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Nickel-Catalyzed Amination of (Hetero)aryl Halides Facilitated by a Catalytic Pyridinium Additive

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Dedicated to the 70th anniversary of Shanghai Institute of Organic Chemistry

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Abstract: An efficient and operationally simple Ni-catalyzed amination protocol has been developed. This methodology features a simple Ni(II) salt, an organic base and catalytic amounts of both a pyridinium additive and Zn metal. A diverse number of (hetero)aryl halides were coupled successfully with primary and secondary alkyl amines, and anilines in good to excellent yields. Similarly, benzophenone imine gave the corresponding *N*-arylation product in an excellent yield.

Aryl amines are the widespread constituents of natural products and pharmaceutical compounds, which render the amination reaction one of the most frequently employed reactions in medicinal chemistry.[1] Over the past 25 years, the Pd-catalyzed cross-coupling of amines with aryl halides or pseudohalides, named Buchwald–Hartwig amination has evolved into a powerful tool for the C(sp^2)–N bond formation through development of the multiple generations of ligands, typically phosphines.[2] Similarly, the Cu-catalyzed Ullmann–Ma coupling has been elevated to an essential transformation by the introduction of diverse nitrogen ligands, such as diamines, amino acids, and oxalic diamides.[3] In recent years, we have observed an ongoing renaissance in nickel catalysis.[4] In fact, the first Ni-catalyzed C–N coupling using $NiCl_2$ at 200 °C dates back to 1950.[5] The seminal contributions from Buchwald, Lipshutz, Chatani, Garg, Hartwig, Montgomery and others have significantly improved Ni-catalyzed amination with Ni(0) catalysts and Ni(II) pre-catalysts.[6,7] It was believed that most of those Ni-catalyzed amination systems involved the Ni(II) amido complexes **I**, followed by the rate-limiting C–N reductive elimination (Figure 1).[8] Stradiotto and co-workers provided an elegant solution to promote Ni-catalyzed C–N coupling by tailored ancillary ligand design.[9] In 2016, MacMillan and Buchwald developed a distinct photoredox protocol to address the challenging reductive elimination issue via the intermediacy of a Ni(III) amido complex **II**.[10] Since then, a variety of photoinduced amination reactions have been reported.[11] Very recently, Baran successfully realized a complementary electrochemical strategy to precisely control the redox states in Ni-catalyzed amination.[12] However, as compared to Pd-catalyzed Buchwald–Hartwig amination and Cu-catalyzed Ullmann–Ma coupling, Ni-catalyzed amination is still not that attractive for industrial applications.

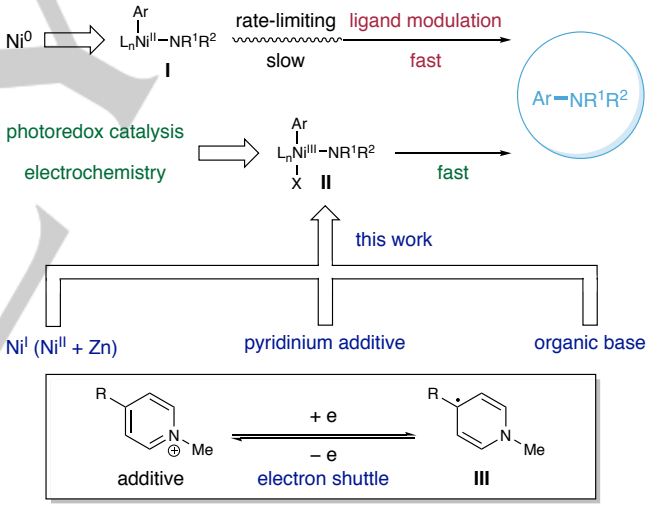

Figure 1. Design Plan for the Nickel-Catalyzed Amination.

