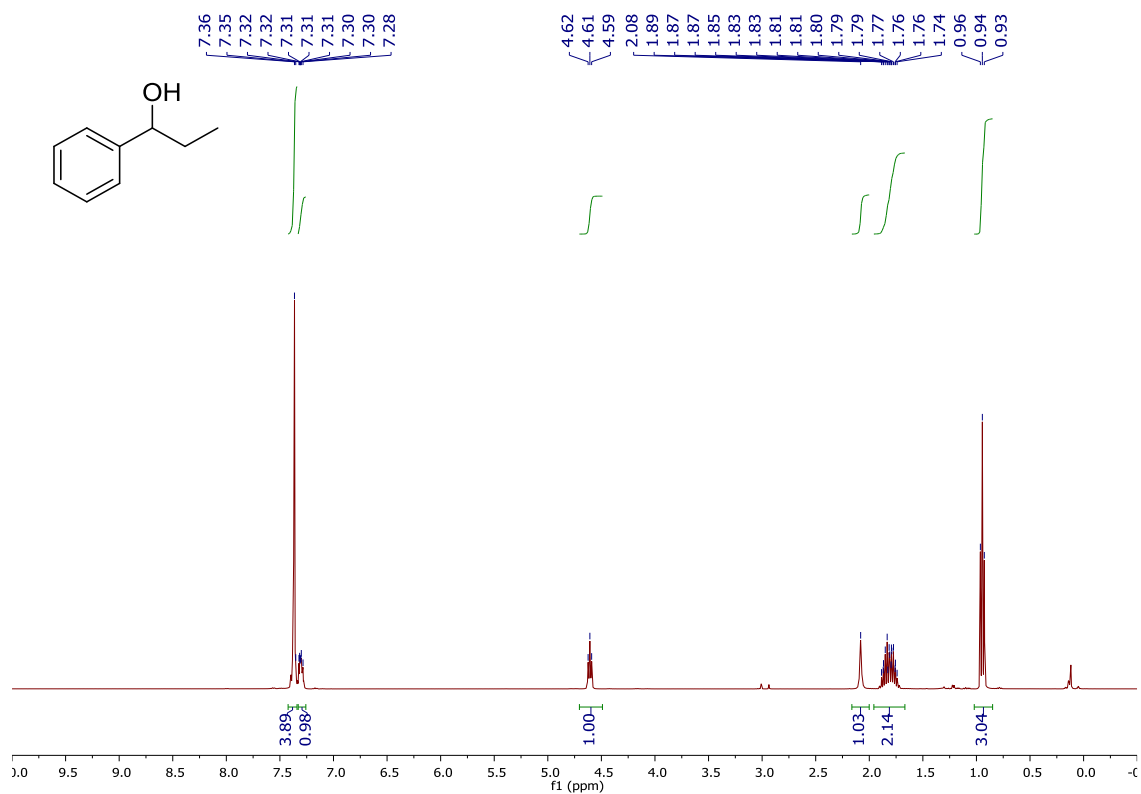


Figure S12: ¹H NMR spectrum of **1-Phenylpropan-1-ol b2** in CDCl₃ recorded at 400MHz.

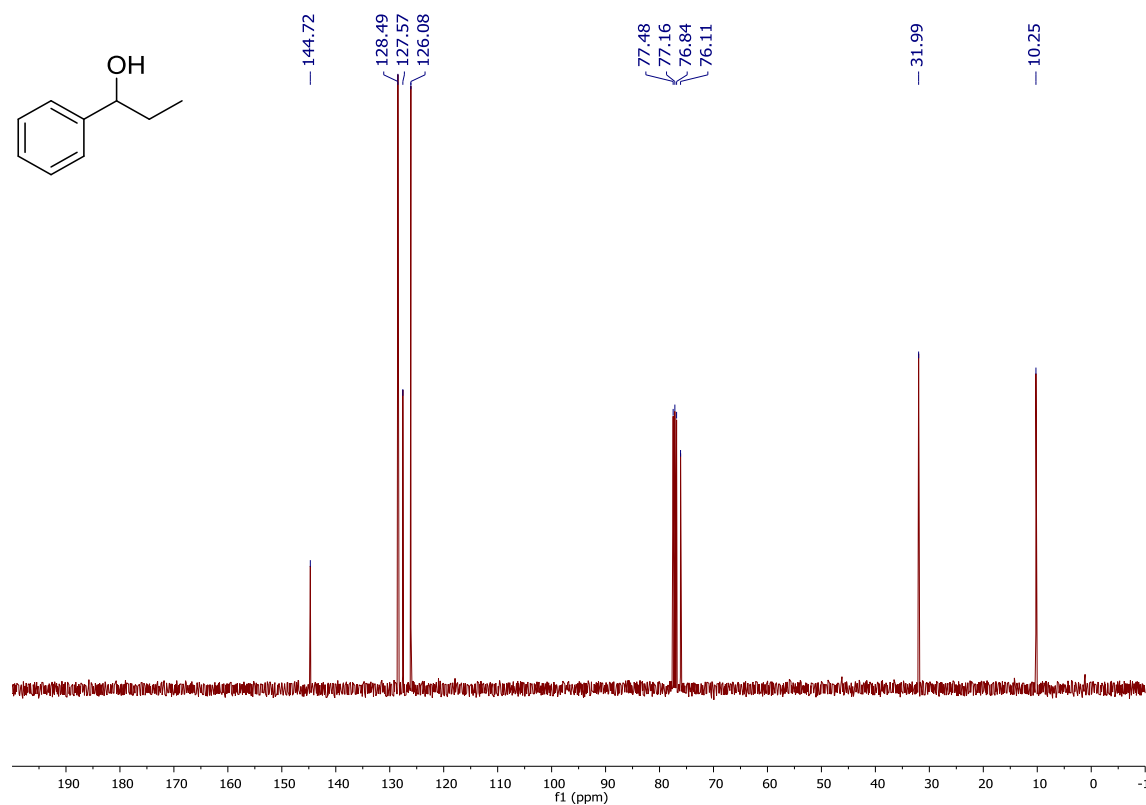


Figure S13: ¹³C{¹H} NMR spectrum of **1-Phenylpropan-1-ol b2** in CDCl₃ recorded at 101 MHz.

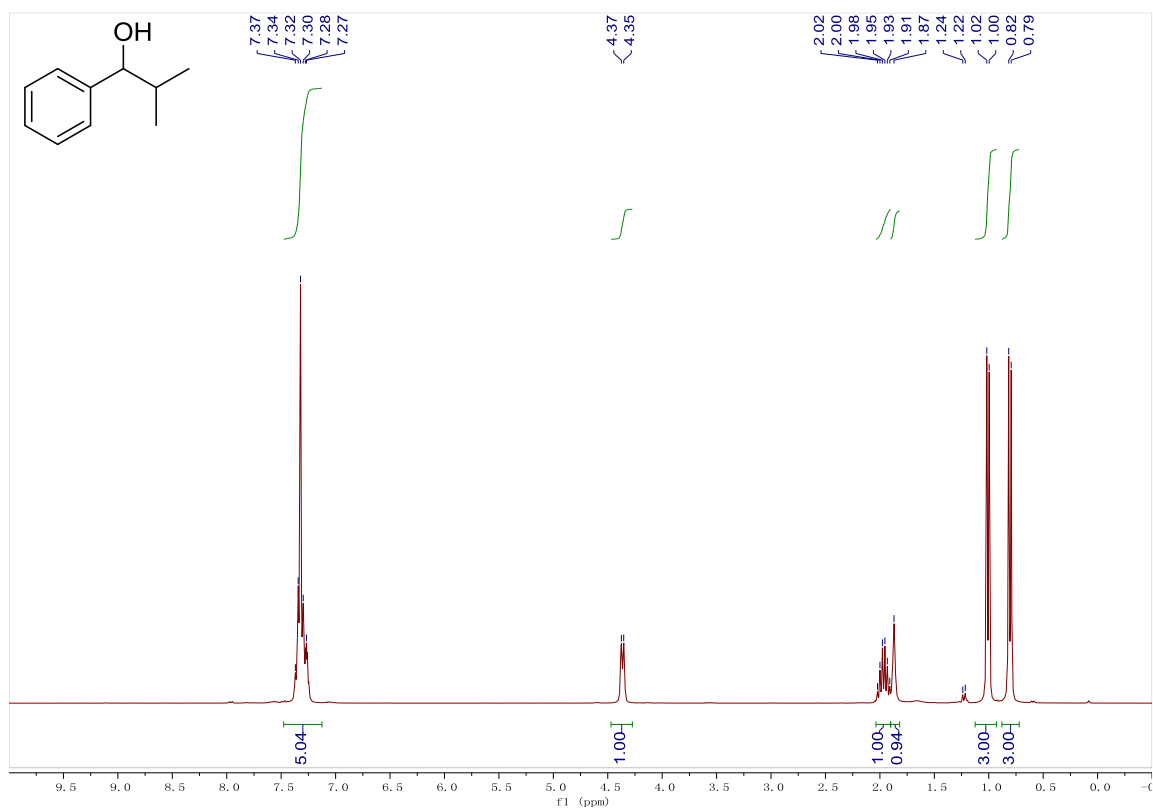


Figure S14: ^1H NMR spectrum of **2-Methyl-1-phenylpropan-1-ol b3** in CDCl_3 recorded at 400MHz.

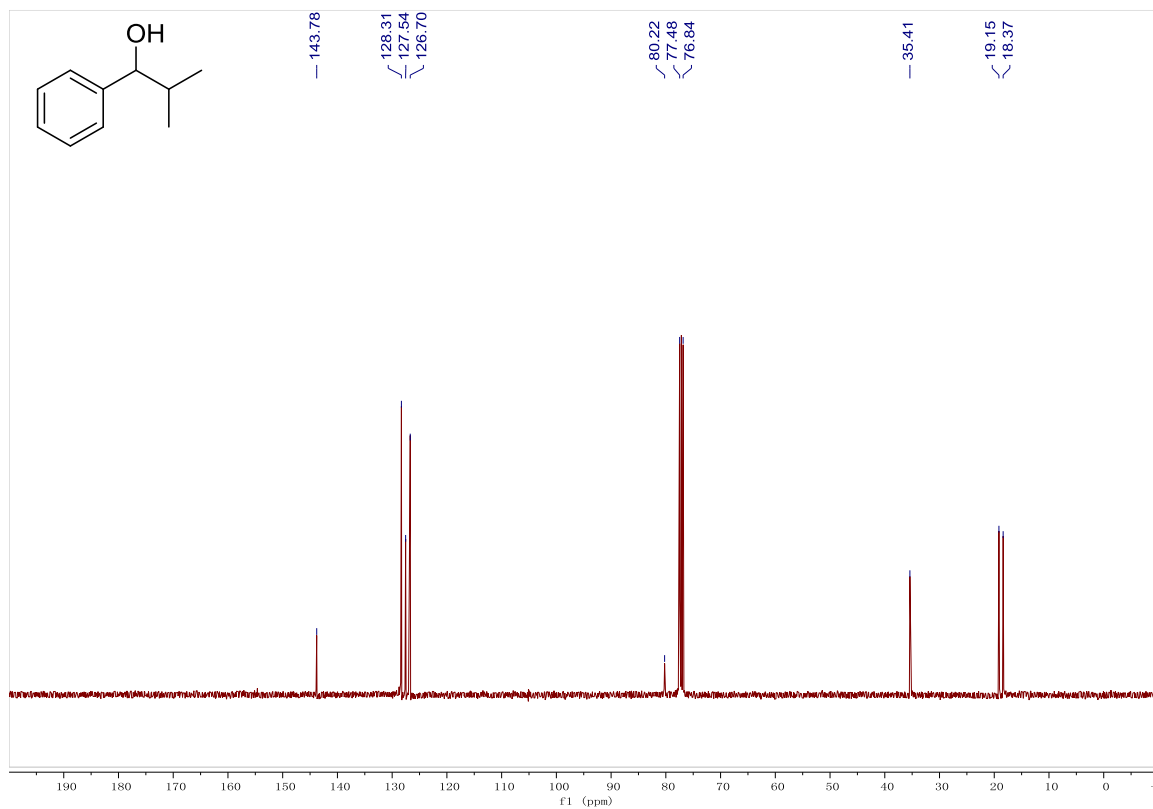


Figure S15: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-Methyl-1-phenylpropan-1-ol b3** in CDCl_3 recorded at 101 MHz.

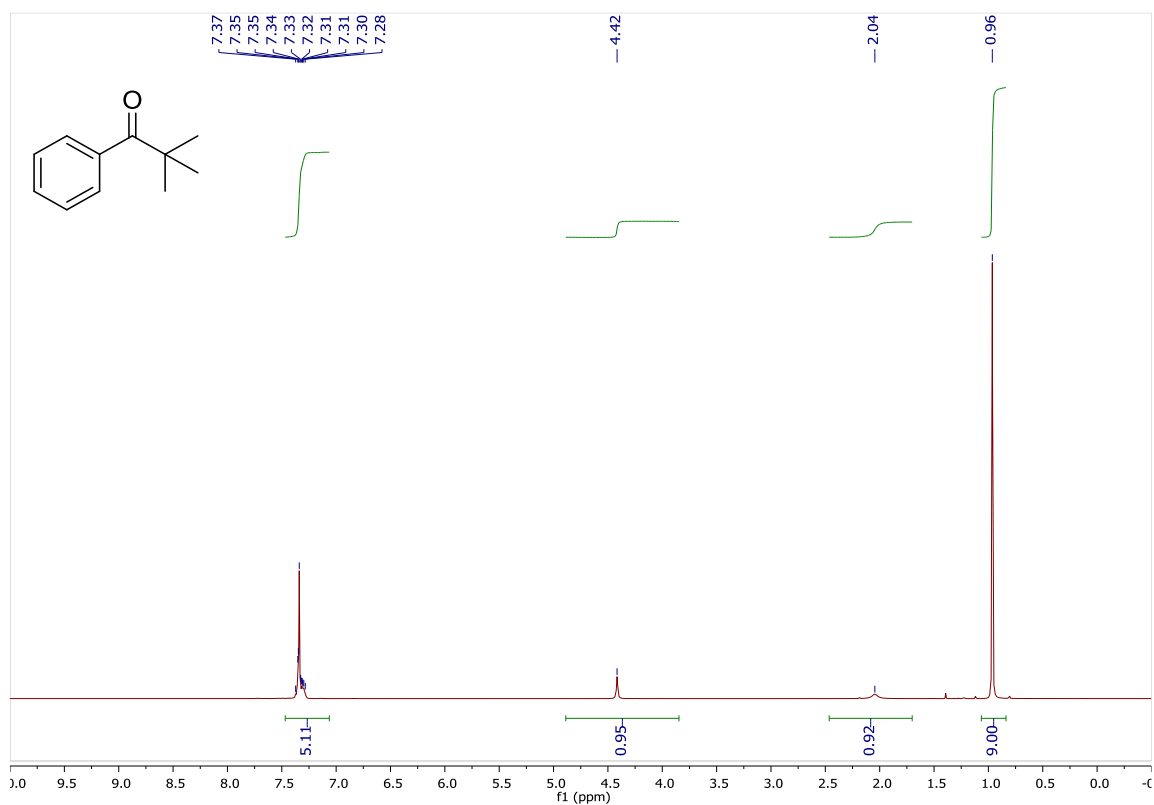


Figure S16: ^1H NMR spectrum of **2,2-Dimethyl-1-phenylpropan-1-ol b4** in CDCl_3 recorded at 400MHz.

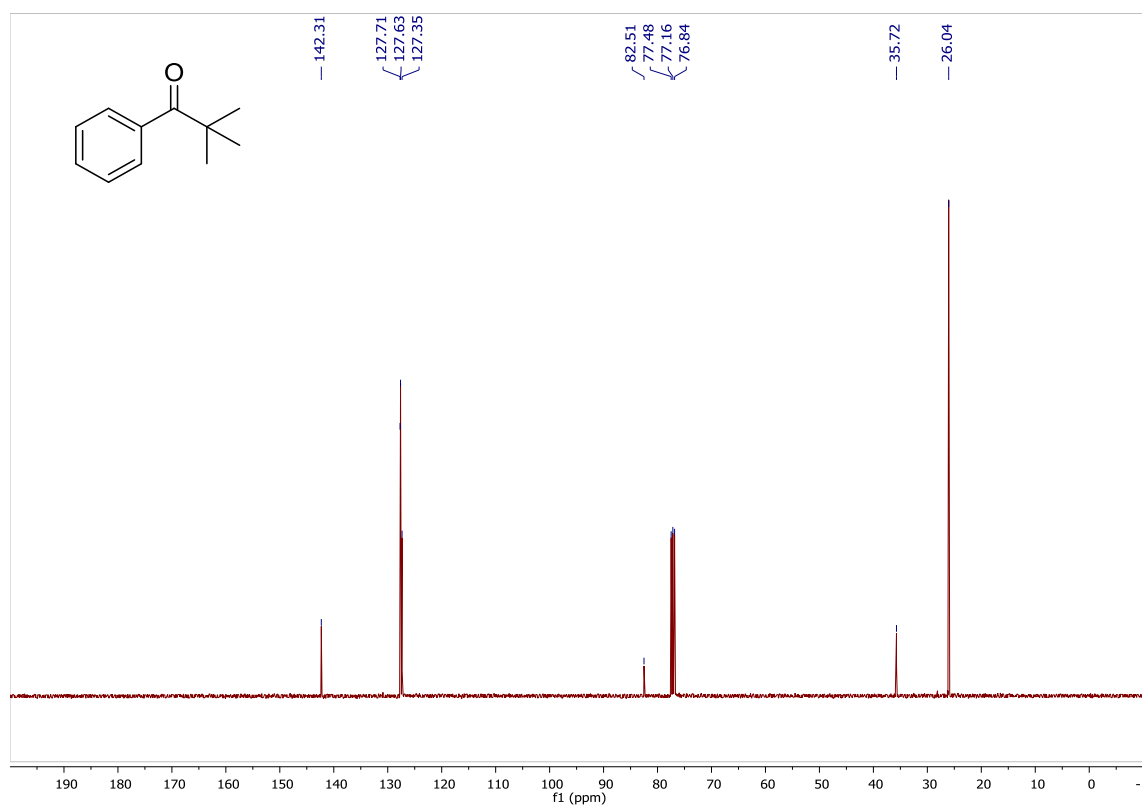


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2,2-Dimethyl-1-phenylpropan-1-ol b4** in CDCl_3 recorded at 101 MHz.

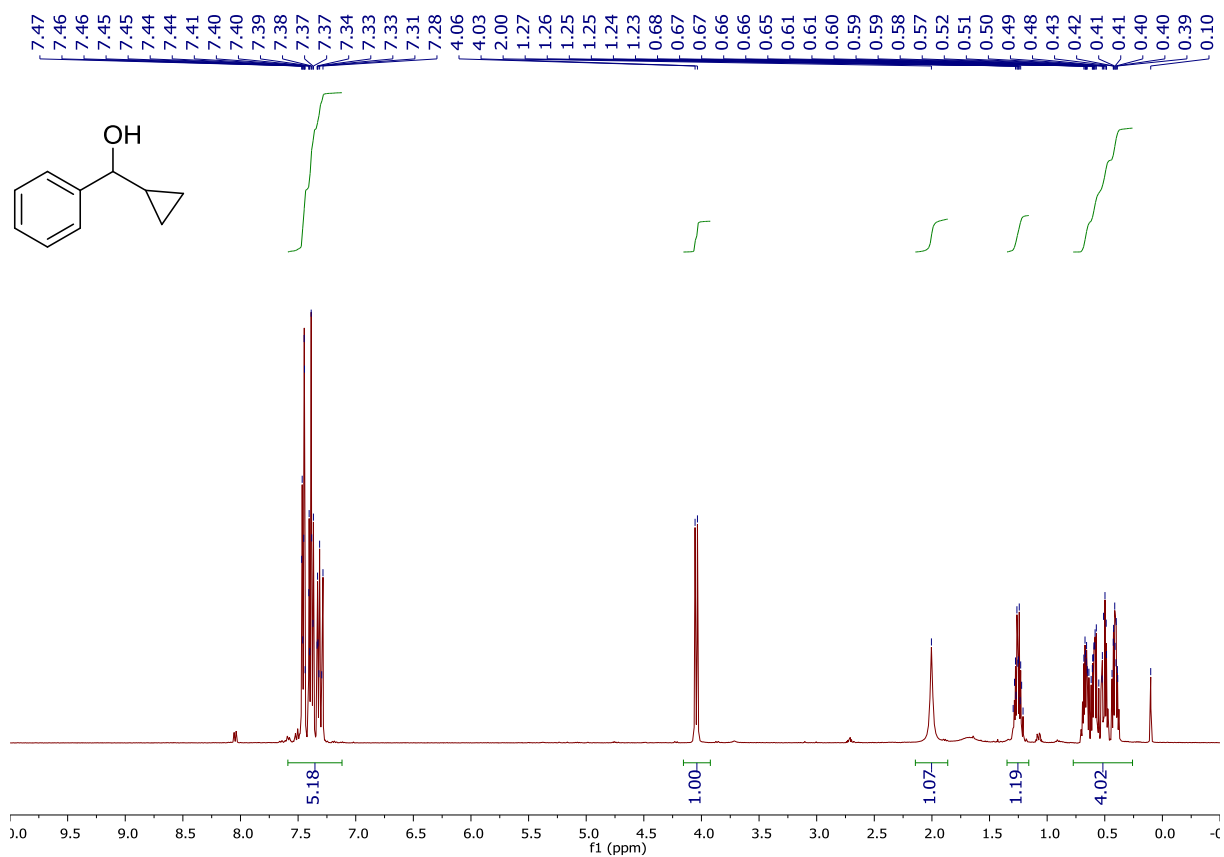


Figure S18: ¹H NMR spectrum of Cyclopropylphenylmethanol **b5** in CDCl₃ recorded at 400MHz.

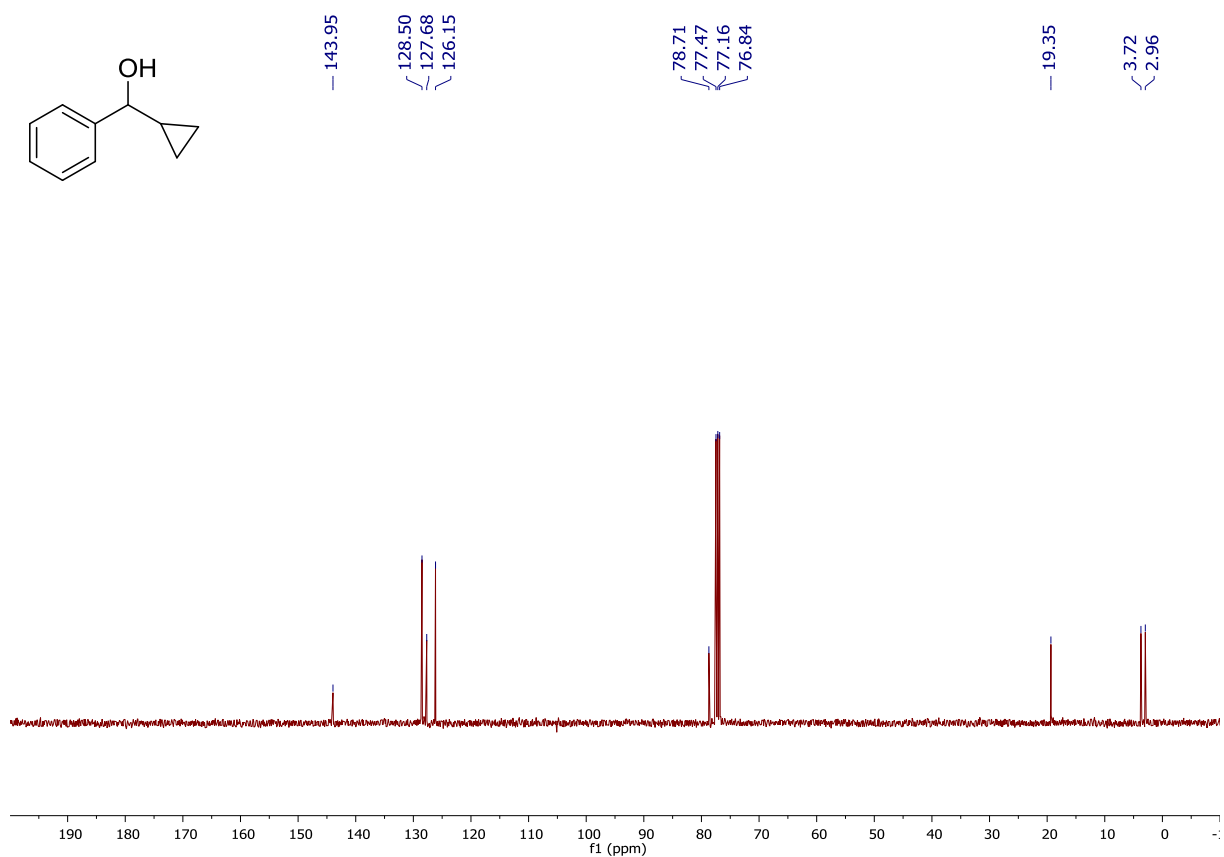


Figure S19: ¹³C{¹H} NMR spectrum of Cyclopropylphenylmethanol **b5** in CDCl₃ recorded at 101 MHz.

