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Copper-Catalyzed Electrophilic Amination of Organoaluminum Nucleophiles with *O*-Benzoyl Hydroxylamines

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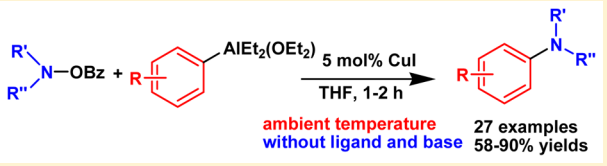
Supporting Information

ABSTRACT: A copper-catalyzed electrophilic amination of aryl and heteroaryl aluminums with *N*,*N*-dialkyl-*O*-benzoyl hydroxylamines that affords the corresponding anilines in good yields has been developed. The catalytic reaction proceeds very smoothly under mild conditions and exhibits good substrate scope. Moreover, the developed catalytic system is also well suited for heteroaryl aluminum nucleophiles, providing facile access to heteroaryl amines.



INTRODUCTION

Aromatic amines are important structural motifs in many bioactive compounds, pharmaceutical and agrochemical targets, and functional materials.[1] Transition metal-catalyzed aromatic C−N cross-coupling reactions are one of the most powerful methods for synthesizing arylamines.[2] After Buchwald−Hartwig's pioneering work on the Pd- or Cu-catalyzed cross-coupling of aryl halides with various amines,[3] Chan and Lam reported the copper-mediated oxidative coupling of nucleophilic arylboronic acids with amines.[4] Although there have been recent improvements to transition metal-catalyzed nucleophilic amination strategies,[5] this approach still suffers from several limitations, including harsh reaction conditions and low functional group tolerance.

Catalytic electrophilic amination using umpolung strategies would provide a complementary method for constructing C−N bonds under mild conditions.[6] An umpolung electrophilic amination using a R_2N^+-type reagent, such as chloroamines and hydroxylamines, has recently received significant attention. In 2004, Johnson and co-workers reported their pioneering research on the Cu-catalyzed amination of organozinc reagents with *N*,*N*-dialkyl-*O*-acyl hydroxylamine derivatives.[7] Barker and Jarvo also developed an analogous Ni-catalyzed reaction with organozinc reagents and *N*,*N*-dialkyl-N-chloramines.[8] Subsequently, R_2N^+ synthons were used as an effective nitrogen source not only for the electrophilic amination of organometallic reagents based on B,[9] Mg,[10] Sn,[11] Ti,[12] Zr,[13] and Si[14] but also for direct (hetero)aromatic C−H amination via a similar catalytic process.[15] More recently, a copper-catalyzed electrophilic amination of organolithiums mediated by siloxane transfer agents with *O*-benzoylhydroxylamines was developed to access various aryl and heteroaryl amines.[16]

Organoaluminum compounds are excellent nucleophiles for organic reactions because of their high reactivities, the high Lewis acidity of the aluminum center, and their low toxicities. Therefore, organoalanes are widely applied in addition to carbonyl compounds[17] and cross-coupling reactions.[18] Moreover, arylalanes have been demonstrated to be highly efficient coupling reagents with aryl bromides and chlorides without the use of a base.[19] As an extension of our research on arylalanes, we herein describe an umpolung strategy for synthesizing tertiary amines via the copper-catalyzed electrophilic amination of (hetero)arylalanes with *O*-benzoyl hydroxylamines.

RESULTS AND DISCUSSION

The reaction of 4-benzoyloxymorpholine (**1a**) with 4-methoxyphenyl aluminum (**2a**) was first tested as the template for optimizing the reaction conditions, and the results are summarized in Table 1. Notably, we found that 5 mol % CuI was effective as a catalyst, even at room temperature, to provide a good yield without ligand and base. Similar to the previously reported coupling of mixed organoalanes, such as $RAlEt_2$ and RAl^iBu_2 (R = Ar, alkenyl, alkynyl), the unsaturated R group was always selectively transferred.[19e,f,20] Further screening of different solvents revealed that performing the reaction in THF afforded the best yield of 87% (entries 1−5, Table 1). It was also found that the reactions provided the product **3aa** in the highest yield at room temperature (entries 2, 6−7, Table 1). The product yields remained almost constant when the equivalent of aryl aluminum was reduced to 1.7 or 1.5 (entries 8 and 9, Table 1). The product yield decreased to 71% when the equivalent of aryl aluminum was decreased to 1.3 (entry 10,