We envisioned an operationally simple approach to establish a Ni(I)/Ni(III) catalytic cycle starting from a Ni(II) precursor by in situ reduction to Ni(I) species with heterogeneous Zn metal.[13] The latter then would undergo oxidative addition with an aryl halide followed by halide-amide exchange to give the Ni(III) amido complex **II** (Figure 1).[14] Amination reactions catalyzed by Pd, Cu, and Ni traditionally employed inorganic bases, such as NaO*t*-Bu and K_3PO_4. There is an increasing interest in the use of soluble organic bases for the cross-coupling.[15] We were interesting in finding an efficient organic base for our Ni-catalyzed amination system. More importantly, we took a different strategy from the prior efforts which were devoted to ligand and precatalyst design to enhance the efficacy of Ni-catalyzed C–N coupling. We assumed that an organic additive would act as an electron shuttle

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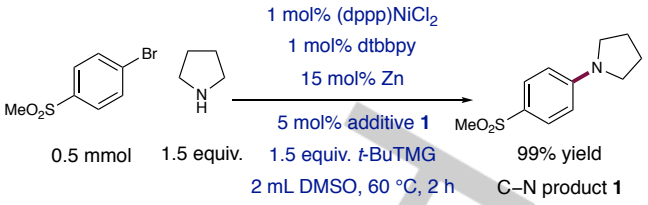
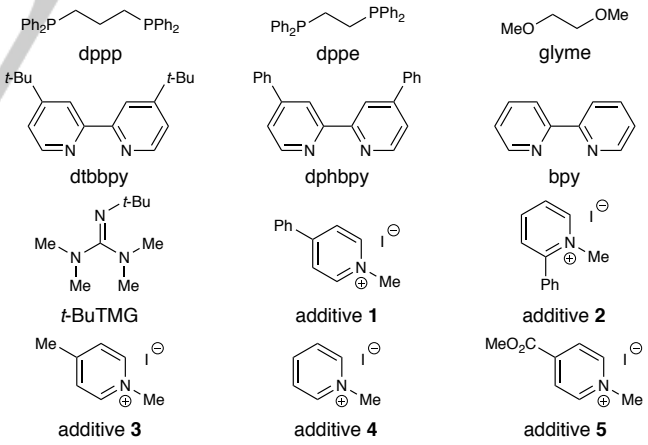
(Figure 1, bottom) to facilitate the inter-transformation of different Ni species, such as in situ reduction of Ni(II) to Ni(I) under heterogeneous conditions. It was noticed that pyridinium salts had been widely explored as electron mediators.[16] And the $E_{1/2}^{red}$ values of pyridiniums [16a] should be comparable to that of Ni^{2+}/Ni^{+}.[12b] We report here on our preliminary results of Ni-catalyzed amination of (hetero)aryl halides facilitated by catalytic amount of a pyridinium additive.

