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Chemoselective Reductive Amination of Carbonyl Compounds for the Synthesis of Tertiary Amines Using $SnCl_2 \cdot 2H_2O$/PMHS/MeOH

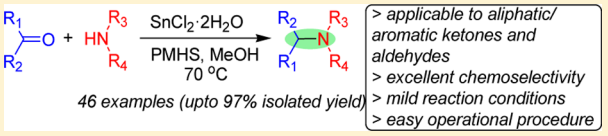
Onkar S. Nayal,[†] Vinod Bhatt,[†,‡] Sushila Sharma,[†,‡] and Neeraj Kumar*[,†,‡]

[†]Natural Product Chemistry and Process Development Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh 176 061, India

[‡]Academy of Scientific and Innovative Research, Anusandhan Bhawan, 2 Rafi Marg, New Delhi 110001, India

Supporting Information

ABSTRACT: Stannous chloride catalyzed chemoselective reductive amination of a variety of carbonyl compounds with aromatic amines has been developed for the synthesis of a diverse range of tertiary amines using inexpensive polymethylhydrosiloxane as reducing agent in methanol. The present method is also applicable for the synthesis of secondary amines including heterocyclic ones.



Tertiary amines are the most common structural feature of naturally occurring biologically active alkaloids, industrial fine chemicals, pharmaceuticals and agrochemicals.[1] Direct reductive amination (DRA) of carbonyl compounds is the most convenient and preferred procedure for the preparation of amines. However, while DRA was widely used for the synthesis of secondary amines in which various types of heterogeneous and homogeneous catalysts have been reported,[2−10] few reports are available for the synthesis of tertiary amines through reductive amination. DRA involving aromatic and aliphatic carbonyl compounds with secondary amines is difficult as the steric hindrance disfavors the iminium ion/enamine formation in equilibrium. Also, the *in situ* transfer hydrogenation of iminium ion is difficult.

Magid et al. reported sodium triacetoxyborohydride as a reagent for the reductive amination of carbonyl compounds with different aliphatic and aromatic primary and sterically unhindered aliphatic secondary amines; however, the method was not applicable to secondary aromatic amines.[11] Ishii and co-workers also developed a method for the alkylation of secondary aliphatic amines with aldehydes.[12] Lee et al. described the reductive amination of aldehydes and aliphatic ketones with secondary amines using $InCl_3$ as catalyst with triethylsilane as reducing agent.[6] Recently, Moulin et al. demonstrated substituted cyclopentadienyl−iron complex catalyzed reductive amination of aliphatic aldehydes with secondary amines using H_2 as hydrogen source.[13] Herein, a protocol has been developed for DRA of carbonyl compounds with primary and secondary amines using easily available, water and air endurance, less corrosive stannous chloride as a catalyst in the presence of polymethylhydrosiloxane (PMHS) and methanol. PMHS is a cheap, easy to handle, air and moisture stable, environment friendly reducing agent, and its byproduct, polysiliconate, is used in silicon industries as an absorbent.[14]

Very few reports have shown the use of tin based catalyst for reductive amination. Xiao group demonstrated reductive amination using catalytic amount of Bu_2SnCl_2 in the presence of phenyl silane[15] and Baba et al. also reported Bu_2SnClH-pyridine-*N*-oxide as a catalyst with diphenylsilane/phenylsilane as a reducing agent.[16] However, these methods were limited for the synthesis of secondary amines.

The present protocol is a versatile method tolerating a variety of carbonyl and amine substrates, including aliphatic and aromatic ketones as well as aldehydes. In our earlier reports, the role of Lewis acidic character of CoPc and $AlCl_3$ was revealed in catalyzing the reductive amination reaction.[9,10] Although these methods were very effective in DRA of carbonyl compounds with primary and secondary amines, unfortunately DRA of ketones with secondary amines was not effective. In this context, we focused on the DRA of carbonyl compounds with secondary amines and screened various Lewis acidic salts. To optimize the reaction conditions, the reductive amination of anisaldehyde with *N*-methylaniline was investigated with variation in reaction parameters such as catalyst, reducing agent, solvent, temperature and time (Table 1). Surprisingly, in the absence of catalyst, the reaction proceeded to afford the product in 15% yield (Table 1, entry 1) which was further lowered in the presence of strong Lewis acids such as $AlCl_3$ and $FeCl_3$ (Table 1, entries 2−3). While no reaction was observed with copper, nickel or cobalt based catalysts (Table 1, entries 4−6), zinc chloride showed some activity toward the reaction (Table 1, entry 7). The best yield of the product was observed with 20 mol % of $SnCl_2 \cdot 2H_2O$ and 2 equiv of PMHS as a reducing agent at 70 °C for 6 h in methanol (Table 1, entry 8). Further, a lower catalyst loading led to lower conversion (Table 1, entry 9), whereas no significant change in the yield of the product was observed with higher catalyst loading (Table 1, entry 10). The investigation of different reducing agents revealed PMHS as the most efficient hydrogen source providing the product in 86% yield (Table 1, entry 8). Comparable yields were recorded with other silanes such as

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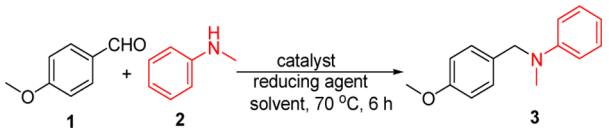
Table 1. Optimisation of Reaction Conditions for DRA of Anisaldehyde with *N*-Methylaniline[a]



entry	catalyst	reducing agent	solvent	yield (%)[b]
1	-	PMHS	MeOH	15
2	$AlCl_3$	PMHS	MeOH	12
3	$FeCl_3$	PMHS	MeOH	9
4	$CuCl_2{\cdot}2H_2O$	PMHS	MeOH	NR
5	$NiCl_2{\cdot}6H_2O$	PMHS	MeOH	NR
6	$CoCl_2{\cdot}6H_2O$	PMHS	MeOH	NR
7	$ZnCl_2$	PMHS	MeOH	33
8	**$SnCl_2{\cdot}2H_2O$**	**PMHS**	**MeOH**	**86**
9	$SnCl_2{\cdot}2H_2O$	PMHS	MeOH	64[c]
10	$SnCl_2{\cdot}2H_2O$	PMHS	MeOH	86[d]
11	$SnCl_2{\cdot}2H_2O$	Et_3SiH	MeOH	57
12	$SnCl_2{\cdot}2H_2O$	Ph_3SiH	MeOH	55
13	$SnCl_2{\cdot}2H_2O$	TMDS	MeOH	61
14	$SnCl_2{\cdot}2H_2O$	$PhSiH_3$	MeOH	68
15	$SnCl_2{\cdot}2H_2O$	PMHS	MeOH	75[e]
16	$SnCl_2{\cdot}2H_2O$	-	MeOH	0[f]
17	$SnCl_2{\cdot}2H_2O$	PMHS	H_2O	55
18	$SnCl_2{\cdot}2H_2O$	PMHS	EtOH	45
19	$SnCl_2{\cdot}2H_2O$	PMHS	*i*PrOH	27
20	$SnCl_2{\cdot}2H_2O$	PMHS	*n*BuOH	24
21	$SnCl_2{\cdot}2H_2O$	PMHS	Toluene	52
22	$SnCl_2{\cdot}2H_2O$	PMHS	THF	31
23	$SnCl_2{\cdot}2H_2O$	PMHS	MeOH	35[g]
24	$SnCl_2{\cdot}2H_2O$	PMHS	MeOH	86[h]

