Clean and Simple Chemoselective Reduction of Imines to Amines Using Boric Acid-Activated Sodium Borohydride under Solvent-Free Conditions

Byung Tae Cho,* Sang Kyu Kang

Department of Chemistry, Hallym University, Chuncheon, Kangwondo 200-702, Republic of Korea
Fax +82(33)2518491; E-mail: btcho@hallym.ac.kr

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Abstract: The first clean and highly effective solvent-free chemoselective reduction of functionalized aldimines and ketimines bearing easily reducible functional groups, such as ketone, carboxylic acid, ester, nitrile, amide, nitro, furyl and alkenyl groups, to the corresponding amines using boric acid-activated sodium borohydride is described.

Key words: imines, reductions, chemoselectivity, sodium borohydride, solvent-free reaction

The reduction of aldimines and ketimines to the corresponding amines is a very useful transformation in organic synthesis because of their versatile utility as intermediates for synthesis of pharmaceuticals[1] and agrochemicals.[2] As effective reducing methods for these conversions, catalytic hydrogenation,[3] metal hydride reductions using $NaBH_3CN$,[1] $LiBH_3CN$,[4b] $(n\text{-}Bu)_4NBH_3CN$,[4c] $NaBH_3CN–ZnCl_2$,[4d] $NaBH_3CN–Ti(O\textit{i}\text{-}Pr)_4$,[4e] $NaBH_3CN–Mg(ClO_4)_2$,[2] $NaBH(OAc)_3$,[3] $NaBH_4–NiCl_2$,[4] $NaBH_4–ZnCl_2$ (nickel boride),[6c] $NaBH_4–ZrCl_4$,[6d] $Ti(O\textit{i}\text{-}Pr)_4–NaBH_4$,[6d] $NaBH_4–H_2SO_4$,[6e] $NaBH_4$–wet clay-microwave,[5] borohydride exchange resin,[6] $Zn(BH_4)_2$,[7] $Zn(BH_4)_2–ZnCl_2$,[8b] $Zn(BH_4)_2–SiO_2$,[8c] pyridine–borane,[8] diborane–MeOH,[9] decaborane,[10] Zn–AcOH,[11] polymethylhydrosiloxane (PMHS)–$Ti(O\textit{i}\text{-}Pr)_4$,[12] PMHS–$ZnCl_2$,[13b] PMHS–$n$-$BuSn(OCOR)_3$,[13c] $Et_3SiH–CF_3CO_2H$,[13d] $PhMe_2SiH–(C_6F_6)_3$,[13e] $Cl_3SiH–DMF$,[13f] $PhSiH_3–n\text{-}Bu_2SnCl_2$,[13g] n-Bu_3SnH–DMF or HMPA,[13] n-$Bu_3SnH–SiO_2$[14b] and n-Bu_2SnIH or n-Bu_2SnClH[14c,d] have been reported. However, most of these reagents have one drawback or another. For example, catalytic hydrogenation is incompatible with compounds containing a carbon-carbon double or triple bond and other reducible functional groups such as nitro, cyano and furyl groups.[3] Cyanoborohydride and tin hydride reagents are highly toxic and generate toxic by-products such as HCN, NaCN or organotin compounds[14] upon workup and may result in the contamination of the product with the toxic compounds. Other hydrides such as zinc borohydride,[16] nickel boride[6b,15] and $PHMS–Ti(O\textit{i}\text{-}Pr)_4$[16] may be not suitable for use in the chemoselective reduction of imines having ketone, ester, amide and nitro groups, since these reagents can reduce those functional groups. Although reductive amination, which involves the initial formation of an imine from the reaction of a carbonyl compound with an amine and its subsequent reduction to an alkylated amine, is an alternative method used for amine synthesis, this process is commonly required for excess amounts of amines to obtain high yields by suppressing undesirable reduction of the starting carbonyls, because metal hydride reagents usually reduce a carbonyl group more rapidly than an imino group due to the lower electrophilicity of an imino group.[4a,5,9b,17] This requires additional purification to remove excess of amines used from the products and causes lower yields. Chemoselective reduction of an imino group in imine compounds containing various reducible functional groups is one of the most important techniques in obtaining amines bearing these functional groups. However, only limited successful reports for such reductions have been published.[10] Recently, considerable efforts have been paid to solvent-free reactions.[18] These 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. Sodium borohydride is an inexpensive, safe to handle and environmental friendly reducing agent, which can reduce aldehydes, ketones and acid chlorides. However, there is no report for reduction of imines using this reagent under solvent-free conditions. We report here the first solvent-free chemoselective reduction of imines to amines using boric acid-activated sodium borohydride.

