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Solvent-free reduction of aldehydes and ketones using solid acid-activated sodium borohydride

Byung Tae Cho,[a,*] Sang Kyu Kang,[a] Min Sung Kim,[b] Soo Ryeon Ryu[b] and Duk Keun An[b,*]

[a]*Department of Chemistry, Hallym University, Chunchon, Kangwondo 200-702, Republic of Korea*
[b]*Department of Chemistry, Kangwon National University, Chunchon, Kangwondo 200-701, Republic of Korea*

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This paper is dedicated to the late Professor Herbert C. Brown and his pioneer works on the hydride reductions

Abstract—A simple and convenient procedure for the reduction of aldehydes and ketones with sodium borohydride activated by solid acids such as boric acid, benzoic acid, and *p*-toluenesulfonic acid monohydrate under solvent-free conditions is described.

1. Introduction

Solvent-free reactions are not only of interest from ecological point of view, but in many cases, also offer considerable synthetic advantages in terms of yield, selectivity, and simplicity of the reaction procedure.[1] Sodium borohydride is an inexpensive, safe to handle, and environmental friendly reducing agent, which rapidly reduce aldehydes, ketones, and acid chlorides.[2] This reagent is commonly employed in hydroxylic solvents, such as methanol, ethanol, and 2-propanol, although it is unstable in both methanol and ethanol due to solvolysis.[2] There are few reports for the reduction of aldehydes and ketones with sodium borohydride under solvent-free conditions.[3] However, the reductions have disadvantage for practical utility, requiring long reaction times. For example, the reduction was complete when a mixture of benzophenone and a 10-fold molar amount of sodium borohydride was kept in a dry box at room temperature with occasional mixing and grinding using an agate mortar and pestle for 5 days.[3a] Very recently, we reported the first solvent-free reduction of imines using solid acid-activated sodium borohydride to give the corresponding amines in near quantitative yields.[4] The results prompted us to study the solvent-free reduction of aldehydes and ketones using the same methodology. This paper includes chemoselective reduction of functionalized aldehydes and ketones bearing other reducible functional groups, regioselective reduction of α,β-unsaturated aldehydes and ketones, and stereoselective reduction of cyclic ketones.

Keywords: Solvent-free reaction; Aldehyde and ketone reduction; Sodium borohydride.
* Corresponding authors. Tel.: +82 33 248 2071; fax: +82 33 251 8491 (B.T.C.); tel.: +82 33 250 8494; fax: +82 33 253 7582 (D.K.A.); e-mail addresses: btcho@hallym.ac.kr; dkan@kangwon.ac.kr

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2. Results and discussion

2.1. Reduction of unfunctionalized aldehydes and ketones

We initially examined solvent-free reductions of benzaldehyde and acetophenone using solid acid-activated sodium borohydride. Boric acid, benzoic acid, and *p*-toluenesulfonic acid were chosen as representative solid acids. We also compared the same reductions using sodium borohydride itself. The reductions were carried out by grinding a 1:1 mixture of the aldehyde (or ketone) and sodium borohydride in the absence and presence of 1 equiv of each solid acid in an agate mortar and pestle at room temperature in air until TLC showed complete disappearance of the starting materials. Product alcohols were isolated by quenching the resulting mixture with saturated aqueous solution of $NaHCO_3$ or 1 N HCl solution to remove solid acid and unreacted sodium borohydride used, followed by extraction with Et_2O or CH_2Cl_2 and yields were determined by capillary GC analysis or column chromatography. As shown in Table 1, benzaldehyde was rapidly reduced to benzyl alcohol even by sodium borohydride alone in the absence of solid acids. In this reduction, effectiveness of activators examined appeared to be not significant, although it was found that they enhanced the reduction. Also, meaningful differences of effects among them were not observed (entries 1–4). Using the same methodology, we examined the reductions of other aromatic, aliphatic, and heterocyclic aldehydes. In all cases, the reductions afforded the corresponding alcohols in high yields (entries 5–14). Unlike those of aldehydes, the reductions of ketones using sodium borohydride itself in the absence of activators proceeded very slowly. For example, the reduction of acetophenone without activators provided 1-phenylethanol in only

Table 1. Solvent-free reduction of simple aldehydes and ketones with sodium borohydride in the presence of activators[a]

