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Amination of Alcohols Catalyzed by Copper-Aluminium Hydrotalcite: A Green Synthesis of Amines

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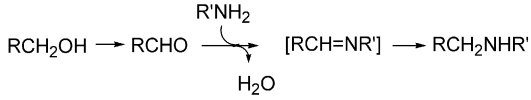
Copper-aluminium hydrotalcite (CuAl-HT)/K_2CO_3 has been employed in the activation of various benzyl alcohols with benzylamines to afford the corresponding amines in good to high yields. Experimentation showed that the reaction takes place through sequential transformations: the oxidation of alcohols into carbonyl compounds, imine formation between amines and carbonyl compounds, and then reduction of imines to amines, heterogeneously catalyzed by non-noble Cu-Al HT catalyst in a one-pot and straightforward fashion. The process was further extended to amination of alcohols with anilines, which are often resistant to alkylation reactions when substituted with strong electron-withdrawing groups.

Introduction

Formation of carbon–nitrogen bonds is of broad interest to synthetic organic chemists because nitrogen-containing compounds, particularly amines and their derivatives, are versatile building blocks for various organic molecules and precursors to a variety of biologically active compounds.[1–4]

With this growing repertoire of applications, the development of efficient methods for the synthesis of amines continues to be a challenging and active area of research. The usual synthetic methods for the synthesis of amines are amination of aryl/alkyl halides[5–7] and reductive amination of carbonyl compounds.[8–11] However, these methods have some drawbacks, such as the need for activation of aryl/alkyl halides, the toxicities of the alkylating agents, and the use of strong reducing reagents, which are undesirable from an environmental point of view. Alternatively, in recent years a number of reports on the hydroamination[12–16] or hydroamino-methylation of olefins or alkynes[17–20] for the synthesis of amines have appeared.

The catalytic amination of alcohols is an atom-economical and environmentally attractive method for the synthesis of amines, thanks to the ubiquitous availability of alcohols. One of the attractive features of this method is the replacement of aryl/alkyl halides by alcohols as alkylating agents; these undergo loss of hydrogen to provide carbonyl intermediate that readily react with amines to form imine or iminium species and then reduce to amines with concomitant formation of water (Scheme 1).



Scheme 1. Catalytic amination of alcohols with amines.

Several catalytic systems for the amination of alcohols have been studied for this oxidation/imination/reduction sequence,[21] based on ruthenium,[22–39] rhodium,[40] platinum,[41] and iridium catalysts[42,43] under homogeneous conditions. Although the reported catalysts are active for this reaction, they are significantly more expensive and non-recoverable. Furthermore, most of the reactions are restricted to the use of primary alcohols at very high reaction temperatures.

The development of heterogeneous catalysts for the synthesis of fine chemicals has become a major area of research, because the potential advantages of these materials (simplified recovery and reusability, the potential for incorporation in continuous reactors and microreactors) over homogeneous systems could have major positive environmental consequences.[44,45] In this context, heterogeneous systems have recently been employed for the amination of alcohols.[46,47]

In our earlier study we reported the preparation of recyclable heterogeneous Cu-exchanged fluoroapatite and *tert*-butoxyapatite catalysts, through the incorporation of the basic species $F^-/tBuO^-$ in apatite in situ by co-precipitation and subsequent exchange with Cu^{II} for the *N*-arylation of imidazoles and other heterocycles with chloroarenes and fluoroarenes, with good to excellent yields,[48,49] together

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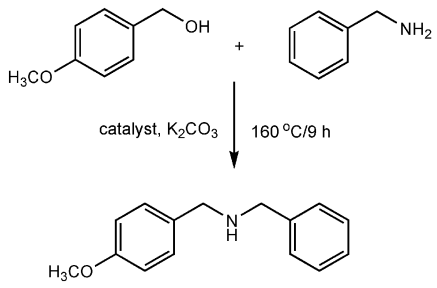
with the CuAl-HT-catalyzed[50] (CuAl-HT: copper-aluminium hydrotalcite) amination of aryl chlorides with benzylamines and cycloalkylamines.[51,52] Here we report a practical and atom-economic synthesis of secondary and tertiary amines by amination of alcohols (primary and secondary alcohols) with the aid of copper-aluminium hydrotalcite as a catalyst in the presence of base under solvent-free conditions.

Results and Discussion

Initially we studied the amination of *p*-methoxybenzyl alcohol with benzylamine in the presence of CuAl-HT and base. Subsequent work was focused on the optimization of this reaction in terms of various reaction parameters such as base, temperature, and time (see the Supporting Information for optimization conditions). Of the various bases screened for this reaction, K_2CO_3 gave the best results. We also studied the catalytic activities of the various copper catalysts under the optimized reaction conditions, and the results are summarized in Table 1. It was observed that Cu(HAP) and Cu(FAP) catalysts, which have been shown to be highly active in *N*-arylation of imidazoles,[46] were ineffective for this reaction. Out of the CuAl-HT catalysts with different Cu/Al ratios (Cu/Al-HT1 3:1), (Cu/Al-HT2 2.5:1) and (Cu/Al-HT3 2:1), Cu/Al-HT2 catalyst was found to be the most effective catalyst for the amination of *p*-methoxybenzyl alcohol with benzylamine.