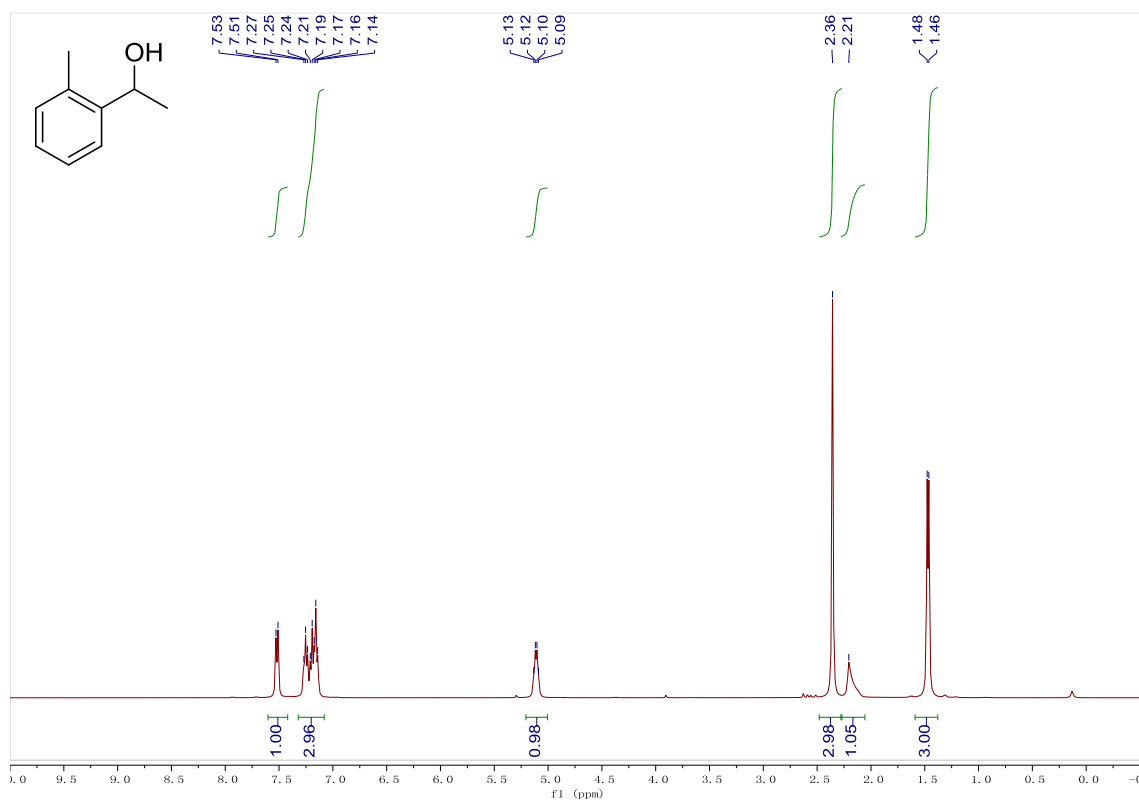


Figure S20: ¹H NMR spectrum of **1-(2-Methylphenyl)ethanol b6** in CDCl₃ recorded at 400MHz.

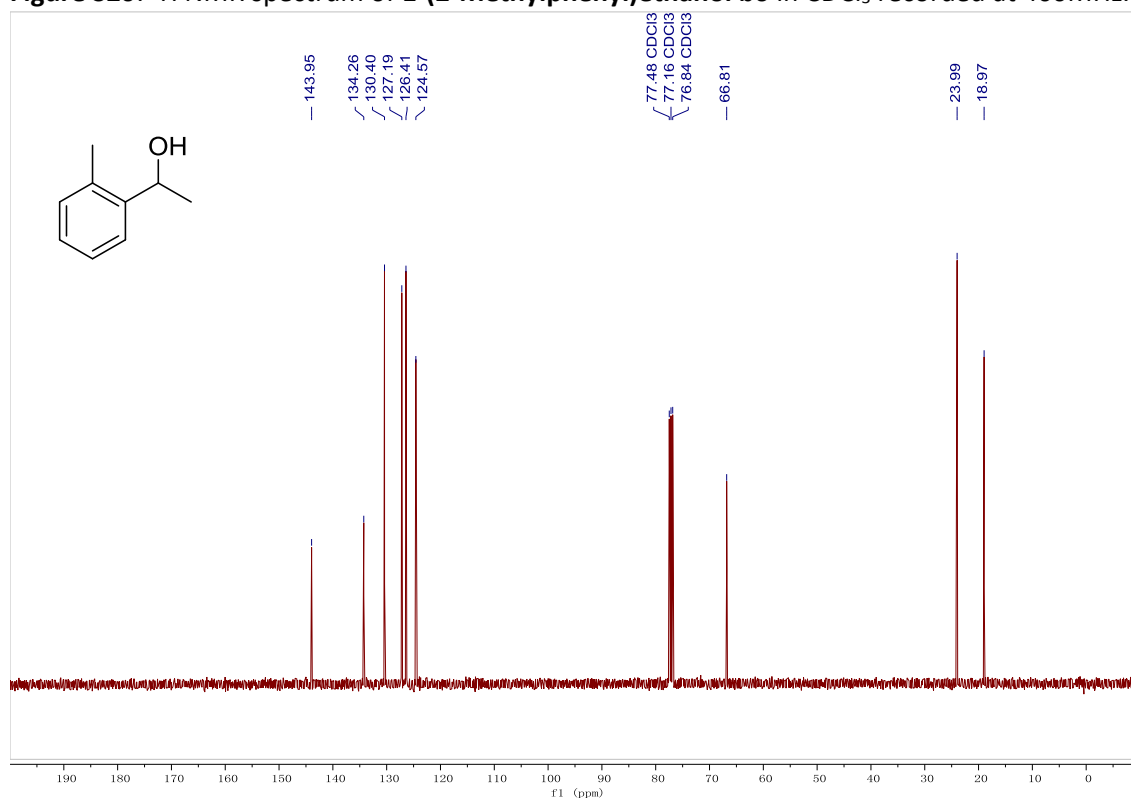


Figure S21: ¹³C{¹H} NMR spectrum of **1-(2-Methylphenyl)ethanol b6** in CDCl₃ recorded at 101 MHz.

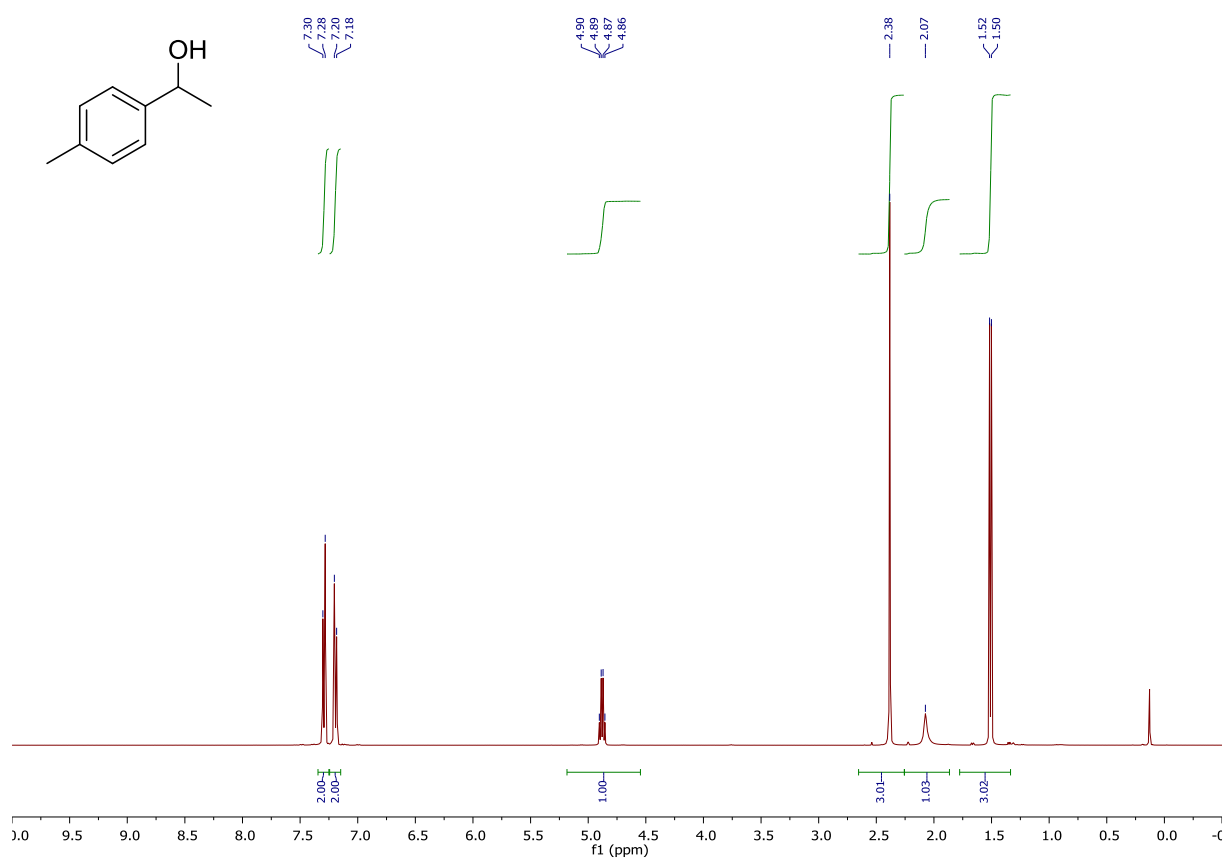


Figure S22: ¹H NMR spectrum of 1-(4-Methylphenyl)ethanol b7 in CDCl₃ recorded at 400MHz.

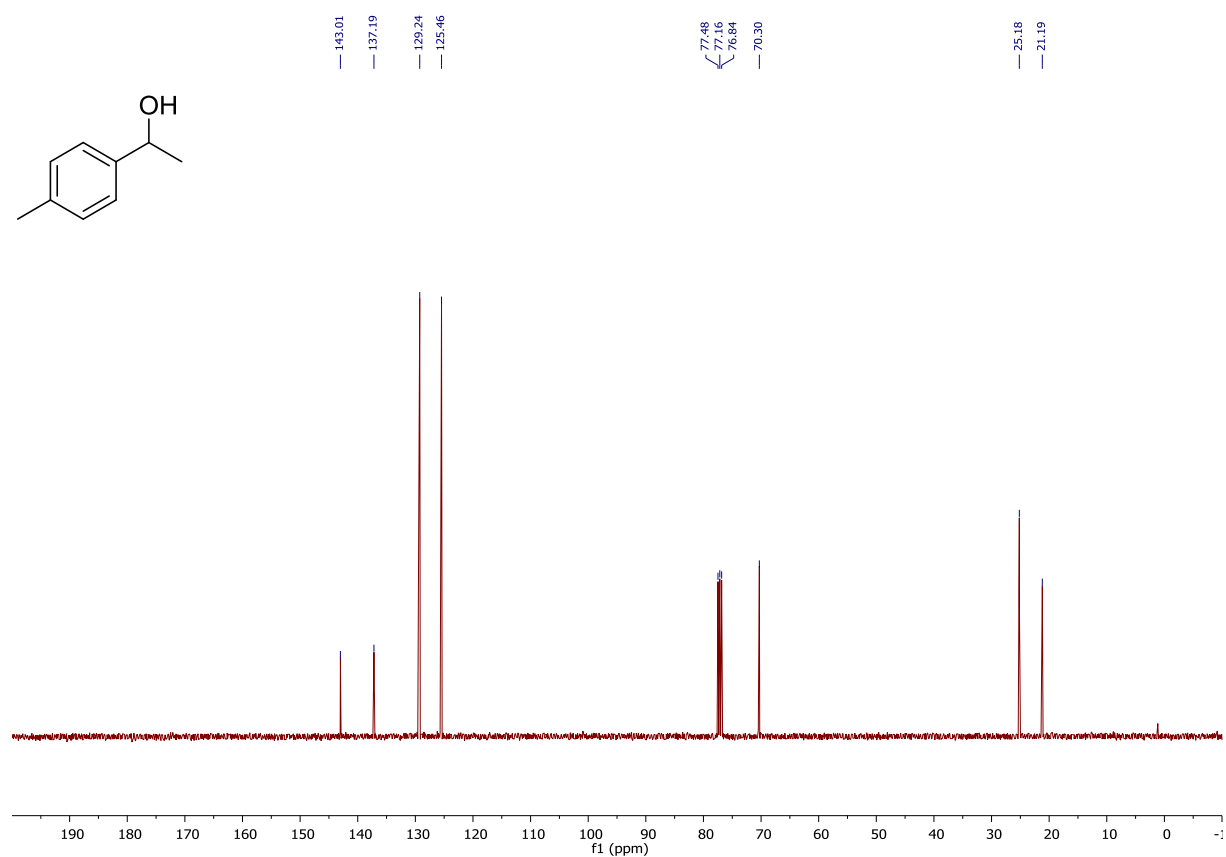


Figure S23: ¹³C{¹H} NMR spectrum of 1-(4-Methylphenyl)ethanol b7 in CDCl₃ recorded at 101 MHz.

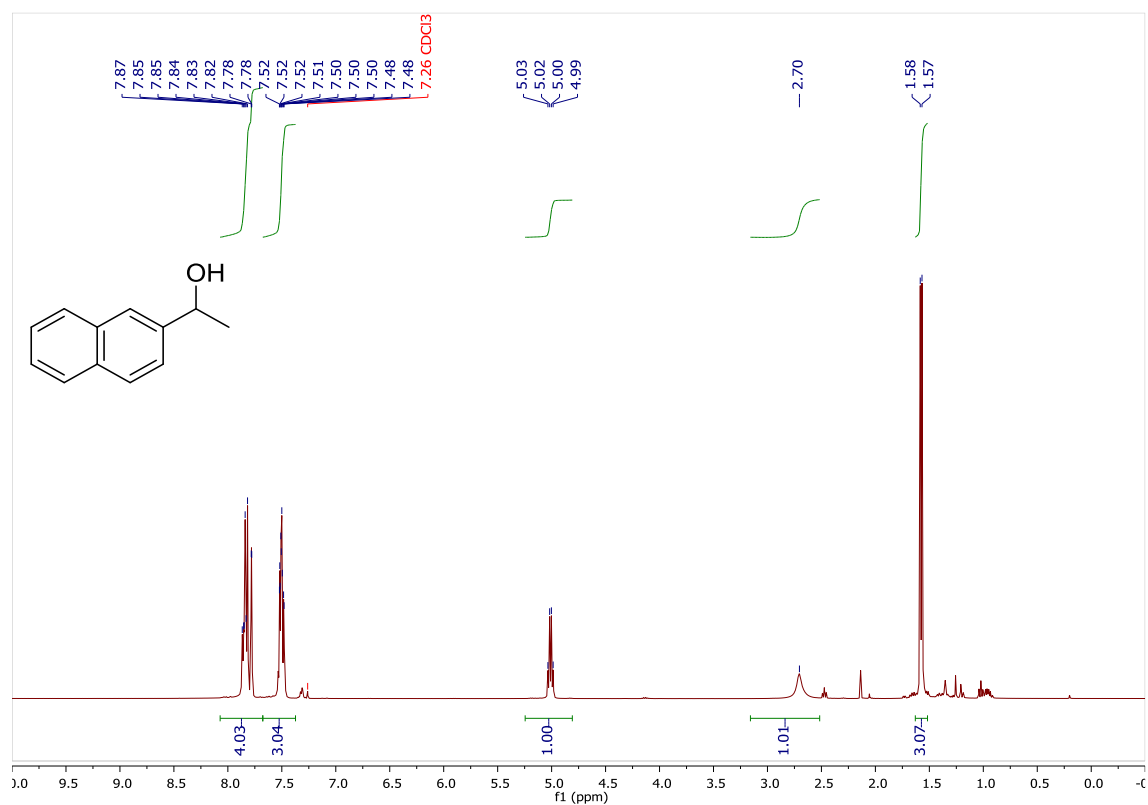


Figure S24: ¹H NMR spectrum of 1-(2-Naphthyl)ethanol b8 in CDCl₃ recorded at 400MHz.

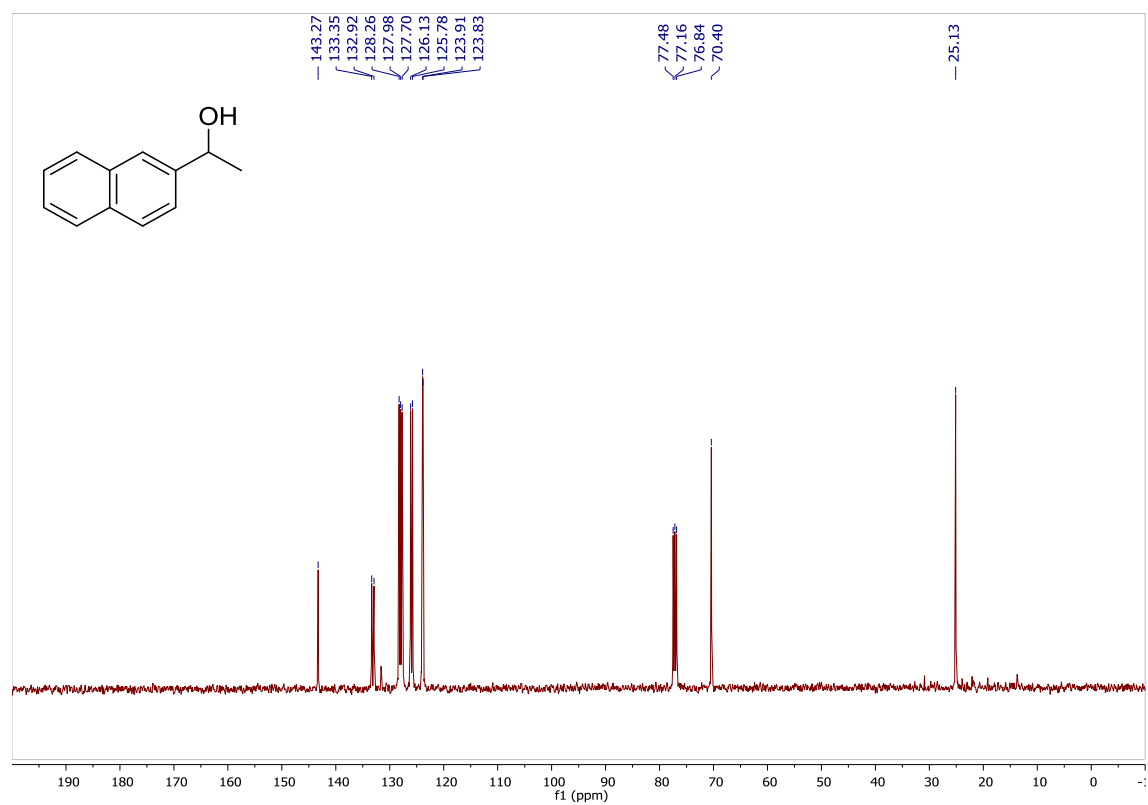


Figure S25: ¹³C{¹H} NMR spectrum of 1-(2-Naphthyl)ethanol b8 in CDCl₃ recorded at 101 MHz.

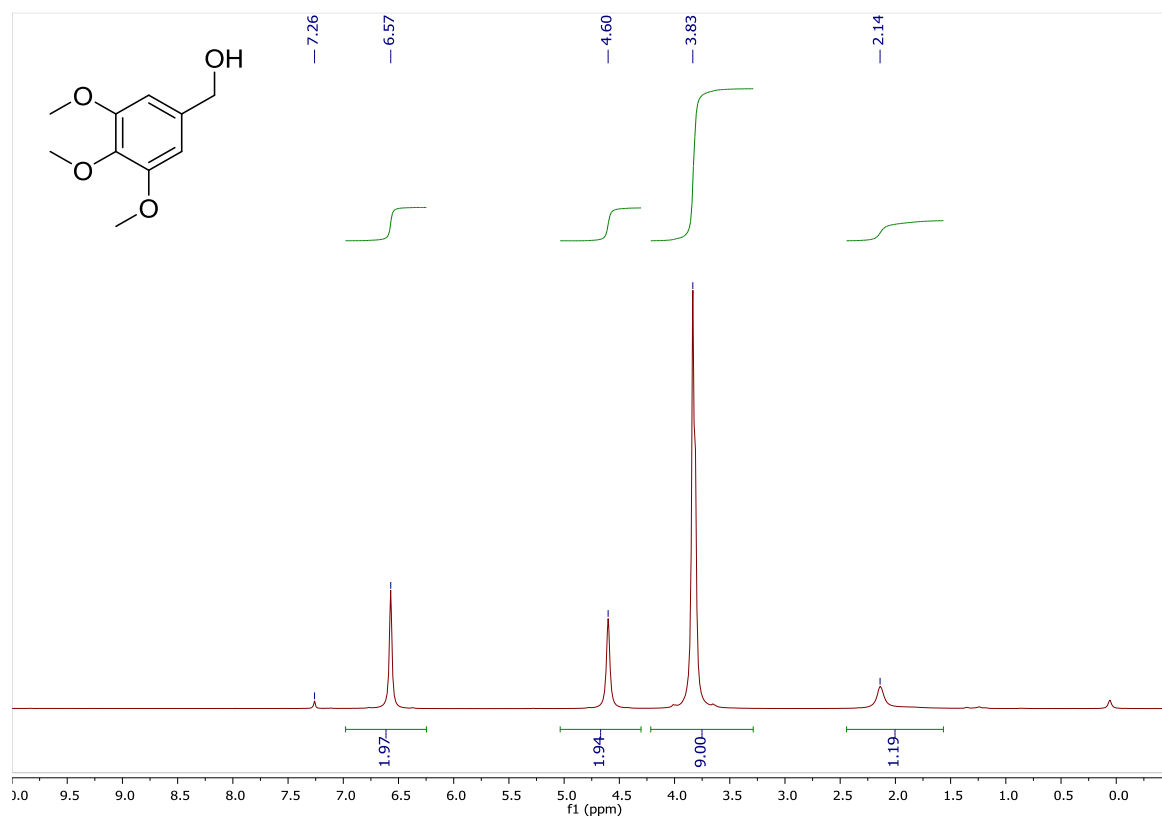


Figure S26: ¹H NMR spectrum of (3,4,5-Trimethoxyphenyl)methanol **b10** in CDCl₃ recorded at 400MHz.

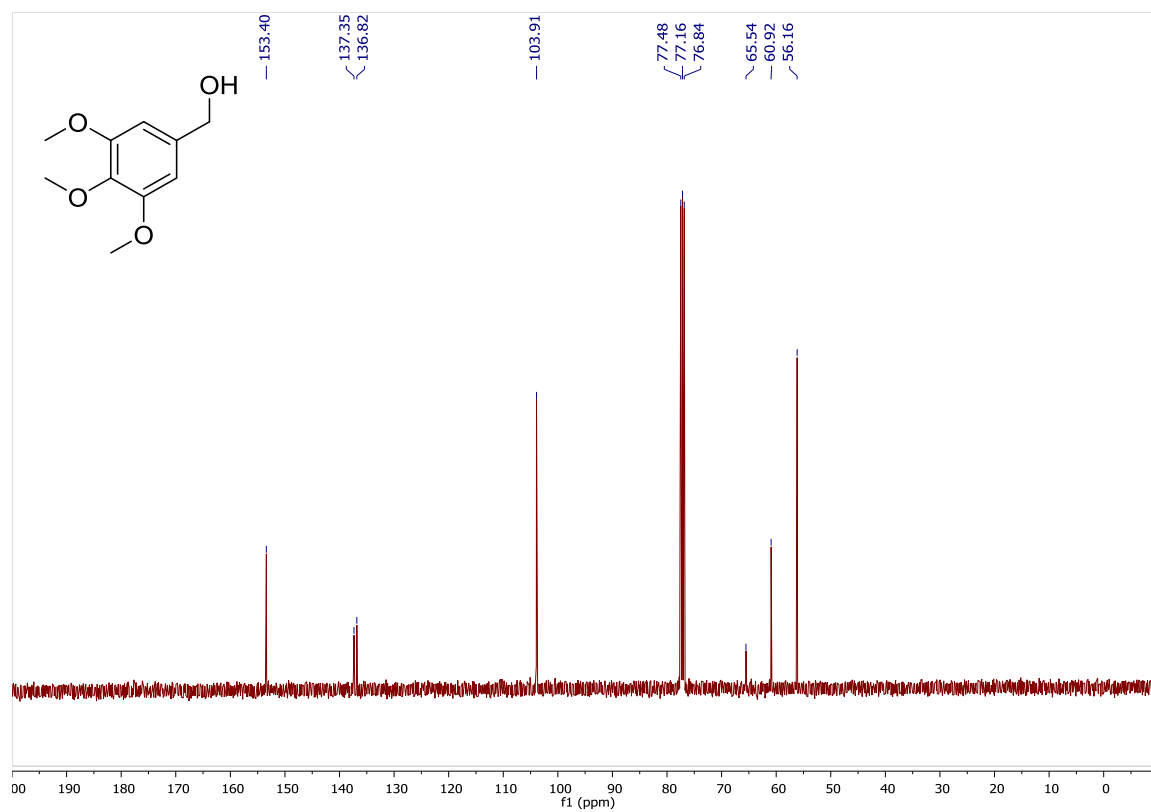


Figure S27: ¹³C{¹H} NMR spectrum of (3,4,5-Trimethoxyphenyl)methanol **b10** in CDCl₃ recorded at 101 MHz.