[a]Reaction conditions: Catalyst (20 mol %), **1** (1.1 mmol), **2** (1 mmol), reducing agent (2 mmol), MeOH (3 mL), 70 °C, 6 h. [b]GC yield using hexadecane as internal standard. [c]Quantity of catalyst used was 15 mol %. [d]Quantity of catalyst used was 25 mol %. [e]The reaction was carried out using 1.5 mmol PMHS. [f]Iminum ion observed. [g]The reaction was carried out at rt. [h]The reaction was carried out at 120 °C.

Et_3SiH, Ph_3SiH, TMDS and $PhSiH_3$ (Table 1, entries 11−14). Lowering the quantity of PMHS resulted in the lower yield of the desired product (Table 1, entry 15). As expected, no product was formed in the absence of PMHS; however, iminium ion was observed as major intermediate (Table 1, entry 16). Further, different solvents were screened to investigate the influence of solvent on the yield as the interaction of solvent molecules with Lewis acids drastically influences catalytic activity and methanol was found to be most efficient compared to other solvents. Moderate yield of the product was observed in water and ethanol (Table 1, entries 17 and 18), whereas sterically hindered alcohols such as *i*PrOH and *n*BuOH gave lower yield of the desired product (Table 1, entries 19−20).

In the case of aprotic solvents such as toluene and THF, moderate yield of the desired product was observed (Table 1, entries 21 and 22) which further decreased in dry toluene. Similarly, in complete anhydrous condition with stannous chloride in dry methanol, significant lowering in the yield was observed which indicated the supportive role of water in catalyzing the reaction (Table S1 in the Supporting Information). A decrease in the yield of the desired product was observed at lower temperature, while no change in the yield was observed at 120 °C (Table 1, entries 23 and 24).

With the best reaction conditions in hand, the scope and limitation of $SnCl_2$ catalyzed reductive amination with PMHS was explored for a variety of carbonyl compounds in combination with different amines. The reactions condition was found to be viable to a wide variety of substrate classes including aromatic and aliphatic aldehydes (Scheme 1).

Halogen substituted aldehydes were well tolerated, and the corresponding amines were obtained in good to excellent yields (Scheme 1, **3a**−**3e**). The reductive amination of aldehydes bearing electron-donating groups with *N*-methylaniline proceeded smoothly to afford the desired product in excellent yields (Scheme 1, **3f**−**3h**). The reaction of polysubstituted aldehydes with *N*-methylaniline, a less studied challenging substrate combination, gave good to excellent yield of the desired product (Scheme 1, **3i**−**3l**). Sterically hindered aldehydes provided the desired product in good yield (Scheme 1, **3m**−**3o**). One of the major predicament associated with reductive amination is intolerance of C=C bonds;[17] however, in the present case >99% chemoselectivity was observed with conjugated as well as isolated C=C bonds containing aldehydes (Scheme 1, **3p**−**3s**). Reductive amination of 2-furaldehyde, anthraldehyde, and aliphatic aldehyde, i.e., 3-phenylpropionaldehyde, proceeded smoothly to give **3t**, **3u**, and **3v** in good (70−87%) yield. The reductive amination of aldehydes with other secondary amines, *N*-ethylaniline and *N*-benzylanisidine, provided an excellent yield of the product (Scheme 1, **3w**−**3x**). Unfortunately, no reaction was observed with aliphatic amines under the present reaction condition (Table S2 in the Supporting Information).

One of the merits of the present method is the reductive amination of aromatic and aliphatic ketones with secondary amines which are otherwise considered difficult substrates for this reaction resulting in low yields of the product.[18] Under the present reaction conditions, the reductive amination of different aliphatic and aromatic ketones with secondary amines afforded the desired products in excellent to moderate yields (Scheme 2). Cyclopentanone and cyclohexanone reacted with *N*-methyl aniline to afford **5a** and **5b** in 83 and 90% yields, respectively. Substituted cyclohexanone also gave excellent yield of the desired product (Scheme 2, **5c**−**5d**). Reductive amination of 4-methylcyclohexanone and cyclopentanone with sterically hindered diphenylamine provided moderate yield of the desired product (Scheme 2, **5e**−**5f**). In the case of acetophenones, while no reaction occurred under the present reaction conditions, moderate yield of the corresponding products were observed when the reaction was carried out in toluene with 3 equiv MeOH at 120 °C (Scheme 2, **5g**−**5i**).

Further, the scope of the method was extended for the reductive animation of carbonyl compounds with primary amines which afforded excellent yield of the corresponding secondary amines with high chemoselectivity (Scheme 3). Excellent yield was observed with electron deficient *N*-heteroaromatic primary amines (Scheme 3, **7a**−**7b**). Bogolubsky et al. reported an efficient method for the reductive amination of heterocyclic amines, but the use of $NaBH(OAc)_3$ as a reducing agent which is not eco-friendly and economically favorable limits its viability.[19] Electron donating substituents present on amines as well as aldehydes were well tolerated and gave excellent yields of the desired products (Scheme 3, **7c**−**7f**). One of the major advantages of the present method is the reductive amination with primary amines bearing electron withdrawing substituents such as −COOH, $-COCH_3$, and $-NO_2$ (Scheme 3, **7g**−**7i**) which were otherwise considered as