Run	Aldehydes and ketones	Activator	Time (min)	Product	Yield (%)[b]
1	C_6H_5CHO	None	10	$C_6H_5CH_2OH$	>99
2		H_3BO_3	5		>99
3		$PhCO_2H$	5		>99
4		PTSA[c]	5		>99
5	2-Naphthaldehyde	None	60	2-Naphthylmethanol	95 (5)[d]
6		$PhCO_2H$	40		>99
7	*n*-$C_6H_{13}CHO$	None	10	*n*-$C_6H_{13}CH_2OH$	98 (2)[d]
8		$PhCO_2H$	5		>99
9	*c*-$C_6H_{11}CHO$	None	20	*c*-$C_6H_{11}CH_2OH$	96 (4)[d]
10		$PhCO_2H$	10		>99
11	Furfural	None	5	Furfuryl alcohol	>99
12		H_3BO_3	5		>99
13	4-Pyridinecarboxaldehyde	None	5	4-Pyridinemethanol	>99
14		H_3BO_3	5		>99
15	$C_6H_5COCH_3$	None	120	$C_6H_5CHOHCH_3$	18 (82)[d]
16		H_3BO_3	10		>99
17		$PhCO_2H$	50		>99
18		PTSA[c]	50		70 (30)[d]
19	2-Acetylnaphthalene[e]	None	100	α-Methyl-2-naphthalenemethanol	17 (83)[d]
20		H_3BO_3	100		97[f]
21	4′-Acetylbiphenyl[e]	None	130	1-(4-Biphenyl)-1-ethanol	16 (84)[d]
22		H_3BO_3	130		80 (20)[d]
23	Benzophenone[e]	None	120	Benzhydrol	1 (99)[d]
24		H_3BO_3	120		98[f]
25	α-Tetralone	None	50	1,2,3,4-Tetrahydro-1-naphthol	5 (95)[d]
26		H_3BO_3	50		>99
27	1-Indanone	None	20	1-Indanol	2 (98)[d]
28		H_3BO_3	20		>99
29	2-Nonanone	None	30	2-Nonanol	2 (98)[d]
30		H_3BO_3	20		>99
31	Cyclohexanone	None	10	Cyclohexanol	>99
32		H_3BO_3	10		>99
33	2-Acetylfuran	None	30	1-(2-Furyl)ethanol	60 (40)[d]
34		H_3BO_3	20		>99
35	5-Methyl-3-acetylfuran[g]	None	40	1-(5-Methyl-2-furyl)ethanol	27 (73)[d]
36		H_3BO_3	20		>99
37	4-Acetylpyridine[g]	None	30	1-(4-Pyridyl)ethanol	78 (22)[d]
38		H_3BO_3	15		>99

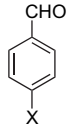
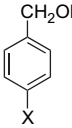
[a] A 1:1 mixture of substrate and $NaBH_4$ or 1:1:1 mixture of substrate, $NaBH_4$, and activator was ground in an agate mortar and pestle at room temperature (ca. 25 °C), unless otherwise indicated.
[b] Determined by capillary GC analysis after quenching the reaction with a saturated aqueous of $NaHCO_3$ or 1 N HCl solution.
[c] PTSA=*p*-toluenesulfonic acid monohydrate.
[d] Figures in parentheses indicate % yield of unreacted starting material.
[e] $NaBH_4$ (5 equiv) or a mixture of $NaBH_4$ (5 equiv) and H_3BO_3 (5 equiv) was used.
[f] Isolated yield.
[g] $NaBH_4$ (3 equiv) or a mixture of $NaBH_4$ (3 equiv) and H_3BO_3 (3 equiv) was used.

