Cobalt(II) Chloride Hexahydrate–Diisopropylamine Catalyzed Mild and Chemoselective Reduction of Carboxylic Esters with Sodium Borohydride

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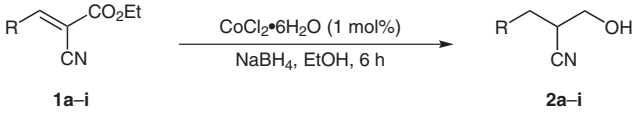
Abstract: The cobalt-catalyzed reduction of unsaturated α-cyano carboxylic esters using sodium borohydride ($NaBH_4$) leads to the corresponding saturated cyano alcohols in high yields. In particular, the new catalytic system cobalt(II) chloride–diisopropylamine in combination with $NaBH_4$ showed excellent activity in the chemoselective reduction of a variety of carboxylic esters to their corresponding alcohols in good to excellent yields under mild conditions.

Key words: reductions, amines, catalysis, esters, alcohols

Sodium borohydride ($NaBH_4$) is a mild, inexpensive yet powerful reducing agent capable of reducing a wide range of functional groups, such as aldehydes, ketones, and imines.[1] Despite its low reactivity towards carboxylic esters,[2] studies have indicated that the reactivity of $NaBH_4$ and its derivatives towards these compounds and carboxylic acids can be enhanced by the addition of certain additives, resulting in the use of reagents such as $NaBH_4$–MX (MX = LiCl, $ZnCl_2$, $AlCl_3$, LiBr, $MgBr_2$, $MgCl_2$, $CaCl_2$),[3] KBH_4–MX (MX = $ZnCl_2$, $AlCl_3$, $MgCl_2$),[4] $NaBH_4$–trifluoroacetic acid,[5] $NaBH_4$–sulfuric acid,[6] $NaBH_4$–iodine,[7] and borane–dimethyl sulfide complex.[8] However, some of the major disadvantages of the reported procedures on ester reduction include the lack of generality[9] and the use of harsh reaction conditions[10] and higher equivalents of $NaBH_4$ and additives.[11] The reduction of esters with hydroxy, amino, and cyano[12] substituents at the α-position and that of carbon–carbon double bonds in α,β-unsaturated esters using $NaBH_4$ have also been reported.[13] In this paper, we report a simple procedure in which cobalt(II) chloride hexahydrate ($CoCl_2·6H_2O$) in combination with diisopropylamine catalyzes the chemoselective reduction of carboxylic esters to saturated alcohols using $NaBH_4$ at ambient conditions.

In continuation of our work[13a,b] on the cobalt-catalyzed reduction of carbon–carbon double bonds and phenyl esters using $NaBH_4$, we became interested in subjecting (*E*)-ethyl 2-cyano-3-phenylacrylate (**1a**) to $CoCl_2$-catalyzed reduction conditions. Surprisingly, we found that ethyl acrylate **1a** underwent reduction using $NaBH_4$ at the carbon–carbon double bond as well as at the ester carbonyl functionality to provide 2-(hydroxymethyl)-3-phenylpropanenitrile (**2a**) in 95% yield (Scheme 1 and Table 1, entry 2). However, when the reaction was carried out without $CoCl_2·6H_2O$ in ethanol at 25 °C, only the reduction of the carbon–carbon double bond was observed to give ethyl 2-cyano-3-phenylpropanoate (Table 1, entry 1).



1a–i **2a–i**

Scheme 1 Cobalt(II) chloride hexahydrate catalyzed reduction of α-cyano-α,β-unsaturated esters using sodium borohydride

Table 1 Cobalt(II) Chloride Hexahydrate Catalyzed Reduction of α-Cyano-α,β-unsaturated Esters Using Sodium Borohydride[a]

Entry	R	Product	Yield[b] (%)
1	Ph	–[c]	80
2	Ph	**2a**	95
3	4-ClC_6H_4	**2b**	90
4	4-$MeOC_6H_4$	**2c**	97
5	4-Tol	**2d**	92
6	3-$F_3CC_6H_4$	**2e**	85
7	3-$O_2NC_6H_4$	**2f**	80
8	3,4-$(MeO)_2C_6H_3$	**2g**	96
9	3,4-$(OCH_2O)C_6H_3$	**2h**	99
10	*n*-C_8H_{17}	**2i**	70

[a] Reaction conditions: cyano ester (10 mmol), $NaBH_4$ (40 mmol), $CoCl_2·6H_2O$ (1 mol%), EtOH (5 mL), 25 °C, 6 h.
[b] Isolated yield after chromatographic purification.
[c] Ethyl 2-cyano-3-phenylpropanoate was isolated when the reaction was carried out in the absence of $CoCl_2·6H_2O$.