To study chemoselective reduction of imines possessing different kinds of reducible functional groups, we initially chose an aldimine bearing a ketone group, 4-acetylbenzaldehyde-*N*-phenylimine (**1a**) and compared its chemoselective reduction with metal hydrides, such as $NaBH_3CN$,[4a] $NaBH(OAc)_3$,[5] $Zn(BH_4)_2$,[8a] pyridine–borane[9] and $PMHS–Ti(O\textit{i}\text{-}Pr)_4$.[13a] The reductions were carried out under the same reaction conditions adopted for the imine reductions using those metal hydrides with a ratio of hydride to **1a** in 1:1. As shown in Table 1, the reduction of **1a** using $NaBH_3CN$ (0.34 equiv) in MeOH at ca pH 3 for 16 hours at room temperature afforded **2a** (97%) and **3a** (3%), which came from reduction of imino and ketone groups of **1a,** respectively (entry 3). Although $NaBH(OAc)_3$ provided only **2a**, the reduction was incomplete even with use of 1.5 equivalents of the reagent for 19 hours (entry 4). The reduction with $Zn(BH_4)_2$ proceeded very slowly with low chemoselectivity to give unreacted **1a** (89%), **2a** (6%), **3a** (3%) and **4a** (2%) even for 38 hours (entry 5). Pyridine–borane also afforded low chemoselectivity to give **2a** (80%) and **4a** (16%) (entry 6).

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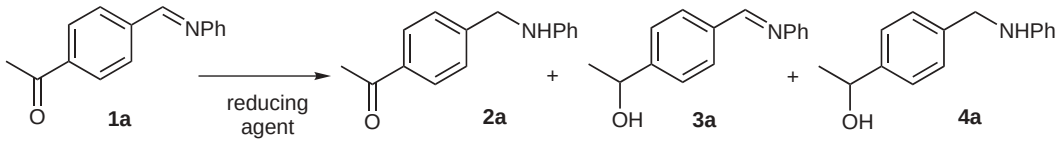
Table 1 Chemoselective Reduction of **1a** with Various Reducing Agents[a]

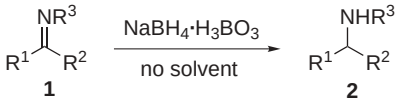


Entry	Reducing agents	Solvent	Time (h)	Product (%)[b]			
				1a	**2a**	**3a**	**4a**
1	$NaBH_4/H_3BO_3$ (1:1)[c]	none	0.5	0	100 (98)[g]	0	0
2	$NaBH_4$[c]	none	2	87 (84)[g]	13 (11)[g]		
3	$NaBH_3CN$[4a]	MeOH	16	0	97 (94)[g]	3	0
4	$NaBH(OAc)_3$[5]	DCE[d,e]	19	6	94	0	0
5	$Zn(BH_4)_2$[8a]	DME[f]	38	89	6	3	2
6	BH_3·Pyridine[9]	Pet. Ether	15	4	80	0	16
7	PMHS/Ti(O*i*-Pr)$_4$[13a]	THF	39	65	0	28	7

[a] [Hydride/imine] = 1.0, unless otherwise indicated.
[b] Determined by ^{1}H NMR analysis.
[c] This study.
[d] DCE = 1,2-dichloroethane.
[e] [Hydride/imine] = 1.5.
[f] DME = 2-dimethoxyethane.
[g] The figures in parentheses indicate isolated yield.