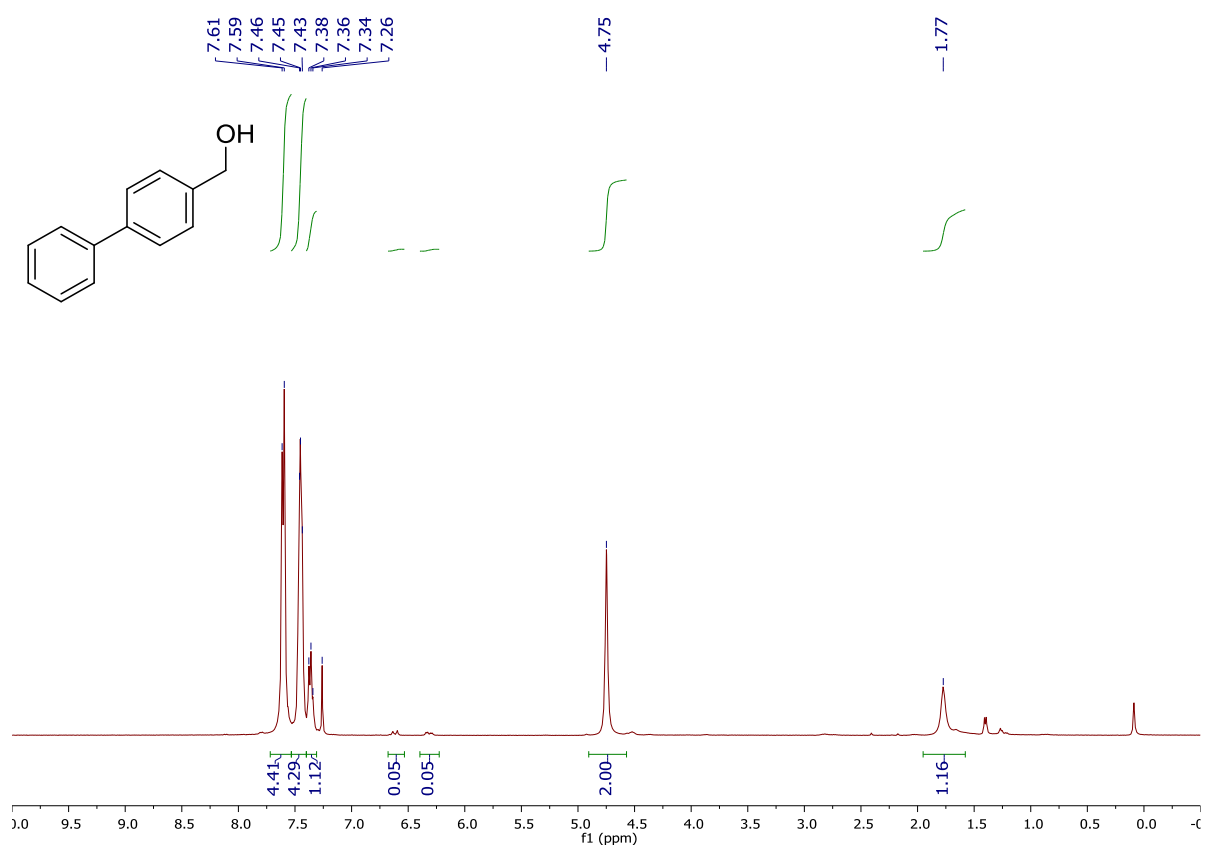


Figure S28: ¹H NMR spectrum of [1,1'-Biphenyl]-4-yl-methanol **b11** in CDCl₃ recorded at 400MHz

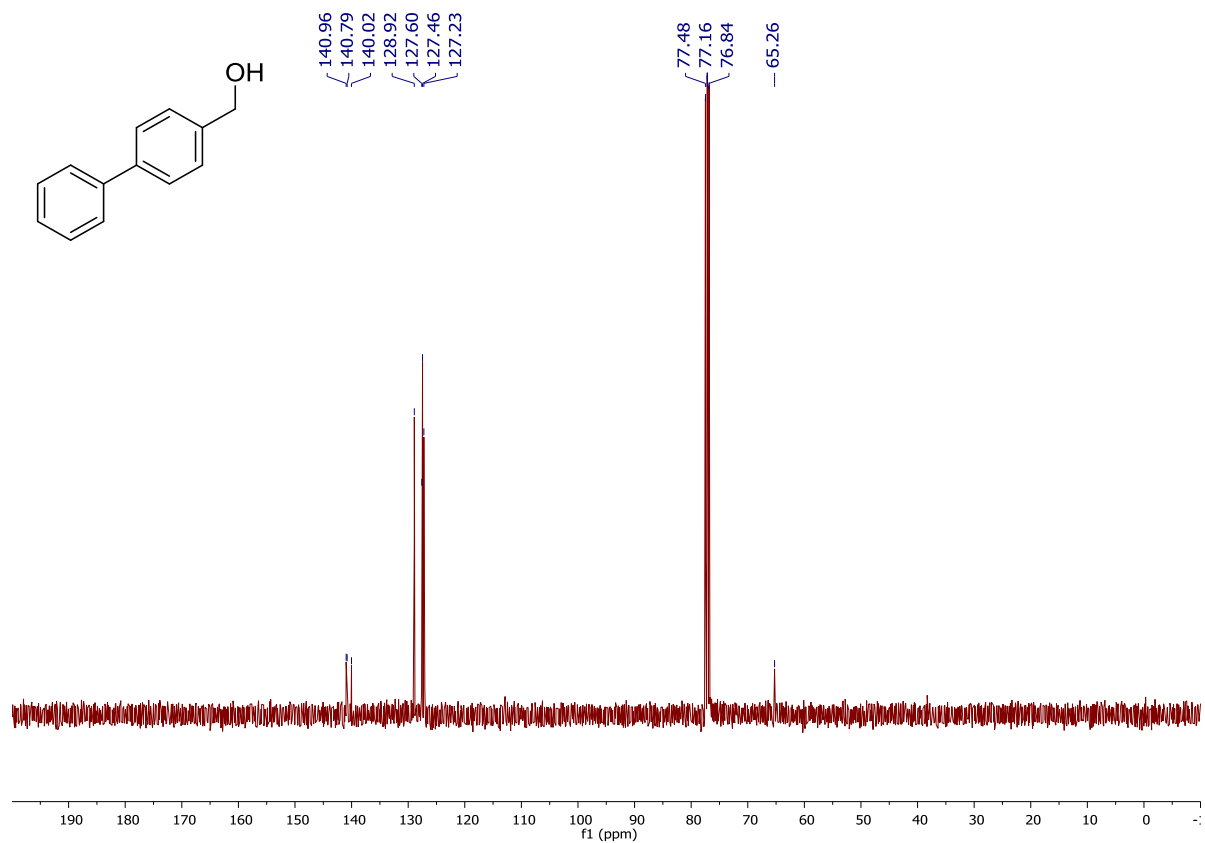


Figure S29: ¹³C{¹H} NMR spectrum of [1,1'-Biphenyl]-4-yl-methanol **b11** in CDCl₃ recorded at 101 MHz.

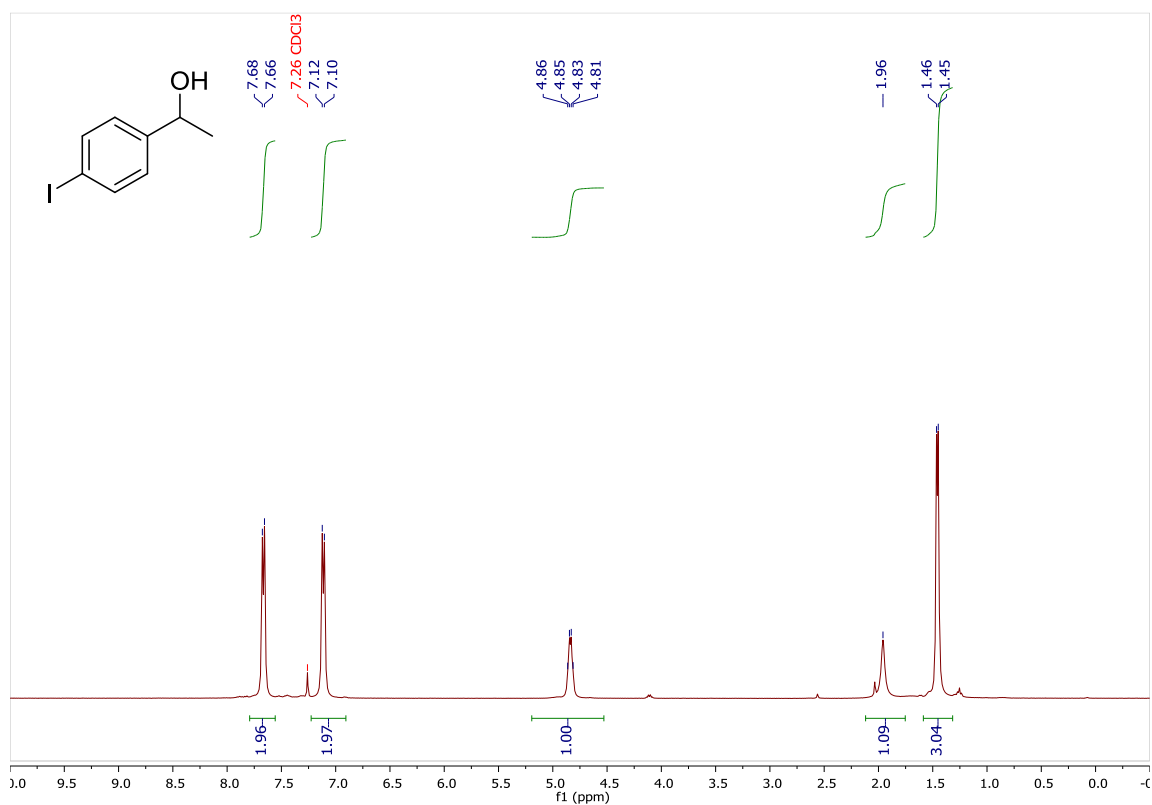


Figure S30: ¹H NMR spectrum of **1-(4-iodophenyl)ethanol b12** in CDCl₃ recorded at 400MHz

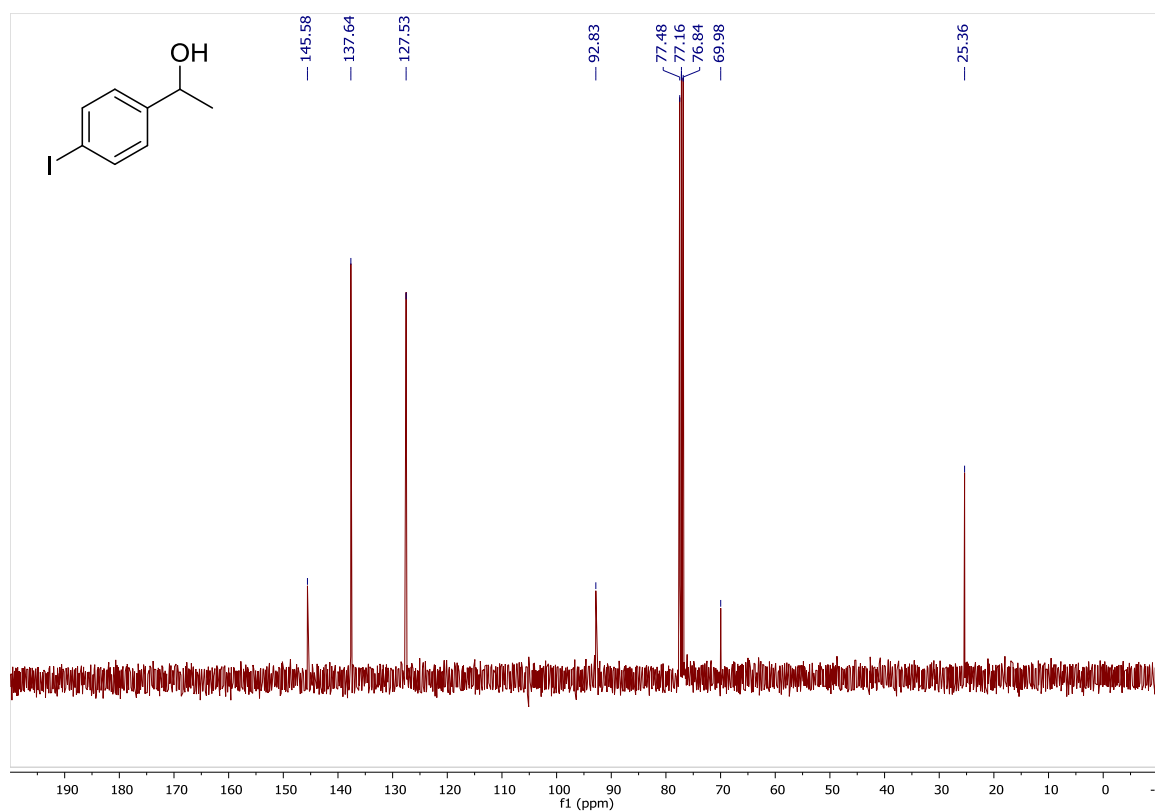


Figure S31: ¹³C{¹H} NMR spectrum of **1-(4-iodophenyl)ethanol b12** in CDCl₃ recorded at 101 MHz.

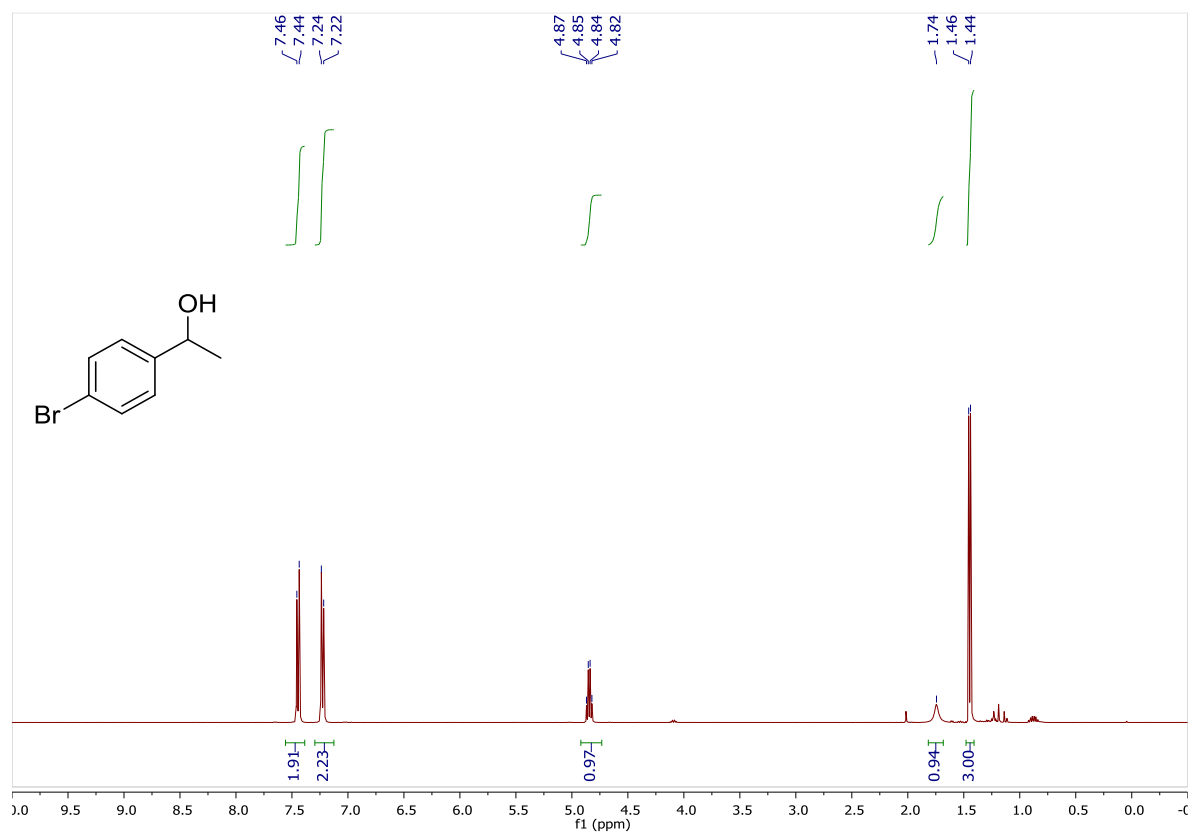


Figure S32: ^1H NMR spectrum of 1-(4-Bromophenyl)ethanol **b13** in CDCl_3 recorded at 400MHz

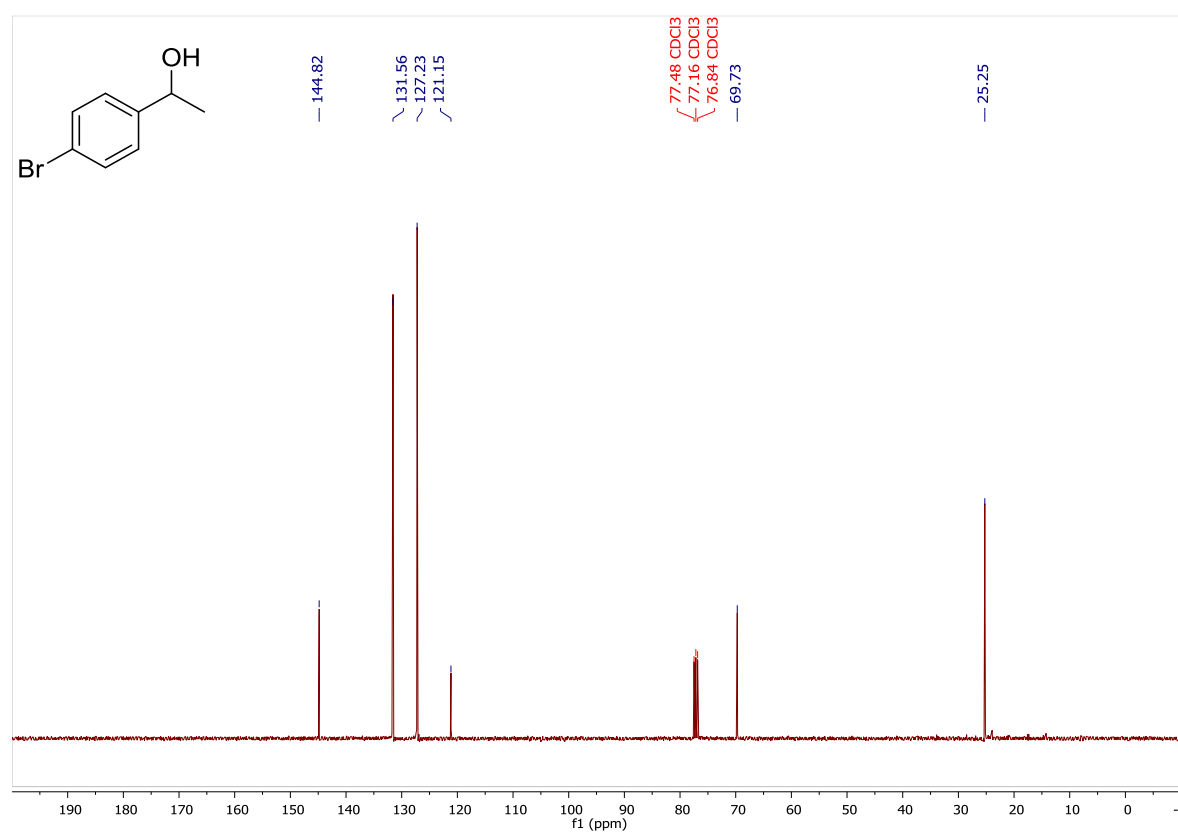


Figure S33: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1-(4-Bromophenyl)ethanol **b13** in CDCl_3 recorded at 101 MHz.

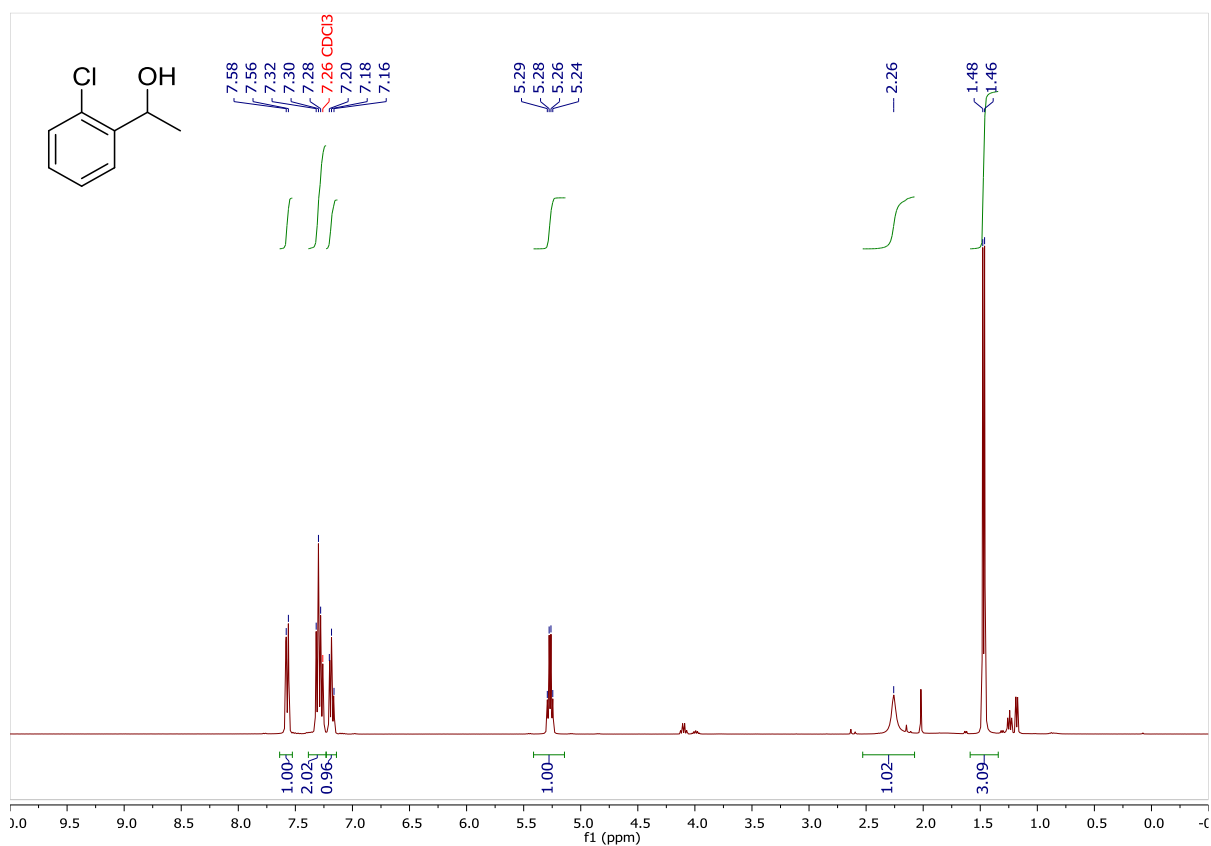


Figure S34: ¹H NMR spectrum of 1-(2-Chlorophenyl)ethanol b14 in CDCl₃ recorded at 400MHz

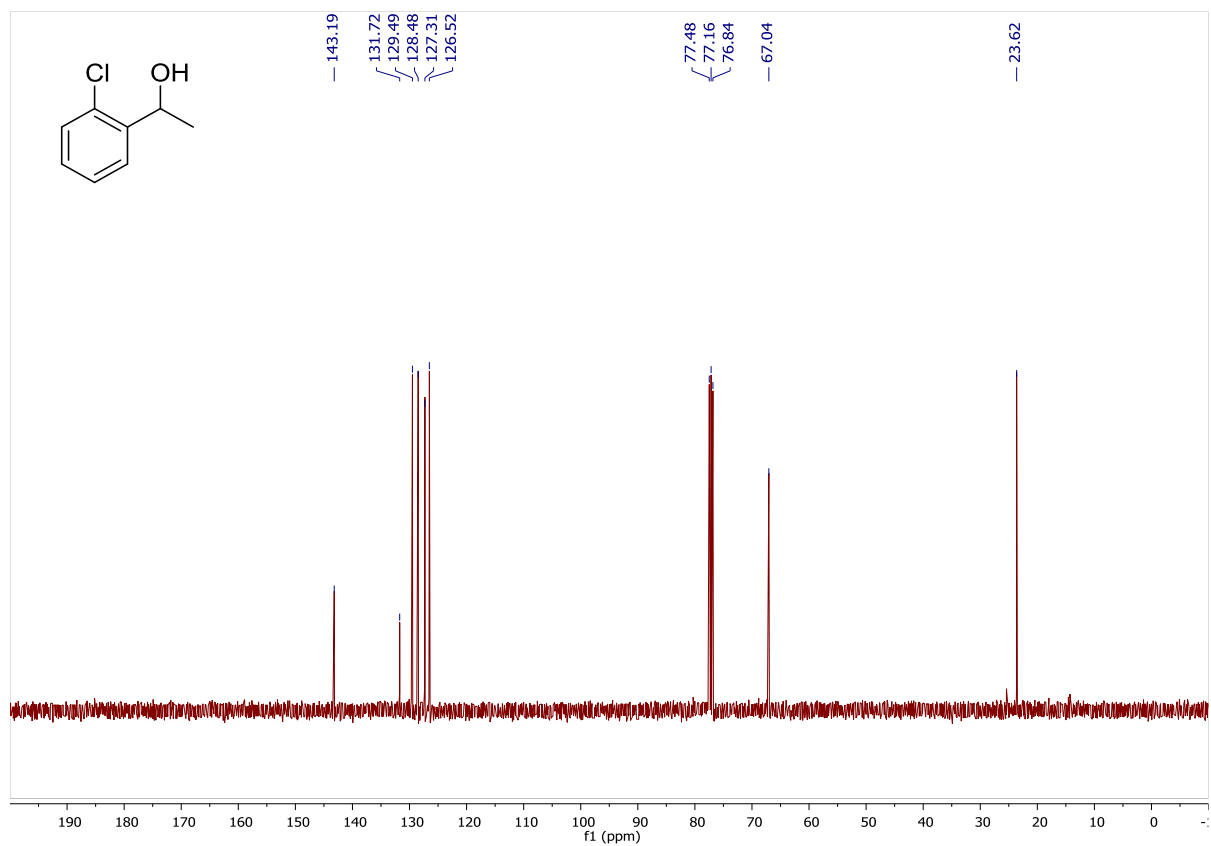


Figure S35: ¹³C{¹H} NMR spectrum of 1-(2-Chlorophenyl)ethanol b14 in CDCl₃ recorded at 101 MHz.

