Copper-TBAF catalyzed arylation of amines and amides with aryl trimethoxysilane†

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A copper-catalyzed C–N bond forming reaction among aryl siloxane and primary, secondary amines as well as amides has been described. The reaction was conducted in the presence of $P(C_6F_5)_3$ and 4 Å molecular sieves in CH_2Cl_2 at room temperature under O_2. A catalytic amount of TBAF was employed to activate aryl siloxanes.

Introduction

C–N bond formation *via* cross-coupling plays an important role in the preparation of nitrogen-containing compounds in pharmaceuticals, crop-protection chemicals and material sciences.[1] The transition-metal-catalyzed cross-coupling reactions between amines with aryl electrophilic reagents such as ArX (X = Cl, Br, I) and ArOTf were powerful tools for the C–N bond formation.[2] Traditional procedures, such as the Ullmann reaction, generally required harsh conditions. Kosugi *et al.* described a palladium-catalyzed amination of halides with tributylstannamines.[3] More recently, the palladium-catalyzed Hartwig-Buchwald amination reactions deserved particular mention due to their high efficiency and good substrate tolerance.[4,5] In addition to palladium,[6] nickel[7] and copper[8] have also been reported for such transformation. In 2007, Bolm and Correa reported an iron-catalyzed *N*-arylation of aryl halides.[9]

Lately, much attention has been paid to the development of transition-metal-catalyzed *N*-arylation through the reaction of amines with nucleophilic arylmetal reagents. Organometals, such as aryllead triacetates,[10] arylboronic acids,[11] arylbismuths,[12] diaryl iodonium salts,[13] and arylstannanes[14] were reported to be efficient reaction partners with nitrogen-containing compounds for the *N*-arylation reaction. The use of organoboronic reagents won high prestige in metal-catalyzed C–N bond formation thanks to their advantages of relative stability toward air and moisture, good functional group tolerance, commercial availability and low toxicity as well as ease of synthesis.[15] An alternative to such a transformation is siloxane methodology, which eliminates the purification difficulties associated with organoboron reagents,[16] and the toxic byproducts associated with the use of organolead and organotin compounds.[17] However, examples of employing arylsilanes in *N*-arylation reaction have been scarcely reported before.[18,19]

In the article of Lam *et al.*, a spectrum of *N*-arylated products was obtained by use of amines and siloxanes as the cross-coupling partners.[19] But this protocol required 1.1 equiv. of copper. Most recently, Li and co-workers reported a solvent-free version of Cu–Fe co-catalyzed *N*-arylation reactions of nitrogen-containing heterocycles with trimethoxysilanes in air.[18] However, one or more than one equiv. of TBAF was still required either in Lam or Li's reaction system. The excess fluoride was environmentally unfriendly, especially in the large scale preparation. Hence, developing an efficient method using a catalytic amount of fluoride salt as the additive to realize the aforementioned transformation is highly desirable. Herein, we report a copper-TBAF catalyzed *N*-arylation of amines and amides with $PhSi(OMe)_3$ in the presence of an electron-deficient triarylphosphine, providing the *N*-arylated products in moderate to good yields at room temperature under an O_2 atmosphere. This method may provide a potential pathway for the development of carbon–carbon or carbon–heteroatom bond forming reactions employing a catalytic amount of TBAF to activate $ArSi(OMe)_3$.

Results and discussion

Parameters in the *N*-arylation reaction

Initial studies of the reaction were conducted using the *N*-arylation of morpholine **1r** as the model reaction. 4 Å molecular sieves were added to eliminate moisture in the reaction system. A series of parameters that had effects on the reaction was tested in the absence of any phosphine ligand. To our disappointment, no desired product was formed. After tedious screening, much to our delight, we found that the combination of CuF_2 (5 mol%), $Cu(OAc)_2$ (10 mol%) and PPh_3 (10 mol%) could produce the desired product in 69% yield (Table 1, entry 2). Further screening showed that KF, CsF, LiF and FeF_3 inhibited the reaction and TBAF was a better additive than CuF_2 in the reaction. Encouraged by this promising result, we then tested some other phosphine ligands in the reaction system. Introducing *ortho* substituents in the aryl group of the phosphine ligands did not increase the yield (Table 1, entry 10). Bidentate phosphine ligands, such as dppe and dppp, were also proper ligands in the reaction (Table 1, entries 7 and 9), while dppb and dppf failed to deliver the product (Table 1, entries 6 and 8). Electron-deficient triarylphosphine ligands were superior to the electron-rich and neutral analogues. For example, the yield increased to 78% with the combination of $TBAF{\cdot}3H_2O$, 4 Å molecular sieves, $Cu(OAc)_2$ and $P(4\text{-Cl-}C_6H_4)_3$

