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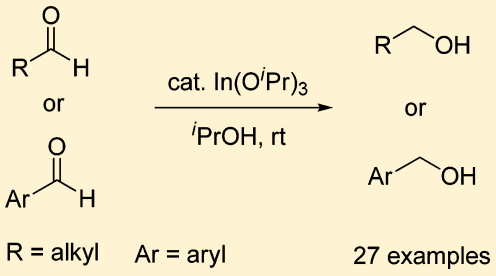
Indium Tri(isopropoxide)-Catalyzed Selective Meerwein–Ponndorf–Verley Reduction of Aliphatic and Aromatic Aldehydes

Jaeyoung Lee, Taekyu Ryu, Sangjune Park, and Phil Ho Lee*

Department of Chemistry, Kangwon National University, Chuncheon 200-701, Republic of Korea

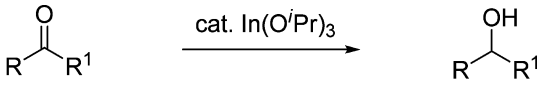
Supporting Information

ABSTRACT: Indium tri(isopropoxide)-catalyzed Meerwein–Ponndorf–Verley reduction of aliphatic and aromatic aldehydes in 2-propanol gave selectively the corresponding primary alcohols in good to excellent yields at room temperature. A wide range of functional groups including alkene, ether, ketone, ester, nitrile, and nitro were tolerated under the optimum reaction conditions. Chemoselective reductions were also achieved not only between aromatic aldehyde, aromatic ketone, and epoxide but also between aliphatic aldehyde and alkene.



The reduction of aldehydes and ketones is one of the important functional group transformations in organic chemistry.[1] Among the various methods for reducing carbonyl groups, the Meerwein–Ponndorf–Verley (MPV) reduction, first reported in 1925, has been recognized as one of most convenient and environmentally benign processes in organic synthesis.[2] In general, the MPV reduction uses inexpensive 2-propanol as a hydride donor and aluminum tri(isopropoxide) as a mediator.[3] Because the MPV reduction is easy to operate and convenient to scale up, it became an attractive green process for reduction of various carbonyl compounds. However, its synthetic utility has been rather limited mainly due to the fact that stoichiometric or excess amounts of aluminum alkoxides are often required at high temperatures. In addition, in situ elimination of generated acetone needs to be carried out in order to maximize the procduct yields in acceptable reaction time.[4] While catalytic MPV reduction was developed by using trimethylaluminum or chlorodimethylaluminum in toluene,[5] an MPV reduction was reported to be accelerated when aluminum tri(isopropoxide) was modified with certain additives such as TFA, HCl, or propionic acid.[2k,l,6] Despite of these recent advances, the chemoselective catalytic MPV reduction of carbonyl compounds is still highly desirable especially without requiring any additives under mild reaction conditions. With regard to this aspect, boron tri(isopropoxide) was examined in the MPV reduction of carbonyl compounds although the system was revealed to reduce only aliphatic aldehydes and ketones.[3c,7] In addition, because the reducing power of boron tri(isopropoxide) is weak, stoichiometric amounts of reagents were needed with long reaction times. Because indium metal is one of the group 13 elements like boron and aluminum, we envisioned that indium might be applied to the reduction of aldehydes and ketones to produce alcohols as shown in Scheme 1. Herein, we report our preliminary results on the development of an indium tri(isopropoxide) reagent that can be employed for the chemoselective catalytic MPV reduction of various aliphatic and aromatic aldehydes under mild reaction conditions.