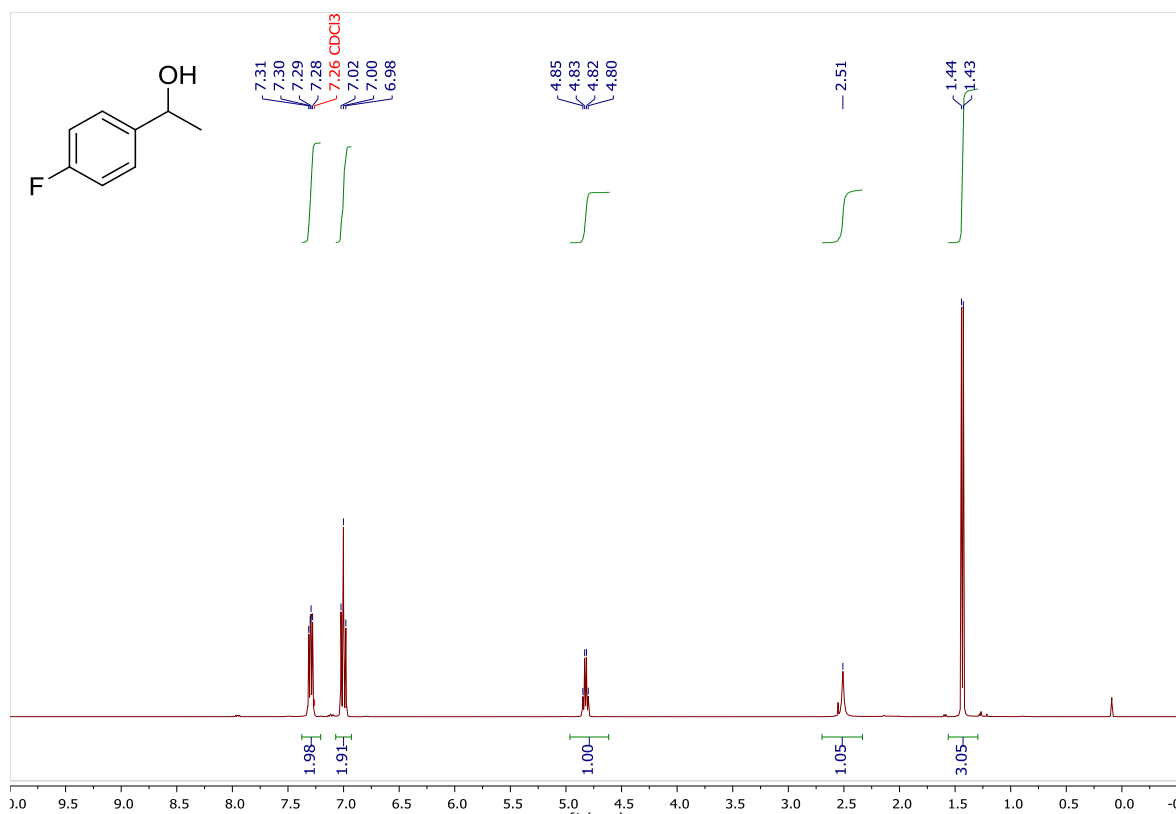


Figure S36: ¹H NMR spectrum of 1-(4-Fluorophenyl)ethanol b15 in CDCl₃ recorded at 400MHz

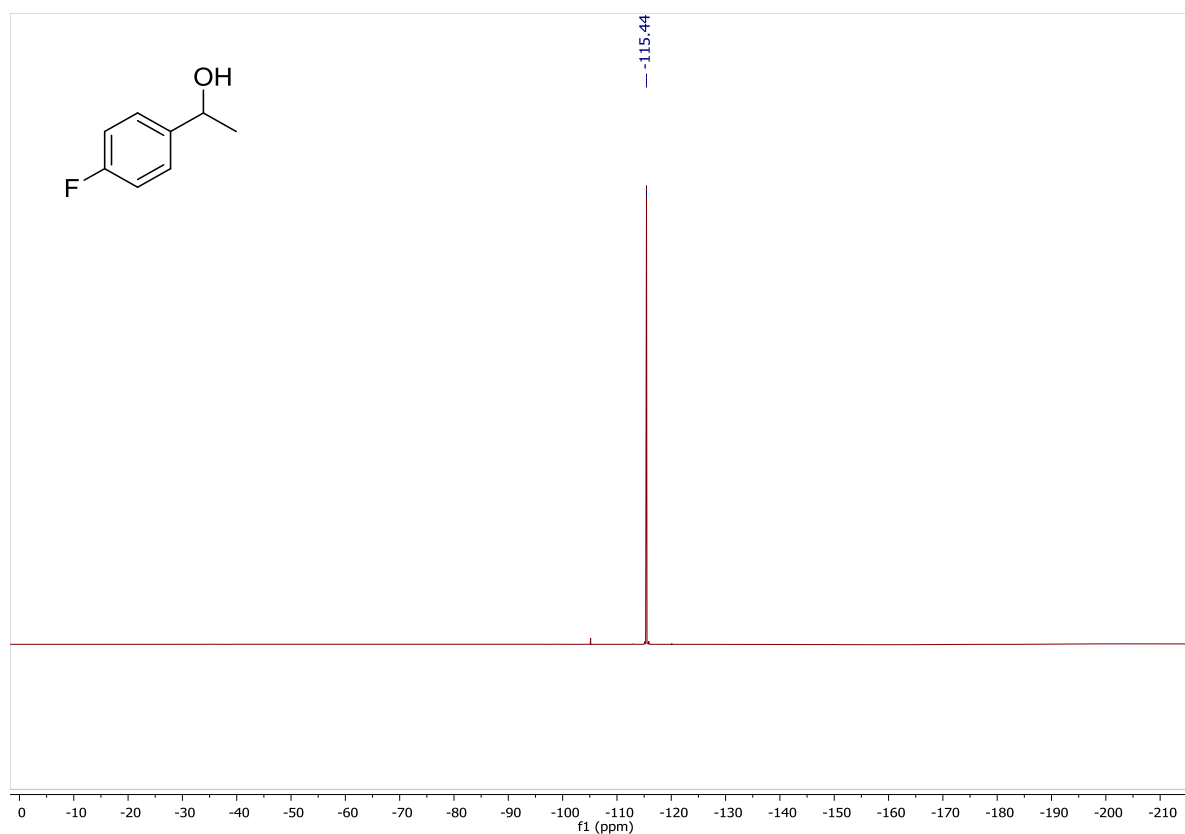


Figure S37: ¹⁹F NMR spectrum of 1-(4-Fluorophenyl)ethanol b15 in CDCl₃ recorded at 376MHz

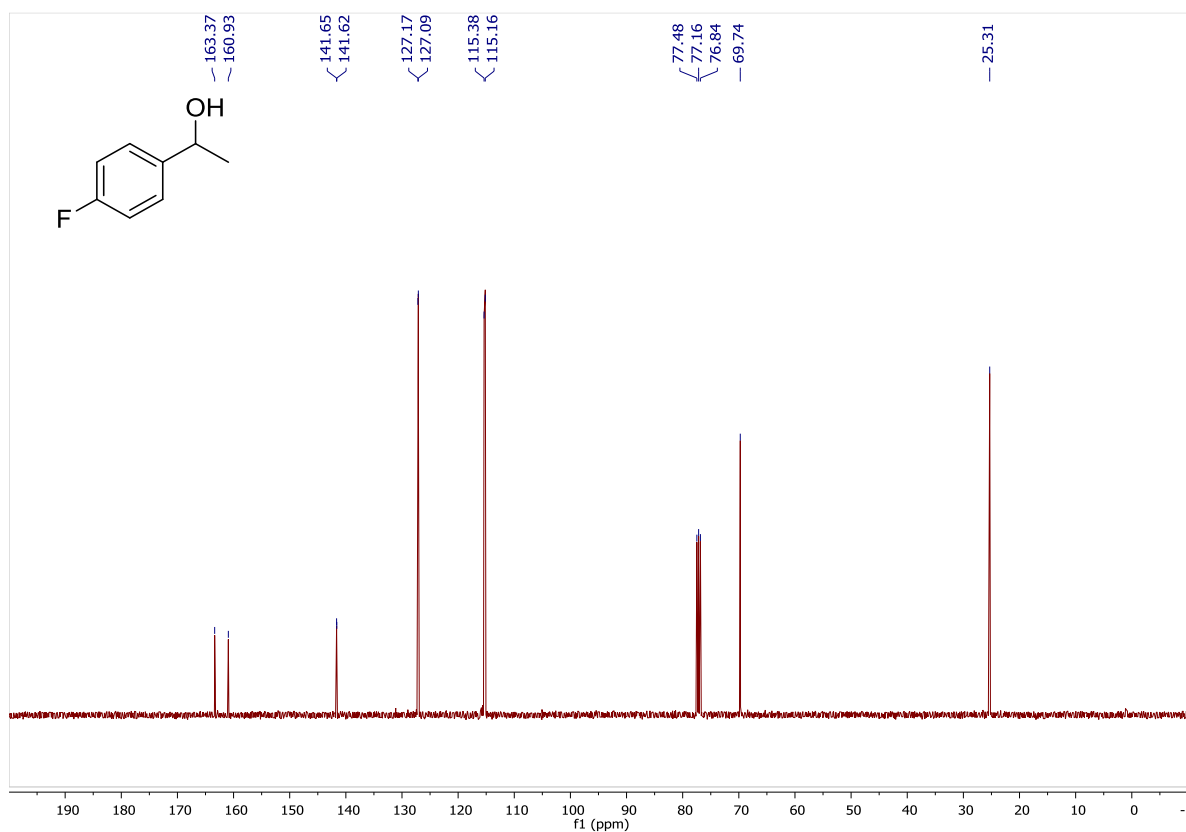


Figure S38: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1-(4-Fluorophenyl)ethanol b15 in CDCl_3 recorded at 101 MHz.

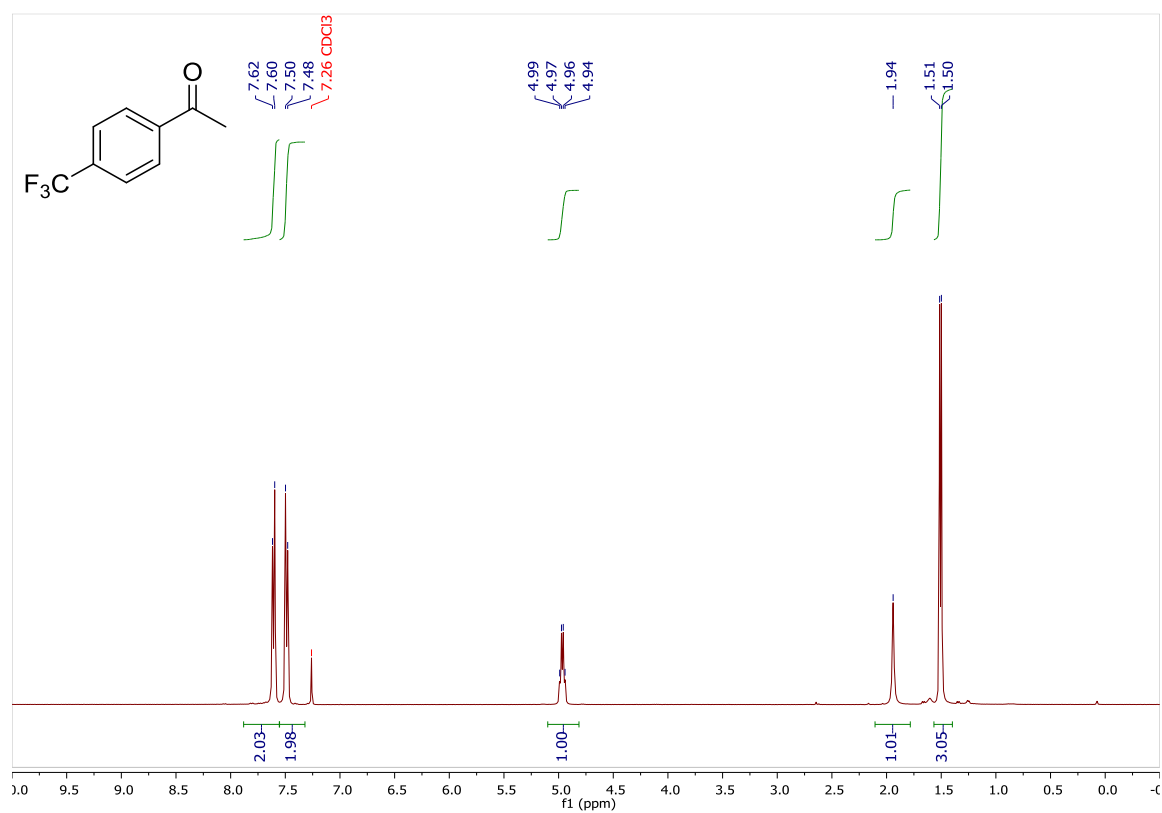


Figure S39: ^1H NMR spectrum of 1-(4-Trifluoromethylphenyl)ethanol b16 in CDCl_3 recorded at 400MHz

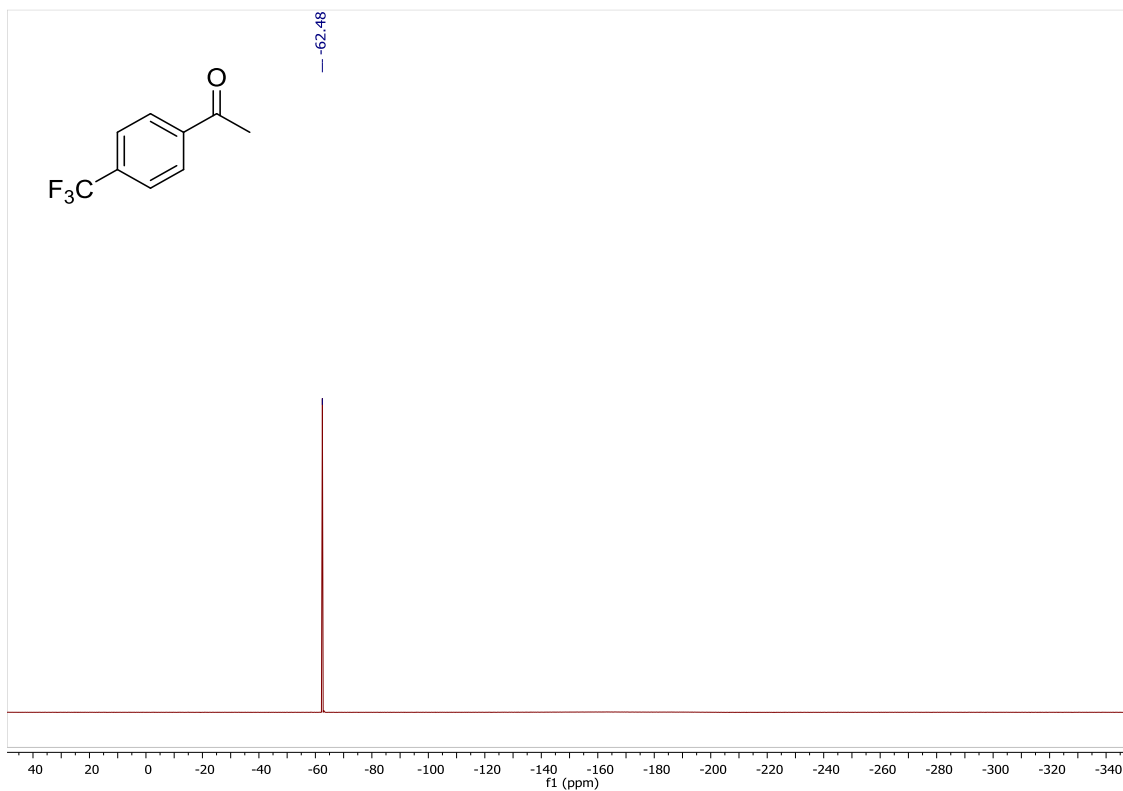


Figure S40: ^{19}F NMR spectrum of **1-(4-Trifluoromethylphenyl)ethanol b16** in CDCl_3 recorded at 376MHz

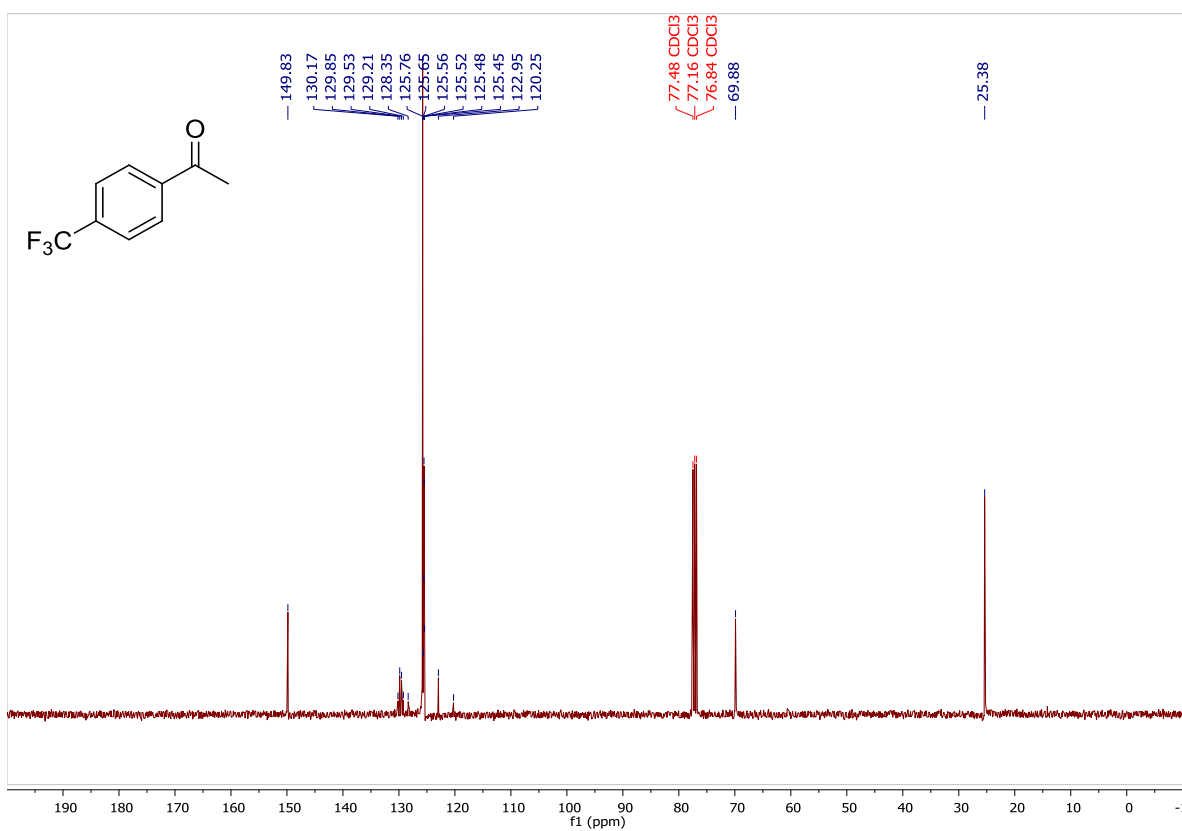


Figure S41: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1-(4-Trifluoromethylphenyl)ethanol b16** in CDCl_3 recorded at 101 MHz.