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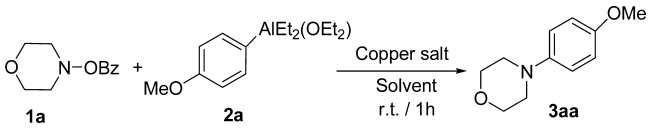
Table 1. Optimization of Copper-Catalyzed Electrophilic Amination of 4-Methoxyphenyl Diethylaluminum (2a) with 4-Benzoyloxymorpholine (1a)[a]



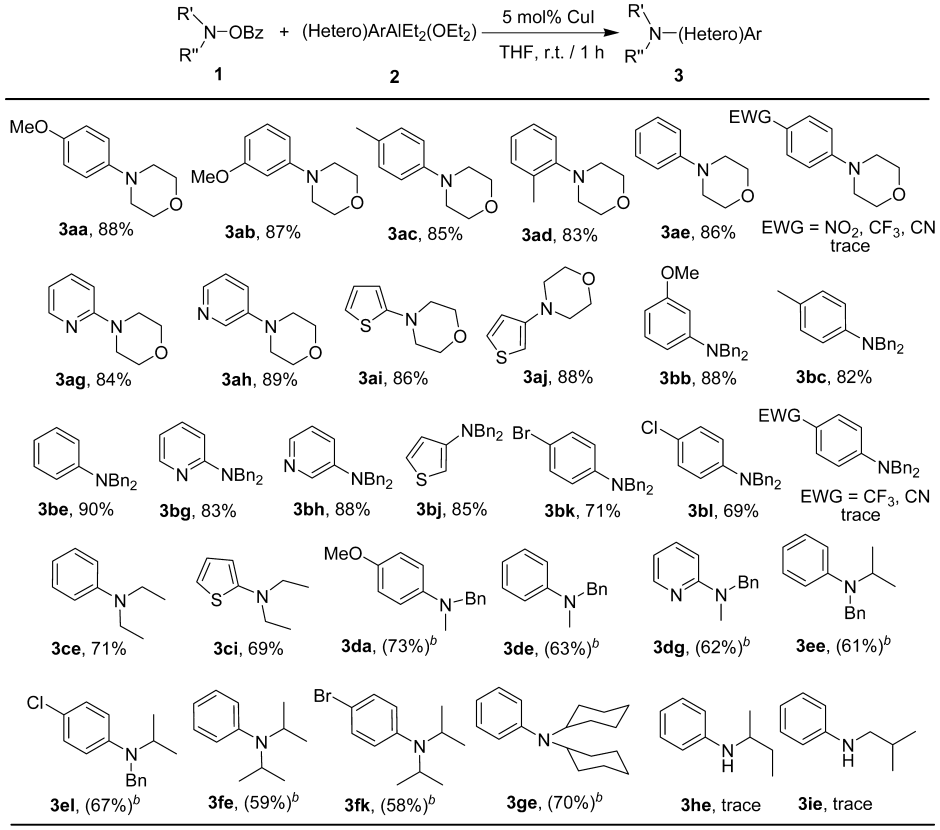
entry	copper salt (mol %)	solvent	$ArAlEt_2(OEt_2)$ (equiv)[b]	temp (°C)	yield (%)
1	CuI (5)	toluene	2.0	rt	78
2	CuI (5)	THF	2.0	rt	87
3	CuI (5)	hexane	2.0	rt	42
4	CuI (5)	Et_2O	2.0	rt	58
5	CuI (5)	CH_2Cl_2	2.0	rt	65
6	CuI (5)	THF	2.0	0	63
7	CuI (5)	THF	2.0	50	73
8	CuI (5)	THF	1.7	rt	86
9	CuI (5)	THF	1.5	rt	88
10	CuI (5)	THF	1.3	rt	71
11	CuI (10)	THF	1.5	rt	90
12	CuI (1)	THF	1.5	rt	62
13	CuI (0)	THF	1.5	rt	NR
14	CuBr (5)	THF	1.5	rt	80
15	CuCl (5)	THF	1.5	rt	78
16	$Cu(OAc)_2$ (5)	THF	1.5	rt	51

[a]Reaction conditions: **1a** (1.0 mmol), solvent (3 mL). [b]Equivalent of $ArAlEt_2(OEt_2)$ relative to **1a**. [c]NR: no reaction.