Table 1. Screening of various copper catalysts for amination of *p*-methoxybenzyl alcohol with benzylamine.[a]

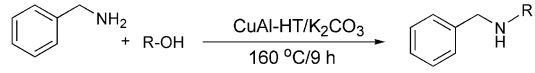


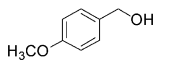
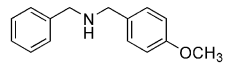
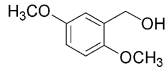
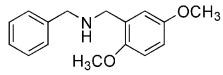
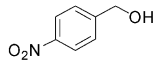
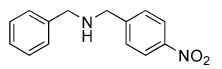
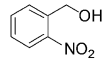
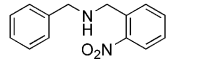
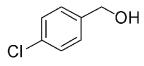
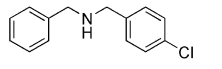
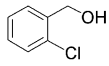
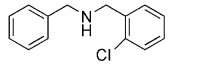
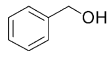
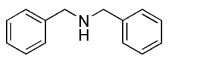
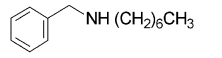
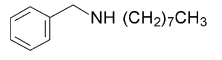
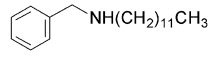
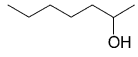
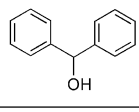
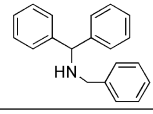
Entry	Catalyst	Yield (%)[b]
1	Cu(HAP)	58
2	Cu(FAP)	35
3	CuAl-HT1	79
4	CuAl-HT2	92
5	CuAl-HT3	65
6	Cu/γAl_2O_3	51
7	$Cu(NO_3)_2$	12

[a] Reaction conditions: *p*-methoxybenzyl alcohol (0.6 g, 4.62 mmol), benzylamine (0.76 mL, 6.93 mmol), catalyst (Cu, 4.0 mol-%), K_2CO_3 (0.8 g, 5.8 mmol), 160 °C, 9 h, under air. Degrees of conversion are based on alcohol. [b] Isolated yield.

Various benzyl and aliphatic alcohols were allowed to react with benzylamine under optimized conditions; the results are summarized in Table 2, from which it can be observed that electron-donating substituents facilitated the amination reaction, to afford excellent yields (Table 2, Entries 1 and 2), whereas lower yields were obtained with electron-withdrawing substituents (Table 2, Entries 3–6). The *ortho*-substituted benzyl alcohols gave lower yields than the *para*-substituted benzyl alcohols because of steric hindrance at the *ortho*-position (Table 2, Entries 4 and 6). In the case of amination of benzyl alcohol with benzylamine, the desired coupling product, dibenzylamine, was isolated in 72% yield at a relatively low temperature after 14 h (Table 2, Entry 7). Long-chain (C7, C8, and C12) aliphatic alcohols were also aminated with benzylamine and it was observed that the yields of the products decreased with increasing carbon chain length (Table 2, Entries 8–10). Further, at-

Table 2. Amination of substituted benzyl alcohols and aliphatic alcohols with benzylamine.[a]



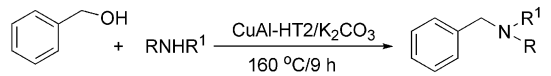
Entry	R-OH	Products[b]	Yield (%)[c]
1			92,91[d]
2			83
3			67
4			35
5			79
6			32
7			72[e]
8	$CH_3(CH_2)_6$-OH		88
9	$CH_3(CH_2)_7$-OH		71
10	$CH_3(CH_2)_{11}$-OH		65
11		--	--
12		--	--
13			87

[a] Reaction conditions: alcohols (4.62 mmol), benzylamine (0.76 mL, 6.93 mmol), catalyst (Cu, 4.0 mol-%), K_2CO_3 (0.8 g, 5.8 mmol), 160 °C, 9 h, under air. [b] All products were characterized by NMR and mass spectroscopy (see the Supporting Information). [c] Isolated yield. [d] Yield after fifth cycle. [e] Reaction temperature 150 °C and reaction time 14 h under air.

tempted amination of aliphatic secondary alcohols (open-chain or cyclic) with benzylamine resulted in no product formation (Table 2, Entries 11 and 12), but the reaction between benzhydrol and benzylamine proceeded well to afford the corresponding secondary amine in excellent yields (Table 2, Entry 13). It is clear from the results that this catalyst system is better suited for arylalkyl secondary alcohols rather than simple aliphatic secondary alcohols.

