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Cobalt-Rhodium Heterobimetallic Nanoparticle-Catalyzed N-Alkylation of Amines with Alcohols to Secondary and Tertiary Amines

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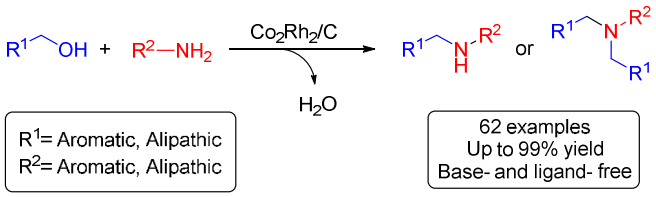


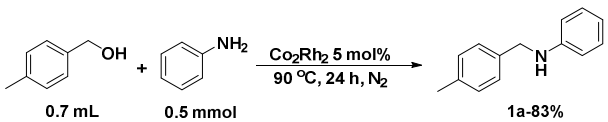
ABSTRACT: Without the requirement for base or other additives, Co_2Rh_2/C can selectively catalyze both mono- and bis-N-alkylation through the coupling of simple alcohols with amines, yielding a range of secondary and tertiary amines in good to excellent isolated yields. The reaction can be applied to benzyl alcohol with optically active 1-phenylethan-1-amines and secondary amines were isolated in quantitative yields with an excellent enantiomeric excess (ee >94%). Selectivity is achieved by varying the reaction temperature and amount of catalyst used. This catalytic system has several advantages including eco-friendliness and a simple workup procedure. The catalyst can be successfully recovered and reused ten times without any significant loss of activity.

Introduction

Secondary and tertiary alkylated amines play an important role as building blocks in many organic synthesis reactions and are important components of agrochemicals, drug molecules, and functional materials.[1] Consequently, many useful synthetic methods have been established.[2] However, they suffer from several drawbacks including low selectivity and the formation of stoichiometric amounts of waste.[3] Recently, the catalytic N-alkylation of amines with alcohols has attracted considerable attention because it provides a green and atom-economic pathway for the synthesis of substituted amines.[4] Since the first report on the catalytic use of a well-defined [$RhH(PPh_3)_4$] in N-alkylations of amines with alcohols in 1981,[5] many useful homogeneous catalysts based on ruthenium,[6] iron,[7] and other transition metals[8] have been developed. However, the homogeneous systems have the drawbacks of low catalyst reusability and/or the indispensable use of large amounts of additives or co-catalysts. Heterogeneous transition metal catalysts[9] can overcome some of the drawbacks of homogeneous catalysts; however, they frequently suffer from harsh reaction conditions, use of toxic and expensive ligands, use of large amount of toxic solvents, catalysts having poor recyclability, and excessive amount of alcohols to obtain satisfactory yields. Therefore, the development of more active and selective heterogeneous catalysts for the N-alkylation of amines with alcohols remains a challenge.

Several years ago, cobalt-rhodium nanoparticles derived from $Co_2Rh_2(CO)_{12}$ were immobilized on charcoal (hereinafter denoted as Co_2Rh_2/C).[10] It was used as a catalyst in the Pauson–Khand reaction and carbonylations.[11] A recent study demonstrated the usefulness of Co_2Rh_2/C in the hydrogenation of nitroarenes.[12] To determine a new catalytic system for the alkylation of amines with alcohols, we decided to use Co_2Rh_2/C as the catalyst without an external base or additive. The catalytic system was determined to be effective in neat at the specific reaction temperature (80–165 °C) depending upon the reaction partners. The proposed catalytic system does not require the addition of a base to function effectively, and thus, represents a greener catalytic system compared to other reported hydrogen borrowing catalysts.

Results and discussion



To examine the catalytic activity of Co_2Rh_2/C, N-alkylation of aniline with 4-methylbenzyl alcohol was chosen initially as a model reaction in the presence of 5 mol% Co_2Rh_2/C at 90 °C for 24 h (eq 1). After workup, a monoalkylation product, N-(4-methylbenzyl)aniline (**1a**), was isolated with 83% yield and no imine was detected. The reactions did not require the addition of molecular sieves

to scavenge the water. Thus, we selected a neat alcohol as the reaction media: the reaction was studied without using a solvent. To optimize the reaction conditions for the mono-alkylation of aniline, reaction parameters such as reaction temperature, reaction time, and the amount of the catalyst used were screened (Table 1). The optimum reaction conditions were established as follows: 5 mol% Co_2Rh_2/C at 100 °C for 24 h for monoalkylation and 10 mol% Co_2Rh_2/C at 140 °C for 24 h for dialkylation.[13]. In a gram scale synthesis, a stoichiometric amount of alcohol was enough to carry out the reaction (see Supporting Information). However, due to the experimental easiness, we used an excess of alcohol in small scale experiments. Other metal nanoparticles such as Co/C and Rh/C, were examined. When Rh/C was used as a catalyst, N-(4-methylbenzyl)aniline was isolated with a 71% yield. Conversely, a trace amount of the secondary amine was formed in the presence of Co/C.

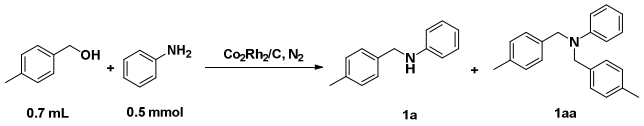


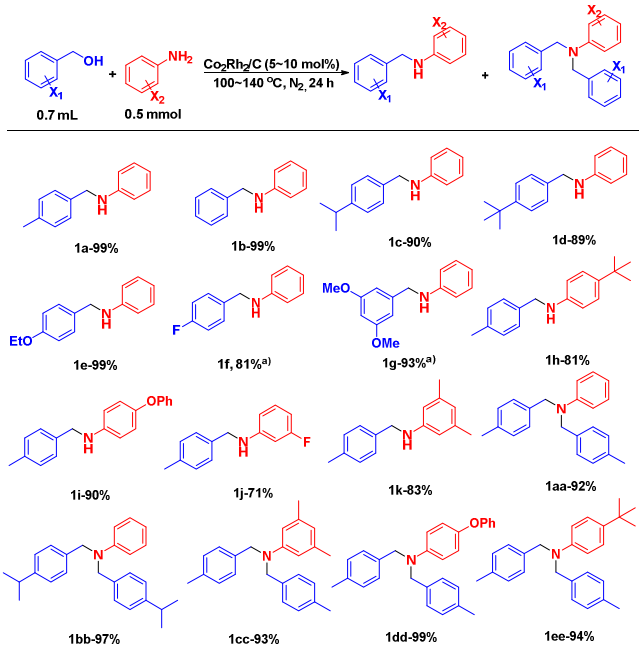
Table 1. Optimization of the Reaction Conditions

Entry	Time (h)	Temp (°C)	Co_2Rh_2 (mol%)	Yield(%)[a]	
				1a	**1aa**
1	24	90	5	83	0
2	24	100	5	99	0
3	18	100	5	74	0
4	24	110	5	99	0
5	24	120	5	87	12
6	24	120	10	54	43
7	24	140	10	7	92
8	24	150	10	10	89
9[b]	24	100	5	98	0

[a]All yields are isolated yields. [b] 6 mmol of amine, 6.5 mmol of alcohol, and 5 mol% (540 mg) of Co_2Rh_2/C.

The substrate scope was next investigated. First, we tested the reactions of aniline with different benzyl alcohols under optimized reaction conditions (5 mol% Co_2Rh_2/C at 100 °C for 24 h); the products were isolated by silica gel column chromatography after workup. The results are listed in Table 2 (compounds **1a – 1g**). High yields were observed. However, steric and electronic effects were observed for the reaction of 3,5-dimethoxybenzyl alcohol (**1g)**: the corresponding sec-amine was isolated with a 42% yield. To our delight, when the reaction was performed at 120 °C, the yield dramatically increased from 42% to 93%. A para-substituent on benzyl alcohol with an electron-withdrawing group such as fluoro resulted in a reduced yield (31%; **1f**). Fortunately, the diminished yield was solved by increasing the reaction temperature to 120 °C (81%). Next, we examined the reaction of 4-methylbenzyl alcohol with substituted anilines (Table 2, **1i – 1k**). It was observed that acceptable yields (**1h** and **1i**, 81% and 90%) were observed for electron-donating substituents such as the t-butyl and phenoxy groups. Interestingly, no steric effect was observed for 3,5-dimethylaniline (**1k,** 83%). Under the reaction conditions for the formation of sec-amines, the formation of the corresponding tert-amines was not observed or negligible for all the substrates. Next, we examined the reactions of different anilines with 4-methylbenzyl alcohol under optimized reaction conditions for double N-alkylations (10 mol% Co_2Rh_2/C at 140 °C for 24 h). Excellent yields (**1aa-1ee,** 92–99%) were obtained with all anilines and alcohol reactants used. However, anilines with 4-chloro or 4-bromo group were not a good substrate under our reaction conditions (5 mol% Co_2Rh_2/C at 100 °C for 24 h). They afforded only ca 10% of their corresponding products. Our results were surprising compared with those of heterogeneous Pt-Sn/γ-Al_2O_3 catalyst.[14] In the presence of Pt-Sn/γ-Al_2O_3, arylamines and heteroarylamines could not be utilized to synthesize tertiary amines, although they could efficiently react with primary alcohols to afford the corresponding secondary amine products.