PMHS–Ti(O*i*-Pr)$_4$ preferentially reduced the ketone group to give **3a** (28%) and **4a** (7%) (entry 7). In contrast, the reduction of **1a** with sodium borohydride in the presence of boric acid under solvent-free conditions provided only **2a** in a quantitative yield (entry 1). ^{1}H NMR analysis of **2a** obtained showed it to be chemically pure. The reduction did not afford any undesirable reduction products, such as **3a** and **4a**. The reduction and work-up procedures were quite simple. A mixture of the 1:1:1 molar ratio of **1a**, sodium borohydride and boric acid was intermittently ground over 30 minutes at room temperature using an agate mortar and pestle in air until TLC showed complete disappearance of the starting material. The mixture was quenched with saturated aqueous solution of $NaHCO_3$, followed by filtration of the resultant suspension to give **2a** with no need of solvent extraction. When **1a** was ground with sodium borohydride alone in the absence of boric acid under the identical conditions, the reduction proceeded more slowly to give **2a** in 11% yield even after 2 hours with recovery of unreacted imine**1a** in 84% yield (entry 2). Based on these results, we carried out the solvent-free chemoselective reduction for various aldimines and ketimines **1a**–**p** bearing other reducible functional groups, such as carboxylic acid, ester, nitrile, amide, nitro, furyl and alkenyl groups using boric acid-activated sodium borohydride.[21] As shown in Table 2, all the reductions examined were complete within 1 hour and provided functionalized amine products **2a**–**p** in 97–99% yields. In this reduction, other functional groups included were not reduced at all, showing that a clean chemoselective reduction of an imino group occurred. To the best of our knowledge, this is the first example for solvent-free and highly effective chemoselective reduction of imines to functionalized amines. When the products were obtained as liquid from the reaction, they were isolated by extraction with CH_2Cl_2 or Et_2O after quenching with saturated aqueous solution of $NaHCO_3$ (entries 2, 8–10, 12, 14 and 15). Influence of substituents on the nitrogen of imines for the reduction was not observed (entries 4, 5 and 6–9). The order of mixing of the reactants had no discernable effect on the rate of reduction, yield and purity of the product. The presence of moisture in air is not critical for the reduction. In this reduction, it is possible that the substrates, imines were activated by boric acid to form iminium salts, which were selectively reduced to the amines. However, it was found that the reduction of imine derivatives with reducing system generated from grinding a 1:1 mixture of sodium borohydride and boric acid was highly chemoselective as well. The results suggest that the reduction also occurs selectively in the condition of little chance of the formation of iminium salts by boric acid. The IR spectrum of this hydride species formed showed at 2381 cm^{-1} a medium peak and a ^{1}H decoupled ^{11}B NMR spectrum of its THF suspension exhibited at –1.91 ppm, which were different spectra from those of sodium borohydride. This hydride species was stable in air at least for few hours with no loss of hydride activity. Although the structure of this reducing species 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

Table 2 Solvent-Free Chemoselective Reduction of Imines with $NaBH_4$/Boric Acid (1:1)



Entry	Imines (**1**)				Amines (**2**)		
	Compound	R^1	R^2	R^3	Product	Time (min)	Yield (%)[a]
1	**1b**	4-$HO_2C_6H_4$	H	Ph	**2b**	40	98
2	**1c**	4-$MeO_2C_6H_4$	H	Ph	**2c**	30	99
3	**1d**	4-$MeO_2C_6H_4$	H	Me	**2d**	30	99
4	**1e**	4-$MeO_2C_6H_4$	H	*t*-Bu	**2e**	30	98
5	**1f**	4-NCC_6H_4	H	Ph	**2f**	30	99
6	**1g**	4-NCC_6H_4	H	Me	**2g**	20	98
7	**1h**	4-NCC_6H_4	H	*n*-C_7H_{15}	**2h**	40	98
8	**1i**	4-NCC_6H_4	H	2-furfuryl	**2i**	20	97
9	**1j**	4-$MeCONHC_6H_4$	H	Ph	**2j**	30	98
10	**1k**	4-$O_2NC_6H_4$	H	Ph	**2k**	40	99
11	**1l**	4-$O_2NC_6H_4$	H	Me	**2l**	30	99
12	**1m**	(*E*)-PhCH=CH	H	Ph	**2m**	20	98
13	**1n**	4-NCC_6H_4	Me	Ph	**2n**	40	98
14	**1o**	4-$O_2NC_6H_4$	Me	Ph	**2o**	60	97
15	**1p**	1-Cyclohexenyl	Me	Ph	**2p**	20	97

[a] Isolated yield.

each case. In fact, the reaction mixture became oily or sticky during grinding the mixtures even though they are powder states before grinding. Further studies on the reduction for other functional groups using this procedure are in progress.

In summary, we established the first solvent-free chemoselective reduction using boric acid-activated sodium borohydride for aldimines and ketimines in the presence of other reducible functional groups, such as ketone, carboxylic acid, ester, nitrile, amide, nitro, furyl and alkenyl groups. This method proves to be a clean, rapid and very simple procedure in preparing functionalized amine compounds in nearly quantitative yields by simply grinding a 1:1:1 mixture of imine, sodium borohydride and boric acid with an agate mortar and pestle at room temperature.