18% yield in 120 min with recovery of the unreacted starting ketone in 82% yield. However, the presence of 1 equiv of boric acid accelerated remarkably the reduction to give the product alcohol in a quantitative yield in 10 min (entry 15 vs 16). Of the activators examined, boric acid provided the best results (entries 15–18). This methodology was successfully applied to the reduction of other aromatic ketones such as 2-acetylnaphthalene, 4′-acetylbiphenyl, benzophenone, α-tetralone, and 1-indanone. Of these, 2-acetylnaphthalene, 4′-acetylbiphenyl, and benzophenone required 5 equiv of the reducing agent for their complete reductions. Again, these reductions with sodium borohydride itself were very sluggish (entries 19–28). In the cases of aliphatic ketones, the reduction of 2-nonanone was remarkably accelerated by the presence of 1 equiv of boric acid, although cyclohexanone was smoothly reduced by sodium borohydride alone (entries 29–32). Similarly, using boric acid-activated sodium borohydride, the reductions of heterocyclic ketones such as 2-acetylfuran, 5-methyl-2-acetylfuran, and 4-acetylpyridin to the corresponding alcohols were successfully achieved (entries 33–38).

2.2. Chemoselective reduction of functionalized aldehydes and ketones bearing other reducible functional groups

We next examined solvent-free chemoselective reduction of functionalized aldehydes and ketones including other reducible functional groups, such as ester, amide, cyano, bromo, and nitro groups, using boric acid-activated sodium borohydride. As shown in Table 2, benzaldehyde derivatives bearing various functional groups were chemoselectively reduced to the corresponding alcohols without reduction of any other functional groups in quantitative yields (entries 1–5). To explore the generality of this methodology, we examined the chemoselective reductions of other functionalized ketone analogues, such as benzoyl cyanide, methyl benzoylformate, benzoylacetonitrile, ethyl benzoylacetate, ethyl

Table 2. Solvent-free chemoselective reduction of aldehydes and ketones containing various functional groups with H_3BO_3-activated sodium borohydride[a]

Run	Aldehydes and ketones		Time (min)	Product		Yield (%)[b]
1		X=CO_2Me	5 (15)[c]		X=CO_2Me	>99 (>99)[d]
2		X=NHCOMe[e]	20 (40)[c]		X=NHCOMe	>99 (>99)[d]
3		X=CN	5 (15)[c]		X=CN	>99 (>99)[d]
4		X=Br	5 (15)[c]		X=Br	>99 (>99)[d]
5		X=NO_2	5 (15)[c]		X=NO_2	>99 (>99)[d]
6	4-$NO_2C_6H_4COCH_3$[e]		10 (30)[c]	4-$NO_2C_6H_4CH(OH)CH_3$		>99 (>99)[d]
7	4-$NCC_6H_4COCH_3$[e]		5 (30)[c]	4-$NCC_6H_4CH(OH)CH_3$		>99 (>99)[d]
8	Benzoyl cyanide		30 (60)[c]	Mandelonitrile		>99 (>99)[d]
9	Methyl benzoylformate		5 (15)[c]	Methyl mandelate		>99 (>99)[d]
10	Benzoylacetonitrile		10 (30)[c]	$PhCH(OH)CH_2CN$		>99 (>99)[d]
11	Ethyl benzoylacetate		40 (60)[c]	$PhCH(OH)CH_2CO_2Et$		>99 (64)[d,f]
12	Ethyl acetoacetate		20 (40)[c]	$MeCH(OH)CH_2CO_2Et$		>99 (>99)[d]
13	2-Methoxycarbonylcycloheptanone		15 (40)[c]	2-Methoxycarbonylcycloheptanol		>99 (>99)[d]
14	Benzoin[e]		40 (120)[c]	Hydrobenzoin		>99 (>99)[d]
15	Methyl 5-acetylsalicylate[e]		90 (90)[c]	5-$MeCH(OH)C_6H_3$-2-$(OH)CO_2Me$		60 (40)[d,f]
16	4-$BrC_6H_4COCH_2Br$[e]		60 (60)[c]	4-$BrC_6H_4CH(OH)CH_2Br$		50 (20)[d,f]