Table 2. Reaction of Anilines with Benzyl Alcohols

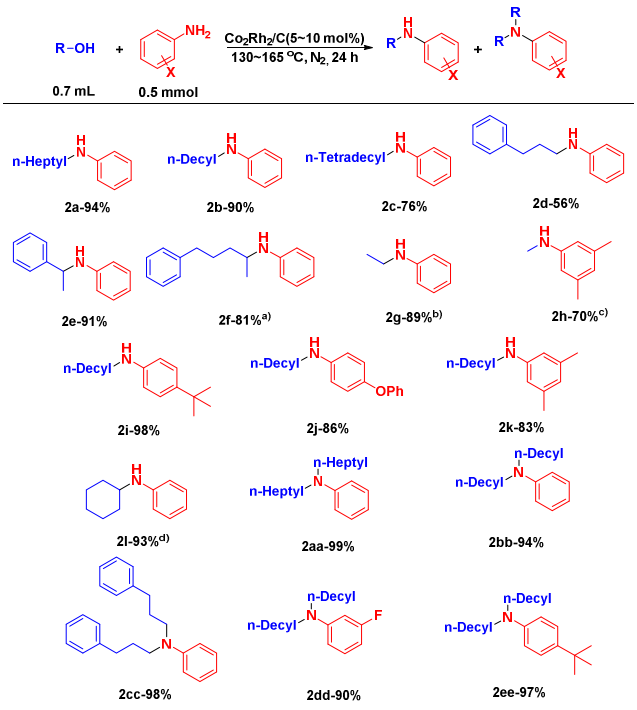


All yields are isolated yields. Reaction conditions for 2° amine: Co_2Rh_2 5 mol% (45 mg), 100 °C, 24 h, N_2. Reaction conditions for 3° amine: Co_2Rh_2 10 mol% (90 mg), 140 °C, 24 h, N_2. [a]120 °C

Encouraged by the above observation, we decided to study the alkylation of aniline with aliphatic alcohols. We optimized the reaction conditions for the alkylation of aniline with 1-decanol (see SI). The optimum reaction conditions were as follows: for monoalkylation, 5 mol% Co_2Rh_2/C at 130 °C for 24 h and for dialkylation, 10 mol% Co_2Rh_2/C at 165 °C for 24 h. First, we examined the reactions of aniline with different aliphatic alcohol derivatives under optimized reaction conditions (5 mol% Co_2Rh_2/C at 130 °C for 24 h) (Table 3). Aliphatic alcohols underwent the N-alkylation reactions with aniline smoothly, affording the desired products in high yields (**2a – 2g**; 56–94%). Peculiarly, a dramatic decrease in the yield was observed for 4-phenyl-2-butanol (**2f**, 27%) when compared to 1-

phenylethan-1-ol (**2e**, 91%). However, increasing the reaction temperature to 150 °C solved this problem (81%). In iridium-catalyzed reactions,[15] 4-phenyl-2-butanol and 1-phenylethan-1-ol displayed reduced activity (19% and 38%, respectively), even with a greater catalyst loading and longer reaction time. In other heterogeneous catalysts, no reaction or poor yields of the corresponding secondary amines were observed with long chain aliphatic alcohols. In the presence of the nanosized zeolite beta,[16] 1-hexanol and 1-octanol provided the respective mono-N-alkylated products in 41% and 10% yields, respectively; no reaction was observed with 1-decanol. Ethanol was also an acceptable substrate (**2g -** 89%). Unfortunately, methanol was not an acceptable substrate[8a,15] under identical reaction conditions (5 mol% Co_2Rh_2/C at 130 °C for 24 h). However, when 3,5-dimethylaniline was methylated at 180 °C in the presence of 5 mol% Co_2Rh_2/C, the mono-methylated 3,5-dimethylaniline product was isolated with a 38% yield. Lengthening the reaction time to 36 h in the presence of 10 mol% Co_2Rh_2/C at 180 °C afforded the mono-methylated 3,5-dimethylaniline at a 70% yield (**2h**). Next, we tested the reaction of 1-decanol with substituted aniline derivatives (**2i – 2k**). The treatment of aniline with cyclohexanol, a secondary alcohol, at 140 °C resulted in N-cyclohexylaniline (**2l**) with a 97% yield. Compared to Zhang's recent study,[17] our result was remarkable. They reported that the same reaction in the presence of a cobalt(II) catalyst based on a pincer PNP ligand afforded a mixture of N-cyclohexylaniline, N-phenylcyclohexanimine, and cyclohexanone after 48 h, with the expected N-cyclohexylaniline being the major product (48% GC yield). Under the reaction conditions of formation of tert-amines (10 mol% Co_2Rh_2/C at 165 °C for 24 h), the corresponding tertiary amines could be obtained with 84–91% yields (**2aa – 2ee**).

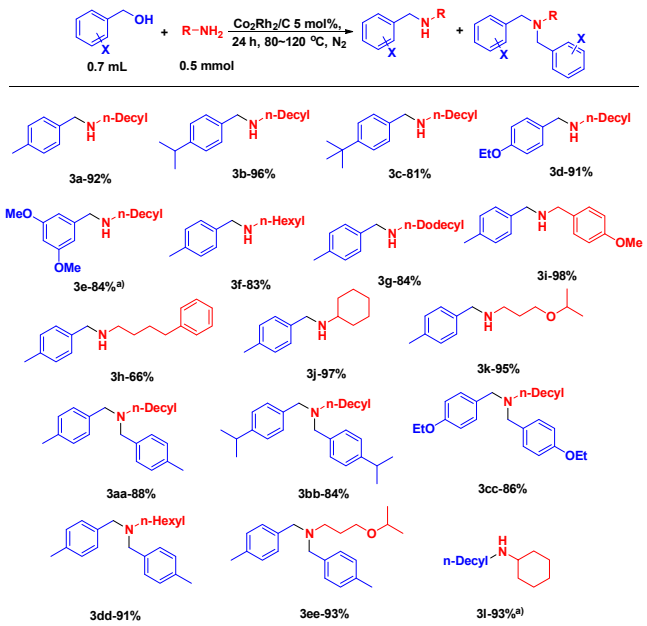
Table 3. Reaction of Anilines with Aliphatic Alcohols



All yields are isolated yields. Reaction conditions for 2° amine: Co_2Rh_2 5 mol% (45 mg), 130 °C, 24 h. Reaction conditions for 3° amine: Co_2Rh_2 10 mol% (90 mg), 165 °C, 24 h. [a] 150 °C [b] 120 °C, alcohol 3 mL [c] Co_2Rh_2 10 mol% (90 mg), 180 °C, 36 h, alcohol 3 mL. [d] 140 °C

Next, we studied the alkylation of aliphatic amines with benzyl alcohols (Table 4). We optimized the reaction conditions for the N-alkylation of decyl amine with 4-methylbenzyl alcohol (see SI). Alkyl amines have a high nucleophilicity compared to those of aryl amines and relative reduced temperatures were required to perform the N-alkylation reactions. Thus, the optimum reaction conditions were as follows: for monoalkylation, 5 mol% Co_2Rh_2/C at 80 °C for 24 h and for dialkylation, 5 mol% Co_2Rh_2/C at 120 °C for 24 h. First, we tested the reactions of 1-decyl amine with substituted benzyl alcohol derivatives under optimized reaction conditions (Co_2Rh_2/C at 80 °C for 24 h). The results are listed in Table 4 (**3a – 3e**). Sec-amines with a long alkyl chain were isolated in acceptable yields except for **3e**. In the case of 3,5-dimethoxybenzyl alcohol, the corresponding sec-amine was isolated at a 48% yield (**3e**). However, increasing the reaction temperature to 100 °C solved the problem (3,5-dimethoxybenzyl alcohol: 84%). We next investigated the reaction between 4-methylbenzyl alcohol with different aliphatic amines (Table 4, **3f – 3k**). N-alkylation produced a secondary amine in high to excellent yield (66–98%), depending upon the amine used. Cyclohexyl amine and 4-methoxybenzyl amine were excellent substrates. Interestingly, in the literature, the alkylation of cyclohexylamine was a challenging reaction.[18] For example, the treatment of cyclohexylamine with benzyl alcohol in the presence of an iridium NHC catalyst afforded a 35% yield of N-benzylcyclohexylamine.[18a] In the reaction with hexyl alcohol in the presence of [Cp*Ir(prolinato)Cl] at 150 °C for 72 h, the formation of N-benzylcyclohexylamine was observed with a 27% yield.[18b] However, when cyclohexyl amine was reacted with decanol under our reaction conditions, N-decylcyclohexanamine was isolated at 93% (**3l**). Under the reaction conditions of the formation of tert-amines (5 mol% Co_2Rh_2/C at 120 °C for 24 h), the corresponding tertiary amines could be obtained with 84–91% yields (**3aa – 3ee**).

