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Nucleophilic Amination and Etherification of Aryl Alkyl Thioethers

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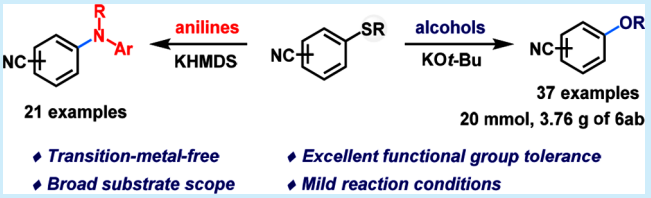
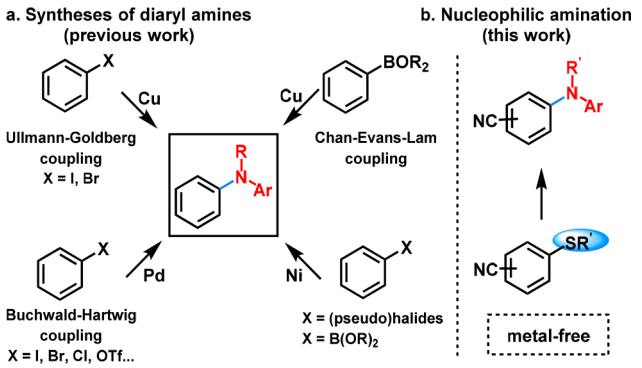
Supporting Information

ABSTRACT: A transition-metal-free protocol capable of synthesizing diarylated aniline derivatives is reported. This method could be further employed to prepare aryl alkyl ethers. A wide range of thioethers, anilines, as well as alcohols were tolerated thanks to the mild reaction conditions. The strength of our method was demonstrated by performing a gram-scale reaction (20 mmol) followed by conversion of the nitrile group into synthetically useful aldehyde, ketone, and carboxylic acid.



Owing to the extensive existence of diarylamines in dyes, pharmaceuticals, agrochemicals, materials, and nature products, intense effort has been dedicated to the exploration of methods for the syntheses of aromatic amines (Scheme 1).[1]

Scheme 1. Methods for Aniline Syntheses



For instance, C−N bond construction has focused on variations of Cu-catalyzed Ullmann−Goldberg coupling between aryl halides and anilines[2] and Chan−Evans−Lam coupling between boronic acids and nitrogen nucleophiles.[3,4] Nevertheless, not many transformations were achieved because of the weak nucleophilicity of aryl amines as compared to aliphatic amines and ammonia. In the past few decades, Buchwald−Hartwig C−N coupling of aryl (pseudo)halides with anilines has emerged as a powerful protocol for the preparation of diarylated amines, allowing rapid development of this significant research area.[5,6] In addition, transition-metal-catalyzed C(sp^2)−H amination has exhibited its capability of incorporating anilines onto arenes.[7] Although transition-metal-free anilines formation protocols are valuable complements to the existing synthetic methods, this research field has received much less attention. Recently, transition-metal-catalyzed conversion of the C(sp^2)−S bond into C−H,[8] C−C,[9] and C−X (X = P,[10] B,[11] S,[12] N[13]) bonds have attracted great attention due to the easy accessibility and handling of aromatic thioethers. Given that the alkylthiolate can poison metal catalysts, the whole catalytic cycle would be suppressed by the *in-situ* generated alkylthiolate.[14] This drawback greatly limits the development of this research area. Therefore, developing metal-free C(sp^2)−S bond cleavage strategies is highly desirable because these techniques could serve as attractive supplements to the ones that need transition-metal catalysts.

