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Copper-Catalyzed $NaBAr_4$-Based N-Arylation of Amines

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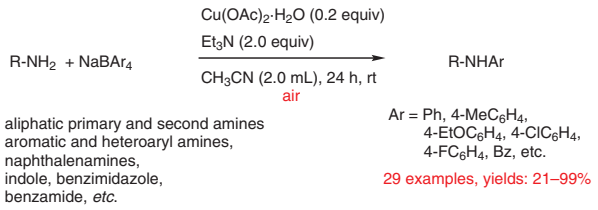

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Abstract Using $NaBAr_4$ as an arylating agent, the formation of carbon–heteroatom bonds by a Cham–Lam cross-coupling reaction in the presence of catalytic copper(II) acetate monohydrate in acetonitrile at room temperature under air is described. The investigation of reaction scope suggests that several aliphatic and aromatic amines are compatible. In particular, the reaction of alkylamine and $NaBAr_4$ proceeds smoothly to offer the corresponding products in good to excellent yields.

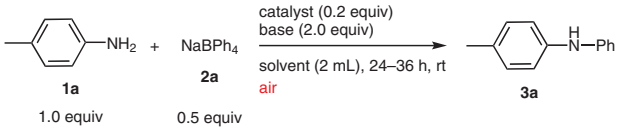
Keywords Cham–Lam cross-coupling reaction, amine, copper acetate monohydrate, tetraphenylborate, N-phenylation

Cross-coupling reaction through a metal catalysis is one of the most important and powerful strategies for the formation of carbon–heteroatom bonds. Among these achievements, the copper-catalyzed reaction of aniline and an organohalide, well-recognized as Ullmann reaction,[1] represents as an efficient synthetic method for C–N bond formation. Additionally, Cham–Evans–Lam cross-coupling reaction[2] mediated by copper salt has emerged as one of significant alternatives for C–N bond formation.[3] Highlighted by a mild reaction condition (room temperature, weak base, and in air), Cham–Evans–Lam reaction always resorted to the usage of arylboronic acid and arylboronates[3a,4] as arylating reagents. In the past decade, organometallic partners including aryllead triacetate,[5] arylbismuth,[6] siloxanes,[7] and hypervalent diaryliodonium salts[8] were also witnessed as efficient aryl sources for this copper-catalyzed N-arylation of anilines. However, synthetic applications of the above reaction were restricted due to the fact that the use of stoichiometric copper salt was required in most of the reactions. As such, tremendous efforts had been made for elaboration of Cham–Evans–Lam reaction with a wish to reduce the loading of copper salt[9–13] and to understand the mechanism of the Chan–Lam amination reaction.[14] An elegant example from Collman indicated that catalytic $[Cu(OH)\cdot TMEDA]_2Cl_2$ enabled this reaction,[9] but it suffered from a limited reaction scope. Assisted by an external oxidant such as molecular oxygen, TEMPO, and pyridine *N*-oxide, Lam[10] found that catalytic cross-coupling of aniline and aromatic amine with arylboronic acids was realized in the presence of catalytic $Cu(OAc)_2$. Batey[12] demonstrated that aliphatic amines were good reaction partners for Cham–Evans–Lam reaction when catalytic copper(II) acetate monohydrate and 4Å molecular sieves were used in dichloromethane at slightly elevated temperatures under an atmosphere of oxygen. On the other hand, $NaBPh_4$ is a stable, non-toxic and commercially available phenylating agent. Compared with other organoboron compounds, $NaBPh_4$ possesses many advantages including lower-cost, easier to handle, and simpler workup. Moreover, it is chemically well-calculated in contrast to the in situ generated organometallic reagents such as arylzinc or cadmium reagents. Mechanistic investigation suggested that σ-phenyl complex of transition metals was observed as a key intermediate in the $NaBPh_4$-based N-phenylation.[15] Consequently, $NaBPh_4$ exhibited excellent versatility in various metal-catalyzed reactions, including palladium-catalyzed phenylation of allylic acetates[16] and chlorides,[17] Suzuki cross-coupling reactions,[18] and hydrophenylation of alkynes[19] and Rh-catalyzed addition reactions.[20] However, application of $NaBPh_4$ in Chan–Lam cross-coupling reaction was not reported so far. Herein we would like to disclose a catalytic version of Chan–Lam cross-coupling using $NaBPh_4$ as a phenyl source. Our primary aim of this study was to develop a suitable reaction condition to realize that in the presence of catalytic copper salt, $NaBPh_4$ reacted with various NH functions (such as aniline, aromatic amines, and aliphatic amines, etc.) to provide N-phenyl architectures with high efficiency and an excellent functional group tolerance.