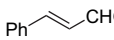
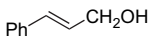
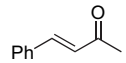
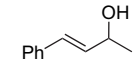
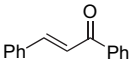
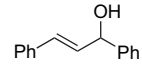
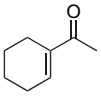
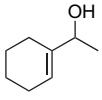
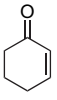
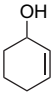
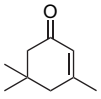
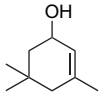
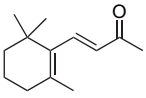
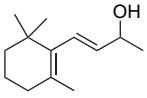
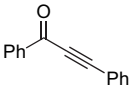
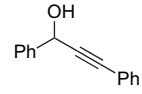
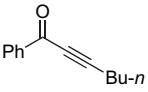
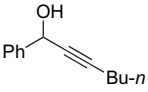
[a,b] See the corresponding footnotes in Table 1.
[c,d] The figures in parentheses indicated reaction time and yield obtained, respectively, when the reaction was carried out with $NaBH_4$ alone.
[e] $NaBH_4$ (3 equiv) or a 1:1 mixture of $NaBH_4$ (3 equiv) and H_3BO_3 (3 equiv) was used.
[f] Unreacted ketones were recovered.

acetoacetate, and 2-ethoxycarbonylcycloheptanone, using the same methodology. In all cases, the reductions provided the corresponding alcohols in high yields and chemoselectivities. The same reductions using sodium borohydride itself with no aid of boric acid underwent more slowly (entries 8–13). For the complete reduction of 4-acetamidobenzaldehyde, 4-nitroacetophenone, 4-cyanoacetophenone, and benzoin, 3 equiv of the activated borohydride was required (entries 2, 6, 7, and 14). However, the reductions of methyl 5-acetylsalicylate and 4′-bromophenacyl bromide under the same conditions were very sluggish (entries 15 and 16).

2.3. Regioselective reduction of α,β-unsaturated aldehydes and ketones

As shown in Table 3, the solvent-free reduction of an α,β-unsaturated aldehyde, (*E*)-cinnamaldehyde using sodium borohydride in the absence and presence of boric acid provided (*E*)-cinnamyl alcohol (1,2-addition product) without the formation of saturated alcohols (1,4-addition product) in quantitative yield.[5a] In this reaction, boric acid did not seem to play a significant role as activator for the reduction (entries 1 and 2). However, this activator was highly effective for accelerating dramatically the reduction of α,β-unsaturated ketones such as (*E*)-4-phenyl-3-butene-2-one,[5b] 1-acetyl-1-cyclohexene, and 2-cyclohexenone,[5c] comparing the same reductions without the activator. The reductions were complete within 10 min to give only 1,2-addition products in quantitative yields (entries 3, 4, and 8–11). For the complete reductions of (*E*)-chalcone and β-ionone to give the corresponding allylic alcohols was required 2 equiv of boric acid-activated borohydride. However, the reduction of isophorone under the identical conditions was more sluggish. Despite use of a large excess of sodium borohydride (5 equiv), these reductions in the absence of activator proceeded very slowly with recovery of unreacted starting ketones (entries 6, 7, and 12–15). In the cases of 2-cyclohexenone and isophorone, the reductions with sodium borohydride alone provided a mixture of 1,2- and 1,4-addition products (entries 10 and 12). On the other hand, the activated borohydride also reduced α,β-ynones such as diphenylpropynone and 1-phenyl-2-heptyn-1-one to the corresponding propargylic alcohols in high yields and regioselectivities (entries 16 and 19).

Table 3. Solvent-free regioselective reduction of α,β-unsaturated aldehydes and ketones using solid acid-activated sodium borohydride[a]

Run	Aldehydes and ketones	Activator	Time (min)	Product	Yield (%)[b]
1		None	10		98
2		H_3BO_3	10		98
3		None	60		96[c]
4		H_3BO_3	10		98[c]
5		$PhCO_2H$	30		96[c]
6		None	120		8[d]
7		H_3BO_3	60		98[e]
8		None	60		27
9		H_3BO_3	10		98
10		None	30		[f]
11		H_3BO_3	10		98
12		None	60		[f]
13		H_3BO_3	60		48[e]
14		None	120		8[d]
15		H_3BO_3	90		98[e]
16		None	90		15[d]
17		H_3BO_3	40		98[e]
18		None	90		21[d]
19		H_3BO_3	40		99[e]

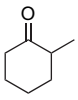
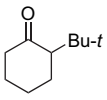
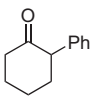
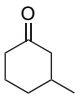
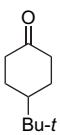
[a,b] See the corresponding footnotes in Table 1.
[c] Isolated yield.
[d] $NaBH_4$ (5 equiv) was used.
[e] A mixture of $NaBH_4$ (2 equiv) and boric acid (2 equiv) was used.
[f] A mixture of 1,2- and 1,4-reduction products was produced.

