Homogeneous Catalysis

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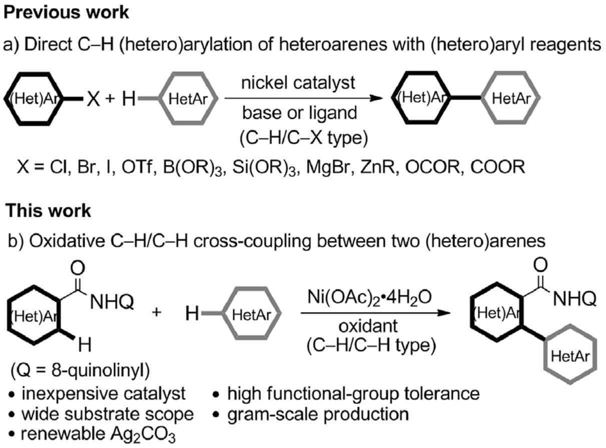
Nickel Catalysis Enables Oxidative C(sp^2)–H/C(sp^2)–H Cross-Coupling Reactions between Two Heteroarenes

*Yangyang Cheng, Yimin Wu, Guangyin Tan, and Jingsong You**

Abstract: *Nickel can be used to promote oxidative C(sp^2)−H/C(sp^2)−H cross-coupling between two heteroarenes. The reaction scope can be extended to aromatic carboxamides as the coupling partner. The reaction exhibits high functional-group compatibility and broad substrate scope. The silver oxidant can be recycled to reduce costs and waste, which is very useful for practical applications.*

Biheteroaryl structural motifs are frequently found in various bioactive molecules, natural products, agrochemicals, pharmaceuticals, and organic functional materials.[1] The development of straightforward access to biheteroarenes has thus been a topic of immense importance in organic synthesis. Over the past few decades, transition-metal-catalyzed cross-coupling reactions with organometallic reagents, organic halides, or pseudohalides have been used to assemble these biheteroaryl units. However, these methods unavoidably require tedious preactivation of substrates and suffer from low efficiency with coupling partners with reactive functional groups. From a step- and atom-economy standpoint, oxidative C−H/C−H cross-coupling between two heteroarenes would be an ideal approach to forge biheteroaryl structural motifs.[2] Tremendous efforts have been focused on the direct C−H/C−H cross-coupling of two (hetero)arenes in recent years. In general, these methods employ a noble-metal catalyst, such as Pd,[3] Rh,[4] Ru,[4b] and Au[5] complexes. However, the rarity and costliness of these complexes often restricts the practicality to some extent. The development of inexpensive and naturally abundant metals (Fe, Co, Ni, Cu, etc.) instead of noble metals as the catalysts is an appealing yet challenging task. To date, only copper-catalyzed or -mediated oxidative C−H/C−H cross-coupling reactions between two heteroarenes have been reported.[6]

As an abundant and low-cost transition metal, nickel has shown its great potential in direct C−H bond functionalizations.[7] Recent reports have disclosed that nickel catalysis assisted by bases or ligands can promote the direct C−H (hetero)arylation of heteroarenes with (hetero)aryl halides, pseudohalides, or organometallic reagents to assemble bi(hetero)arenes (Scheme 1a).[8] Unlike other metal catalysts, nickel catalysts have also been utilized to catalyze the direct (hetero)arylation of heteroarenes with inexpensive and readily available aryl esters and phenol derivatives.[9] Recently, nickel salts have emerged as effective catalysts for direct C−H/C−H cross-coupling reactions. Chatani and Shi have disclosed that a nickel/N,N-bidentate directing group can be used to promote oxidative C(sp^2)−H/C(sp^3)−H and C(sp^2)−H/C(sp)−H cross-coupling reactions.[7g,10] However, except for examples of deprotonative dimerization of heteroarenes,[11] nickel-catalyzed oxidative C(sp^2)−H/C(sp^2)−H cross-coupling of two heteroarenes has not yet been achieved. Herein, we wish to demonstrate the potential of nickel catalysis in oxidative C−H/C−H cross-coupling reactions between two heteroarenes (Scheme 1b).