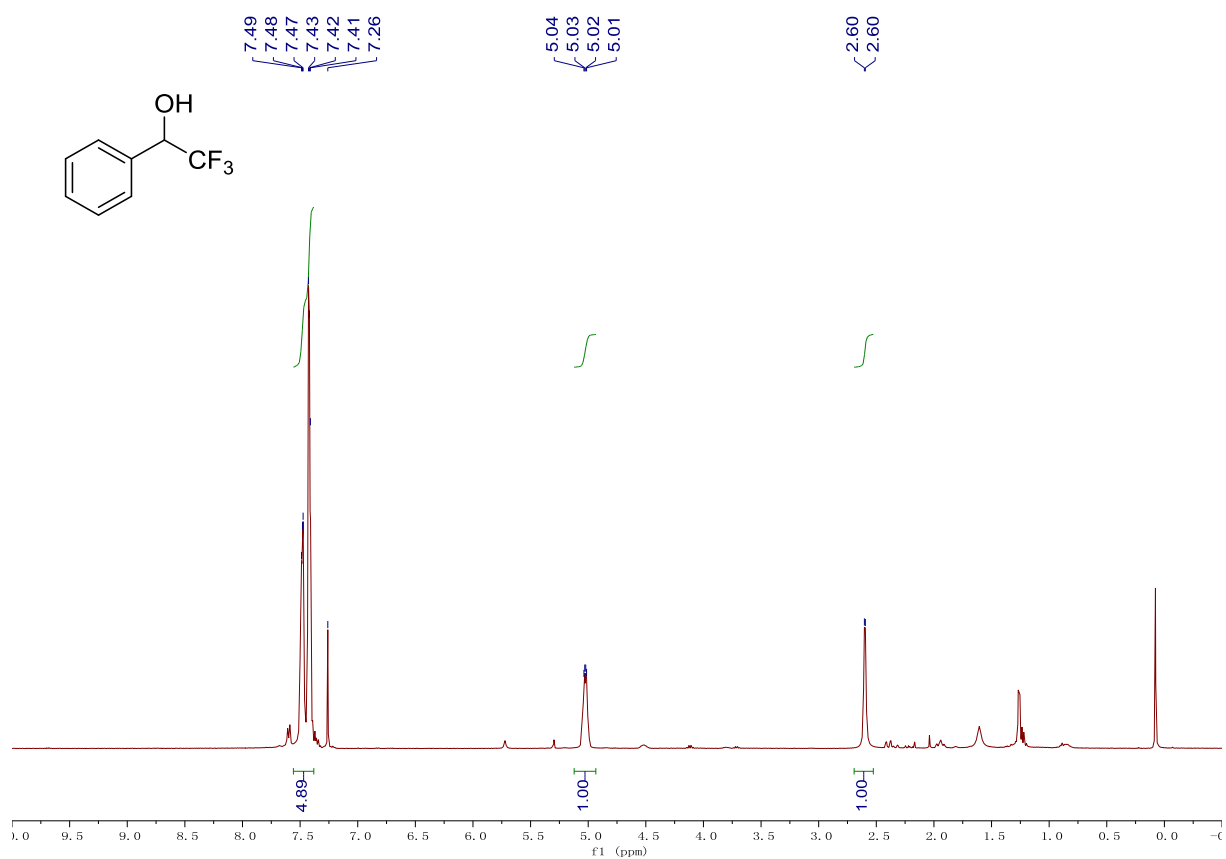


Figure S42: ¹H NMR spectrum of **2,2,2-trifluoro-1-phenylethanol b17** in CDCl₃ recorded at 400MHz

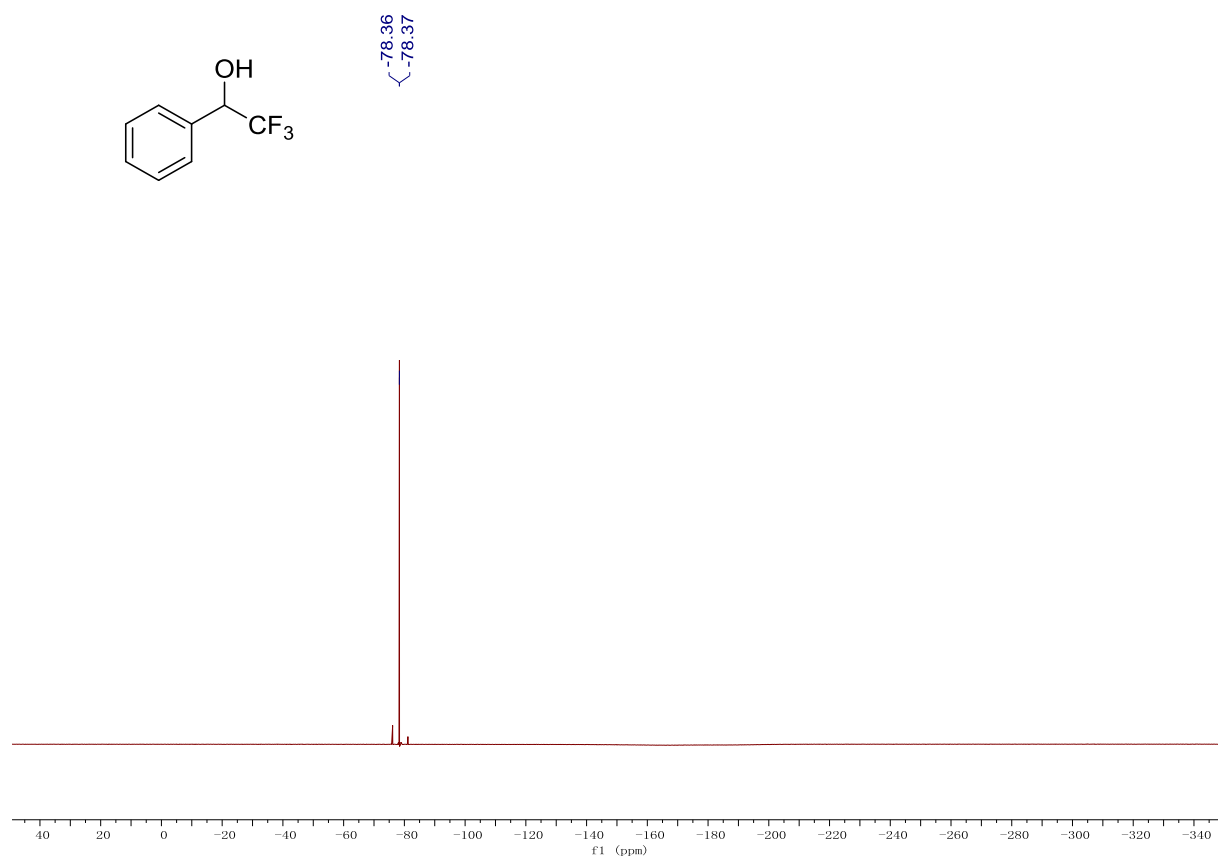


Figure S43: ¹⁹F NMR spectrum of **2,2,2-trifluoro-1-phenylethanol b17** in CDCl₃ recorded at 376MHz

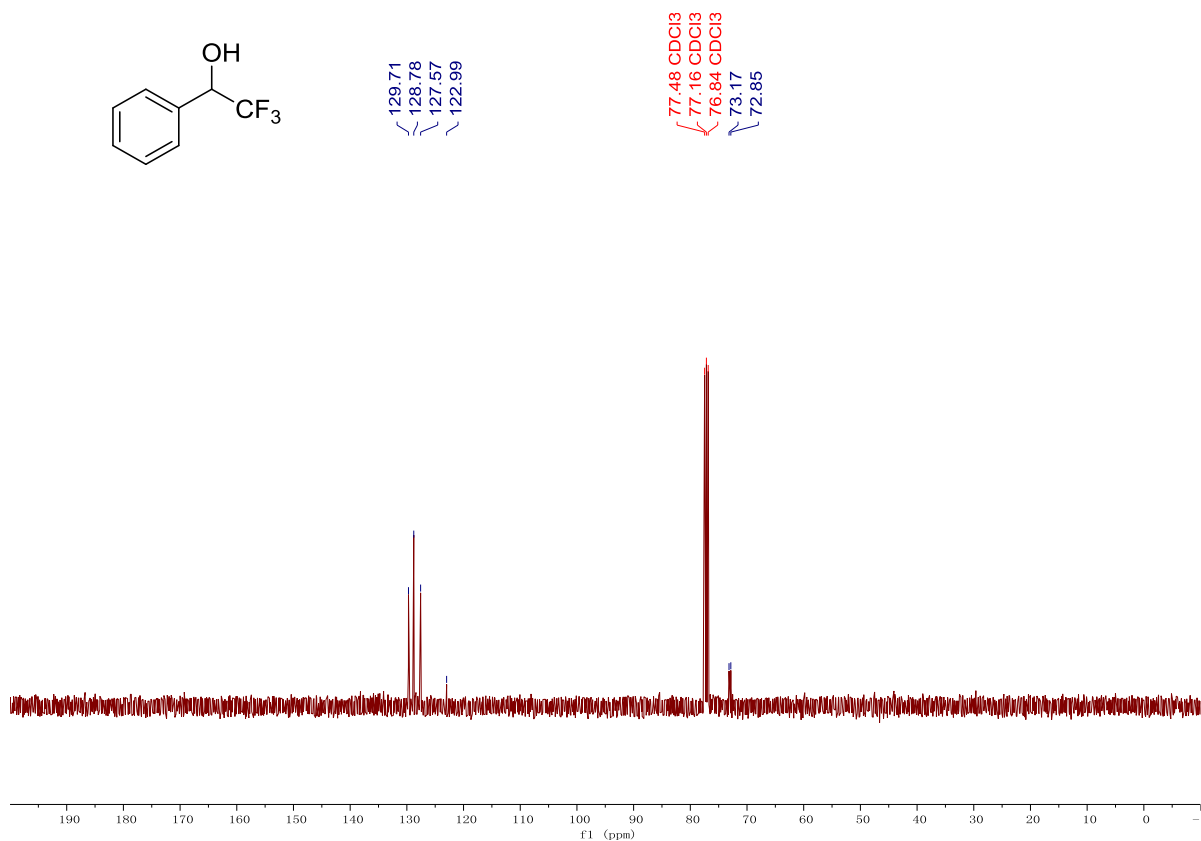


Figure S44: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2,2,2-Trifluoro-1-phenylethanol b17** in CDCl_3 recorded at 101 MHz.

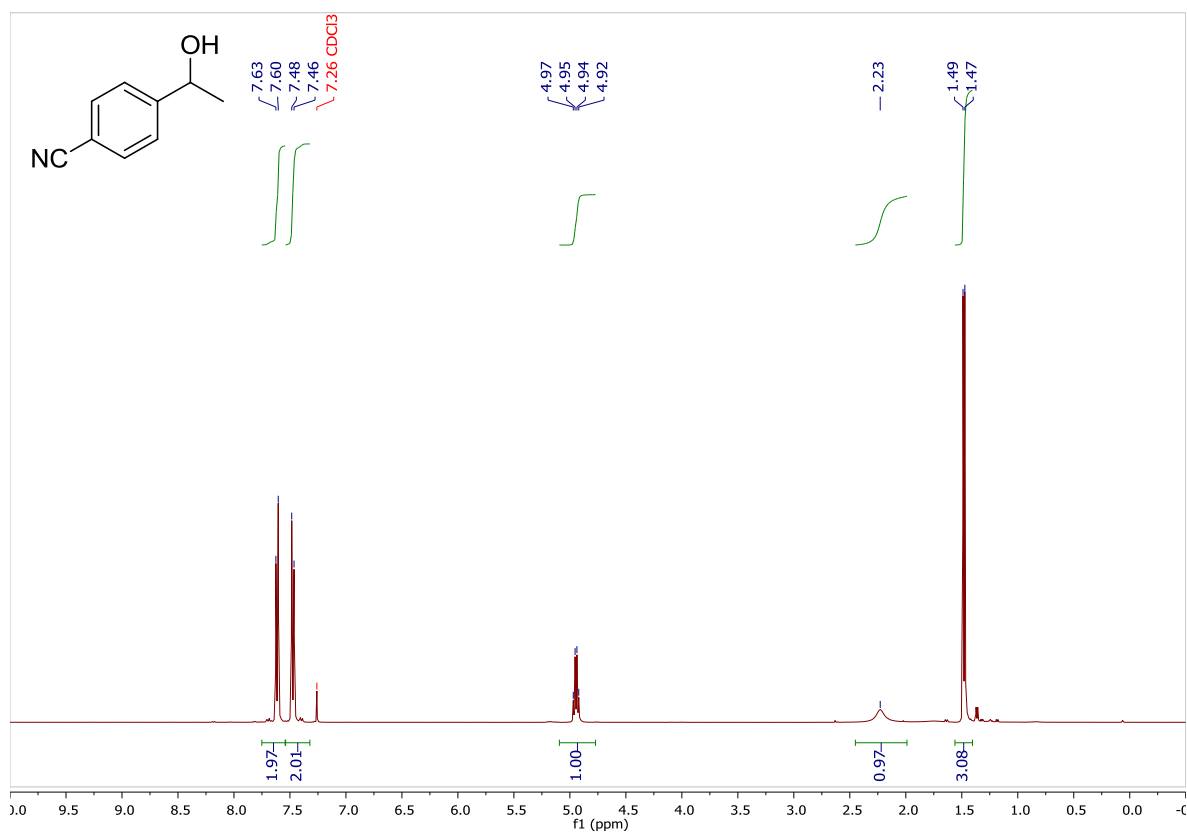


Figure S45: ^1H NMR spectrum of **4-(1-Hydroxyethyl)benzotrile b18** in CDCl_3 recorded at 400MHz

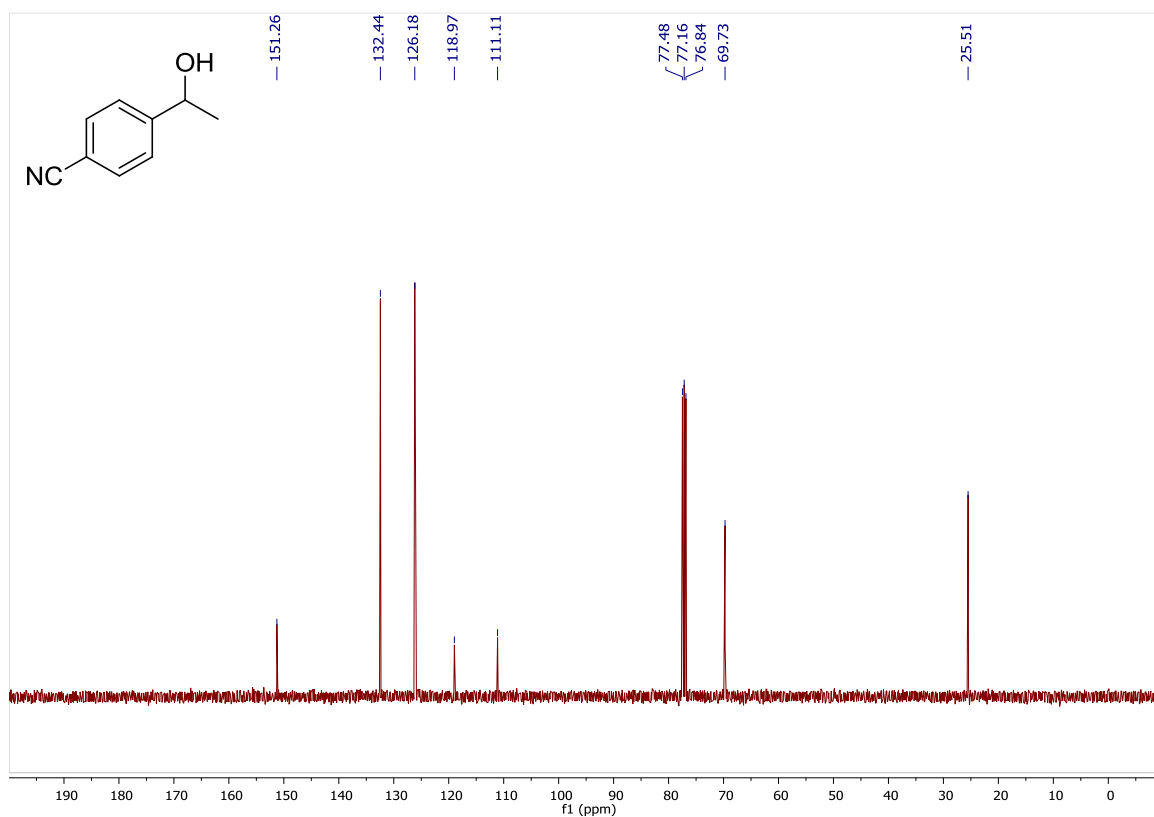


Figure S46: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-(1-Hydroxyethyl)benzonitrile **b18** in CDCl_3 recorded at 101 MHz.

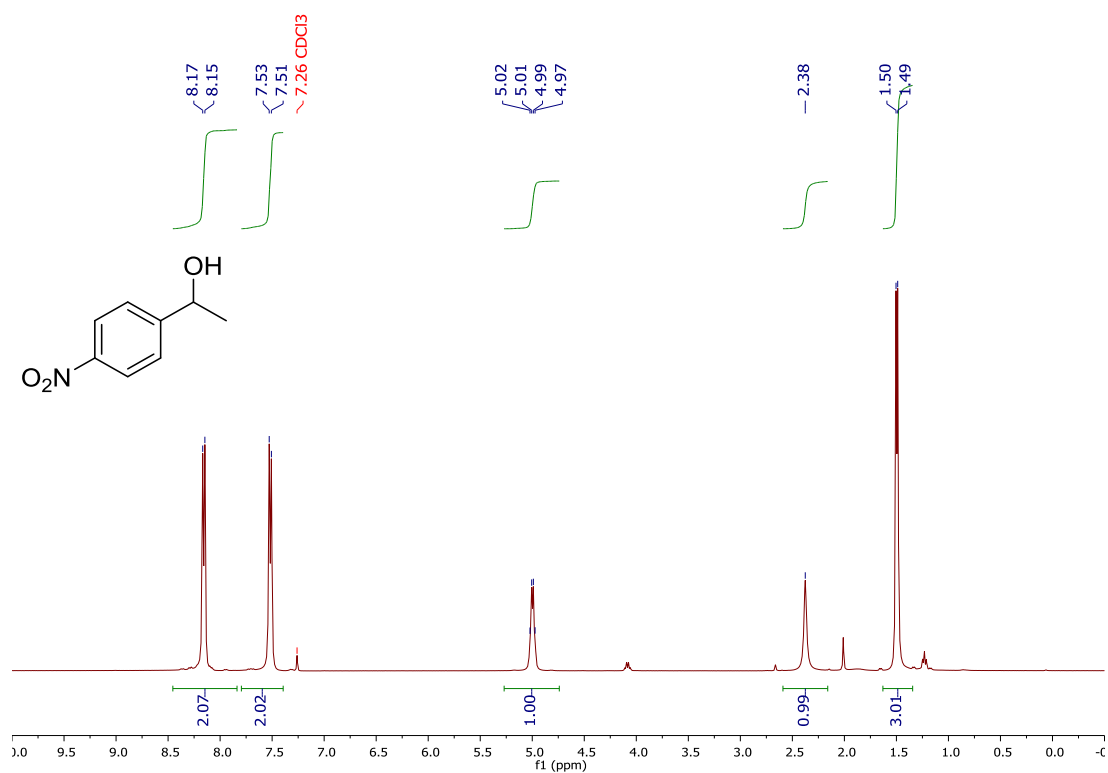


Figure S47: ^1H NMR spectrum of 1-(4-Nitrophenyl)ethanol **b19** in CDCl_3 recorded at 400 MHz.

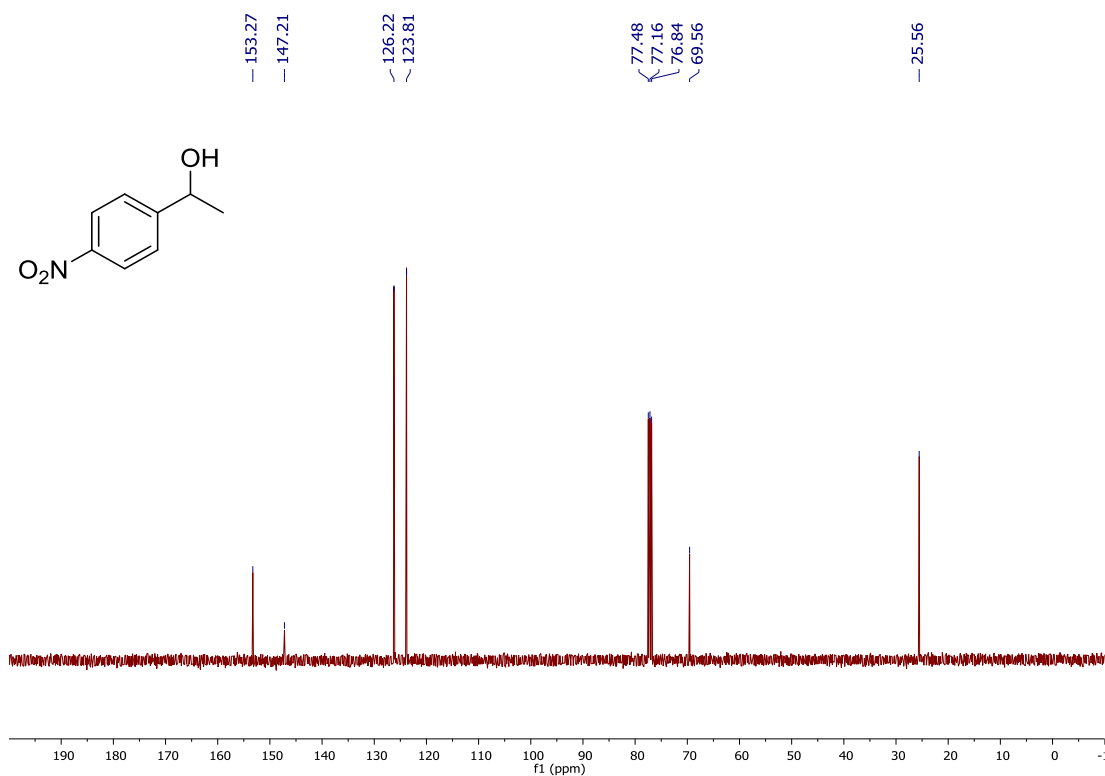


Figure S48: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1-(4-nitrophenyl)ethanol b19 in CDCl_3 recorded at 101 MHz.

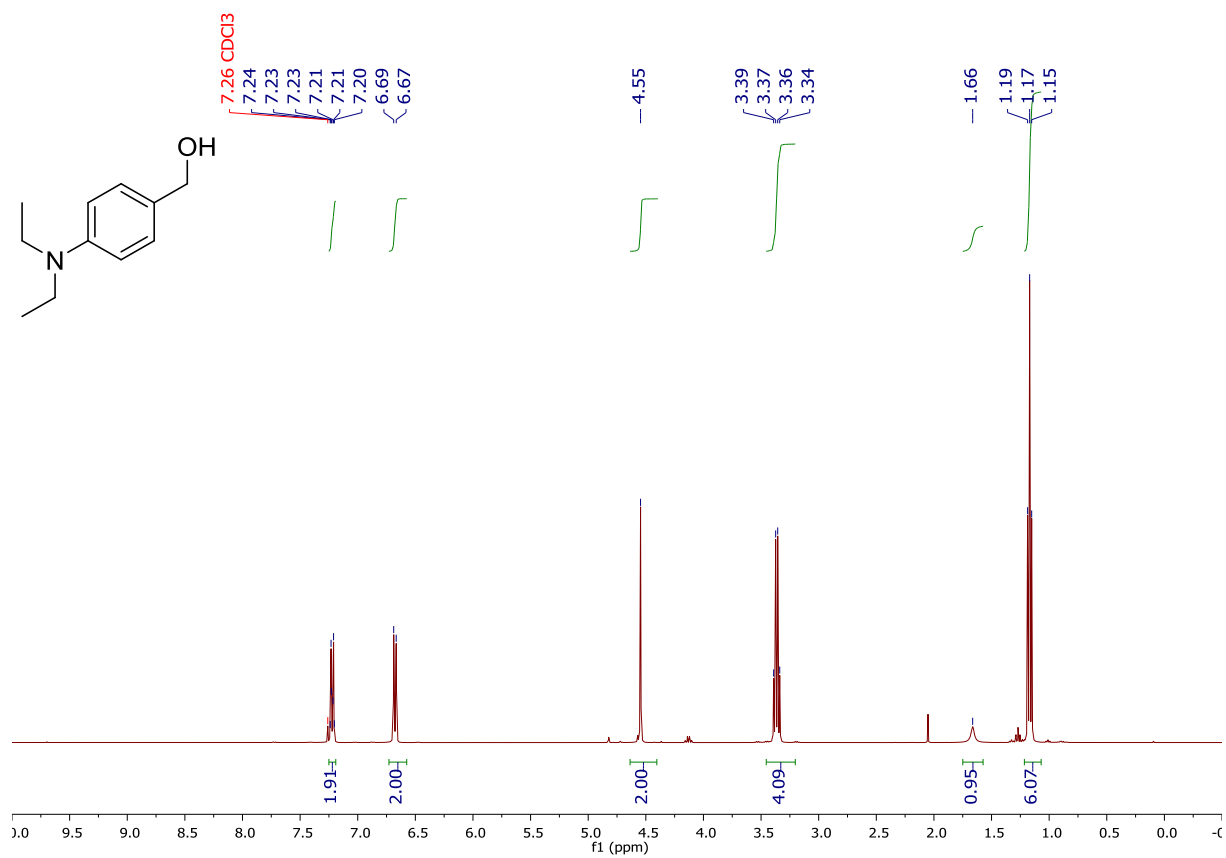


Figure S49: ^1H NMR spectrum of 4-(diethylamino)phenylmethanol b21 in CDCl_3 recorded at 400 MHz.

