Homogeneous Catalysis

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Nickel-Catalyzed Amination of Silyloxyarenes through C–O Bond Activation

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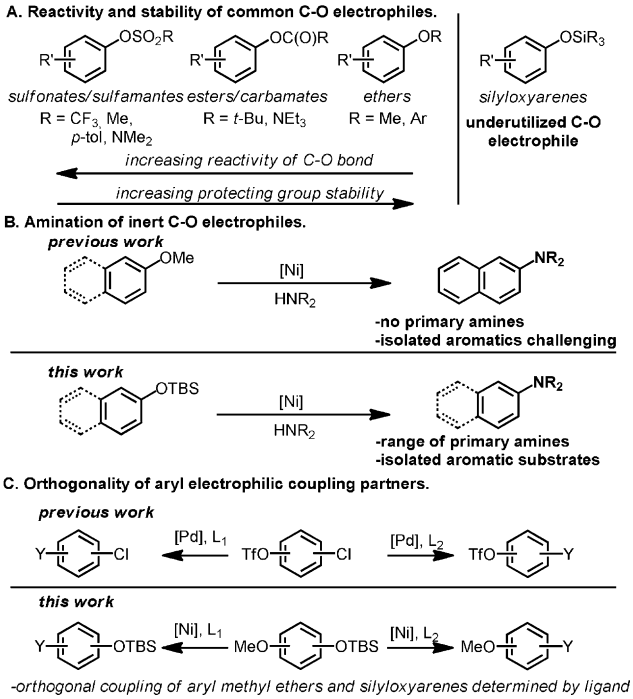
Abstract: *Silyloxyarenes were utilized as electrophilic coupling partners with amines in the synthesis of aniline derivatives. A diverse range of amine substrates were used, including cyclic or acyclic secondary amines, secondary anilines, and sterically hindered primary anilines. Additionally, a range of sterically hindered and unhindered primary aliphatic amines were employed, which have previously been challenging with other classes of aryl ether electrophiles. Orthogonal couplings of silyloxyarenes with aryl methyl ethers are illustrated, where selectivity between the two C–O electrophiles is determined by ligand control, thereby allowing complementary and selective late-stage diversification of either electrophile. Finally, a sequential coupling displays the utility of this amination method along with the reversal in intrinsic reactivity between aryl methyl ethers and silyloxyarenes.*

Aryl amines are among the most abundant motifs in biologically active molecules, and methods for aryl C–N bond formation have revolutionized the synthesis of aniline derivatives.[1] Building on the pioneering work of the Buchwald[2] and Hartwig[3] groups, many methods have been developed to enable difficult couplings at low catalyst loadings,[4] with recent methods using photoredox catalysis greatly expanding the utility of nickel-catalyzed processes.[4h] Recently, there has been significant interest in developing reactions complementary to those using aryl halides, thereby enabling sequential or orthogonal methods that can eliminate protecting-group manipulations while utilizing alternative feedstocks.[5] Phenol derivatives are attractive alternatives to aryl halides due to their relative abundance and complementary reactivity (Scheme 1 A), and those possessing non-activating protecting groups with low reactivity are particularly appealing for late-stage diversification due to their high stability through earlier synthetic steps.

The exploration of using aryl ethers as cross-coupling electrophiles began with the seminal work by Wenkert et al.,[6] where aryl methyl ether derivatives were used with Grignard reagents in Kumada couplings under nickel catalysis. Since this work, numerous methods have been developed exploring a range of more activating groups for C–O bonds in a wide variety of catalytic methods.[7–9] While these methods



Scheme 1. Aryl electrophiles for amination and orthogonal couplings.

are high yielding and practical, the involvement of more stable phenol derivatives has also been explored in order to improve the ability to carry substrates through multiple synthetic steps prior to coupling. In particular, beginning with fundamental work from Chatani, aryl methyl ethers have proven to be very practical due to their availability and masked reactivity, which allows increased stability through a greater array of synthetic steps.[8e,10–12] Important recent work has allowed even unprotected phenols to be directly utilized in C–N bond-forming processes.[13] Despite many impressive advances in this area, remaining challenges include more completely addressing the lower reactivity of isolated aromatic substrates, further expanding substrate scope, and identifying strategies for establishing orthogonal reactivity of different substrate classes that possess strong C–O bonds.

Silyloxyarenes have rarely been utilized as substrates in cross-couplings, typically with activated nucleophilic partners,[10a–d,14a] although recent reports have illustrated the conversion of silyloxyarenes to reduced products under milder conditions.[14b–c] Given their broad utility as protecting groups in organic synthesis,[15] the use of silyl ethers as aryl electrophiles in cross-couplings presents unique potential due to their facile installation and stability across a large range of reaction conditions. The availability of such a large variety of

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silyl protecting groups commonly used in organic synthesis allows the stability and reactivity of the C–O bond to be easily tuned according to the precise properties desired. The focus of this study has been to develop nickel-catalyzed carbon–nitrogen bond-forming processes by coupling silyloxyarenes with amines (Scheme 1B) and to benchmark the reactivity of silyloxyarenes in multistep sequences with substrates that possess other types of C–O bonds (Scheme 1C).