We also examined the amination of benzyl alcohols with primary and secondary amines, benzylamines, and long-chain aliphatic amines. The results are summarized in Table 3, from which it can be seen that benzylamines containing either electron-donating groups (Table 3, Entry 1) or electron-withdrawing groups (Table 3, Entry 2) displayed similar reactivity patterns, thus implying that the electronic nature of the substituent on benzylamine does not have any noticeable influence on the reaction. Amination of benzyl alcohol with decylamine also afforded the corresponding aminated product but in diminished yields (Table 3, Entry 4). When the secondary amine dibenzylamine was employed in the reaction, tribenzylamine was obtained in excellent yields (Table 3, Entry 5) within 5 h.

Table 3. Amination of benzyl alcohols with various amines.[a]

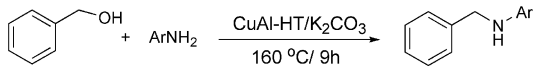


Entry	R,R1	Products	Yield (%)[b]
1	R = H_3CO–C_6H_4–CH_2–, R^1 = H	H_3CO–C_6H_4–CH_2–NH–CH_2–C_6H_5	86
2	R = Cl–C_6H_4–CH_2–, R^1 = H	Cl–C_6H_4–CH_2–NH–CH_2–C_6H_5	91
3	R = C_6H_5–CH_2–, R^1 = H	C_6H_5–CH_2–NH–CH_2–CH_2–C_6H_5	73
4	R = $CH_3(CH_2)_8CH_2$–, R^1 = H	$CH_3(CH_2)_8CH_2NH(CH_2)_8CH_3$	65
5	R = C_6H_5–CH_2–, R^1 = C_6H_5–CH_2–	$(C_6H_5CH_2)_3N$	98[c]

[a] Reaction conditions: benzyl alcohol (0.5 g, 4.62 mmol), amines (6.93 mmol), catalyst (Cu, 4.0 mol-%), K_2CO_3 (0.8 g, 5.8 mmol), 160 °C, 9 h, under air. [b] Isolated yield. [c] Reaction time 5 h.

Later, we successfully extended the scope of the methodology by using anilines as coupling partners under similar reaction conditions, to produce amines useful in the fine chemicals industries (Table 4). The use of anilines in the amination of alcohols is usually unsuccessful, especially with anilines possessing strongly electron-withdrawing groups (*p*-nitroaniline), which are often resistant to alkylation reactions. We were delighted to observe that the CuAl-HT2/K_2CO_3 combination was successful for the formation of a range of *N*-phenylamines (Table 4, Entries 1–9). All the catalytic reactions were attempted under the same optimal reaction conditions to allow observation of the effects of steric and electronic parameters. The electron-rich 4-methoxyaniline and 3,5-dimethoxyaniline gave excellent yields (Table 4, Entries 2 and 3), whereas anilines with electron-withdrawing substituents (Table 4, Entries 4–9) were *N*-alkylated in yields ranging from moderate to excellent. The *ortho*-substituted anilines gave lower yields than their *para*-substituted counterparts (Table 4, Entries 6 vs. 7 and 8 vs. 9), which might be due to the steric hindrance of the substituent at the *ortho*-position.

Table 4. Amination of benzyl alcohols with anilines.[a]



Entry	$ArNH_2$	Product[b]	Yield (%)[c]
1	$C_6H_5NH_2$	$C_6H_5CH_2NHC_6H_5$	91
2	H_3CO–C_6H_4–NH_2	H_3CO–C_6H_4–NH–CH_2–C_6H_5	97
3	H_3CO, OCH_3–C_6H_3–NH_2	H_3CO, OCH_3–C_6H_3–NH–CH_2–C_6H_5	98
4	HOOC–C_6H_4–NH_2	HOOC–C_6H_4–NH–CH_2–C_6H_5	57
5	Cl–C_6H_4–NH_2	Cl–C_6H_4–NH–CH_2–C_6H_5	87
6	CN–C_6H_4–NH_2	CN–C_6H_4–NH–CH_2–C_6H_5	41
7	NC–C_6H_4–NH_2	NC–C_6H_4–NH–CH_2–C_6H_5	69
8	NO_2–C_6H_4–NH_2	NO_2–C_6H_4–NH–CH_2–C_6H_5	70
9	O_2N–C_6H_4–NH_2	O_2N–C_6H_4–NH–CH_2–C_6H_5	98,97[d]

[a] Reaction conditions: benzyl alcohol (0.5 g, 4.62 mmol), anilines (6.93 mmol), catalyst (Cu, 4.0 mol-%), K_2CO_3 (0.8 g, 5.8 mmol), 160 °C, 9 h, under air. [b] All products are characterized by NMR and mass spectroscopy (see the Supporting Information). [c] Isolated yield. [d] Yield after fifth cycle.