Initially, *p*-toluidine (**1a**) was chosen as model coupling partner to react with $NaBPh_4$ under conditions presented as following: 20 mol% $Cu(OAc)_2{\cdot}H_2O$, 2.0 equivalents of Et_3N, dichloromethane as solvent, and at room temperature in air. To our delight, the model reaction afforded the desired product **3a** in 72% yield (Table 1, entry 1). Encouraged by this result, we screened diverse result-affecting factors including catalyst, base, and solvent. The results are outlined in Table 1. Various catalysts were first examined for this reaction. It seemed that the transformation worked uniquely well when the reaction was treated with catalytic $Cu(OAc)_2{\cdot}H_2O$ or $CuCl_2$ (entries 1, 2). Other transitional metals such as Cu_2O, $FeCl_3$, $Co(OAc)_2$, and AgOAc did not promote the model reaction (entries 3–6). Subsequently, various bases were elaborated. From the results, we were pleased to find that Et_3N was the best choice, and other bases gave inferior yields (entries 1, 7–9). Particularly, a control experiment without a base offered a negative outcome, indicating the necessity for the presence of a base (entry 10). Based on screening of solvent, the reaction was extremely sensitive to the solvent. Of the solvent detected, MeCN was found to be the best solvent for this reaction (entry 11), leading to the desired product **3a** in 80%. Water as solvent just delivered a moderate yield of the arylated product **3a** (entry 12). No desired product **3a** was detected in PEG-400, DME, and 1,4-dioxane (entries 13–15). The control experiment indicated that only trace amount of the desired product was obtained when reaction was performed under N_2 (entry 16). Thus, the optimized conditions are as follows: 0.5 equivalent $NaBPh_4$, 20 mol% $Cu(OAc)_2{\cdot}H_2O$, 200 mol% Et_3N in MeCN at room temperature in air for 24 hours.

With the optimized conditions in hand, the reaction scope was exploited and the results are presented in Table 2. From the results, it seemed that various arylamines, attached with either electron-donating or electron-withdrawing groups on the phenyl ring afforded the coupling products **3a–i** in moderate to good yields (Table 2, entries 1–9). Anilines with electron-rich groups were more favorable for the reaction under standard conditions. For example, the reaction of 4-ethoxylphenylamine (**1d**) afforded the *N*-phenyl-4-ethoxylphenylamine (**3d**) in 92% yield, while 4-nitrophenylamine (**1j**) just provided the desired product **3j** in 43% yield (entry 10). Notably, the formation of biaryl byproduct derived from homocoupling of 4-methoxyphenylamine (**1c**) was obtained in 24% yield (entry 3). Naphthyl-linked amines **1k** and **1l** were also good reaction partners, leading to the desired *N*-phenyl products **3k** and **3l** in good to excellent yields (entries 11 and 12). Interestingly, this reaction conditions could also be utilized to heteroarylamine **1m** and indole **1n** (entries 13, 14). However, the corresponding reactions did not work well, just giving the desired products **3m** and **3n** in a yield of 37% and 31%, respectively. Surprisingly, under standard conditions the reaction of benzimidazole (**1o**) offered the corresponding *N*-phenylbenzimidazole (**3o**) in 97% yield (entry 15). Subsequently, aliphatic amines were then examined. Pleasingly, various aliphatic amines were suitable for the reaction, providing the desired products **3p–t** in moderate to excellent yields. For instance, the reaction of morpholine (**1q**) gave the *N*-phenylmorpholine (**3q**) in 99% yield, and the reaction of benzylamine (**1t**) provided **3t** in 67% yield. Moreover, aliphatic secondary amines seemed to be more efficient reaction partners. For example, the reaction of piperidine (**1p**) gave the desired *N*-phenylpiperidine (**3p**) in 90% yield while the reaction of cyclohexylamine (**1r**) produced **3r** only in 60% yield. The reaction of *n*-butylamine provided the desired product **3s** in a reasonable yield (entry 19). The standard conditions were not well compatible for the reaction of benzamide (**1u**) (entry 21), and just gave the desired product **3u** in 23% yield.