Scheme 1. Nickel-catalyzed C−H (hetero)arylation of heteroarenes.

Given that 8-aminoquinoline is a highly efficient N,N-bidentate directing group in transition metal-catalyzed C−H bond activation,[12] we initially focused on the nickel-catalyzed oxidative C−H/C−H cross-coupling of *N*-(quinolin-8-yl)thiophene-2-carboxamide **1a** with benzothiazole **2a** [Eq. (1); Table S1 in the Supporting Information]. To our delight, the desired product **3a** was obtained in 28% yield when employing 15 mol% of $NiCl_2{\cdot}6H_2O$ as the catalyst, 2.0 equiv of AgOAc as the oxidant, and 1.0 equiv of PivOH as the additive in 1,2-dichloroethane at 120 °C for 12 h (Table S1,

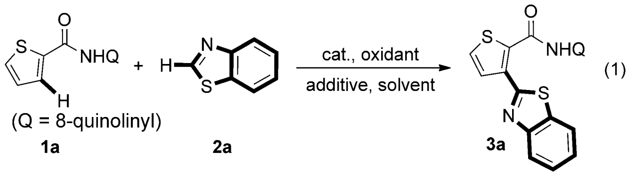


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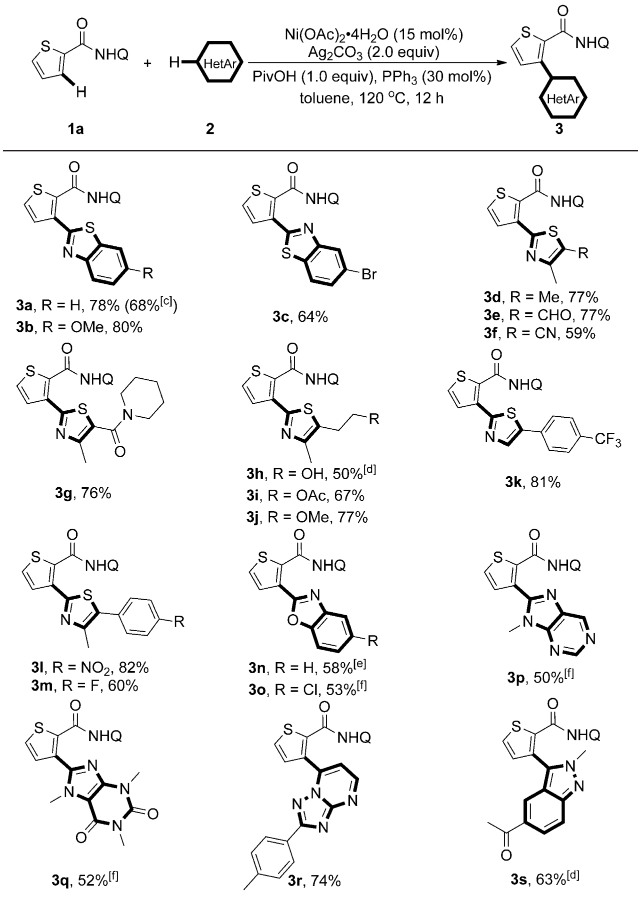
Table 1: The scope with respect to the heteroarenes.[a,b]



3a, R = H, 78% (68%[c])
3b, R = OMe, 80%

3c, 64%

3d, R = Me, 77%
3e, R = CHO, 77%
3f, R = CN, 59%

3g, 76%

3h, R = OH, 50%[d]
3i, R = OAc, 67%
3j, R = OMe, 77%

3k, 81%

3l, R = NO_2, 82%
3m, R = F, 60%

3n, R = H, 58%[e]
3o, R = Cl, 53%[f]

3p, 50%[f]

3q, 52%[f]