Although this methodology requires relatively high reaction temperatures and excesses of amines, it offers several advantages such as the use of the cheap heterogeneous catalyst Cu-Al hydrotalcite in place of expensive and non-recoverable homogeneous catalysts, its applicability for a wide range of alcohols in combination with benzyl and aromatic amines, and the easy separation and recovery of the catalyst.

In order to examine the role of base in the aminations of the alcohols, we performed the reactions in the absence of base and no products were observed. We thus speculated that the oxidation step may possibly proceed through the formation of an alkoxide by the abstraction of a proton from the alcohol in the presence of base and binding to the copper atom in the hydrotalcite. The copper alkoxide could be transformed into the aldehyde through β-hydride elimination, which could result in the concomitant formation of mono(hydrido)copper. The condensation of the aldehyde with the amine could result in the imine, which could be reduced by the mono(hydrido)copper[53,54] to form an (amido)copper species. Ligand exchange between the copper amide and the alcoholic substrate (or alkoxide) could afford the desired amination product. To obtain an insight into the reaction pathway, we monitored the amination of *p*-methoxybenzyl alcohol (PMBA) with benzylamine (BA) in the presence of CuAl-HT2 and K_2CO_3 at 160 °C for 9 h by GC analysis and plotted the assessment of reactant and product over time. As shown in Figure 1, in the first part of the reaction, *p*-anisaldehyde (PAA) was rapidly generated from the copper alkoxide with a subsequent β-hydride elimination process. The formation of PAA was at its maximum at 2 h. Subsequently, the yield of PAA decreased, and the yield of *N*-alkylated product increased.

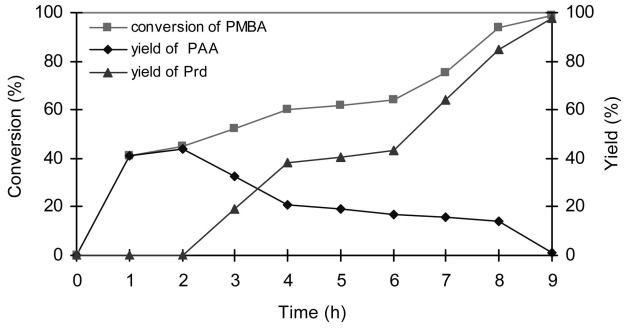


Figure 1. PAA and *N*-alkylated product over time in the CuAl-HT2/K_2CO_3-catalyzed amination of PMBA with BA (160 °C, 9 h).

However, we could not detect the imine species, the condensation product of PAA and BA, during the course of the reaction. The sequential conversion of PMBA into PAA and the formation of the product was almost constant in the second part of the reaction. The above observation clearly suggests the possible intermediacy of the aldehyde derived from the alcohol in the *N*-alkylation reaction. Indeed, in a separate experiment, using only PMBA in the presence of catalyst and base at 160 °C for 2.5 h, we obtained PAA in 98% isolated yield.

Further, to verify the role of CuAl-HT in the reduction of imines to amines, we conducted a separate reaction between PAA and BA at 160 °C in the presence of CuAl-HT2 with monitoring for 9 h. We observed no formation of the *N*-alkylated amine during the course of the reaction. From this study, it is clear that the reaction proceeds through an oxidation/imination/reduction sequence[21] with in situ generation of metal hydride species and their subsequent participation in reduction of imine, which indicated no net hydrogen loss or gain at the end of the catalytic cycle. This was further confirmed by an X-ray photoelectron spectroscopic study (see Figure 2, XPS spectra for Cu^{II}) in which the XPS spectra for the fresh CuAl-HT2 and for the recovered catalyst each show a 2p peak at 936.3 eV corresponding to Cu in the +2 oxidation state (no reduction of Cu^{II} was observed).

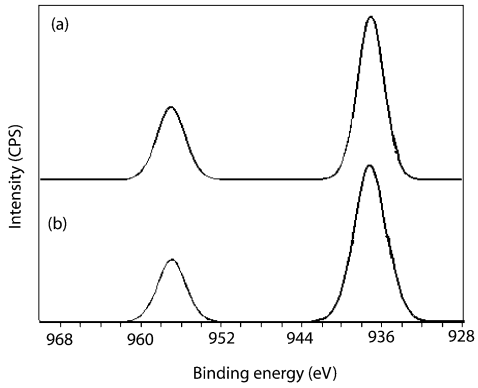


Figure 2. High-resolution XPS narrow scans of Cu 2p for (a) fresh CuAl-HT2, and (b) recovered catalyst after the 5th cycle.