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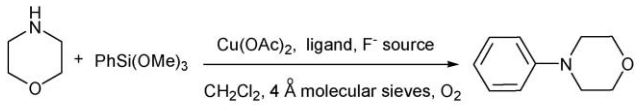
Table 1 Screening of parameters in the *N*-arylation reaction[a]



1r 2a 3ra

Entry	F^- sources	Ligand	Solvent	Yield (%)[b]
1	CuF_2	None	CH_2Cl_2	<5
2	CuF_2	PPh_3	CH_2Cl_2	69
3	TBAF	PPh_3	CH_2Cl_2	75
4	TBAF	dppe	CH_2Cl_2	64
5	TBAF	*i*-Pr_2NPPh_2	CH_2Cl_2	64
6	TBAF	dppb	CH_2Cl_2	<5
7	TBAF	dppe	CH_2Cl_2	64
8	TBAF	dppf	CH_2Cl_2	<5
9	TBAF	dppp	CH_2Cl_2	65
10	TBAF	P(2-tol)$_3$	CH_2Cl_2	53
11	TBAF	P(3,5-di-Me-C_6H_3)$_3$	CH_2Cl_2	56
12	TBAF	P(4-MeO-C_6H_4)$_3$	CH_2Cl_2	58
13	TBAF	P(C_6F_5)$_3$	CH_2Cl_2	90 (57[c], 46[d])
14	TBAF	P(1-naph)$_3$	CH_2Cl_2	63
15	TBAF	1-(Dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-yl)piperidine	CH_2Cl_2	76
16	TBAF	P(4-Cl-C_6H_4)$_3$	CH_2Cl_2	78
17	TBAF	P(C_6F_5)$_3$	Toluene	48
18	TBAF	P(C_6F_5)$_3$	DMF	75
19	TBAF	P(C_6F_5)$_3$	DCE	76
20	TBAF	P(C_6F_5)$_3$	$CHCl_3$	35

[a] Reaction conditions: $PhSi(OMe)_3$ (198 mg, 1 mmol), copper source (10 mol%), F^- source (10 mol%), ligand (10 mol% or 5 mol% for bidendate ligand), morpholine (36 mg, 0.5 mmol), 4 Å molecular sieves (100 mg) and indicated solvent (4 mL) under O_2 at room temperature for 24 h. [b] Isolated yield. [c] Under air, molecular sieves. [d] Under air, no molecular sieves.

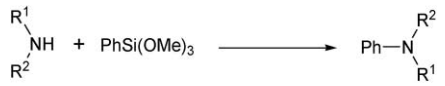
under O_2 in CH_2Cl_2 (Table 1, entry 16). By employing the electron-rich phosphine ligand P(4-MeO-C_6H_4)$_3$, the yield decreased to 58% (Table 1, entry 12). In light of this, more electron-deficient triarylphosphine ligands were tested. Finally, we were pleased to find that by employing the more electron-deficient phosphine ligand P(C_6F_5)$_3$ (10 mol%), the yield increased dramatically to 90% (Table 1, entry 13). The yield was quickly decreased when the reaction was performed under air or in the absence of molecular sieves. The solvents also had an obvious effect on the reaction. Among the solvents tested, CH_2Cl_2 was the best.

The substrate scope

Once the optimized conditions were obtained, the scope of the reaction was examined. As expected, a variety of amines ran smoothly, including primary and secondary, or aliphatic and aromatic amines, providing the *N*-arylation product in moderate to good yields, respectively. Aniline and its derivatives proved to be good cross-coupling substrates under these conditions, affording the diarylamine products in good yield. The sterics of the amines had an obvious effect on the reaction. For example, **3oa** and **3qa** were only isolated in 44% and 50% yields, respectively, while **3fa** and **3pa** were formed in 67% and 71% yield, respectively (Table 2, entries 15, 17, 6 and 16).