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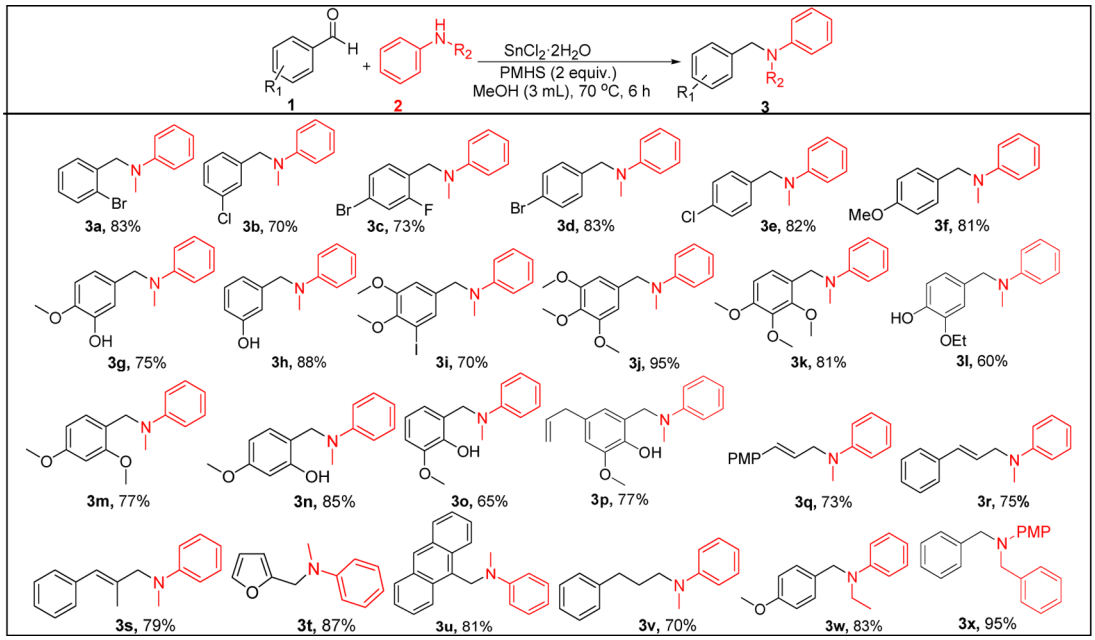
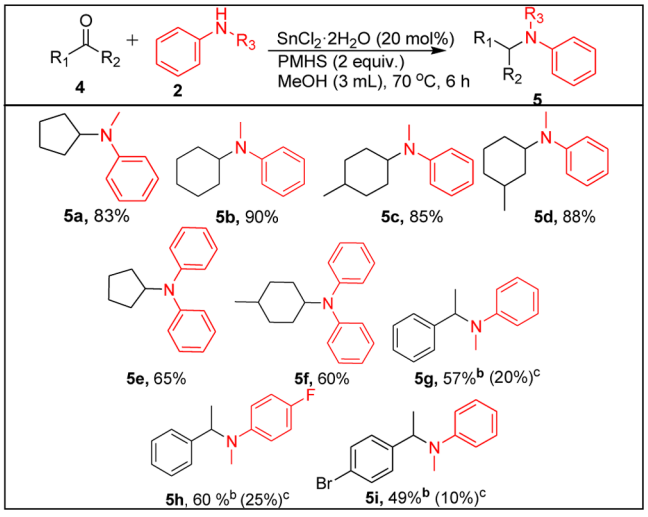
Scheme 1. Reductive Amination of Aldehydes with Secondary Amines[a]



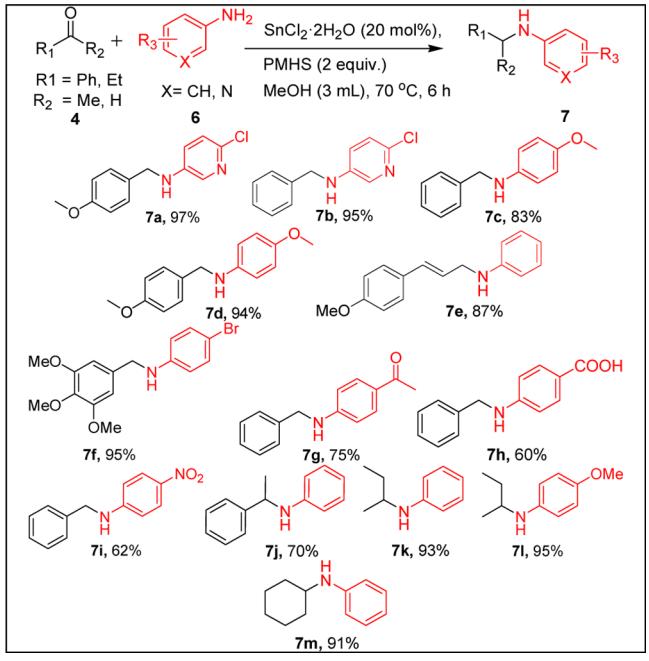
[a]Reaction conditions: $SnCl_2{\cdot}2H_2O$ (20 mol %), **1** (1.1 mmol), **2** (1 mmol), PMHS (2 mmol), MeOH (3 mL), 70 °C, 6 h. Isolated yield.

Scheme 2. Reductive Amination of Ketones with Secondary Amines[a]



[a]Reaction condition: $SnCl_2{\cdot}2H_2O$ (20 mol %), **4** (1.1 mmol), **2** (1 mmol), PMHS (2 mmol),MeOH (3 mL), at 70 °C for 6 h. Isolated yield. [b]Reaction carried out at 120 °C, MeOH (3 mmol) in toluene (3 mL). [c]Reaction carried out at 120 °C in toluene (3 mL).

Scheme 3. Reductive Amination of Carbonyl Compounds with Primary Amines[a]



[a]Reaction conditions: $SnCl_2{\cdot}2H_2O$ (20 mol %), **4** (1 mmol), **6** (1 mmol), PMHS (2 mmol), 3 mL MeOH, 70 °C, 6 h. Isolated yield.

difficult substrates.[20] Aliphatic as well as aromatic ketones were transformed to the desired products in excellent yields (Scheme 3, **7j**–**7m**).

To get insight into the reaction mechanism, different control experiments were carried out. ESI-MS, UV–vis, and FT-IR spectra of $SnCl_2{\cdot}2H_2O$/MeOH indicated the initial formation of tin methanol complex (**A**). Although exact role of tin catalyst is not clear, the *in situ* formation of tin hydride complex has been assumed. Being highly unstable,[21] direct detection of tin hydride complex (**B**) was not possible; however, various indirect evidence in favor of **B** were collected. Addition of PMHS to $SnCl_2{\cdot}2H_2O$/MeOH led to the disappearance of ν_{Si-H} (2162 cm^{-1}) band in FT-IR spectrum. ^1H NMR of PMHS/$SnCl_2{\cdot}2H_2O$/MeOH mixture also showed disappearance of δ_H 4.75 signal of Si-**H**. Furthermore, the reduction of imine did not proceed in the presence of PMHS/MeOH system alone, hence indicating the formation of **B** *via* activation of PMHS by **A**. The hydride transfer from **B** to *in situ* generated iminium ion resulted in the formation of product. It has been observed that the role of water as an additive is crucial for the product formation as complete anhydrous condition led to

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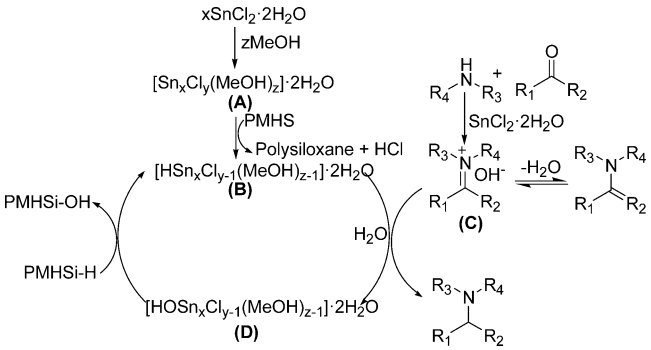
significant decrease in product yield (Table S1 in the Supporting Information).

