Supporting Information

$B(C_6F_5)_3$-Catalyzed Transfer Hydrogenation of Esters and Organic Carbonates Towards Alcohols with Ammonia Borane

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Contents

1. General information

1.1 General experimental details

All experiments were performed under argon atmosphere by using standard Schlenk techniques, if not stated otherwise. All solvents were dried, stored in septum-sealed flasks over molecular sieves, degassed and purged with argon prior to use. Unless otherwise noted, all reagents were obtained from Sigma Aldrich, Alfa Aesar, TCI., Abcr, and Acros Organics GmbH. Aluminum TLC plates coated with silica gel 60 F_{254} were purchased from Merck, spots were detected with UV light and revealed with $KMnO_4$. Deuterated solvents were ordered from Deutero GmbH and stored over molecular sieves. Deuterium of BH_3NH_3 compounds were synthesized according to previous reports.[1, 2]

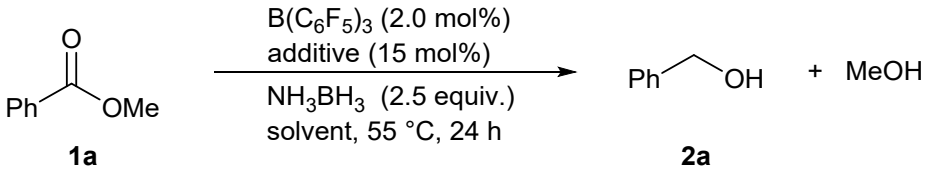
1.2 Instrumentation

NMR spectra were collected using *Bruker* 300 Fourier, *Bruker* AV 300 and *Bruker* AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). Abbreviations are: s: singlet, d: doublet, t: triplet and m: multiplet. GC analyses were performed on a Trace 1310 chromatograph with a 29 m HP5 column and the yields, and the data of GC was based on a calibrated area of mesitylene as internal standard. GC-MS spectra were recorded with a combination of an Agilent Technologies GC Mass 5973 Network MSD and an Agilent Technology 6890N Network GC System at LIKAT.

2. Screening of reaction conditions

2.1 Catalysts and co-catalysts

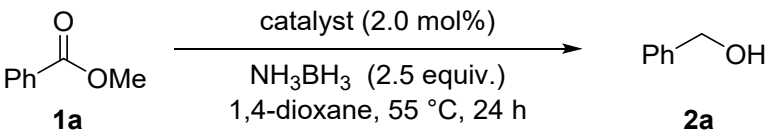
Table S1. Conditions' screening for the $B(C_6F_5)_3$-catalyzed transfer hydrogenation of methyl benzoate (**1a**) with ammonia borane[a]



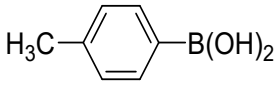
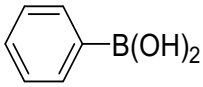
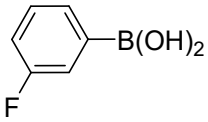
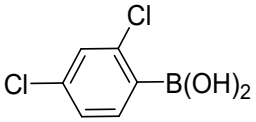
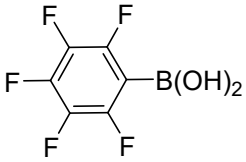
entry	additive	solvent	conv./ %	**2a**/ %
1	-	1,4-dixoane	63	59
2	TsOH	1,4-dixoane	7	traces
3	AgF	1,4-dixoane	18	traces
4	$Al(OTf)_3$	1,4-dixoane	63	59
5	$In(OTf)_3$	1,4-dixoane	65	64
6	$Sc(OTf)_3$	1,4-dixoane	61	58
7	$BF_3{\cdot}OEt_2$	1,4-dixoane	79	73
8[b]	$BF_3{\cdot}OEt_2$	1,4-dixoane	37	33
9	$BF_3{\cdot}OEt_2$	THF	41	39
10	$BF_3{\cdot}OEt_2$	toluene	22	trace
11	$BF_3{\cdot}OEt_2$	DCE	96	94
12	$BF_3{\cdot}OEt_2$	H_2O	-	-

[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (2.0 mol%), NH_3BH_3 (1.25 mmol, 2.5 equiv.), additive (15 mol%), solvent (1.0 mL) at 55 °C for 24 h. The conversions and yields were determined by GC using mesitylene as the internal standard. [b]without $B(C_6F_5)_3$.

Table S2. Catalysts screening for the transfer hydrogenation of methyl benzoate (**1a**).[a]



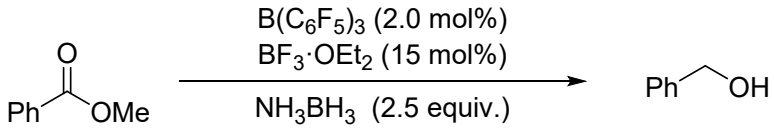
entry	catalyst	conv./ %	**2a**/ %[b]
1	-	13	-

2		21	-
3		31	-
4		22	14
5		27	-
6		26	19
7	$B(Ph)_3$	25	20
8	$BF_3{\cdot}OEt_2$	24	22

[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), catalyst (2.0 mol%), NH_3BH_3 (1.25 mmol, 2.5 equiv.), 1,4-dioxane (1.0 mL) at 55 °C for 24 h; [b] The conversion and yields were determined by GC using mesitylene as the internal standard.

2.2 Reaction temperature

Table S3. Effect of reaction temperature on the transfer hydrogenation of methyl benzoate (**1a**).[a]



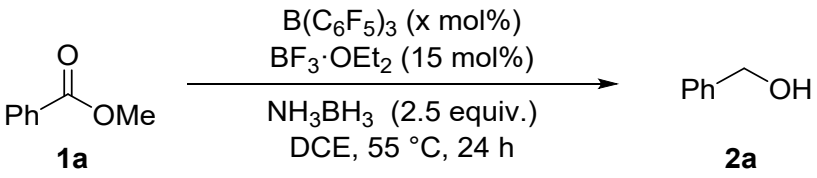
1a **2a**

entry	*T*/ °C	conv./ %	**2a**/ %[b]
1	35	32	19
2	45	68	53
3	55	96	94
4	65	>99	93
5	75	>99	93
6	85	>99	94
7	95	>99	89
8[c]	95	>99	84

[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (2.0 mol%), NH_3BH_3 (1.25 mmol, 2.5 equiv.), $BF_3{\cdot}OEt_2$ (15 mol%), DCE (1.0 mL) at *T* °C for 24 h; [b] The conversion and yields were determined by GC using mesitylene as the internal standard; [c] without additive.

2.3 Catalyst loading

Table S4. Catalyst loading effect on the transfer hydrogenation of methyl benzoate (**1a**).[a]



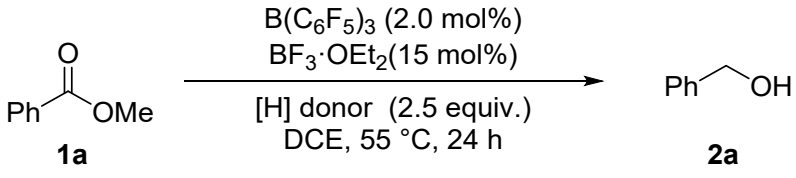
1a **2a**

entry	x/ mol%l	conv./ %	**2a**/ %[b]
1	0.0	34	32
2	1.0	81	77
3	2.0	96	94
4	3.0	>99	94
5	4.0	>99	94
6	5.0	>99	93

[a] Reaction conditions: **1a** (0.50 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (x mol%), $BF_3{\cdot}OEt_2$ (15 mol%), NH_3BH_3 (1.25 mmol, 2.5 equiv.), DCE (1.0 mL) at 55 °C for 24 h; [b] The conversions and yields were determined by GC using mesitylene as the internal standard.

2.4 Hydrogen source

Table S5. Transfer hydrogenation of methyl benzoate (**1a**) with various hydrogen source.[a]



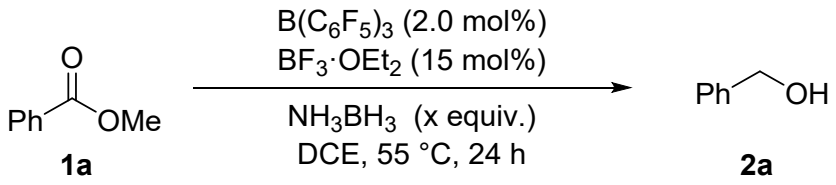
1a **2a**

entry	[H] donor	conv./ %	**2a**/ %[b]
1	Hantzsch ester (4.5 equiv.)	-	-
2	Isopropanol (96 equiv.)	-	-
3	$NHMe_2BH_3$ (2.5 equiv.)	35	17
4	$HCOOH/Et_3N$ (6 equiv.)	-	-
5	H_2 (40 bar)	25	22
6	NH_3BH_3 (2.5 equiv.)	96	94
7	NMe_3BH_3 (2.5 equiv.)	28	5
8	$NH_2{}^t BuBH_3$ (2.5 equiv.)	11	-

[a] Reaction conditions: **1a** (0.50 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (2.0 mol%), $BF_3{\cdot}OEt_2$ (15 mol%), hydrogen donor, DCE (1.0 mL) at 55 °C for 24 h; [b] The conversions and yields were determined by GC using mesitylene as the internal standard.

2.5 Amount of hydrogen donor

Table S6. Transfer hydrogenation of methyl benzoate (**1a**) with various amount of hydrogen donors.[a]



1a **2a**

entry	x/ mmol	conv./ %	**2a**/ %[b]
1	0.50	41	37
2	0.75	69	63
3	1.00	87	85
4	1.25	96	94
5	1.5	>99	92

[a] Reaction conditions: **1a** (0.50 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (2.0 mol%), $BF_3{\cdot}OEt_2$ (15 mol%), NH_3BH_3 (x mmol), DCE (1.0 mL) at 55 °C for 24 h; [b] The conversions and yields were determined by GC using mesitylene as the internal standard.

3. Reaction scope

3.1 General method for transfer hydrogenation reaction

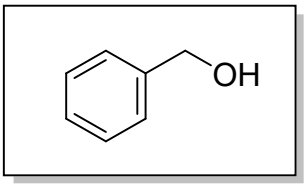
General Procedure 1 (GP-1): In an oven-dried 10 mL pressure tube equipped with a stirring bar, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%) was dissolved in DCE (1.0 mL). The substrates **1** (0.5 mmol), NH_3BH_3 (38.7 mg, 1.25 mmol) and co-catalyst $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%) were added to the tube under Argon atmosphere. Then, the tube was sealed, and the reaction mixture was stirred at 55 °C for 24 h. After this time, the reaction mixture was allowed to cool to room temperature. The solvent and other volatile materials were removed by rotary evaporation, and the resulting the crude mixture was purified by column chromatography on silica gel to afford the desired products.

General Procedure 2 (GP-2): The same as Procedure 1, but using 78.10 mg (2.5 mmol) of NH_3BH_3.

General Procedure 3 (GP-3): The same as Procedure 1, but using 54.5 mg (1.75 mmol) of NH_3BH_3.

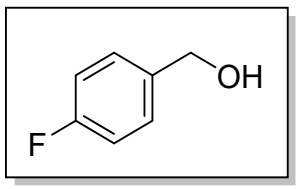
3.2 Characterization data of transfer hydrogenation products

Benzyl alcohol (2a)



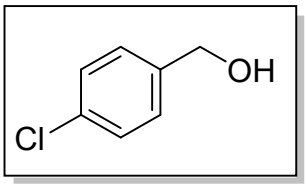
According to the **GP-1**, $B(C_6F_5)_3$ (5.1 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1a** (68.2 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2a** (47.6 mg, 0.44 mmol, 88%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.31 – 7.14 (m, 5H), 4.55 (t, J = 0.5 Hz, 2H), 2.09 (s, 1H) ppm.**^{13}C NMR** (75 MHz, $CDCl_3$) δ = 140.90, 128.57, 127.64, 127.02, 65.25 ppm. The spectroscopic data match those reported in the literature.[3]

4-Fluorobenzylic alcohol (2b)



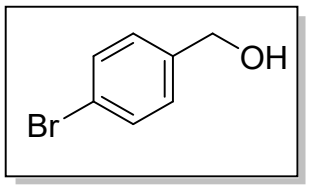
According to the **GP-1**, $B(C_6F_5)_3$ (5.1 mg, 2.0 mol%), NH_3BH_3 (38.6 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.7 mg, 15 mol%), **1f** (77.1 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2b** (60.5 mg, 0.48 mmol, 96%) was obtained as pale yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.43 – 7.17 (m, 2H), 7.13 – 6.94 (m, 2H), 4.60 (d, J = 1.6 Hz, 2H), 2.34 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 163.84, 160.59, 136.52, 136.48, 128.73, 128.62, 115.41, 115.12, 64.39 ppm. The spectroscopic data match those reported in the literature.[3]

4-Chlorobenzyl alcohol (2c)



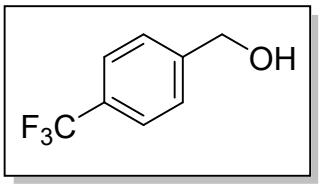
According to the **GP-1**, $B(C_6F_5)_3$ (5.1 mg, 2.0 mol%), NH_3BH_3 (38.5 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1g** (89.2 mg, 0.52 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2c** (68.6 mg, 0.48 mmol, 93%) was obtained as white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.26 – 7.15 (m, 4H), 4.54 (d, J = 0.8 Hz, 2H), 2.13 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 139.24, 133.33, 128.67, 128.29, 64.45 ppm. The spectroscopic data match those reported in the literature.[3]

4-Bromobenzyl alcohol (2d)



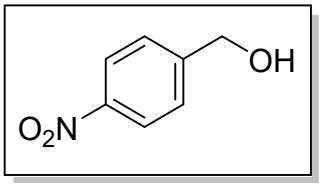
According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 20 mol%), **1h** (107.5 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2d** (75.7 mg, 42.6 mmol, 81%) was obtained as white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.41 – 7.33 (m, 2H), 7.15 – 7.04 (m, 2H), 4.52 (s, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 139.76, 131.62, 128.60, 121.44, 64.49 ppm. The spectroscopic data match those reported in the literature.[3]

4-(Trifluoromethyl)benzyl alcohol (2e)



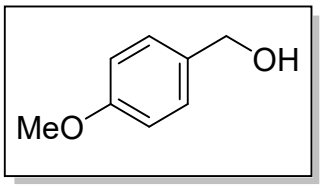
According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.6 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1i** (109.7 mg, 0.54 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2e** (87.4 mg, 0.49 mmol, 92%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.57 – 7.33 (m, 4H), 4.66 (s, 2H), 2.11 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 144.67, 144.65, 126.86, 126.82, 126.80, 126.76, 125.50, 125.45, 125.40, 125.35, 64.33 ppm. The spectroscopic data match those reported in the literature.[4]

4-Nitrobenzyl alcohol (2f)



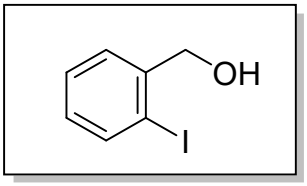
According to the **GP-1**, $B(C_6F_5)_3$ (5.1 mg, 2.0 mol%), NH_3BH_3 (38.60 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.7 mg, 15 mol%), **1j** (91.1 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2f** (59.7 mg, 0.4 mmol, 78%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.22 – 8.14 (m, 2H), 7.55 – 7.48 (m, 2H), 4.82 (s, 2H), 2.42 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 148.24, 147.14, 126.93, 123.63, 63.86 ppm. The spectroscopic data match those reported in the literature.[5]

4-Methoxybenzyl alcohol (2g)



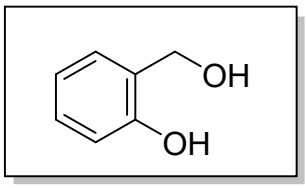
According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.7 mg, 15 mol%), **1k** (83.1 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2g** (52.5 mg, 0.38 mmol, 76%) was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.26 – 7.13 (m, 2H), 6.85 – 6.72 (m, 2H), 4.51 (s, 2H), 3.72 (s, 3H), 1.92 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 159.18, 133.15, 128.67, 113.95, 64.98, 64.96, 55.31 ppm. The spectroscopic data match those reported in the literature.[4]

2-Iodobenzyl alcohol (2h)



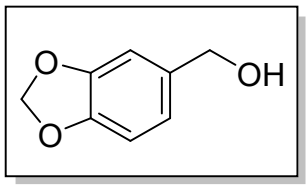
According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1l** (131.0 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2h** (72.6 mg, 0.31 mmol, 62%) was obtained as white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.74 (dd, J = 7.9, 1.2 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.28 (td, J = 7.5, 1.2 Hz, 1H), 6.91 (dddd, J = 7.9, 7.3, 1.7, 0.6 Hz, 1H), 4.58 (s, 2H), 2.12 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 142.61, 139.21, 129.33, 128.52, 128.46, 97.49, 69.30 ppm. The spectroscopic data match those reported in the literature.[6]

2-Hydroxybenzyl alcohol (2i)



According to the **GP-1**, $B(C_6F_5)_3$ (5.1 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 20 mol%), **1m** (76.2 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2i** (55.8 mg, 0.45 mmol, 89%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.20 – 7.16 (m, 1H), 7.13 (ddt, J = 7.8, 1.7, 0.5 Hz, 1H), 6.97 (ddt, J = 6.9, 1.8, 0.6 Hz, 1H), 6.85 – 6.74 (m, 2H), 4.80 (s, 2H), 2.15 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 156.13, 129.56, 127.81, 124.59, 120.10, 116.60, 64.75 ppm. The spectroscopic data match those reported in the literature.[6]

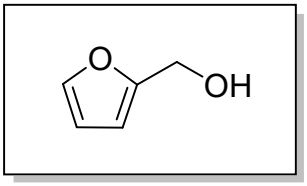
Piperonyl alcohol (2j)