Table 4. Reaction of Aliphatic Amines

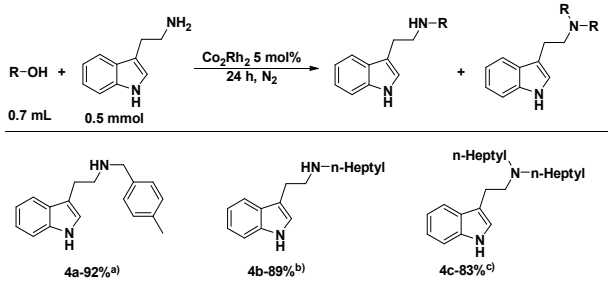


All yields are isolated yields. Reaction conditions for 2° amine: Co_2Rh_2 5 mol% (45 mg), 80 °C, 24 h. Reaction conditions for 3° amine: Co_2Rh_2 5 mol% (45 mg), 120 °C, 24 h. [a] 100 °C

We performed additional experiments to further assess the ability of Co_2Rh_2/C to promote the reactions of other types of substrates (Scheme 1). Tryptamine, containing an indole ring joined to an amino (NH_2) group via an ethyl ($-CH_2-CH_2-$) sidechain, is the common functional group in a set of compounds termed collectively serotonin analogues. Under our reaction conditions, mono and di-alkylation of an amino group were observed with high yields: 92% for the mono-benzylation, and 89% and 83% for the mono and bis-heptylation, respectively.

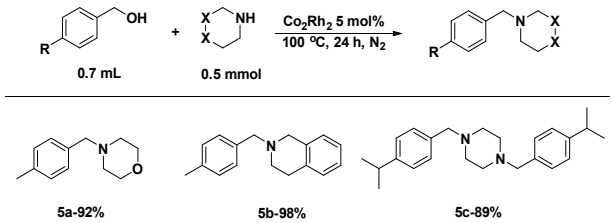
We also examined the reaction of cyclic amines with 4-methylbenzyl alcohol in the presence of 5 mol% Co_2Rh_2/C at 100 °C for 24 h (Scheme 2). High yields were observed for morpholine (**5a**-92%), piperazine (**5c**-89%), and 1,2,3,4-tetrahydroisoquinoline (**5b**-98%). Interestingly, a two-N-alkylation was observed in the case of piperazine.

Scheme 1. Reaction of Tryptamine



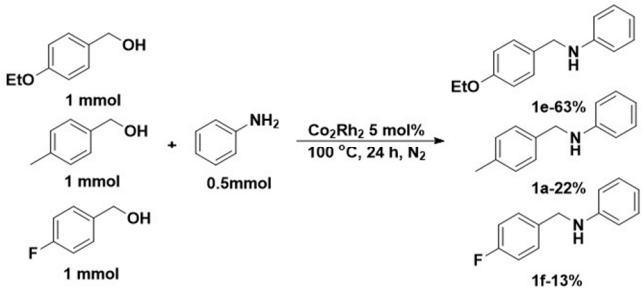
All yields are isolated yields. [a] 80 °C. [b] 100 °C. [c] 130 °C.

Scheme 2. Reaction of Cyclic Amines[a]



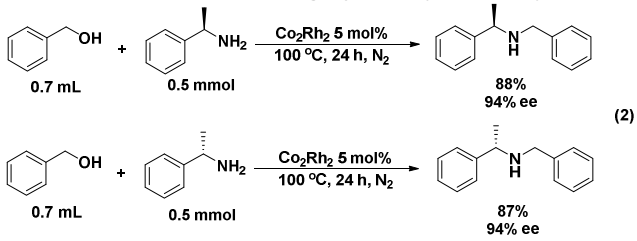
[a] Isolated yields.

To investigate the substitution effects of different functional groups, competitive reactions of 4-methylbenzyl alcohol, 4-fluorobenzylalcohol, and 4-ethoxybenzylalcohol with aniline were performed (Scheme 3). Based on GC-MS analysis, the yields of the corresponding sec-anilines were 22%, 13%, and 63%, respectively. Thus, the electron-rich group on the aromatic ring of benzyl alcohols remarkably enhanced the coupling reaction.



Scheme 3. Competitive Reaction

To illustrate the synthetic utility of our catalytic system, our reaction conditions were applied to benzyl alcohol and optically active 1-phenylethan-1-amines (eq 2). Secondary amines were isolated in high yields (84 ~87%) with an

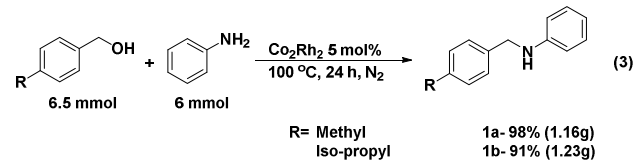


(2)

excellent enantiomeric excess (ee >94%).

In the literature, the reaction of aliphatic alcohol with aliphatic amines by heterogeneous catalysts is rare. However, our results suggest that Co_2Rh_2/C demonstrated high catalytic activities for the coupling of benzylic and aliphatic alcohols, and aliphatic and aromatic amines to produce secondary and tertiary amines selectively under base and ligand-free conditions.

To verify the practicality of the developed method, a gram scale reaction was performed (eq 3): a reaction of 6.5 mmol of benzyl alcohol (R = Me, 0.78 g; R = iPr, 0.96 g) with 6 mmol of aniline afforded high yields of the corresponding secondary amine (R = Me, 98%; 1.16 g; R = iPr, 91%; 1.23 g). Thus, secondary amines can be synthesized

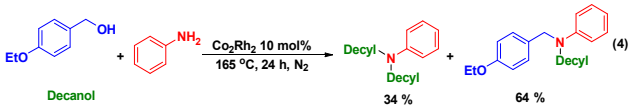


(3)

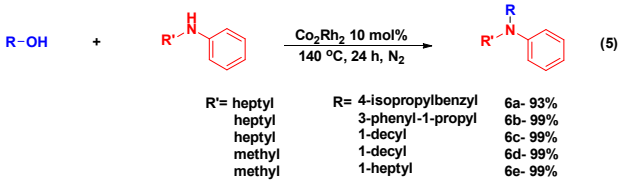
by the alkylation of amine with virtually a theoretical equivalent of primary alcohols.

To demonstrate the usefulness of the present system, we explored the synthesis of unsymmetrically substituted tertiary amines. When aniline, 4-ethoxybenzyl alcohol, and 1-decanol in a mole ratio of 1:1:1.5 were reacted in a one-

step and one-pot reaction, N-decyl-N-(4-ethoxybenzyl)aniline and N,N-decylaniline were isolated in 64% and 34% yields, respectively, with a trace amount of N,N-bis(4-ethoxybenzyl)aniline (eq 4).



Thus, the attempt was a "half way" to success. Then, a two-step reaction was employed for the synthesis of unsymmetrically substituted tertiary amines: aniline was treated with an alcohol to obtain a secondary amine. Then, the synthesized secondary amine was reacted with another alcohol to produce unsymmetrically substituted tertiary amines. After workup, the corresponding tertiary amines (*N*-heptyl-*N*-(4-isopropylbenzyl)aniline), (*N*-heptyl-*N*-(3-phenylpropyl)aniline), (*N*-decyl-*N*-heptylaniline), (*N*-decyl-*N*-methylaniline), and (*N*-heptyl-*N*-methylaniline) from their corresponding alcohol, were isolated in excellent yields(**6a-**93%, **6b-**99%, **6c-**99%, **6d-**99%, and **6e-**99%), respectively (eq 5).



The reusability of Co_2Rh_2/C was investigated by performing the alkylation of aniline with 4-methylbenzyl alcohol (Table 5). A high level of activity (97–99%) was maintained even after ten cycles of reuse. The catalytic system demonstrated an excellent capability of reuse and a significant air-stability under the reaction conditions.

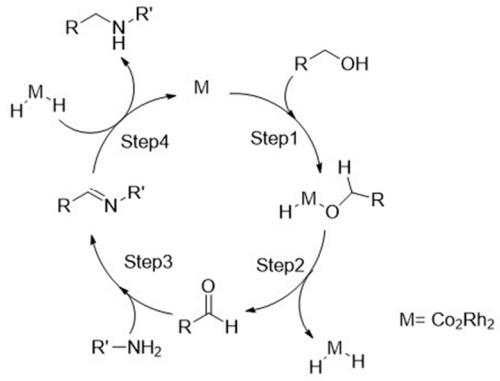
Table 5. Recycle test

Run	Yield (%)[a)]
	1a
1	99
2	99
3	98
4	99
5	97
6	98
7	98
8	99
9	97
10	99

[a)] Isolated yields.

The Co_2Rh_2/C-catalyzed dehydrogenative N-alkylation of amines with alcohols may proceed through a number of sequential reactions. (Scheme 4) An alcohol coordinates to a metal with the formation of a metal-hydride species (step 1). Then, the metal complex transforms into a metal-dihydride and an aldehyde by a β-hydride elimination (step 2). An amine readily forms an imine with the aldehyde (step 3). Finally, a hydrogen transfer from the metal dihydride to the imine intermediate proceeds to afford a desired secondary amine (step 4). Tertiary amine formation should proceed through similar sequential processes.

Scheme 4. Proposed Catalytic Cycle



Conclusion

In summary, a chemoselective method for the preparation of secondary or tertiary amines from primary amines with alcohols was successfully realized with a heterogeneous bimetallic Co_2Rh_2/C catalyst through a borrowing hydrogen strategy. The catalyst exhibited excellent catalytic activity and selectivity and could be readily recycled. The advantages of this method are the general applicability with different amines and alcohols in high yields and the observed selectivity, which provide an attractive and useful methodology for secondary and tertiary amine synthesis. The present protocol provides a green and concise benign method to access higher-order amines.