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(21) **General Procedure for Chemoselective Reduction of Aldimines and Ketimines**. A mixture of imine derivatives **1** (10 mmol), $NaBH_4$ (10 mmol) and boric acid (10 mmol) was ground with an agate mortar and pestle for 0.5–1.0 h until TLC showed complete disappearance of the starting material. The mixture was quenched with a sat. aq solution of $NaHCO_3$, followed by filtration of the resultant suspension to give product amines **2**. When the product was liquid, it was isolated from extraction with CH_2Cl_2 or Et_2O instead of filtration. ***N*-Phenyl-4-acetylbenzylamine (2a)**: Yield: 98%; white solid; mp 74–75 °C. IR (KBr): 3379, 3024, 2994, 2838, 1663, 1602, 1507, 1273, 749, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.58 (s, 3 H), 4.17 (br s, 1 H), 4.40 (s, 2 H), 6.58 (d, *J* = 8.80 Hz, 2 H), 6.70 (t, *J* = 7.29 Hz, 1 H), 7.14 (t, *J* = 7.56 Hz, 2 H), 7.43 (d, *J* = 7.98 Hz, 2 H), 7.90 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.0, 48.2, 113.1, 118.1, 121.1, 127.5, 128.9, 129.1, 129.5, 136.3, 145.4, 147.9, 197.8. Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.96; H, 6.73; N, 6.22. ***N*-Phenyl-4-carboxybenzylamine (2b)**: Yield: 99%; white solid; mp 196–198 °C. IR (KBr): 3412, 3360, 3050, 2933, 2836, 1684, 1603, 1317, 1291, 760 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 3.64 (br s, 1 H), 4.31 (s, 2 H), 6.35 (br s, 1 H), 6.48 (t, *J* = 7.15 Hz, 1 H), 6.52 (d, *J* = 7.43 Hz, 2 H), 7.00 (t, *J* = 7.84 Hz, 2 H), 7.42 (d, *J* = 7.98 Hz, 2 H), 7.87 (d, *J* = 7.98 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.9, 112.9, 116.5, 127.7, 129.5, 130.0, 130.4, 146.2, 149.0, 168.2. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.98; H, 5.75; N, 6.18. ***N*-Phenyl-4-methoxycarbonylbenzylamine (2c)**: Yield: 98%; oil. IR (neat): 3415, 3024, 2951, 2840, 1698, 1616, 1521, 1123, 763, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 4.15 (br s, 1 H), 4.35 (s, 2 H), 6.56 (d, *J* = 7.70 Hz, 2 H), 6.69 (t, *J* = 7.43 Hz, 1 H), 7.13 (t, *J* = 7.84 Hz, 2 H), 7.38 (d, *J* = 7.98 Hz, 2 H), 7.96 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.3, 52.4, 113.1, 118.0, 127.3, 129.2, 129.5, 130.1, 145.2, 148.0, 167.1. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.70; H, 6.37; N, 5.86. ***N*-Methyl-4-methoxycarbonylbenzylamine (2d)**: Yield: 99%; white solid; mp 152–153 °C. IR (KBr): 3236, 3018, 1004, 2952, 1704, 1428, 1286, 1168, 894 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (d, *J* = 5.78 Hz, 3 H), 3.59 (dd, *J* = 9.77, 13.62 Hz, 1 H), 3.93 (s, 3 H), 4.30 (dd, *J* = 2.89, 13.89 Hz, 1 H), 4.39 (br s, 1 H), 7.39 (d, *J* = 8.25 Hz, 2 H), 8.05 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.8, 60.7, 129.7, 130.5, 130.8, 166.6. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.01; H, 7.33; N, 7.83. ***N-tert*-Butyl-4-methoxycarbonylbenzylamine (2e):** Yield: 98%; white solid; mp 30–31 °C. IR (KBr): 3316, 3187, 2961, 2877, 1716, 1437, 1281, 1110, 1019, 769 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 9 H), 1.43 (s, 1 H), 3.77 (s, 2 H), 3.90 (s, 3 H), 7.40 (d, *J* = 7.98 Hz, 2 H), 7.96 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5, 47.3, 51.2, 52.5, 128.3, 128.7, 129.9, 147.1, 167.3. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.58; H, 8.67; N, 6.33. ***N*-Phenyl-4-cyanobenzylamine (2f)**: Yield: 99%; mp 83–84 °C. IR (KBr): 3425, 3047, 2911, 2864, 2220, 1600, 1507, 1332, 1266, 818, 765, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.20 (br s, 1 H), 4.40 (s, 2 H), 6.55 (d, *J* = 7.70 Hz, 2 H), 6.71 (t, *J* = 7.29 Hz, 1 H), 7.14 (t, *J* = 7.01 Hz, 2 H), 7.44 (d, *J* = 7.98 Hz, 2 H), 7.58 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.1, 111.1, 113.1, 118.3, 119.1, 127.9, 129.6, 132.6, 145.6, 147.6. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.76; H, 5.78; N, 13.46. ***N*-Methyl-4-cyanobenzylamine (2g)**: Yield: 98%; white solid; mp 108–109 °C. IR (KBr): 3158, 3013, 2854, 2260, 1520, 1350, 1169, 853 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.43 (d, *J* = 5.50 Hz, 3 H), 3.64 (dd, *J* = 7.35, 13.75 Hz, 1 H), 4.26 (dd, *J* = 3.58, 13.75 Hz, 1 H), 4.68 (br s, 1 H), 7.47 (d, *J* = 8.25 Hz, 2 H), 7.70 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.0, 60.4, 112.9, 118.6, 130.6, 133.0, 139.1. Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.99; H, 6.95; N, 19.17. ***N-n*-Heptyl-4-cyanobenzylamine (2h)**: Yield: 98%, white solid; mp 63–64 °C. IR (KBr): 3193, 2955, 2926, 2856, 2228, 1457, 1160, 897, 854 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.60 Hz, 3 H), 1.13–1.27 (m, 6 H), 1.58–1.74 (m, 4 H), 2.61–2.67 (m, 2 H), 3.77 (dd, *J* =8.12, 13.34 Hz, 1 H), 4.08 (br s, 1 H), 4.17 (dd, *J* = 4.26, 13.34 Hz, 1 H), 7.46 (d, *J* = 8.25 Hz, 2 H), 7.69 (d, *J* = 8.53 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 22.9, 26.6, 27.0, 29.2, 31.9, 54.3, 59.2, 112.9,