As part of our long-term interest in heteroatom-heteroatom and carbon-heteroatom bond formation,[17] we started our exploration into Ni-catalyzed amination of aryl halides (Table 1). 4-Bromophenyl methyl sulfone and pyrrolidine were chosen as the model substrates. To our delight, after extensive evaluation of various reaction parameters, the desired C–N coupling product **1** was obtained in 99% yield with 1 mol% of (dppp)$NiCl_2$/dtbbpy as the precatalyst, 15 mol% of zinc metal as the Ni(II) reductant, 5 mol% of 1-methyl-4-phenylpyridinium iodide as the additive, and *t*-BuTMG as the organic base. The essential roles of nickel salt, bipyridine ligand, Zn metal, organic base, and additive were firstly demonstrated by the control experiments (entries 1–5). Without any one of these reagents, it led to 0 to 7% yields of the amination product. The other common Ni(II) salts afforded similar catalytic efficiency with slightly decreased yields (entries 6–8). It is worth mentioning that $NiCl_2{\cdot}6H_2O$ performed well for the amination protocol, implying that a phosphine ligand is not required. The Ni(0) complex exhibited similar catalytic efficacy with Ni(II) precatalysts under otherwise the same conditions. However, it lost the catalytic ability without Zn metal and additive **1**, suggesting that Ni(0) might not be the productive catalyst (entries 9 and 10). Notably, replacement of dtbbpy with dphbpy and even the parent bipyridine ligand bpy could maintain the high yields (entries 11 and 12). Although Mn metal only furnished the product **1** in 29% yield after 2 h (entry 13), in some cases superiority of Mn to Zn could be observed (*vide infra*). Experiments were also carried out to replace 1-methyl-4-phenylpyridinium iodide by other pyridinium salts (entries 14–17). The pyridinium additives **2** and **3** with the C2-phenyl and C4-methyl groups, respectively, provided the amination product in 78-87% yields, while the pyridium additive **4** and **5** only afforded 51% and 18% of the amination product, respectively. Moreover, 4-phenylpyridine, *n*-Bu_4NI and KI almost had no impact on the reaction, demonstrating that the pyridinium moiety was critical for the promoting effect (entries 18–20). It was noted that the amination could proceed successfully in DMF and NMP, although not efficiently in MeCN, under the standard conditions (entries 21–23). Other transition metals were ruled out by the control experiments (entry 24). No product was formed when $CrCl_3$, $FeCl_2$, $MnCl_2$, $CoCl_2$, $CuCl_2$, or $PdCl_2$ was used under otherwise the same conditions. Finally, a number of common organic bases, such as Et_3N, *i*-Pr_2NEt, DABCO and DBU were screened for the amination reaction, but <10% yields of the product **1** were observed.



entry	variation from standard conditions	yield [%]
1	no nickel salt	0
2	no bipyridine ligand	3
3	no Zn	4
4	no additive **1**	7
5	no *t*-BuTMG	7
6	$NiCl_2{\cdot}6H_2O$ instead of (dppp)$NiCl_2$	91
7	(glyme)$NiCl_2$ instead of (dppp)$NiCl_2$	93
8	(dppe)$NiCl_2$ instead of (dppp)$NiCl_2$	94
9	$Ni(cod)_2$ instead of (dppp)$NiCl_2$	91
10	$Ni(cod)_2$ instead of (dppp)$NiCl_2$, no Zn, no additive **1**	7
11	dphbpy instead of dtbbpy	97
12	bpy instead of dtbbpy	94
13	Mn instead of Zn	29
14	additive **2** instead of additive **1**	78
15	additive **3** instead of additive **1**	87
16	additive **4** instead of additive **1**	51
17	additive **5** instead of additive **1**	18
18	4-phenylpyridine instead of additive **1**	6
19	*n*-Bu_4NI instead of additive **1**	5
20	KI instead of additive **1**	6
21	DMF instead of DMSO	94
22	NMP instead of DMSO	90
23	MeCN instead of DMSO	54
24	Cr, Fe, Mn, Co, Cu or Pd salt instead of Ni salt	0
25	Et_3N, *i*-Pr_2NEt, DABCO, DBU instead of *t*-BuTMG	<10



[a] Yields determined by ^1H NMR using 1,3-benzodioxole as an internal standard in $CDCl_3$.

Table 1. Optimization for the Nickel-Catalyzed Amination[a].

Encouraged by the preliminary results, we sought to evaluate the generality of this nickel-catalyzed amination protocol. The scope of (hetero)aryl electrophiles was examined using pyrrolidine as the amine coupling partner, that is the most common five-membered heterocycle in medicines.[18] For every substrate in this work, two sets of reactions were performed with and without the additive **1**. As illustrated in Scheme 1, the catalytic amount of additive **1** could have an impressive promoting effect for most of the substrates. A wide range of (hetero)aryl bromides