On the basis of the above experimental results and literature findings,[22] a plausible reaction mechanism is proposed in Scheme 4. First, $SnCl_2·2H_2O$ in the presence of MeOH formed

Scheme 4. Plausible Reaction Mechanism



the complex **A** which further reacted with PMHS and resulted in the formation of tin hydride complex **B**.[22b] Water promoted reduction of *in situ* generated iminium ion (**C**) in the presence of **B** resulted in the formation of product along with tin hydroxide complex (**D**). Finally, the complex **B** was regenerated in the presence of PMHS for another catalytic cycle.[22c]

In conclusion, the present paper discloses $SnCl_2·2H_2O$ as highly efficient and versatile catalyst for the synthesis of a series of tertiary and secondary amines by reductive amination of aliphatic as well as aromatic carbonyl compounds utilizing inexpensive, stable and easy to handle PMHS as reducing agent. The reductive amination of a variety of substrates in high yield and chemoselectivity with broad functional group tolerance, air insensitive, and ambient reaction conditions are the remarkable features of the present protocol.

EXPERIMENTAL SECTION

General. High grade solvents were used for all reactions. Column chromatography was carried out with 60−120 mesh silica gel and monitored with TLC on silica gel 60 F254 plates using UV light as visualizing agent. ^{1}H NMR and ^{13}C NMR experiments were recorded on 300 and 600 MHz instruments. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. Mass spectra were recorded on electrospray ionization quadrupole time-of-flight (ESI-QTOF-MS) mass spectrometer. The GC analysis was carried out on Gas Chromatogram, an AOC-20i autosampler coupled, and a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm). The initial temperature of the column was held at 70 °C for 4 min and was programmed to 230 °C at 4 °C min^{-1}, then held for 15 min at 230 °C; the sample injection volume was 1 μL in GC grade dichloromethane. Nitrogen was used as the carrier gas at a flow rate of 1.1 mL min^{-1} on split mode (1:50). UV−vis spectra were recorded on a UV−vis spectrophotometer.

Typical Procedure for the Reductive Amination. To a stirred solution of $SnCl_2·2H_2O$ (0.2 mmol) in MeOH (3 mL) were added carbonyl compound (1.1 mmol), amine (1.0 mmol) and PMHS (2.0 H equiv) at room temperature, and then the temperature was raised to 70 °C. After 6 h, the reaction mixture was allowed to cool, filtered and passed through anhydrous sodium sulfate. The crude product was purified by column chromatography over silica gel (60−120 mesh) with an appropriate mixture of *n*-hexane and ethyl acetate.

*N-(2-Bromobenzyl)-N-methylaniline (**3a**).* Pale yellow oil (124 mg, 83% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.13 (s, 3H), 4.59 (s, 2H), 6.71 (d, 2H, J = 8.1 Hz), 6.76 (t, 1H, J = 7.1 Hz), 7.14−7.19 (m, 2H), 7.24−7.27 (m, 3H), 7.62 (d, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.8, 57.4, 112.0, 116.6, 122.7, 127.5, 127.9, 128.4, 129.2, 132.8, 137.4, 149.2; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{15}BrN$ 276.0388; found 276.0367.

*N-(3-Chlorobenzyl)-N-methylaniline (**3b**).* Pale yellow oil (162 mg, 70% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.06 (s, 3H), 4.53 (s, 2H), 6.78−6.81 (m, 3H), 7.16−7.12 (m, 1H), 7.26−7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.6, 56.4, 112.5, 117.0, 124.9, 126.8, 127.1, 129.3, 129.9, 134.6, 141.5, 149.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{15}ClN$ 232.0893; found 232.0875.

*N-(4-Bromo-2-fluorobenzyl)-N-methylaniline (**3c**).* Pale yellow oil (214.6 mg, 73% yield), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.10 (s, 3H), 4.59 (s, 2H), 6.78−6.85 (m, 3H), 7.12 (t, 1H, J = 8.07 Hz), 7.24−7.33 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.1, 50.7 (d, J = 3.6 Hz), 112.8, 117.5, 119.4 (d, J = 24.6 Hz), 121.1 (d, J = 9.3 Hz), 125.4 (d, J = 14.7 Hz), 127.9 (d, J = 3.3 Hz), 129.7, 130.2 (d, J = 5.2 Hz), 149.6, 161.0 (d, J = 249.9 Hz); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{14}BrFN$ 294.0294; found 294.0289.

*N-(4-Bromobenzyl)-N-methylaniline (**3d**).* Colorless oil (229 mg, 83% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.04 (s, 3H), 4.51 (s, 2H), 6.78 (overlapped, 3H), 7.15 (d, 2H, J = 7.9 Hz), 7.26−7.29 (m, 2H), 7.47 (dd, 2H, J = 6.8, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.6, 56.2, 112.5, 116.9, 120.6, 128.5, 129.3, 131.7, 138.1, 149.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{15}BrN$ 276.0388; found 276.0345.

*N-(4-Chlorobenzyl)-N-methylaniline (**3e**).* Colorless oil (189.4 mg, 82% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.13 (s, 3H), 4.61 (s, 2H), 6.89 (d, 3H, J = 7.5 Hz), 7.31 (t, 2H, J = 7.7 Hz), 7.39−7.42 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.5, 56.2, 112.5, 116.9, 128.1, 128.7, 129.2, 132.5, 137.5, 149.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{15}ClN$ 232.0893; found 232.0876.

*N-(4-Methoxybenzyl)-N-methylaniline (**3f**).* Yellow oil (183.8 mg, 81% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.04 (s, 3H), 3.36 (s, 3H), 4.13 (s, 2H), 6.76 (t, 1H, J = 7.1 Hz), 6.81 (d, 2H, J = 8.1 Hz), 6.90 (d, 2H, J = 8.3 Hz), 7.20 (d, 2H, J = 8.2 Hz), 7.27 (t, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.3, 55.3, 56.1, 112.5, 114.0, 116.5, 128.0, 129.2, 130.9, 149.9, 158.6. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{18}NO$ 228.1388; found 228.1380.

*N-(3-Hydroxy-4-methoxybenzyl)-N-methylaniline (**3g**).* Pale yellow solid (120 mg, 75% yield), mp. 73−74 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.06 (s, 3H), 3.90 (s, 3H), 4.50 (s, 2H), 6.79−6.86 (m, 5H), 6.91 (d, 1H, J = 1.7 Hz), 7.27−7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.8, 56.4, 56.6, 111.2, 112.9, 113.6, 116.9, 118.6, 129.6, 132.7, 146.0, 146.2, 150.2; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{18}NO_2$ 244.1338; found 244.1341.