According to the **GP-1**, $B(C_6F_5)_3$ (5.1 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (14.20 mg, 20 mol%), **1n** (90.2 mg, 0.50 mmol) and DCE (1.00 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2j** (74.5 mg, 0.49 mmol, 97%) was obtained as white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 6.78 (dt, J = 1.6, 0.6 Hz, 1H), 6.75 – 6.67 (m, 2H), 5.87 (s, 2H),

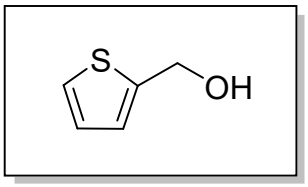
4.49 (d, *J* = 0.5 Hz, 2H), 1.82 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* = 147.83, 147.10, 134.89, 120.53, 108.22, 107.91, 101.03, 65.24 ppm. The spectroscopic data match those reported in the literature.[7]

Furfuryl alcohol (2k)



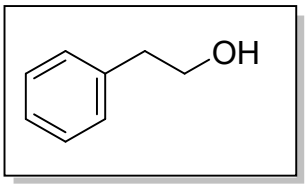
According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1o** (62.5 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2k** (39.2 mg, 0.4 mmol, 80%) was obtained as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) *δ* = 7.43 – 7.38 (m, 1H), 6.35 (ddd, *J* = 3.2, 1.9, 0.5 Hz, 1H), 6.29 (dp, *J* = 3.2, 0.6 Hz, 1H), 4.58 (q, *J* = 0.5 Hz, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* = 154.08, 142.52, 110.35, 107.71, 57.28 ppm. The spectroscopic data match those reported in the literature.[3]

2-Thiophenemethanol (2l)



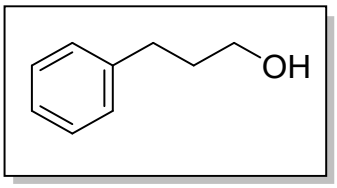
According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1p** (71.1 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2l** (42.3 mg, 0.37 mmol, 74%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) *δ* = 7.29 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.12 – 6.91 (m, 2H), 4.79 (s, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* = 144.03, 126.89, 125.58, 125.50, 59.82 ppm. The spectroscopic data match those reported in the literature.[6]

2-Phenylethanol (2m)



According to the **GP-1**, $B(C_6F_5)_3$ (5.1 mg, 2.0 mol%), NH_3BH_3 (38.7 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1q** (75.2 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2m** (48.8 mg, 0.4 mmol, 79%) was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* = 7.48 – 7.21 (m, 5H), 3.85 (t, *J* = 6.7 Hz, 2H), 2.89 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* = 138.69, 129.11, 128.59, 126.46, 63.61, 39.22 ppm. The spectroscopic data match those reported in the literature.[4]

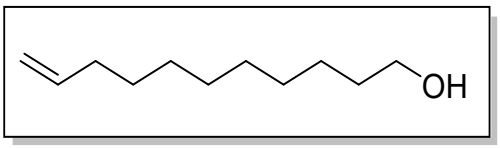
3-Phenyl-1-propanol (2n)



According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.6 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1r** (82.3 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2,

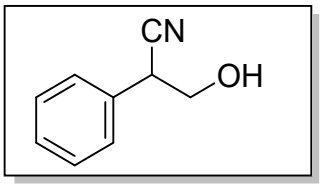
CH_2Cl_2/MeOH = 95:5) the title compound **2n** (49.0 mg, 0.36 mmol, 72%) was obtained as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.23 (m, 5H), 3.71 (td, J = 6.6, 1.7 Hz, 2H), 2.90 (dd, J = 32.8, 16.8 Hz, 1H), 2.81 – 2.72 (m, 2H), 1.96 (ddt, J = 8.0, 6.4, 3.3 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.00, 141.97, 128.52, 128.47, 125.92, 62.08, 62.06, 34.25, 32.15 ppm. The spectroscopic data match those reported in the literature.[8]

10-Undecen-1-ol (2o)



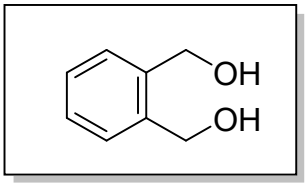
According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.6 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1s** (98.9 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2o** (35.7 mg, 0.21 mmol, 41%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 5.79 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H), 5.06 – 4.82 (m, 2H), 3.59 (td, J = 6.7, 1.1 Hz, 2H), 2.55 (t, J = 12.0 Hz, 1H), 2.02 (tdd, J = 6.5, 5.2, 1.5 Hz, 2H), 1.62 – 1.44 (m, 2H), 1.43 – 1.02 (m, 13H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 139.12, 114.08, 62.73, 33.78, 32.70, 29.55, 29.43, 29.11, 28.91, 25.75 ppm. The spectroscopic data match those reported in the literature.[9]

3-Hydroxy-2-phenylpropanenitrile (2p)



According to the **GP-1**, $B(C_6F_5)_3$ (5.3 mg, 2.0 mol%), NH_3BH_3 (38.6 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 20 mol%), **1t** (94.6 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2p** (47.1 mg, 0.32 mmol, 64%) was obtained as yellow liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.38 – 7.25 (m, 5H), 3.97 – 3.79 (m, 3H), 2.42 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 132.18, 129.29, 128.68, 127.83, 119.50, 65.30, 41.00 ppm. The spectroscopic data match those reported in the literature.[10]

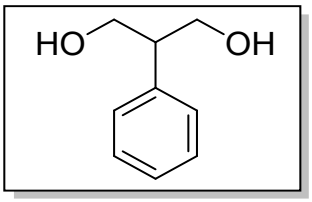
1,2-Benzenedimethanol (2q)



According to the **GP-2**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (78.1 mg, 2.5 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1u** (111.2 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2q** (24.9 mg, 0.18 mmol, 35%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.23 (d, J = 1.0 Hz, 4H), 4.57 (s, 4H), 3.36 (s, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 139.38, 129.71, 128.56, 64.03 ppm. The spectroscopic data match those reported in the literature.[11]

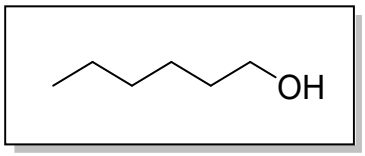
2-Phenyl-1,3-propanediol (2r)

According to the **GP-2**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (78.1 mg, 2.5 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1v** (118.2 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2r** (25.7 mg, 0.17 mmol, 33%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.30 – 7.11 (m, 5H), 3.95 – 3.80 (m, 4H), 3.01 (tt, *J* = 7.6, 5.6 Hz, 1H), 2.28 (dd, *J* = 2.5, 1.5 Hz, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 139.33, 128.82, 128.05, 127.24, 66.02, 49.76 ppm. The spectroscopic data match those reported in the literature.[12]



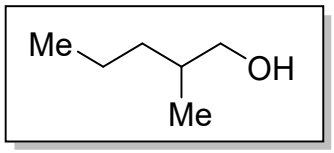
Hexan-1-ol (2s)

According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.6 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1y** (64.9 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2s** (27.6 mg, 0.27 mmol, 54%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 3.58 (t, *J* = 6.7 Hz, 2H), 2.62 – 2.53 (m, 1H), 1.61 – 1.46 (m, 2H), 1.40 – 1.20 (m, 6H), 0.94 – 0.81 (m, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 62.74, 32.65, 31.63, 25.42, 22.60, 13.96 ppm. The Spectroscopic data match those reported in the literature.[3]



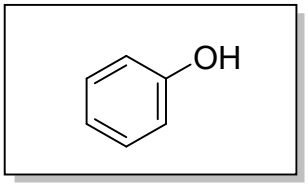
2-Methyl-1-pentanol (2t)

According to the **GP-1**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (38.6 mg, 1.25 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **1z** (65.1 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2t** (26.1 mg, 0.26 mmol, 52%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 3.60 – 3.37 (m, 2H), 1.72 – 1.57 (m, 1H), 1.52 (dq, J = 1.4, 0.7 Hz, 1H), 1.47 – 1.24 (m, 3H), 1.18 – 1.02 (m, 1H), 0.96 – 0.87 (m, 6H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 68.43, 35.49, 35.41, 20.07, 16.54, 14.33 ppm. The Spectroscopic data match those reported in the literature.[13]



Phenol (2u)

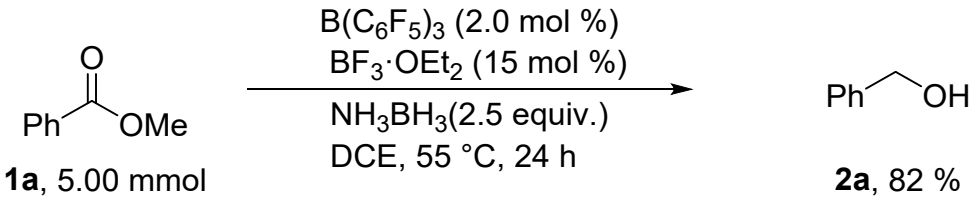
According to the **GP-3**, $B(C_6F_5)_3$ (5.2 mg, 2.0 mol%), NH_3BH_3 (54.5 mg 1.75 mmol), $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%), **4a** (107.1 mg, 0.5 mmol) and DCE (1.0 mL) were used. The mixture was put in a preheated oil bath (55 °C) and stirred for 24 h. After column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) the title compound **2u** (83.8 mg, 0.89 mmol, 89%) was obtained as colorless liquid. **^{1}H NMR** (300 MHz $CDCl_3$) δ = 7.33 – 7.24 (m, 2H), 7.03 – 6.95 (m, 1H), 6.92 – 6.84 (m, 2H),



5.29 (s, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 155.36, 129.76, 120.94, 115.39 ppm. Spectroscopic data match those reported in the literature.[9]

3.3 Scale-up experiments

1) Ester



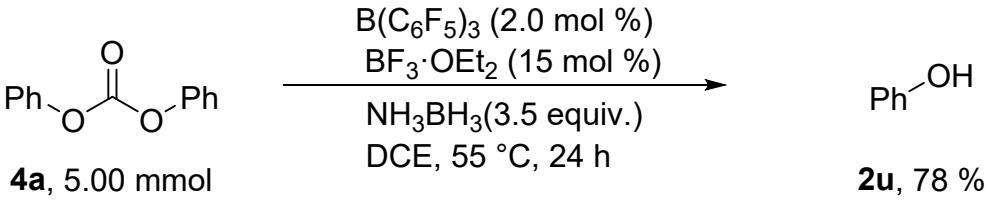
1a, 5.00 mmol

2a, 82 %

Scheme S1. Transfer hydrogenation of gram-scale ester (**1a**).

In an oven-dried 20 mL pressure tube equipped with a stirring bar, $B(C_6F_5)_3$ (0.052 g, 0.1 mmol) was dissolved in DCE (10.0 mL). The substrates **1a** (0.685 g, 5.00 mmol), NH_3BH_3 (0.386 g, 12.5 mmol) and co-catalyst $BF_3{\cdot}OEt_2$ (0.108 g, 15 mol%) were added to the tube under Argon atmosphere. Then, the tube was sealed, and the reaction mixture was stirred at 55 °C for 24 h. After this time, reaction mixture was allowed to cool to room temperature, extracted with diethyl ether and concentrated under reduced pressure. The yield was calculated by GC using mesitylene as internal standard.

2) Carbonate



4a, 5.00 mmol

2u, 78 %

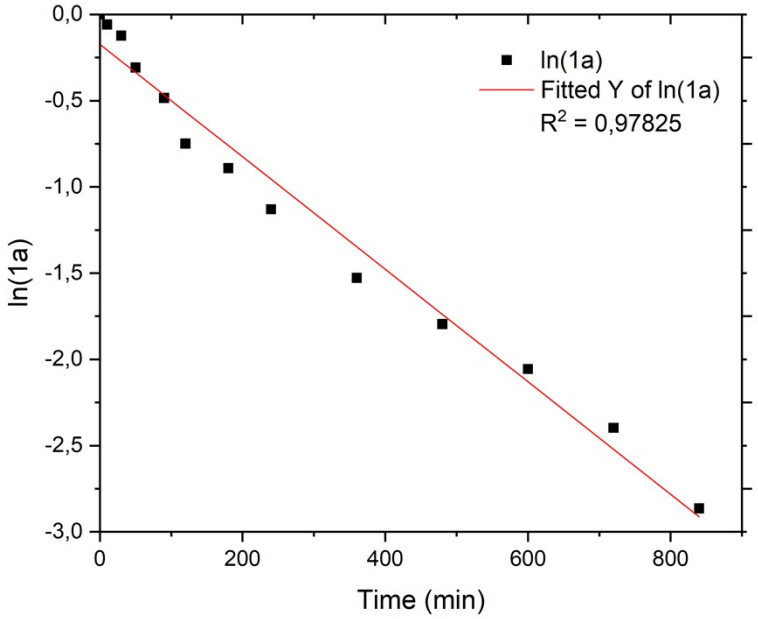
Scheme S2. Transfer hydrogenation of large-scale carbonate (**4a**).

In an oven-dried 20 mL pressure tube equipped with a stirring bar, $B(C_6F_5)_3$ (0.052 g, 0.1 mmol) was dissolved in DCE (10.0 mL). The substrates **4a** (1. 080 g, 5.00 mmol), NH_3BH_3 (0.543 g, 17.5 mmol) and co-catalyst $BF_3{\cdot}OEt_2$ (0.108 g, 15 mol%) were added to the tube under Argon atmosphere. Then, the tube was sealed, and the reaction mixture was stirred at 55 °C for 24 h. After this time, reaction mixture was allowed to cool to room temperature, extracted with diethyl ether and concentrated under reduced pressure. The yield was calculated by GC using mesitylene as internal standard.

4. Mechanistic studies

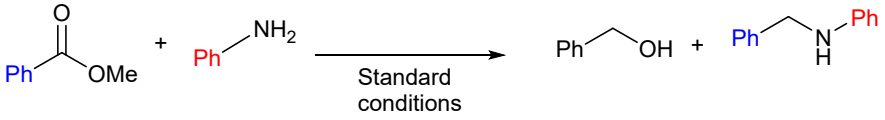
The following scheme presents an overview of the performed mechanistic investigations. For further details see the following sub-sections.

Kinetic profile (first order on substrate)



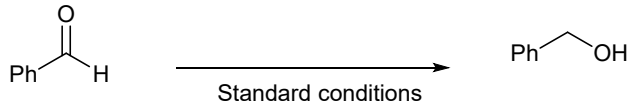
Control experiments

A



1a **5** **2a**, n.d. **6**, 42%

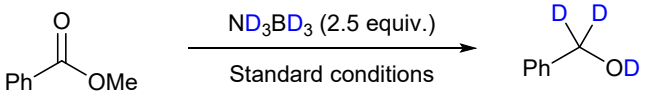
B



7 **2a**, 98 %[b]

Deuterium experiments

C



1a **[D]-2a**, 73 %

Scheme S3. Mechanistic studies on the transfer hydrogenation of methyl benzoate with ammonia borane. Standard conditions: **4** (0.5 mmol), $B(C_6F_5)_3$ (2 mol%), NH_3BH_3 (1.75 mmol), $BF_3{\cdot}OEt_2$ (15 mol%), DCE (1.0 mL) at 55 °C for 24 h. n.d. = not detected. *Yields determined by GC.

4.1 Analysis of products from dehydrogenation of ammonia borane

After the reactions, an insoluble material was obtained. ^{11}B-[^1H] NMR spectroscopy (Figure S1a) confirmed that this insoluble material are the by-products of the dehydrogenation of ammonia borane (Figure S1b).[14, 15]

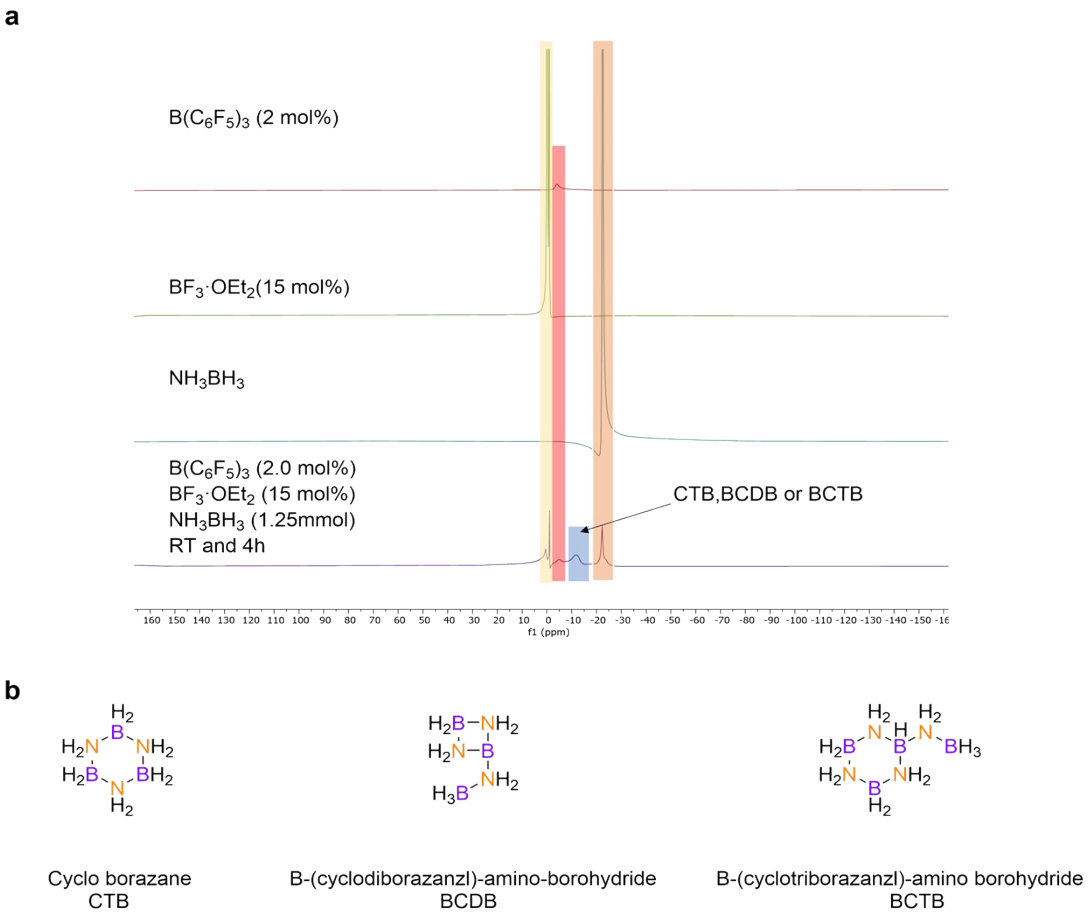


Figure S1. (a) ^{11}B-[^{1}H] NMR spectra for dehydrogenation products of ammonia borane at room temperature and (b) structures of the identified dehydrogenation products.