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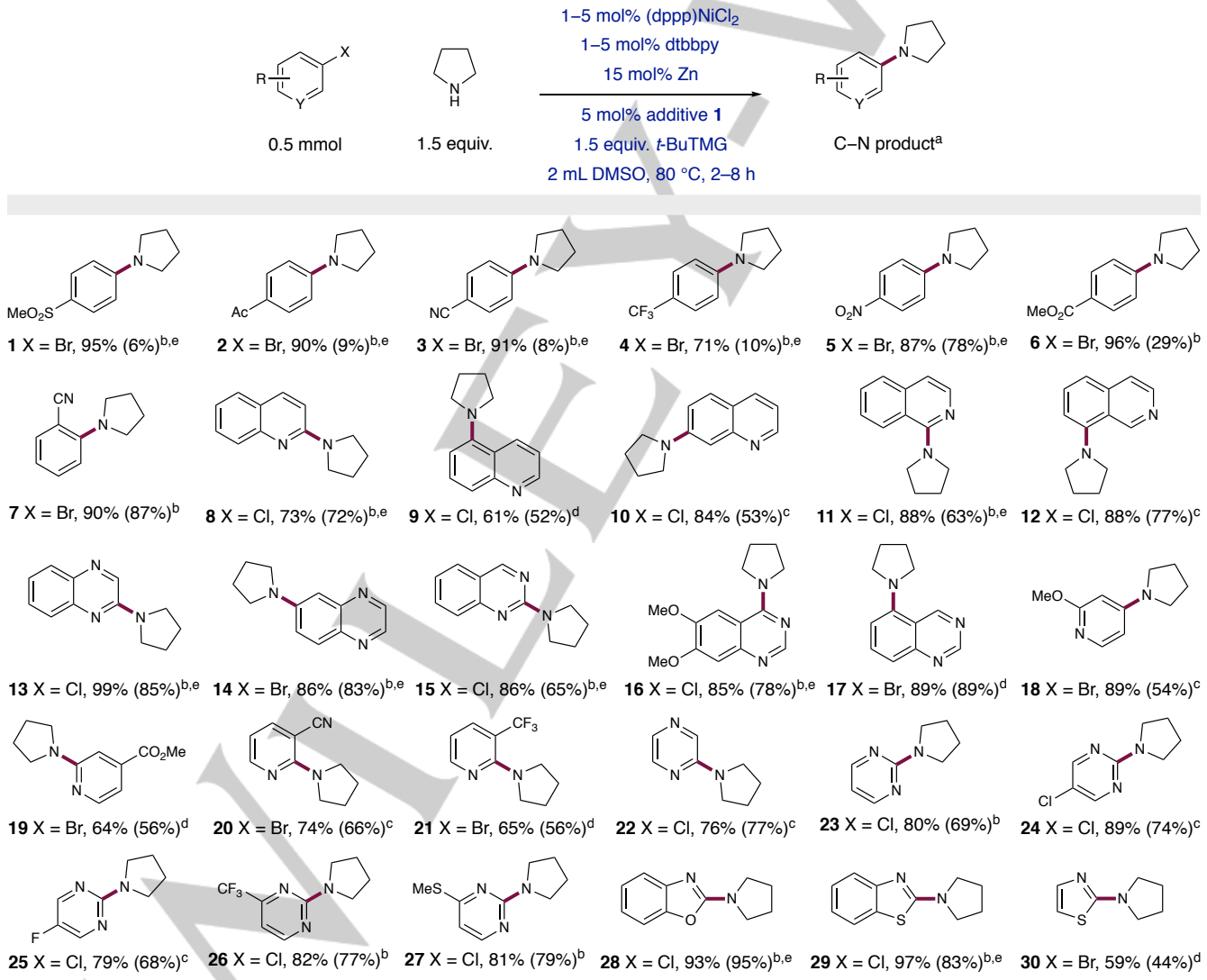
and chlorides were found to be competent coupling partner for the reaction. Electron-poor aryl bromides reacted readily to form the amination products in high yields (**1**–**7**) while electron-rich aryl halides gave very poor yields of <20% (data not shown). The 4-nitrophenyl bromide (**5**) and 2-cyanophenyl bromide (**7**) exerted a diminished additive effect. We speculated that the strong electron-withdrawing effect of *para*-nitro and *ortho*-CN groups rendered these substrates already highly reactive. A variety of six-membered heteroaromatic halides performed well under the reaction conditions to furnish the heteroaryl amines of medicinal relevance. The halogen derivatives of quinoline (**8**–**10**), isoquinoline (**11** and **12**), quinoxaline (**13** and **14**), quinazoline (**15**–**17**), pyridine (**18**–**21**), pyrazine (**22**), and pyrimidine (**23**–**27**) were successfully coupled with pyrrolidine, demonstrating the high functional group tolerance of this method. Moreover, five-membered heteroaromatic halides were also amenable to this reaction, including but not limited to benzoxazole (**28**), benzothiazole (**29**), and thiazole (**30**). Remarkedly, sulfur-based functional groups were compatible with the Ni-catalyzed system (**27**, **29** and **30**).