The results of the reduction of several α-cyano-α,β-unsaturated esters are presented in Table 1; those groups in the ester substrates capable of being reduced, such as nitro and cyano groups, were found to be unaffected under the reduction conditions. The high yields obtained, coupled with the use of ethanol as solvent over diglyme, makes this procedure straightforward and highly economical. It may be that the strong electron-withdrawing nature of the cyano group as well as that of the ester functionality results in the β-positions of the α-cyano esters being more

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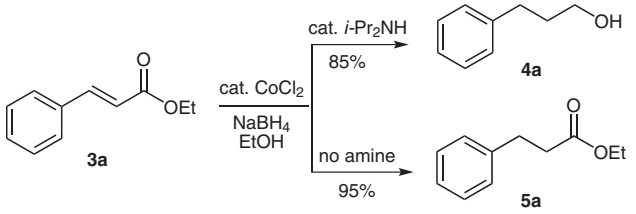
electrophilic for carbon–carbon double bond reduction to occur.

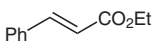
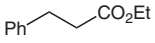
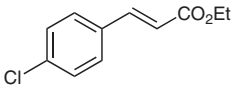
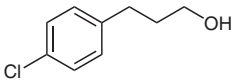
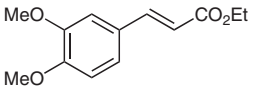
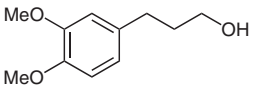
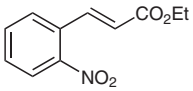
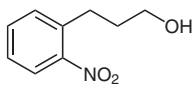
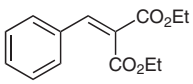
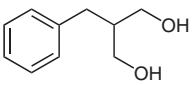
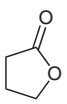
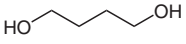
This catalytic procedure provides 3-aryl-2-(hydroxymethyl)propanenitriles **2a**–**h** and 3-*n*-octyl derivative **2i** in high yields; such compounds are potential intermediates in the synthesis of aminooxazolines.[11c–e] We noticed that the reduction of α-cyano esters is more facile compared with that of alkyl carboxylic esters with an α-cyano group. To make the ester reduction procedure more general and practical, we became interested in enhancing the reactivity of $NaBH_4$ by the addition of additives.[14,15] Thus, the addition of various amines (i.e., Et_3N, DMAP, Me_2NPh, or *i*-Pr_2NH) in catalytic amounts was shown to enhance the rate of reduction of carboxylic esters at 50 °C, for example the reduction of ethyl cinnamate (Scheme 2 and Table 2, entries 1–6). After careful study, we found that the combination of $CoCl_2·6H_2O$–*i*-Pr_2NH in catalytic amounts is an effective catalytic system in the reduction of a variety of esters, including α,β-unsaturated, aliphatic, and aromatic ones and lactones, giving the corresponding saturated alcohols **4** in high yields.



Scheme 2 Cobalt-catalyzed reduction of ethyl cinnamate with sodium borohydride

The simultaneous reduction of the carbon–carbon double bond along with the carboxylic ester functionality was also observed in the case of (*E*)-ethyl 3-arylacrylates (Table 2, entries 7–9). In addition, diethyl 2-benzylidenemalonate smoothly underwent reduction to provide 2-benzylpropane-1,3-diol (**4e**) in 94% yield (entry 10). Aromatic esters were reduced to the corresponding benzyl alcohols (entries 11 and 12). More interestingly, aliphatic esters and lactones were reduced to the corresponding alcohols in good yields under mild conditions (entries 13