Scheme 1. MPV Reduction of Aldehydes and Ketones Using Indium Catalyst



In order to examine the feasibility of reduction of carbonyl compounds using indium catalyst, we first investigated a reaction of benzaldehyde (**1a**) with indium tri(isopropoxide) under nitrogen atmosphere (Table 1). When **1a** was treated with 5 mol % of $In(O^iPr)_3$ and 10 equiv of 2-propanol in toluene, benzyl alcohol (**2a**) was obtained in 12% yield at 25 °C after 1.5 h (entry 1). The use of 10 and 15 mol % of $In(O^iPr)_3$ gave **2a** in 40% and 78% yields, respectively (entries 2 and 4). Toluene was more effective for the reaction compared to other solvents, representatively dichloromethane (entries 3 and 5). Exposure of **1a** to 20 mol % of $In(O^iPr)_3$ in the presence of 1 equiv of 2-propanol in toluene afforded **2a** in 73% yield (entry 6). Increasing the amounts of 2-propanol to 5 and 10 equiv resulted in higher product yields of 81% and 86%, respectively, in toluene (entries 7 and 8). Although the use of 5 and 10 mol % of $In(O^iPr)_3$ in 2-propanol as a solvent provided **2a** in low yield (entries 9 and 10), treatment of **1a** with 20 mol % of $In(O^iPr)_3$ in 2-propanol produced **2a** in 91% yield at 25 °C for 3 h (entry 11).

To demonstrate the efficiency and scope of the present method, we applied this catalytic reduction system to a wide range of aromatic aldehyde substrates (Table 2). When 2- and 4-tolualdehyde were treated with 20 mol % $In(O^iPr)_3$, the corresponding alcohols were obtained in good to excellent yields (93% and 86%) at 25 °C for 0.25 h (entries 2 and 3).

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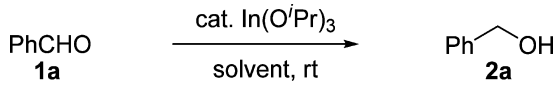
Table 1. Optimization of Indium Tri(isopropoxide)-Catalyzed MPV Reduction of Benzaldehyde[a]



entry	$In(O^iPr)_3$ (mol %)	^{i}PrOH (equiv)	solvent	time (h)	yield[b] (%)
1	5	10	toluene	1.5	12
2	10	10	toluene	3	40
3	10	10	CH_2Cl_2	5	37
4	15	10	toluene	5	78
5	15	10	CH_2Cl_2	3	72
6	20	1	toluene	7	73 (71)[c]
7	20	5	toluene	5	81 (79)[c]
8	20	10	toluene	3	86 (83)[c]
9	5		^{i}PrOH	6	3
10	10		^{i}PrOH	3	9
11	20		^{i}PrOH	3	91 (88)[c]

[a]Reactions were carried out with **1a** (0.5 mmol) in solvent (1.5 mL) under nitrogen atmosphere. [b]GC yields using dodecane as an internal standard. [c]Isolated yields.

Table 2. Indium Tri(isopropoxide)-Catalyzed MPV Reduction of Aryl and Heteroaryl Aldehydes[a]

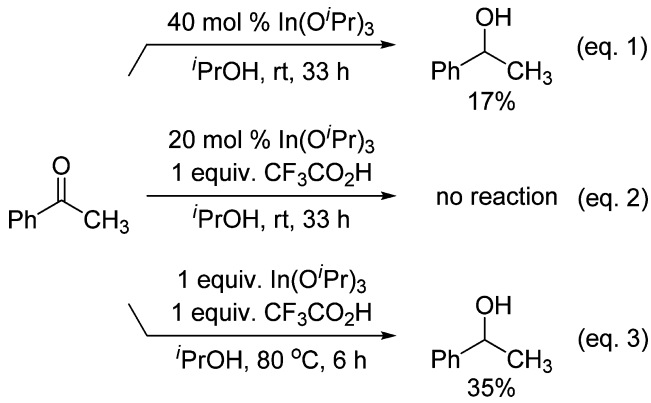
entry	Ar		time (h)	yield[b] (%)
1	Ph	**a**	3	88
2	2-Me-C_6H_4	**b**	0.25	93
3	4-Me-C_6H_4	**c**	0.25	86
4	2,4,6-$(Me)_3$-C_6H_2	**d**	24	47 (42)[c]
5	2,4,6-$(Me)_3$-C_6H_2	**d**	4.5	92[d]
6	2-MeO-C_6H_4	**e**	0.25	90
7	3-MeO-C_6H_4	**f**	0.5	97
8	4-MeO-C_6H_4	**g**	5.5	78
9	3,5-$(MeO)_2$-C_6H_3	**h**	0.5	93
10	3,4-(OCH_2O)-C_6H_3	**i**	2	83
11	4-AcO-C_6H_4	**j**	24	41 (47)[e]
12	2−Br-C_6H_4	**k**	0.5	91
13	3−Br-C_6H_4	**l**	6	89
14	2−I-C_6H_4	**m**	6	94
15	4−Ac-C_6H_4	**n**	1.5	87
16	4-MeO_2C−C_6H_4	**o**	0.5	94
17	3-NC-C_6H_4	**p**	1	90
18	4-O_2N−C_6H_4	**q**	3	94
19	2-F-3-MeO-C_6H_3	**r**	0.08	98
20	3-pyridyl	**s**	1	90
21	5-Br-thienyl	**t**	1	89