Table 1). A further increase in the copper catalyst (10 mol %) afforded the product **3aa** in slightly high yield (entry 11, Table 1). However, the product was obtained in the low yield of 62% when the catalyst loading was increased to 1 mol % (entry 12, Table 1). When the reaction was conducted in the absence of catalyst, no electrophilic amination product **3aa** was isolated under the same conditions (entry 13, Table 1). Nonoxygenated Cu(I) sources, such as CuBr and CuCl, afforded similar yields (entries 14 and 15, Table 1), whereas the Cu(II) source $Cu(OAc)_2{\cdot}H_2O$ afforded the lowest yield of 51% (entry 16, Table 1).

With the optimized conditions established, the scope of this transformation was explored using various arylalanes and *O*-benzoyl hydroxylamines (Table 2). The treatment of morpholino benzoate (**1a**) with a series of arylalanes indicated that the reaction is significantly affected by the electronic effect of the substituents on the aromatic ring of arylalanes. The electron-rich aryl-substituted alanes were effective, affording the corresponding products **3aa–ad** in high yields. In contrast, no reaction was observed in the case of the electron-deficient aryl-substituted alanes such as 4-nitrophenyl, 4-cyanophenyl, and 4-trifluomethylphenyl aluminum reagents. Notably, the reaction also performed well with heteroarylalanes such as pyridyl aluminums and thienyl aluminums to afford the corresponding products **3ag–aj** in good yields. In particular, 3-thienyl amines have potential use in the synthesis of polythiophene derivatives, which have been the focus of many studies because of their promising applications in polymer solar cells,[21] light-emitting diodes,[22] and field-effect transistors.[23]

Table 2. Substrate Scope for the Copper-Catalyzed Electrophilic Amination of (Hetero)arylalanes.[a]



[a]Reaction conditions: CuI (0.05 mmol), **1** (1.0 mmol), **2** (1.5 mmol), THF (3 mL). [b]Reaction time: 2 h.

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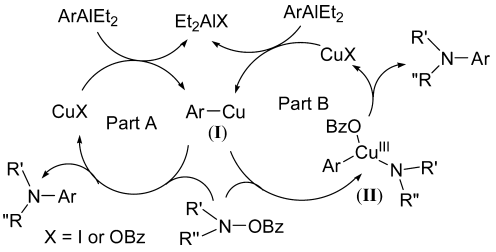
Considering the convenience of the subsequent derivatization of the corresponding products, *O*-benzoyl-*N*,*N*-dibenzylhydroxylamine (**1b**) was employed as another electrophilic nitrogen source for this reaction (Table 2). Similarly, various arylalanes exhibited high reactivities in this transformation, affording the corresponding products in high yields of 82−90%, except for the electron-deficient aryl-substituted alanes such as 4-cyanophenyl and 4-trifluomethylphenyl aluminum reagents. For heteroarylalanes such as pyridyl aluminums and thienyl aluminums, the corresponding heteroaryl amines **3bg**, **3bh**, and **3bj** were also obtained in good yields. Notably, the reactions of **1b** with halogenated arylalanes, such as 4-bromophenyl aluminum and 4-chlorophenyl aluminum, afforded the corresponding halogenated arylamines **3bk** and **3bl**, which may allow further useful transformations via halogen-exchange reactions.

Next, the reactions of a series of *O*-benzoyl hydroxylamines **1c−i** with arylalanes were examined under the optimized reaction conditions (Table 2). In general, the amination reactions with **1** derived from secondary amines proceeded smoothly to provide the desired products in moderate to good yields. It is worth mentioning that the reactions of sterically hindered amines such as *O*-benzoyl-*N*,*N*-isopropylbenzylhydroxylamine (**1e**), *O*-benzoyl-*N*,*N*-diisopropylhydroxylamine (**1f**), and *O*-benzoyl-*N*,*N*-dicyclohexylhydroxylamine (**1g**) with the corresponding arylalanes afforded the corresponding products **3ee−ge** in moderate yields (58−70%). However, this reaction was ineffective for *O*-benzoyl-*N*-alkylhydroxylamine **1h** and **1i**, which are derived from primary amines, probably due to the protonation of arylalanes by the corresponding amines.