3r, 74%

3s, 63%[d]

[a] Reaction conditions: *N*-(Quinolin-8-yl)thiophene-2-carboxamide **1a** (0.2 mmol), heteroarene (1.5 equiv), $Ni(OAc)_2{\cdot}4H_2O$ (15 mol%), Ag_2CO_3 (2.0 equiv), and PivOH (1.0 equiv) in toluene (0.5 mL) at 120°C for 12 h under N_2 atmosphere. [b] Yield of isolated product. [c] 4.0 mmol scale. [d] 24 h. [e] PivOH (2.0 equiv) and *o*-xylene instead of toluene. [f] PivOH (2.0 equiv) and *o*-xylene instead of toluene at 140°C for 24 h.

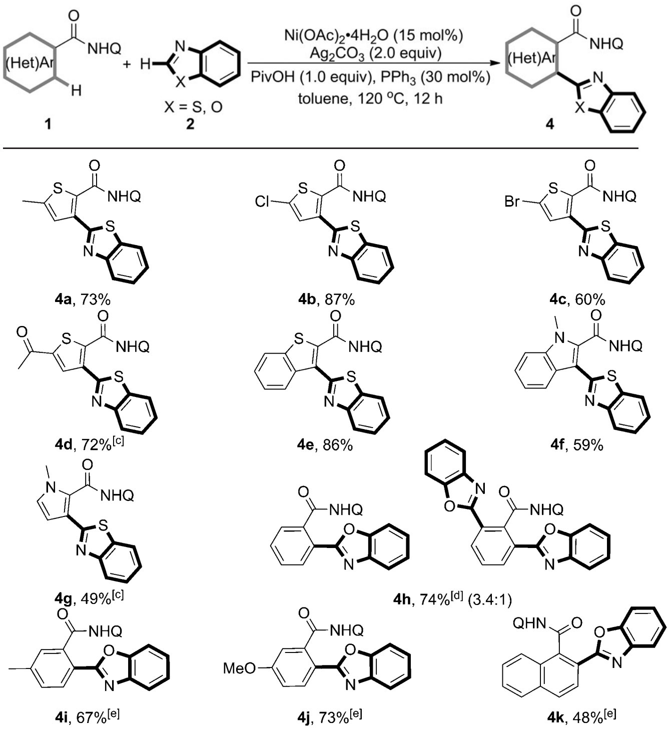
entry 1). Analysis of the single crystal X-ray diffraction pattern of **3a** demonstrated that the reaction selectively occurred at the thiophene C3 position (Figure S1 in the Supporting Information).[13] After screening several solvents (*N*,*N*-dimethylformamide (DMF), 1,4-dioxane, toluene, and *o*-xylene), toluene proved to be the best choice, and the yield was improved to 44% (Table S1, entries 2–5). Further optimization of the silver oxidants showed that Ag_2CO_3 was the most efficient oxidant (Table S1, entries 8–10). Other oxidants such as manganese salt ($Mn(OAc)_2{\cdot}4H_2O$), chlorate ($NaClO_3$), persulfate ($K_2S_2O_8$), and organic oxidants (BQ and DDQ) were ineffective (Table S1, entries 11–15). It is worth noting that PivOH as an additive was necessary. Only 34% yield was achieved in the absence of PivOH (Table S1, entry 16). Further addition of PPh_3 increased the yield to 76% (Table S1, entry 17). Subsequently, both the amount of nickel catalyst and the nickel source were investigated. Using 10 mol% of $NiCl_2{\cdot}6H_2O$ resulted in a decreased yield of 63% (Table S1, entry 18). The more inexpensive $Ni(OAc)_2{\cdot}4H_2O$[14] proved to be the most efficient catalyst and delivered the desired product in 78% yield (Table S1, entries 19–24). Finally, the best result was observed under a catalytic system comprising $Ni(OAc)_2{\cdot}4H_2O$ (15 mol%), Ag_2CO_3 (2.0 equiv), PivOH (1.0 equiv), and PPh_3 (30 mol%) in toluene at 120°C for 12 h. Under the optimized conditions, several structurally similar thiophene-2-carboxamides were examined and no desired product was observed (Scheme S1). These control experiments suggest that the 8-aminoquinoline moiety plays an indispensable role. It is notable that only trace amounts of the homocoupled product of **1a** was produced and no homocoupling reaction of **2a** was detected under the catalytic system.