[a]Reactions were carried out with **1** (0.5 mmol) in 2-propanol (1.5 mL) under nitrogen atmosphere. [b]Isolated yield. [c]Recovery yield of aldehyde. [d]Reaction was carried out at 80 °C. [e]4-Hydroxybenzaldehyde.

While 2,4,6-trimethylbenzaldehyde was reduced to **2d** in 47% yield at 25 °C even after 24 h presumably due to steric effect (entry 4), the same reaction at higher temperatures (80 °C) afforded **2d** in 92% yield for 4.5 h (entry 5). Subjecting 2- and 3-methoxybenzaldehyde (**1e** and **1f**) to indium catalyst afforded **2e** and **2f** in excellent yield (90% and 97%) (entries 6 and 7). 4-Methoxybenzaldehyde required longer reaction time (5.5 h) (entry 8). 3,5-Dimethoxybenzaldehyde was converted to the corresponding alcohol in 93% yield (entry 9). Benzo[1,3]dioxole-5-carbaldehyde was reduced with indium catalyst to furnish **2i** in 83% yield (entry 10). However, when 4-acetoxybenzaldehyde **1j** was treated with 20 mol % of $In(O^iPr)_3$, the corresponding alcohol **2j** was obtained in 41% yield together with 4-hydroxybenzaldehyde (47%), which was a byproduct derived from the ester cleavage in **1j** (entry 11). The presence of halide groups in the aromatic ring did not deteriorate the reaction efficiency of the MPV reactions (entries 12−14). The reduction of aromatic aldehydes (**1n**, **1o**, **1p**, and **1q**) having acetyl, methoxycarbonyl, nitrile, and nitro groups provided selectively the corresponding primary alcohols in good to excellent yields under the standard conditions (entries 15−18). 2-Fluoro-3-methoxybenzaldehyde (**1r**) was smoothly reduced to give **2r** in 98% yield at 25 °C for 5 min (entry 19). Heteroaromatic aldehydes turned out to be compatible with the employed reaction conditions. Indeed, 3-pyridinecarboxaldehyde and 5-bromo-2-thiophenecarboxaldehyde were converted to the desired alcohols in 90% and 89% yields, respectively (entries 20 and 21).[5]

Similarly, this catalytic system was successfully applied in the reduction of a wide range of aliphatic aldehydes (Table 3). Reaction of undecylenic aldehyde (**3a**) with 20 mol % of $In(O^iPr)_3$ in 2-propanol afforded selectively 10-undecen-1-ol (**4a**) in 82% yield at 25 °C for 3 h with the double bond intact (entry 1). The present method worked equally well with 2-ethylbutanal (**3b**) and 2,6-dimethyl-5-heptenal (**3c**), leading to the selective formation of 2-ethyl-1-butanol (**4b**) and 2,6-dimethyl-5-hepten-1-ol (**4c**) in 88% and 83% yields, respectively (entries 2 and 3). Cyclohexanecarboxaldehyde (**3d**) was reduced efficiently under the standard conditions (entry 4). Treatment of cinnamaldehyde and 2-bromocinnamaldehyde with indium catalyst produced selectively cinnamyl alcohol and 2-bromocinnamyl alcohol in 82% and 96% yields, respectively, at 25 °C without the reduction of conjugated olefinic or carbon−bromine bonds (entries 5 and 6). Under the optimum reaction conditions, (**3g**) was converted to the alcohol (**4g**) in 81% yield (entry 7).