The CuAl-HT2 catalyst was readily separated from the reaction mixture by simple filtration. The recovered catalyst, after washing with acetone followed by drying at 65 °C, was used in the next run and consistent activity was observed (Table 4, Entry 9, first cycle 98%; fifth cycle 97%). In order to examine whether CuAl-HT2-catalyzed amination of alcohols with amines is heterogeneous, we terminated the reaction between *o*-nitroaniline and benzyl alcohol after 45 min at 20% conversion and the catalyst was filtered hot. The reaction was continued with the filtrate for 9 h and no change in the conversion of *o*-nitroaniline was observed. Further, the filtrate was tested by AAS analysis for metal content and no copper was found in the filtrate.

We also studied the XRD patterns of fresh CuAl-HT2 catalyst and of recovered catalyst from the fifth reaction cycle (see the Supporting Information), which suggested that there is no difference between the XRD patterns of the fresh catalyst and of the recovered catalyst. This study illustrates that the catalyst is very robust and efficient and works purely heterogeneously.

Conclusions

In conclusion, we have developed an efficient and inexpensive CuAl-HT2/K_2CO_3 catalyst system for the amin-

ation of various alcohols. The catalyst system shows excellent selectivity and good to high yields in the amination of benzyl alcohols with aliphatic/aromatic amines, including anilines, to provide the corresponding amines. Moreover, the catalyst can be easily separated by simple filtration and reused for several cycles with consistent activity.

Experimental Section

General: All chemicals were purchased from Aldrich and were used as received. All solvents used were of analytical grade and were used as received from Merck India Pvt. Ltd. X-ray powder diffraction (XRD) data were collected with a Simens/D-5000 diffractometer with use of Cu-K_α radiation. XPS spectra were recorded with a Kratos AXIS 165 apparatus with a dual anode (Mg and Al) with use of the Mg K_α anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration we used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted with the aid of the Sun Solaris-based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined from the spectrum of a pure sample, and the locations and FWHMs of the products not obtained as pure species were adjusted until the best fits were obtained. Symmetric Gaussian shapes were used in all cases. The Cu/Al ratio was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). GC analysis was performed with a Shimadzu GC-2010 instrument and a ZB-5 capillary column. ^{1}H and ^{13}C spectra were recorded with a Bruker Avance 300 (300 MHz ^{1}H and ^{13}C) spectrometer at room temperature with respect to TMS and $CDCl_3$ for ^{1}H and ^{13}C NMRs, respectively. Chemical shifts are reported in ppm relative to residual $CHCl_3$ or to $CDCl_3$ (δ = 7.28 ppm for ^{1}H; δ = 77.0 ppm for ^{13}C). Coupling constants (J) are reported in Hertz. The copper-aluminium hydrotalcite catalysts CuAl-HT1, CuAl-HT2, and CuAl-HT3 were prepared by the literature procedure.[48]

General Procedure for the Amination of Alcohols with Amines: Benzylamine (0.76 mL, 6.93 mmol), *p*-methoxybenzyl alcohol (0.6 g, 4.62 mmol), Cu/Al-HT2 (4 mol-%), and K_2CO_3 (0.8 g, 5.8 mmol) were placed in a 50 mL round-bottomed flask containing a Teflon-coated magnetic stirring bead and introduced into a pre-heated oil bath at 160 °C. The mixture was stirred for 9 h. The progress of the reaction was monitored by TLC, and on completion of the reaction the reaction mixture was centrifuged to separate the catalyst, the solid residue was washed with EtOAc (1 × 5 mL) to make the catalyst free of organic matter, and the reaction mixture was diluted with water (20 mL) and then extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to yield the crude product. This was then purified by flash chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate (98:2 v/v) as eluent to afford the pure product.

Benzyl(4-methoxybenzyl)amine: See Table 2, Entry 1; yellow solid (0.9648 g, 4.2504 mmol, 92%); m.p. 192–194 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.10 (m, 9 H), 3.85 (s, 4 H), 3.76 (s, 3 H), 1.75 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 139.6, 130.2, 128.8, 128.7, 128.5, 126.8, 57.9, 57.1 ppm. GC-MS: m/z = 228 $[M + H]^+$. $C_{15}H_{17}NO$ (227.31): calcd. C 79.26, H 7.54, N 6.16; found C 79.29, H 7.55, N 6.20.

Benzyl(2,5-dimethoxybenzyl)amine: See Table 2, Entry 2; yellow semisolid (0.9854 g, 3.835 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.20 (m, 5 H), 6.81–6.71 (m, 3 H), 3.87 (s, 4 H), 3.72 (s, 6 H), 2.20 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0, 153.8, 128.4, 127.9, 126.9, 123.8, 114.8, 114.4, 113.5, 57.9, 57.7, 57.5, 50.3 ppm. EI-MS: m/z = 257 $[M]^+$. $C_{16}H_{19}NO_2$ (257.33): calcd. C 74.68, H 7.44, N 5.44; found C 75.05, H 7.45, N 5.42.