Table 1 Conditions Screened for C–N Bond Formation with $NaBPh_4$[a]

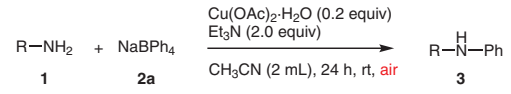


1a (1.0 equiv) 2a (0.5 equiv) 3a

Entry	Catalyst	Base	Solvent	Time (h)	Yield (%)[b]
1	$Cu(OAc)_2{\cdot}H_2O$	Et_3N	CH_2Cl_2	24	72
2	$CuCl_2$	Et_3N	CH_2Cl_2	24	51
3	Cu_2O	Et_3N	CH_2Cl_2	36	trace
4	$FeCl_3$	Et_3N	CH_2Cl_2	36	0
5	$Co(OAc)_2$	Et_3N	CH_2Cl_2	36	0
6	AgOAc	Et_3N	CH_2Cl_2	36	0
7	$Cu(OAc)_2{\cdot}H_2O$	pyridine	CH_2Cl_2	36	0
8	$Cu(OAc)_2{\cdot}H_2O$	K_2CO_3	CH_2Cl_2	24	55
9	$Cu(OAc)_2{\cdot}H_2O$	NaOH	CH_2Cl_2	24	68
10	$Cu(OAc)_2{\cdot}H_2O$	–	CH_2Cl_2	36	0
11	$Cu(OAc)_2{\cdot}H_2O$	Et_3N	MeCN	24	80
12	$Cu(OAc)_2{\cdot}H_2O$	Et_3N	H_2O	24	32
13	$Cu(OAc)_2{\cdot}H_2O$	Et_3N	PEG-400	24	0
14	$Cu(OAc)_2{\cdot}H_2O$	Et_3N	DME	24	0
15	$Cu(OAc)_2{\cdot}H_2O$	Et_3N	1,4-dioxane	24	0
16[c]	$Cu(OAc)_2{\cdot}H_2O$	Et_3N	MeCN	24	trace

[a] All reactions were performed in 0.2 mmol scale, standard conditions: **1a** (0.2 mmol), $NaBPh_4$ (0.1 mmol), 20 mol% catalyst, 200 mol% Et_3N, solvent (2.0 mL), r.t. in air.
[b] Isolated yield.
[c] The reaction was performed under N_2.

Table 2 Copper-Catalyzed Coupling of N–H Substrates with $NaBPh_4$[a]



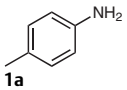
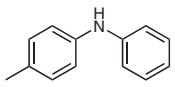
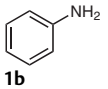
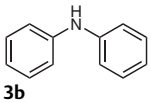
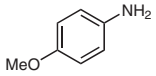
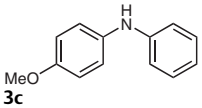
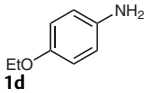
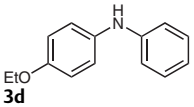
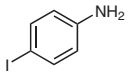
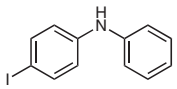
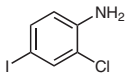
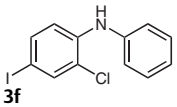
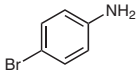
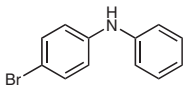
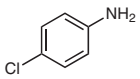
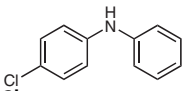
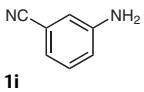
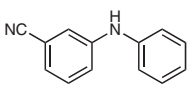
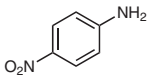
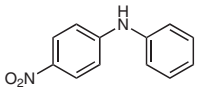
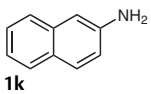
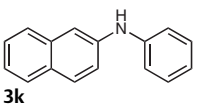
Entry	Substrate	Product	Yield (%)[b]
1	 **1a**	 **3a**	80
2	 **1b**	 **3b**	77
3	 **1c**	 **3c**	62[c]
4	 **1d**	 **3d**	92
5	 **1e**	 **3e**	75
6	 **1f**	 **3f**	87
7	 **1g**	 **3g**	75
8	 **1h**	 **3h**	55
9	 **1i**	 **3i**	71
10	 **1j**	 **3j**	43
11	 **1k**	 **3k**	99