Next, the scope of amine nucleophiles was explored to gain further insight into the capability of pyridinium-facilitated amination (Scheme 2). Generally, the conversion of secondary alkyl amines to the corresponding C–N coupling products was dramatically improved in the presence of additive **1**. A series of cyclic secondary amines with different ring sizes provided good to excellent yields of the desired amination products. A broad variety of functional groups on the amine substrates were feasible, such as Boc (**35** and **54**) and acetal (**45**) protecting groups, morpholinyl (**42**), difluoromethylene (**46**), alkenyl (**52**), and pyridinyl (**53**) groups. The C–N coupling reaction showed excellent chemo- and regio-selectivity. For instance, the amine was arylated smoothly leaving the hydroxy group untouched (**43**). Also, the arylation preferentially occurred at the less sterically congested site for 2-methylpiperazine (**48**). It is of note that acyclic secondary amines worked as well in this C–N coupling reaction (**57**–**60**).



Scheme 1. Scope of (Hetero)aryl Halides for the Amination Reaction. [a] Isolated yields and in parentheses the yields of control reactions without additive. [b] 1 mol% nickel salt and 1 mol% dtbbpy. [c] 3 mol% nickel salt and 3 mol% dtbbpy. [d] 5 mol% nickel salt and 5 mol% dtbbpy. [e] 60 ºC.