Next, the MPV reduction of aromatic ketone with indium tri(isopropoxide) was briefly investigated. Although 40 mol % of $In(OiPr)_3$ was used, 1-phenylethanol was obtained in only 17% yield at 25 °C after 33 h (eq 1). The use of trifluoroacetic



acid (1 equiv) as an additive was not effective (eq 2). In addition, treatment of acetophenone with 1 equiv of $In(O^iPr)_3$ and 1 equiv of trifluoroacetic acid in 2-propanol gave rise to 1-phenylethanol in 35% yield at 80 °C after 6 h (eq 3).

These results led us to predict that an aromatic aldehyde can be selectively reduced in the presence of aromatic ketones (Scheme 2). In fact, when a mixture of benzaldehyde and acetophenone was subjected to the reaction conditions, benzyl alcohol was selectively isolated in 88% yield at 25 °C for 3 h. Interestingly, an exposure of a mixture of benzaldehyde and styrene oxide to indium catalyst led to only benzyl alcohol in 83% yield without the formation of 1- or 2-phenylethanol.

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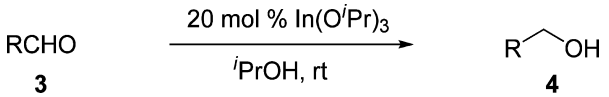
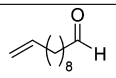
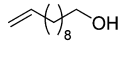
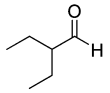
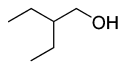
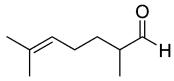
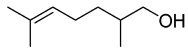
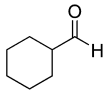
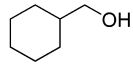
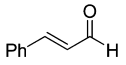
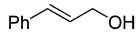
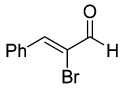
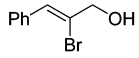
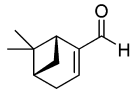
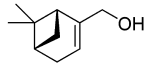
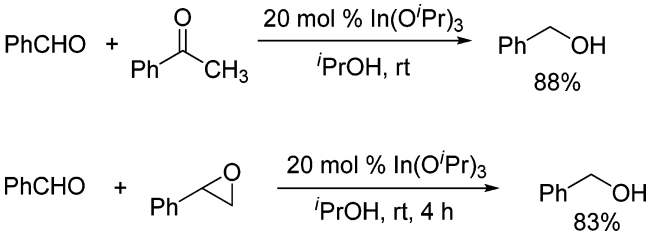
Table 3. Indium Tri(isopropoxide)-Catalyzed MPV Reduction of Aliphatic Aldehydes[a]



entry	aldehyde		time (h)	alcohol	Yield[b] (%)
1		**a**	3		82
2		**b**	3		88[c]
3		**c**	3		83
4		**d**	1		90
5		**e**	5		82
6		**f**	0.5		96
7		**g**	0.5		81[d]

[a]Reactions were carried out with **3** (0.5 mmol) in solvent (1.5 mL) under nitrogen atmosphere. [b]Isolated yield. [c]GC yield using naphthalene as an internal standard. [d]Reaction was carried out at 80 °C.

Scheme 2. Selective Reduction between Aldehyde and Ketone or Epoxide



In summary, we have developed a new indium catalyst system for the selective Meerwein-Ponndorf-Verley reduction of aliphatic and aromatic aldehydes in 2-propanol to give the corresponding primary alcohols in good to excellent yields at room temperature. A wide range of functional groups such as alkene, ether, ketone, ester, nitrile, and nitro are tolerated under the optimized reaction conditions. Chemoselective reductions were also achieved not only between aromatic aldehyde, aromatic ketone, and epoxide but also between aliphatic aldehyde and alkene.

EXPERIMENTAL SECTION

Indium Tri(isopropoxide)-Catalyzed MPV Reduction of Benzaldehyde. Benzaldehyde (53.1 mg, 0.5 mmol) was added to a solution of $In(O^iPr)_3$ (29.2 mg, 0.1 mmol, 20 mol %) purchased from a commercial supplier in 2-propanol (1.5 mL) under nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 3 h. The reaction mixture was quenched with 1 N HCl solution (4 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:5) to give benzyl alcohol (**2a**) (47.7 mg, 88%):[8] colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.37−7.34 (m, 4H), 7.32−7.25 (m, 1H), 4.69 (d, J = 5.9 Hz, 2H), 1.73 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 141.3, 129.0, 128.1, 127.4, 65.8; IR (film) 3230 (OH), 3056, 3012, 2982, 1610, 1589, 1219, 1005 cm^{-1}.