4.2 Deuterium experiments

4.2.1 Synthesis of deuterated ammonia borane (ND_3BD_3)

$$2\ NaBD_4 + (NH_4)_2SO_4 \xrightarrow[16h,\ 40\ °C]{THF} NH_3BD_3 \xrightarrow[24h,\ 25\ °C]{CD_3OD} ND_3BD_3$$

Scheme S4. Reaction sequence for the preparation of deuterated ammonia borane

The reaction was performed according to the previous reports.[1, 2] In a dried Schlenk tube, $NaBD_4$ (90 %-D, 0.50 g, 12.0 mmol, 1.0 equiv.) and ammonium sulfate (1.66 g, 12.5 mmol, 1.04 equiv.) were added and dissolved in dry THF (75 mL) under Argon atmosphere. The reaction mixture was stirred for 16 h at 40°C. After cooling to room temperature, the solvent was removed by rotary evaporation. The crude product was dissolved in dry diethyl ether and filtered to remove any insoluble materials (repeated 3 times). The solvent was removed, and the product dried in *vacuo* at room temperature to obtain a white solid (NH_3BD_3) in 61.5 % yield. The deuterium content was determined by ^{1}H-NMR spectroscopy and calculated by the integrals of $NH_3B\boldsymbol{H}_3$ (0.44) and $NH_3B\boldsymbol{D}_3$ (3.0) (Figure S2). Deuterium content = 1-(0.44/3.0) = 0.85 = 85%

NH_3BD_3. Then, using another dried Schlenk tube, NH_3BD_3 (169.2mg, 5.0 mmol) was dissolved in 10 mL CD_3OD and stirred for 24 h. After evaporation of the solvent, the residue was dried in *vacuo* to obtain the final product as a white solid (yield 62 %). The deuteration degree of the compound was determined by ^{1}H-NMR spectroscopy and calculated from the integral of residual $NH_3B(\boldsymbol{H/D})_3$ (Figure S5). Deuterium content = [(1-(0.55/3.0)]*0.85 = 0.70 = 70% ND_3BD_3.

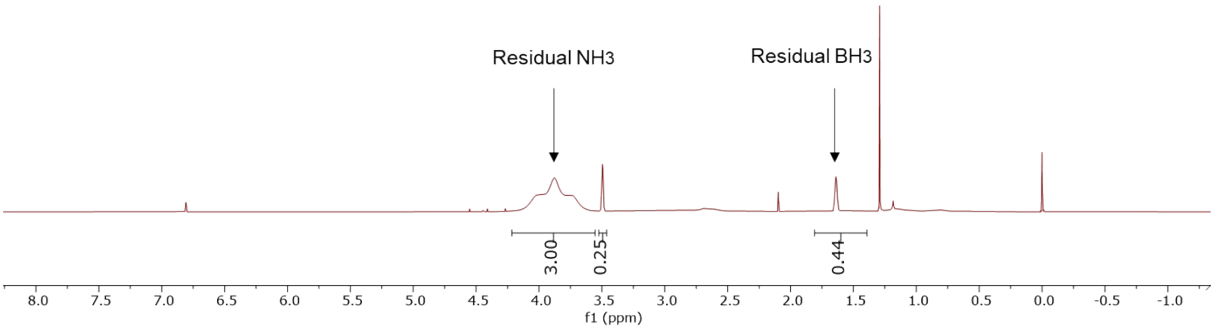


Figure S2. ^{1}H-NMR spectrum (400 MHz, THF-d_8) of NH_3BD_3.

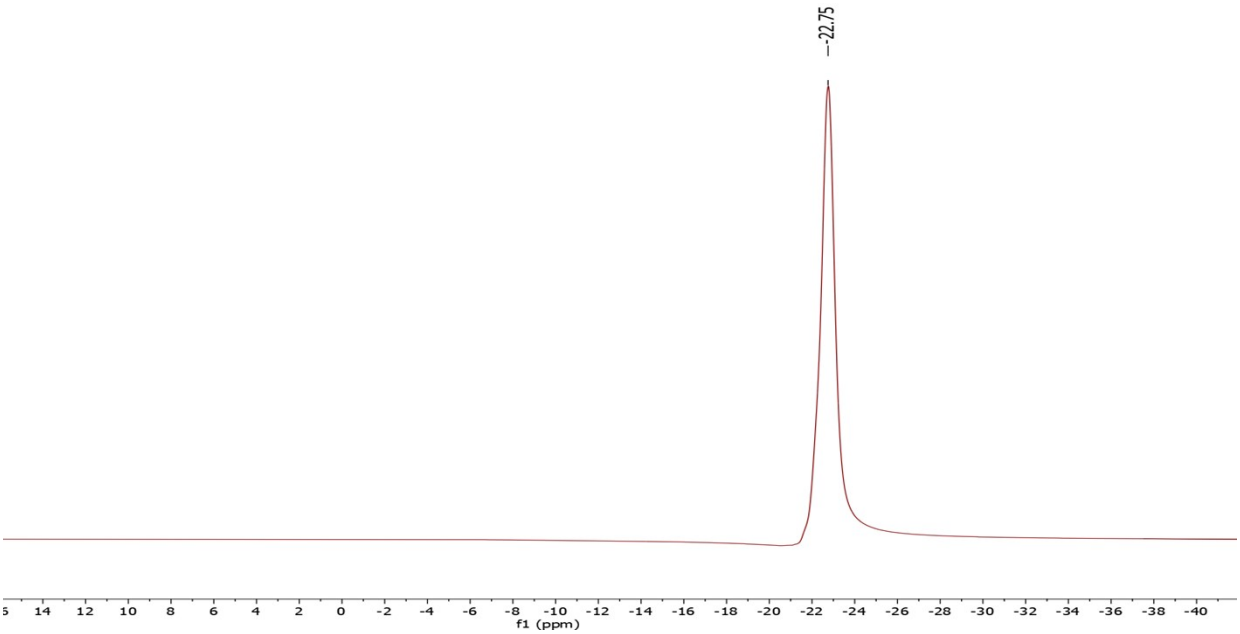


Figure S3. ^{11}B-NMR spectrum (400 MHz, THF-d_8) of NH_3BD_3.

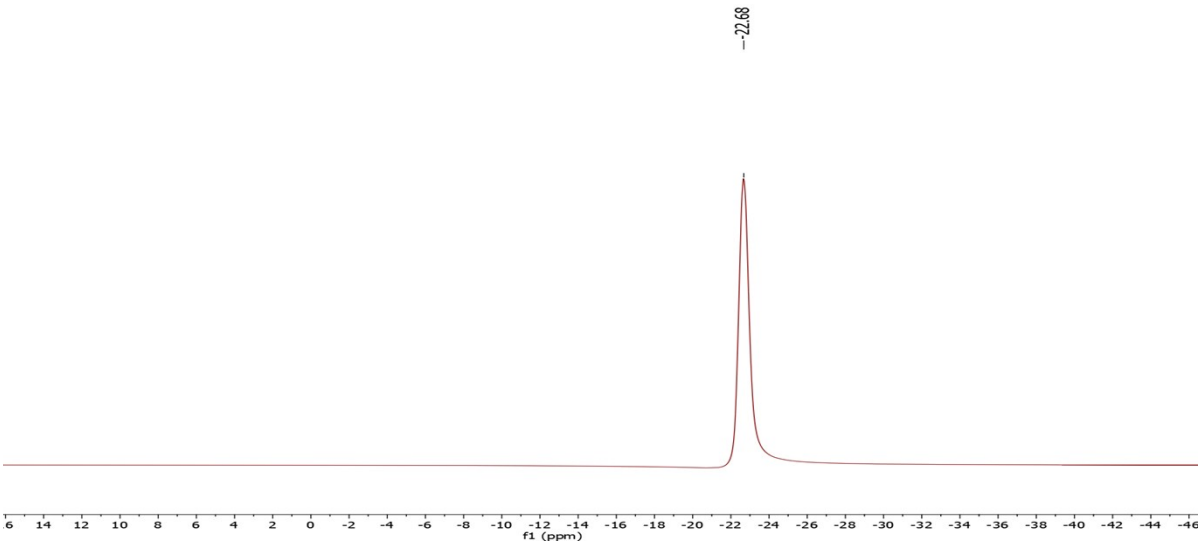


Figure S4. ^{11}B-[^{1}H] NMR spectrum (400 MHz, THF-d_8) of NH_3BD_3.

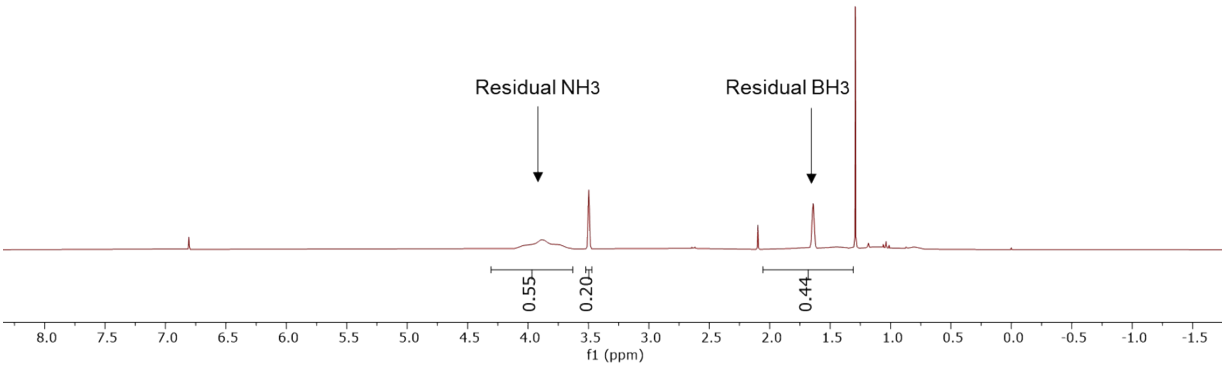


Figure S5. ^{1}H-NMR spectrum (400 MHz, THF-d_8) of ND_3BD_3.

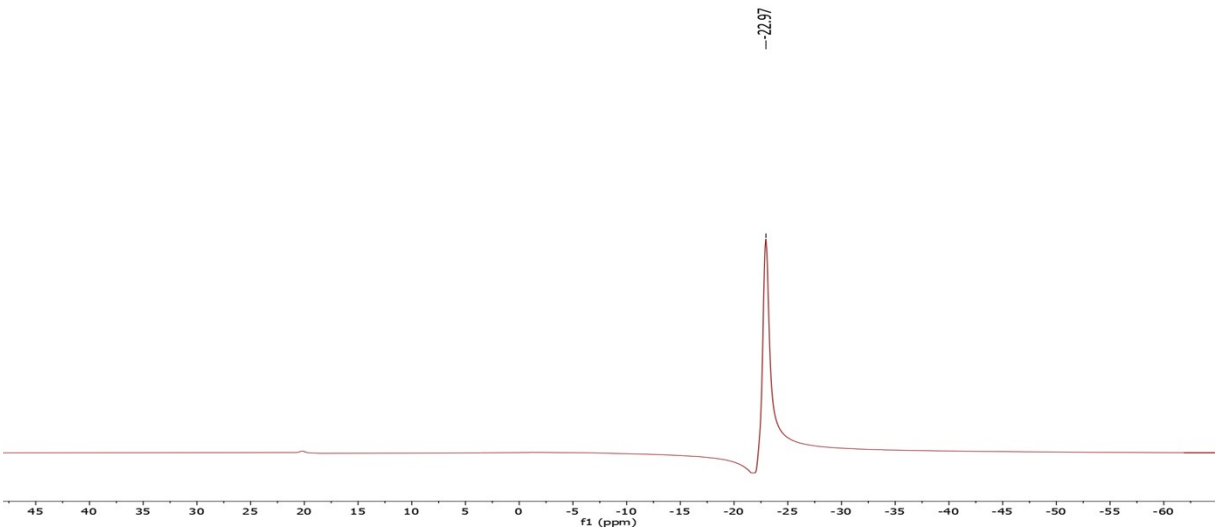


Figure S6. ^{11}B-NMR spectrum (400 MHz, THF-d_8) of ND_3BD_3.

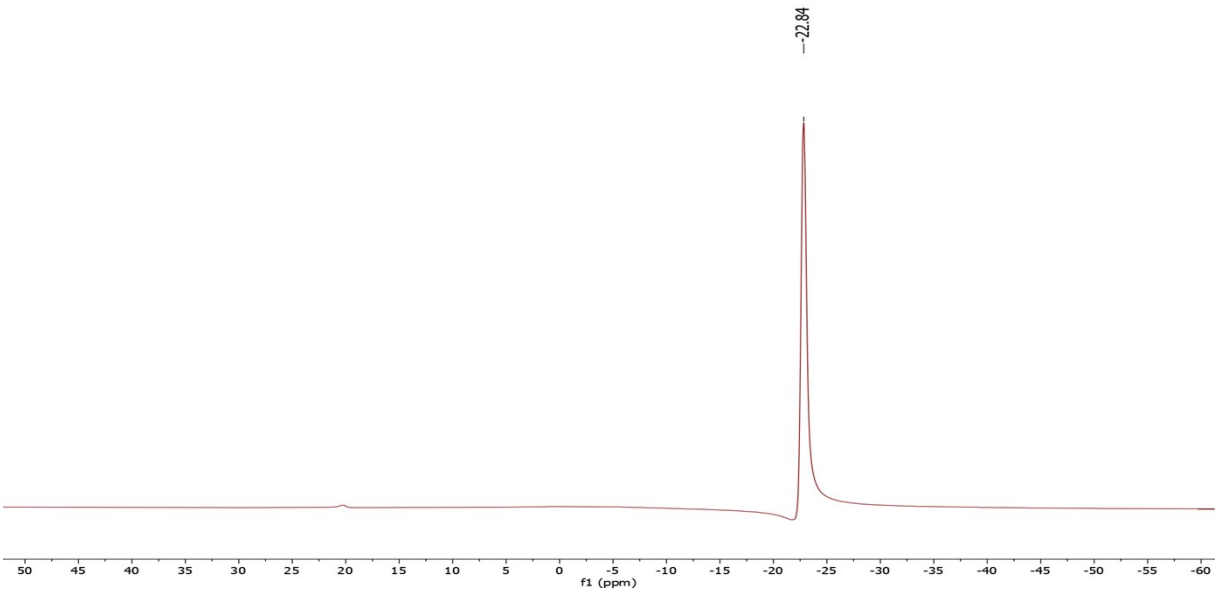
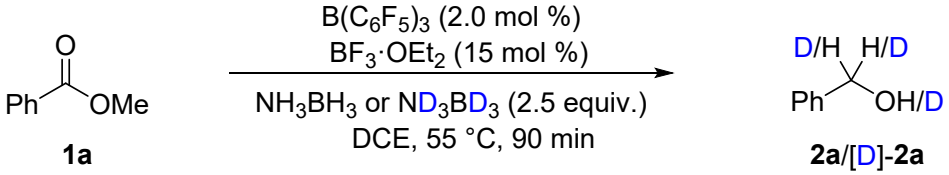


Figure S7. ^{11}B-[^{1}H] NMR spectrum (400 MHz, THF-d_8) of ND_3BD_3.

4.2.2 Determination of kinetic isotope effects



1a **2a**/[D]-**2a**

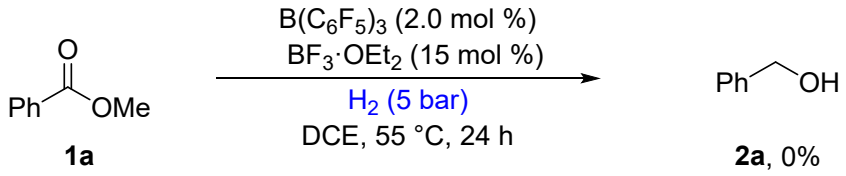
	NH_3BH_3	ND_3BD_3
2a	26.2%	-
[D]-**2a**	-	18.3%

Scheme S5. Transfer hydrogenation of esters using normal and labeled ammonia borane.

In an oven-dried 10 mL pressure tube equipped with a stirring bar, $B(C_6F_5)_3$ (5.0 mg, 2.0 mol%) which was dissolved in DCE (1.0 mL). The substrates **1a** (68.2 mg, 0.5 mmol), NH_3BH_3 (38.6 mg, 1.25 mmol) and $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%) were added under argon atmosphere. Then, the tube was sealed, and reaction mixture was stirred at 55 °C for 90 min; Another parallel reaction was carried out with using fully deuterated labeled AB (41.2 mg, 1.25 mmol). After this time, reaction mixtures were allowed to cool to room temperature, extracted with diethyl ether and concentrated under reduced pressure, respectively. The yields were calculated by GC using mesitylene as internal standard. Comparing the yield of reactions using deuterated AB with normal AB the kinetic isotope effect (KIE) was calculated as:

KIE = Yield (NH_3BH_3)/Yield (ND_3BD_3) = 1.43

4.3 Hydrogenation under standard conditions with low-pressure H_2



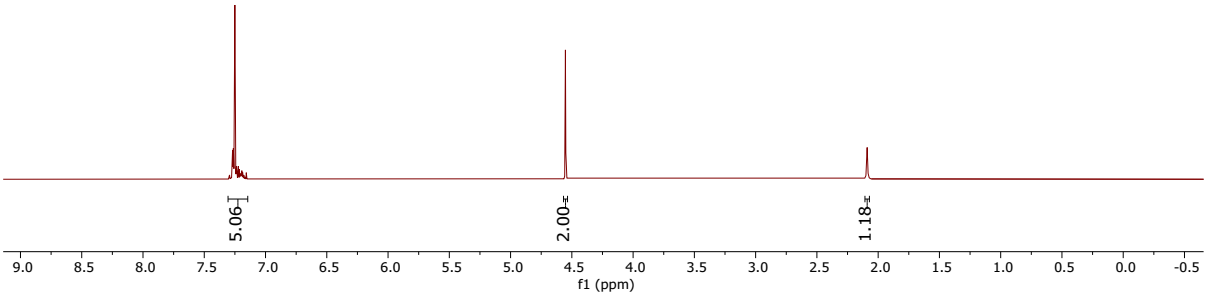
1a **2a**, 0%

Scheme S6. Hydrogenation of methyl benzoate **1a** with 5 bar H_2. The yield was determined by GC using mesitylene as the internal standard.