Table 2 (continued)

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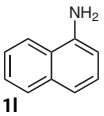
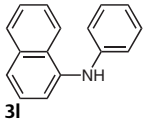
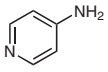
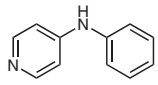
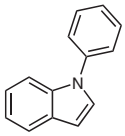
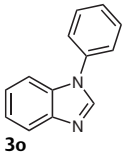
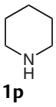
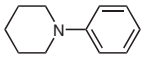
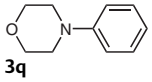
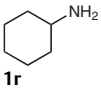
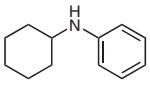
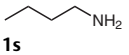
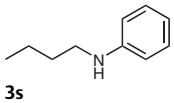
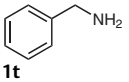
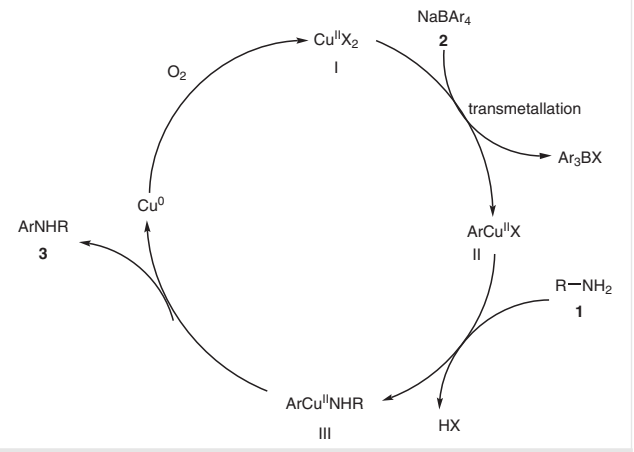
12	 **1l**	 **3l**	73
13	 **1m**	 **3m**	37
14	 **1n**	 **3n**	31
15	 **1o**	 **3o**	97
16	 **1p**	 **3p**	90
17	 **1q**	 **3q**	99
18	 **1r**	 **3r**	60
19	 **1s**	 **3s**	39
20	 **1t**	**3t**	67
21	**1u**	**3u**	23

[a] All reactions were performed in 0.2 mmol scale, standard conditions: **1a** (0.2 mmol), $NaBPh_4$ (**2a**; 0.1 mmol), 20 mol% catalyst, 200 mol% Et_3N, solvent (2.0 mL), r.t. in air.
[b] Isolated yield.
[c] The isolated compound was a mixture of **3c** (62%) and the biaryl by-product (24%).