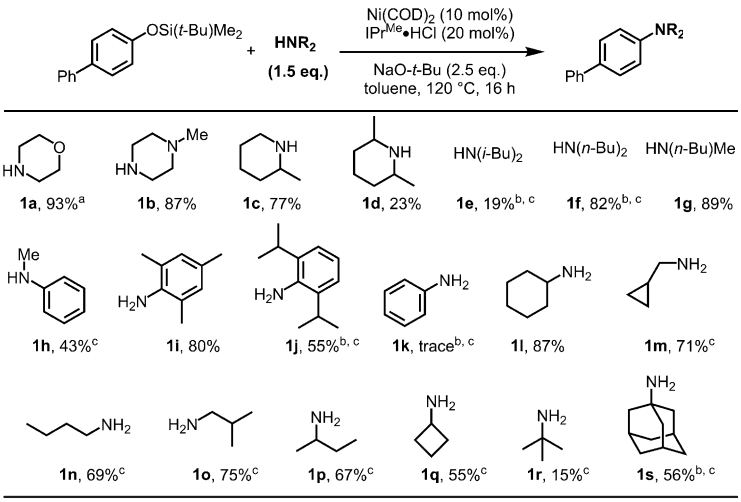
Our efforts to develop a method for efficient catalytic amination of silyloxyarenes began with an evaluation of nickel catalysts and silyl protecting groups. Previous work from our group in evaluating the reactivity of silyloxyarenes towards nickel catalysts demonstrated that electron-rich NHC-Ni catalysts promoted reductions of TBS-protected silyloxyarenes with silanes or titanium reductants.[14c] Based on these findings, and building on prior studies of C–O bond aminations,[12,16] we explored electron-rich phosphines and NHCs with $Ni(COD)_2$ to examine the feasibility of silyloxyarene amination. Using a model substrate and morpholine in toluene, a wide array of phosphines and NHCs were examined as ligands, and IPr^{Me} was found to be uniquely effective in the desired aminations to generate product **1a** (Table 1, see the Supporting Information for optimization details). Other common aryl electrophiles resulted in inferior results, with OMe only showing trace product and other phenol-derived electrophiles, including OPh, OPiv, and OTf, resulting in decreased yields. Additionally, aryl halides (Br, F) resulted in low yields due to conversion of the aryl halide to biphenyl through reduction with the amine.

With optimized conditions in hand, the scope with respect to the amine component was explored. Several cyclic amines resulted in good yields, including amines with basic functionality such as a piperazine derivatives (Table 1, **1b**), or sterically hindered amines such as 2-methylpiperidine (**1c**). However, very sterically hindered cyclic amines, such as 2,6-dimethylpiperidine, resulted in lower yields (**1d**). Acyclic secondary aliphatic amines were then explored, and very sterically hindered amines such as diisobutylamine (**1e**) were poor substrates, but other acyclic secondary amines **1f**–**1g** underwent coupling in high yields. Utilizing secondary aniline derivative **1h** resulted in moderate yields, and sterically hindered primary anilines **1i**–**1j** reacted in moderate to good yields. Steric hindrance in couplings of anilines was necessary, since using unhindered aniline **1k** only yielded trace product, presumably due to C–N reductive elimination being promoted by steric crowding. However, exploring the use of primary aliphatic amines showed promising results (**1l**–**1m**). Primary aliphatic amines have been difficult to couple with aryl ethers using previously reported methods.[12,17] However, in this method using silyloxyarenes, unhindered, primary aliphatic amines such as *n*-butylamine (**1n**) provided products in good yields. A series of increasingly encumbered nucleophilic amines was explored with primary aliphatic amines from *n*-butyl to cyclobutyl, all resulting in high yields (**1n**–**1q**). Increasing to more sterically hindered *tert*-butylamine (**1r**) gave poor yield, but even 1-aminoadamantane (**1s**) coupled in high yield, showing good generality in couplings of primary aliphatic amines.