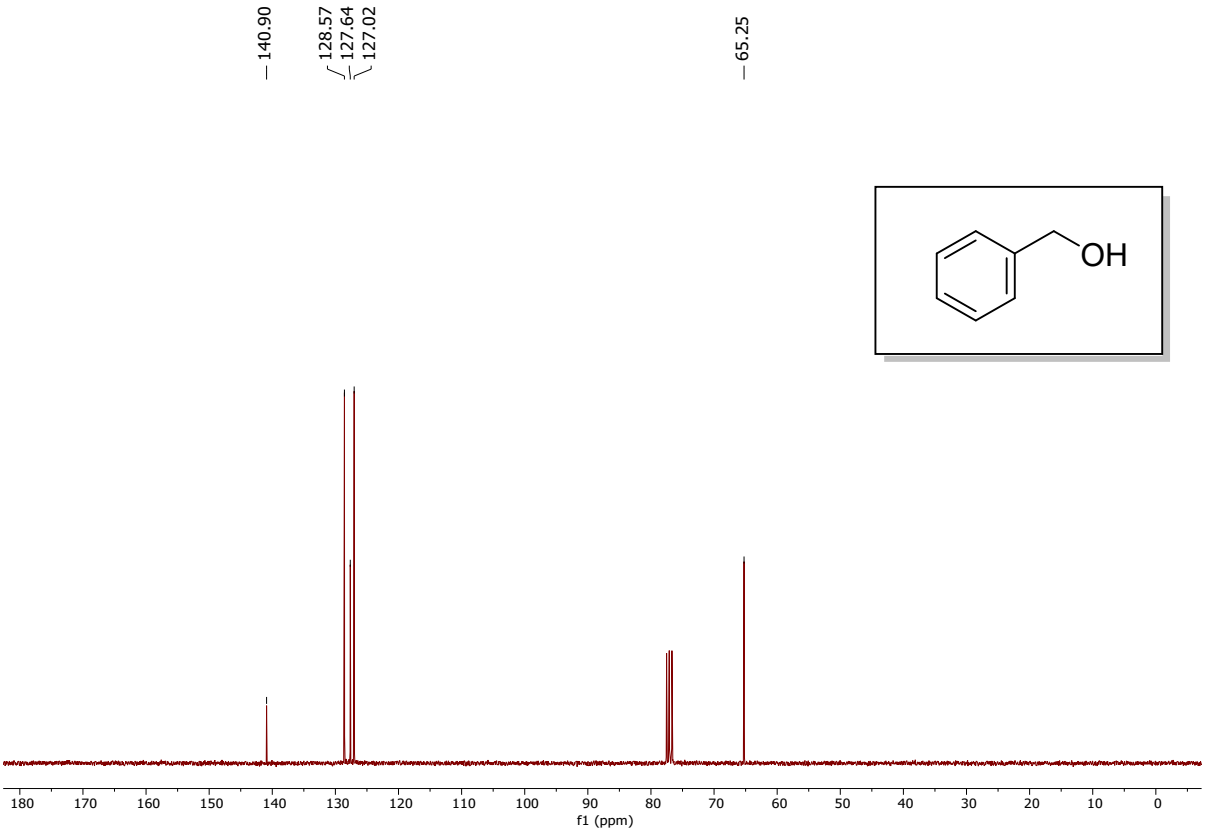
To prove that the reduction reaction is a transfer hydrogen process rather than a direct hydrogenation by H_2 (in-situ released from decomposition of ammonia borane), we used low-pressure H_2 gas (5 bar) instead of NH_3BH_3 to run the model reaction under the standard conditions. In an oven-dried 12 mL glass vial equipped with a stirring bar, $B(C_6F_5)_3$ (5.0 mg, 2.0 mol%) was dissolved in DCE (1.0 mL). The substrates **1a** (68.0 mg, 0.5 mmol) and $BF_3{\cdot}OEt_2$ (10.8 mg, 15 mol%) were added under argon atmosphere. Then, the vial was sealed, the septum was pierced with a needle, and the vial was placed in a steel autoclave. The reactor was flushed tree times with hydrogen at a pressure of 5 bar. The reaction mixture was stirred at 55 °C in an aluminum block for 24 h. After this time, reaction mixture was cooled to room temperature, extracted it with diethyl ether and concentrated under reduced pressure. The target product was not detected in the residue.

5. NMR-spectra

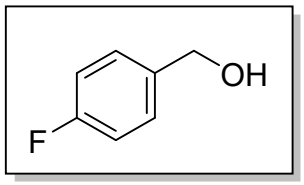
Benzyl alcohol (**2a**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

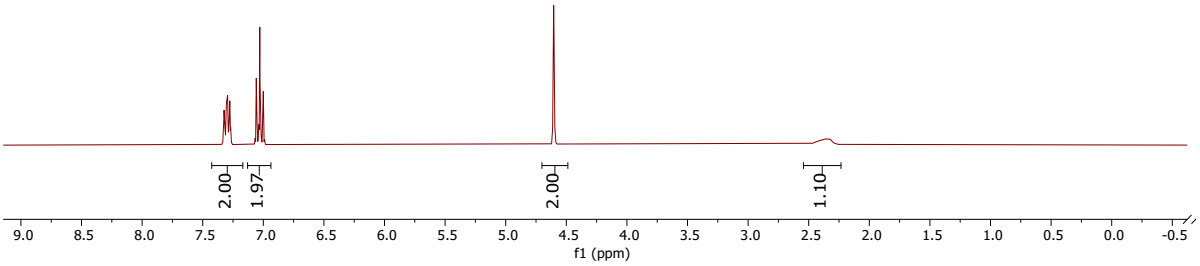


Benzyl alcohol (**2a**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

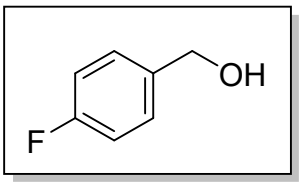


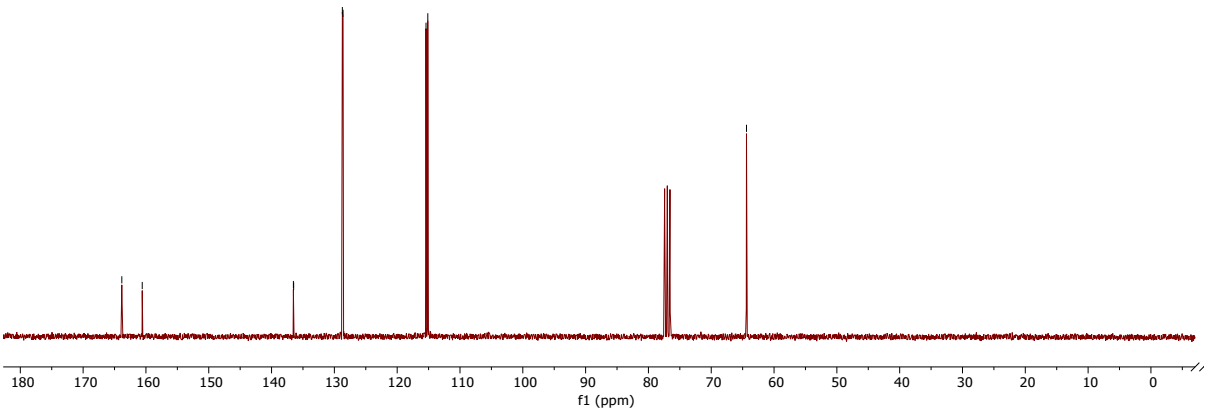
4-Fluorobenzylic alcohol (**2b**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$



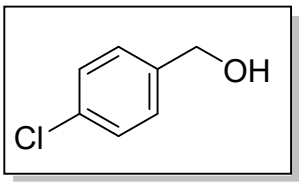


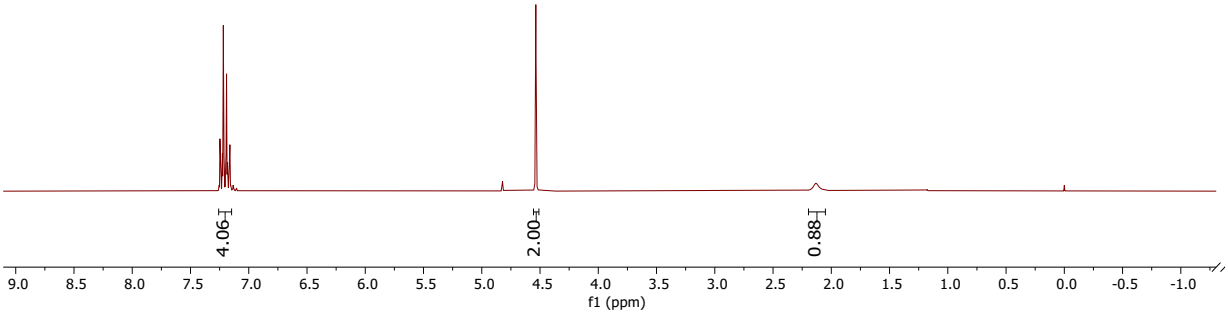
4-Fluorobenzylic alcohol (**2b**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



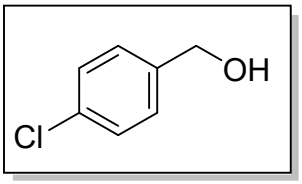


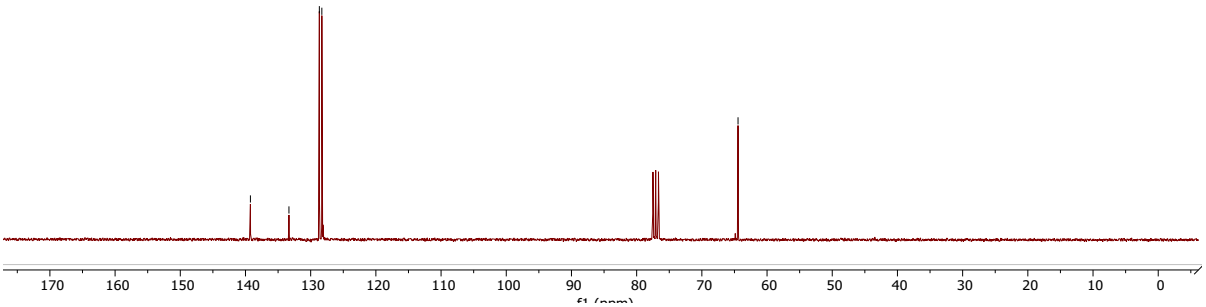
4-Chlorobenzyl alcohol (**2c**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$



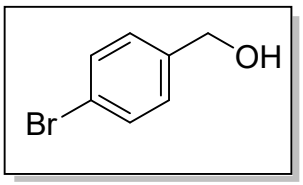


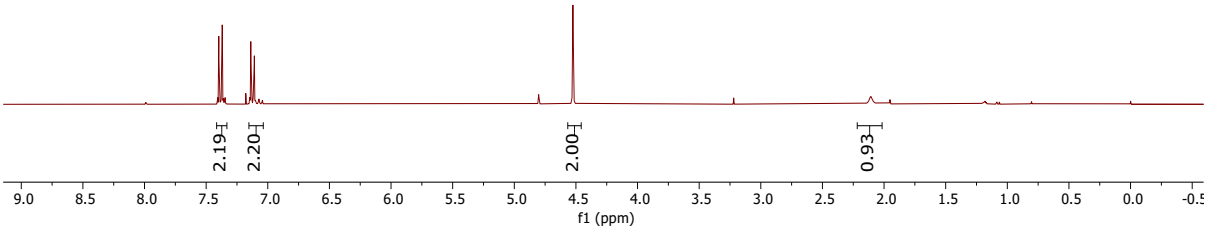
4-Chlorobenzyl alcohol (**2c**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



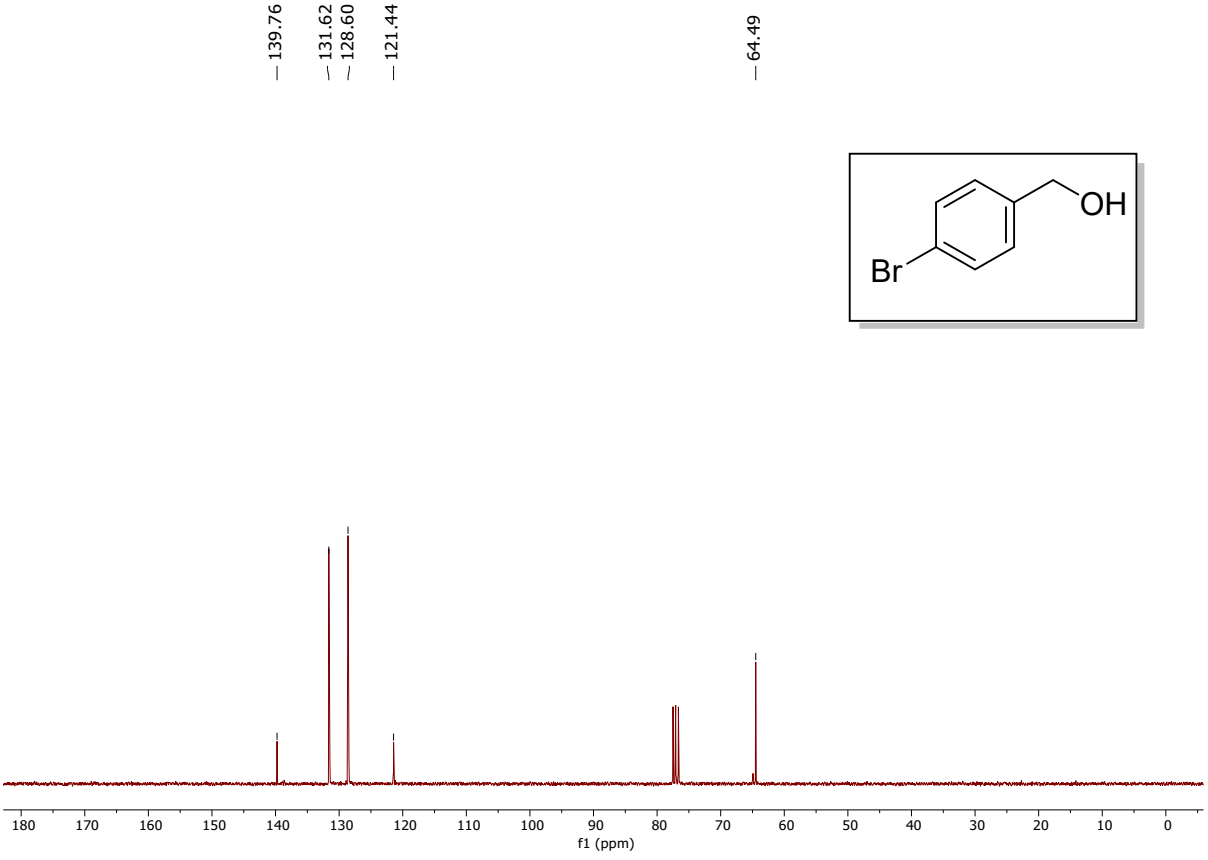


4-Bromobenzyl alcohol (**2d**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

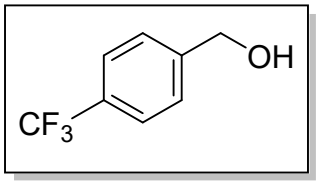


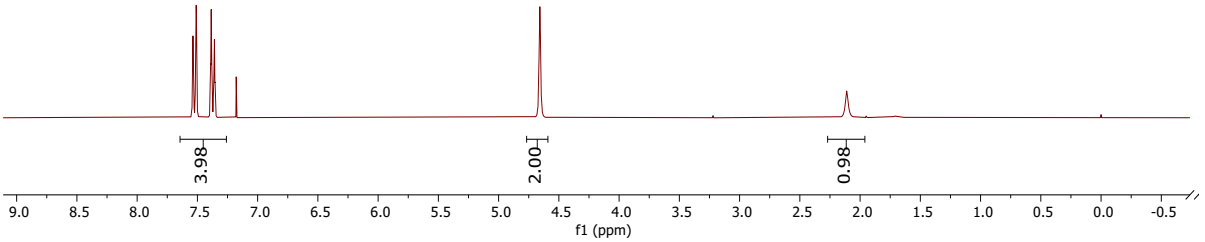


4-Bromobenzyl alcohol (**2d**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

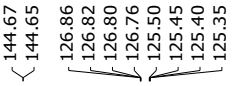


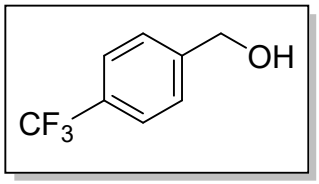
4-(Trifluoromethyl)benzyl alcohol (**2e**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

