OL Organic Letters

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Copper-Catalyzed 8-Aminoquinoline-Directed Oxidative C−H/N−H Coupling for *N*-Arylation of Sulfoximines

Gowri Sankar Grandhi, Suman Dana, Anup Mandal, and Mahiuddin Baidya*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c00545 Read Online

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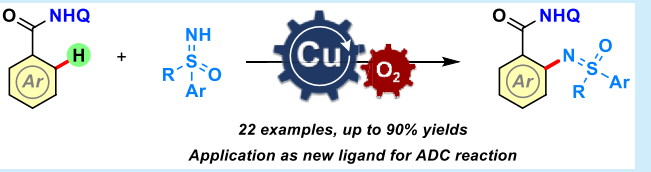
ABSTRACT: A copper-catalyzed cross-dehydrogenative C−H/N−H coupling has been devised to access a series of *N*-arylated sulfoximines in high yield from 8-aminoquinoline-derived benzamides and sulfoximines. The reaction is scalable, and mechanistic studies favor the involvement of an organometallic pathway, where C−H bond cleavage is presumed to be the kinetically relevant step. The utility of sulfoximine-coupled benzamides was displayed through the nickel-catalyzed acceptorless dehydrogenative olefination of benzyl alcohols.



N-Arylated sulfoximines, the chemically and metabolically stable monoaza S(VI)-congeners of sulfones, are emerging as an eminent class of bioactive molecules in marketed drugs, clinical drug candidates, and agrochemicals with unique physicochemical and biological properties (Figure 1).[1] They

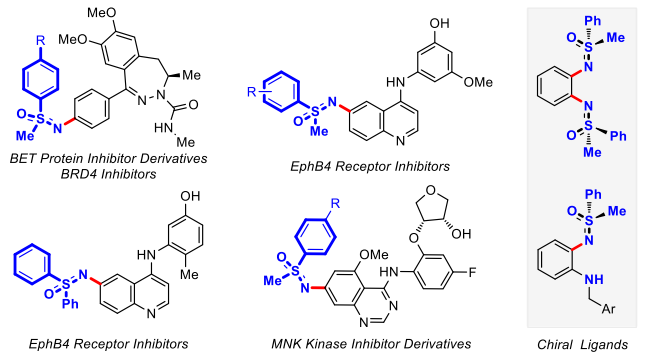
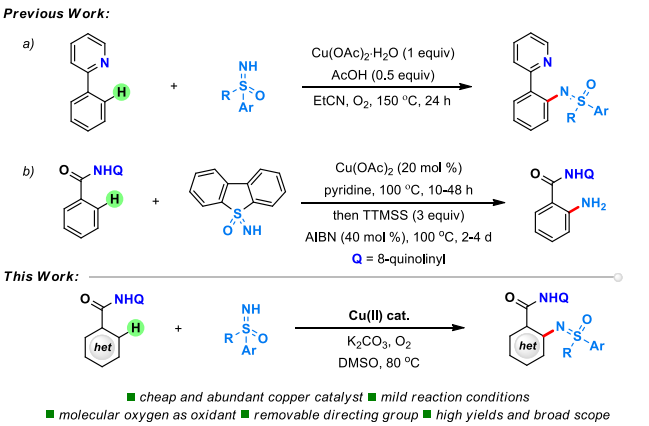


Figure 1. Some Important *N*-Aryl Sulfoximine Derivatives.

also serve as useful structural building blocks and chiral ligands for asymmetric catalysis in contemporary organic synthesis (Figure 1).[2] Consequently, the succinct synthesis of *N*-arylated sulfoximines is highly demanding. Over the years, several protocols have been developed for the *N*-arylation of sulfoximines based on metal-mediated/catalyzed cross-coupling reactions of aryl halides, triflates, tosylates, silanes, boronic acids, and so on.[3] Whereas these processes are very efficient, the necessity for prefunctionalized coupling partners restricts their synthetic efficiency.