*N-(3-Hydroxybenzyl)-N-methylaniline (**3h**).* Greenish oil (187.4 mg, 88% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.03 (s, 3H), 4.50 (s, 2H), 6.72 (t, 2H, J = 7.3 Hz), 6.78−6.81 (m, 3H), 6.85 (d, 1H, J = 7.5 Hz), 7.21 (t, 1H, J = 7.7 Hz), 7.26−7.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.6, 56.5, 112.6, 113.6, 114.0, 116.8, 119.2, 129.3, 129.9, 141.0, 149.7, 155.9; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{14}H_{16}NO$ 214.1232; found 214.1242.

*N-(3-Iodo-4,5-dimethoxybenzyl)-N-methylaniline (**3i**).* Greenish yellow solid (268 mg, 70% yield), mp 69−70 °C. IR $\tilde{\nu}$ (KBr) (cm^{-1}): 690, 744, 835, 997, 1032, 1120, 1255,1371, 1479, 1508, 2929. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.02 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 4.44 (s, 2H), 6.77−6.80 (m, 4H), 7.27 (t, 3H J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.6, 56.0, 56.3, 60.4, 92.6, 111.3, 112.8, 117.1, 128.4, 129.2, 137.3, 147.8, 149.8, 152.8; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{19}INO_2$ 384.0461; found 384.0482.

*N-(3,4,5-Trimethoxybenzyl)-N-methylaniline (**3j**).* Brown solid (272.6 mg, 95% yield), mp 50−51 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.04 (s, 3H), 3.83 (s, 6H), 3.90 (s, 3H), 4.49 (s, 2H), 6.53 (s, 2H), 6.76−6.85 (m, 3H), 7.25−7.31 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.8, 56.4, 57.5, 61.2, 103.9, 113.1, 117.3, 129.6, 135.3, 137.2, 150.4, 153.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{22}NO_3$ 288.1600; found 288.1621.

*N-(2,3,4-Trimethoxybenzyl)-N-methylaniline (**3k**).* Pale yellow oil (232.5 mg, 81% yield), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.07 (s, 3H), 3.89 (s, 3H), 3.99−4.00 (overlapped, 6H), 4.58 (s, 2H), 6.65 (d, 1H, J

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= 8.5 Hz), 6.78 (t, 1H, J = 7.1 Hz), 6.85 (d, 2H, J = 8.1 Hz), 6.89 (d, 1H, J = 8.5 Hz), 7.30 (t, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.3, 51.7, 56.0, 60.7, 60.8, 107.2, 112.4, 116.4, 122.2, 124.4, 129.2, 142.4, 149.4, 151.7, 152.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}NO_3$ 288.1600; found 288.1621.

*N-(3-Ethoxy-4-hydroxybenzyl)-N-methylaniline (**3l**).* Brown solid (154 mg, 60% yield), mp 50−51 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), δ 1.46 (t, 3H, J = 6.9 Hz), 3.30 (s, 3H), 4.06−4.13 (q, 2H, J = 6.9 Hz), 4.50 (s, 2H), 6.78−6.87 (m, 5H), 6.95 (d, 1H, J = 8.5 Hz), 7.30 (t, 2H, J = 5.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 38.6, 57.0, 64.8, 110.7, 113.2, 114.7, 117.2, 120.0, 129.6, 131.1, 145.1, 146.4, 150.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO_2$ 258.1494; found 258.1490.

*N-(2,4-Dimethoxybenzyl)-N-methylaniline (**3m**).* Yellow oil (197.8 mg, 77% yield), IR $\tilde{\nu}$ (KBr) (cm^{-1}): 690, 744, 821, 1033, 1116, 1153, 1207, 1247, 1298, 1379, 1456, 1500, 1585, 1614, 2924. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.08 (s, 3H), 3.83 (s, 3H), 3.88 (s, 3H), 4.52 (s, 2H), 6.45 (d, 1H, J = 3.6 Hz), 6.55 (d, 1H, J = 2.3 Hz), 6.75 (t, 1H, J = 7.2 Hz), 6.79 (d, 2H, J = 8.2 Hz), 7.04 (d, 1H, J = 8.3 Hz), 7.25−7.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.4, 51.5, 55.2, 55.3, 98.5, 103.8, 112.2, 116.1, 118.0, 128.0, 129.1, 149.8, 158.2, 159.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO_2$ 258.1494; found 258.1478.

*N-(2-Hydroxy-4-methoxybenzyl)-N-methylaniline (**3n**).* Yellow oil (206.5 mg, 85% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.83 (s, 3H), 3.77 (s, 3H), 4.34 (s, 2H), 6.67 (brs, 1H), 6.76−6.78 (m, 1H), 6.82 (d, 1H, J = 8.7 Hz), 7.03 (t, 1H, J = 7.3 Hz), 7.14 (d, 2H, J = 8.2 Hz), 7.33 (t, 2H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 40.2, 55.7, 59.0, 113.6, 114.5, 116.8, 118.5, 122.1, 123.0, 129.3, 150.7, 150.7, 153.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO_2$ 244.1338; found 244.1345.

*N-(2-Hydroxy-3-methoxybenzyl)-N-methylaniline (**3o**).* Brown solid (158 mg, 65% yield), mp 56−57 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.05 (s, 3H), 3.93 (s, 3H), 4.58 (s, 2H), 6.79 (d, 1H, J = 6.9 Hz), 6.82−6.88 (m, 3H), 6.94 (d, 2H, J = 8.1 Hz), 7.31 (t, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 39.2, 53.7, 56.0, 109.8, 114.3, 118.2, 119.4, 120.2, 124.0, 129.2, 144.2, 146.9, 150.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO_2$ 244.1338; found 244.1327.

*N-(2-Hydroxy-3-methoxy-5-prop-2-eneylbenzyl)-N-methylaniline (**3p**).* Dark brown oil (218 mg, 77% yield), IR $\tilde{\nu}$ (KBr) (cm^{-1}): 1070, 1143, 1188, 1207, 1230, 1255, 1292, 1303, 1342, 1355, 1371, 1435, 1492, 1598,2914, 3442. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.01 (s, 3H), 3.34 (d, 2H, J = 6.5 Hz), 3.92 (s, 3H), 4.53 (s, 2H), 5.09−5.13 (m, 2H), 5.96−6.02 (m, 1H), 6.63 (s, 1H), 6.70 (s, 1H), 6.88 (t, 1H, J = 7.2 Hz), 6.97 (d, 2H, J = 8.0 Hz), 7.32 (t, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 39.2, 40.0, 54.2, 56.0, 110.3, 114.7, 115.5, 118.5, 120.1, 123.6, 129.2, 131.2, 137.9, 142.6, 146.9, 150.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}NNaO_2$ 306.1470; found 306.1462.