EXPERIMENTAL SECTION

General Information. Workup procedures were done in air. Toluene was used after purification. The other solvents were used without further purification. Unless otherwise noted, all commercial materials were used without purification. Commercial available reagents were used as received. High purity Ar (99.999%) was used. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates. TLC plates were visualized by ultraviolet light and treated with $KMnO_4$ stain followed by gentle heating. Flash column chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with Agilent 400-MR DD2 (400 MHz and 100 MHz, respectively) and Varian (500 MHz and 125 MHz, respectively) spectrometer. ^1H NMR spectra were taken in $CDCl_3$ and were referenced to residual TMS (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of the $^{13}C\{^1H\}$ NMR spectra were measured relative to $CDCl_3$ (77.16 ppm). High-Resolution Mass Spectra were obtained at the Korea Basic Science Institute (Daegu, South Korea) on a Jeol JMS 700 high resolution mass spectrometer. All reactants are commercially available compounds.

Synthesis of Co/Rh Nanoparticles on Charcoal To a two-neck flask were added *o*-dichlorobenzene (10 mL), oleic acid (0.2 mL), and trioctylphosphine oxide (0.4 g). While the solution was

heated at 180°C, a solution of metal carbonyl $Co_2Rh_2(CO)_{12}$ (0.8 g) in 25 mL of *o*-dichlorobenzene was injected into the flask. The resulting solution was heated to 180°C for 2 h and then concentrated to a volume of 5 mL. The concentrated solution was cooled to room temperature. To the cooled solution was added 30 mL of THF. After the solution was well stirred for 10 min, flame-dried charcoal (1.6 g) was added to the solution. After the resulting solution had been refluxed for 12 h, the precipitates were filtered and washed with diethyl ether (20 mL), dichloromethane (20 mL), acetone (20 mL), and methanol (20 mL). Vacuum dry gave a black solid.

General Procedure for Synthesis and Characterization for reaction of Anilines Reactions were performed in a 20 mL Schlenk flask equipped with a stirring bar and the followings were placed in the Schlenk flask in the order: amine (0.5 mmol), alcohol (0.7 mL) and 5 mol% ~ 10 mol% Co_2Rh_2 (45 mg ~ 90 mg of the immobilized Co_2Rh_2/C). The flask was purged with N_2 gas, and heated at 100 °C~165 °C for 24 h. After the flask was cooled to room temperature, the solution was filtered and the product was isolated by chromatography on a silica gel column eluting with hexane and ethyl acetate (silica, 1/80 – 1/150 EtOAc/hexane).

General Procedure for Synthesis and Characterization for reaction of Aliphatic amines Reactions were performed in a 20 mL Schlenk flask equipped with a stirring bar and the followings were placed in the Schlenk flask in the order: amine (0.5 mmol), alcohol (0.7 mL) and 5 mol% Co_2Rh_2 (45 mg of the immobilized Co_2Rh_2/C). The flask was purged with N_2 gas, and heated at 80 °C~120 °C for 24 h. After the flask was cooled to room temperature, the solution was filtered and the product was isolated by chromatography on a silica gel column eluting with hexane and ethyl acetate for 3aa-3ee (silica, 1/100 EtOAc/hexane), dichloromethane and methanol for 3a-3l (silica, 1/100 CH_2Cl_2/MeOH) .

General Procedure for Synthesis and Characterization for reaction of cyclic amines Reactions were performed in a 20 mL Schlenk flask equipped with a stirring bar and the followings were placed in the Schlenk flask in the order: amine (0.5 mmol), alcohol (0.7 mL) and 5 mol% Co_2Rh_2 (45 mg of the immobilized Co_2Rh_2/C). The flask was purged with N_2 gas, and heated at 100 °C for 24 h. After the flask was cooled to room temperature, the solution was filtered and the product was isolated by chromatography on a silica gel column eluting with dichloromethane and methanol (silica, 1/100 CH_2Cl_2/MeOH).

General Procedure for Synthesis and Characterization for methylation and ethylation of aniline Reactions were performed in a 30 mL stainless steel autoclave equipped with a stirring bar and the followings were place in the autoclave in the order: amine (0.5 mmol), alcohol (3 mL) and 5 mol% for ethylation ~ 10 mol% for methylation Co_2Rh_2 (45 mg~ 90 mg of the immobilized Co_2Rh_2/C). The reactor was purged with Ar gas, and charged with 1 atm of Ar and heated at (ethylation: 120 °C for 24 h) or (methylation: 180 °C for 48 h). After the reactor was cooled to room temperature, the solution was filtered and concentrated, and the product was isolated by chromatography on a silica gel column eluting with hexane and ethyl acetate. (silica, 1/150 EtOAc/hexane)

General Procedure for Synthesis and Characterization for reaction of asymmetric tertiary amine(eq5) Reactions were performed in a 20 mL schlenk flask equipped with a stirring bar and the followings were placed in the schlenk flask in the order: amine (0.5 mmol), alcohol (0.7 mL) and 10 mol% Co_2Rh_2 (90 mg of the immobilized Co_2Rh_2/C). The flask was purged with N_2 gas, and heated at 140 °C for 24 h. After the flask was cooled to room temperature, the solution was filtered and the product was isolated by chromatography on a silica gel column eluting with hexane and ethyl acetate (silica, 1/100 EtOAc/hexane).

Gram scale experiment Reactions were performed in a 20 mL schlenk flask equipped with a stirring bar and the followings were place in the schlenk flask in the order: aniline (6 mmol), alcohol (6.5 mmmol) and 5 mol% Co_2Rh_2 (540 mg of the immobilized Co_2Rh_2/C). The flask was purged with Ar gas and heated at 100 °C for 24 h. After the reactor was cooled to room temperature, the solution was filtered and concentrated, and the product was isolated by chromatography on a silica gel column eluting with hexane and ethyl acetate (silica, 1/100 EtOAc/hexane).

*N-(4-Methylbenzyl)aniline (**1a**)*. Colorless oil (98 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.7 Hz, 2 H), 7.04 (m, 4 H), 6.59 (t, *J* = 7.3 Hz, 1 H), 6.48 (d, *J* = 7.9 Hz, 2 H), 4.11 (s, 2 H), 3.79 (s, 1 H), 2.27 – 2.18 (m, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.3, 136.8, 136.5, 129.33, 129.27, 127.5, 117.5, 112.9, 48.1, 21.1; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{14}H_{15}N]^+$: 197.1204, found 197.1205.

*N-(4-Isopropylbenzyl)aniline (**1c**). C*olorless oil (112 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2 H), 7.14 – 7.04 (m, 4 H), 6.62 (t, *J* = 7.3 Hz, 1 H), 6.55 (d, *J* = 7.6 Hz, 2 H), 4.18 (s, 2 H), 3.86 (s, 1 H), 2.81 (m, 1H), 1.17 (d, *J* = 6.9 Hz, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.39, 148.07, 136.86, 129.36, 127.75, 126.79, 117.58, 112.92, 48.22, 33.94, 24.16; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{16}H_{19}N]^+$: 225.1517, found 225.1518.

*N-(4-(tert-Butyl)benzyl)aniline (**1d**).* White solid(107 mg, 89%); m.p. 38.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.3 Hz, 2 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 7.08 (m, 2 H), 6.62 (t, *J* = 7.3 Hz, 1 H), 6.55 (d, *J* = 7.7 Hz, 2 H), 4.19 (s, 2 H), 3.86 (s, 1 H), 1.23 (s, 9 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 150.6, 148.4, 136.5, 129.4, 127.5, 125.7, 117.6, 112.9, 48.1, 34.6, 31.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{17}H_{21}N]^+$: 239.1674, found 239.1672.

*N-(4-Ethoxybenzyl)aniline (**1e**).* Colorless oil (112 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.6 Hz, 2 H), 7.08 (t, *J* = 7.3 Hz, 2 H), 6.78 (d, *J* = 7.3 Hz, 2 H), 6.62 (t, *J* = 7.2 Hz, 1 H), 6.54 (d, *J* = 7.8 Hz, 2 H), 4.14 (s, 2 H), 3.92 (q, *J* = 6.9 Hz, 2 H), 3.83 (s, 1 H), 1.31 (m, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.3, 148.6, 131.4, 129.3, 128.9, 117.6, 114.7, 112.9, 63.6, 47.9, 14.97; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{15}H_{17}NO]^+$: 227.1310, found 227.1312.

*N-(4-Fluorobenzyl)aniline (**1f**).* Yellow oil (82 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2 H), 7.10 (t, *J* = 7.3 Hz, 2 H), 6.95 (t, *J* = 8.0 Hz, 2 H), 6.65 (t, *J* = 7.0 Hz, 1 H), 6.55 (d, *J* = 8.2 Hz, 2 H), 4.23 (s, 2 H), 3.94 (s, 1 H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.4, 161.0, 148.0, 135.24, 135.21, 129.4, 129.18, 129.10, 117.9, 115.7, 115.5, 113.0, 47.8; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{13}H_{12}NF]^+$: 201.0954, found 201.0952.

*N-(3,5-Dimethoxybenzyl)aniline (**1g**).* Colorless oil (101 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.6 Hz, 2 H), 6.64 (t, *J* = 7.2 Hz, 1 H), 6.55 (d, *J* = 7.9 Hz, 2 H), 6.46 (s, 2 H), 6.30 (s, 1 H), 4.19 (s, 2 H), 3.95 (s, 1 H), 3.70 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.2, 148.3, 142.2, 129.4, 117.8, 113.0, 105.4, 99.2, 55.5, 48.7; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{15}H_{17}NO_2]^+$: 243.1259, found 243.1261.