Modern organic synthesis has largely focused on the use of the C−H bond as a staple for molecular diversification.[4] In this context, copper-mediated/catalyzed cross-dehydrogenative C−H/N−H coupling reactions have turned out to be a compelling route for manipulating C−H bonds into diverse *N*-centered functionalities.[5] Whereas these strategies have been rapidly adopted for the direct amination and amidation of unactivated as well as activated C−H bonds, the examples of C−H/N−H coupling toward the *N*-arylation of sulfoximines are elusive. Notable contributions were accomplished by the Bolm and Miura groups, who demonstrated the examples of the Cu(II)-mediated C−H sulfoximination of activated azoles as well as polyfluoroarenes[6] and later uncovered a non-removable pyridine-assisted C−H sulfoximination of 2-arylpyridines at elevated temperature (Scheme 1a).[7] Recently,

Scheme 1. Cross-Dehydrogenative *N*-Arylation of Sulfoximines with Copper Catalysts



Received: February 11, 2020

https://dx.doi.org/10.1021/acs.orglett.0c00545
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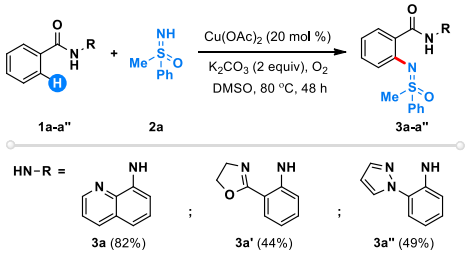
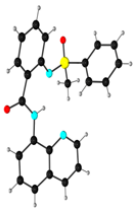
Bolm et al. also delineated a Cu(II)-catalyzed direct amination of benzamide derivatives utilizing *N*-arylated dibenzothiophene sulfoximine as an intermediate, where pyridine was used as the solvent (Scheme 1b).[8] With our continuous interest in developing general protocols toward carbon−heteroatom bonds,[9] we envisaged that the Cu(II)-catalyzed bidentate auxiliary-directed *ortho*-C−H bond activation of benzamides and the concomitant C−N bond-forming reaction with readily available sulfoximines can provide an easy entry to *N*-arylated sulfoximines. However, the materialization of this concept in a catalytic fashion is increasingly challenging as the product formed in this process can act as a tridentate *N*,*N*,*N*-type pincer ligand, which can form a complex with the Cu(II) catalyst and diminish the catalytic efficacy.

Our investigation began by following the reaction of benzamide derivatives **1** with methyl phenyl sulfoximine **2a** (Table 1). We first screened various bidentate directing groups

Table 1. Optimization of Reaction Conditions[a]





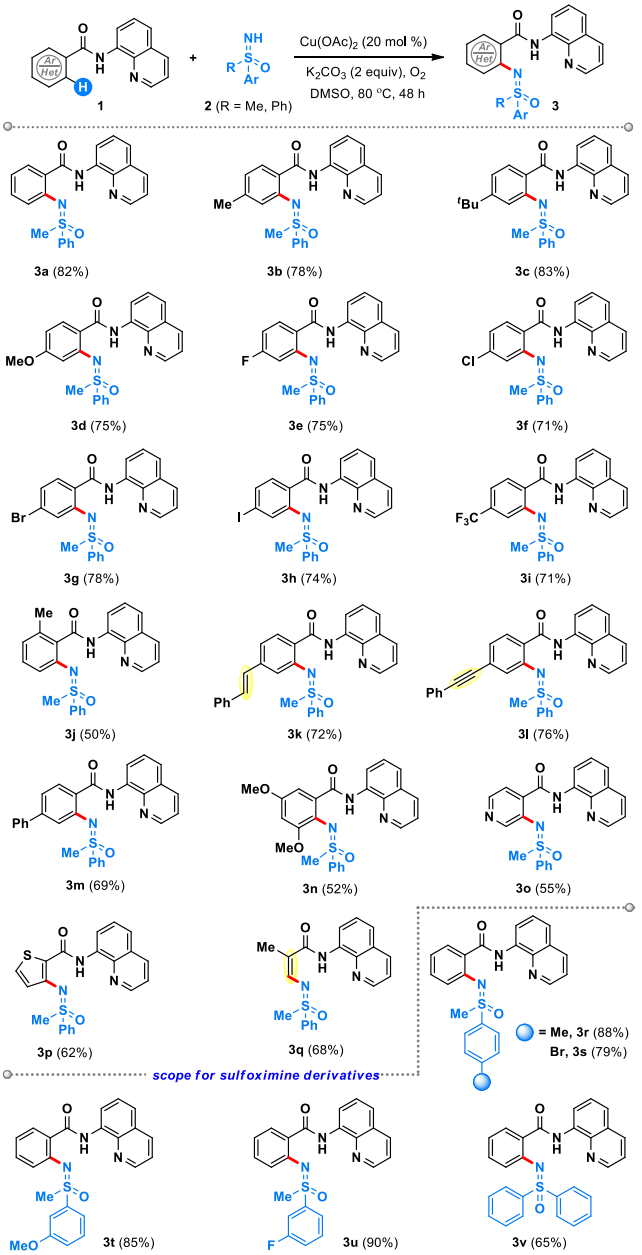
entry	deviation from standard conditions	yield (%)[b]
1	**none**	**82**
2	Na_2CO_3 instead of K_2CO_3	28
3	Li_2CO_3/Cs_2CO_3 instead of K_2CO_3	21/36
4	KOAc/NaOAc/K_3PO_4 instead of K_2CO_3	<5
5	DMF/DME/CH_3CN instead of DMSO	38/18/NR
6	toluene/DCE instead of DMSO	NR
7	at 60 °C/100 °C	trace/52
8	air instead of O_2	45
9	10 mol % $Cu(OAc)_2$	51
10	without $Cu(OAc)_2$	NR
11	without K_2CO_3	NR