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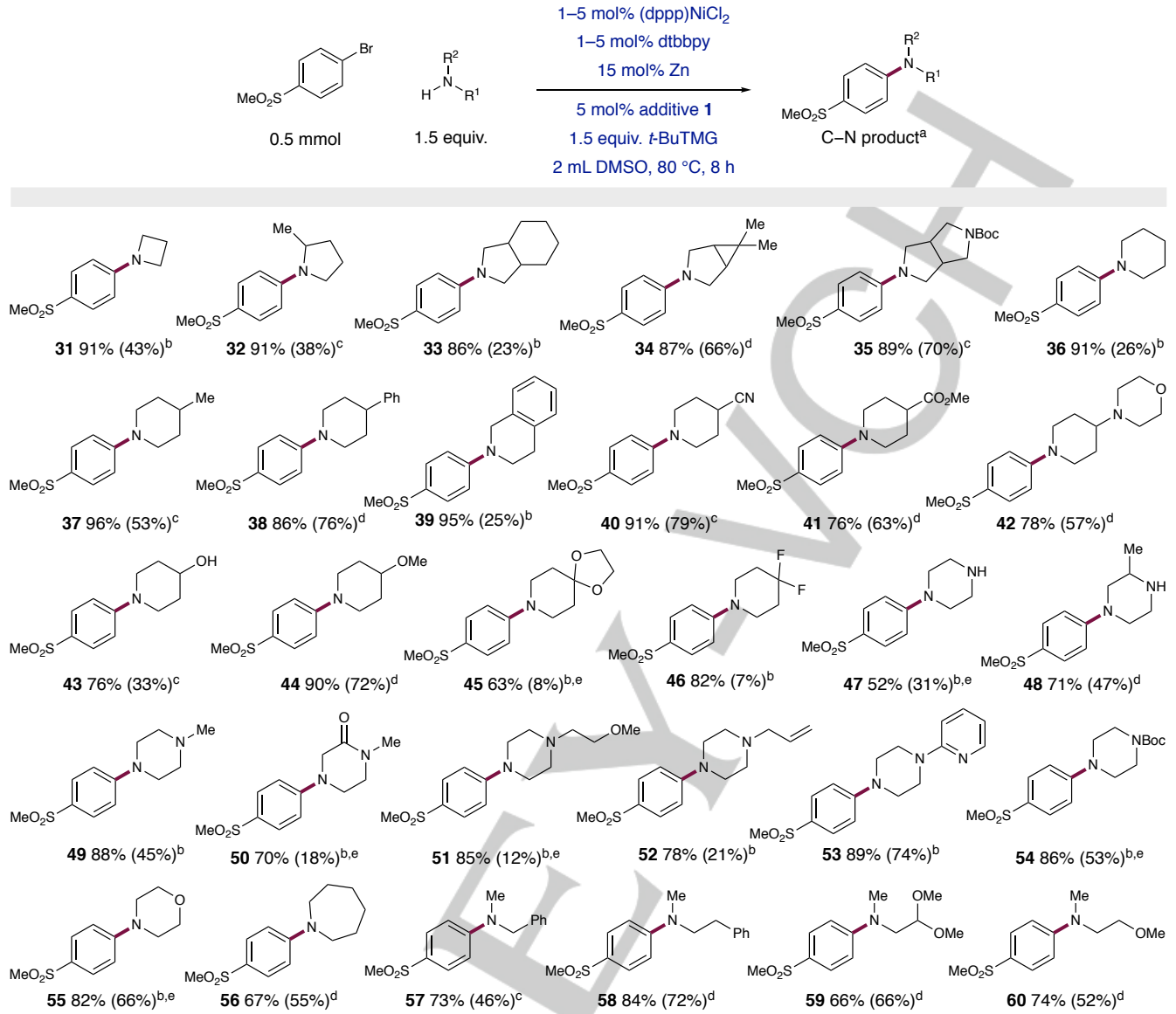

Scheme 2. Scope of Secondary Amines for the Amination Reaction. [a] Isolated yields and in parentheses the yields of control reactions without additive. [b] 1 mol% nickel salt and 1 mol% dtbbpy. [c] 3 mol% nickel salt and 3 mol% dtbbpy. [d] 5 mol% nickel salt and 5 mol% dtbbpy. [e] Mn instead of Zn used.