2-Methylbenzyl alcohol[9] (2b): white solid; mp = 30−35 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.36−7.33 (m, 1H), 7.23−7.16 (m, 3H), 4.69 (d, J = 3.7 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 139.1, 136.5, 130.8, 128.2, 128.0, 126.5, 64.0, 19.1; IR (film) 3248 (OH), 3032, 2936, 2912, 1557, 1446, 1154, 788 cm^{-1}.

4-Methylbenzyl alcohol[8] (2c): white solid; mp = 58−63 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.25 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 4.64 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 138.3, 137.8, 129.7, 127.5, 65.7, 21.6; IR (film) 3348 (OH), 3022, 2956, 2920, 1517, 1446, 1034, 808 cm^{-1}.

Mesitylmethanol[8] (2d): white solid; mp = 85−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 6.87 (s, 2H), 4.71 (d, J = 3.3 Hz, 2H), 2.39 (s, 6H), 2.27 (s, 3H), 1.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 138.2, 137.7, 134.1, 129.6, 59.6, 21.4, 19.8; IR (film) 3280 (OH), 3000, 2970, 2915, 1613, 1445, 992, 851 cm^{-1}.

2-Methoxybenzyl alcohol[10] (2e): colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.31−7.26 (m, 2H), 6.94 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 4.69 (d, J = 5.0 Hz, 2H), 3.87 (s, 3H), 2.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 157.9,

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129.43, 129.40, 129.2, 121.1, 110.6, 63.6, 55.7; IR (film) 3374 (OH), 2938, 2836, 1602, 1492, 1242, 1030, 754 cm^{-1}.

3-Methoxybenzyl alcohol[11] (2f): colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.29−7.25 (m, 1H), 6.94 (d, J = 7.4 Hz, 2H), 6.83 (dd, J = 7.1, 2.1 Hz, 1H), 4.67 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 160.3, 142.9, 130.0, 119.5, 113.7, 112.7, 65.7, 55.6; IR (film) 3356 (OH), 2938, 2835, 1601, 1488, 1263, 1039, 782 cm^{-1}.

4-Methoxybenzyl alcohol[8] (2g): colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.30 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6, Hz, 2H), 4.62 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 159.6, 133.5, 129.1, 114.4, 65.5, 55.7; IR (film) 3352 (OH), 3030, 3000, 2956, 2934, 1612, 1512, 1247, 1032, 816 cm^{-1}.

3,5-Dimethoxybenzyl alcohol[12] (2h): pale yellow solid; mp = 40−45 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 6.52 (d, J = 2.2 Hz, 2H), 6.39 (t, J = 2.3 Hz, 1H), 4.63 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 161.4, 143.8, 105.1, 100.0, 65.8, 55.8; IR (film) 3397 (OH), 3000, 2938, 2838, 1598, 1463, 1205, 1060, 834 cm^{-1}.

Benzo[1,3]dioxolo-5-methanol[8] (2i): yellow solid; mp = 50−55 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 6.86 (s, 1H), 6.80 (dd, J = 8.0, 1.4 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 5.94 (s, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 148.2, 147.5, 135.3, 120.9, 108.6, 108.3, 101.4, 65.6; IR (film) 3321 (OH), 3078, 3011, 2989, 2905, 1489, 1444, 1252, 807 cm^{-1}.

4-Acetoxybenzyl alcohol[13] (2j): white solid; mp = 30−35 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.38 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 4.68 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 170.0, 150.5, 138.9, 128.5, 122.1, 65.1, 21.5; IR (film) 3336 (OH), 3059, 3005, 2845, 1699, 1678, 1266, 1204, 825 cm^{-1}.