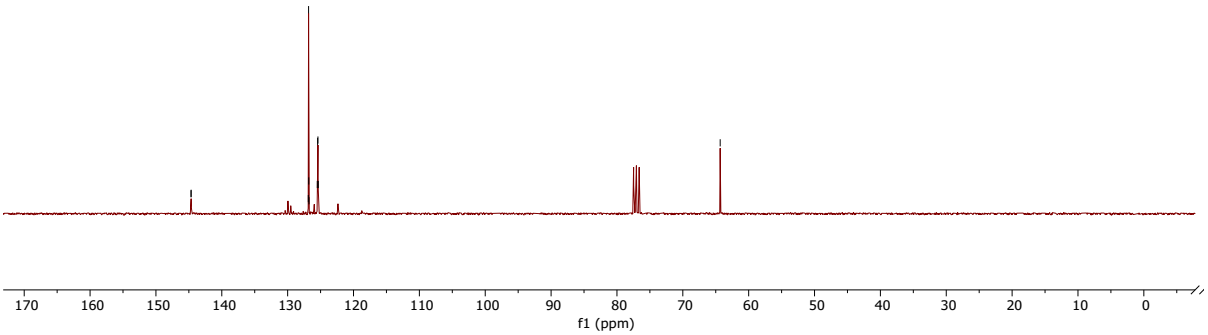




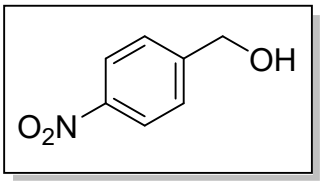
4-(Trifluoromethyl)benzyl alcohol (**2e**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

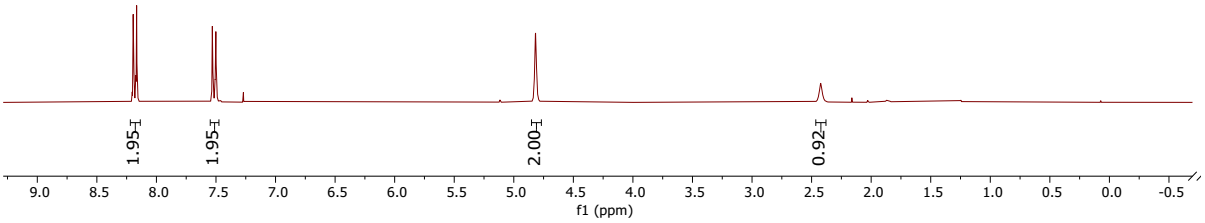






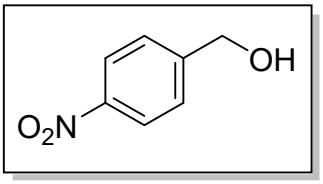
4-Nitrobenzyl alcohol (**2f**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

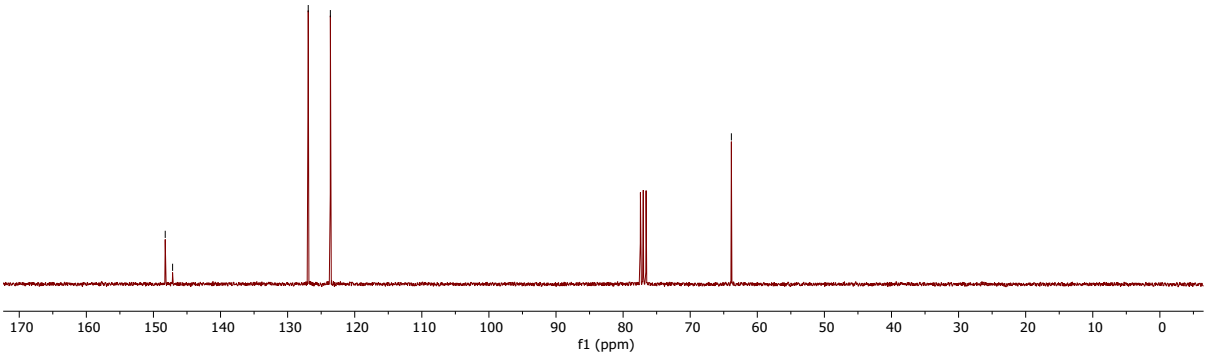




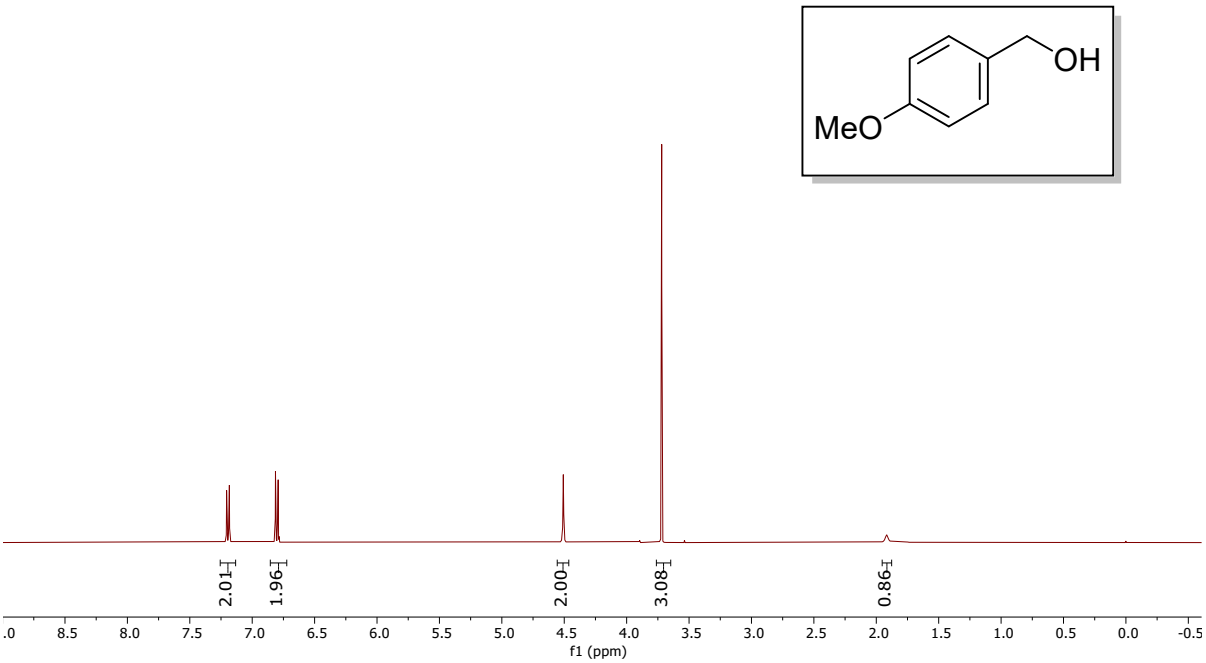
4-Nitrobenzyl alcohol (**2f**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

148.24
147.14
126.93
123.63
63.86

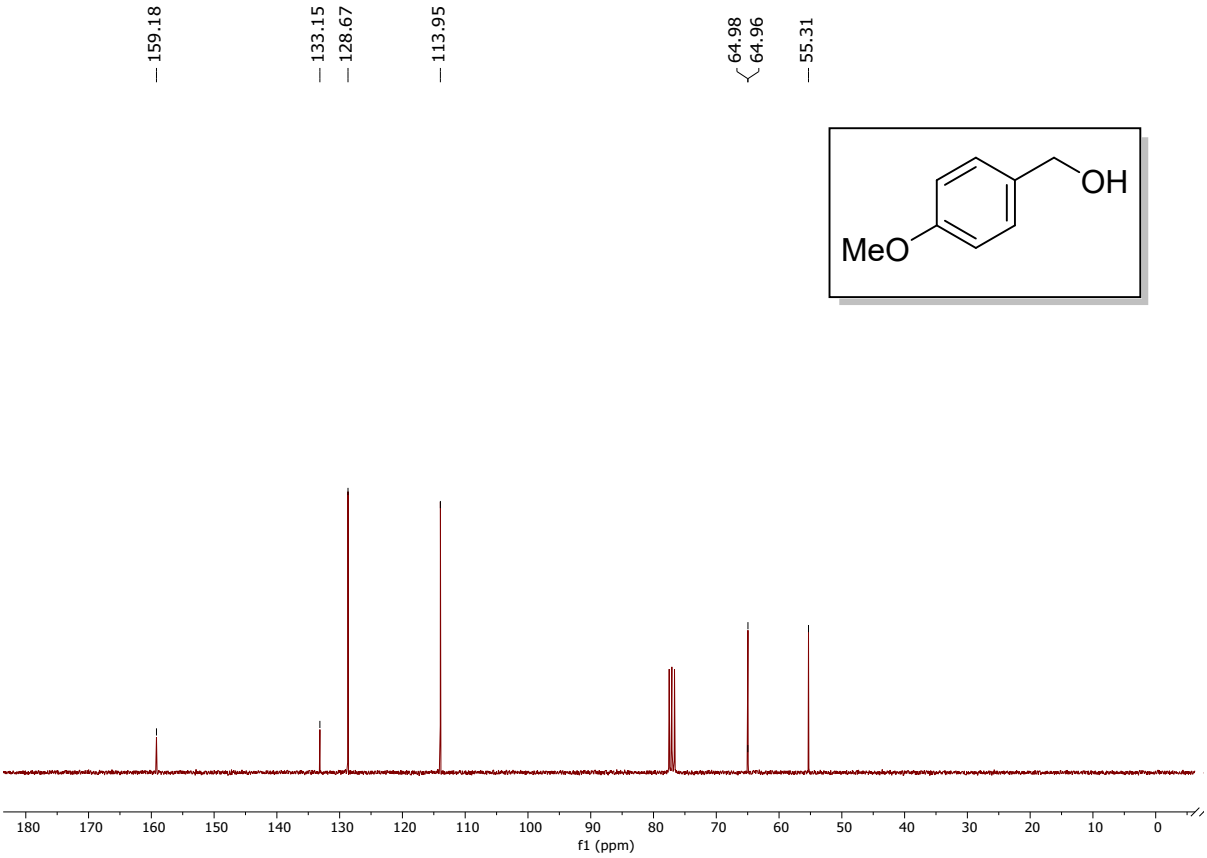




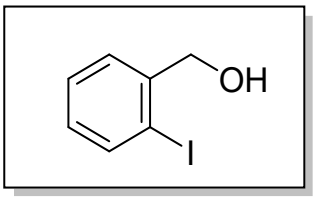
4-Methoxybenzyl alcohol (**2g**) ^{1}H-NMR spectrum (400 MHz) in $CDCl_3$

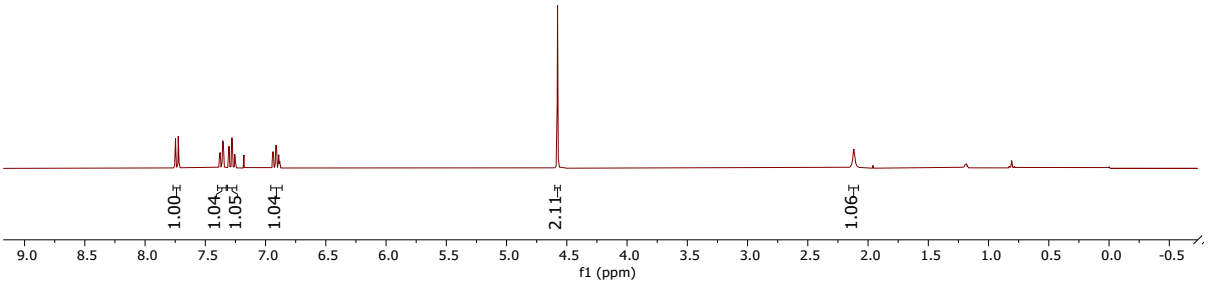


4-Methoxybenzyl alcohol (**2g**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

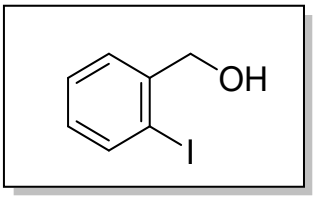


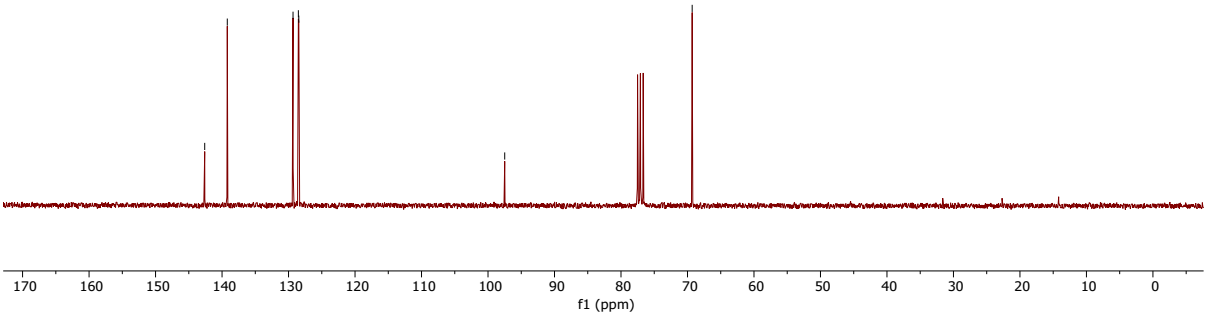
2-Iodobenzyl alcohol (**2h**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$



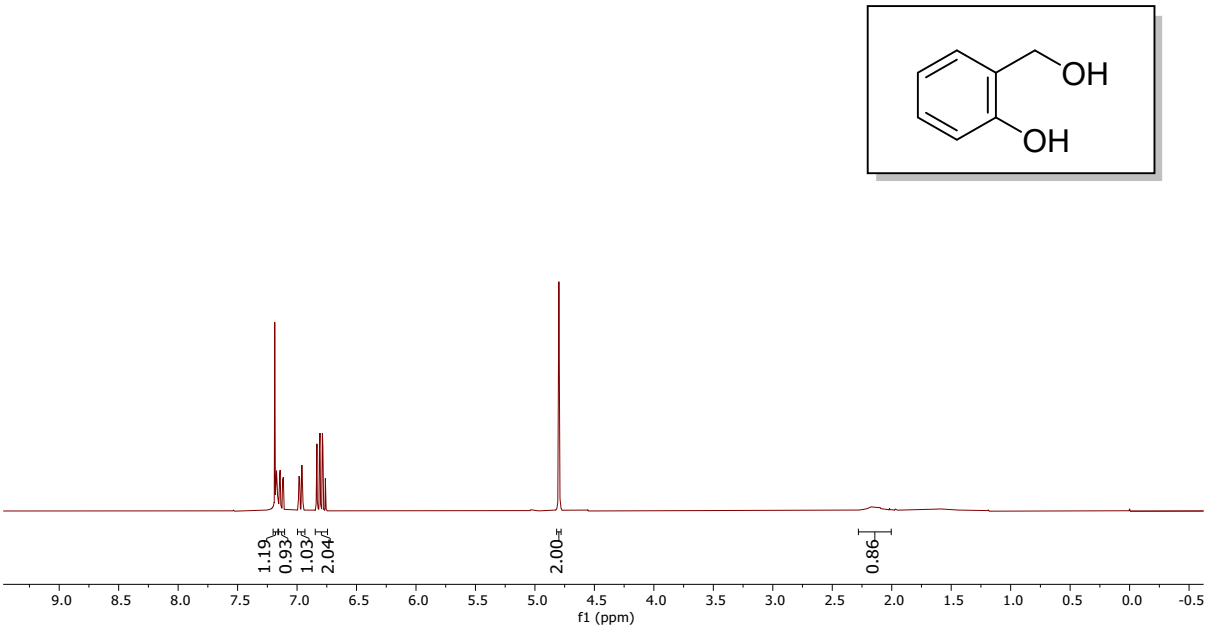


2-Iodobenzyl alcohol (**2h**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

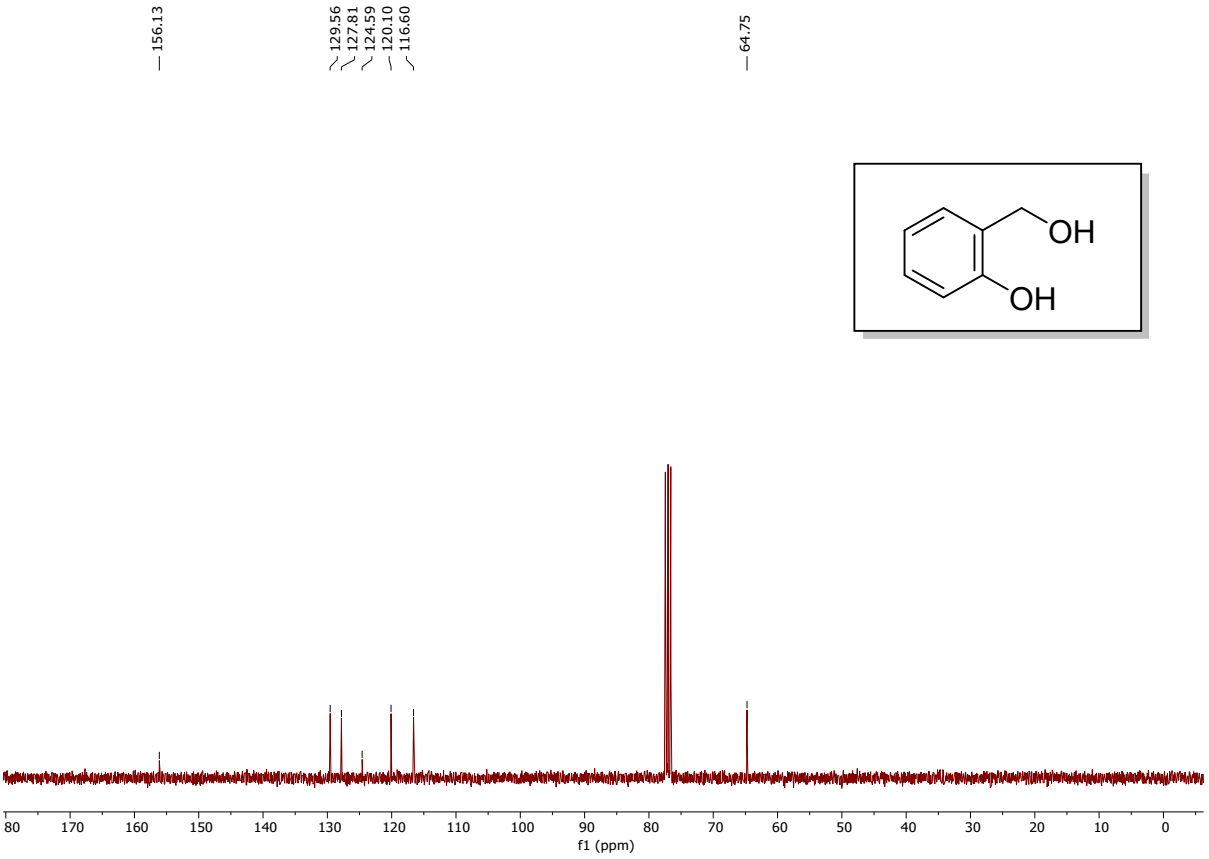




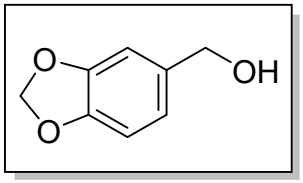
2-Hydroxybenzyl alcohol (**2i**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