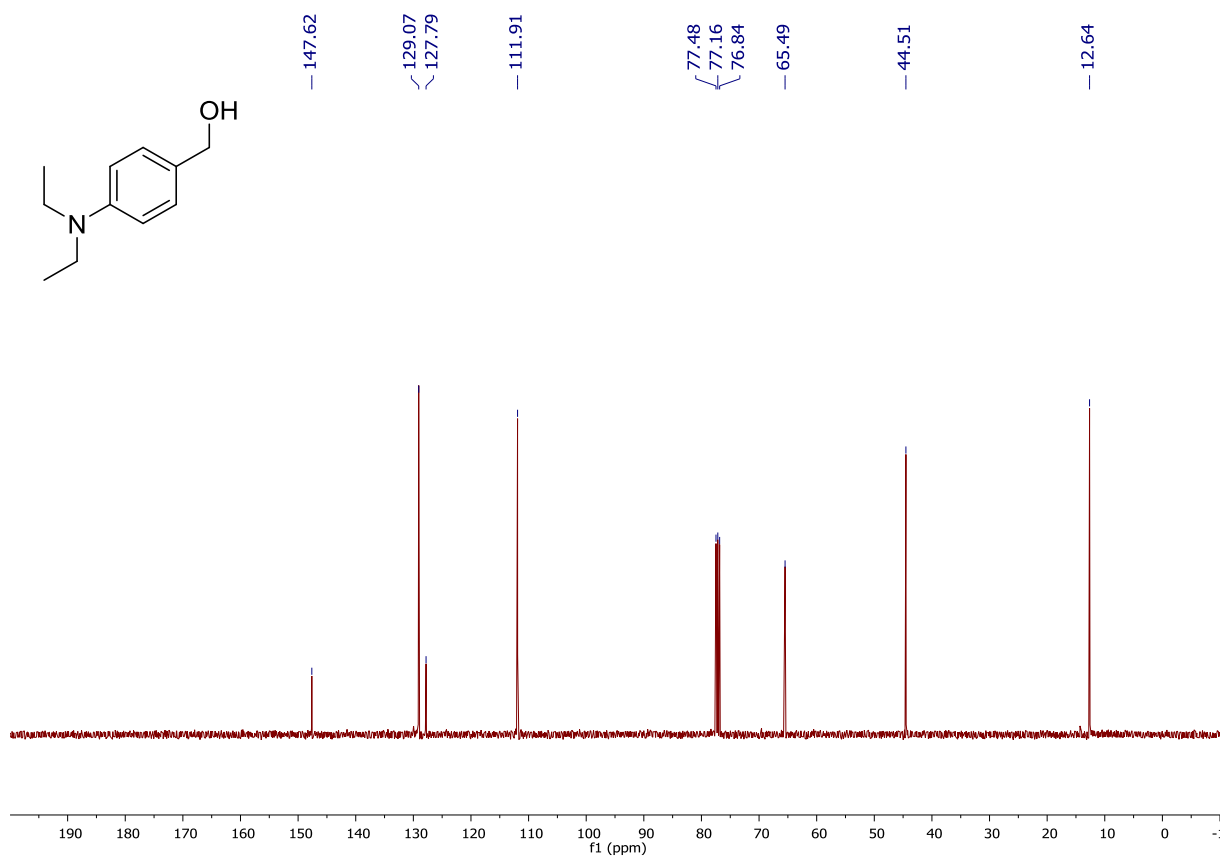


Figure S50: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (4-(Diethylamino)phenyl)methanol b21 in CDCl_3 recorded at 101 MHz.

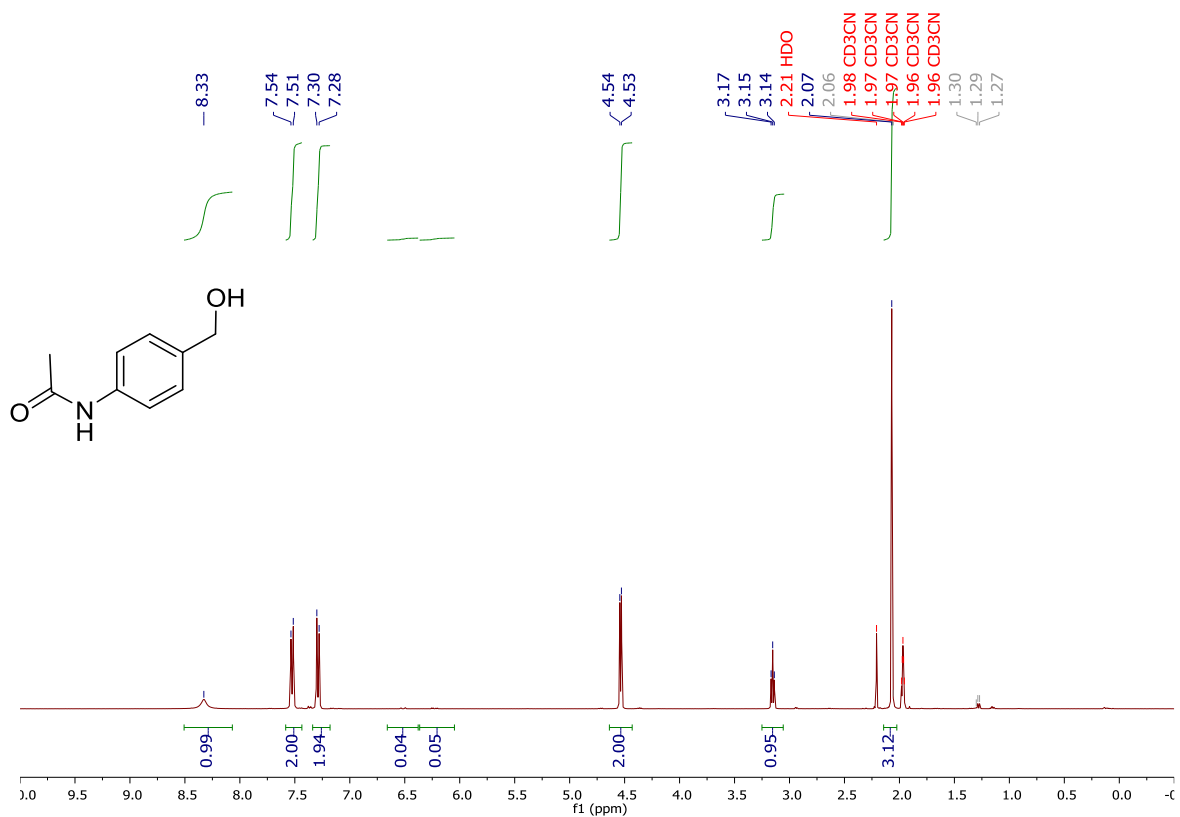


Figure S51: ^1H NMR spectrum of *N*-(4-(hydroxymethyl)phenyl)acetamide b23 in CD_3CN recorded at 400 MHz.

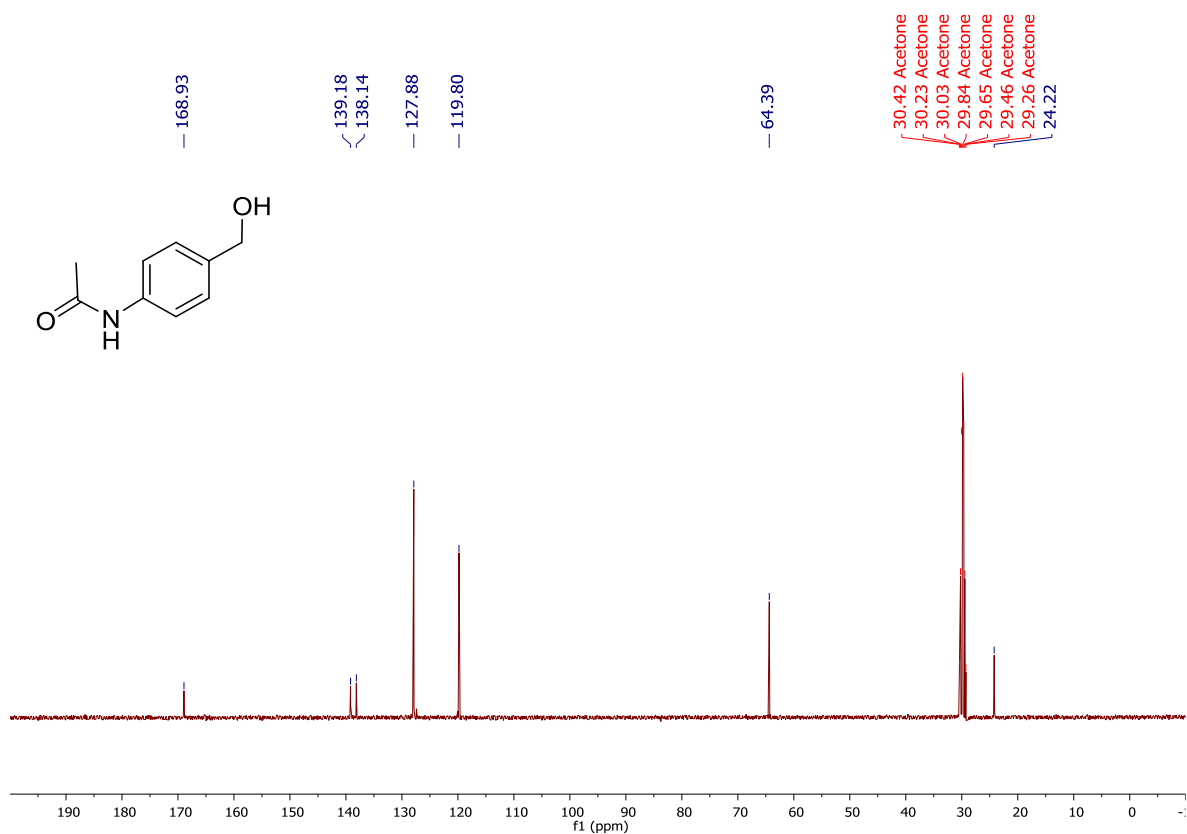


Figure S52: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *N*-(4-(hydroxymethyl)phenyl)acetamide **b23** in $(\text{CD}_3)_2\text{CO}$ recorded at 101 MHz.

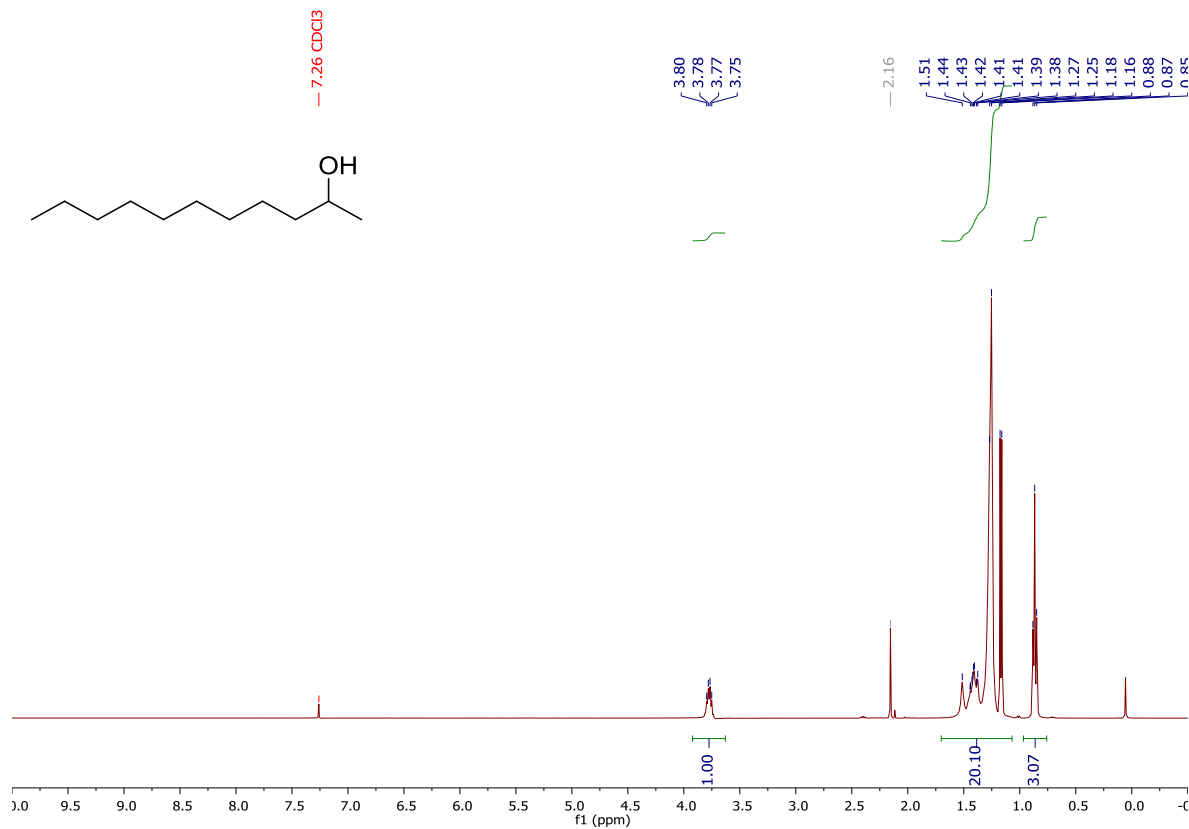


Figure S53: ^1H NMR spectrum of Undecan-2-ol **b25** in CDCl_3 recorded at 400MHz

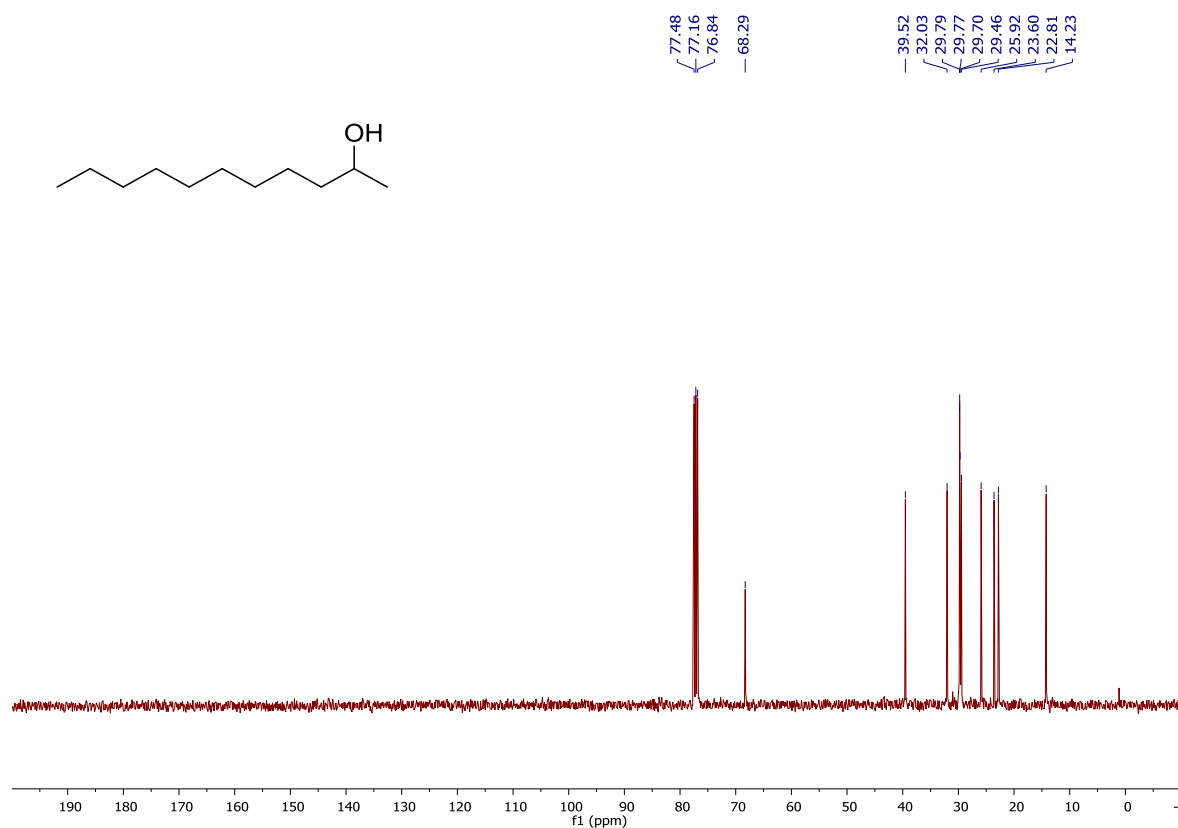


Figure S54: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Undecan-2-ol b25** in CDCl_3 recorded at 101 MHz.

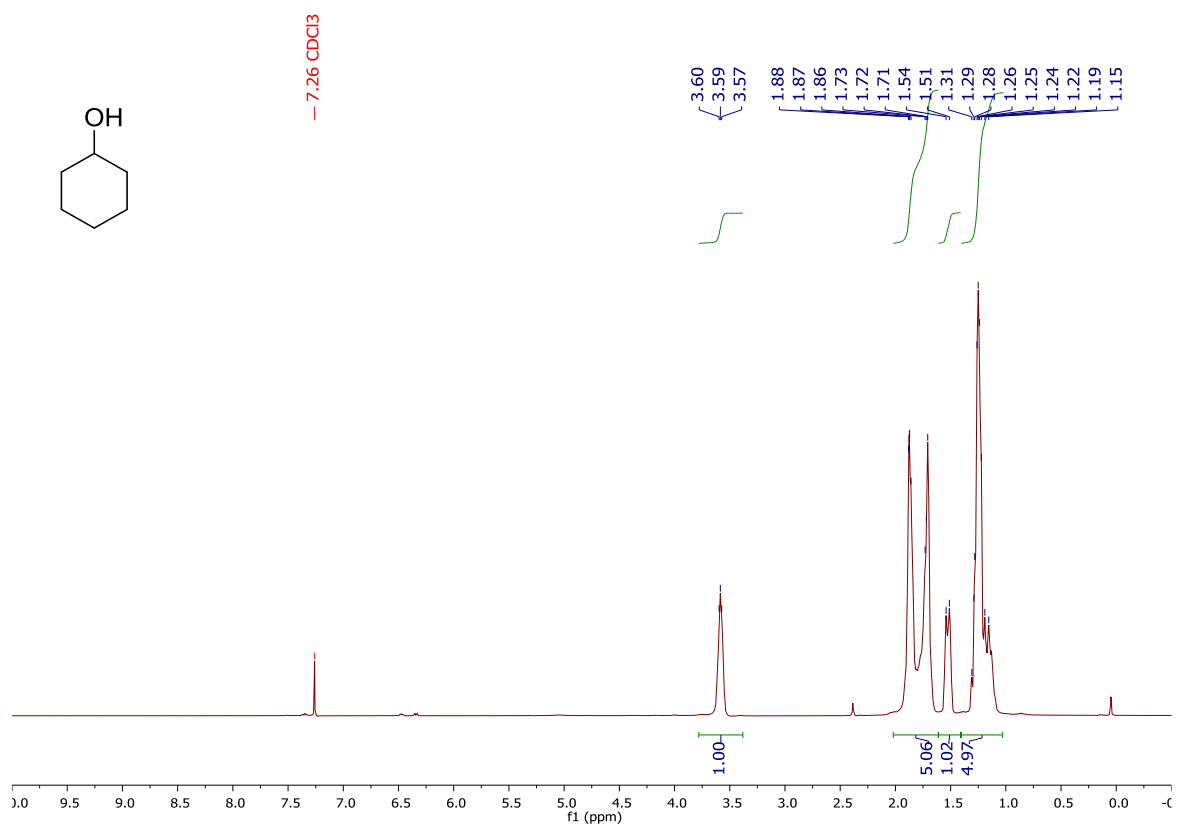


Figure S55: ^1H NMR spectrum of **Cyclohexanol b26** in CDCl_3 recorded at 400 MHz.

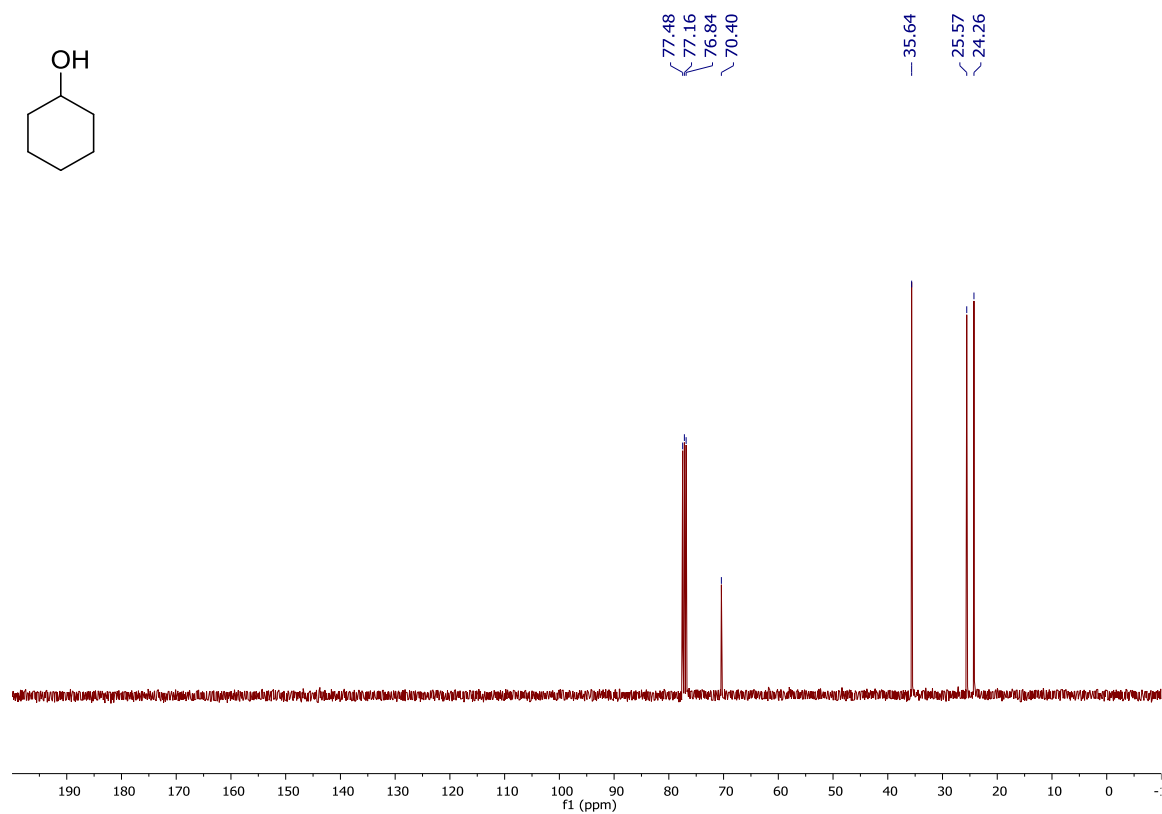


Figure S56: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Cyclohexanol b26** in CDCl_3 recorded at 101 MHz.