Benzyl(4-nitrobenzyl)amine: See Table 2, Entry 3; yellow solid (0.7490 g, 3.0954 mmol, 67%); m.p. 246–249 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.4 Hz, 2 H), 7.41–7.20 (m, 5 H), 6.61 (d, J = 8.4 Hz, 2 H), 4.75 (br. s, 1 H), 4.41 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 144.0, 137.5, 129.0, 128.4, 128.1, 123.6, 56.1 ppm. EI-MS: m/z = 242 $[M]^+$. $C_{14}H_{14}N_2O_2$ (242.28): calcd. C 69.41, H 5.82, N 11.56; found C 70.01, H 6.00, N 11.61.

Benzyl(2-nitrobenzyl)amine: See Table 2, Entry 4; yellow solid (0.3913 g, 1.617 mmol, 35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.35 (br. s, 1 H), 8.15 (dd, J = 10.19, 8.7 Hz, 1 H), 7.72 (t, J = 8.7, 7.9 Hz, 1 H), 7.57 (d, J = 8.8 Hz, 1 H), 7.44–7.36 (m, 6 H), 4.50 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 137.2, 134.6, 132.4, 129.0, 128.4, 128.1, 127.8, 127.3, 123.1, 57.0, 46.4 ppm. EI-MS: m/z = 243 $[M + H]^+$. $C_{14}H_{14}N_2O_2$ (242.28): calcd. C 69.41, H 5.82, N 11.56; found C 68.99, H 5.79, N 11.54.

Benzyl(4-chlorobenzyl)amine: See Table 2, Entry 5; colorless liquid (0.8449 g, 3.6498 mmol, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.21 (m, 4 H), 7.19–6.98 (m, 5 H), 3.73 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 135.2, 132.0, 131.3, 128.7, 128.4, 128.1, 126.8, 55.6 ppm. EI-MS: m/z = 232 $[M]^+$. $C_{14}H_{14}ClN$ (231.72): calcd. C 72.57, H 6.09, N 6.04; found C 72.67, H 5.92, N 5.99.

Benzyl(2-chlorobenzyl)amine: See Table 2, Entry 6; pale yellow liquid (0.3422 g, 1.4784 mmol, 32%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25–8.15 (m, 2 H), 7.61–7.50 (m, 7 H), 4.95 (d, J = 5.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 136.9, 134.0, 129.4, 128.8, 128.4, 128.1, 126.9, 57.3, 46.4 ppm. EI-MS: m/z = 232 $[M]^+$. $C_{14}H_{14}ClN$ (231.72): calcd. C 75.57, H 6.09, N 6.04; found C 75.90, H 6.05, N 6.05.

Dibenzylamine: See Table 2, Entry 7; colorless liquid (0.8919 g, 4.53 mmol, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.12–5.90 (m, 10 H), 3.73 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.4, 128.2, 127.0, 53.0 ppm. GC-MS: m/z = 197 $[M]^+$. $C_{14}H_{15}N$ (197.28): calcd. C 85.24, H 7.66, N 7.10; found C 85.12, H 7.75, N 7.12.

***N*-Benzylheptan-1-amine:** See Table 2, Entry 8; colorless liquid (0.8904 g, 4.0656 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–6.67 (m, 5 H), 3.52–3.40 (m, 2 H), 3.85 (s, 4 H), 2.84 (br. s, 2 H), 1.36–1.16 (m, 10 H), 0.88 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 128.1, 127.2, 126.6, 54.5, 42.0, 32.9, 31.6, 29.1, 26.6, 22.5, 13.9 ppm. EI-MS: m/z = 206 $[M]^+$. $C_{14}H_{23}N$ (205.34): calcd. C 81.89, H 11.29, N 6.82; found C 81.60, H 11.25, N 6.85.

***N*-Benzyloctan-1-amine:** See Table 2, Entry 9; colorless liquid (0.7643 g, 3.2802 mmol, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–6.80 (m, 5 H), 3.47 (d, J = 5.6 Hz, 2 H), 2.80 (br. s, 1 H), 1.55–1.36 (m, 2 H), 1.35–1.14 (m, 12 H), 0.88 (t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8, 128.2, 127.2, 126.7, 54.5, 41.4, 32.9, 31.6, 29.9, 26.6, 22.5, 13.9 ppm. EI-MS: m/z = 219 $[M]^+$. $C_{15}H_{25}N$ (219.37): calcd. C 82.13, H 11.49, N 6.39; found C 82.09, H 11.33, N 6.38.