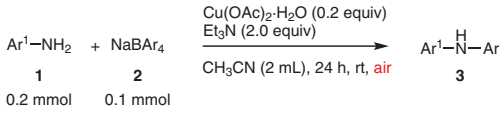
Then, sodium tetraarylborates **2b–f** were prepared[21] in our laboratory for investigating the generality in borate compounds (Table 3). The results in Table 3 indicate that the electronic nature of the borate compounds had significant effect on the reaction efficiency. The electron-rich $NaBAr_4$ are favorable for the reaction under standard conditions and gave higher yields. For example, the reactions of **1a** with $NaB(4\text{-}MeC_6H_4)_4$ (**2b**) or $NaB(4\text{-}EtOC_6H_4)_4$ (**2c**) afforded the corresponding *N*-aryl-4-methylphenylamine **3ab** and **3ac** in 91% and 88% yield, respectively (Table 3, entries 1, 2). The reaction of $NaBAr_4$ with an electron-withdrawing substituent such as $NaB(4\text{-}ClC_6H_4)_4$ (**2d**) and $NaB(4\text{-}FC_6H_4)_4$ (**2e**) gave the corresponding product only in 23% and 21% yield, respectively, (entries 3, 4). When the more electron-deficient [3,5-bis(trifluoromethyl)phenyl]borate (**2f**) was employed, no desired product was obtained (not listed in Table 3). Finally, good to excellent yields were obtained when various amines **1e**, **1h**, **1k**, and **1q** were reacted with **2b** (entries 5–8).

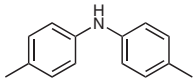
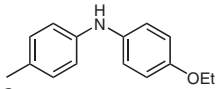
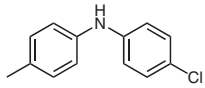
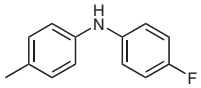
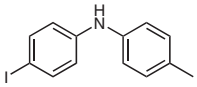
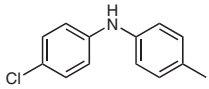
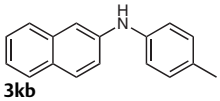
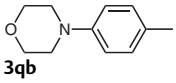
As regards the reaction mechanism, we propose that the process begins from the catalyst Cu(II) **I**, which undergoes transmetalation with $NaBAr_4$ **2** to deliver arylCu(II) species **II** (Scheme 1). Amine **1** reacts with **II** to form $ArCu^{II}NHR$ **III**. Finally, $ArCu^{II}NHR$ undergoes reductive elimination to give the product **3** and releases Cu^0, which is oxidized by O_2 to liberate Cu(II), and complete the cycle.



Scheme 1 Proposed reaction mechanism

Table 3 Copper-Catalyzed Coupling of N–H Substrates with $NaBAr_4$[a]



Entry	Amine	X-C_6H_4	Product	Yield (%)[b]
1	**1a**	4-Me **2b**	 **3ab**	91
2	**1a**	4-EtO **2c**	 **3ac**	88
3	**1a**	4-Cl **2d**	 **3ad**	23
4	**1a**	4-F **2e**	 **3ae**	21
5	**1e**	**2b**	 **3eb**	80
6	**1h**	**2b**	 **3ad**	54
7	**1k**	**2b**	 **3kb**	92
8	**1q**	**2b**	 **3qb**	96

[a] All reactions were performed in 0.2 mmol scale, standard conditions: **1** (0.2 mmol), $NaBAr_4$ **2** (0.1 mmol), 20 mol% catalyst, 200 mol% Et_3N, solvent (2.0 mL), r.t. in air.
[b] Isolated yield.

In conclusion, we have described a $NaBPh_4$-based Chan–Lam cross-coupling reaction. The transformation proceeded smoothly under mild conditions. The investigation of reaction scope suggested that several tetraarylborates, aliphatic and aromatic amines were compatible. Particularly, the reaction of alkylamine and $NaBPh_4$ worked well to deliver the corresponding products in high efficiency.

All reactions were performed in reaction tubes under air. Reagents and solvents were purchased and used without further purification. Flash column chromatography was performed using 200–300 mesh silica gel using EtOAc and petroleum ether as eluent. Analytical TLC was carried out using glass plates pre-coated with GF254 silica gel impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated by rotary evaporator. NMR spectra are recorded in ppm from internal TMS the δ scale. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in

ppm and coupling constants in Hz. IR spectra were recorded using KBr cells or mixture of compounds/KBr on an FT-IR spectrophotometer.