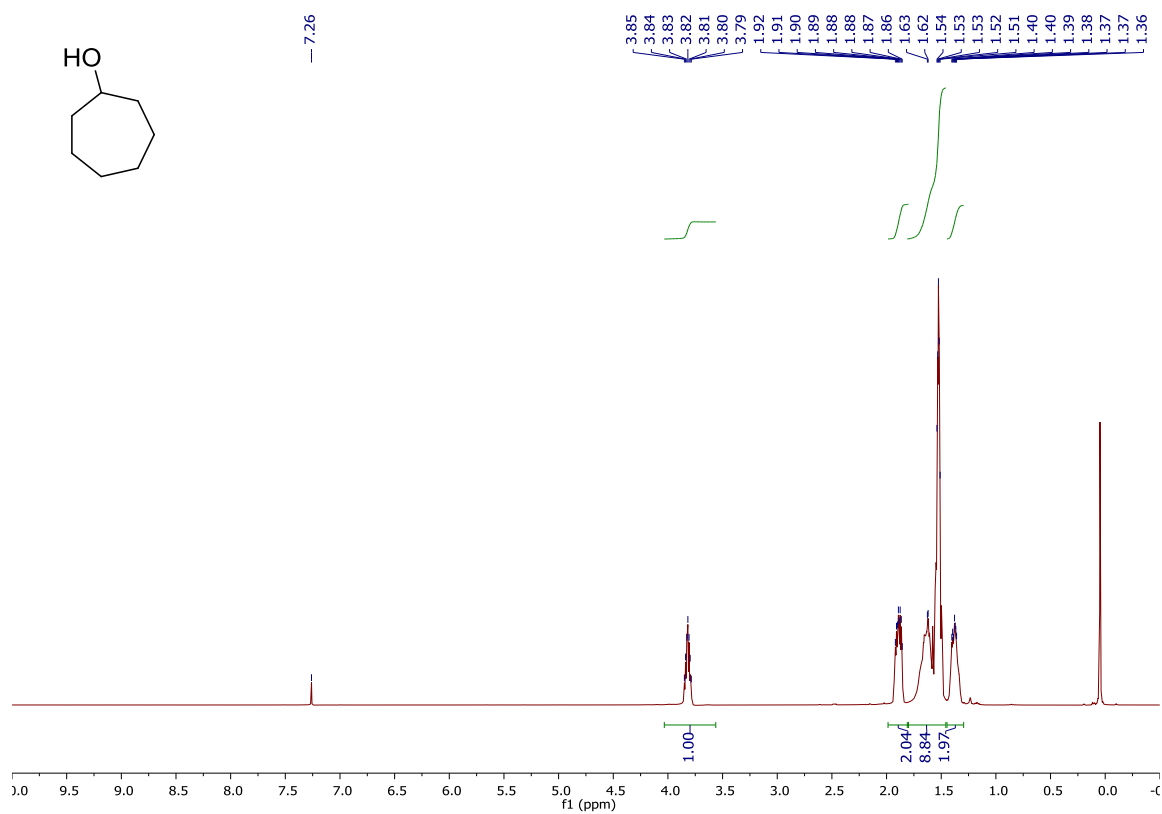


Figure S57: ^1H NMR spectrum of **Cycloheptanol b27** in CDCl_3 recorded at 400MHz

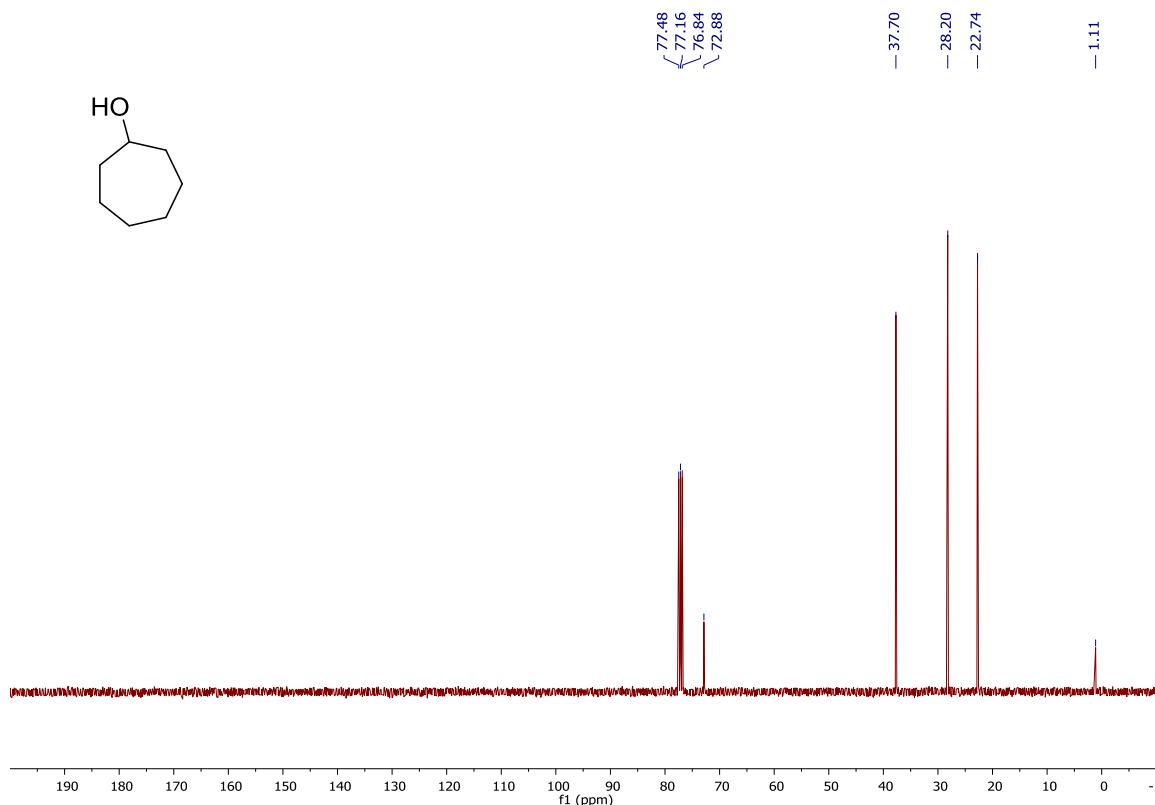


Figure S58: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Cycloheptanol b27** in CDCl_3 recorded at 101 MHz.

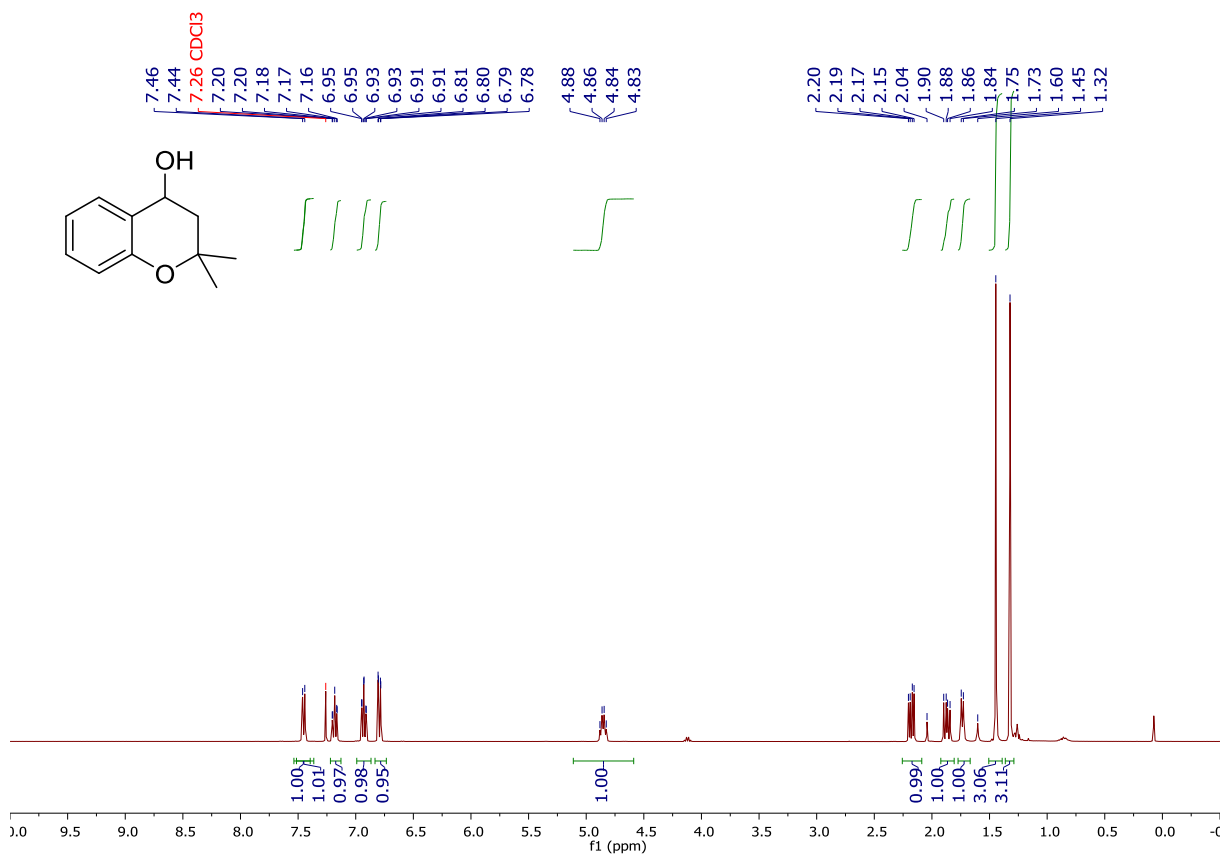


Figure S59: ^1H NMR spectrum of **2,2-Dimethylchroman-4-ol b28** in CDCl_3 recorded at 400MHz

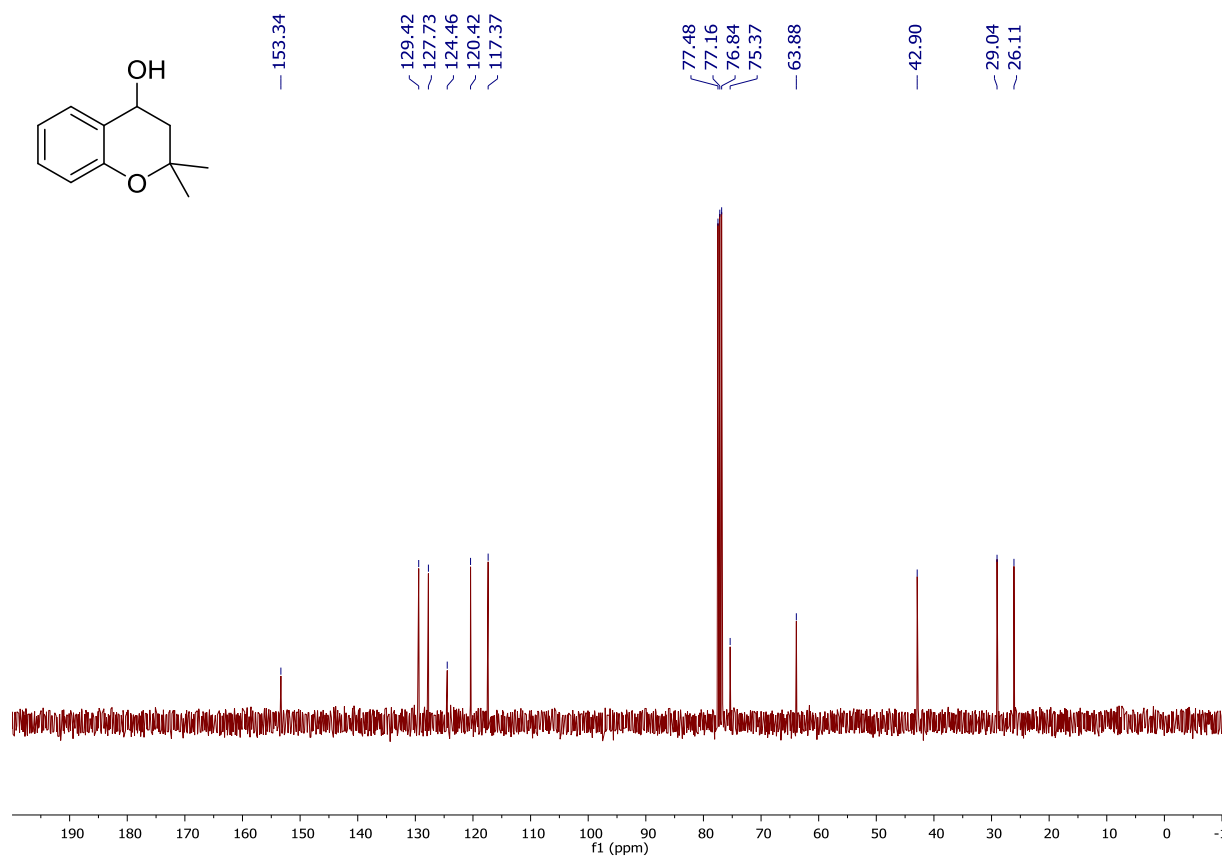


Figure S60: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2,2-Dimethylchroman-4-ol b28** in CDCl_3 recorded at 101 MHz.

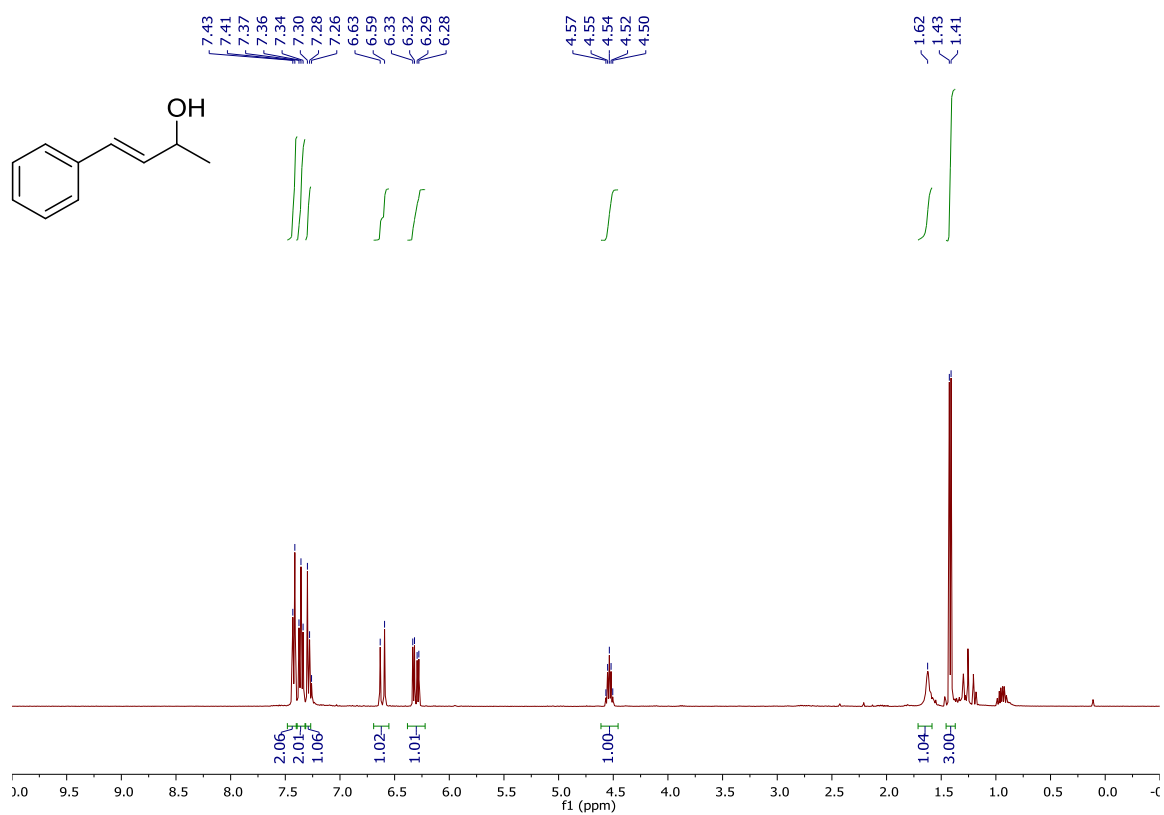


Figure S61: ^1H NMR spectrum of **4-Phenylbut-3-en-2-ol b30** in CDCl_3 recorded at 400 MHz.

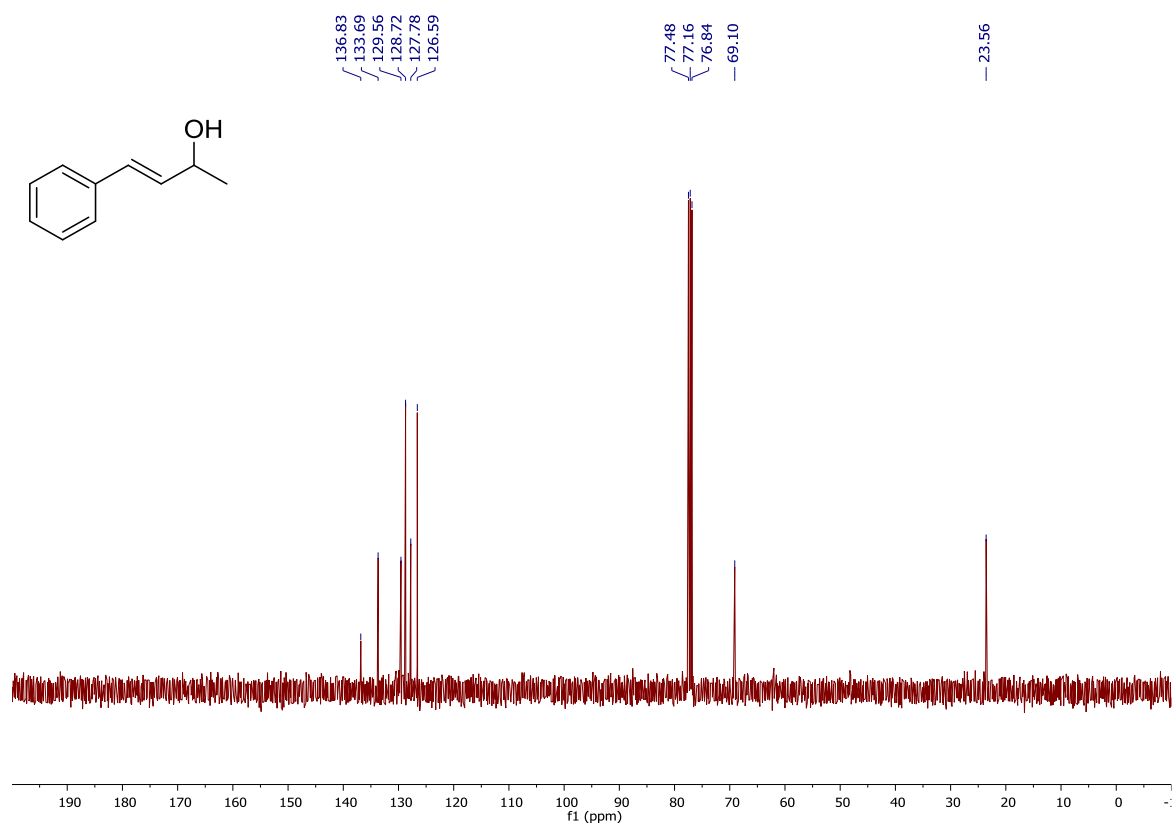


Figure S62: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4-Phenylbut-3-en-2-ol b30** in CDCl_3 recorded at 101 MHz.

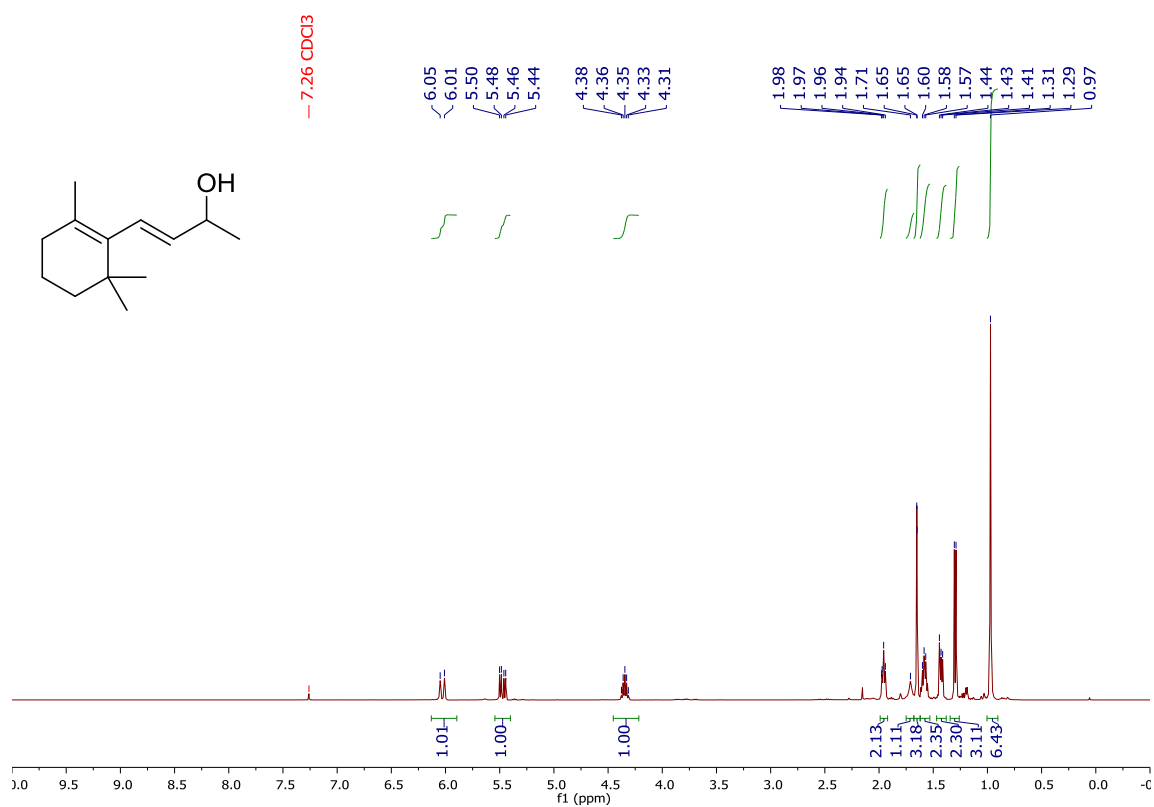


Figure S63: ^1H NMR spectrum of **beta-ionol b31** in CDCl_3 recorded at 400 MHz.

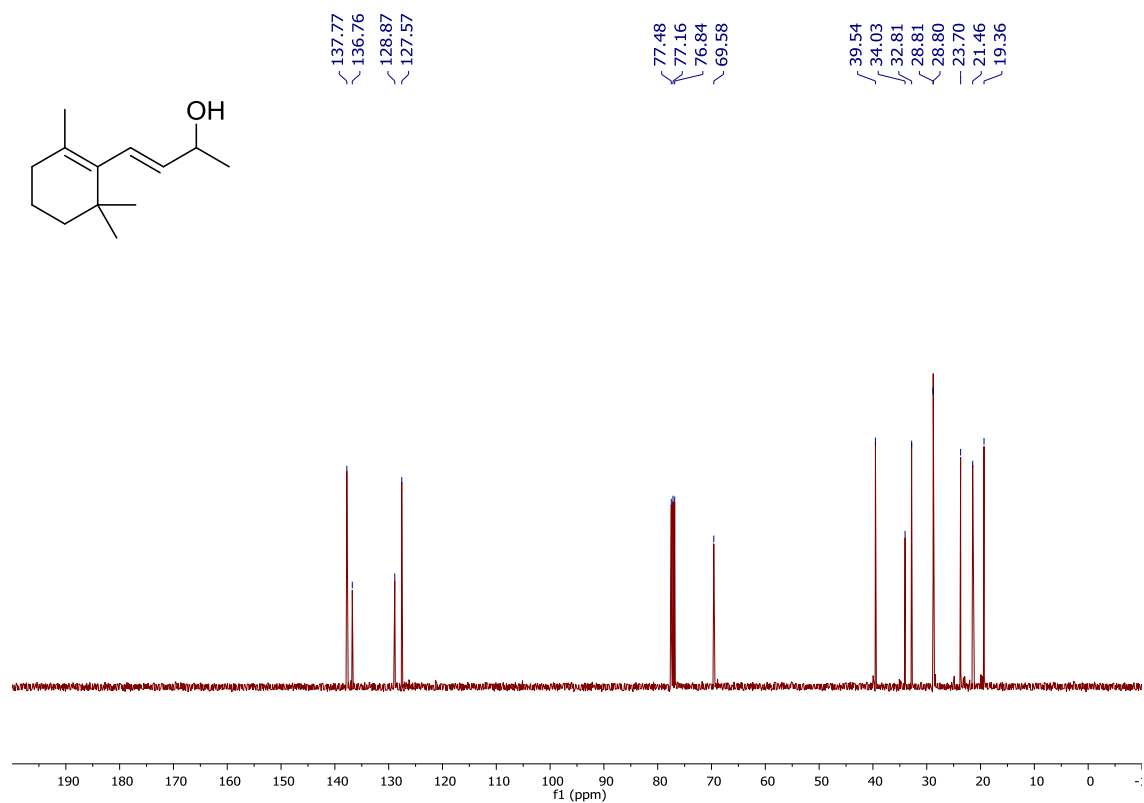


Figure S64: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **beta-ionol b31** in CDCl_3 recorded at 101 MHz.