[a]Reaction conditions: **1a**−**a**′′ (0.1 mmol), **2a** (0.15 mmol), $Cu(OAc)_2$ (20 mol %), base (2 equiv), O_2, solvent (0.5 mL), 80 °C for 48 h. [b]Isolated yields.

such as 8-aminoquinoline (**1a**), 2-aminophenyl-2-oxazoline (**1a**′), and 2-aminophenylpyrazole (**1a**′′). When corresponding benzamides **1a**−**1a**′′ were treated with sulfoximine **2a** in the presence of $Cu(OAc)_2$ (20 mol %) and K_2CO_3 (2 equiv) in DMSO solvent under an oxygen atmosphere at 80 °C, we observed that the desired C−H/N−H cross-coupling reaction is indeed operational (Table 1). The 8-aminoquinoline auxiliary served as the best directing group for this process, providing 82% yield of the desired product **3a** (Table 1, entry 1). The screening of other carbonate bases provided inferior results, whereas acetate and phosphate bases turned out to be inefficient to supply the desired product (Table 1, entries 2−4). The choice of solvent was decisive for this reaction, as other common organic solvents such as DMF, DME, CH_3CN, toluene, and DCE delivered detrimental results or no product formation with the recovery of starting materials (Table 1, entries 5 and 6). The increase in reaction temperature reduced the catalytic efficacy, whereas the decrease in the temperature produced the desired product in only a trace amount (entry 7). Notably, ambient air as an oxidant was found to be incompetent and reduced the catalytic turnover number (entry 8). Further screening suggested that lowering the catalyst loading displayed a depleting trend in reactivity (entry 9), and both $Cu(OAc)_2$ and K_2CO_3 played an imperative role for this C−N bond formation process (Table 1, entries 10 and 11).

Having acquired the optimal conditions in hand, we next intended to explore the scope of the reaction. Various substituted benzamides having electron-donating or electron-withdrawing substituents delivered the desired *N*-arylated sulfoximines in good to excellent yield (Scheme 2). Alkyl

Scheme 2. Substrate Scope of the *N*-Arylation Reaction[a]



[a]Reaction conditions: **1** (0.1 mmol), **2** (0.15 mmol), $Cu(OAc)_2$ (20 mol %), K_2CO_3 (2 equiv), O_2, DMSO (0.5 mL), 80 °C for 48 h. Yields of isolated products are given.