Table 2 Cobalt(II) Chloride Hexahydrate–Diisopropylamine Catalyzed Chemoselective Reduction of Esters Using Sodium Borohydride: The Role of Diisopropylamine[a]

Entry	Ester	Additive		Product	Yield[b] (%)
1		no catalyst	**5a**		5
2		no amine	**5a**		95
3		*i*-Pr_2NH	**4a**		85
4		DMAP	**4a**		12
5		Et_3N	**4a**		30
6		Me_2NPh	**4a**		21
7		*i*-Pr_2NH	**4b**		87
8		*i*-Pr_2NH	**4c**		82
9		*i*-Pr_2NH	**4d**		87
10		*i*-Pr_2NH	**4e**		94
11	$PhCO_2Et$	*i*-Pr_2NH	**4f**	$PhCH_2OH$	87
12	4-$BrC_6H_4CO_2Et$	*i*-Pr_2NH	**4g**	4-$BrC_6H_4CH_2OH$	82
13	4-$O_2NC_6H_4CH_2CO_2Et$	*i*-Pr_2NH	**4h**	4-$O_2NC_6H_4CH_2CH_2OH$	79
14		*i*-Pr_2NH	**4i**		81

[a] Reaction conditions: carboxylic ester (2 mmol), $NaBH_4$ (4 mmol), $CoCl_2·6H_2O$ (10 mol%), *i*-Pr_2NH (20 mol%), EtOH (12 mL), 50 °C, 24 h.
[b] Isolated yield after chromatographic purification.

and 14, respectively). The results of the $CoCl_2·6H_2O$–*i*-Pr_2NH/$NaBH_4$ reduction clearly showed that esters can be reduced under mild conditions even when they contain various reducible groups, such as nitro and halo groups; such reactions are quite difficult with other strong reducing agents, e.g. lithium aluminum hydride. Mechanistically, the role of diisopropylamine is probably to enhance the nucleophilicity of the borohydride reagent by way of coordination.[15a]

In conclusion, we have demonstrated a simple catalytic combination comprising $CoCl_2·6H_2O$–*i*-Pr_2NH with stoichiometric $NaBH_4$ that reduces both the carbon–carbon double bond and ester carbonyl functionality in unsaturated carboxylic esters containing other reducible groups, such as halo, cyano, and nitro groups. Mild reaction conditions, easy-to-handle reagents, and good chemoselectivity are distinct features of this methodology; this procedure is a promising alternative to those involving expensive and difficult-to-handle lithium aluminum hydride.

The IR spectra were collected on a Shimadzu FTIR-8400 spectrometer. The NMR spectroscopy was performed on Bruker AV-200 and AV-400 NMR spectrometers with TMS as an internal standard. Quantitative analyses were determined using a Carlo Erba CHNS-O apparatus. Melting points are uncorrected. Solvents were purified and dried by standard procedures before use; petroleum ether of boiling range 60–80 °C was used.

2-(Hydroxymethyl)-3-phenylpropanenitrile (2a); Typical Procedure

To cyano ester **1a** (2.01 g, 10 mmol) in a 10-mL round-bottomed flask was added a solution of $CoCl_2·6H_2O$ (0.024 g, 0.11 mmol) in EtOH (10 mL) under a nitrogen atmosphere. Then, $NaBH_4$ (1.51 g, 40 mmol) was added, and the mixture was stirred at 25 °C for 6 h. After completion of the reaction (monitored by TLC), the mixture was transferred to a separating funnel containing EtOAc–H_2O (1:1, 100 mL), diluted with ice water (25 mL), and extracted with EtOAc (3 × 300 mL). The organic layer was washed with brine soln (2 × 400 mL), dried (anhyd Na_2SO_4), and concentrated under reduced pressure. The product was purified by column chromatography (EtOAc–petroleum ether, 3:1) to afford 2-(hydroxymethyl)-3-phenylpropanenitrile (**2a**) as a colorless solid. Yield: 1.53 g (95%); mp 75–78 °C [following recrystallization from $CHCl_3$ (91% yield)].