In view of the mechanism previously proposed for the electrophilic amination of aryl zincs and boronic esters,[7c,9c] we proposed that this reaction involved transmetalation from aluminum to copper, affording aryl copper [ArCu] species as intermediate (**I**) and subsequent electrophilic amination of the aryl copper intermediate (**I**) to afford the final products (Scheme 1, part A). To obtain a preliminary understanding of

Scheme 1. Proposed Mechanism for the Copper-Catalyzed Coupling of *O*-Benzoyl Hydroxylamines with Organoalanes



the mechanism, the reaction of **1b** with [PhCu], generated in situ from PhMgCl and CuI, afforded the amination product **3be** in a comparable yield of 87%. It should be noted that the result was different from the reaction of [PhCu] with *N*-chloroamides to afford biphenyl as the homocoupling products in electrophilic amination of arylboronic acids with *N*-chloroamides catalyzed by CuCl,[9b] indicating that the transmetalation of aryl aluminum to aryl copper was a favorable route in our current reaction system. However, an alternative catalytic mechanism, which proceeds by the further oxidative addition of [PhCu] (**I**) to afford the intermediate (**II**) and next reductive elimination of the intermediate (**II**) to afford the final product, cannot be ruled out (Scheme 1, part B).

CONCLUSION

In summary, an umpolung strategy for preparing various tertiary amines via the copper-catalyzed electrophilic amination of arylalanes with *O*-benzoyl hydroxylamines has been developed. The reaction afforded the corresponding arylamines in moderate to good yields in the presence of 5 mol % CuI without the need for ligand and base. The developed catalytic system exhibited good substrate scope in terms of both the functional groups tolerated on the nucleophilic component and the steric hindrance of the coupling partners. Moreover, the catalytic system could also be applied to heteroaryl aluminum nucleophiles to provide facile access to heteroaryl amines. This reaction provides an alternative method for accessing various aromatic amines.

EXPERIMENTAL SECTION

General Methods. All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were refluxed and distilled over sodium/benzophenone (THF, Et_2O, *n*-hexane, and toluene) and P_2O_5 (CH_2Cl_2) under argon prior to use. *N*,*N*-Dialkyl-*O*-benzoyl hydroxylamines[7a,b] and (hetero)-$ArAlEt_2(OEt_2)$[17j,19f] were prepared according to previously reported procedures. ^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded at 300 MHz/75 MHz (^1H NMR/^{13}C NMR) or 500 MHz/125 MHz (^1H NMR/^{13}C NMR) with chemical shifts given in ppm from the internal TMS. High resolution mass spectral (HRMS) data were obtained with an ionization mode of ESI and a TOF analyzer.

General Procedures for Copper-Catalyzed Electrophilic Amination of Organoaluminum Nucleophiles with *O*-Benzoyl Hydroxylamines. Under a dry argon atmosphere, an oven-dried 25 mL Schlenk tube was charged with CuI (9.5 mg, 0.05 mmol), *O*-benzoyl hydroxylamine (1.0 mmol), and anhydrous THF (3 mL) at room temperature. The solution was stirred for 10 min, followed by the addition of (hetero)arylaluminum reagent (1.5 mmol). After being stirred at ambient temperature for 1−2 h, the resulting mixture was quenched with water. The mixture was diluted with ethyl acetate (40 mL) and then passed through a filter and concentrated. The crude product was purified by column chromatography (silica gel), eluting with petroleum ether and ethyl acetate to give the product **3**.

4-(4-Methoxyphenyl)morpholine (3aa).[7b] White solid (171 mg, 88% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 6.91−6.83 (m, 4H), 3.86 (t, J = 4.5 Hz, 4H), 3.77 (s, 3H), 3.06 (t, J = 4.8 Hz, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 154.0, 145.6, 117.8, 114.5, 67.0, 55.5, 50.8. HRMS (ESI) calcd for $C_{11}H_{16}NO_2$ [M + H^+] 194.1176, found 194.1177.