N-Arylation of Amines 3; General Procedure

A 10 mL vial was charged with the substrate amine **1** (0.2 mmol), $NaBPh_4$ or $NaBAr_4$ (0.1 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (0.2 equiv) in MeCN (2 mL). To this mixture was added Et_3N (2.0 equiv). The reaction mixture was then stirred at r.t. for 24 h. After completion of the reaction as monitored by TLC, the mixture was then concentrated through a rotary evaporator to yield the product, which was purified by direct flash column chromatography (Tables 2 and 3).

N-Phenyl-4-methylaniline (3a)[22a]

Yield: 29 mg (80%); yellow solid; mp 88.2–89.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.17 (m, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.03–6.95 (m, 4 H), 6.88 (t, *J* = 7.2 Hz, 1 H), 5.60 (s, 1 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 140.3, 130.9, 129.9, 129.4, 129.3, 120.3, 118.9, 116.9, 20.7.

Diphenylamine (3b)[22b]

Yield: 26 mg (77%); white solid; mp 48.5–49.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.18 (m, 4 H), 7.11–7.00 (m, 4 H), 6.95–6.85 (m, 2 H), 5.71 (s, 1 H).

N-(4-Methoxyphenyl)aniline (3c)[22b]

Yield: 25 mg (62%). The isolated compound was a mixture of **3c** and the biaryl by-product (2.92:1, calculated by ^{1}H NMR analysis).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.8 Hz, 2 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 6.86–6.80 (m, 3 H), 5.43 (s, 1 H), 3.78 (s, 3 H).

4-Ethoxy-*N*-phenylaniline (3d)[22b]

Yield: 39 mg (92%); white solid; mp 72.9–73.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (t, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 4.8 Hz, 2 H), 6.90 (d, *J* = 7.2 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 4.04–3.99 (m, 2 H), 1.40 (t, *J* = 7.2 Hz, 3 H).

N-Phenyl-4-iodoaniline (3e)[22c]

Yield: 44 mg (75%); light yellow solid; mp 101.7–103.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.48 (m, 2 H), 7.28 (t, *J* = 8.0 Hz, 2 H), 7.09–7.03 (m, 2 H), 6.97 (t, *J* = 7.4 Hz, 2 H), 6.86–6.79 (m, 2 H), 5.68 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 142.2, 138.2, 138.0, 129.6, 129.4, 119.3, 119.0, 118.5, 82.1.

2-Chloro-4-iodo-*N*-phenylaniline (3f)

Yield: 57 mg (87%); wine-colored oil.

IR (KBr): 3402.6, 1579.1, 1503.9, 1463.9, 1313.6, 1046.9, 869.3, 805.6, 756.5, 693.0, 495.9 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (t, *J* = 2.0 Hz, 1 H), 7.38–7.28 (m, 3 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.07 (t, *J* = 7.4 Hz, 1 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 6.07 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7, 140.4, 137.5, 136.2, 129.6, 123.4, 122.0, 120.8, 118.9, 116.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_9ClIN$: 329. 9546; found: 329.9547.

N-Phenyl-4-bromoaniline (3g)[12b]

Yield: 37 mg (75%); brown solid; mp 87.6–88.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.4 Hz, 2 H), 7.26 (t, *J* = 7.8 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.96 (t, *J* = 7.2 Hz, 1 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 5.66 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.40, 142.37, 132.2, 129.4, 121.6, 119.0, 118.3, 112.6.

N-Phenyl-4-chloroaniline (3h)[22b]

Yield: 22 mg (55%); white solid; mp 66.5–67.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.4 Hz, 2 H), 7.27 (t, *J* = 7.8 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.96 (t, *J* = 7.2 Hz, 1 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 5.66 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 141.9, 129.5, 129.4, 125.5, 121.5, 118.8, 118.1.

3-(Phenylamino)benzonitrile (3i)

Yield: 28 mg (71%); dark green solid; mp 68.7–69.4 °C.

IR (KBr): 3339.9, 3124.6, 2234.4, 1593.5, 1580.1, 1496.1, 1456.1, 1339.4, 1152.9, 763.8, 722.5, 695.7 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.30 (m, 3 H), 7.25 (s, 1 H), 7.21–7.15 (m, 1 H), 7.14–6.98 (m, 4 H), 5.90 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 141.1, 130.2, 129.7, 123.5, 123.0, 120.7, 119.8, 119.1, 118.8, 113.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}N_2$: 195.0922; found: 195.0957.