*N-Benzylaniline (**1b**)*. Colorless oil (90 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 4 H), 7.19 (m, 1 H), 7.10 (t, *J* = 7.6 Hz, 2 H), 6.64 (t, *J* = 7.3 Hz, 1 H), 6.57 (d, *J* = 8.5 Hz, 2 H), 4.25 (s, 2 H), 4.06 (s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.2, 139.5, 129.4, 128.8, 127.7, 127.4, 117.8, 113.1, 48.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{13}H_{13}N]^+$: 183.1048, found 183.1049.

*4-(tert-Butyl)-N-(4-methylbenzyl)aniline (**1h**).* Off-white solid (103 mg, 81 %); m.p. 42 - 44 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 7.04 (d, *J* = 7.8 Hz, 2 H), 6.48 (d, *J* = 8.5 Hz, 2 H), 4.14 (s, 2 H), 3.74 (s, 1 H), 2.23 (s, 3 H), 1.18 (s, 9 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.0, 140.3, 136.84, 136.75, 129.4, 127.7, 126.1, 112.7, 48.5, 34.0, 31.7, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{18}H_{23}N]^+$: 253.1830, found 253.1832.

*N-(4-Methylbenzyl)-4-phenoxyaniline (**1i**).* Colorless to yellow oil (130 mg, 90 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (m, 4 H), 7.02 (d, *J* = 7.8 Hz, 2 H), 6.85 (t, *J* = 7.3 Hz, 1 H), 6.77 (m, 4 H), 6.45 (d, *J* = 8.8 Hz, 2 H), 4.09 (s, 2 H), 3.74 (s, 1 H), 2.21 (s, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.2, 147.7, 145.0, 136.9, 136.4, 129.5, 129.4, 127.6, 122.0, 121.3, 117.2, 113.9, 48.6, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{20}H_{19}NO]^+$: 289.1467, found 289.1468.

*3-Fluoro-N-(4-methylbenzyl)aniline (**1j**).* Colorless to yellow oil (77 mg, 71 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.9 Hz, 2 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 7.14 (m, 1 H), 6.48 – 6.40 (m, 2 H), 6.36 (m, 1H), 4.30 (s, 2 H), 4.14 (s, 1 H), 2.41 (s, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.2, 163.3, 150.0, 137.2, 135.9, 130.4, 130.3, 129.5, 127.6, 108.8, 104.0, 103.9, 99.7, 99.5, 48.1, 21.2; ^{19}F NMR (376 MHz, cdcl$_3$) δ -115.60, -115.62, -115.63, -115.64, -115.65, -115.66, -115.68; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{14}H_{14}NF]^+$: 215.1110, found 215.1107.

*3,5-Dimethyl-N-(4-methylbenzyl)aniline (**1k**).* Colorless oil (94 mg, 83 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.9 Hz, 2 H), 7.03 (d, *J* = 7.8 Hz, 2 H), 6.28 (s, 1 H), 6.16 (s, 2 H), 4.12 (s, 2 H), 3.69 (s, 1 H), 2.23 (s, 3 H), 2.12 (s, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.5, 138.9, 136.8, 136.7, 129.3, 127.6, 119.6, 110.9, 48.2, 21.6, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{16}H_{19}N]^+$: 225.1517, found 225.1515.

*N,N-bis(4-Methylbenzyl)aniline (**1aa**).* Colorless oil (139 mg, 92 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31 – 6.21 (m, 10 H), 5.87 (d, *J* = 8.0 Hz, 2 H), 5.82 (t, *J* = 7.2 Hz, 1 H), 3.73 (s, 4 H), 1.47 (s, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.6, 135.7, 129.4, 129.3, 126.82, 116.7, 112.7, 54.0, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{22}H_{23}N]^+$: 301.1830, found 301.1833.

*N,N-bis(4-Isopropylbenzyl)aniline (**1bb**).* Colorless oil (173 mg, 97 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.05 (m, 10 H), 6.67 (d, *J* = 8.0 Hz, 2 H), 6.61 (t, *J* = 7.3 Hz, 1 H), 4.54 (s, 4 H), 2.82 (m, 2 H), 1.17 (t, *J* = 6.8 Hz, 12 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.5, 147.6, 136.1, 129.3, 126.78, 126.75, 116.6, 112.5, 54.0, 33.9, 24.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{26}H_{31}N]^+$: 357.2457, found 357.2459.

*3,5-Dimethyl-N,N-bis(4-methylbenzyl)aniline (**1cc**).* Colorless oil (153 mg, 93 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (m, 8 H), 6.31 (m, 3 H), 4.47 (s, 4 H), 2.26 (s, 6 H), 2.13 (s, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.9, 138.9, 136.4, 135.9, 129.4, 126.9, 118.8, 110.4, 53.5, 21.9, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{24}H_{27}N]^+$: 329.2143, found 329.2141.

N,N-bis(4-Methylbenzyl)-4-phenoxyaniline (***1dd**).* Yellow oil (195 mg, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (m, 3 H), 7.06 (m, 7H), 6.95 – 6.74 (m, 5 H), 6.62 (m, 2 H), 4.49 (m, 4 H), 2.25 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.1, 147.3, 146.2, 136.6, 135.7, 129.6, 129.4, 126.8, 122.1, 121.0, 117.4, 113.8, 54.6, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{28}H_{27}NO]^+$: 393.2093, found 393.2095.

*4-(tert-Butyl)-N,N-bis(4-methylbenzyl)aniline (**1ee**).* Colorless to yellow oil (168 mg, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 6.99 (m, 10 H), 6.58 (m, 2 H), 4.47 (s, 4 H), 2.23 (s, 6 H), 1.16 (m, 9 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.3, 139.2, 136.4, 136.0, 129.4, 126.9, 126.0, 112.2, 54.1, 33.9, 31.7, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{26}H_{31}N]^+$: 357.2457, found 357.2454.

*N-Decylaniline (**2a**).* Colorless oil (110 mg, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (m, 2 H), 6.60 (m, 1 H), 6.51 (d, *J* = 8.3 Hz, 2 H), 3.49 (s, 1 H), 3.01 (t, *J* = 7.1 Hz, 2 H), 1.53 (m, 2 H), 1.36 – 1.13 (m, 14 H), 0.81 (t, *J* = 6.7 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.7, 129.3, 117.2, 112.8, 44.2, 32.0, 29.8, 29.7, 29.6, 29.5, 27.3, 22.8, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{16}H_{27}N]^+$: 233.2143, found 233.2145.

*N-Heptylaniline (**2b**).* Colorless oil (86 mg, 90 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (m, 2 H), 6.60 (m, 1 H), 6.51 (m, 2 H), 3.49 (s, 1 H), 3.07 – 2.95 (m, 2 H), 1.63 – 1.43 (m, 2 H), 1.26 (m, 8 H), 0.81 (m, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.66, 129.31, 117.16, 112.79, 44.2, 31.9, 29.7, 29.3, 27.3, 22.8, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{13}H_{21}N]^+$: 191.1674, found 191.1672.

*N-Tetradecylaniline (**2c**).* White solid (110 mg, 76 %); m.p. 32.3 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 – 7.05 (m, 2 H), 6.60 (t, *J* = 7.3 Hz, 1 H), 6.53 – 6.50 (m, 2 H), 3.50 (s, 1 H), 3.02 (t, *J* = 7.1 Hz, 2 H), 1.53 (m, 2 H), 1.37 – 1.13 (m, 22 H), 0.81 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.7, 129.3, 117.2, 112.8, 44.2, 32.1, 29.82, 29.75, 29.6, 29.5, 27.3, 22.9, 14.3; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{20}H_{35}N]^+$: 289.2770, found 289.2767.

*N-(3-Phenylpropyl)aniline (**2d**).* Colorless oil (60 mg, 56 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 2 H), 7.09 (m, 5 H), 6.60 (t, *J* = 7.3 Hz, 1 H), 6.48 (d, *J* = 7.7 Hz, 2 H), 3.49 (s, 1 H), 3.05 (t, *J* = 7.0 Hz, 2 H), 2.64 (t, *J* = 7.6 Hz, 2 H), 1.85 (m, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.4, 141.7, 129.3, 128.49, 128.46, 126.0, 117.3, 112.8, 43.5, 33.5, 31.1; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{15}H_{17}N]^+$: 211.1361, found 211.1362.

*N-(1-Phenylethyl)aniline (**2e**).* Colorless oil (90 mg, 91 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 4 H), 7.13 (t, *J* = 7.2 Hz, 1 H), 7.00 (t, *J* = 7.3 Hz, 2 H), 6.56 (t, *J* = 7.3 Hz, 1 H), 6.42 (d, *J* = 7.8 Hz, 2 H), 4.40 (q, *J* = 6.5 Hz, 1 H), 3.92 (s, 1 H), 1.42 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 145.3, 129.2, 128.7, 127.0, 126.0, 117.4, 113.4, 53.6, 25.1; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{14}H_{15}N]^+$: 197.1204, found 197.1207.