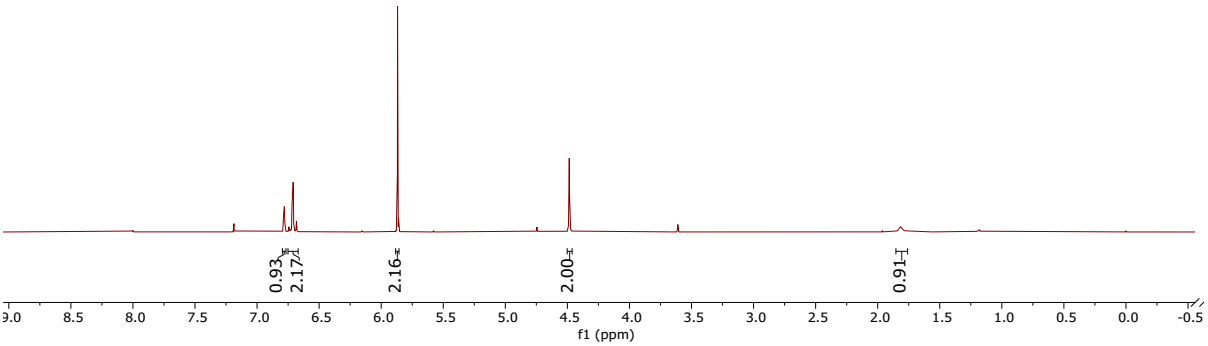


2-Hydroxybenzyl alcohol (**2i**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



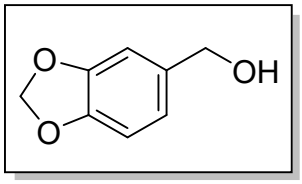
Piperonyl alcohol (**2j**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

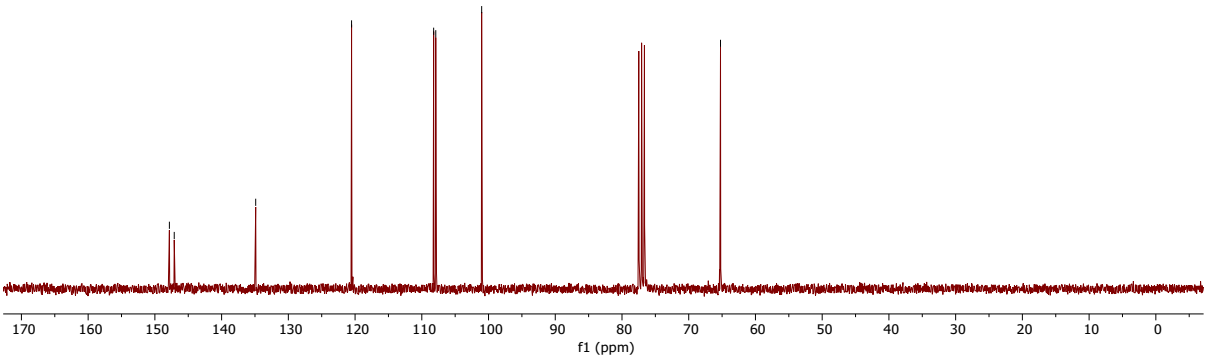




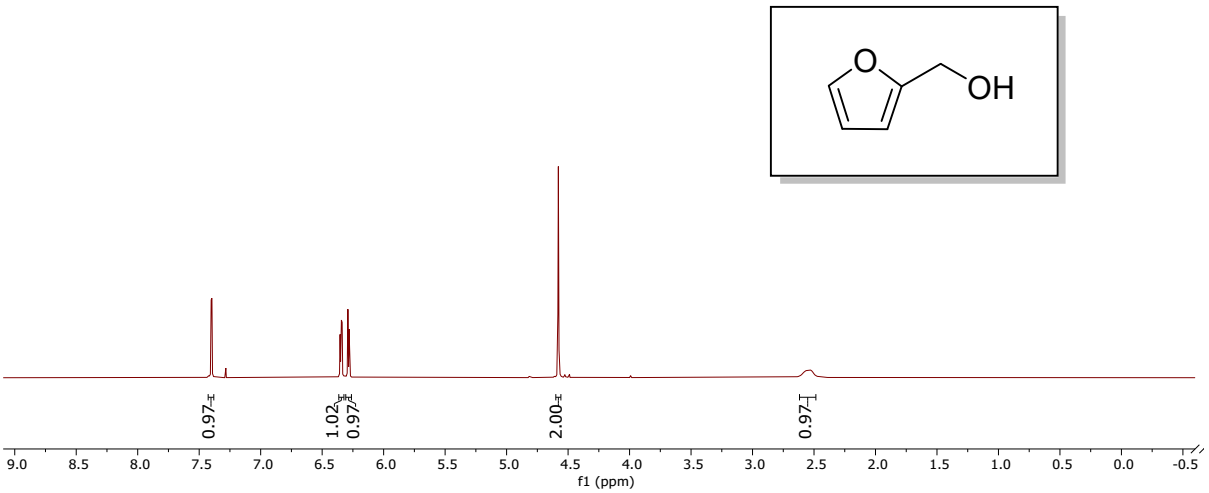
Piperonyl alcohol (**2j**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

147.83
147.10
134.89
120.53
108.22
107.91
101.03
65.24

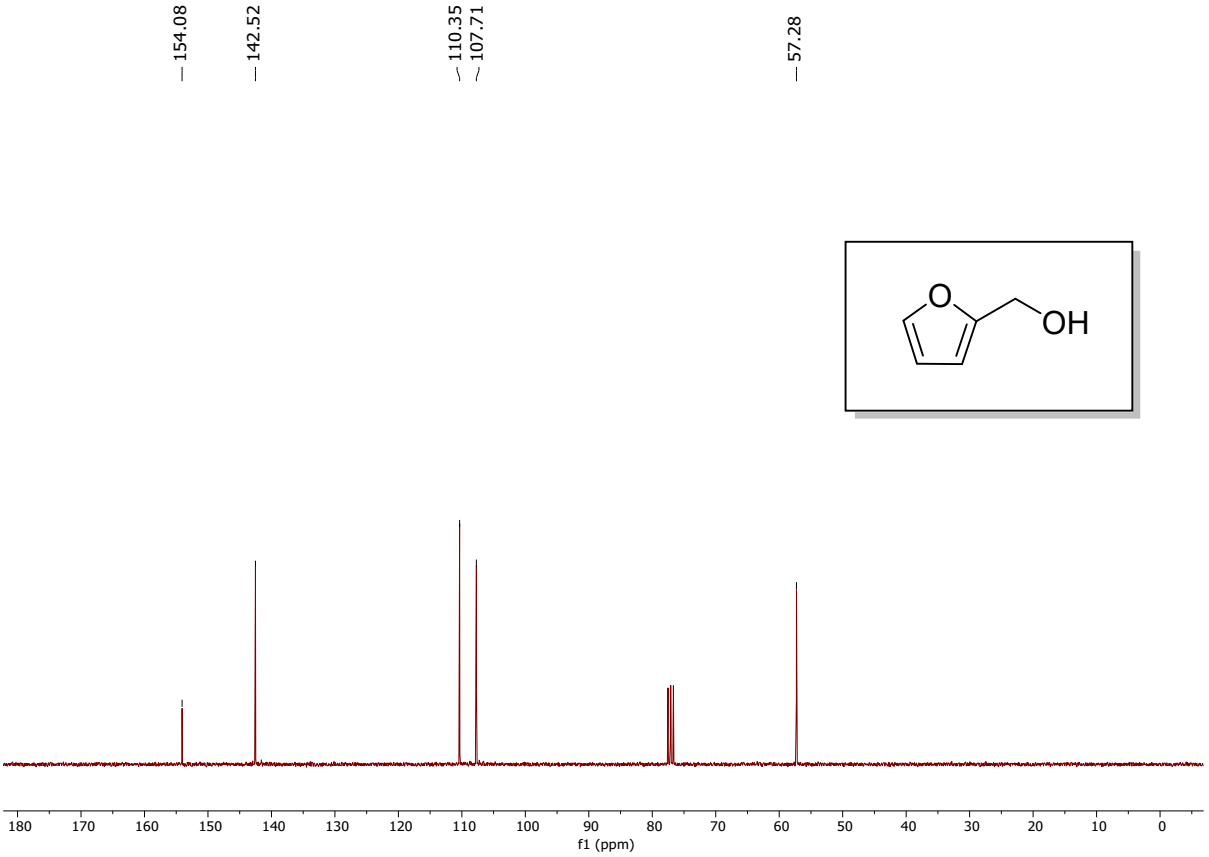




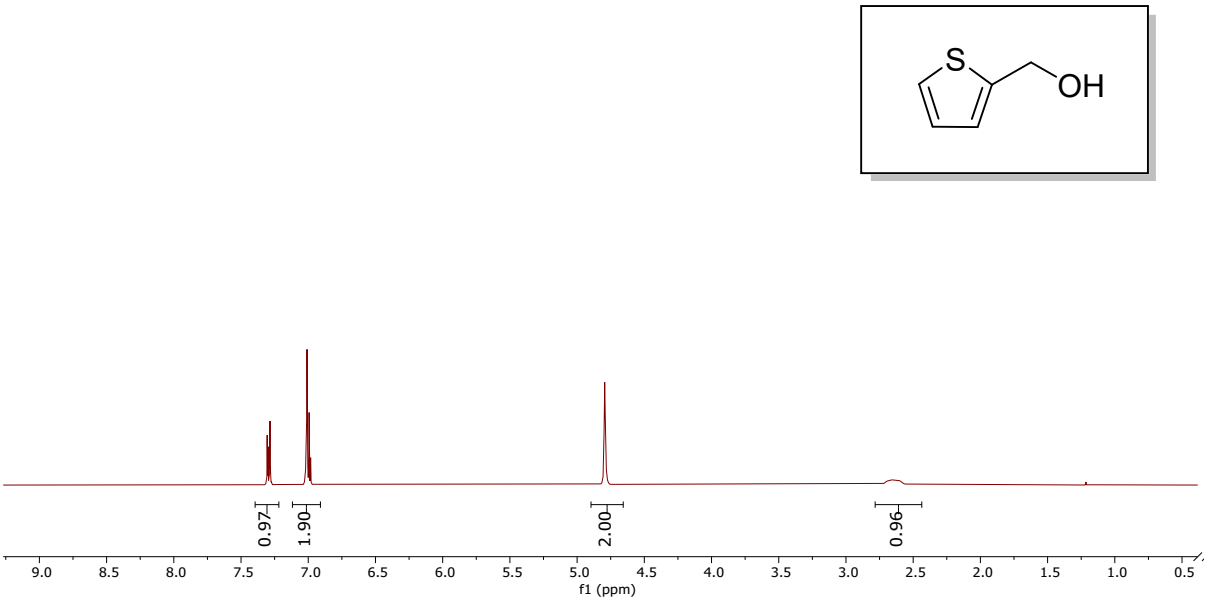
Furfuryl alcohol (**2k**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$



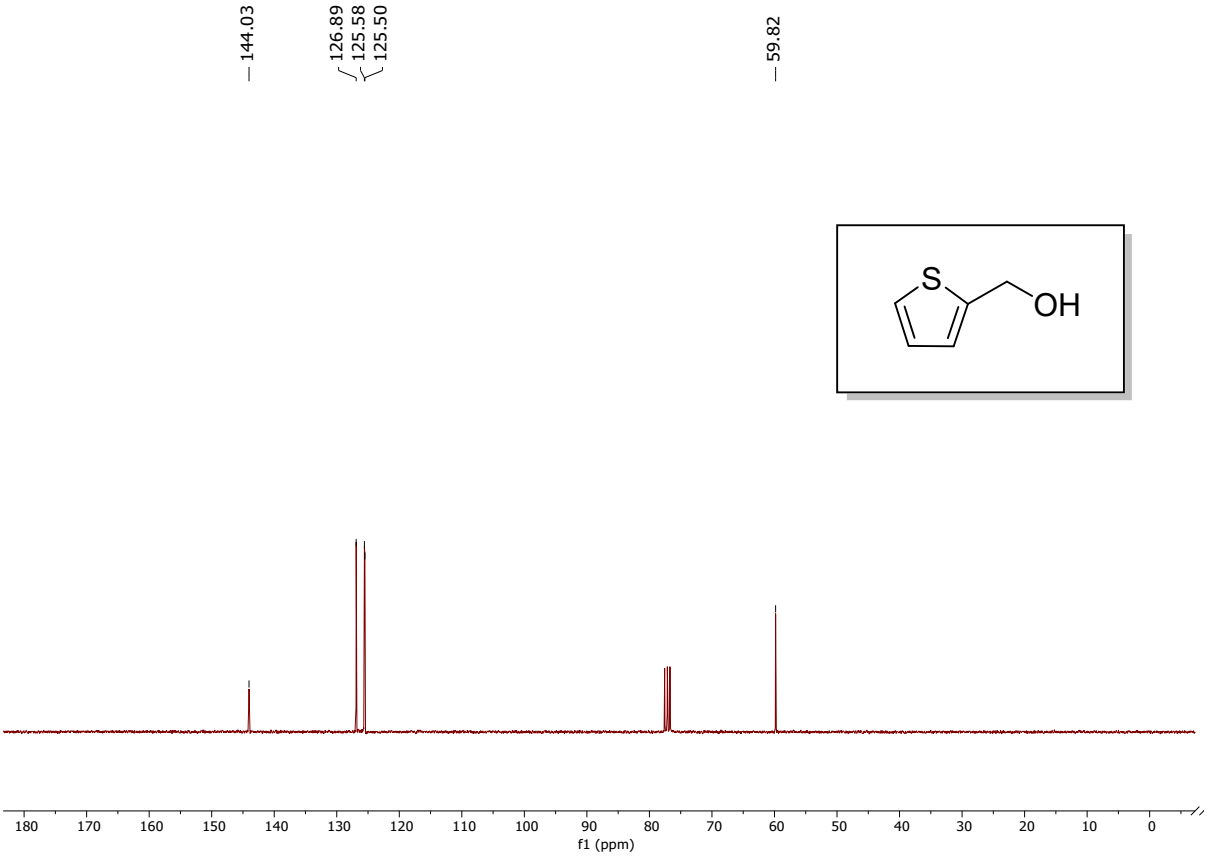
Furfuryl alcohol (**2k**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



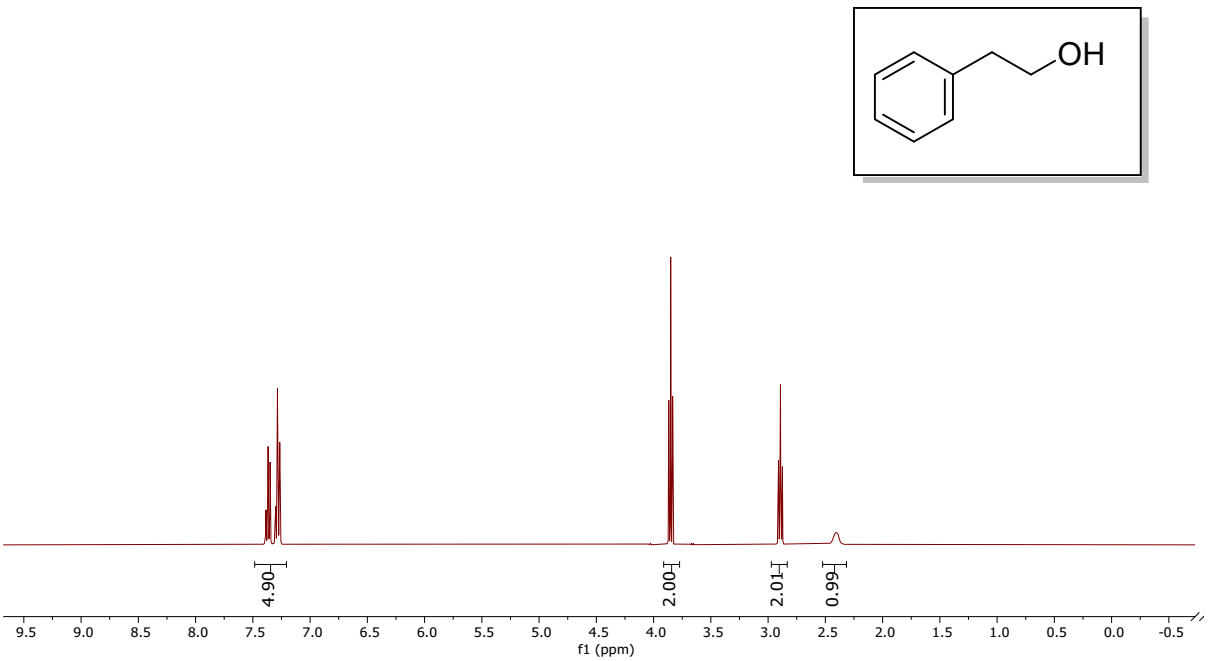
2-Thiophenemethanol (**2l**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$