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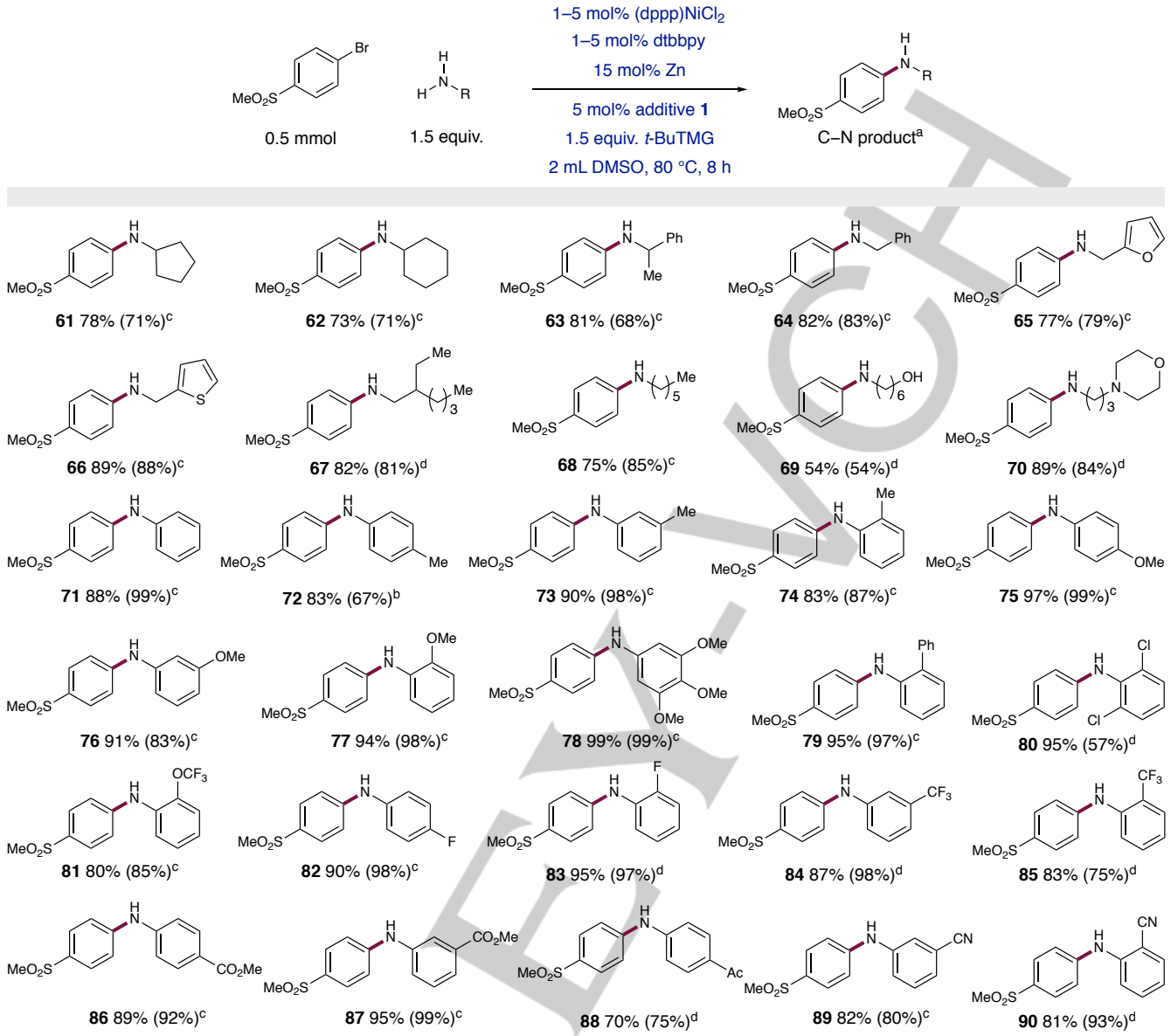
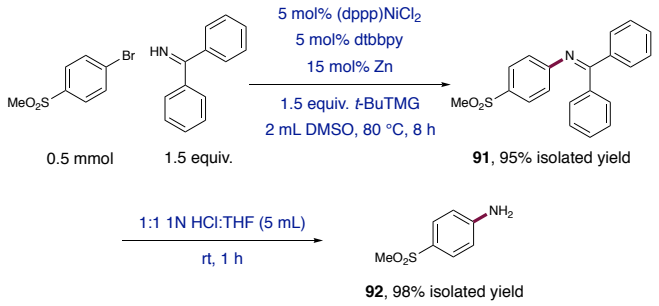


Scheme 3. Scope of Primary Amines for the Amination Reaction. [a] Isolated yields and in parentheses the yields of control reactions without additive. [b] 1 mol% nickel salt and 1 mol% dtbbpy. [c] 3 mol% nickel salt and 3 mol% dtbbpy. [d] 5 mol% nickel salt and 5 mol% dtbbpy.