*N-(4-Phenylbutan-2-yl)aniline (**2f**).* Colorless oil (91 mg, 81 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 2 H), 7.14 – 7.03 (m, 5 H), 6.57 (t, *J* = 7.3 Hz, 1 H), 6.43 (d, *J* = 8.6 Hz, 2 H), 3.39 (m, 1 H), 3.32 (s, 1 H), 2.63 (t, *J* = 7.9 Hz, 2 H), 1.77 (m, 1 H), 1.67 (m, 1 H), 1.11 (d, *J* = 6.3 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.7, 142.1, 129.3, 128.53, 128.48, 125.9, 117.0, 113.3, 48.0, 38.9, 32.6, 21.0; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{16}H_{19}N]^+$: 225.1517, found 225.1516.

*4-(tert-Butyl)-N-decylaniline (**2i**).* Colorless to red oil (142 mg, 89 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2 H), 6.47 (d, *J* = 8.2 Hz, 2 H), 3.40 (s, 1 H), 3.00 (t, *J* = 7.0 Hz, 2 H), 1.57 – 1.46 (m, 2 H), 1.37 – 1.12 (m, 23 H), 0.81 (t, *J* = 6.4 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.4, 139.9, 126.1, 112.5, 44.4, 33.9, 32.0, 31.7, 29.84, 29.76, 29.72, 29.6, 29.5, 27.4, 22.8, 14.3; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{20}H_{35}N]^+$: 289.2770, found 289.2771.

*N-Decyl-4-phenoxyaniline (**2j**).* Colorless oil (140 mg, 86 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.2 Hz, 2 H), 6.90 (t, *J* = 7.3 Hz, 1 H), 6.86 – 6.73 (m, 4 H), 6.50 (d, *J* = 7.8 Hz, 2 H), 3.44 (s, 1 H), 3.00 (t, *J* = 6.9 Hz, 2 H), 1.53 (m, 2 H), 1.25 (m, 14 H), 0.80 (t, *J* = 6.2 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.4, 147.6, 145.4, 129.6, 122.0, 121.4, 117.2, 113.8, 44.8, 32.1, 29.81, 29.75, 29.71, 29.6, 29.5, 27.4, 22.8, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{22}H_{31}NO]^+$: 325.2406, found 325.2408.

*N-Decyl-3,5-dimethylaniline (**2k**).* Colorless to yellow oil (109 mg, 83 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.43 (s, 1 H), 6.32 (s, 2 H), 3.55 (s, 1 H), 3.15 (t, *J* = 7.1 Hz, 2 H), 2.32 (s, 6 H), 1.66 (m, 2 H), 1.50 – 1.29 (m, 14 H), 0.97 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.8, 138.9, 119.2, 110.8, 44.2, 32.0, 29.79, 29.76, 29.72, 29.6, 29.5, 27.3, 22.8, 21.6, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{18}H_{31}N]^+$: 261.2457, found 261.2459.

*N-3,5-Trimethylaniline (**2h**).* Colorless to yellow oil (47 mg, 70 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (s, 1 H), 6.22 (s, 2 H), 2.76 (s, 3 H), 2.19 (s, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.0, 119.7, 110.7, 31.1, 21.6; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_9H_{13}N]^+$: 135.1048, found 135.1049.

*N,N-Didecylaniline (**2bb**).* Colorless oil (175 mg, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 2 H), 6.81 – 6.64 (m, 3 H), 3.43 – 3.29 (m, 4 H), 1.68 (m, 4 H), 1.41 (m, 28 H), 1.08 – 0.97 (m, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.3, 129.23, 115.2, 111.9, 51.2, 32.1, 29.8, 29.74, 29.71, 29.5, 27.42, 27.37, 22.8, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{26}H_{47}N]^+$: 373.3709, found 373.3710 .

*N,N-Diheptylaniline (**2aa**).* Colorless oil (143 mg, 99 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.07 (m, 2 H), 6.56 (m, 3 H), 3.24 – 3.10 (m, 4 H), 1.58 – 1.46 (m, 4 H), 1.24 (m, 16 H), 0.83 (t, *J* = 7.0 Hz, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.6, 129.3, 115.2, 111.8, 51.2, 32.1, 29.4, 27.4, 27.3, 22.8, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{20}H_{35}N]^+$: 289.2770, found 289.2771.

*N,N-bis(3-Phenylpropyl)aniline (**2cc**).* Colorless oil (161 mg, 98 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (m, 4 H), 7.11 – 7.00 (m, 8 H), 6.53 (t, *J* = 7.2 Hz, 1 H), 6.47 (d, *J* = 8.6 Hz, 2 H), 3.22 – 3.12 (m, 4 H), 2.53 (t, *J* = 7.7 Hz, 4 H), 1.86 – 1.73 (m, 4 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.2, 141.9, 129.3, 128.51, 128.47, 126.0, 115.8, 112.3, 50.7, 33.5, 28.9; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{24}H_{27}N]^+$: 329.2143, found 329.2147.

*N,N-Didecyl-3-fluoroaniline (**2dd**).* Colorless oil (176 mg, 90 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.1 Hz, 1 H), 6.28 (d, *J* = 8.3 Hz, 1 H), 6.23 – 6.15 (m, 2 H), 3.24 – 3.03 (m, 4 H), 1.48 (m, 4 H), 1.21 (m, 28 H), 0.81 (t, *J* = 6.5 Hz, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.5, 163.6, 150.2, 150.1, 130.2, 130.1, 107.4, 101.7, 101.5, 98.8, 98.5, 51.3, 32.1, 29.8, 29.74, 29.69, 29.5, 27.4, 27.3, 22.8, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.80, -112.82, -112.83, -112.84, -112.85, -112.87; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{26}H_{46}FN]^+$: 391.3614, found 391.3611.

*4-(tert-Butyl)-N,N-didecylaniline (**2ee**).* Colorless oil (208 mg, 97 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.5 Hz, 2 H), 6.50 (d, *J* = 8.5 Hz, 2 H), 3.16 – 3.09 (m, 4 H), 1.46 (m, 4 H), 1.20 (m, 37 H), 0.80 (t, *J* = 6.8 Hz, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.2, 137.8, 126.1, 111.5, 51.3, 33.8, 32.1, 31.7, 29.9, 29.8, 29.5, 27.5, 27.4, 22.9, 14.3; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{30}H_{55}N]^+$: 429.4355, found 429.4332.

*N-(4-Methylbenzyl)decan-1-amine (**3a**).* Colorless oil (120 mg, 92 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.20 (d, *J* = 7.9 Hz, 2 H), 7.13 (d, *J* = 7.9 Hz, 2 H), 3.70 (s, 2 H), 2.62 – 2.50 (m, 2 H), 2.31 (s, 3 H), 1.59 – 1.45 (m, 2 H), 1.30 (m,14 H), 0.89 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.0, 137.0, 130.1, 129.6, 54.0, 49.8, 33.0, 30.7, 30.6, 30.4, 30.1, 28.4, 23.7, 21.2, 14.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{18}H_{31}N]^+$: 261.2457, found 261.2457.

N-(4-Isopropylbenzyl)decan-1-amine *(**3b**).* Colorless oil (138 mg, 96 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.26 (d, *J* = 8.1 Hz, 2 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 3.75 (s, 2 H), 2.94 – 2.81 (m, 1 H), 2.66 – 2.55 (m, 2 H), 1.61 – 1.49 (m, 2 H), 1.36 – 1.25 (m, 14 H), 1.23 (d, *J* = 7.0 Hz, 6 H), 0.89 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 149.2, 136.8, 129.7, 127.5, 53.9, 49.7, 35.0, 33.0, 30.6, 30.5, 30.4, 29.9, 28.3, 24.5, 23.7, 14.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{20}H_{35}N]^+$: 289.2770, found 289.2767.

*N-(4-(tert-Butyl)benzyl)decan-1-amine (**3c**).* White solid (123 mg, 81 %); m.p. 73 - 75 ^{o}C. ^{1}H NMR (500 MHz, CD_3OD) δ 7.37 (d, *J* = 8.1 Hz, 2 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 3.74 (s, 2 H), 2.66 – 2.54 (m, 2 H), 1.55 (m, 2 H), 1.30 (m, 20 H), 0.90 (t, *J* = 6.7 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 151.4, 136.6, 129.4, 126.4, 53.9, 49.8, 35.3, 33.0, 31.9, 30.7, 30.6, 30.4, 30.0, 28.4, 23.7, 14.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{21}H_{37}N]^+$: 303.2926, found 303.2923.

*N-(4-Ethoxybenzyl)decan-1-amine (**3d**).* Colorless oil (133 mg, 91 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.24 (d, *J* = 8.6 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 4.00 (q, *J* = 7.0 Hz, 2 H), 3.71 (s, 2 H), 2.63 – 2.55 (m, 2 H), 1.60 – 1.46 (m, 2 H), 1.36 (t, *J* = 7.0 Hz, 3 H), 1.28 (m, 14 H), 0.89 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 159.9, 131.3, 131.0, 115.6, 64.5, 53.6, 49.6, 33.1, 30.7, 30.6, 30.4, 29.9, 28.4, 23.7, 15.2, 14.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{19}H_{33}NO]^+$: 291.2562, found 291.2563.

*N-(3,5-Dimethoxybenzyl)decan-1-amine (**3e**).* Colorless oil (128 mg, 84 %). ^{1}H NMR (500 MHz, CD_3OD) δ 6.51 (d, *J* = 2.2 Hz, 2 H), 6.37 (t, *J* = 2.2 Hz, 1 H), 3.75 (s, 6 H), 3.67 (s, 2 H), 2.60 – 2.51 (m, 2 H), 1.56 – 1.48 (m, 2 H), 1.28 (m, 14 H), 0.89 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 162.4, 142.5, 107.4, 100.2, 55.7, 54.5, 49.8, 33.0, 30.7, 30.6, 30.4, 30.2, 28.4, 23.7, 14.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{19}H_{33}NO_2]^+$: 307.2511, found 307.2507.