*N-(4-Methoxycinnamyl)-N-methylaniline (**3q**).* Yellow solid (185 mg, 73% yield), mp 61−62 °C. IR $\tilde{\nu}$ (KBr) (cm^{-1}): 690, 748, 802, 974, 1035, 1228, 1240, 1346, 1448, 1463, 1502, 1593, 2954. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.02 (s, 3H), 3.38 (s, 3H), 4.51 (s, 2H), 6.14−6.20 (m, 1H), 6.54 (d, 1H, J = 15.7 Hz), 6.81−6.92 (m, 5H), 7.30−7.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.4, 55.4, 55.7, 113.1, 114.4, 117.0, 123.8, 127.9, 129.6, 130.1, 131.2, 150.0, 159.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO$ 254.1545; found 254.1529.

*N-Cinnamyl-N-methylaniline (**3r**).* Colorless oil (167 mg, 75% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.01 (s, 3H), 4.11 (d, 2H, J = 4.9 Hz), 6.27−6.30 (m, 1H), 6.56 (d, 1H, J = 15.8 Hz), 6.76 (t, 1H, J = 6.9 Hz), 6.88 (d, 2H, J = 7.8 Hz), 7.23−7.34 (m, 5H), 7.38 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.0, 54.9, 112.7, 116.7, 125.7, 126.3, 127.4, 128.5, 129.2, 131.3, 136.9, 149.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}N$ 224.1439; found 224.1429.

*N-(3-Phenyl-2-methylpropeneyl)-N-methylaniline (**3s**).* Brown solid (187 mg, 79% yield), mp 45−46 °C. IR $\tilde{\nu}$ (KBr) (cm^{-1}): 686, 740, 933, 1031, 1120, 1192, 1215, 1257, 1363, 1440, 1492, 1504, 1597, 2852, 2914, 3059. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00 (s, 3H), 3.12 (s, 3H), 4.06 (s, 2H), 6.51 (s, 1H), 6.83−6.91 (m, 3H), 7.28−7.47 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.4, 38.6, 61.4, 112.7, 116.8, 125.3, 126.7, 128.5, 129.4, 129.6, 135.2, 138.3, 150.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}N$ 238.1596; found 238.1575.

*N-2-Furfuryl-N-methylaniline (**3t**).* Pale yellow oil (163 mg, 87% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.06 (s, 3H), 4.53 (s, 2H), 6.21−6.22 (m, 1H), 6.36−6.37 (m, 1H), 6.83 (t, 1H, J = 7.2 Hz), 6.91 (d, 2H, J = 7.9 Hz), 7.33 (dd, 2H, J = 3.2 Hz), 7.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.3, 49.9, 107.3, 110.2, 113.1, 117.2, 129.2, 141.9, 149.4, 152.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}NO$ 188.1075; found 188.1067.

*N-(9-Anthracenylmethyl)-N-methylaniline (**3u**).* Yellow solid (229 mg, 81% yield), mp 145−146 °C. IR $\tilde{\nu}$ (KBr) (cm^{-1}): 688, 731, 746, 885, 1315, 1344, 1371, 1442, 1436, 1597, 2846, 2916. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.58 (s, 3H), 5.23 (s, 2H), 6.96 (t, 1H, J = 7.3 Hz), 7.13 (d, 2H, J = 7.9 Hz), 7.45−7.48 (m, 2H), 7.51−7.54 (s, 4H), 8.06−8.08 (m, 2H), 8.27−8.28 (m, 2H), 8.50 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 34.7, 46.9, 113.2, 117.4, 124.4, 125.1, 126.4, 128.0, 128.7, 129.2, 129.4, 131.5, 131.5, 150.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}$ N 298.1596; found 298.1585.

*N-(3-Phenylpropyl)-N-methylaniline (**3v**),.* Colorless oil (157.5 mg, 70% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.90−1.95 (m, 2H), 2.66 (t, 2H, J = 7.6 Hz), 2.93 (s, 3H), 3.35 (t, 2H, J = 7.4 Hz), 6.68 (d, 2H, J = 8.3 Hz), 7.20−7.23 (m, 5H), 7.26−7.31 (m, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 28.1, 33.3, 38.2, 52.2, 112.2, 116.0, 125.8, 128.3, 128.3, 129.1, 141.8, 149.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}N$ 226.1596; found 226.1578.

*N-(4-Methoxybenzyl)-N-ethylaniline (**3w**).* Pale yellow oil (178.4 mg, 83% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.23 (t, 3H, J = 6.9 Hz), 3.49 (q, 2H, J = 6.4 Hz), 3.82 (s, 3H), 4.50 (s, 2H), 6.71 (t, 1H, J = 6.9 Hz), 6.75 (d, 2H, J = 7.5 Hz), 6.89 (d, 2H, J = 4.1 Hz), 7.20−7.26 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 12.1, 44.9, 53.3, 55.3, 112.3, 114.0, 116.0, 127.7, 129.2, 131.1, 148.6, 158.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO$ 242.1545; found 242.1535.

*N,N-Dibenzyl-4-methoxyaniline (**3x**).* Brown solid (288 mg, 95% yield), mp 76−77 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.75 (s, 3H), 4.60 (s, 4H), 6.74 (d, 2H, J = 9.0 Hz), 6.80 (d, 2H J = 9.1 Hz), 7.26−7.30 (m, 6H), 7.35 (t, 4H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 55.2, 55.7, 114.6, 114.7, 126.8, 126.9, 128.5, 139.0, 143.8, 151.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO$ 304.1701; found 304.1691.

*N-Cyclopentyl-N-methylaniline (**5a**).* Colorless oil (145 mg, 83% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.62−1.64 (m, 4H), 1.74−1.76 (m, 2H), 1.88−1.92 (m, 2H), 2.82 (s, 3H), 4.16−4.21 (m, 1H), 6.74 (t, 1H, J = 7.2 Hz), 6.87 (d, 2H, J = 8.1 Hz), 7.25−7.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 24.3, 28.7, 32.6, 60.3, 114.1, 116.8, 129.0, 151.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{18}N$ 176.1439; found 176.1428.

*N-Cyclohexyl-N-methylaniline (**5b**).* Yellow oil (170 mg, 90% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.22−1.29 (m, 2H), 1.45−1.51 (m, 2H), 1.54−1.60 (m, 2H), 1.81 (d, 1H, J = 12.7 Hz), 1.94 (dd, 4H, J = 12.6, 11.8), 2.89 (s, 3H), 3.69 (t, 1H, J = 11.3 Hz), 6.81 (t, 1H, J = 8.0 Hz), 6.90 (d, 2H, J = 7.9 Hz), 7.35 (t, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 26.1, 26.4, 30.2, 31.3, 58.3, 113.4, 116.4, 129.0, 150.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{20}N$ 190.1596; found 190.1589.