IR ($CHCl_3$): 700, 750, 1070, 1218, 1454, 1496, 1602, 1641, 1718, 1955, 2245, 2887, 2935, 3028, 3064, 3421 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.94 (s, 3 H), 3.71 (m, 3 H), 7.26 (m, 5 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 34.1, 36.6, 61.1, 120.5, 127.0, 128.5, 128.8, 136.4.

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.45; H, 6.85; N, 8.70.

3-(4-Chlorophenyl)-2-(hydroxymethyl)propanenitrile (2b)

Yield: 90% (1.18 g); colorless solid; mp 118–120 °C ($CHCl_3$).

IR ($CHCl_3$): 669, 757, 1215, 1492, 2400, 3020, 3433 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.98 (s, 3 H), 3.78 (m, 3 H), 7.47 (d, *J* = 8.72 Hz, 2 H), 7.75 (d, *J* = 7.12 Hz, 2 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 34.2, 36.7, 61.2, 120.2, 122.3, 128.2, 128.5, 134.1, 136.0, 140.2.

Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.39; H, 5.15; N, 7.16. Found: C, 61.42; H, 5.11; N, 7.21.

2-(Hydroxymethyl)-3-(4-methoxyphenyl)propanenitrile (2c)

Yield: 97% (1.22 g); gray solid; mp 122–124 °C ($CHCl_3$).

IR ($CHCl_3$): 667, 756, 837, 1033, 1068, 1111, 1180, 1249, 1301, 1442, 1463, 1514, 1612, 1660, 2244, 2837, 2935, 3014, 3448 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.70–3.10 (m, 4 H), 3.70–3.90 (m, 5 H), 6.8 (d, *J* = 8.0 Hz, 2 H), 7.01 (d, *J* = 7.12 Hz, 2 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 32.8, 38.0, 55.2, 61.1, 114.3, 114.4, 119.9, 130.2, 130.6, 131.4, 163.4.

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.10; H, 6.80; N, 7.28.

2-(Hydroxymethyl)-3-(4-tolyl)propanenitrile (2d)

Yield: 92% (1.46 g); colorless solid; mp 100–101 °C ($CHCl_3$).

IR ($CHCl_3$): 667, 757, 1070, 1214, 1381, 1446, 1516, 1625, 1903, 2245, 2887, 2927, 3018, 3444 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 2.91 (s, 3 H), 3.35 (s, 2 H), 3.71 (m, 1 H), 7.14 (m, 4 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 20.7, 33.7, 36.5, 61.2, 120.5, 128.6, 129.1, 133.3, 136.3.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.32; H, 7.35; N, 8.00.

2-(Hydroxymethyl)-3-[3-(trifluoromethyl)phenyl]propanenitrile (2e)

Yield: 85% (1.48 g); colorless solid; mp 105–108 °C ($CHCl_3$).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.00 (s, 3 H), 3.54 (br s, 1 H), 3.76 (m, 2 H), 7.44–7.53 (m, 4 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 33.9, 36.4, 61.2, 120.2, 121.1, 124.0, 125.5, 129.2, 131.1, 132.4, 137.4.

Anal. Calcd for $C_{11}H_{10}F_3NO$: C, 57.64; H, 4.40; N, 6.11. Found: C, 57.50; H, 4.45; N, 6.10.

2-(Hydroxymethyl)-3-(3-nitrophenyl)propanenitrile (2f)

Yield: 80% (1.43 g); yellowish solid; mp 182–184 °C (EtOH–$CHCl_3$).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.10 (s, 3 H), 3.84 (m, 3 H), 7.56 (d, *J* = 8.72 Hz, 2 H), 8.14 (d, *J* = 6.19 Hz, 2 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 33.8, 36.2, 61.3, 119.7, 122.4, 123.9, 129.8, 135.4, 138.5, 148.3.

Anal. Calcd for $C_{10}H_{10}N_2O_3$: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.22; H, 4.85; N, 13.60.

3-(3,4-Dimethoxyphenyl)-2-(hydroxymethyl)propanenitrile (2g)

Yield: 96% (1.61 g); brown solid; mp 170–171 °C ($CHCl_3$).