The scope with respect to the silyloxyarene component was next explored by utilizing challenging amine or silyloxyarene coupling partners. Naphthyl substrates substituted at the 1- or 2-positions resulted in good yields with primary aliphatic amines (Table 2, **2** and **3**). A variety of substitution patterns were tolerated on the silyloxyarene substrate, including other silyl groups (**4**) and *ortho* substitution (**5**). However, large *ortho* substituents, such as phenyl, resulted in low reactivity, and for a bis-silylated 2-phenylhydroquinone derivative, the *meta* silyloxy group was preferred in a 5.7:1 ratio favoring product **6**. A variety of heterocycles are tolerated, including quinolines, pyridines, and carbazoles (**7**, **8**, and **9**). Additionally, substrates with silyloxy groups substituted on the heterocyclic ring are coupled in high yield, such as quinoline substrate **10**. Other protecting groups for alcohols or amines, such as aryl methyl ethers or *tert*-butyloxycarbonyl (Boc) are tolerated, thereby allowing further derivatization of complex substrates **11** and **12**. Finally, C–O bonds substituted on isolated phenyl substrates are reactive, including electron-rich silyloxyarenes **13** and **14**, resulting in good yields. A coupling with acetaminophen derivative **14** also displays the tolerance of unprotected amides. High yields are observed with isolated aromatics that are not as electron-rich (**15**), including estradiol derivative **16**, which also displays tolerance of alkyl silyl ethers. The high efficiencies with substrates **15** and **16** are noteworthy given that many methods involving nickel-catalyzed couplings of aryl ethers require naphthyl-type extended conjugation in the substrates.

Having found that the silyloxyarene amination tolerates aryl methyl ethers, an orthogonal coupling was envisioned to demonstrate the complementarity of this method to other methods that activate aryl methyl ethers. Selective activation of one electrophile over another, ideally with catalyst control over selectivity, is a highly sought-

Table 1: Amine scope for C–O bond amination of silyloxyarenes.



[a] 5 mol% $Ni(COD)_2$ and 10 mol% IPr^{Me}·HCl. [b] 15 mol% $Ni(COD)_2$ and 30 mol% IPr^{Me}·HCl. [c] 2.5 equiv of amine.

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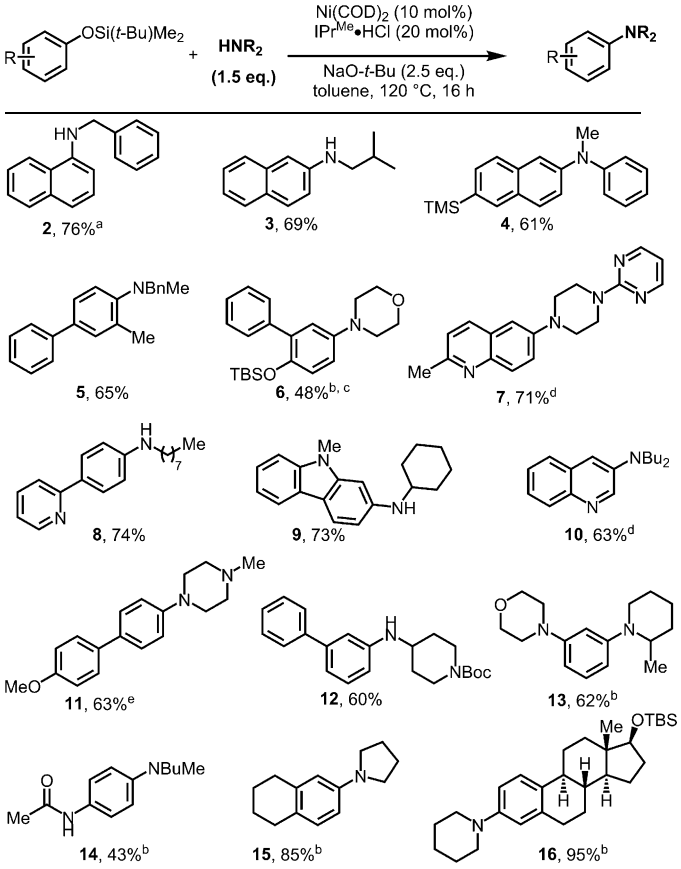
Table 2: Silyloxyarene scope for C–O bond amination.

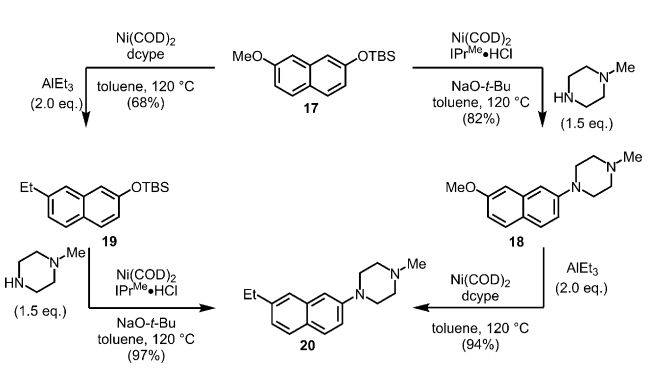


[a] 4 equiv of base. [b] 15 mol% $Ni(COD)_2$, 30 mol% IPr^{Me}·HCl, 4 equiv base, 2.5 equiv amine at 130°C. [c] Reaction gave a 5.7:1 ratio of 6:4-([1,1′-biphenyl]-3-yl)morpholine. [d] 2.5 equiv of amine. [e] 15 mol% $Ni(COD)_2$, 30 mol% IPr^{Me}·HCl and 4 equiv base.