118.5, 130.6, 132.9, 139.4. Anal. Calcd for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.23; H, 9.64; N, 12.17. ***N*-2-Furfuryl-4-cyanobenzyl-amine (2i)**: Yield: 97%; oil. IR (neat): 3203, 2962, 2927, 2852, 2230, 1504, 1167, 1010, 821, 739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.72 (dd, *J* = 8.94, 14.99 Hz, 1 H), 3.83 (d, *J* = 5.50 Hz, 2 H), 3.87 (br s, 1 H), 4.10 (dd, *J* = 3.30, 14.30 Hz, 1 H), 6.30–6.34 (m, 2 H), 7.25 (d, *J* = 8.53 Hz, 2 H), 7.35 (m, 1 H), 7.55 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.9, 57.4, 111.3, 111.9, 112.8, 118.6, 130.8, 132.7, 139.0, 143.7, 147.5. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.55; H, 5.69; N, 13.22. ***N*-Phenyl-4-acetamido-benzylamine (2j)**: Yield: 98%; oil. IR (neat): 3426, 3301, 3193, 3050, 2931, 2840, 1662, 1601, 1511, 1315, 745, 689 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 4.03 (br s, 1 H), 4.24 (s, 2 H), 6.58 (dd, *J* = 1.10, 8.53 Hz, 2 H), 6.68 (t, *J* = 7.30 Hz, 1 H), 7.13 (dd, *J* = 7.43, 8.53 Hz, 2 H), 7.25 (d, *J* = 8.25 Hz, 2 H), 7.42 (d, *J* = 8.25 Hz, 2 H), 7.76 (br s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9, 48.1, 113.1, 117.8, 120.6, 128.2, 129.5, 135.6, 137.1, 148.2, 168.9. Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.95; H, 6.75; N, 11.68. ***N*-Phenyl-4-nitrobenzyamine (2k)**: Yield: 99%; oil. IR (neat): 3423, 3052, 2923, 2843, 1614, 1506, 1334, 761, 701 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.27 (br s, 1 H), 4.43 (s, 2 H), 6.54 (d, *J* = 8.53 Hz, 2 H), 6.70 (t, *J* = 7.29 Hz, 1 H), 7.13 (t, *J* = 7.70 Hz, 2 H), 7.47 (d, *J* = 8.25 Hz, 2 H), 8.12 (d, *J* = 8.44 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.9, 113.1, 118.3, 124.1, 127.9, 129.6, 147.2, 147.5, 147.8. Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.43; H, 5.32; N, 12.25. ***N*-Methyl-4-nitrobenzyamine (2l)**: Yield: 99%; yellow solid; mp 111–112 °C. IR (KBr): 3200, 3069, 2999, 2951, 1465, 1290, 1164, 894 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.47 (d, *J* = 5.78 Hz, 3 H), 3.72 (dd, *J* = 9.35, 13.75 Hz, 1 H), 4.30 (dd, *J* = 3.85, 13.75 Hz, 1 H), 4.71 (br s, 1 H), 7.54 (d, *J* = 8.53 Hz, 2 H), 8.25 (d, *J* = 8.80 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.1, 60.1, 124.4, 130.9, 140.9, 148.2. Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.84; H, 6.10; N, 16.87. ***N*-Phenyl-*trans*-cinnamylamine (2m)**: Yield: 98%; oil. IR (neat): 3416, 3023, 2925, 2833, 1601, 1505, 1320, 1251, 747, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.77 (br s, 1 H), 3.88 (dd, *J* = 1.22, 5.49 Hz, 2 H), 6.29 (m, 1 H), 6.55–6.75 (m, 4 H), 7.13–7.37 (m, 7 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.8, 113.7, 118.2, 127.0, 127.7, 128.2, 129.2, 129.9, 132.1, 137.5, 148.7. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.09; H, 6.67; N, 6.68. ***N*-Phenyl-α-methyl-(4-cyanobenzyl)amine (2n)**: Yield: 98%; mp 99–101 °C. IR (KBr): 3373, 3029, 2962, 2864, 2228, 1605, 1512, 1497, 1324, 1259, 832, 754, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.51 (d, *J* = 6.60 Hz, 3 H), 4.07 (br s, 1 H), 4.49 (q, *J* = 6.79 Hz, 1 H), 6.41 (d, *J* = 7.70 Hz, 2 H), 6.66 (t, *J* = 7.43 Hz, 1 H), 7.07 (dd, *J* = 7.56, 8.39 Hz, 2 H), 7.46 (d, *J* = 8.53 Hz, 2 H), 7.58 (d, *J* = 8.25 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.4, 53.7, 101.9, 113.4, 118.0, 119.2, 126.8, 129.4, 132.8, 146.7, 151.2. Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.07; H, 6.37; N, 12.65. ***N*-Phenyl-α-methyl-(4-nitrobenzyl)amine (2o)**: Yield: 97%; oil. IR (neat): 3409, 3052, 2971, 2927, 2869, 1614, 1588, 1450, 1013, 744, 702 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 6.72 Hz, 3 H), 4.09 (br s, 1 H), 4.57 (q, *J* = 6.72 Hz, 1 H), 6.44 (d, *J* = 7.63 Hz, 2 H), 6.68 (t, *J* = 7.33 Hz, 1 H), 7.10 (t, *J* = 7.94 Hz, 2 H), 7.55 (d, *J* = 8.85 Hz, 2 H), 8.18 (d, *J* = 8.85 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.6, 54.0, 114.0, 118.7, 124.8, 127.4, 129.9, 147.2, 147.8, 153.9. Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.43; H, 5.82; N, 11.55. ***N*-Phenyl-2-(1′-cyclohexenyl)ethyl-amine (2p):** Yield: 97%; oil. IR (neat): 3410, 3050, 2925, 2855, 1602, 1504, 1319, 749, 691 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 (d, *J* = 6.88 Hz, 3 H), 1.48–1.64 (m, 4 H), 1.94–1.99 (m, 4 H), 3.75 (q, *J* = 6.60 Hz, 1 H), 3.76 (m, 1 H), 5.66 (s, 1 H); 6.54 (d, *J* = 7.43 Hz, 2 H), 6.63 (t, *J* = 7.29 Hz, 1 H), 7.11 (dd, *J* = 7.15, 8.53 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 23.1, 23.2, 24.7, 25.4, 55.1, 113.3, 117.0, 121.8, 129.2, 139.6, 147.9. Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.52; H, 9.54; N, 6.98.