IR ($CHCl_3$): 765, 812, 858, 1026, 1072, 1141, 1157, 1238, 1263, 1336, 1421, 1465, 1515, 1591, 1724, 2243, 2837, 2937, 3494 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.11 (s, 3 H), 3.48 (br s, 1 H), 3.71 (m, 2 H), 3.81 (s, 6 H), 6.58–6.72 (m, 3 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 33.7, 36.3, 56.3, 61.1, 114.7, 115.7, 132.2, 132.6, 138.2, 144.5, 147.1.

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.11; H, 6.80; N, 6.35.

3-Benzo[1,3]dioxol-5-yl-2-(hydroxymethyl)propanenitrile (2h)

Yield: 99% (1.66 g); colorless solid; mp 190–192 °C ($CHCl_3$).

IR ($CHCl_3$): 771, 813, 864, 927, 1039, 1091, 1193, 1247, 1365, 1444, 1510, 1608, 1728, 1843, 2245, 2781, 2893, 3452 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.97 (s, 3 H), 3.44 (br s, 1 H), 3.62 (m, 2 H), 5.87 (s, 2 H), 6.53–6.62 (m, 3 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 34.1, 35.3, 61.1, 91.1, 115.3, 115.9, 132.3, 132.8, 138.4, 145.1, 146.8.

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.43; H, 5.36; N, 6.70.

2-(Hydroxymethyl)undecanenitrile (2i)
Yield: 70% (1.21 g); colorless solid; mp 50–53 °C ($CHCl_3$).

IR (KBr): 667, 757, 1047, 1215, 1377, 1465, 1670, 1730, 2200, 2854, 2925, 3018, 3386 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.66 Hz, 3 H), 1.27–1.57 (m, 16 H), 1.90 (br s, 1 H), 3.88 (m, 2 H), 4.49 (m, 1 H).

^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.1, 17.8, 54.0, 59.2, 99.3, 126.3, 127.3, 128.4, 144.9, 148.4, 152.2, 165.4.

Anal. Calcd for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 73.98; H, 11.95; N, 7.60.

Cobalt(II) Chloride Hexahydrate–Diisopropylamine Catalyzed Reduction of Esters to Alcohols 4; General Procedure
To a solution of the appropriate carboxylic ester (2 mmol) and $CoCl_2·6H_2O$ (4.72 mg, 0.2 mmol) in distilled EtOH (8 mL) was added 1 M *i*-Pr_2NH (20 mol%) in distilled EtOH (4 mL). To the stirred mixture was then added $NaBH_4$ (156 mg, 4 mmol) portionwise. The mixture was stirred at 50 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was diluted with H_2O (50 mL) and EtOAc (50 mL). The organic layer was separated, washed with brine soln (2 × 20 mL), dried (anhyd Na_2SO_4), and concentrated under reduced pressure to give the crude product. Flash column chromatography (silica gel, 230–400 mesh, petroleum ether–EtOAc, 3:2) afforded the saturated alcohol **4** in pure form.

The reaction of ethyl cinnamate without the use of *i*-Pr_2NH resulted in the formation of the saturated ester **5a**.

3-Phenylpropan-1-ol (4a)
Yield: 85% (300 mg); colorless liquid.

IR ($CHCl_3$): 698, 744, 968, 1029, 1060, 1454, 1495, 3325 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.44 (br s, 1 H), 1.84–1.95 (m, 2 H), 2.70 (t, *J* = 8.0 Hz, 2 H), 3.65 (t, *J* = 6.3 Hz, 2 H), 7.13–7.31 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.1, 33.7, 63.3, 126.7, 127.1, 128.1, 140.4.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.32; H, 8.82.

Ethyl 3-Phenylpropanoate (5a)
Yield: 95% (354 mg); colorless liquid.

IR ($CHCl_3$): 698, 744, 968, 1029, 1060, 1454, 1495, 1747 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.3 Hz, 3 H), 2.65–2.72 (m, 2 H), 2.81–2.91 (m, 2 H), 4.15 (q, *J* = 7.3 Hz, 2 H), 7.15–7.33 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 30.6, 35.3, 59.8, 125.9, 127.9, 128.1, 140.3, 172.6.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.11; H, 7.95.