***N*-Benzyldodecan-1-amine:** See Table 2, Entry 10; colorless liquid (0.8258 g, 3.003 mmol, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =

7.40–7.08 (m, 5 H), 3.49 (d, J = 5.7 Hz, 2 H), 3.05 (br. s, 1 H), 1.68–1.48 (m, 2 H), 1.40–1.20 (m, 20 H), 0.90 (t, J = 6.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7, 128.1, 127.1, 126.7, 54.4, 42.4, 32.3, 31.7, 29.4, 29.2, 29.1, 25.5, 13.9 ppm. EI-MS: m/z = 276 $[M + H]^+$. $C_{19}H_{33}N$ (275.48): calcd. C 82.84, H 12.07, N 5.08; found C 82.73, H 12.11, N 4.94.

***N*-Benzyldiphenylmethanamine:** See Table 2, Entry 13; yellow solid (1.0972 g, 4.0914 mmol, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.10 (m, 15 H), 5.65 (s, 1 H), 3.75 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7, 140.6, 128.2, 127.2, 126.8, 126.4, 64.6, 45.8 ppm. EI-MS: m/z = 273 $[M]^+$. $C_{20}H_{19}N$ (273.38): calcd. C 87.87, H 7.01, N 5.12; found C 87.84, H 6.98, N 4.99.

***N*-Benzyl-2-phenylethanamine:** See Table 3, Entry 3; colorless liquid (0.7117 g, 3.373 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.12 (m, 10 H), 4.45 (s, 2 H), 2.85 (s, 2 H), 2.55 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5, 138.2, 128.5, 127.9, 126.9, 126.5, 125.8, 54.0, 48.8, 38.5 ppm. EI-MS: m/z = 211 $[M]^+$. $C_{15}H_{17}N$ (211.31): calcd. C 85.26, H 8.11, N 6.63; found C 85.37, H 8.99, N 6.56.

***N*-Benzyldecan-1-amine:** See Table 3, Entry 4; colorless liquid (0.7430 g, 3.003 mmol, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (d, J = 9.8 Hz, 2 H), 7.15–7.10 (m, 3 H), 3.91 (s, 2 H), 1.40–1.21 (m, 16 H), 0.90 (t, J = 6.8, 6.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6, 130.8, 130.5, 127.1, 55.8, 50.9, 33.8, 32.7, 31.0, 30.9, 29.3, 24.7, 14.3 ppm. EI-MS: m/z = 247 $[M]^+$. $C_{17}H_{29}N$ (247.42): calcd. C 82.52, H 11.81, N 5.66; found C 82.63, H 12.11, N 5.69.

Tribenzylamine: See Table 3, Entry 5; white crystalline solid (1.2994 g, 4.5276 mmol, 98%); m.p. 92–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.6 Hz, 6 H), 7.27 (t, J = 7.6, 6.8 Hz, 6 H), 7.17 (t, J = 7.6, 6.8 Hz, 3 H), 3.55 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6, 128.7, 128.1, 126.8, 57.8 ppm. GC-MS: m/z = 288 $[M + H]^+$. $C_{21}H_{21}N$ (287.40): calcd. C 87.76, H 7.36, N 4.87; found C 87.77, H 7.39, N 4.76.

***N*-Benzylbenzenamine:** See Table 4, Entry 1; colorless liquid (0.7693 g, 4.2042 mmol, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.35 (m, 5 H), 6.85–6.70 (m, 5 H), 4.50 (d, J = 5.6 Hz, 2 H), 4.00 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.7, 140.6, 128.6, 127.7, 126.6, 126.3, 117.9, 114.8, 53.7 ppm. EI-MS: m/z = 183 $[M]^+$. $C_{13}H_{13}N$ (183.25): calcd. C 85.21, H 7.15, N 7.64; found C 85.07, H 7.19, N 7.55.

Benzyl(4-methoxyphenyl)amine: See Table 4, Entry 2; pale yellow solid (0.9545 g, 4.4814 mmol, 97%); m.p. 48–50 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.9 Hz, 2 H), 6.88–6.76 (m, 5 H), 6.56 (d, J = 7.9 Hz, 2 H), 4.22 (d, J = 5.6 Hz, 2 H), 4.0 (br. s, 1 H), 3.75 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 141.5, 135.8, 128.4, 126.9, 126.4, 114.4, 113.9, 56.9, 56.5 ppm. GC-MS: m/z = 214 $[M + H]^+$. $C_{14}H_{15}NO$ (213.28): calcd. C 78.84, H 7.09, N 6.57; found C 79.19, H 7.05, N 6.60.

Benzyl(3,5-dimethoxyphenyl)amine: See Table 4, Entry 3; yellow liquid (1.1002 g, 4.5276 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85–6.60 (m, 5 H), 5.51–5.24 (m, 3 H), 4.15 (d, J = 5.6 Hz, 2 H), 4.00 (br. s, 1 H), 3.75 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.1, 145.1, 143.3, 127.9, 126.9, 126.5, 90.1, 87.7, 57.0, 56.1 ppm. GC-MS: m/z = 243 $[M]^+$. $C_{15}H_{17}NO_2$ (243.30): calcd. C 74.05, H 7.04, N 5.76; found C 74.19, H 7.05, N 6.01.