4-(3-Methoxyphenyl)morpholine (3ab).[5h] Colorless oil (168 mg, 87% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.25−7.15 (m, 1H), 6.55−6.42 (m, 3H), 3.84 (t, J = 4.8 Hz, 4H), 3.79 (s, 3H), 3.14 (t, J = 4.8 Hz, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.6, 152.7, 129.8, 108.5, 104.7, 102.2, 66.9, 55.2, 49.3. HRMS (ESI) calcd for $C_{11}H_{16}NO_2$ [M + H^+] 194.1176, found 194.1177.

4-(4-Methylphenyl)morpholine (3ac).[24] White solid (151 mg, 85% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.09 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 3.86 (t, J = 4.5 Hz, 4H), 3.11 (t, J = 4.5 Hz, 4H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 149.2, 129.7, 129.6, 116.0, 67.0, 49.9, 20.4. HRMS (ESI) calcd for $C_{11}H_{16}NO$ [M + H^+] 178.1226, found 178.1229.

4-(2-Methylphenyl)morpholine (3ad).[7b] Pale yellow oil (147 mg, 83% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.19−7.15 (m, 2H), 7.02−6.98 (m, 2H), 3.84 (t, J = 4.5 Hz, 4H), 2.90 (t, J = 4.5 Hz, 4H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 151.2, 132.6, 131.1, 126.6, 123.4, 118.9, 67.4, 52.2, 17.8. HRMS (ESI) calcd for $C_{11}H_{16}NO$ [M + H^+] 178.1226, found 194.1228.

4-Phenylmorpholine (3ae).[7b] White solid (140 mg, 86% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.16−7.23 (m, 2H), 6.85−6.80 (m, 3H), 3.78−3.75 (m, 4H), 3.08−3.04 (m, 4H). $^{13}C\{^1H\}$ NMR (75

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MHz, $CDCl_3$): δ 151.2, 129.1, 120.0, 115.7, 66.9, 49.3. HRMS (ESI) calcd for $C_{10}H_{14}NO$ [M + H$^+$] 164.1070, found 164.1072.

4-Pyridin-2-ylmorpholine (3ag).[7b] Yellow oil (138 mg, 84% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21−8.19 (m, 1H), 7.53−7.47 (m, 1H), 6.68−6.62 (m, 2H), 3.83 (t, *J* = 4.8 Hz, 4H), 3.49 (d, *J* = 4.8 Hz, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.5, 147.9, 137.5, 113.8, 106.9, 66.7, 45.6. HRMS (ESI) calcd for $C_9H_{13}N_2O$ [M + H$^+$] 165.1022, found 165.1024.

4-Pyridin-3-ylmorpholine (3ah). Yellow oil (146 mg, 89% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.14−8.11 (m, 1H), 7.19−7.17 (m, 2H), 3.88 (t, *J* = 4.8 Hz, 4H), 3.18 (t, *J* = 4.8 Hz, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 146.8, 141.0, 138.2, 123.5, 122.0, 66.6, 48.5. HRMS (ESI) calcd for $C_9H_{12}N_2O$ [M + H$^+$] 165.1022, found 165.1028.

4-Thien-2-ylmorpholine (3ai). Yellow oil (146 mg, 86% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.81−6.77 (m, 1H), 6.64−6.61 (m, 1H), 6.16−6.13 (m, 1H), 3.85−3.80 (m, 4H), 3.13−3.09 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.3, 126.1, 112.7, 105.6, 66.4, 51.9. HRMS (ESI) calcd for $C_8H_{11}NOS$ [M + H$^+$] 170.0634, found 170.0638.

4-Thien-3-ylmorpholine (3aj). White solid (149 mg, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26−7.24 (m, 1H), 6.87−6.84 (m, 1H), 6.21−6.19 (m, 1H), 3.84 (d, *J* = 4.8 Hz, 4H), 3.08 (d, *J* = 4.8 Hz, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 152.4, 125.6, 119.6, 100.4, 66.7, 50.7. HRMS (ESI) calcd for $C_8H_{11}NOS$ [M + H$^+$] 170.0634, found 170.0639.

***N*-(3-Methoxyphenyl)dibenzylamine (3bb).** Yellow oil (267 mg, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.21 (m, 10H), 7.08−7.05 (m, 1H), 6.38−6.34 (m, 1H), 6.30−6.26 (m, 2H), 4.63 (s, 4H), 3.69 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 160.7, 150.6, 138.5, 129.9, 128.6, 126.8, 126.6, 105.6, 101.4, 98.9, 55.0, 54.2. HRMS (ESI) calcd for $C_{21}H_{21}NO$ [M + H$^+$] 304.1696, found 304.1701.