*N-(4-Methylcyclohexyl)-N-methylaniline (**5c**).* Colorless oil (173 mg, 85% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.01 (cis, d, 3H, J = 6.4 Hz), 1.10 (trans, d, 3H, J = 7.1 Hz), 1.09−1.17 (m, 2H), 1.43 (s, 1H), 1.58−1.63 (m, 4H), 1.69−1.88 (m, 10H), 2.03 (s, 1H), 2.84 (cis, s, 3H), 2.88 (trans, s, 3H), 3.60−3.66 (m, 2H), 6.76−6.88 (m, 2H), 6.87 (t, 4H, J = 6.7 Hz), 7.31 (t, 4H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (cis + trans) 17.6, 22.4, 24.1, 26.7, 29.6, 31.3, 31.5, 31.7, 32.5, 34.9, 58.2, 58.5, 113.3, 113.5, 116.3, 116.5, 129.2, 150.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}N$ 204.1752; found 204.1776.

*N-(3-Methylcyclohexyl)-N-methylaniline (**5d**).* Yellow oil (178.7 mg, 88% yield), IR $\tilde{\nu}$ (KBr) (cm^{-1}): 688, 744, 1103, 1321, 1454, 1502, 1597, 2922. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (cis, d, 3H, J = 6.4 Hz), 1.16 (trans, d, 3H, J = 7.1 Hz), 1.34−1.91 (m, 17H), 2.22−2.26

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(m, 1H), 2.83 (cis+trans, s, 6H), 3.64−3.72 (m, 1H), 3.87−3.96 (m, 1H), 6.76 (t, 2H, J = 7.1 Hz), 6.85 (d, 4H, J = 7.9 Hz), 7.29 (t, 4H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) 75 MHz) δ (cis+trans) 18.6, 21.2, 23.0, 25.9, 28.7, 29.7, 30.9, 31.6, 31.7, 33.1, 35.1, 35.7, 39.0, 52.8, 58.3, 113.7, 116.7, 129.5, 150.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}N$ 204.1752; found 204.1732.

*N-Cyclopentyl-N,N-diphenylamine (**5e**).* Colorless oil (154 mg, 65% yield), IR $\tilde{\nu}$ (KBr) (cm^{-1}): 690, 742, 1236, 1283, 1319, 1489, 1587, 2868, 2957. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.51−1.56 (m, 2H), 1.63−1.66 (m, 4H), 2.04−2.08 (m, 2H), 4.31−4.37 (m, 1H), 6.96 (d, 4H, J = 7.6 Hz), 7.07 (t, 2H, J = 7.3 Hz), 7.34 (t, 4H, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 23.1, 30.5, 60.0, 121.7, 123.2, 129.1, 147.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}N$ 238.1596; found 238.1591.

*N-(4-Methylcyclohexyl)-N,N-diphenylamine (**5f**).* Brownish oil (159 mg, 60% yield), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (cis, d, 3H, J = 7.1 Hz), 0.91 (trans, d, 3H, J = 6.4 Hz), 1.13−1.25 (m, 6H), 1.37−1.46 (m, 2H), 1.57 (d, 2H, J = 13.9 Hz), 1.66−1.71 (m, 2H), 1.78 (t, 4H, J = 13.5 Hz), 2.03 (d, 2H, J = 12.0 Hz), 3.82−3.86 (cis +trans, m, 2H), 6.86 (t, 8H, J = 8.2), 7.00(t, 4H, J = 6.9 Hz), 7.26−7.30 (m, 8H, J = 7.1 Hz); ^{13}CNMR ($CDCl_3$, 75 MHz) δ 17.6, 22.3, 25.9, 26.7, 31.3, 31.5, 32.2, 34.8, 56.6, 57.1, 121.9, 121.5, 122.8, 122.8, 129.1, 129.2, 146.4, 146.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}N$ 266.1909; found 266.1901.

*N-(1-Phenylethyl)-N-methylaniline (**5g**).* Yellow oil (120 mg, 57% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.61 (d, 3H, J = 6.9 Hz), 2.74 (s, 3H), 5.19 (q, 1H, J = 6.8 Hz), 6.79 (t, 1H, J = 7.2 Hz), 6.91 (d, 2H, J = 8.1 Hz), 7.29−7.33 (m, 3H), 7.38−7.40 (m, 4H) ^{13}CNMR ($CDCl_3$, 150 MHz) δ 16.3, 31.9, 56.6, 113.1, 116.1, 126.8, 126.9, 128.4, 129.2, 142.8, 150.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}N$ 212.1439; found 212.1425.

*N-(1-Phenylethyl)-N-methyl-4-fluoroaniline (**5h**).* Yellow oil (137 mg, 60% yield), IR $\tilde{\nu}$ (KBr) (cm^{-1}): 698, 783, 812, 1109, 1109, 1226, 1373, 1448, 1506, 2924. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.54 (d, 3H, J = 6.8 Hz), 2.67 (s, 3H), 5.01 (q, 1H, J = 6.6 Hz), 6.80 (q, 2H, J = 4.2 Hz), 6.98 (t, 2H, J = 8.5 Hz), 7.28 (q, 1H, J = 7.4 Hz), 7.33−7.38 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.3, 32.6, 58.1, 115.0 (d, J = 7.0 Hz), 115.5 (d, J = 21.9 Hz), 126.9, 128.4, 142.7, 147.0, 155.6 (d, J = 235.7 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{17}NF$ 230.1345; found 230.1342.

*N-(1-(4-Bromophenyl)ethyl)-N-methylaniline (**5i**).* Yellow oil (142 mg, 49% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.56 (d, 3H, J = 6.9 Hz), 2.69 (s, 3H), 5.09 (q, 1H, J = 6.7 Hz), 6.78 (t, 1H, J = 7.0 Hz), 6.86 (d, 2H, J = 8.2 Hz), 7.22 (d, 2H, J = 8.2 Hz), 7.28 (t, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.3, 31.9, 56.3, 113.3, 117.1, 120.7, 128.7, 129.3, 131.5, 141.9, 150.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{17}BrN$ 290.0544; found 290.0534.

*(6-Chloropyridin-3-yl)-N-(4-methoxybenzyl)amine (**7a**).* Yellow solid (240.5 mg, 97% yield), mp 87−88 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.79 (s, 3H), 4.23 (s, 2H), 6.83−6.89 (m, 3H), 7.03−7.06 (d, 1H, J = 8.5 Hz), 7.25 (d, 2H, J = 8.2 Hz), 7.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 47.7, 55.7, 114.5, 122.6, 124.4, 129.0, 130.4, 134.9, 139.1, 143.6, 159.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}ClN_2O$ 249.0795; found 249.0793.