N-(4-Nitrophenyl)aniline (3j)[22d]

Yield: 18 mg (43%); yellow solid; mp 134.6–136.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 9.2 Hz, 2 H), 7.39 (t, *J* = 7.8 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 6.95 (d, *J* = 9.2 Hz, 2 H), 6.32 (s, 1 H).

N-Phenyl-2-naphthalenamine (3k)[22e]

Yield: 43 mg (99%); white solid; mp 106.4–108.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.77 (m, 2 H), 7.66 (d, *J* = 8.0 Hz, 1 H), 7.52 (s, 1 H), 7.44–7.37 (m, 1 H), 7.34–7.21 (m, 6 H), 7.02 (t, *J* = 7.2 Hz, 1 H).

N-Phenyl-1-naphthalenamine (3l)[22e]

Yield: 32 mg (73%); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 7.6 Hz, 1 H), 7.63–7.53 (m, 1 H), 7.53–7.43 (m, 2 H), 7.42–7.34 (m, 2 H), 7.30–7.19 (m, 2 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.92 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 138.7, 134.7, 129.5, 129.3, 128.6, 128.5, 127.7, 126.1, 126.0, 121.8, 120.6, 117.5.

N-Phenylpyridin-4-amine (3m)[22f]

Yield: 13 mg (37%); white solid; mp 174.2–176.1 °C.

IR (KBr): 3488.7, 3376.2, 2961.3, 1722.1, 1634.9, 1521.0, 1431.8, 1295.7, 1077.2, 834.4, 729.1, 704.1 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.20–7.12 (m, 5 H), 7.12–7.04 (m, 3 H), 7.00 (t, *J* = 6.8 Hz, 1 H), 5.60 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 134.7, 133.7, 127.1, 126.7, 124.4, 108.8.

1-Phenyl-1*H*-indole (3n)[22g]

Yield: 12 mg (31%); light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.6 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.54–7.49 (m, 4 H), 7.35 (d, *J* = 3.2 Hz, 2 H), 7.23–7.14 (m, 2 H), 6.69 (d, *J* = 3.2 Hz, 1 H).

1-Phenyl-1*H*-benzo[*d*]imidazole (3o)[22b]

Yield: 38 mg (97%); brown solid; mp 95.3–96.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.94–7.85 (m, 1 H), 7.61–7.51 (m, 5 H), 7.48 (t, *J* = 7.2 Hz, 1 H), 7.38–7.29 (m, 2 H).

1-Phenylpiperidine (3p)[12b]

Yield: 29 mg (90%); light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.19 (m, 2 H), 6.97–6.90 (m, 2 H), 6.82 (t, *J* = 7.2 Hz, 1 H), 3.18–3.08 (m, 4 H), 1.74–1.68 (m, 4 H), 1.59–1.55 (m, 2 H).

4-Phenylmorpholine (3q)[12b]

Yield: 32 mg (99%); light yellow solid; mp 52.7–53.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, *J* = 8.0 Hz, 2 H), 6.92–6.86 (m, 3 H), 3.84 (t, *J* = 4.8 Hz, 4 H), 3.13 (t, *J* = 4.8 Hz, 4 H).

***N*-Cyclohexylaniline (3r)**[22b]

Yield: 21 mg (60%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (t, *J* = 7.8 Hz, 2 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 6.58 (d, *J* = 8.2 Hz, 2 H), 3.50 (s, 1 H), 3.27–3.22 (m, 1 H), 2.05 (d, *J* = 12.0 Hz, 2 H), 1.77–1.74 (m, 2 H), 1.66 (d, *J* = 12.8 Hz, 1 H), 1.41–1.32 (m, 2 H), 1.26–1.09 (m, 3 H).