It was noteworthy that amides were also good reaction partners in the procedure, although the yields were moderate. For example, **3ea**, **3ja**, **3la** and **3na** were isolated in 52%, 34%, 52% and 50%

Table 2 *N*-Arylation of the amines or amides with $PhSi(OMe)_3$[a]



1 2a 3

Entry	R^1R^2NH	Yield (%)[b]	Entry	R^1R^2NH	Yield (%)[b]
1	*n*-$BuNH_2$ **1a**	**3aa** 48	10	**1j**	**3ja** 34
2	**1b**	**3ba** 73	11	**1k**	**3ka** 60
3	**1c**	**3ca** 67	12	**1l**	**3la** 52
4	**1d**	**3da** 85	13	*n*-$C_{18}H_{37}NH_2$ **1m**	**3ma** 60
5	**1e**	**3ea** 52	14	**1n**	**3na** 50
6	**1f**	**3fa** 67	15	**1o**	**3oa** 44
7	**1g**	**3ga** 66	16	**1p**	**3pa** 71
8	**1h**	**3ha** 62	17	**1q**	**3qa** 50
9	**1i**	**3ia** 64	18	**1r**	**3ra** 90

[a] Reaction conditions: $PhSi(OMe)_3$ (198 mg, 1 mmol), $R^1R^2NH_2$ (0.5 mmol), $Cu(OAc)_2$ (9 mg, 10 mol%), TBAF·$3H_2O$ (15 mg, 10 mol%), P(C_6F_5)$_3$ (27 mg, 10 mol%), CH_2Cl_2 (4 mL) and 100 mg of 4 Å MS under O_2 at room temperature for 24 h. [b] Isolated yield.

yield, respectively (Table 2, entries 5, 10, 12 and 14). This may be at least partly caused by the low nucleophilic ability of the nitrogen atom in the presence of the electron-withdrawing groups. Notably, 2-chloroacetamide **3la** and 4-chlorobenzenamine **3ga** ran smoothly in the procedure and kept the chloro group untouched (Table 2, entries 12 and 7).

Having demonstrated the utility of the addition reaction conditions on $PhSi(OMe)_3$, we chose to test the generality of the functional group tolerance of the $ArSi(OMe)_3$, as shown in Fig. 1.

The reaction may proceed as follows: (1) $ArSi(OMe)_3$ is activated by F^- to form $[PhSi(OMe)_3F]^-$; (2) $[PhSi(OMe)_3F]^-$ enters the catalytic cycle, which is similar to the reported *N*-arylation reaction of amines with boronic acids.[20] It is interesting to note that the Ar group in $ArSi(OMe)_3$ was transferred to the product in the presence of a catalytic amount of TBAF; however, the catalytic cycle of fluoride is still unclear.[21]

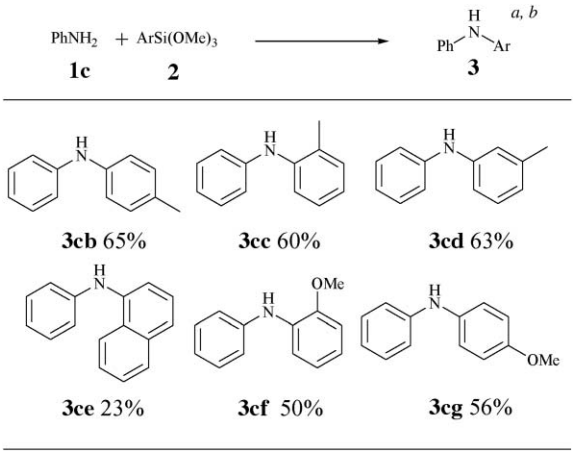


Fig. 1 *N*-Arylation of $PhNH_2$ with $ArSi(OMe)_3$.

Conclusions

In conclusion, we have developed a mild $Cu(OAc)_2$-TBAF co-catalyzed *N*-arylation reaction of amines and amides with $ArSi(OMe)_3$, which was activated by catalytic amounts of TBAF under nearly neutral conditions, providing the *N*-arylation products in moderate to good yields. The reaction has a wide substrate scope, including amides, primary and secondary or aliphatic and aromatic amines, and may provide a potential pathway for the development of carbon–carbon or carbon–heteroatom bond forming reactions related to catalytic TBAF activation of $ArSi(OMe)_3$. Mechanistic investigations and the application of the catalytic fluoride system with $ArSi(OMe)_3$ are the focus of ongoing efforts in our laboratory currently.