By using the optimized conditions, we set out to explore the scope with respect to the heteroarenes, as summarized in Table 1. To our delight, a variety of heteroarenes could directly couple with **1a** in moderate to good yields. Thiazoles and benzothiazoles with both electron-donating and electron-withdrawing groups could be engaged in this transformation (Table 1, **3a**–**m**). A series of sensitive functional groups, including aldehyde, cyano, ester, nitro, acyl, chloro, bromo, and even hydroxy groups, were well tolerated under the current conditions, which may allow high diversity in the synthesis of functionalized biheteroarenes. Other heteroarenes such as benzoxazole, purine, and caffeine could also be converted into the desired products (Table 1, **3n**–**q**). [1,2,4]Triazolo[1,5-*a*]pyrimidine reacted with **1a** at the C7 position to deliver **3r** in 74% yield. To our delight, besides 1,3-azoles, the 1,2-azole-like indazole also smoothly underwent the heteroarylation in 63% yield (Table 1, **3s**). It is worthy of note that these reactions proceeded at the relatively acidic C−H bond of the azoles. The pK_a range of reactive C−H bonds is approximately 25–35 (benzothiazole: ca. 27, thiazole: ca. 29, benzoxazole: ca. 25, purine: ca. 29; indazole: ca. 35).[15] However, the pK_a value is not the sole governing factor determining reactivity and thus cannot be used to forecast the reactivity of other (hetero)arenes. For example, pentafluorobenzene bearing an acidic C−H bond (pK_a: 29) did not undergo coupling under the optimized conditions. It is worthy of note that the reaction of **1a** with **2a** could be carried out on a gram scale (4.0 mmol), and an acceptable yield of 68% was obtained (Table 1, **3a**), thus demonstrating the applicability of this method for mass production.

Next, we turned our efforts to the scope with respect to the heteroaromatic carboxamide derivatives (Table 2). An array of electron-rich heteroaromatic carboxamides, such as thienyl, benzothienyl, indolyl, and pyrrolyl carboxamides, underwent the coupling reaction in satisfactory yields (Table 2, **4a**–**g**). Chloro and bromo groups on the thienyl moiety were tolerated, which could provide an opportunity for further functionalization through cross-coupling (Table 2, **4b**–**c**). It is worth noting that our method was also suitable for benzamide derivatives (Table 2, **4h**–**k**). For unsubstituted benzamide, which bears two potentially reactive sites, the disubstituted product was detected (Table 2, **4h**). Reactions of *meta*-substituted benzamide derivatives only occurred at the less sterically hindered position (Table 2, **4i**,**j**). 1-Naphthamide could also be transformed into the corresponding bi(hetero)arene (Table 2, **4k**).

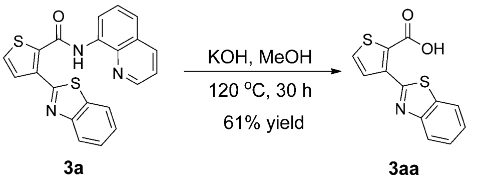
Subsequently, we attempted to remove the directing group. Gratifyingly, the 8-aminoquinoline moiety could be

Table 2: The scope with respect to the (hetero)aromatic carboxamides.[a,b]