At the beginning of our investigations, it was uncertain whether such a protocol could be achieved as several challenges still exist: (1) the electronegativity of sulfur is very close to a sp^2-hybridized carbon atom, and the C−S bond thus is not significantly polarized; (2) the increased electron density of the aromatic ring, which stems from strong electron-donating −SR group might suppress the reaction; (3) the nucleophilicity of aniline is quite low. We started our study by evaluating the amination of **1a** with **2a**. After careful optimization, we found that the use of KO*t*-Bu as base in 1,4-dioxane at 60 °C could generate the expected product in 23% isolated yield (Table 1, entry 1).[15] NaO*t*-Bu was much less efficient than KO*t*-Bu, and only a trace amount of product was observed (entry 2). To our delight, the use of KHMDS could improve the yield to 50% in 1,4-dioxane (entry 3), while other solvents such as THF, diethyl ether, and methyl *tert*-butyl ether afforded the targeted aniline in slightly lower yields (entries 4−6). Interestingly, 85% of yield was detected when the reaction conducted in a mixed solvent and lower concentration in the presence of KHMDS (entry 7). Changing

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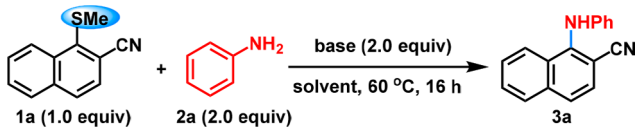
Table 1. Optimization of Reaction Conditions[a]



entry	base[b]	solvent	conv[c] (%)	yield[c] (%)
1	KO*t*-Bu	1,4-dioxane	100	23[d]
2	NaO*t*-Bu	1,4-dioxane	30	trace
3	KHMDS	1,4-dioxane	70	50
4	KHMDS	THF	64	48
5	KHMDS	Et_2O	62	42
6	KHMDS	*t*-BuOMe	64	46
7	KHMDS (1 M in THF)	1,4-dioxane	100	85 (80[d])
8	NaHMDS (2.0 M in THF)	1,4-dioxane	100	84
9	LiHMDS (1 M in THF)	1,4-dioxane	100	60
10	KHMDS (1 M in THF)	1,4-dioxane	99	35[e]
11	KHMDS (1 M in THF)	1,4-dioxane	100	33[f]
12	none	1,4-dioxane	0	

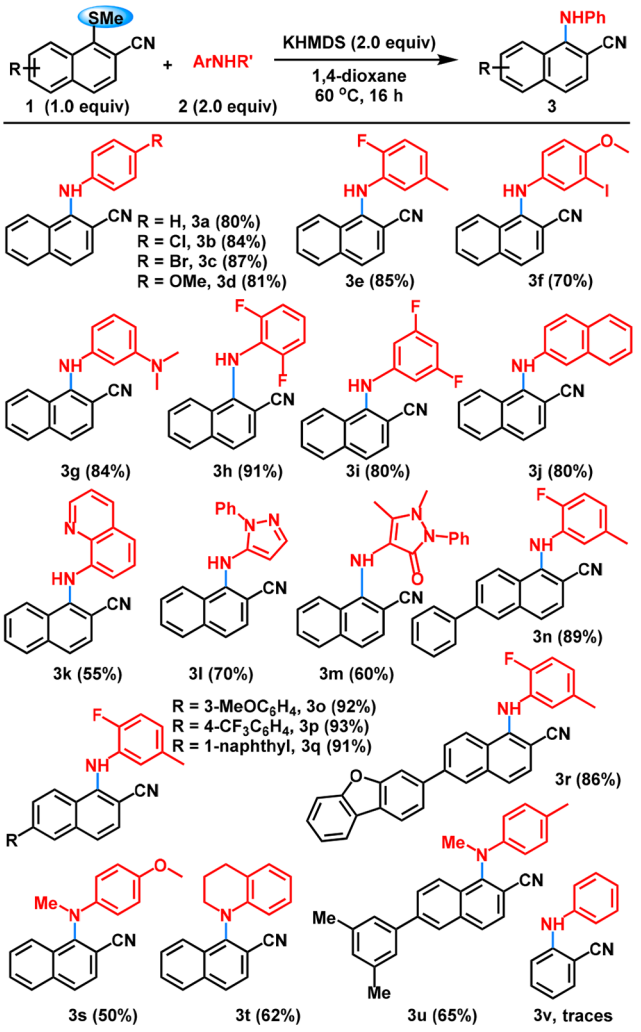
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), base (1.0 mmol), 60 °C, 16 h. [b]KHMDS = potassium hexamethyldisilazane; NaHMDS = sodium hexamethyldisilazane; LiHMDS = lithium hexamethyldisilazane. [c]NMR conversions and yields using naphthalene as internal standard. [d]Isolated yield. [e]KHMDS (1.5 equiv). [f]**2a** (1.5 equiv).

the base to NaHMDS provided a similar yield of 84%, and a moderate yield was observed with LiHMDS (entries 8 and 9). Decreasing the loading of KHMDS or **2a** to 1.5 equiv led to inferior yields of 35% and 33%, respectively (entries 10 and 11). Not surprisingly, the control experiment without KHMDS did not deliver any targeted aniline (entry 12).