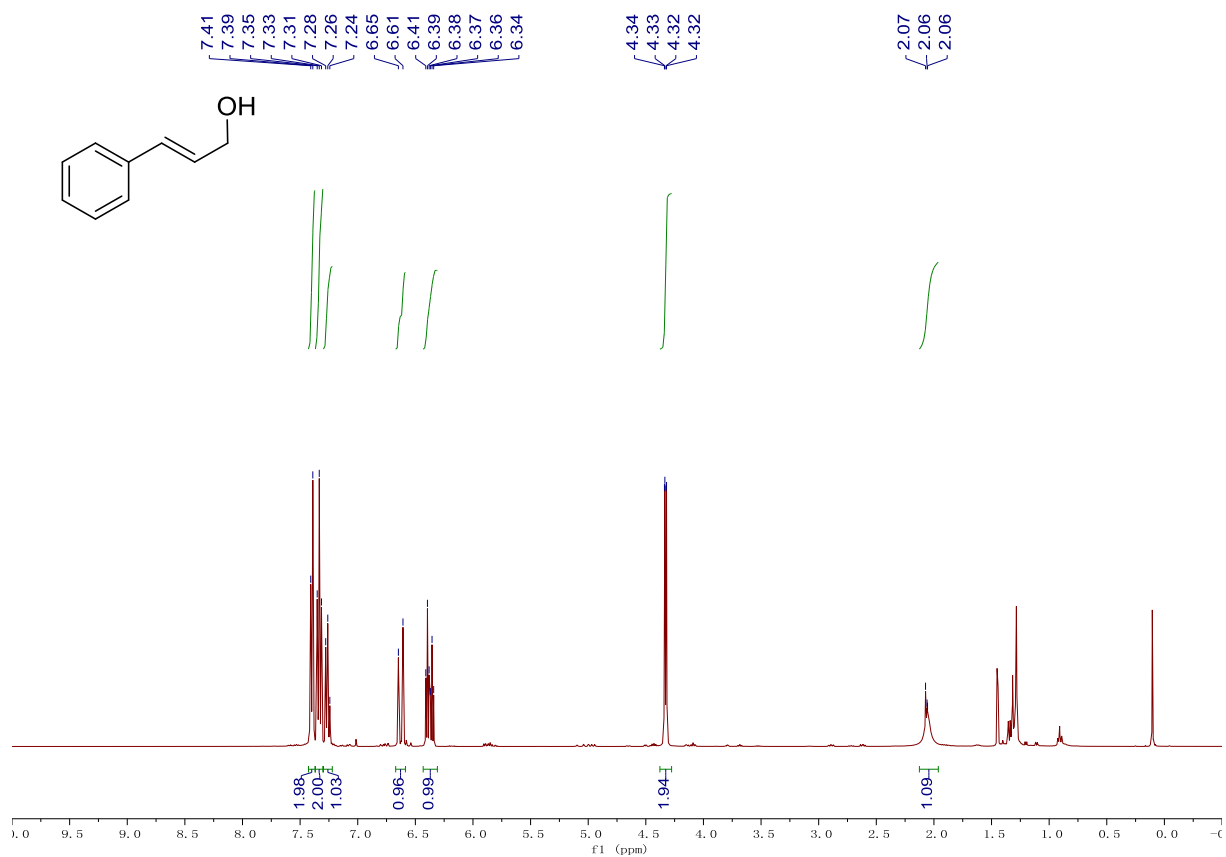


Figure S65: ^1H NMR spectrum of **cinnamyl alcohol b32** in CDCl_3 recorded at 400 MHz.

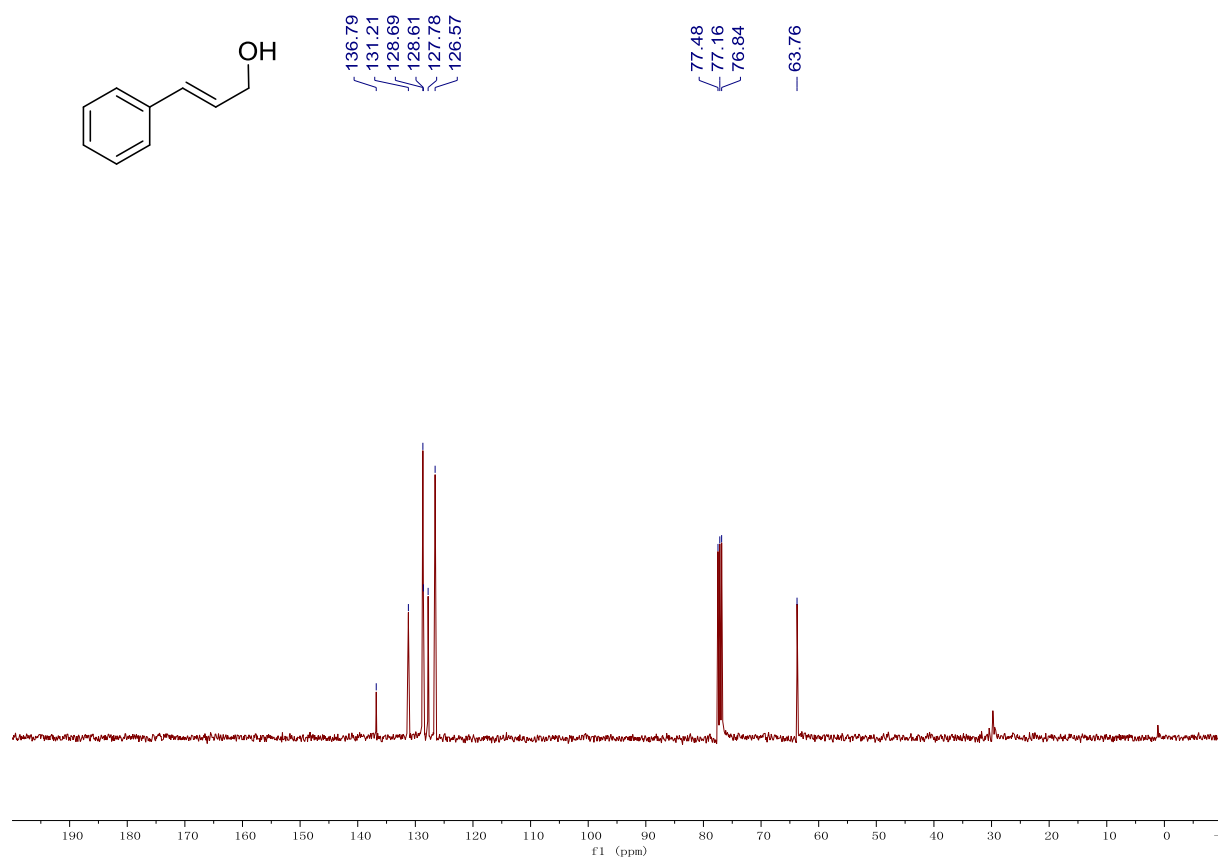


Figure S66: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **cinnamyl alcohol b32** in CDCl_3 recorded at 101 MHz.

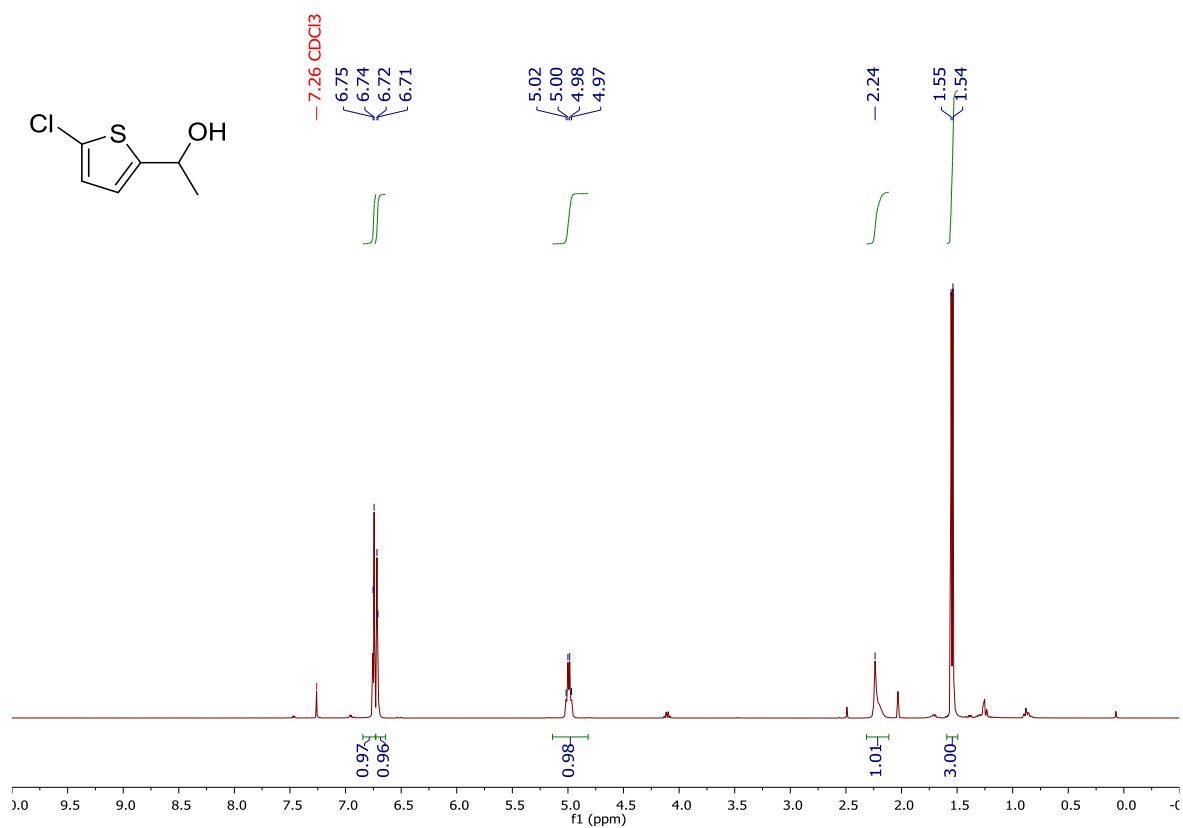


Figure S67: ^1H NMR spectrum of **1-(5-chlorothiophen-2-yl)ethanol b33** in CDCl_3 recorded at 400MHz

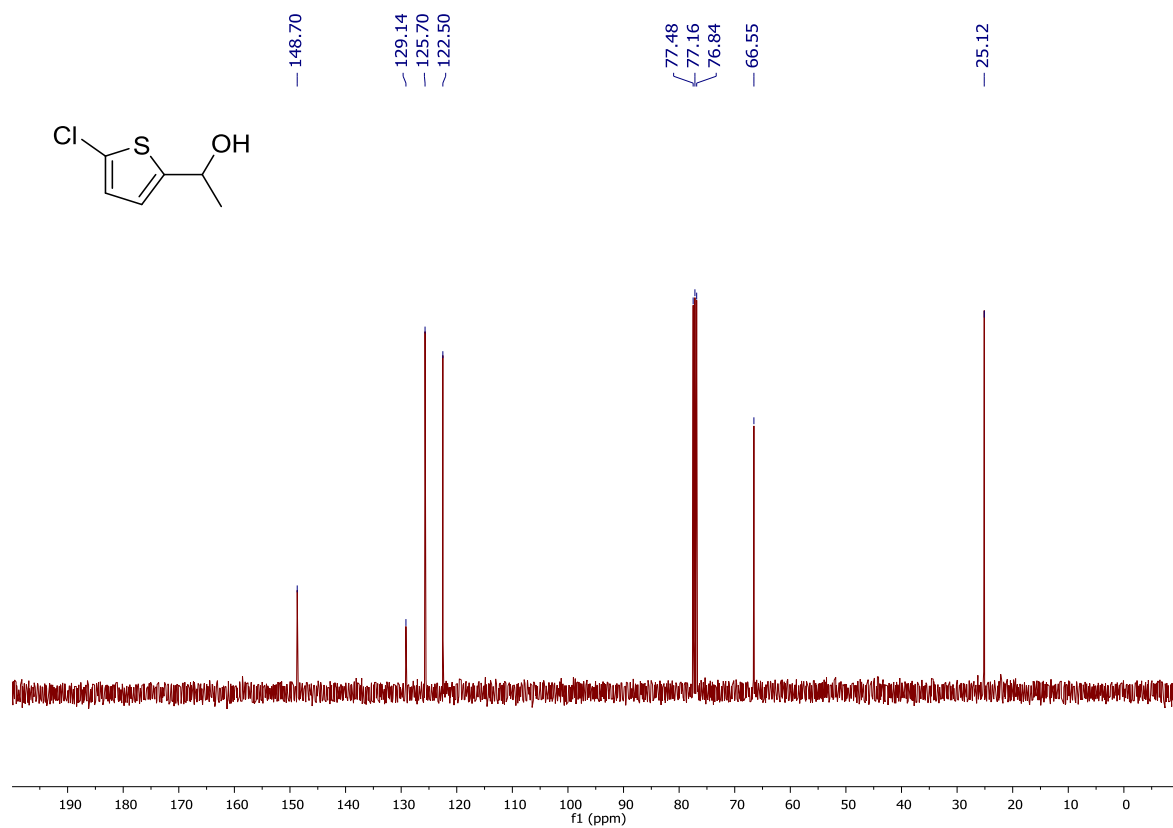


Figure S68: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1-(5-Chlorothiophen-2-yl)ethanol b33** in CDCl_3 recorded at 101 MHz.

Typical ^1H NMR of crude mixture after reaction

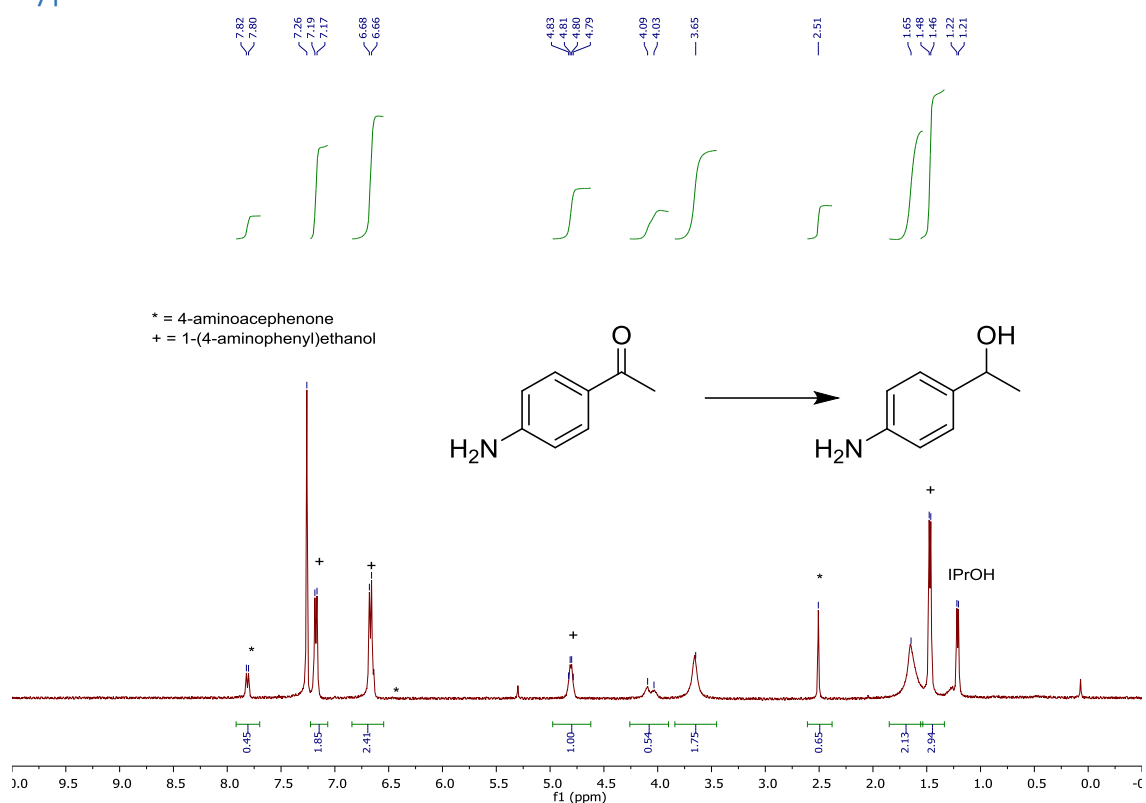


Figure S69: ^1H NMR spectrum of the crude mixture for the reduction of 4-aminoacetophenone **a22** recorded after 20 min at 80 °C at 300 MHz (82 % conversion).

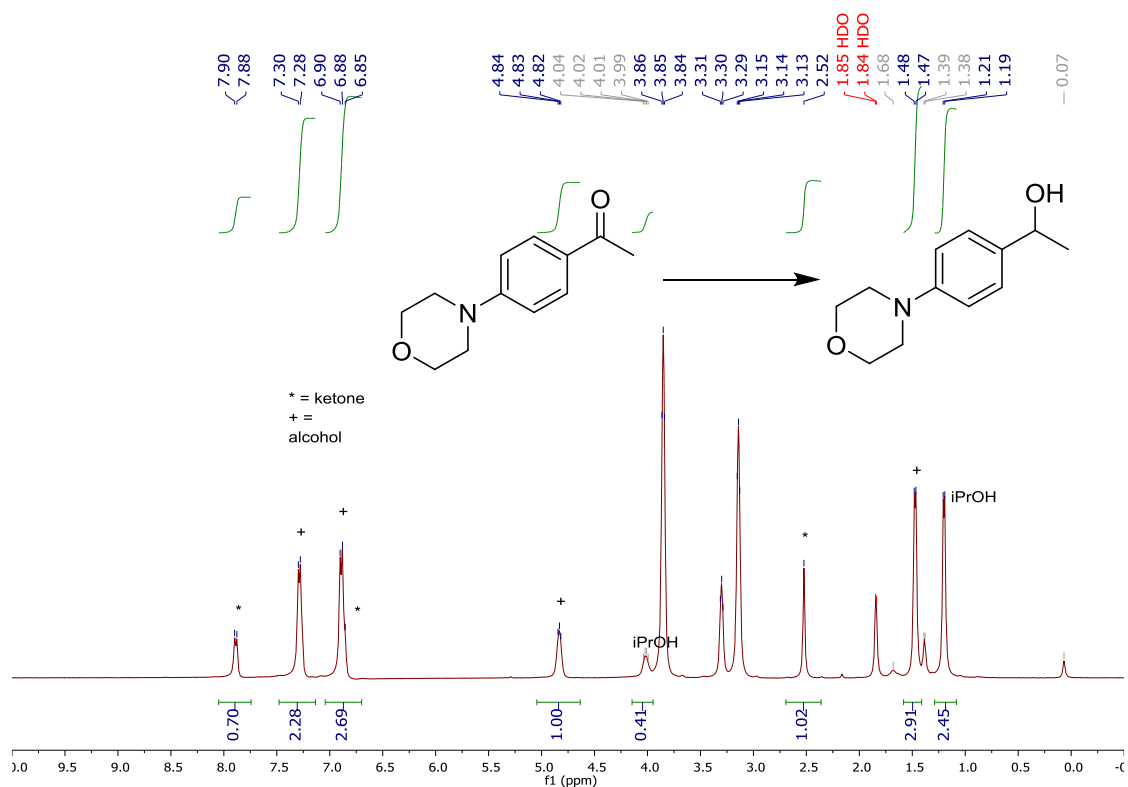


Figure S70: ^1H NMR spectrum of the crude mixture for the reduction of 4-morpholinoacetophenone **a20** recorded after 20 min at 80 °C at 300 MHz (74 % conversion).

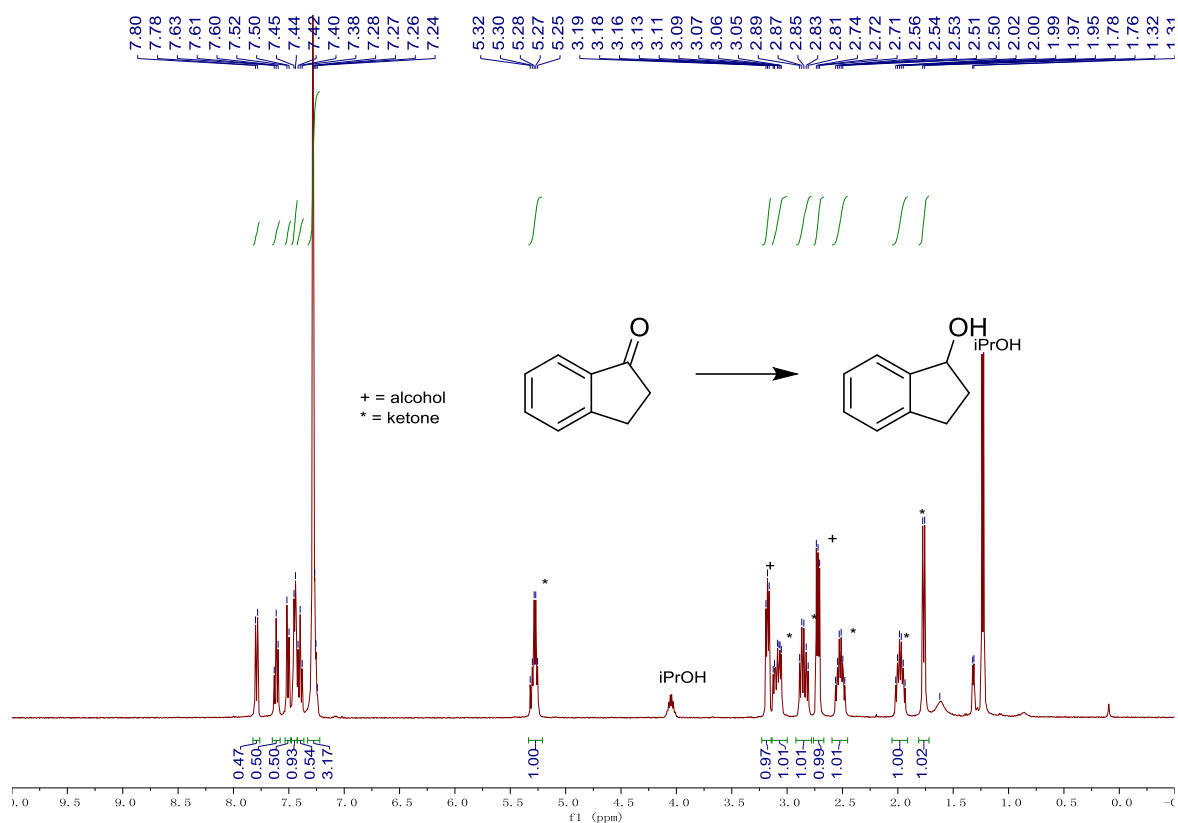


Figure S71: ^1H NMR spectrum of the crude mixture for the reduction of indanone **a29** recorded after 20 min at 80 °C at 300 MHz (67 % conversion).

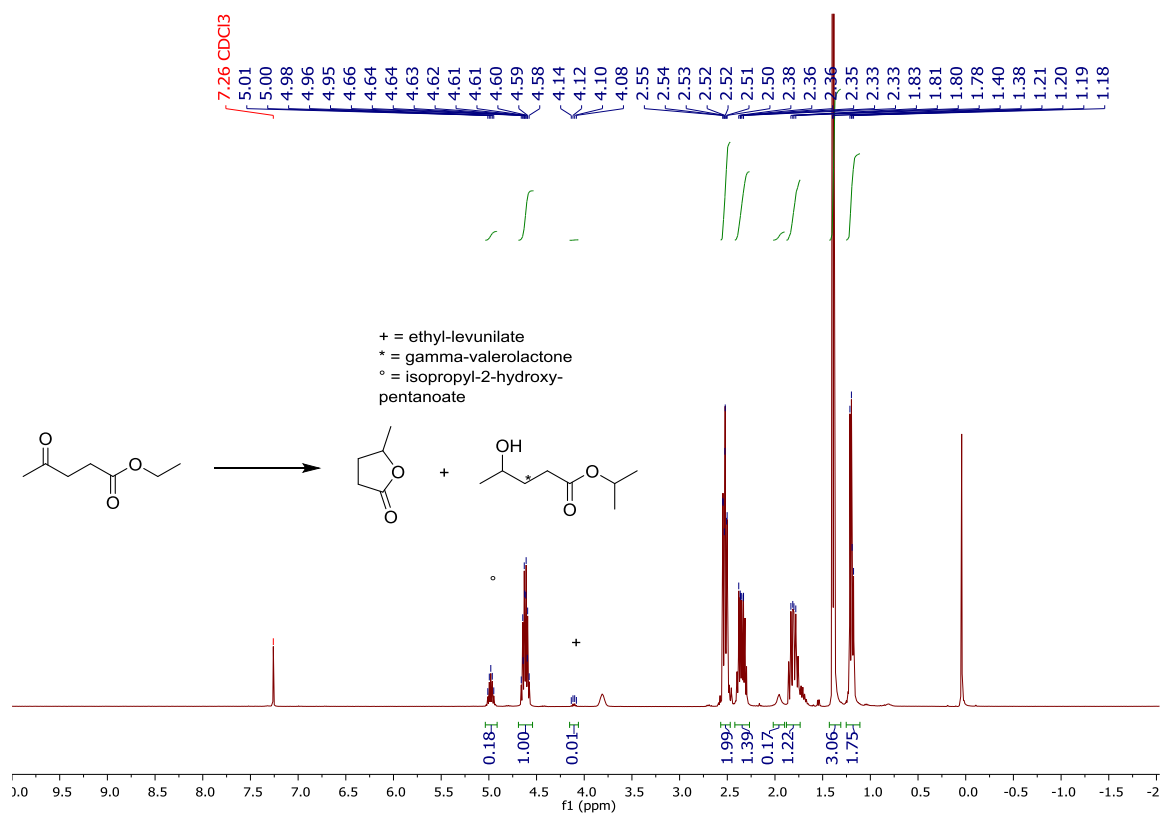


Figure S72: ^1H NMR spectrum of the crude mixture for the reduction of ethyl-levunilate **a24** recorded after 20 min at 80 °C at 300 MHz (67 % conversion).

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