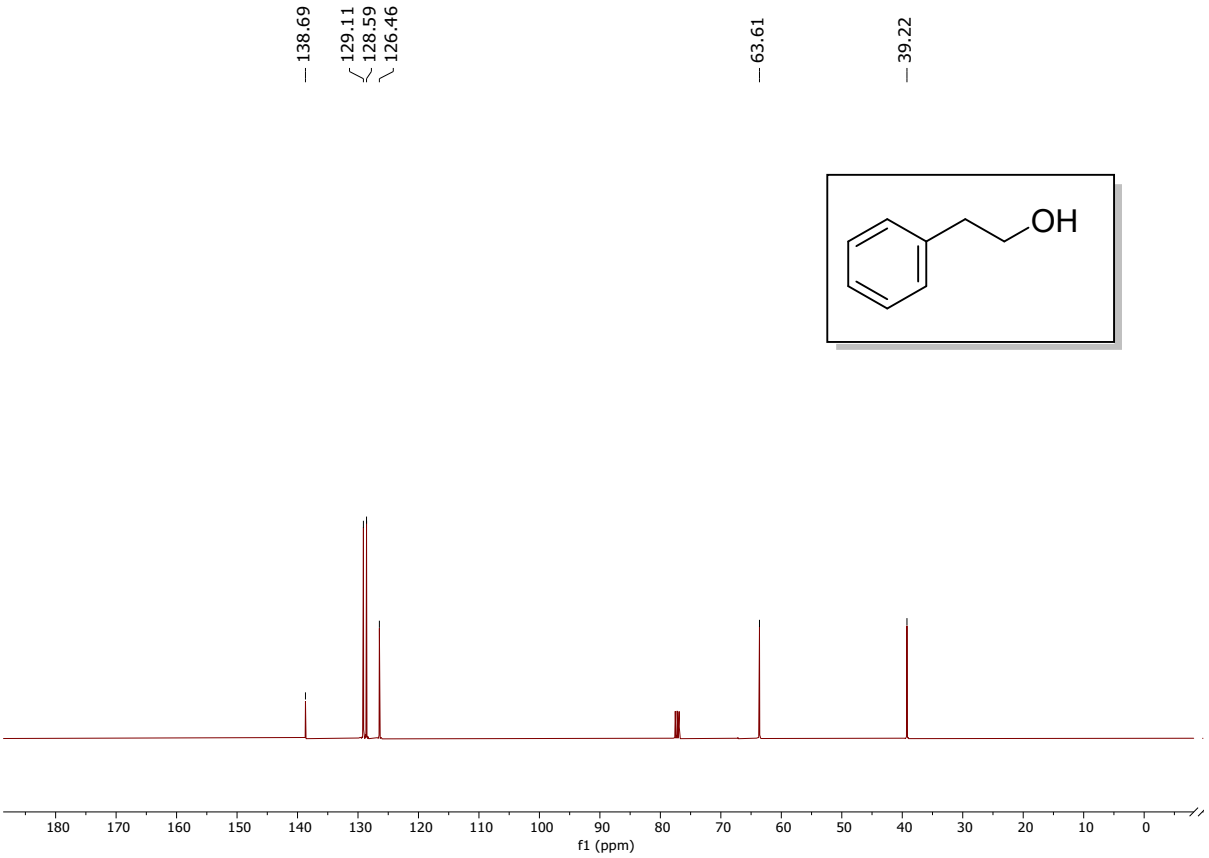
2-Thiophenemethanol (**2l**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



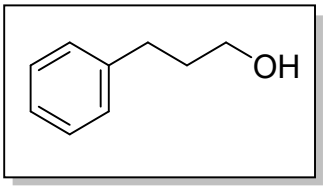
2-Phenylethanol (**2m**) ^{1}H-NMR spectrum (400 MHz) in $CDCl_3$

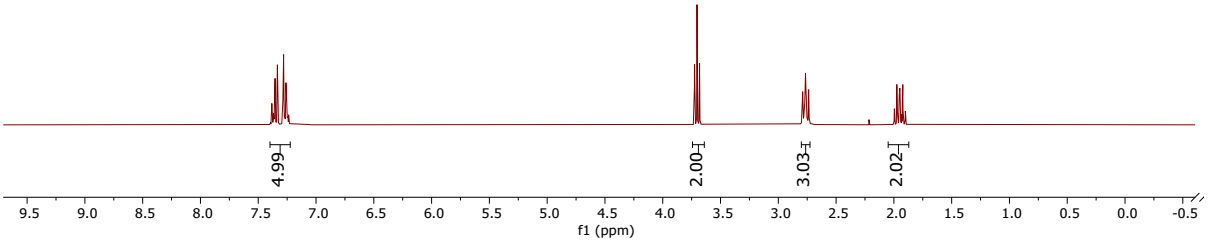


2-Phenylethanol (**2m**) ^{13}C-NMR spectrum (101 MHz) in $CDCl_3$

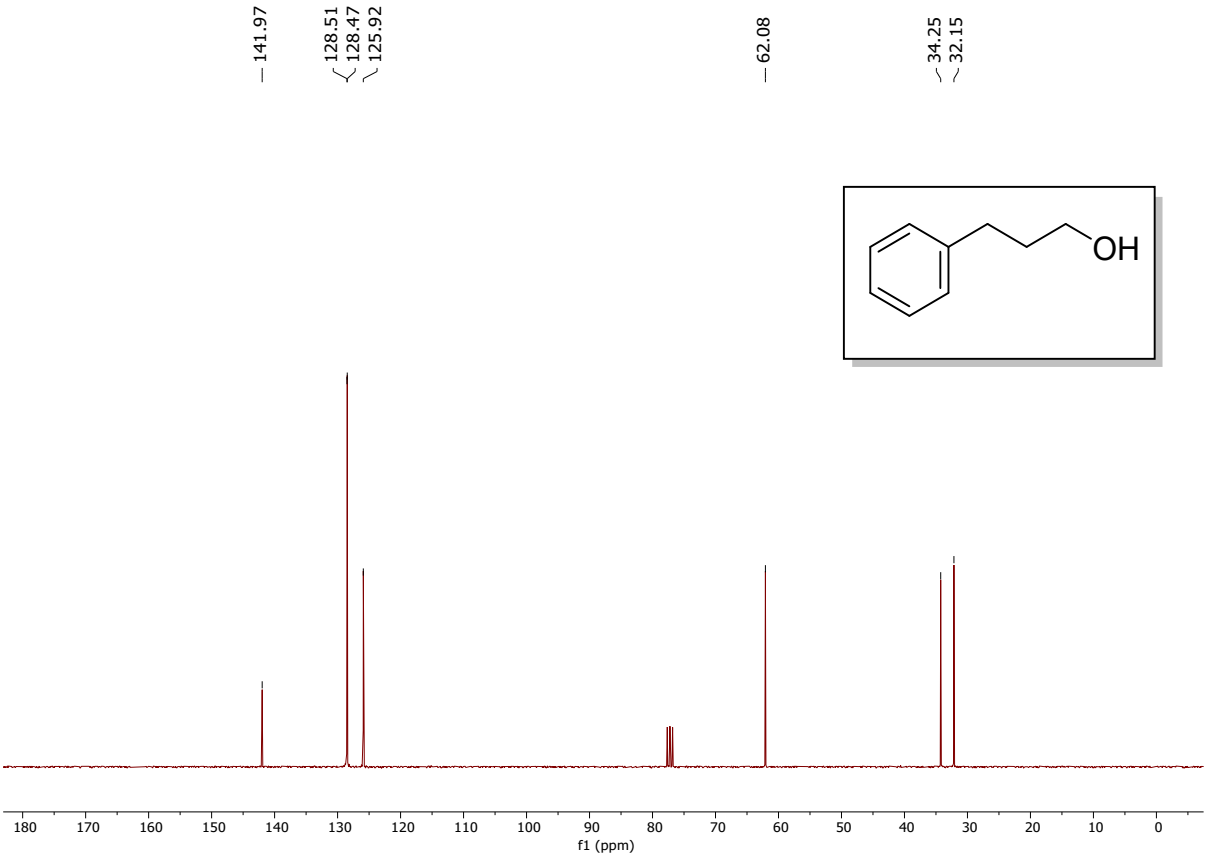


3-Phenyl-1-propanol (**2n**) ^{1}H-NMR spectrum (400 MHz) in $CDCl_3$

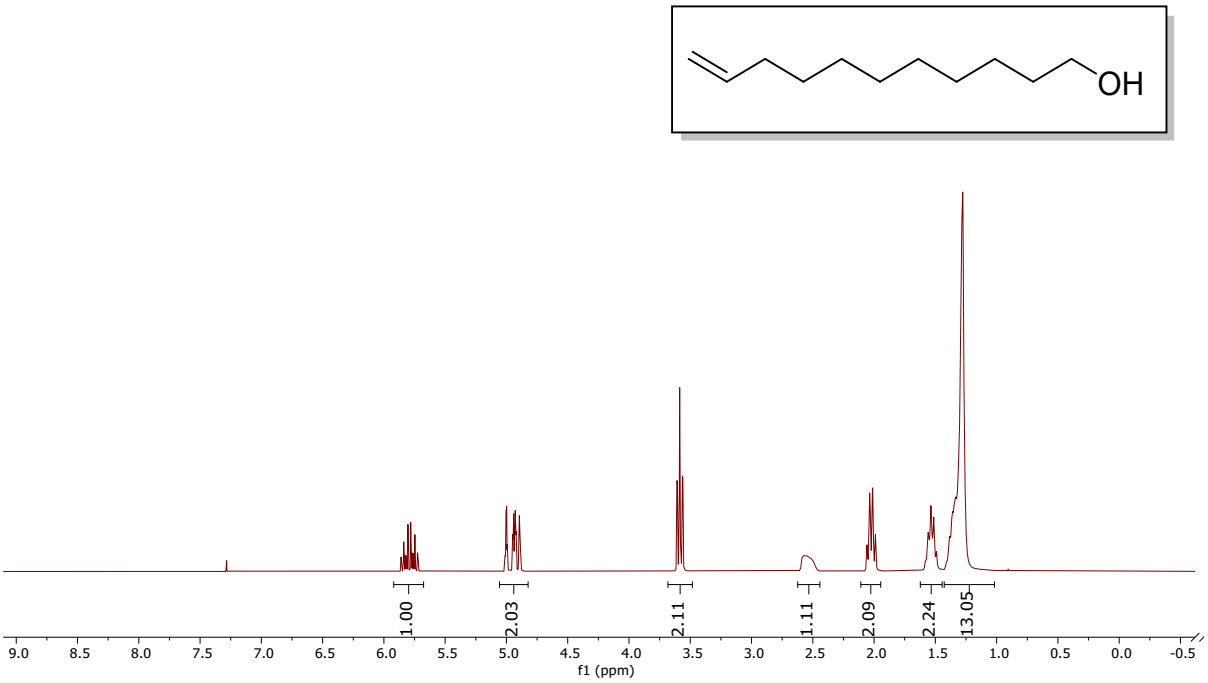




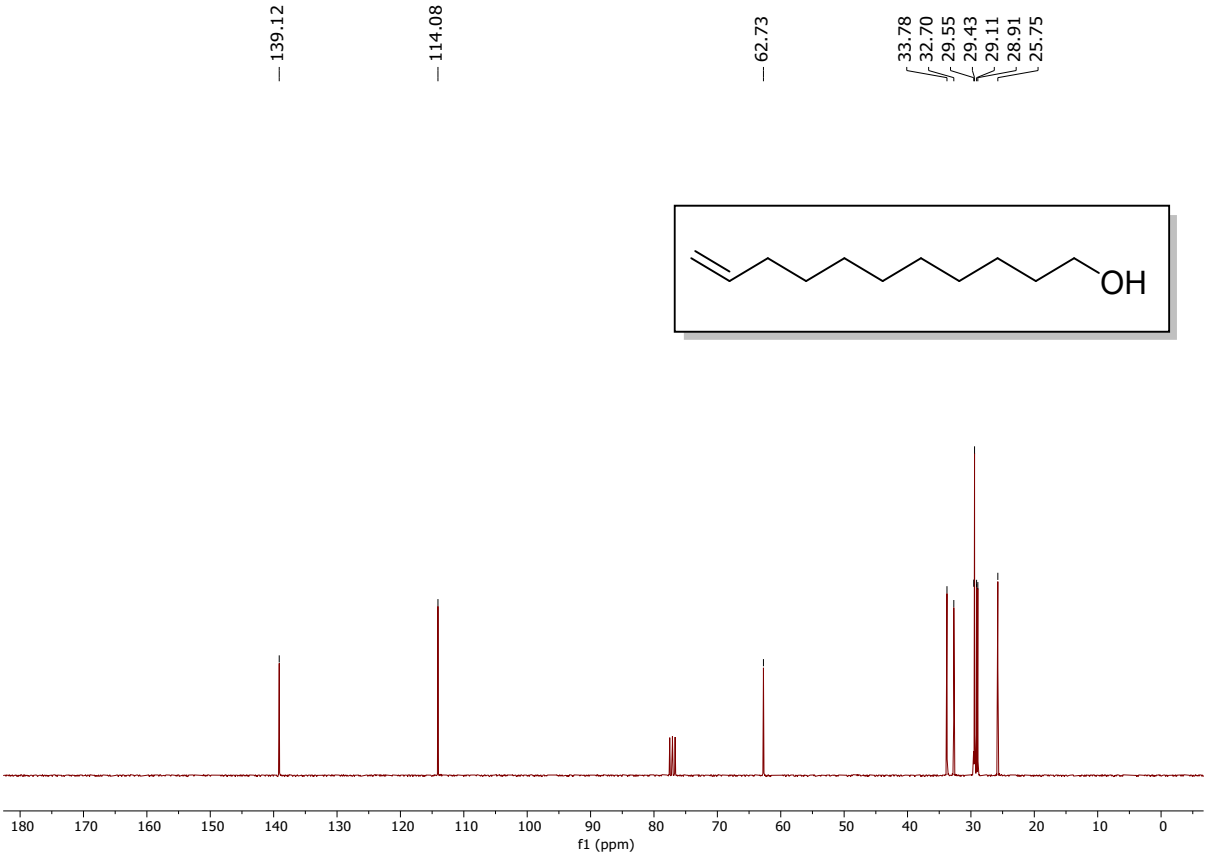
3-Phenyl-1-propanol (**2n**) ^{13}C-NMR spectrum (101 MHz) in $CDCl_3$



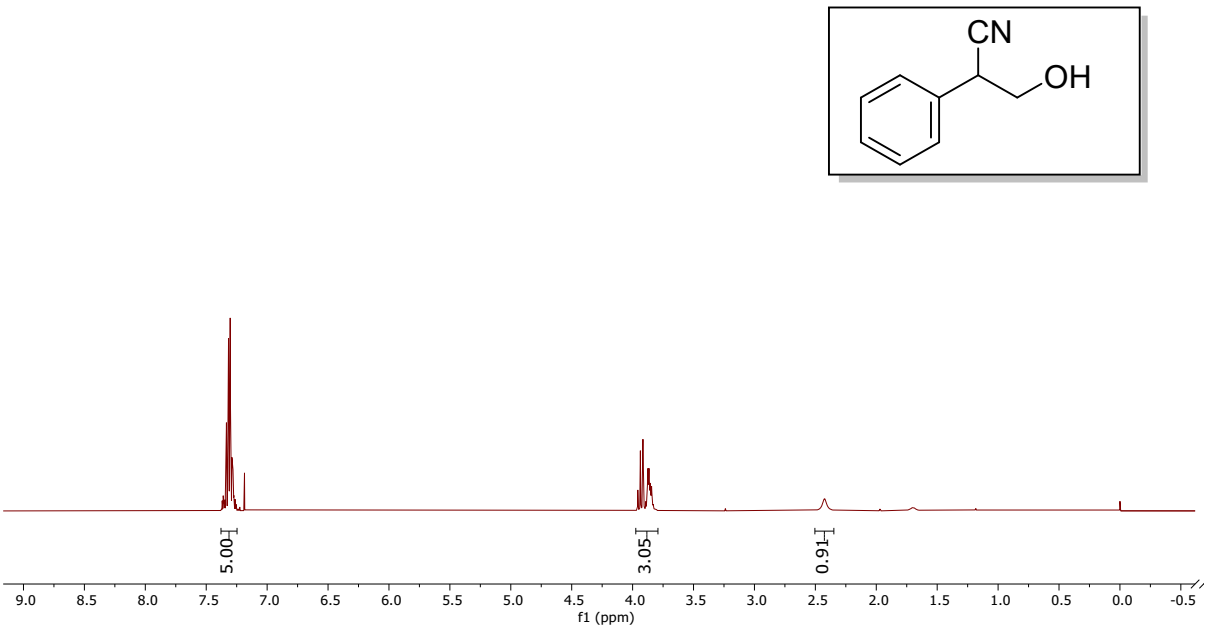
10-Undecen-1-ol (**2o**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$