2-Bromobenzyl alcohol[14] (2k): pale brown solid; mp = 75−80 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.55 (dd, J = 8.0, 1.0 Hz, 1H), 7.49 (dd, J = 7.6, 1.4 Hz, 1H), 7.34 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 7.17 (ddd, J = 7.7, 7.7, 1.6 Hz, 1H), 4.76 (d, J = 6.4 Hz, 2H), 2.00 (t, J = 6.5 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 139.7, 132.6, 129.1, 128.9, 127.7, 122.6, 65.1; IR (film) 3204 (OH), 3066, 2913, 2858, 1456, 1442, 1055, 1024, 749 cm^{-1}.

3-Bromobenzyl alcohol[15] (2l): pale yellow liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.53 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.29−7.21 (m, 2H), 4.68 (d, J = 5.1 Hz, 2H), 1.79 (t, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 143.5, 131.1, 130.5, 130.3, 125.7, 123.1, 64.9; IR (film) 3323 (OH), 3055, 2934, 2873, 1570, 1428, 1069, 777 cm^{-1}.

2-Iodobenzyl alcohol[16] (2m): pale yellow solid; mp = 90−95 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.83 (dd, J = 7.8, 1.0 Hz, 11H), 7.47 (dd, J = 7.6, 1.5 Hz, 1H), 7.37 (ddd, J = 7.5, 7.5, 0.9 Hz, 1H), 7.01 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 4.69 (d, J = 6.1 Hz, 2H), 1.98 (t, J = 6.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 143.0, 139.6, 129.8, 128.92, 128.90, 97.9, 69.8; IR (film) 3187 (OH), 3060, 2897, 1458, 1434, 1036, 1012, 740 cm^{-1}.

4-Acetylbenzyl alcohol[17] (2n): yellow solid; mp = 30−35 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.92 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 4.76 (s, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 198.6, 146.8, 136.6, 129.0, 127.0, 64.9, 27.0; IR (film) 3434 (OH), 3050, 3005, 2956, 2926, 1653, 1266, 1048, 814 cm^{-1}.

4-Methoxycarbonyl benzyl alcohol[8] (2o): white solid; mp = 45−50 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.02 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 4.76 (s, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 167.4, 146.4, 130.2, 129.7, 126.9, 65.0, 52.5; IR (film) 3225 (OH), 3077, 3022, 3010, 2956, 1725, 1619, 1278, 1010, 823 cm^{-1}.

3-Cyanobenzyl alcohol[8] (2p): white solid; mp = 25−30 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.68 (s, 1H), 7.61−7.57 (m, 3H), 4.75 (s, 2H), 2.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 142.7, 131.6, 131.4, 1306, 129.7, 119.2, 112.9, 64.4; IR (film) 3413 (OH), 3075, 3014, 2983, 1405, 808 cm^{-1}.

4-Nitrobenzyl alcohol[8] (2q): yellow solid; mp = 90−95 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.23 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.9 Hz, 2H), 4.84 (d, J = 5.5 Hz, 2H), 1.90 (t, J = 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 148.1, 147.4, 127.0, 123.8, 64.1; IR (film) 3521 (OH), 3110, 3070, 2944, 2869, 1509, 1345, 1056, 735 cm^{-1}.

2-Fluoro-5-methoxybenzyl alcohol[18] (2r): colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 6.99−6.94 (m, 2H), 6.79−6.75 (m, 1H), 4.73 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 156.4, 156.22, 156.20, 154.0, 128.9, 128.8, 116.3, 116.1, 114.6, 114.5, 114.25, 114.21, 59.9, 59.8, 56.2; IR (film) 3398 (OH), 2942, 2837, 1740, 1504, 1203, 1033, 811, 711 cm^{-1}.

3-Pyridinemethanol[8] (2s): light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.45 (s, 1H), 8.38 (d, J = 4.0 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.26 (dd, J = 7.8, 4.9 Hz, 1H), 4.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 148.5, 148.3, 137.6, 135.6, 124.0, 62.4; IR (film) 3210 (OH), 3066, 3000, 2949, 2866, 1600, 1583, 1450, 1190, 1042, 800 cm^{-1}.

(5-Bromothiophen-2-yl)methanol[19] (2t): yellow liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 6.92 (d, J = 3.8 Hz, 1H), 6.76 (d, J = 3.5 Hz, 1H), 4.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 146.1, 1300, 1261, 1127, 60.6; IR (film) 3347 (OH), 3088, 3044, 2926, 2866, 1440, 1357, 1014, 795 cm^{-1}.