2.4. Stereoselective reduction of cyclic ketones

Using the same methodology, solvent-free stereoselective reductions of cyclic ketones, namely 2-methylcyclohexanone, 2-*tert*-butylcyclohexanone, 2-phenylcyclohexanone, 3-methylcyclohexanone, and 4-*tert*-butylcyclohexanone, were studied. As shown in Table 4, all the ketones examined were smoothly reduced to the corresponding alcohols in quantitative yields. All the reductions with one exception were satisfactorily accomplished even by sodium borohydride alone in the absence of activators. The reduction of 2-*tert*-butylcyclohexanone with sodium borohydride alone was very sluggish, giving the product alcohol in only 5% yield in 210 min. However, the same reduction with boric acid-activated sodium borohydride was completed in 120 min (entries 3 and 4). Comparing effectiveness of activators for the reduction of 2-phenylcyclohexanone and 4-*tert*-butylcyclohexanone, boric acid among solid acids selected provided the best results (entries 6–8 and 12–14). With respect to the stereoselection of product alcohols, all the reduction of cyclic ketones examined predominantly produced thermodynamically more stable alcohols, such as the ratio of 65% for *trans*-2-methylcyclohexanol, 40% for *trans*-2-*tert*-butylcyclohexanol, 65% for *trans*-2-phenylcyclohexanol, 86% for *cis*-3-methylcyclohexanol, and 92% for *trans*-4-*tert*-butylcyclohexanol. The results indicate that the reducing agents used preferentially attacks unhindered site of the carbonyl group of cyclic ketones examined.[6] Comparing the stereoselective ratios of product alcohols obtained, the effect of activators on the stereoselective reduction of the ketones examined was not significant.

On the other hand, in all the solvent-free reductions examined above, it was found that the order of mixing of the reactants had no discernible effects on the rate of reduction, yields, and the chemoselectivity, regioselectivity, and stereoselectivity of products. Also, the presence of moisture in air is not critical for the reduction. This hydride species of the mixture were stable in air at least for few hours with no loss of hydride activity. Although the structure of this reducing species of solid acid-activated sodium borohydride[7] and the mechanism of this reduction are unclear so far, it appears that a eutectic temperature with melting point lower than the ambient temperature exists in each case. In fact, the reaction mixture became oily or sticky during grinding the mixtures even though they are in powder states before grinding.

Table 4. Solvent-free stereoselective reduction of cyclic ketones using solid acid-activated sodium borohydride[a]

Run	Ketone	Activator	Time (min)	Product alcohol		Yield (%)[b]
				cis	*trans*	
1		None	45	38	62	>99
2		H_3BO_3	15	35	65	>99
3		None	210	53	47	5
4		H_3BO_3	120	56	43	>99
5		None	30	31	69	>99
6		H_3BO_3	20	35	65	>99
7		$PhCO_2H$	20	38	62	>99
8		PTSA[c]	30	36	64	>99
9		None	20	83	16	>99
10		H_3BO_3	10	86	14	>99
11		None	20	8	92	>99
12		H_3BO_3	10	8	92	>99
13		$PhCO_2H$	10	7	93	>99
14		PTSA[c]	10	8	92	80 (20)[d]

[a–d] See the corresponding footnotes in Table 1.

3. Conclusion

We have established a convenient solvent-free reduction of aldehydes and ketones using solid acid-activated sodium borohydride. The reductions provided not only high chemoselectivity for functionalized aldehydes and ketones including other reducible functional groups, but also high regioselectivity for α,β-unsaturated aldehydes and ketones to give only the corresponding allylic alcohols. This is the first example for highly effective reduction of aldehydes and ketones under solvent-free conditions.

4. Experimental

4.1. General

The reactions were monitored by TLC using silica gel plates. GC analyses were performed on a Donam DS 6200 FID chromatograph, using a HP-1 (crosslinked methyl siloxane) capillary column (30 m). All GC yields were determined with use of a suitable internal standard and authentic mixture. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX FT (400 MHz) or Bruker Avance (300 MHz) spectrometer. The chemical shifts are expressed as units with Me_4Si as the internal standard in $CDCl_3$. IR-spectra were recorded on a JASCO FTIR-460 and absorptions are reported in wave numbers (cm^{-1}).