***N*-(4-Methylphenyl)dibenzylamine (3bc).** Colorless oil (236 mg, 82% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−7.16 (m, 10H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.60 (s, 4H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 147.0, 138.8, 129.7, 128.6, 126.8, 126.7, 125.8, 112.6, 54.3, 20.2. HRMS (ESI) calcd for $C_{21}H_{21}N$ [M + H$^+$] 288.1747, found 288.1752.

***N,N*-Dibenzylaniline (3be).**[7b] White solid (246 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24−7.03 (m, 10H), 6.65−6.57 (m, 4H), 4.56 (s, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.1, 138.5, 129.2, 128.6, 126.8, 126.6, 116.7, 112.3, 54.1. HRMS (ESI) calcd for $C_{20}H_{20}N$ [M + H$^+$] 274.1590, found 274.1597.

***N*-(2-Pyridyl)dibenzylamine (3bg).** Yellow oil (228 mg, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14−8.10 (m, 1H), 7.24−7.13 (m, 11H), 6.51−6.46 (m, 1H), 6.38−6.35 (m, 1H), 4.71 (s, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.6, 148.0, 138.4, 137.4, 128.5, 127.0, 126.9, 112.2, 105.8, 50.8. HRMS (ESI) calcd for $C_{19}H_{18}N_2$ [M + H$^+$] 275.1543, found 275.1548.

***N*-(3-Pyridyl)dibenzylamine (3bh).**[25] Yellow oil (241 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 3.5 Hz, 1H), 7.94 (d, *J* = 4.0 Hz, 1H), 7.35−7.28 (m, 8H), 7.18−7.16 (m, 4H), 4.72 (s, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 147.1, 134.3, 129.5, 128.6, 128.3, 127.9, 126.7, 126.2, 124.5, 54.9. HRMS (ESI) calcd for $C_{19}H_{19}N_2$ [M + H$^+$] 275.1543, found 274.1548.

***N*-(3-Thienyl)dibenzylamine (3bj).** Yellow oil (237 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.17 (m, 10H), 7.10−7.08 (m, 1H), 6.74−6.72 (m, 1H), 5.92 (s, 1H), 4.48 (s, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 150.6, 138.6, 128.4, 127.2, 126.9, 124.9, 119.1, 96.9, 56.0. HRMS (ESI) calcd for $C_{18}H_{17}NS$ [M + H$^+$] 280.1154, found 280.1160.

***N*-(4-Bromophenyl)dibenzylamine (3bk).**[9g] White solid (250 mg, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.20 (m, 12H), 6.50−6.57 (m, 2H), 4.63 (s, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 148.1, 140.0, 131.9, 128.7, 127.1, 126.5, 111.4, 108.6, 54.4.

***N*-(4-Chlorophenyl)dibenzylamine (3bl).**[6] White solid (212 mg, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.20 (m, 10H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.63 (s, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 147.7, 138.1, 128.9, 128.7, 127.0, 126.5, 121.5, 113.7, 54.5. HRMS (ESI) calcd for $C_{20}H_{19}ClN$ [M + H$^+$] 308.1201, found 308.1202.

***N,N*-Diethylaniline (3ce).**[7b] Pale yellow oil (106 mg, 71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.19 (m, 2H), 6.71−6.64 (m, 3H), 3.35 (q, *J* = 6.9 Hz, 4H), 1.16 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.2, 129.6, 115.8, 112.3, 44.7, 12.9. HRMS (ESI) calcd for $C_{10}H_{15}N$ [M + H$^+$] 150.1277, found 150.1281.

***N,N*-Diethylthiophen-2-amine (3ci).**[26] Pale yellow oil (107 mg, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21−7.18 (m, 1H), 6.78−6.75 (m, 1H), 5.90−5.88 (m, 1H), 3.25 (q, *J* = 7.2 Hz, 4H), 1.13 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.4, 125.2, 119.6, 96.2, 45.9, 12.7. HRMS (ESI) calcd for $C_8H_{14}NS$ [M + H$^+$] 156.0841, found 156.0844.