3-(4-Chlorophenyl)propan-1-ol (4b)
Yield: 87% (358 mg); gum.

IR ($CHCl_3$): 754, 968, 1029, 1060, 1454, 1495, 3325 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.76 (br s, 1 H), 1.78–1.92 (m, 2 H), 2.67 (t, *J* = 7.3 Hz, 2 H), 3.61 (t, *J* = 7.3 Hz, 2 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 7.24 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.1, 33.7, 61.3, 128.1, 129.5, 131.2, 140.0.

Anal. Calcd for $C_9H_{11}ClO$: C, 63.35; H, 6.50. Found: C, 63.32; H, 6.52.

3-(3,4-Dimethoxyphenyl)propan-1-ol (4c)
Yield: 82% (320 mg); gum.

IR ($CHCl_3$): 745, 857, 968, 1029, 1060, 1460, 1495, 3498 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.64 (br s, 1 H), 1.61–1.95 (m, 2 H), 2.67 (t, *J* = 8.1 Hz, 2 H), 3.68 (t, *J* = 8.1 Hz, 2 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 6.72–6.86 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.5, 34.2, 55.7, 55.8, 62.1, 111.2, 111.6, 120.1, 134.3, 147.0, 147.7.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.28; H, 8.21.

3-(2-Nitrophenyl)propan-1-ol (4d)
Yield: 87% (326 mg); gum.

IR ($CHCl_3$): 857, 968, 1029, 1060, 1245, 1440, 1507, 3430 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.67 (br s, 1 H), 1.87–2.01 (m, 2 H), 1.99 (t, *J* = 7.6 Hz, 2 H), 3.72 (t, *J* = 6.2 Hz, 2 H), 7.31–7.60 (m, 3 H), 7.92 (dd, *J* = 1.2, 8.1 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.1, 33.2, 61.6, 124.4, 126.8, 131.8, 132.8, 136.7, 149.1.

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.63; H, 6.10; N, 7.75.

2-Benzylpropane-1,3-diol (4e)
Yield: 94% (342 mg); gum.

IR ($CHCl_3$): 745, 857, 968, 1029, 1060, 1454, 1498, 3400 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.99–2.27 (m, 1 H, and br s, 2 H), 2.62 (d, *J* = 7.6 Hz, 2 H), 3.63–3.85 (m, 4 H), 7.17–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 34.1, 43.7, 64.9, 126.0, 128.9, 139.8.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.23; H, 8.44.

Phenylmethanol (4f)
Yield: 87% (322 mg); gum.

IR ($CHCl_3$): 857, 968, 1495, 3498 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.99 (br s, 1 H), 4.66 (s, 2 H), 7.25–7.37 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 64.3, 126.7, 127.1, 128.1, 140.6.

Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.72; H, 7.45.

(4-Bromophenyl)methanol (4g)
Yield: 82% (332 mg); gum.

IR ($CHCl_3$): 968, 1029, 1060, 1501, 3390 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.88 (br s, 1 H), 4.64 (s, 2 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 7.48 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 63.9, 121.1, 128.4, 131.3, 139.5.

Anal. Calcd for C_7H_7BrO: C, 44.95; H, 3.77. Found: C, 44.92; H, 3.73.

2-(4-Nitrophenyl)ethanol (4h)
Yield: 79% (319 mg); gum.

IR ($CHCl_3$): 857, 1063, 1245, 1498, 3450 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.70 (br s, 1 H), 2.96 (t, *J* = 6.3 Hz, 2 H), 3.91 (m, 2 H), 7.40 (d, *J* = 8.7 Hz, 2 H), 8.15 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 67.2, 121.2, 128.6, 146.1, 147.1.

Anal. Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.44; H, 5.40; N, 8.35.

Butane-1,4-diol (4i)
Yield: 85% (312 mg); gum.

IR ($CHCl_3$): 837, 938, 1291, 3098, cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.42–1.48 (m, 4 H), 1.94 (br s, 2 H), 3.51–3.58 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.1, 64.3.

Anal. Calcd for $C_4H_{10}O_2$: C, 53.31; H, 11.18. Found: C, 53.61; H, 11.33.

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