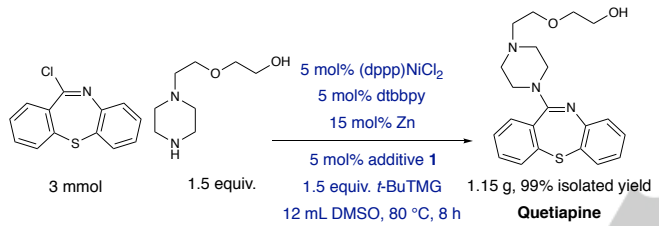
Gratifyingly, this C–N coupling protocol could be applied to the primary alkyl and aryl amines successfully (Scheme 3). While the primary alkyl amine substrates benefited moderately from the addition of additive 1, the circumstances of anilines were much complicated. In some cases better yields were obtained with additive 1 (**72**, **76**, **80** and **85**), however, in the other cases the pyridinium additive decreased the yields to some extent (**71**, **73**, **82**, **84**, and **90**). The primary alkyl amines bearing a diverse of functional groups were transformed into the arylation products efficiently (**61**–**70**). Besides, no matter with electron-donating or withdrawing groups, anilines proved perfect substrates for the coupling reaction (**71**–**90**). Notably, the steric congestion was well tolerated in this coupling protocol. Anilines with *ortho*-substituents, including methyl (**74**), methoxy (**77**), phenyl (**79**), chloro (**80**), trifluoromethoxy (**81**), fluoro (**83**), trifluoromethyl (**85**), and cyano (**90**) groups, all underwent the cross-coupling in high yields.

Then we turned our attention to the synthesis of primary amines by this amination protocol. The cross-coupling of ammonia and (hetero)aryl halides, however, only afforded poor yields of desired products under the standard conditions. To our delight, the benzophenone imine coupled with 4-bromophenyl methyl sulfone smoothly to provide the product **91** (95%), which could be hydrolyzed to give the primary amine **92** quantitatively (Scheme 4).[19,20]



Scheme 4. Cross-Coupling of the Hydrolysable Amine Partner.

Finally, the practical application of our C–N coupling protocol was demonstrated by the gram-scale synthesis of Quetiapine, a medicine used to treat certain mental/mood conditions (Scheme 5). The coupling of 11-chlorodibenzo[*b,f*][1,4]thiazepine and 2-(2-(piperazin-1-yl)ethoxy)ethan-1-ol efficiently furnished 1.15 g of Quetiapine.



Scheme 5. Gram-Scale Synthesis of Medicine Quetiapine.

In summary, we have developed a novel nickel-catalyzed amination protocol featuring a simple Ni(II) precatalyst (1–5 mol%), an organic base (*t*-BuTMG) and catalytic amounts of a pyridinium additive (5 mol%) and Zn metal (15 mol%). A diverse of (hetero)aryl halides were coupled successfully with primary and secondary alkyl amines, and anilines to furnish the corresponding amination products in good to excellent yields. Generally, moderate to high promoting effect of catalytic pyridinium additive was observed on the Ni-catalyzed C–N coupling reaction. Further exploration into the reaction mechanism is undergoing in our lab.

Acknowledgements

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Keywords: nickel-catalyzed • amination • C–N coupling • aryl halides • anilines

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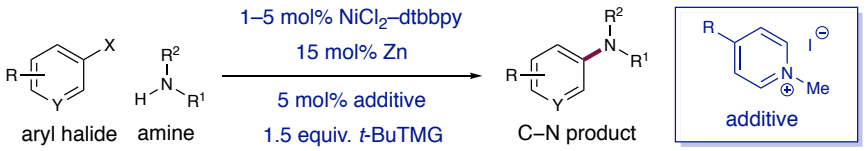

Pyridinium salt gives a hand to nickel. A Ni-catalyzed amination has been developed as an efficient synthetic tool of promising potential for application in industry. A diverse of (hetero)aryl halides were coupled successfully with primary and secondary alkyl amines, and anilines in good to excellent yields. This C–N coupling features with low $NiCl_2$–dtbbpy loadings, catalytic amounts of Zn metal and a pyridinium additive, and an organic base.

Keywords: nickel-catalyzed; amination; C–N coupling; aryl halides; anilines