4.2. Materials

Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation when necessary. Sodium borohydride, *p*-toluenesulfonic acid monohydrate, and benzoic acid were purchased from Aldrich or Lancaster and used without further purification.

4.2.1. Solvent-free reduction of aldehydes and ketones using solid acid-activated sodium borohydride.

4.2.1.1. General procedure. A mixture of aldehyde or ketone (10 mmol), $NaBH_4$ (10 mmol), and boric acid, benzoic acid, or *p*-toluenesulfonic acid monohydrate (10 mmol) was ground with an agate mortar and pestle until TLC showed complete disappearance of the starting material. The mixture was quenched with a saturated aqueous solution of $NaHCO_3$ or 1 N HCl solution, followed by filtration of the resultant suspension to give product alcohol. When the product was liquid, it was isolated from extraction with CH_2Cl_2 or Et_2O instead of filtration. All products were characterized by IR, ^{1}H, and ^{13}C NMR spectra. In the case of known compounds, their spectra were compared with those of authentic samples.

4.2.1.2. 1-(5-Methyl-2-furyl)ethanol (Table 1, entry 36). IR (neat, cm^{-1}): 3349, 2979, 2924, 2884, 1564, 1517, 1450, 1370, 1319, 1289, 1221, 1078, 1017; ^1H NMR ($CDCl_3$): δ 6.10 (d, J=3.1 Hz, 1H), 5.91–5.89 (m, 1H), 4.82 (q, J=6.6 Hz, 1H), 2.28 (s, 3H), 1.98 (br s, 1H), 1.52 (d, J=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 13.53, 21.17, 63.62, 105.81, 105.96, 151.67, 155.81.

4.2.1.3. 4-Methoxycarbonylbenzyl alcohol (Table 2, entry 1). IR (KBr, cm^{-1}): 3308, 3210, 3015, 2914, 2861, 1721, 1448, 1433, 1415, 1312, 1284, 1193, 1111, 1049; ^1H NMR ($CDCl_3$): δ 8.03 (d, J=8.3 Hz, 2H), 7.43 (d, J=8.6 Hz, 2H), 4.77 (s, 2H), 3.92 (s, 3H), 1.99 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 52.13, 64.70, 126.47, 129.32, 129.86, 145.98, 166.98.

4.2.1.4. 4-Acetamidobenzyl alcohol (Table 2, entry 2). IR (KBr, cm^{-1}): 3421, 3246, 3188, 3126, 3074, 2924, 2882, 1670, 1608, 1549, 1517, 1411, 1371, 1323, 1273, 1211, 1002; ^1H NMR (DMSO): δ 9.88 (s, 1H), 7.50 (d, J=8.5 Hz, 2H), 7.21 (d, J=8.5 Hz, 2H), 5.08 (s, 1H), 4.41 (s, 2H), 2.01 (s, 3H); ^{13}C NMR (DMSO): δ 23.92, 62.60, 118.67, 126.86, 137.03, 137.91, 168.08.

4.2.1.5. 4-Cyanobenzyl alcohol (Table 2, entry 3). IR (neat, cm^{-1}): 3838, 3419, 2975, 2929, 2881, 2229, 1610, 1503, 1451, 1407, 1370, 1287, 1206, 1119, 1090, 1013; ^1H NMR ($CDCl_3$): δ 7.64 (d, J=8.4 Hz, 2H), 7.49 (d, J=8.1 Hz, 2H), 4.97 (q, J=6.5 Hz, 1H), 2.13 (s, 1H), 1.50 (d, J=6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 25.42, 69.66, 111.07, 118.87, 126.07, 136.36, 151.12.

4.2.1.6. 2-Methoxycarbonylcycloheptanol (Table 2, entry 13). IR (neat, cm^{-1}): 3481, 2928, 2859, 1723, 1436, 1263, 1198, 1127, 1034; ^1H NMR ($CDCl_3$): δ 4.24–4.19 (m, 1H), 3.71 (s, 3H), 2.84 (s, 1H), 2.62 (dt, J=2.6, 10.0 Hz, 1H), 1.37–2.05 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 21.94, 24.18, 26.62, 27.82, 34.94, 49.76, 51.79, 70.27, 176.79.