*N-(4-Methylbenzyl)hexan-1-amine (**3f**).* Colorless oil (85 mg, 83 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.21 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 3.72 (s, 2 H), 2.64 – 2.52 (m, 2 H), 2.30 (s, 3 H), 1.58 – 1.44 (m, 2 H), 1.37 – 1.22 (m, 6 H), 0.89 (t, *J* = 6.7 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.1, 136.6, 130.1, 129.6, 53.9, 49.8, 32.8, 30.0, 28.0, 23.6, 21.2, 14.4; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{14}H_{23}N]^+$: 205.1830, found 205.1829.

*N-(4-Methylbenzyl)dodecan-1-amine (**3g**).* White sloid (121 mg, 84 %); m.p. 62 - 64 ^{o}C. ^{1}H NMR (500 MHz, CD_3OD) δ 7.22 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 3.74 (s, 2 H), 2.65 – 2.54 (m, 2 H), 2.30 (s, 3 H), 1.58 – 1.49 (m, 2 H), 1.28 (m, 18 H), 0.89 (t, *J* = 7.0 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.3, 136.1, 130.2, 129.7, 53.8, 49.6, 33.1, 30.8, 30.7, 30.7, 30.6, 30.5, 29.8, 28.3, 23.7, 21.3, 14.5; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{20}H_{35}N]^+$: 289.2770, found 289.2766.

*N-(4-Methylbenzyl)-4-phenylbutan-1-amine (**3h**).* Yellow oil (84 mg, 66 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.25 – 7.15 (m, 4 H), 7.12 (m, 5 H), 3.66 (s, 2 H), 2.56 (m, 4 H), 2.29 (s, 3 H), 1.55 (m, 4 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 143.4, 138.0, 136.8, 130.1, 129.6, 129.4, 129.3, 126.7, 53.9, 49.5, 36.6, 30.2, 29.6, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{18}H_{23}N]^+$: 253.1830, found 253.1830.

*N-(4-Methoxybenzyl)-1-(p-tolyl)methanamine (**3i**).* Colorless oil (118 mg, 98 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.22 (d, *J* = 8.7 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 7.9 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 3.76 (s, 3 H), 3.65 (s, 2 H), 3.64 (s, 2 H), 2.30 (s, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 160.4, 137.9, 137.5, 132.6, 130.8, 130.1, 129.5, 114.9, 55.7, 53.2, 52.9, 21.1; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{16}H_{19}NO]^+$: 241.1467, found 241.1464.

*N-(4-Methylbenzyl)cyclohexanamine (**3j**).* Colorless oil (98 mg, 97 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.21 (d, *J* = 7.9 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 3.74 (s, 2 H), 2.50 (m, 1 H), 2.29 (s, 3 H), 1.99 – 1.90 (m, 2 H), 1.78 – 1.69 (m, 2 H), 1.62 (m, 1 H), 1.32 – 1.09 (m, 5 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.1, 136.8, 130.2, 129.6, 57.1, 50.8, 33.3, 27.1, 26.1, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{14}H_{21}N]^+$: 203.1674, found 203.1676.

*3-Isopropoxy-N-(4-methylbenzyl)propan-1-amine (**3k**).* Colorless oil (105 mg, 95 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.20 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 3.71 (s, 2 H), 3.59 – 3.49 (m, 1 H), 3.46 (t, *J* = 6.1 Hz, 2 H), 2.68 (t, *J* = 7.1 Hz, 2 H), 2.29 (s, 3 H), 1.80 – 1.70 (m, 2 H), 1.09 (d, *J* = 6.2 Hz, 6 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.1, 136.6, 130.1, 129.6, 72.9, 67.8, 54.0, 47.7, 30.3, 22.4, 21.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{14}H_{23}NO]^+$: 221.1780, found 221.1783.

*N,N-bis(4-Methylbenzyl)decan-1-amine (**3aa**).* Colorless oil (161 mg, 88 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (m, 4 H), 7.04 (m, 4 H), 3.43 (s, 4 H), 2.35 – 2.28 (m, 2 H), 2.26 (s, 6 H), 1.46 – 1.39 (m, 2 H), 1.29 – 1.07 (m, 14 H), 0.82 (t, *J* = 7.0 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.2, 136.2, 128.91, 128.86, 58.0, 53.4, 32.1, 29.82, 29.77, 29.69, 29.5, 27.5, 27.1, 22.9, 21.2, 14.3; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{26}H_{39}N]^+$: 365.3083, found 365.3083.

*N,N-bis(4-Isopropylbenzyl)decan-1-amine (**3bb**).* Colorless oil (177 mg, 84 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 4 H), 7.07 (m, 4 H), 3.43 (s, 4 H), 2.80 (m, 2 H), 2.38 – 2.25 (m, 2 H), 1.45 – 1.38 (m, 2 H), 1.15 (m, 26 H), 0.80 (t, *J* = 7.0 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.3, 137.6, 128.8, 126.2, 58.1, 53.6, 33.9, 32.1, 29.83, 29.79, 29.7, 29.5, 27.4, 27.2, 24.2, 22.9, 14.3; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{30}H_{47}N]^+$: 421.3709, found 421.3710.

*N,N-bis(4-Isopropylbenzyl)decan-1-amine (**3cc**).* Colorless oil (182 mg, 86 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (m, 4 H), 6.72 (m, 4 H), 3.89 (q, *J* = 7.0 Hz, 4 H), 3.35 (s, 4 H), 2.30 – 2.21 (m, 2 H), 1.41 – 1.34 (m, 2 H), 1.28 (t, *J* = 7.0 Hz, 6 H), 1.25 – 1.02 (m, 14 H), 0.79 (t, *J* = 7.0 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.9, 132.1, 129.9, 114.2, 63.4, 57.6, 53.2, 32.1, 29.80, 29.75, 29.6, 29.5, 27.4, 27.1, 22.8, 15.0, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{28}H_{43}NO_2]^+$: 425.3294, found 425.3291.

N,N-bis(4-Methylbenzyl)hexan-1-amine (**3dd**). Colorless oil (140 mg, 91 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (m, 4 H), 7.01 (s, 4 H), 3.40 (m, 4 H), 2.28 (t, *J* = 7.2 Hz, 2 H), 2.22 (s, 6 H), 1.46 – 1.32 (m, 2 H), 1.13 (m, 6 H), 0.75 (t, *J* = 7.1 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.1, 136.2, 128.90, 128.85, 58.0, 53.4, 31.9, 27.12, 27.11, 22.8, 21.2, 14.2; HRMS (EI$^+$): m/z M$^+$ calcd for $[C_{22}H_{31}N]^+$: 309.2457, found 309.2454.

*3-Isopropoxy-N,N-bis(4-methylbenzyl)propan-1-amine (**3ee**).* Colorless oil (151 mg, 93 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.9 Hz, 4 H), 7.02 (d, *J* = 7.8 Hz, 4 H), 3.42 (s, 4 H), 3.38 – 3.32 (m, 1 H), 3.30 (t, *J* = 6.8 Hz, 2 H), 2.39 (t, *J* = 6.9 Hz, 2 H), 2.23 (s, 6 H), 1.72 – 1.63 (m, 2 H), 0.99 (d, *J* = 6.1 Hz, 6 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 136.9, 136.3, 128.8, 128.86, 71.4, 66.4, 58.0, 50.2,

27.9, 22.2, 21.2; HRMS (EI+): m/z M+ calcd for $[C_{22}H_{31}NO]^+$: 325.2406, found 325.2403.

*N-Decylcyclohexanamine (**3l**).* Colorless oil (111 mg, 93 %). ^{1}H NMR (500 MHz, CD_3OD) δ 2.59 – 2.53 (m, 2 H), 2.42 (m, 1 H), 1.94 – 1.85 (m, 2 H), 1.78 – 1.71 (m, 2 H), 1.66 – 1.59 (m, 1 H), 1.52 – 1.44 (m, 2 H), 1.35 – 1.22 (m, 16 H), 1.22 – 1.13 (m, 1 H), 1.13 – 1.02 (m, 2 H), 0.88 (t, *J* = 7.0 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 58.1, 47.6, 33.7, 33.1, 30.71, 30.68, 30.63, 30.5, 28.5, 27.2, 26.2, 23.7, 14.5; HRMS (EI+): m/z M+ calcd for $[C_{16}H_{33}N]^+$: 239.2613, found 239.2610.

*2-(1H-Indol-3-yl)-N-(4-methylbenzyl)ethan-1-amine (**4a**).* Colorless oil (121 mg, 92 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.50 (d, *J* = 7.9 Hz, 1 H), 7.33 (d, *J* = 8.1 Hz, 1 H), 7.15 – 7.03 (m, 5 H), 6.99 (m, 2 H), 3.68 (s, 2 H), 2.96 (t, *J* = 6.9 Hz, 2 H), 2.89 (t, *J* = 6.7 Hz, 2 H), 2.27 (s, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.21, 138.16, 136.3, 130.1, 129.5, 128.6, 123.5, 122.4, 119.6, 119.3, 113.0, 112.3, 53.7, 50.0, 25.7, 21.1; HRMS (EI+): m/z M+ calcd for $[C_{18}H_{20}N_2]^+$: 264.1626, found 264.1629.