With optimized conditions in hand, we then investigated the generality of our newly developed amination protocol. Notably, electron-deficient amines that possess halides such as fluoride (Scheme 2, **3e**, **3h**, **3i**), chloride (**3b**), and bromide (**3c**) all reacted smoothly with **1a** to produce the corresponding products in excellent yields. The aminations of **1a** with a series of electron-rich or electron-neutral amines competently afforded the diarylated amines (**3a**, **3d**, **3f**, **3g**, **3j**). Furthermore, the mild reaction conditions are compatible with a variety of heterocycles, such as quinoline (**3k**), pyrazole (**3l**), and pyrazol-3-one (**3m**). In addition, we also tested the substrate scope of aryl alkyl thioether, and a range of naphthyl methyl thioethers possessing various substituents at the 6-position were also suitable for this transformation, giving the desired products in excellent yields (**3n**–**r**). Remarkably, we found that secondary amines could also be used to provide arylated products in moderate yields, which can be explained by the increased bulkiness of the amines (**3s**–**u**). Unfortunately, traces amount of desired amine could be observed when benzonitrile was employed as starting material (**3v**).

Encouraged by these results, we questioned whether we could further apply our method to prepare aryl alkyl ethers, not only because of their significant roles in producing of catalysts, cosmetics, fragrances, and functional materials[16,17] but also because of their wide existence in biologically active agents and pharmaceutically significant compounds.[18] After a quick optimization, we found 86% yield of **6a** was isolated, while KO*t*-Bu served as base in dioxane at 80 °C. We next focused our attention on the representative examples of this interesting etherification reaction. As summarized in Scheme 3, all of the

Scheme 2. Substrate Scope of Amination Reaction[a]



[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), KHMDS (1 M in THF, 1.0 mmol), 1,4-dioxane (0.5 mL), 60 °C, 16 h. [b]Isolated yield. [c]KHMDS = potassium hexamethyldisilazane

2-SMe-substituted benzonitriles produced the corresponding products in high yields regardless of the nature of the substituents on phenyl ring (Scheme 3, **6a**–**d**). The reactions of starting materials with heterocycles such as thiophene and benzofuran occurred in high efficiency, affording **6e** and **6f** in 63% and 68% of yields, respectively. In addition, 4-SMe-substituted benzonitriles could also take part in the reaction, albeit with slightly lower yields (**6g**, **6h**). Intriguingly, the position of the −SMe group does have a profound influence on reactivity for the naphthonitrile substrate, and **6j** was delivered in 55% yield while 93% of yield was obtained for **6i**. We next explored the scope of alcohols under otherwise identical reaction conditions. A variety of primary alcohols were found to be suitable for this transformation, generating the corresponding ethers in good to excellent yields (**6k**–**q**). It is worth noting that secondary alcohols reacted well with both benzonitrile and naphthonitirles, resulting in the formation of desired products (**6r**, **6s**). Remarkably, tertiary alkoxides such as KO*t*-Bu could be employed in this reaction, although their reactivity is much lower than primary and secondary ones (**6t**–**v**). Owing to the mild reaction conditions, good functional group compatibility was observed, and a variety of groups such