Undec-10-en-1-ol[20] (4a): colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 5.87−5.76 (m, 1H), 5.02−4.97 (m, 1H), 4.95−4.91 (m, 1H), 3.66−3.62 (m, 2H), 2.07−2.01 (m, 2H), 1.58−1.53 (m, 2H), 1.39−1.29 (m, 12H), 1.24−1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 139.2, 114.1, 63.1, 33.8, 32.8, 29.5, 29.4, 29.1, 28.9, 25.7; IR (film) 3245 (OH), 3078, 3000, 2905, 2855, 1624, 1425, 1305 cm^{-1}.

2-Ethyl-1-butanol[21] (4b): colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 3.56 (d, J = 3.0 Hz, 2H), 1.67 (s, 1H), 1.41−1.32 (m, 4H), 1.25 (s, 1H), 0.92−0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 64.5, 43.4, 22.7, 11.0; IR (film) 3336 (OH), 2962, 2932, 2875, 1461, 1380, 1112, 1052, 1010 cm^{-1}.

2,6-Dimethylhept-5-en-1-ol[22] (4c): colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 5.13−5.09 (m, 1H), 3.54−3.41 (m, 2H), 2.08−1.95 (m, 2H), 1.69 (s, 3H), 1.66−1.63 (m, 1H), 1.61 (s, 3H), 1.48−1.39 (m, 1H), 1.20−1.11 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 131.5, 124.6, 68.3, 35.3, 33.2, 25.7, 25.4, 17.7, 16.5; IR (film) 3339 (OH), 2965, 2915, 2873, 1453, 1376, 1041 cm^{-1}.

Cyclohexanemethanol[14] (4d): pale brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 3.44 (d, J = 6.43 Hz, 2H), 1.78−1.65 (m, 5H), 1.51−1.44 (m, 1H), 1.34 (bs, 1H), 1.30−1.11 (m, 3H), 0.98−0.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 69.2, 40.9, 30.0, 27.0, 26.2; IR (film) 3335 (OH), 2945, 2855, 1420, 788 cm^{-1}.

Cinnamyl alcohol[8] (4e): white solid; mp = 30−35 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.40−7.38 (m, 2H), 7.34−7.29 (m, 2H), 7.26−7.22 (m, 1H), 6.62 (d, J = 15.9 Hz, 1H), 6.37 (dt, J = 16.0, 5.7 Hz, 1H), 4.33 (dd, J = 5.3, 1.3 Hz, 2H)), 1.48 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 137.1, 131.6, 129.0, 128.9, 128.1, 126.9, 64.2; IR (film) 3323 (OH), 3058, 3025, 2862, 1493, 1448, 1009, 967, 734, 692 cm^{-1}.

***β*-Bromocinnamyl alcohol[23] (4f):** colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.63 (d, J = 1.5 Hz, 2H), 7.39−7.35 (m, 2H), 7.34−7.32 (m, 1H), 7.09 (s, 1H), 4.42 (d, J = 5.9 Hz, 2H), 2.14 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 135.4, 129.4, 128.6, 128.3, 125.7, 69.8; IR (film) 3341 (OH), 3050, 3014, 2920, 2837, 1652, 1069, 878, 745 cm^{-1}.

(1*R*)-(−)-Myrtenol[24] (4g): colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 5.49−5.47 (m, 1H), 3.99 (s, 2H), 2.42 (dt, J = 8.6, 5.6 Hz, 1H), 2.34−2.21 (m, 2H), 2.16−2.10 (m, 2H), 1.30 (s, 3H), 1.26 (s, 1H), 1.18 (d, J = 8.6 Hz, 1H), 0.84 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 147.8, 117.9, 66.0, 43.4, 40.9, 38.0, 31.6, 31.1, 26.1, 21.1; IR (film) 3322 (OH), 2987, 2912, 2831, 1655, 1468, 1056 cm^{-1}.

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■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: phlee@kangwon.ac.kr.

Notes

The authors declare no competing financial interest.

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