*N-Benzyl-(6-chloropyridin-3-yl)amine (**7b**).* White solid (207 mg, 95% yield), mp 95−96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.32 (s, 2H), 6.84−6.88 (dd, 1H, J = 5.8 Hz), 7.06 (d, 1H, J = 8.5 Hz), 7.27−7.34 (m, 5H), 7.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.3, 122.6, 124.4, 127.7, 128.0, 129.2, 135.0, 138.4, 139.3, 143.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{11}ClN_2Na$ 241.0508; found 241.0503.

*N-Benzyl-4-methoxyaniline (**7c**).* Yellow solid (178 mg, 83% yield), mp 50−51 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.53 (s, 3H), 4.06 (s, 2H), 6.40 (d, 2H, J = 8.8 Hz), 6.61 (d, 2H, J = 8.8 Hz), 7.09 (t, 1H, J = 7.0 Hz), 7.15−7.19 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 49.3, 55.8, 114.2, 115.0, 127.3, 127.7, 128.7, 139.9, 142.6, 152.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO$ 214.1232; found 214.1224.

*N-(4-Methoxybenzyl)-4-methoxyaniline (**7d**).* White solid (228 mg, 94% yield), mp 95−96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77 (s, 3H), 3.83 (s, 3H), 4.23 (s, 2H), 6.64 (d, 2H, J = 8.8 Hz), 6.81 (d, 2H, J = 8.8 Hz), 6.91 (d, 2H, J = 8.5 Hz), 7.32 (d, 2H, J = 8.1 Hz), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 49.1, 55.6, 56.2, 114.4, 114.5, 115.3, 129.2, 142.9, 152.5, 159.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO_2$ 244.1338; found 244.1328.

*N-(4-Methoxycinnamyl)aniline (**7e**).* White solid (208 mg, 87% yield), mp 75−76 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.85 (s, 3H), 3.95 (d, 2H, J = 5.8 Hz), 6.16−6.29 (m 1H), 6.57−6.81 (m, 4H), 6.91 (d, 2H, J = 8.6 Hz), 7.25 (t, 2H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 46.7, 55.7, 113.4, 114.4, 117.9, 125.1, 127.9, 129.7, 130.1, 131.5, 148.5, 159.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{17}NNaO$ 262.1208; found 262.1225

*N-(3,4,5-Trimethoxybenzyl)-4-bromoaniline (**7f**).* Yellow oil (126 mg, 95% yield), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.84 (s, 9H), 4.22 (s, 2H), 6.51 (d, 2H, J = 8.6 Hz), 6.58 (s, 2H), 7.24 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.9, 56.5, 61.2, 104.6, 109.5, 114.8, 132.3, 135.1, 137.4, 147.5, 153.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}BrNO_3$ 352.0548; found 352.0538.

*1-(4-Benzylaminophenyl)ethanone (**7g**).* Yellow solid (168 mg, 75% yield), mp 95−96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.49 (s, 3H), 4.41 (s, 2H), 6.61 (d, 2H, J = 8.7 Hz), 7.36 (brd s, 5H), 7.83 (d, 2H, J = 8.7 Hz), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.4, 47.9, 112.0, 127.2, 127.7, 127.9, 129.2, 131.2, 138.7, 152.5, 196.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232; found 226.1224.

*N-Benzyl-4-carboxyaniline (**7h**).* White solid (136 mg, 60% yield), mp 163−164 °C. ^{1}H NMR (CD_3OD, 600 MHz) δ 4.18 (s, 2H), 6.41 (d, 2H, J = 7.2 Hz), 7.03 (t, 1H, J = 6.4 Hz), 7.11−7.15 (m, 4H), 7.58 (d, 2H, J = 8.7 Hz), ^{13}C NMR (CD_3OD, 150 MHz) δ 49.1, 113.8, 119.8, 129.3, 129.5, 130.8, 134.0, 141.9, 155.6, 172.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1025; found 228.1024.

*N-Benzyl 4-nitroaniline (**7i**).* Dark yellow solid (141.4 mg, 62% yield), mp 148−149 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.43 (s, 2H), 4.98 (brd s, 1H NH), 6.57 (d, 2H, J = 9.0 Hz), 7.31−7.38 (m, 5H), 8.06 (d, 2H, J = 8.9 Hz),^{13}C NMR ($CDCl_3$, 150 MHz) δ 47.6, 111.3, 126.4, 127.3, 127.8, 128.9, 137.4, 138.3, 153.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{13}N_2O_2$ 229.0977; found 229.0974.

*N-(1-Phenylethyl)aniline (**7j**).* Yellow oil (138 mg, 70% yield), ^{1}HNMR ($CDCl_3$, 600 MHz) δ 1.56 (d, 3H, J = 6.7 Hz), 4.53 (q, 1H, J = 6.7 Hz), 6.56 (d, 2H, J = 7.9 Hz), 6.70 (t, 1H, J = 7.2 Hz), 7.14 (t, 2H, J = 7.8 Hz), 7.28 (t, 2H, J = 7.2 Hz), 7.37 (t, 2H, J = 7.6 Hz), 7.42 (d, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 25.0, 53.3, 113.3, 117.3, 125.9, 126.9, 128.7, 129.1, 145.2, 147.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}N$ 198.1283; found 198.1279.

*N-Isobutylaniline (**7k**).* Colorless oil (138.6 mg, 93% yield), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.06 (t, 3H, J = 7.4 Hz), 1.28 (d, 3H, J = 6.3 Hz), 1.53−1.75 (m, 2H), 3.47−3.53 (m, 1H), 6.67−6.80 (m, 3H), 7.27 (t, 2H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 10.8, 20.7, 30.1, 50.2, 113.6, 117.2, 129.7, 148.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{16}N$ 150.1283; found 150.1274.

*N-Isobutyl-4-methoxyaniline (**7l**).* Yellow oil (170 mg, 95% yield), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (t, 3H, J = 7.4 Hz), 1.21 (d, 3H, J = 6.3 Hz), 1.43−1.70 (m, 2H), 3.32−3.43 (m, 1H), 3.79 (s, 3H), 6.62 (d, 2H, J = 8.9 Hz), 8.84 (d, 2H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.8, 20.6, 30.0, 51.2, 56.1, 115.1, 115.3, 142.4, 152.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{18}NO$ 180.1388; found 180.1374.

*N-Cyclohexyl aniline (**7m**).* Greenish yellow oil (159.2 mg, 91% yield), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23−1.62 (m, 6H), 1.79−1.96 (m, 3H), 2.22 (q, 2H, J = 4.2 Hz), 3.36−3.46 (m, 1H), 6.75 (d, 2H, J = 7.7 Hz), 6.84 (t, 1H, J = 7.3 Hz), 7.33 (t, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.6, 26.5, 34.0, 52.2, 113.7, 117.3, 129.8, 147.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{18}N$ 176.1439; found 176.1425.

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■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C NMR, ESI-MS, IR and UV−vis spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00156.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: neerajnpp@rediffmail.com, neeraj@ihbt.res.in.

Notes

The authors declare no competing financial interest.

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