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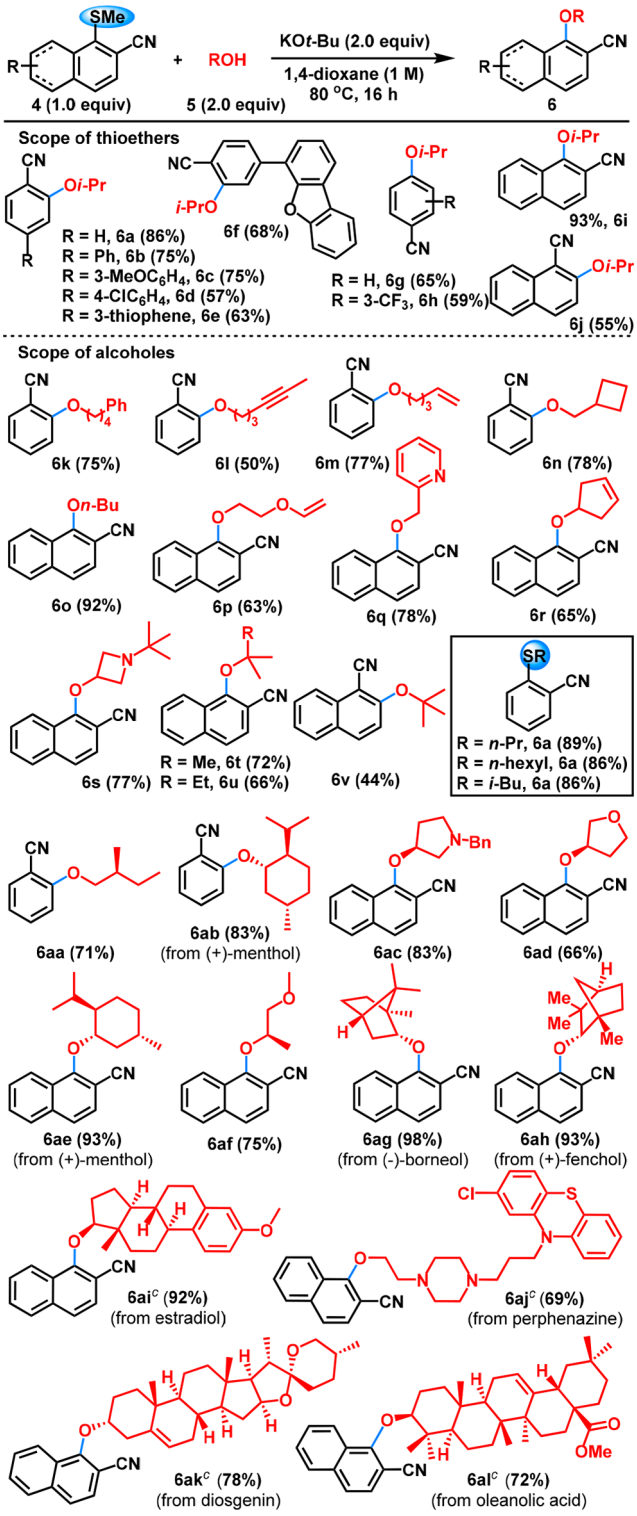
Scheme 3. Substrate Scope of Thioethers and Alcohols[a]

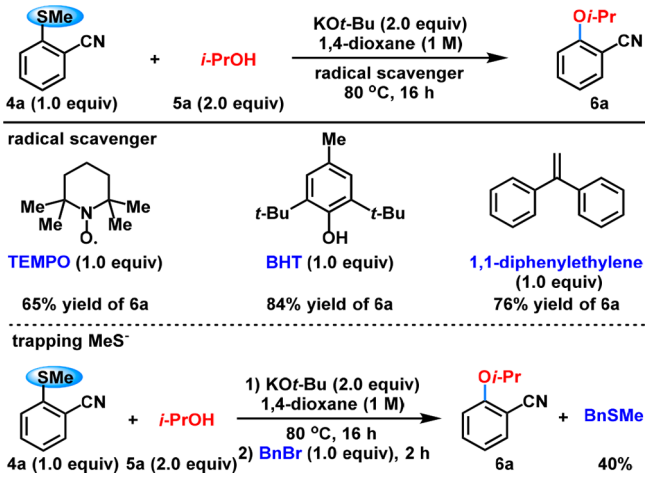


[a]Reaction conditions: **4** (0.5 mmol), **5** (1.0 mmol), KO*t*-Bu (1.0 mmol), dioxane (0.5 mL, 1M), 60 °C, 16 h. [b]Isolated yield. [c]1.5 mL 1,4-dioxane, 30 °C