Experimental

General

Under atmosphere a reaction tube was charged with $PhSi(OMe)_3$ (198 mg, 1 mmol), $Cu(OAc)_2$ (18 mg, 10 mol%), $TBAF{\cdot}3H_2O$ (15 mg, 10 mol%), $P(C_6F_5)_3$ (27 mg, 10 mol%), CH_2Cl_2 (3 mL) and 100 mg of 4 Å MS at room temperature. After stirring for 5 min, 0.5 mmol of amine or amide was added and the reaction tube was purged with O_2. The mixture kept stirring at room temperature for 24 h. After the completion of the reaction, as monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel column to give the product. The NMR data of all the products match the literature data.

1-Phenylpiperidine (3ba)[22]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.23 (m, 2H), 6.97–6.95 (m, 2H), 6.86–6.81 (m, 1H), 3.18–3.15 (m, 4H), 1.76–1.69 (m, 4H), 1.62–1.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 129.5, 119.2, 117.6, 50.7, 25.9, 24.3.

Diphenylamine (3ca)[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.23 (m, 4H), 7.08–7.05 (m, 4H), 6.94–6.89 (m, 2H), 5.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.0, 129.4, 129.3, 120.9, 117.8.

N-Benzylaniline (3da)[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.31 (m, 5H), 7.27–7.19 (m, 2H), 6.66–6.65 (m, 2H), 4.36 (s, 2H), 4.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.8, 139.2, 129.0, 128.4, 127.3, 127.0, 117.3, 112.6, 48.1.

N-Phenylbenzamide (3ea)[24]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88–7.85 (m, 3H), 7.66–7.63 (m, 2H), 7.55–7.46 (m, 4H), 7.18–7.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 65.5, 137.6, 134.7, 131.6, 128.9, 128.6, 126.8, 124.3, 119.9.

4-Methyl-*N*-phenylaniline (3fa)[22]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.23 (m, 2H), 7.12–7.09 (d, J = 8.2 Hz, 2H), 7.04–7.00 (m, 4H), 6.92–6.87 (m, 1H), 5.61 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 140.3, 130.9, 129.9, 129.3, 120.3, 118.9, 116.8, 20.7.

4-Chloro-*N*-phenylaniline (3ga)[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.19 (m, 4H), 7.05–6.95 (m, 5H), 5.66 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142, 141.8, 129.4, 129.3, 125.5, 121.5, 118.8, 118.1.

N-Phenylpyridin-2-amine (3ha)[26]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22–8.21 (m, 1H), 7.50–7.49 (m, 1H), 7.35–7.33 (m, 4H), 7.08–7.06 (m, 1H), 6.92–6.89 (m, 1H), 6.76–6.73 (m, 1H), 2.12 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.8, 148.1, 140.2, 137.5, 129.0, 122.6, 120.1, 114.7, 107.9.

N-(1-Phenylethyl)aniline (3ia)[27]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–6.51 (m, 10H), 4.50 (s, 1H), 4.00 (s, 1H), 1.53 (d, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.3, 145.2, 129.1, 128.6, 126.9, 125.8, 117.2, 113.3, 53.4, 25.1.

N-Phenylacetamide (3ja)[28]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.49–7.47 (m, 2H), 7.31–7.25 (m, 2H), 7.09–7.07 (m, 1H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 137.9, 128.9, 124.3, 120.0, 24.5.

N-(3-Methoxyphenyl)benzenamine (3ka)[29]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.24 (m, 2H), 7.19–7.07 (m, 3H), 6.95–6.92 (m, 1H), 6.66–6.63 (m, 2H), 6.50–6.46 (m, 1H), 5.71 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.7, 144.6, 142.8, 130.1, 129.3, 121.2, 118.3, 110.2, 106.1, 103.3, 55.2.

2-Chloro-*N*-phenylacetamide (3la)[30]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.55–7.53 (m, 2H), 7.38–7.33 (m, 2H), 7.19–7.14 (m, 1H), 4.18 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.7, 136.6, 129.1, 125.2, 120.1, 42.9.