***N*-Benzyl-4-methoxy-*N*-methylaniline (3da).** Red oil (166 mg, 73% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22−7.14 (m, 5H), 6.76−6.64 (m, 4H), 4.34 (s, 2H), 3.66 (s, 3H), 2.83 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 152.2, 145.2, 139.6, 128.9, 127.6, 127.3, 115.2, 115.0, 58.5, 56.2, 39.5. HRMS (ESI) calcd for $C_{15}H_{17}NO$ [M + H$^+$] 228.1383, found 228.1388.

***N*-Benzyl-*N*-methylaniline (3de).** Yellow oil (124 mg, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34−7.19 (m, 7H), 6.76−6.68 (m, 3H), 4.54 (s, 2H), 3.02 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 150.2, 139. 5, 129.6, 129.0, 127.3, 127,2, 116.9, 112.8, 57.0, 39.0. HRMS (ESI) calcd for $C_{14}H_{15}N$ [M + H$^+$] 198. 1277, found 198.1283.

***N*-Benzyl-*N*-methylpyridin-2-amine (3dg).** Yellow oil (123 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20−8.17 (m, 1H), 7.45−7.39 (m, 1H), 7.33−7.20 (m, 5H), 6.58−6.48 (m, 2H), 4.80 (s, 2H), 3.07 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.3, 148.4, 139.1, 137.7, 128.9, 127.4, 127.3, 112.2, 106.1, 53.6, 36.6. HRMS (ESI) calcd for $C_{13}H_{14}N_2$ [M + H$^+$] 199.1230, found 199.1235.

***N*-Benzyl-*N*-isopropylbenzenamine (3ee).**[27] Pale yellow oil (129 mg, 61% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−7.13 (m, 7H), 6.72−6.66 (m, 3H), 4.41 (s, 2H), 4.34−4.20 (dt, 1H), 1.20 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.4, 140.9, 129.2, 128.5, 126.5, 126.3, 116.5, 113.2, 48.5, 48.3, 20.0. HRMS (ESI) calcd for $C_{16}H_{20}N$ [M + H$^+$] 226.1596, found 260.1593.

***N*-Benzyl-4-chloro-*N*-isopropylbenzenamine (3el).** Pale yellow oil (200 mg, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31−7.21 (m, 5H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.38 (s, 2H), 4.26−4.16 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 147.8, 140.1, 128.8, 128.5, 126.6, 126.1, 121.1, 114.4, 48.6, 48.3, 19.8. HRMS (ESI) calcd for $C_{16}H_{19}NCl$ [M + H$^+$] 260.1206, found 260.1202.

***N,N*-Diisopropylbenzenamine (3fe).**[9c] Colorless oil (105 mg, 59% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22−7.16 (m, 2H), 6.91−6.88 (m, 2H), 6.79−6.74 (m, 1H), 3.81−3.72 (m, 2H), 1.20 (d, *J* = 6.6 Hz, 12H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 148.0, 128.4, 119.4, 118.2, 47.5, 21.3. HRMS (ESI) calcd for $C_{12}H_{20}N$ [M + H$^+$] 178.1590, found 178.1593.

4-Bromo-*N,N*-diisopropylbenzenamine (3fk).[9c] Colorless oil (91 mg, 58% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, *J* = 6.0 Hz, 2H), 6.74 (d, *J* = 6.0 Hz, 2H), 3.78−3.69 (m, 2H), 1.20 (d, *J* = 6.6 Hz, 12H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 147.1, 137.2, 120.3, 109.9, 47.6, 21.2. HRMS (ESI) calcd for $C_{12}H_{19}BrN$ [M + H$^+$] 256.0695, found 256.0697.

***N,N*-Dicyclohexylbenzenamine (3ge).**[9d] Pale yellow oil (180 mg, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25−7.15 (m, 2H), 6.95−6.92 (m, 2H), 6.82−6.77 (m, 1H), 3.27−3.20 (m, 2H), 1.78−1.08 (m, 20H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 148.7, 128.2, 121.0, 119.0, 57.5, 32.0, 26.3, 26.0. HRMS (ESI) calcd for $C_{18}H_{28}N$ [M + H$^+$] 258.2216, found 258.2218.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of the compounds **3**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00767.

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Notes

The authors declare no competing financial interest.

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