***N*-Butylaniline (3s)**[22b]

Yield: 12 mg (39%); light brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 8.0 Hz, 2 H), 6.68 (t, *J* = 7.2 Hz, 1 H), 6.60 (d, *J* = 7.8 Hz, 2 H), 3.59 (s, 1 H), 3.10 (t, *J* = 7.2 Hz, 2 H), 1.65–1.54 (m, 2 H), 1.49–1.35 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H).

***N*-Benzylaniline (3t)**[22b]

Yield: 25 mg (67%); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 4 H), 7.27–7.23 (m, 1 H), 7.15 (t, *J* = 8.0 Hz, 2 H), 6.70 (t, *J* = 7.2 Hz, 1 H), 6.61 (d, *J* = 8.4 Hz, 2 H), 4.29 (s, 2 H), 3.97 (s, 1 H).

***N*-Phenylbenzamide (3u)**[22g]

Yield: 9 mg (23%); white solid; mp 164.2–166.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 6.8 Hz, 2 H), 7.81 (s, 1 H), 7.65 (d, *J* = 7.8 Hz, 2 H), 7.56 (d, *J* = 6.8 Hz, 1 H), 7.52 (t, *J* = 7.2 Hz, 2 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.16 (t, *J* = 7.2 Hz, 1 H).

Di-*p*-Tolylamine (3ab)[22h]

Yield: 36 mg (91%); white solid; mp 70.5–71.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.2 Hz, 4 H), 6.96 (d, *J* = 8.0 Hz, 4 H), 5.51 (s, 1 H), 2.31 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 130.2, 129.8, 118.0, 20.6.

4-Ethoxy-*N*-(*p*-tolyl)aniline (3ac)[22i]

Yield: 40.1 mg (88%); white solid; mp 58.5–60.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–6.95 (m, 4 H), 6.90–6.78 (m, 4 H), 5.38 (s, 1 H), 4.01 (q, *J* = 6.8 Hz, 2 H), 2.28 (s, 3 H), 1.41 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.2, 142.5, 136.6, 129.8, 129.3, 121.2, 116.6, 115.5, 63.9, 20.5, 14.9.

4-Chloro-*N*-(*p*-tolyl)aniline (3ad)[22j]

Yield: 10 mg (23%) and 23 mg (54%) (entries 3 and 6, respectively, in Table 3); white solid; mp 76.5–78.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 5.57 (s, 1 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 139.8, 131.6, 129.9, 129.2, 124.7, 119.2, 117.9, 20.69.

4-Fluoro-*N*-(*p*-tolyl)aniline (3ae)[22k]

Yield: 8.0 mg (21%); white solid; mp 49.5–51.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 8.0 Hz, 2 H), 7.01–6.88 (m, 4 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 5.47 (s, 1 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7 (d, *J* = 240.0 Hz), 141.2, 139.9, 130.6, 130.0, 119.4 (d, *J* = 7.7 Hz), 117.9 (s), 115.8 (d, *J* = 22.3 Hz), 20.6.

4-Iodo-*N*-(*p*-tolyl)aniline (3eb)[22j]

Yield: 49.6 mg (80%); white solid; mp 96.5–97.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.8 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.76 (d, *J* = 8.4 Hz, 2 H), 5.57 (s, 1 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 139.4, 138.0, 131.9, 130.0, 119.7, 118.5, 81.2, 20.7.

***N*-(*p*-Tolyl)naphthalen-2-amine (3kb)**[22e]

Yield: 40.6 mg (92%); white solid; mp 92.5–94.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.71 (m, 2 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.45–7.36 (m, 2 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.22–7.14 (m, 3 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 5.77 (s, 1 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 140.2, 134.8, 131.4, 130.0, 129.2, 129.0, 127.7, 126.43, 126.40, 123.2, 119.6, 119.4, 110.4, 20.8.

4-(*p*-Tolyl)morpholine (3qb)[22l]

Yield: 31.3 mg (96%); white solid; mp 39.5–41.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.4 Hz, 2 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 3.87 (t, *J* = 4.6 Hz, 4 H), 3.12 (t, *J* = 4.8 Hz, 4 H), 2.29 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.3, 129.7, 129.6, 116.1, 67.0, 50.0, 20.4.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610251.

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