4.2.1.7. 1-(4′-Hydroxy-3′-methoxycarbonylphenyl)-ethanol (Table 2, entry 15). IR (neat, cm^{-1}): 3341, 2972, 1684, 1617, 1595, 1490, 1442, 1318, 1214, 1086; ^1H NMR ($CDCl_3$): δ 10.71 (s, 1H), 7.84 (d, J=2.1 Hz, 1H), 7.48 (dd, J=2.2, 8.6 Hz, 1H), 6.97 (d, J=8.6 Hz, 1H), 4.86 (q, J=6.4 Hz, 1H), 3.96 (s, 3H), 1.79 (br s, 1H), 1.48 (d, J=6.39 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 25.12, 52.32, 69.64, 112.02, 117.76, 126.71, 133.16, 136.62, 160.96, 170.48.

4.2.1.8. 2-Bromo-1-(4′-bromophenyl)ethanol (Table 2, entry 16). IR (KBr, cm^{-1}): 3390, 2959, 2917, 1593, 1488, 1420, 1403, 1218, 1195, 1071, 1011; ^1H NMR ($CDCl_3$): δ 7.51 (d, J=8.4 Hz, 2H), 7.27 (d, J=8.1 Hz, 2H), 4.90 (dd, J=3.4, 8.8 Hz, 1H), 3.61 (dd, J=3.4, 10.5 Hz, 1H), 3.50 (dd, J=8.7, 10.1 Hz, 1H), 2.59 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 39.89, 73.10, 122.37, 127.68, 131.82, 139.21.

4.2.1.9. 1-(Cyclohexen-1-yl)ethanol (Table 3, entry 9). IR (neat, cm^{-1}): 3349, 2972, 2929, 2858, 2837, 2661, 1668, 1437, 1366, 1293, 1166, 1137, 1096, 1060, 1007; ^1H NMR ($CDCl_3$): δ 5.67 (s, 1H), 4.17 (q, J=6.4 Hz, 1H), 1.97–2.05 (m, 4H), 1.53–1.67 (m, 4H), 1.26 (d, J=6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 21.52, 22.61, 22.67, 23.67, 24.90, 72.18, 121.54, 141.27.

4.2.1.10. 3,5,5-Trimethyl-2-cyclohexen-1-ol (Table 3, entry 13). IR (neat, cm^{-1}): 3324, 3035, 2952, 2825, 2724, 1673, 1455, 1437, 1364, 1284, 1200, 1170, 1129, 1100, 1043, 1020; ^1H NMR ($CDCl_3$): δ 5.43 (s, 1H), 4.20–4.27 (m, 1H), 1.64–1.88 (m, 4H), 1.68 (s, 3H), 1.23 (dd, J=9.1, 12.4 Hz, 1H), 0.99 (s, 3H), 0.88 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 23.54, 26.20, 31.07, 31.24, 44.12, 45.24, 66.84, 123.65, 136.02.

4.2.1.11. 1,3-Diphenylpropyn-1-ol (Table 3, entry 17). IR (neat, cm^{-1}): 3549, 3365, 3062, 3031, 2871, 2228, 1598, 1490, 1455, 1443, 1305, 1190, 1070, 1030; ^1H NMR ($CDCl_3$): δ 7.62–7.49 (m, 10H), 5.68 (s, 1H), 2.43 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 65.10, 86.66, 88.70, 122.40, 126.74, 128.31, 128.44, 128.61, 128.67, 131.75, 140.62.

4.2.1.12. 1-Phenyl-2-heptynol (Table 3, entry 19). IR (neat, cm^{-1}): 3365, 3063, 3031, 2957, 2933, 2872, 2227, 1603, 1493, 1455, 1135, 1003; ^1H NMR ($CDCl_3$): δ 7.55–7.41 (m, 5H), 5.46 (s, 1H), 2.28 (dt, J=2.0, 6.9 Hz, 2H), 1.93 (br s, 1H), 1.89–1.56 (m, 4H), 0.92 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 13.59, 18.51, 21.99, 30.66, 64.81, 79.95, 87.65, 125.92, 126.64, 128.18, 128.42, 128.52, 141.31.

References and notes

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