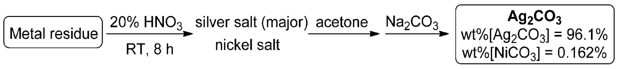
[a] Reaction conditions: heteroaromatic carboxamide (0.2 mmol), heteroarene (1.5 equiv), Ni(OAc)$_2$·4 H$_2$O (15 mol%), Ag$_2$CO$_3$ (2.0 equiv), and PivOH (1.0 equiv) in toluene (0.5 mL) at 120°C for 12 h under N$_2$ atmosphere. [b] Yield of isolated product. [c] 140°C for 24 h. [d] AgOAc (2.5 equiv) instead of Ag$_2$CO$_3$, and PivOH (2.0 equiv) in *o*-xylene (0.5 mL). [e] AgOAc (2.5 equiv) instead of Ag$_2$CO$_3$, and PivOH (2.0 equiv) in *o*-xylene (0.5 mL) at 140°C.

smoothly removed through base-assisted hydrolysis of heteroaromatic carboxamide. For example, the coupled product **3a** was hydrolyzed to produce the corresponding biheteroaromatic acid **3aa** in a 61% yield in the presence of KOH [Eq. (2)].



(2)

In order to reduce the cost and waste of the reaction, we attempted to recycle the silver salt on a gram scale. To our delight, Ag$_2$CO$_3$ could be simply regenerated after successive dissolution of the silver residue with nitric acid, washing with acetone, and precipitation with sodium carbonate [Eq. (3)]. The regenerated Ag$_2$CO$_3$ could smoothly promote the coupling reaction to afford **3a** in approximately 80% yield without loss of activity even after third-round recovery [Eq. (4); for details, see Section IX in the Supporting Information].



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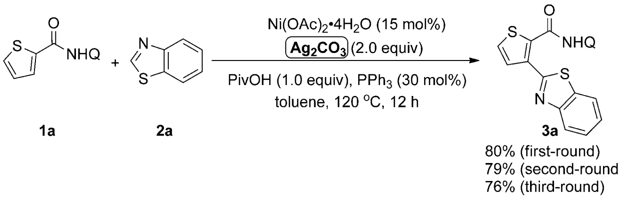
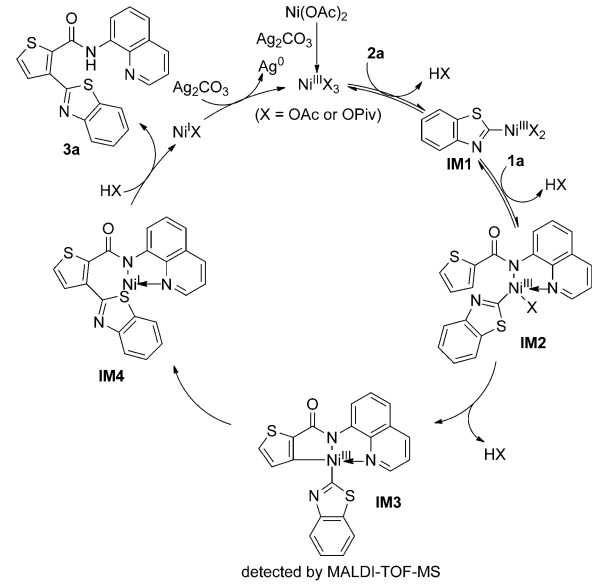


(4)