4-(Benzylamino)benzoic Acid: See Table 4, Entry 4; yellow solid (0.5978 g, 2.6334 mmol, 57%); m.p. 142–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.4 Hz, 2 H), 7.40–7.25 (m, 5 H), 6.55 (d, J = 8.4 Hz, 2 H), 4.75 (br. s, 1 H), 4.40 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 153.1, 138.2, 137.3, 130.2, 128.9, 127.2, 126.3, 117.4, 111.2, 47.5 ppm. EI-MS: m/z = 228 $[M + H]^+$. $C_{14}H_{13}NO_2$ (227.26): calcd. C 73.99, H 5.77, N 6.16; found C 74.00, H 5.55, N 6.20.

Benzyl(4-chlorophenyl)amine: See Table 4, Entry 5; light yellow liquid (0.8742 g, 4.0197 mmol, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (br. s, 1 H), 7.41–7.34 (m, 5 H), 6.62 (d, J = 8.4 Hz, 2 H), 6.32 (d, J = 8.4 Hz, 2 H), 3.45 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 140.4, 128.4, 127.8, 126.8, 122.5, 116.1, 45.8 ppm. EI-MS: m/z = 218 $[M + H]^+$. $C_{13}H_{12}ClN$ (217.70): calcd. C 71.72, H 5.56, N 6.43; found C 71.80, H 5. 55, N 6.39.

2-(Benzylamino)benzonitrile: See Table 4, Entry 6; white solid (0.3939 g, 1.8942 mmol, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (br. s, 1 H), 7.7 (d, J = 8.5 Hz, 1 H), 7.40–7.20 (m, 7 H), 6.66 (d, J = 8.5 Hz, 1 H), 4.40 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 147.1, 134.0, 133.1, 128.5, 126.9, 117.4, 116.3, 113.9, 95.4, 43.8 ppm. GC-MS: m/z = 208 $[M]^+$. $C_{14}H_{12}N_2$ (208.26): calcd. C 80.74, H 5.81, N 13.45; found C 81.02, H 5.85, N 14.20.

4-(Benzylamino)benzonitrile: See Table 4, Entry 7): Yellow solid (0.6631 g, 3.187 mmol, 69%); m.p. 80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.4 Hz, 2 H), 7.36–7.28 (m, 5 H), 6.53 (d, J = 8.4 Hz, 2 H), 4.85 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2, 143.7, 133.1, 129.0, 126.9, 126.0, 117.0, 113.9, 99.9, 45.8 ppm. GC-MS: m/z = 209 $[M + H]^+$. $C_{14}H_{12}N_2$ (208.26): calcd. C 80.74, H 5.81, N 13.45; found C 81.72, H 5.88, N 13.90.

Benzyl(2-nitrophenyl)amine: See Table 4, Entry 8; orange crystalline solid (0.7374 g, 3.234 mmol, 70%); m.p. 76–78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (br. s, 1 H), 8.21 (dd, J = 8.3, 1.5 Hz, 1 H), 7.42–7.31 (m, 6 H), 6.80 (d, J = 8.3 Hz, 1 H), 6.68 (t, J = 7.6 Hz, 1 H), 4.57 (d, J = 6.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 137.3, 136.2, 128.9, 127.6, 127.0, 125.1, 116.3, 114.1, 47.0 ppm. EI-MS: m/z = 228 $[M]^+$. $C_{13}H_{12}N_2O_2$ (228.25): calcd. C 68.41, H 5.30, N 12.27; found C 68.59, H 5.25, N 12.25.

Benzyl(4-nitrophenyl)amine: See Table 4, Entry 9; orange solid (1.0323 g, 4.5276 mmol, 98%); m.p. 146–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (dd, J = 9.8, 8.3 Hz, 2 H), 8.12 (br. d, J = 6.8 Hz, 1 H), 7.38 (t, J = 8.3, 7.6 Hz, 2 H), 6.85 (d, J = 9.1 Hz, 2 H), 6.60 (t, J = 8.3, 7.6 Hz, 3 H), 3.55 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 145.2, 136.2, 128.9, 127.7, 127.0, 122.5, 114.1, 47.1 ppm. GC-MS: m/z = 228 $[M]^+$. $C_{13}H_{12}N_2O_2$ (228.25): calcd. C 68.41, H 5.30, N 12.27; found C 68.30, H 5.25, N 12.25.

Supporting Information (see also the footnote on the first page of this article): General remarks, preparation of catalysts, experimental procedures, optimization of reaction conditions, ^{1}H NMR and ^{13}C NMR, XRD spectra of fresh and reused catalyst, catalyst recyclability chart, GC spectra for the sequential formation of *p*-anisaldehyde and benzyl(4-methoxybenzyl)amine in the amination of *p*-methoxybenzyl alcohol with benzylamine, references.

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