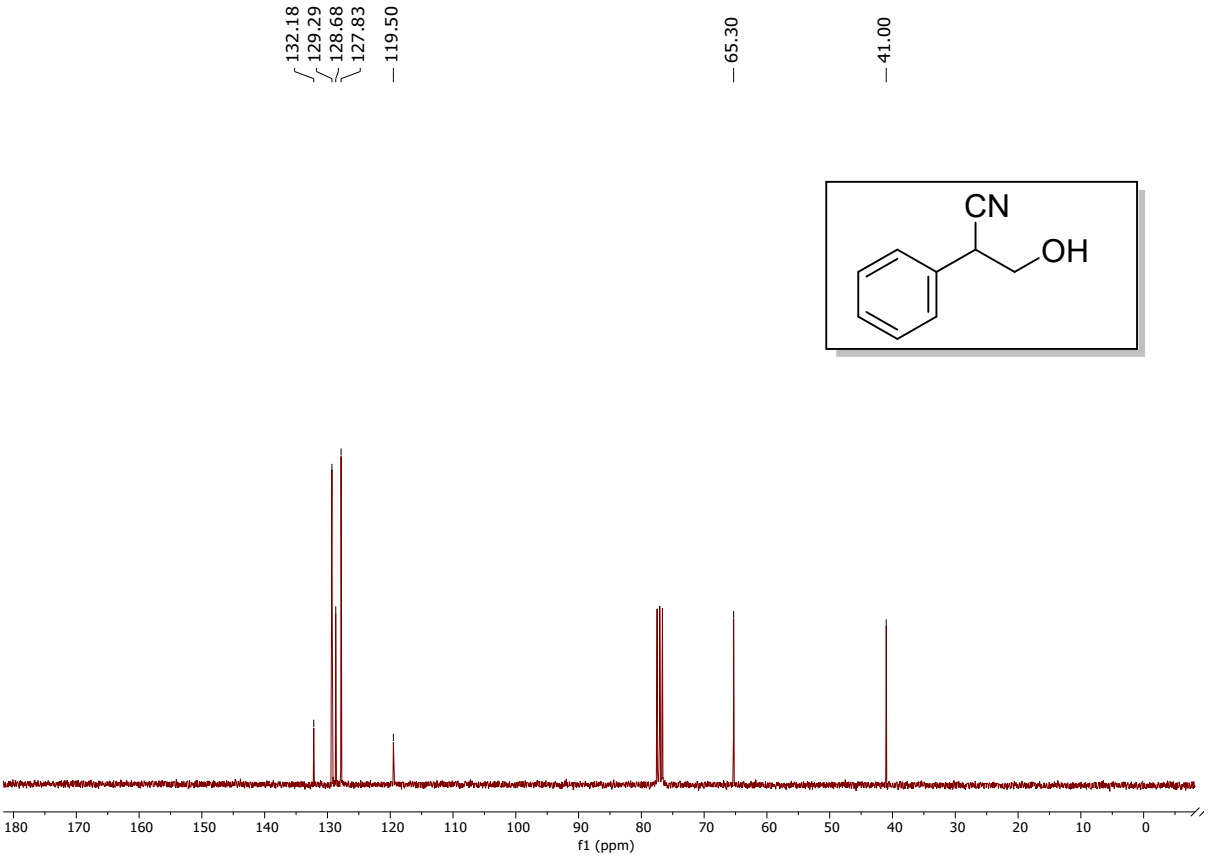
10-Undecen-1-ol (**2o**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



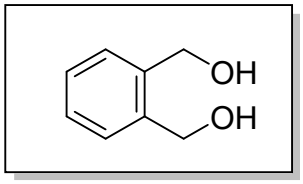
3-Hydroxy-2-phenylpropanenitrile (**2p**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

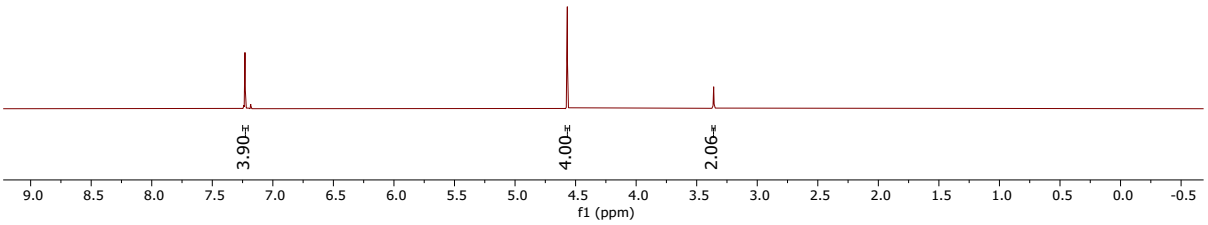


3-Hydroxy-2-phenylpropanenitrile (**2p**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

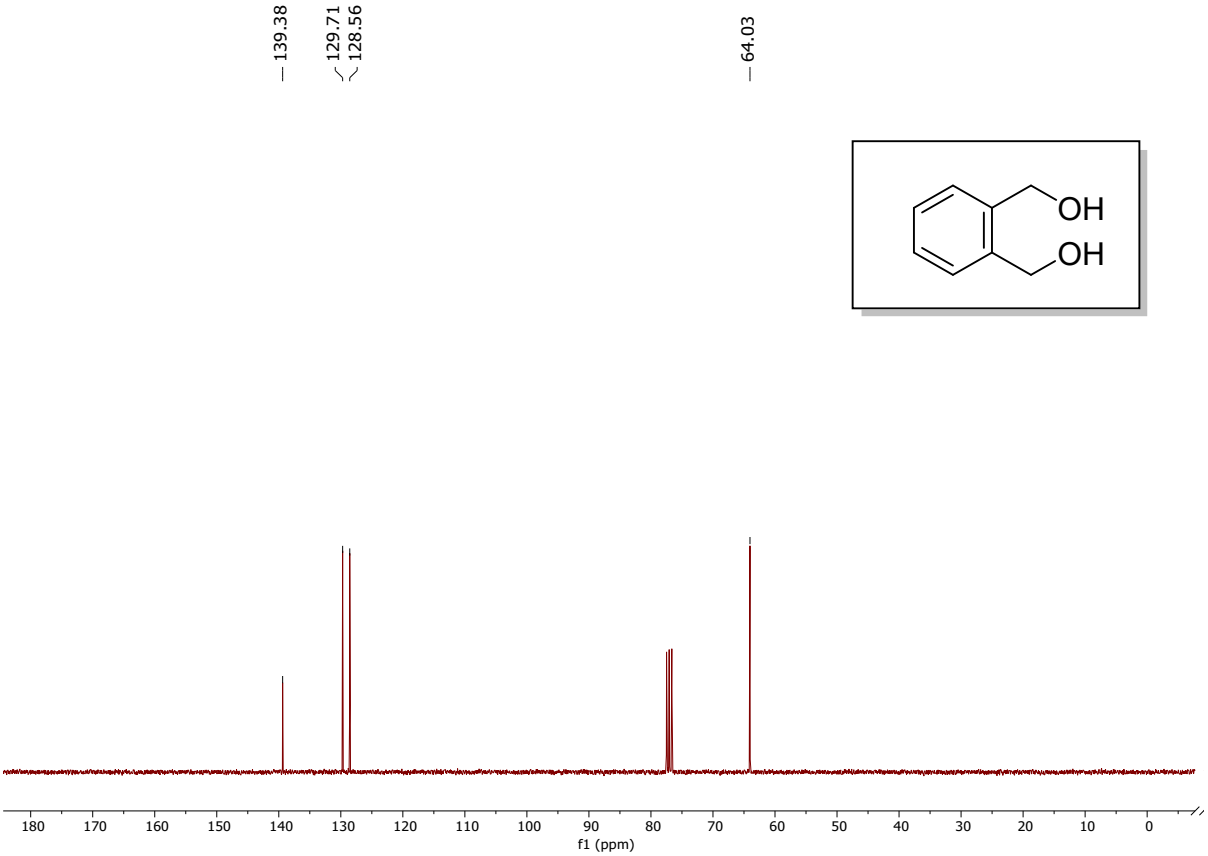


1,2-Benzenedimethanol (**2q**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

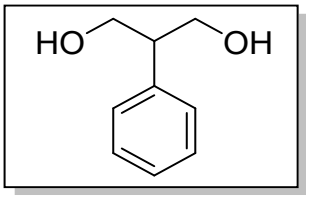


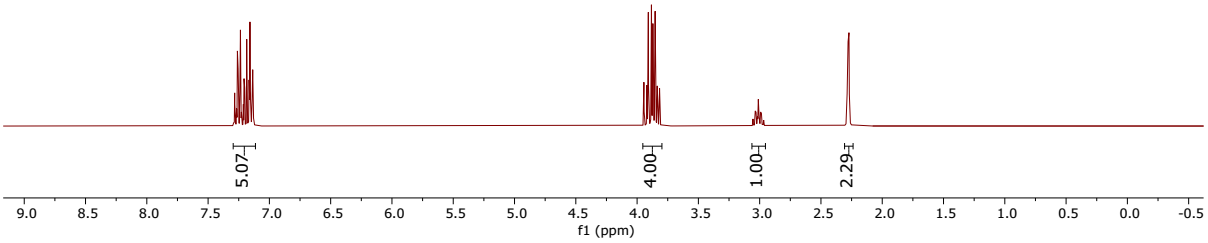


1,2-Benzenedimethanol (**2q**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

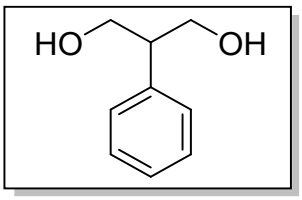


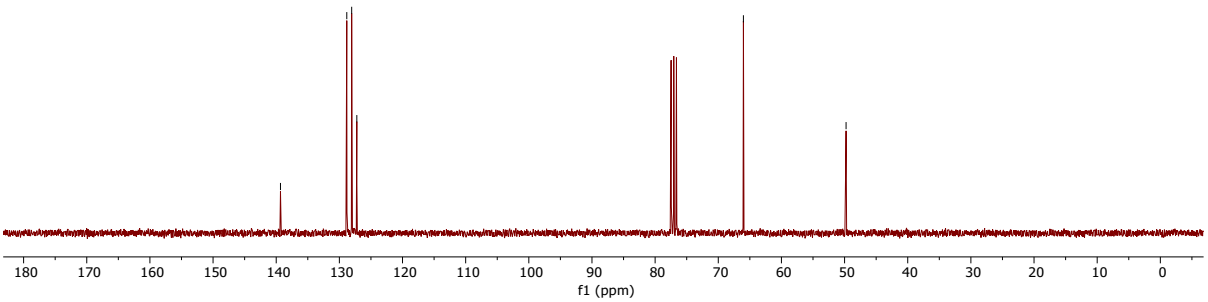
2-Phenyl-1,3-propanediol (**2r**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$



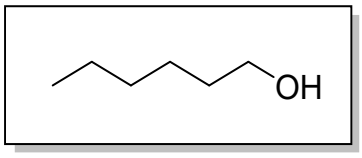


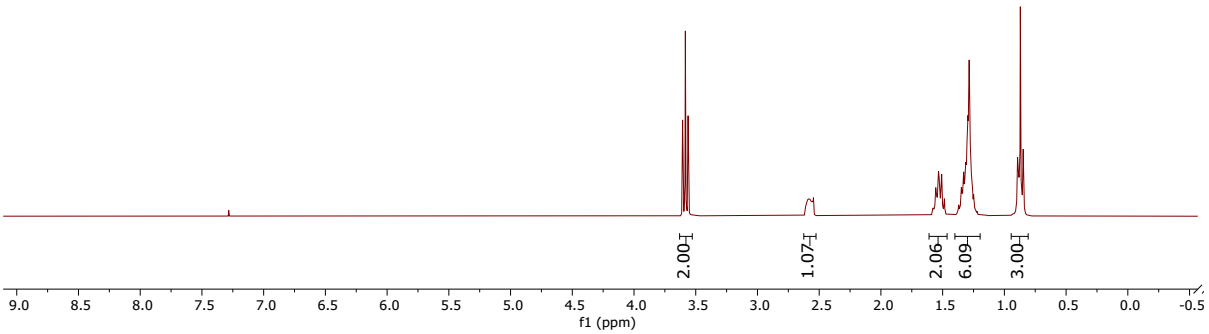
2-Phenyl-1,3-propanediol (**2r**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



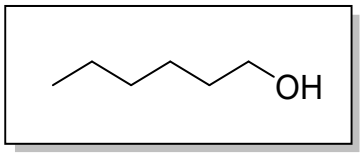


Hexan-1-ol (**2s**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

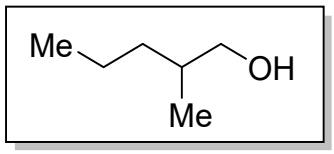


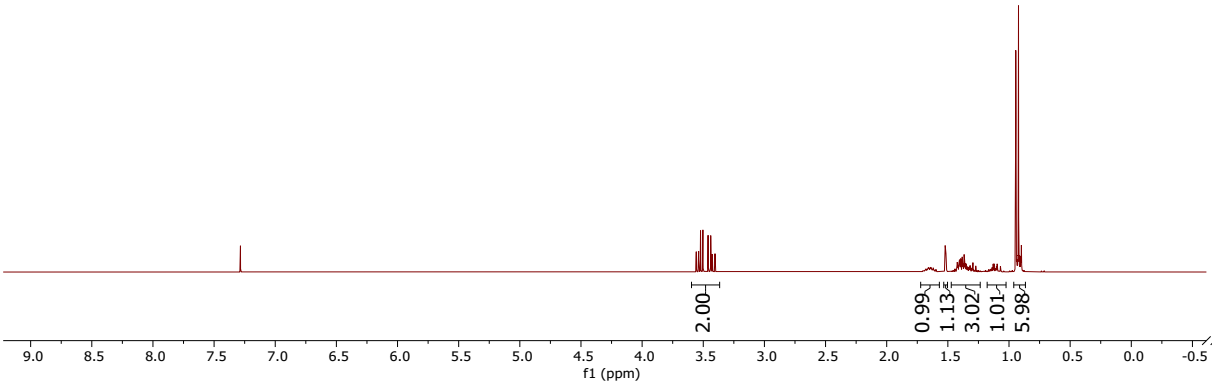


Hexan-1-ol (**2s**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

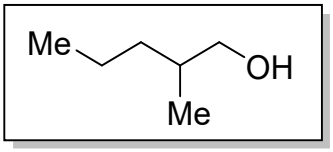


2-Methyl-1-pentanol (**2t**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$

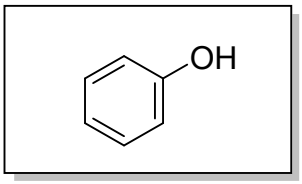


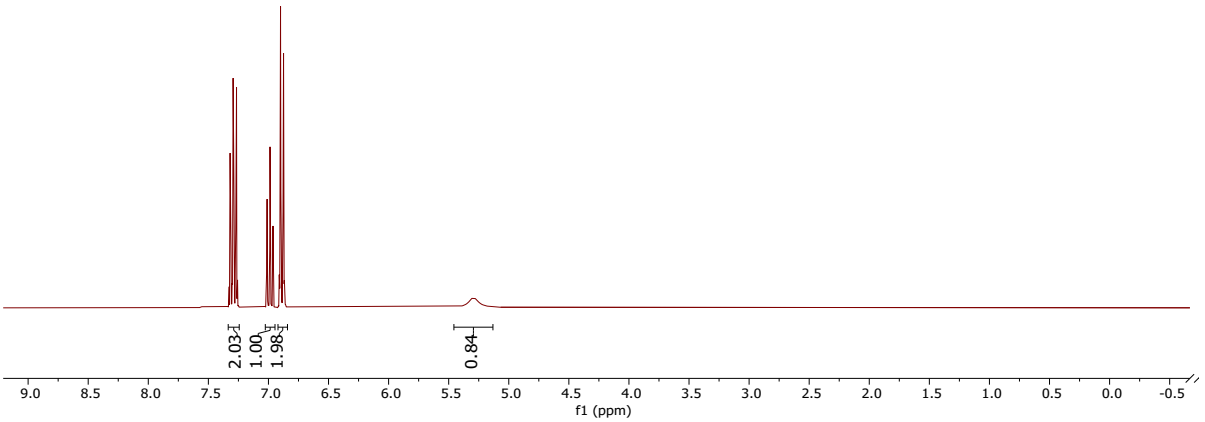


2-Methyl-1-pentanol (**2t**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$

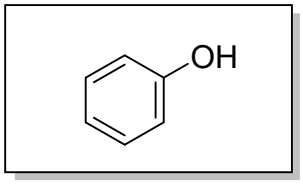


Phenol (**2u**) ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$





Phenol (**2u**) ^{13}C-NMR spectrum (75 MHz) in $CDCl_3$



References

1. T. M. M. S. Sandl, I. G. Shenderovich, A. Jacobi von Wangelin, J. J. Weigand, R. Wolf, *Chem. Eur. J.*, 2019, **25**, 238-245.
2. L. Zhou, D. Zhang, J. Hu, Y. Wu, J. Geng and X. Hu, *Organometallics*, 2021, **40**, 2643-2650.
3. R. A. Farrar-Tobar, B. Wozniak, A. Savini, S. Hinze, S. Tin and J. G. de Vries, *Angew. Chem. Int. Ed.*, 2019, **58**, 1129-1133.
4. S. Chakraborty, H. G. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause and H. R. Guan, *J. Am. Chem. Soc.*, 2014, **136**, 7869-7872.
5. M. Flinker, H. F. Yin, R. W. Juhl, E. Z. Eikeland, J. Overgaard, D. U. Nielsen and T. Skrydstrup, *Angew. Chem. Int. Ed.*, 2017, **56**, 15910-15915.
6. M. K. Barman, K. Das and B. Maji, *J. Org. Chem.*, 2019, **84**, 1570-1579.
7. G. Q. Zhang, J. Cheng, K. Davis, M. G. Bonifacio and C. Zajaczkowski, *Green Chem.*, 2019, **21**, 1114-1121.
8. M. Szostak, M. Spain and D. J. Procter, *Org. Lett.*, 2012, **14**, 840-843.
9. N. Kern, T. Dombray, A. Blanc, J. M. Weibel and P. Pale, *J. Org. Chem.*, 2012, **77**, 9227-9235.
10. E. Farber, J. Herget, J. A. Gascon and A. R. Howell, *J. Org. Chem.*, 2010, **75**, 7565-7572.
11. T. Zell, Y. Ben-David and D. Milstein, *Angew. Chem. Int. Ed.*, 2014, **53**, 4685-4689.
12. W. Q. Yang, J. J. Yan, Y. Long, S. S. Zhang, J. G. Liu, Y. L. Zeng and Q. Cai, *Org. Lett.*, 2013, **15**, 6022-6025.
13. A. Kaithal, P. van Bonn, M. Hölscher and W. Leitner, *Angew. Chem. Int. Ed.*, 2020, **59**, 215-220.
14. X. Yang, L. Zhao, T. Fox, Z. X. Wang and H. Berke, *Angew. Chem. Int. Ed.*, 2010, **49**, 2058-2062.
15. A. Rossin and M. Peruzzini, *Chem. Rev.*, 2016, **116**, 8848-8872.