N-Octadecylbenzenamine (3ma)[31]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21–7.15 (m, 2H), 6.72–6.67 (m, 1H), 6.62–6.60 (m, 2H), 3.60 (s, 1H), 3.13–3.08 (m, 2H), 1.64–1.60

(m, 2H), 1.39–1.24 (m, 30H), 0.91–0.86 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.6, 129.1, 117.0, 112.6, 43.9, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.2, 22.7, 14.1.

3-Phenyloxazolidin-2-one (3na)[32]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–7.53 (m, 2H), 7.40–7.35 (m, 2H), 7.17–7.12 (m, 1H), 4.49–4.44 (m, 2H), 4.07–4.02 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 138.2, 129.0, 124.0, 118.2, 61.3, 45.1.

2-Methyl-*N*-phenylaniline (3oa)[33]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.20 (m, 5H), 6.99–6.89 (m, 4H), 5.39 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7, 146.0, 135.7, 134.1, 133.0, 131.5, 126.7, 125.2, 123.5, 122.2, 22.7.

***N*-(4-Methoxyphenyl)benzenamine (3pa)[34]**

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24–7.18 (m, 2H), 7.08–7.05 (m, 2H), 6.91–6.83 (m, 5H), 5.48 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.7, 129.3, 124.3, 122.2, 119.5, 115.6, 114.6, 114.1, 55.6.

2-Methoxy-*N*-phenylaniline (3qa)[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.25 (m, 2H), 7.16 (d, J = 7.6 Hz, 2H), 6.95–6.87 (m, 5H), 6.16 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.2, 142.7, 132.9, 129.3, 121.1, 120.8, 119.9, 118.5, 114.6, 110.5, 55.6.

4-Phenylmorpholine (3ra)[33]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.25 (m, 2H), 6.93–6.88 (m, 3H), 3.87–3.84 (m, 2H), 3.17–3.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.3, 129.2, 120.1, 115.7, 66.9, 49.3.

3-Methyl-*N*-phenylbenzenamine (3cd)[35]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27–7.22 (m, 3H), 7.13–7.11 (m, 1H), 7.06–7.03 (m, 2H), 6.90–6.86 (m, 2H), 6.74–6.72 (m, 1H), 5.65 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.0, 131.3, 129.3, 129.2, 121.9, 120.8, 119.5, 118.5, 117.8, 114.9. 21.5.

***N*-Phenylnaphthalen-1-amine (3ce)[36]**

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99–7.98 (m, 1H), 7.90–7.82 (m, 3H), 7.52–7.44 (m, 5H), 6.98–6.88 (m, 3H), 5.89 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.0, 129.3, 129.1, 128.5, 126.1, 126.0, 125.7, 122.9, 122.8, 121.8, 120.5, 117.3, 115.8.

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21 In the ^{19}F NMR, the signal of TBAF in CD_2Cl_2 appeared at −127.9 ppm (Fig. 1 in ESI†). Adding 20 equiv. of $PhSi(OMe)_3$ in the reaction system, the signal shifted to −145.5 ppm, which was ascribed to the $[PhSi(OMe)_3F]^-$ species (Fig. 2 in ESI). After $Cu(OAc)_2$ (1 equiv.) was added, one signal at −129.9 ppm appeared within 3 min, accompanied by the signal at −145.5 ppm (Fig. 3 in ESI). The signal at −145.5 ppm almost disappeared after 12 h (Fig. 4, 5 in ESI). In addition to $Cu(OAc)_2$, $CuBr_2$ had almost the same effect on the system. CuI had little effect, but when the mixture was exposed to air for one week, the signal at −145.5 ppm all shifted to −129.9 ppm. In the presence of 1 equiv. of $P(C_6F_5)_3$, together with 1 equiv. of $Cu(OAc)_2$, the signal at −145.5 ppm immediately and almost totally shifted to −128.6 ppm within 3 min (Fig. 6, 7 in ESI). The phosphine ligand may play dual roles in the reaction. One is to increase the solubility of $Cu(OAc)_2$ by coordination of the copper and phosphine in the reaction system. The other is to alter the electron potential of copper in the catalytic cycles.
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