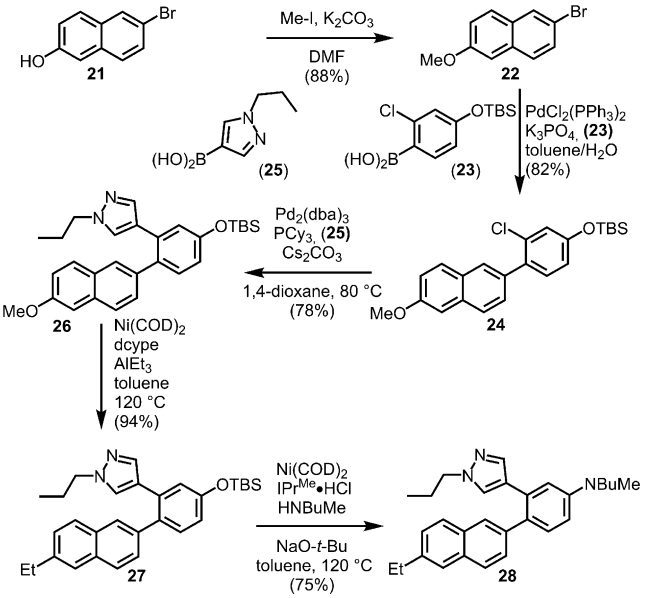
after goal in catalysis. Development of such a method would be analogous to orthogonal couplings of aryl triflates and aryl chlorides or bromides with palladium catalysts.[18] Through optimization of the silyloxyarene amination, we found that common ligands utilized in the activation of aryl methyl ethers (ICy, IAd, PCy_3) did not typically activate the C–O bond of silyloxyarenes.

By utilizing the amination method optimized above, selective coupling of the silyloxy group, leaving the aryl methyl ether intact, was illustrated in the conversion of **17** to **18** (Scheme 2). Alternatively, beginning with the same starting material **17** under similar reaction conditions, but following the method developed by Rueping,[19] produced **19** in high yield, leaving the silyloxyarene functionality untouched. Next, coupling of the silyloxyarene product (**19**), utilizing the silyloxyarene amination method, resulted in product **20** in high yield. Alternatively, the same product can be accessed by utilizing the aryl methyl ether compound **18** and triethylaluminum.

Having explored the orthogonality of silyloxyarenes to aryl methyl ethers, applications alongside other aryl electrophiles were also explored in a sequential coupling,[20] which demonstrated that this method can be used to conduct chemoselective bond formations without requiring functional-group manipulations. The sequence began by protecting 6-bromo-2-naphthol (Scheme 3, **21**), resulting in aryl methyl ether **22**. A palladium-catalyzed Suzuki coupling of **22** with a difunctionalized boronic acid containing an aryl chloride and silyloxyarene resulted in **24**, where boronic acid and bromoaryl functional groups reacted in the presence of chloro, methoxy, and silyloxy functionalities. Subsequent Suzuki coupling to install a pyrazole with boronic acid **25** was then carried out successfully. Next, utilizing the catalyst selectivity observed between silyloxyarenes and aryl methyl ethers (see above), the aryl methyl ether was reacted under nickel catalysis with triethylaluminum to give **27** in high yield, without activating the silyloxyarene C–O bond. Finally, late-stage silyloxyarene amination gave the final product **28**. This sequence displays four sequential couplings without any protecting-group manipulations and utilizes the catalyst-controlled selectivity between aryl methyl ethers and silyloxyarenes. These examples further illustrate how silyloxyarenes can be utilized alongside



Scheme 2. Orthogonal coupling with silyloxyarenes and aryl methyl ethers.



Scheme 3. Sequential coupling of aryl electrophiles with silyloxyarenes.

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known cross-coupling strategies and can be carried through syntheses as late-stage electrophilic partners.

In summary, this work illustrates the versatility of silyloxyarenes as coupling partners with nickel catalysts in the synthesis of aniline derivatives, thus enabling a commonly employed protecting group class to be directly used in C–N bond-forming processes. The direct coupling of silyloxyarenes with a large range of amines enables an increase in complexity from abundant and robust phenol derivatives. Additionally, reactivity was observed with primary aliphatic amines, which have previously proven difficult with other types of aryl ether electrophiles. Finally, catalyst selectivity between silyloxyarenes and aryl methyl ethers was demonstrated in a sequential coupling, thus illustrating that these findings complement previously developed strategies for utilizing strong C–O bonds in nickel catalysis.

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Conflict of interest

The authors declare no conflict of interest.

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