as alkyne (**6l**), alkene (**6m**, **6p**, **6r**), amine (**6s**), ether (**6p**), and pyridine (**6q**) were well tolerated. It is noteworthy that the other alkyl thioethers such as *n*-PrS−, *n*-hexylS−, and *i*-BuS− could also participate the etherification, generating **6a** in excellent yields. To further validate the generality of our method, we then conducted the etherifications of **4** with various chiral alcohols, natural products, and pharmaceutical related alcohols.[12] As shown in Scheme 3, benzonitrile was found to effortlessly react with (*S*)-(−)-2-methyl-1-butanol (**6aa**) and secondary alcohol such as (+)-menthol (**6ab**). We were pleased to find that the utilization of nitrogen- or oxygen-containing alcohols could generate the desired ether products in high yields (**6ac**, **6ad**, **6af**). Surprisingly, steric bulkier secondary alcohols such as (−)-borneol and (+)-fenchol were efficiently incorporated into arenes with 98% (**6ag**) and 93% (**6ah**) of yields. Promoted by these promising results, estradiol (**6ai**), perphenazine (**6aj**), diosgenin (**6ak**), and oleanolic acid derivative (**6al**) were subjected to the standard reaction conditions. Gladly, all the cases we tested were all reacted, delivering the targeted aryl alkyl ethers in good yields.

To shed light on the mechanism of our protocols, we next decided to carry out mechanistic studies. The addition of radical scavengers such as TEMPO, BHT, and 1,1-diphenylethylene to the etherification reaction did not suppress the reaction, and the targeted product **6a** was obtained in slightly lower yields as shown in Scheme 4. These results might allow

Scheme 4. Mechanistic Studies of Etherification



us to exclude the possibility of a radical pathway. We also trapped MeS^- by adding benzyl bromide, and benzyl methyl thioether was detected in 40% yield. Although the proposal of a detailed mechanism should await further investigations, we suggest this transformation should take a nucleophilic aromatic substitution course.

The practicality of our synthetic method is demonstrated in Scheme 5. As shown, the reaction could be scaled up to 20 mmol, affording the desired product **6ab** in 73% isolated yield (3.76 g). The practicality of this protocol was further verified by converting the etherification product **6a** into reduced product **7a** in 98% yield and carboxylic acid **7c** in 60% yield under basic reaction conditions. Additionally, **6ab** could undergo reduction with DIBAL-H and addition with MeMgBr, generating the aldehyde **7b** and ketone **7d** in 97% and 95% of yield, respectively.

In summary, we described a transition-metal-free protocol capable of efficiently incorporating weak nucleophilic anilines into nitrile substituted aryl alkylthio ethers. It is worth noting that the mild reaction conditions could tolerate a variety of aryl alkylthio ethers and anilines. Moreover, secondary amine also participated the amination reactions, generating the targeted

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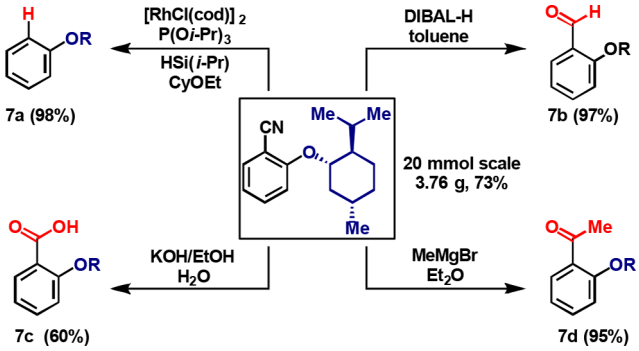
Scheme 5. Gram-Scale Reaction and Applications



tertiary amines in good yields. Importantly, we could further apply this strategy to synthesize aryl alkyl ethers. Likewise, a variety of alcohols include primary, secondary, bulky tertiary alcohols, drugs and even biologically active molecules were suitable for this transformation. The value of our method has been verified by the gram-scale-reaction and the derivatization of nitrile into synthetically significant building blocks. We anticipate this technique would find wide applications in different research fields.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01758.

Experimental procedures, characterization data, and spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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