To gain some insights into the reaction mechanism, hydrogen/deuterium (H/D) exchange control experiments were first conducted [Eq. (S2)–(S4)]. When *N*-(quinolin-8-yl)benzamide **1i** was treated with D$_2$O under the optimized conditions, 14% of **1i** was deuterated in 2 h [Eq. (S2)]. On the other hand, 85% H/D scrambling was obtained with benzoxazole **2n** [Eq. (S3)]. Treatment of **1i** and **2n** with D$_2$O gave a similar H/D exchange ratio for **2n**, whereas deuterated [D$_n$]-**1i** was not obtained [Eq. (S4)]. These results suggest that the metalation order **2n** then **1i** could be reasonable. Subsequently, kinetic isotope effect (KIE) experiments for both coupling partners were carried out [Eq. (S5),(S6)]. The KIE value of two parallel competition reactions of **1i** and [D$_5$]-**1i** with **2n** was found to be 1.92, while a value of 1.03 was observed for the reactions of **2n** and [D$_1$]-**2n** with **1i**, which implies that C−H bond cleavage of **1i** could be involved in the rate-determining step.[16] Furthermore, radical trapping experiments were conducted. The reaction of **1a** with **2a** gave only a slightly decreased yield in the presence of 1.0 equiv of 2,2,6,6-tetramethylpiperidine oxide (TEMPO; for details, see Section XI in the Supporting Information). A mixture of Ni(OAc)$_2$·4 H$_2$O and **2a** in toluene did not show a significant electron paramagnetic resonance (EPR) signal with the addition of free-radical spin-trapping agent DMPO (5,5-dimethyl-1-pyrroline *N*-oxide). These observations indicate a low possibility that a free-radical pathway is involved in the reaction.

Based on the above results and some relevant publications,[6e,17] a plausible mechanism is proposed as shown in Scheme 2. Initially, benzothiazole **2a** reacts with the Ni^{III} species to give the intermediate **IM1**. Next, coordination of *N*-(quinolin-8-yl)thiophene-2-carboxamide (**1a**) to the Ni^{III} center generates the nickel complex **IM2**. The resulting **IM2** undergoes an intramolecular cyclonickelation to give the diaryl nickel complex **IM3**, which was detected by MALDI-TOF-MS (See Section XIII in the Supporting Information). Reductive elimination of **IM3** affords the Ni^{I} intermediate **IM4**, which is then protonated to deliver the desired product **3a**. Finally, reoxidation of the Ni^{I} species with Ag$_2$CO$_3$ regenerates the Ni^{III} species to complete the catalytic cycle.

In conclusion, we have disclosed for the first time a nickel-catalyzed oxidative C−H/C−H cross-coupling reaction between two heteroarenes with the aid of the 8-aminoquinoline group. The method can also be applied with aromatic carboxamides as the coupling partner. This reaction features broad substrate scope, good functional-group tolerance, gram-scale production capability, and recycling of the silver



detected by MALDI-TOF-MS

Scheme 2. Proposed reaction mechanism.

oxidant. Preliminary mechanistic studies suggest that C–H bond cleavage of (hetero)aromatic carboxamide is involved in the rate-determining step. Further mechanistic studies and applications of this method are ongoing in our laboratory.

Acknowledgements

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Keywords: heteroarenes · homogeneous catalysis · nickel · oxidative cross-coupling · synthetic methods

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[13] CCDC 1447854 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[14] Prices of frequently used nickel complexes from Aldrich: Ni(OAc)$_2$·4H$_2$O: \$170/1 kg, NiCl$_2$·6H$_2$O: \$206/1 kg, Ni(OTf)$_2$: \$38.1/1 g, Ni(cod)$_2$: \$33.8/1 g, Ni(acac)$_2$: \$33.2/5 g.

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Communications

Homogeneous Catalysis

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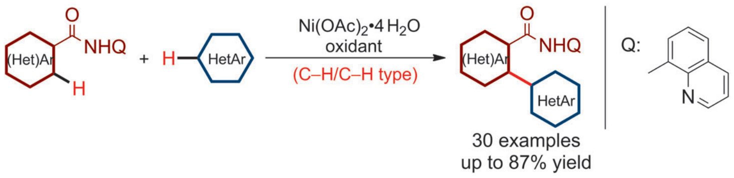
Nickel Catalysis Enables Oxidative C(sp^2)–H/C(sp^2)–H Cross-Coupling Reactions between Two Heteroarenes



An odd couple: The title reaction with the aid of the 8-aminoquinoline group gives biheteroaryl structural motifs. The reaction exhibits high functional-group compatibility and broad substrate scope, and the silver oxidant can be recycled to reduce costs and waste.