*2-(1H-Indol-3-yl)-N-(4-methylbenzyl)ethan-1-amine (**4b**).* White solid (115 mg, 89 %); m.p. 166 - 168 °C. ^{1}H NMR (400 MHz, CD_3OD) δ 7.58 (d, *J* = 7.9 Hz, 1 H), 7.36 (d, *J* = 8.1 Hz, 1 H), 7.16 (s, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 7.04 (t, *J* = 7.0 Hz, 1 H), 3.25 – 3.17 (m, 2 H), 3.17 – 3.09 (m, 2 H), 2.97 – 2.87 (m, 2 H), 1.70 – 1.57 (m, 2 H), 1.44 – 1.17 (m, 8 H), 0.90 (t, *J* = 6.8 Hz, 3 H); ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 138.3, 128.2, 124.1, 122.7, 120.0, 119.0, 112.5, 110.7, 49.6, 32.8, 29.9, 27.70, 27.65, 23.8, 23.6, 14.4; HRMS (EI+): m/z M+ calcd for $[C_{17}H_{26}N_2]^+$: 258.2096, found 258.2093.

*N-(2-(1H-Indol-3-yl)ethyl)-N-heptylheptan-1-amine (**4c**).* Colorless oil (147 mg, 83 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.52 (d, *J* = 7.9 Hz, 1 H), 7.34 (d, *J* = 8.1 Hz, 1 H), 7.08 (m, 2 H), 7.03 – 6.97 (m, 1 H), 2.93 (m, 4 H), 2.72 – 2.60 (m, 4 H), 1.59 – 1.45 (m, 4 H), 1.32 (m, 16 H), 0.92 (t, *J* = 7.0 Hz, 6 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.2, 128.6, 123.3, 122.4, 119.6, 119.1, 113.3, 112.4, 55.5, 55.0, 33.0, 30.3, 28.5, 27.0, 23.7, 22.9, 14.4; HRMS (EI+): m/z M+ calcd for $[C_{24}H_{40}N_2]^+$: 356.3191, found 356.3187.

*N-Cyclohexylaniline (**2l**).* Colorless oil (81 mg, 93 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.04 (m, 2 H), 6.58 (t, *J* = 7.3 Hz, 1 H), 6.50 (d, *J* = 7.7 Hz, 2 H), 3.42 (s, 1 H), 3.17 (m, 1 H), 2.03 – 1.92 (m, 2 H), 1.74 – 1.64 (m, 2 H), 1.64 – 1.52 (m, 1 H), 1.37 – 1.25 (m, 2 H), 1.20 – 0.97 (m, 4 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.5, 129.3, 116.9, 113.2, 51.8, 33.6, 26.1, 25.1; HRMS (EI+): m/z M+ calcd for $[C_{12}H_{17}N]^+$: 175.1361, found 175.1363.

*2-(4-Methylbenzyl)-1,2,3,4-tetrahydroisoquinoline (**5b**).* Colorless oil (116 mg, 98 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.9 Hz, 2 H), 7.03 (d, *J* = 7.9 Hz, 2 H), 7.01 – 6.95 (m, 3 H), 6.86 (d, *J* = 7.1 Hz, 1 H), 3.52 (m, 4 H), 2.78 (t, *J* = 5.9 Hz, 2 H), 2.61 (t, *J* = 5.9 Hz, 2 H), 2.24 (s, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.7, 135.4, 135.1, 134.5, 129.11, 129.05, 128.7, 126.7, 126.1, 125.6, 62.6, 56.2, 50.7, 29.3, 21.2; HRMS (EI+): m/z M+ calcd for $[C_{17}H_{19}N]^+$: 237.1517, found 237.1516.

*4-(4-Methylbenzyl)morpholine (**5a**).* Colorless oil (88 mg, 92 %). ^{1}H NMR (500 MHz, CD_3OD) δ 7.19 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 3.69 – 3.61 (m, 4 H), 3.44 (s, 2 H), 2.41 (d, *J* = 4.1 Hz, 4 H), 2.30 (s, 3 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 138.1, 135.0, 130.6, 129.9, 67.7, 64.1, 54.5, 21.2; HRMS (EI+): m/z M+ calcd for $[C_{12}H_{17}NO]^+$: 191.1310, found 191.1310.

1,4-bis(4-Isopropylbenzyl)piperazine (**5c**). White solid (156 mg, 89 %); m.p. 58 - 60 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 7.21 (d, *J* = 8.2 Hz, 4 H), 7.17 (d, *J* = 8.1 Hz, 4 H), 3.48 (s, 4 H), 2.87 (m, 2 H), 2.48 (s, 8 H), 1.23 (m, 12 H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 149.3, 135.4, 130.8, 127.3, 63.6, 53.6, 35.1, 24.4; HRMS (EI+): m/z M+ calcd for $[C_{24}H_{34}N_2]^+$: 350.2722, found 350.2719.

*N-Benzyl-1-phenylethan-1-amine (**eq2**).* Colorless oil (D-form 93 mg, 88 %) (L-form 92 mg, 87%)). ^{1}H NMR (400 MHz, CD_3OD) δ 7.29 – 7.06 (m, 10 H), 3.66 (q, *J* = 6.7 Hz, 1 H), 3.45 (m, 2 H), 1.27 (d, *J* = 6.7 Hz, 3 H); ^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ 145.9, 140.8, 129.6, 129.4, 128.2, 128.1, 128.0, 58.5, 52.2, 23.8; HRMS (EI+): m/z M+ calcd for $[C_{15}H_{17}N]^+$: 211.1361, found D-form - 211.1360 L-form – 211.1362.

*N-Heptyl-N-(4-isopropylbenzyl)aniline (**6a**).* Colorless oil (150 mg, 93 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (m, 6 H), 6.57 (m, 3 H), 4.42 (s, 2 H), 3.33 – 3.23 (m, 2 H), 2.86 – 2.73 (m, 1 H), 1.58 (m, 2 H), 1.30 – 1.11 (m, 14 H), 0.80 (t, *J* = 6.7 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.8, 147.4, 136.6, 129.3, 126.7, 126.6, 115.9, 112.2, 54.3, 51.4, 33.9, 32.0, 29.3, 27.3, 27.2, 24.2, 22.7, 14.2; HRMS (EI+): m/z M+ calcd for $[C_{23}H_{33}N]^+$: 323.2613, found 323.2611.

*N-Heptyl-N-(3-phenylpropyl)aniline (**6b**).* Colorless oil (153 mg, 99 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.4 Hz, 2 H), 7.08 (t, *J* = 7.2 Hz, 5 H), 6.52 (m, 3 H), 3.22 – 3.15 (m, 2 H), 3.15 – 3.09 (m, 2 H), 2.54 (t, *J* = 7.7 Hz, 2 H), 1.81 (m, 2 H), 1.52 – 1.39 (m, 2 H), 1.19 (m, 8 H), 0.80 (t, *J* = 6.5 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.2, 141.9, 129.3, 128.5, 128.4, 126.0, 115.5, 112.0, 51.2, 50.6, 33.5, 32.0, 29.3, 28.9, 27.4, 27.3, 22.7, 14.2; HRMS (EI+): m/z M+ calcd for $[C_{22}H_{31}N]^+$: 309.2457, found 309.2457.

*N-Decyl-N-heptylaniline (**6c**).* Colorless oil (164 mg, 99 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 2 H), 6.54 (m, 3 H), 3.20 – 3.11 (m, 4 H), 1.50 (m, 4 H), 1.31 – 1.09 (m, 22 H), 0.81 (m, 6 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.4, 129.3, 115.2, 111.9, 51.2, 32.1, 29.8, 29.74, 29.72, 29.5, 29.4, 27.42, 27.37, 27.35, 22.8, 22.8, 14.3; HRMS (EI+): m/z M+ calcd for $[C_{23}H_{41}N]^+$: 331.3239, found 331.3237.

*N-Decyl-N-methylaniline (**6d**).* Colorless oil (123 mg, 99 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 2 H), 6.61 (m, 3 H), 3.26 – 3.18 (m, 2 H), 2.85 (s, 3 H), 1.57 – 1.43 (m, 2 H), 1.31 – 1.16 (m, 14 H), 0.83 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.5, 129.2, 115.9, 112.2, 53.0, 38.4, 32.0, 29.8, 29.73, 29.71, 29.5, 27.3, 26.8, 22.8, 14.3; HRMS (EI+): m/z M+ calcd for $[C_{17}H_{29}N]^+$: 247.2300, found 247.2301.

*N-Heptyl-N-methylaniline (**6e**).* Colorless oil (123 mg, 99 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 2 H), 6.62 (m, 3 H), 3.25 – 3.17 (m, 2 H), 2.85 (s, 3 H), 1.57 – 1.44 (m, 2 H), 1.25 (m, 8 H), 0.83 (t, *J* = 6.9 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.5, 129.2, 115.9, 112.2, 53.0, 38.4, 32.0, 29.4, 27.3, 26.8, 22.8, 14.2; HRMS (EI+): m/z M+ calcd for $[C_{17}H_{23}N]^+$: 205.1830, found 205.1832.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Additional experimental data and copies of ^{1}H, ^{13}C, or ^{19}F spectra for compounds and HPLC chromatograms (PDF).

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