https://dx.doi.org/10.1021/acs.orglett.0c00545
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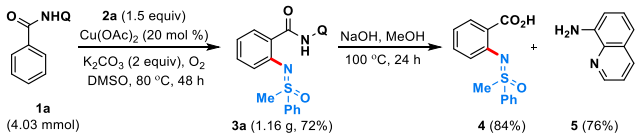
(**3b**,**c**) and alkoxy (**3d**) substituents in the para position of amides dispensed the desired products in 75−83% yield. Notably, sensitive and synthetically modifiable halo-functionalities remained untouched, and the corresponding C−N coupled products (**3e**−**h**) were obtained in very high yield. The protocol also functioned smoothly with benzamides having electron-withdrawing trifluoromethyl (**3i**) and bulky *ortho*-methyl (**3j**) substituents. Reactive alkenyl (**3k**) and alkynyl (**3l**) substituents in the para position were also sustained under the catalytic conditions. The protocol was successful with biphenyl-derived benzamide, furnishing a 69% yield of **3m**. Sterically hindered 3,5-dimethoxybenzamide gave **3n** in moderate yield (52%). Delightfully, various heteroarene amides also participated in the transformation, furnishing *N*-heteroaryl sulfoximines **3o** and **3p** in 55 and 62% yield, respectively. The olefin congener of benzamide **1q** was also suited under this protocol, offering **3q** in 68% yield. Notably, this is the first example of C−H bond activation reaction, where high-value *N*-3-pyridyl (**3o**), *N*-3-thiophenyl (**3p**), and *N*-alkenyl (**3q**) sulfoximines can be accessed directly through a C−H/N−H cross-dehydrogenative coupling. We also examined the diversity of sulfoximine coupling partners. Satisfyingly, various functional groups, for example, alkyl (**3r**), bromo (**3s**), methoxy (**3t**), and fluoro (**3u**) substituents in para or meta positions of the aryl ring in sulfoximine, delivered the desired products in uniformly high yield (79−90%). Also, oxidative C−H/N−H coupling was fruitful with diphenyl sulfoximine to offer compound **3v** in 65% isolated yield.

The synthetic utility of the reaction was then showcased through a gram-scale reaction, and the reaction efficacy did not significantly hamper upon the scale-up (Scheme 3).

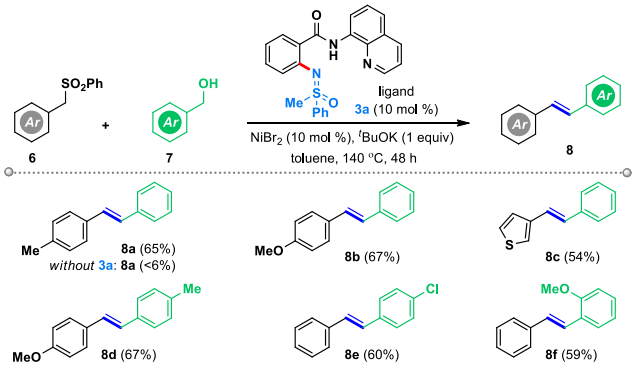
Scheme 3. Gram-Scale Reaction and Removal of the Directing Group



Furthermore, the bidentate auxiliary can also be easily removed by exposing the product **3a** to methanolic NaOH, producing functionalized benzoic acid **4** in excellent yield (Scheme 3). Also, no hydrolysis of sulfoximine unit was detected during the course of the reaction. Of note, base-metal-catalyzed acceptorless dehydrogenative coupling (ADC) reactions of alcohol have gained significant attention owing to their innate greenness and atom-economic profile, and often these processes are highly governed by the judicious ligand design.[10] The possibility that product **3** could serve as a useful *N*,*N*,*N*-type pincer ligand encouraged us to investigate its potential as a ligand in transition-metal-catalyzed olefination reactions. Gratifyingly, the olefination of sulfones **6** with benzyl alcohols **7** proceeded smoothly in the presence of a catalytic amount of $NiBr_2$ in combination with product **3a** as a ligand, forging olefins **8a**−**f** in good yield (Scheme 4). These findings reveal the potential of the C−N-coupled products as a new class of *N*,*N*,*N*-type tridentate ligands.

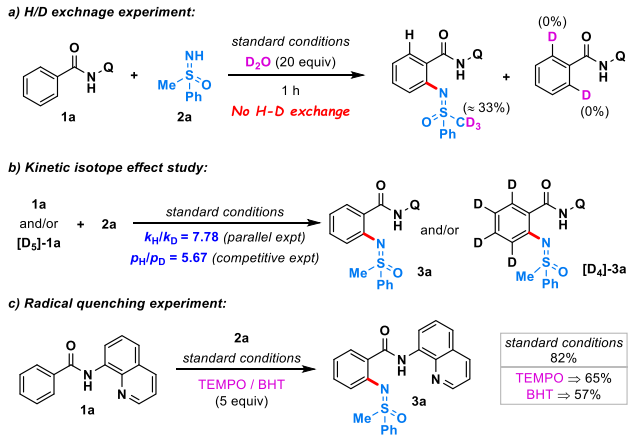
We next sought to gain the mechanistic insights into this reaction. To probe into the nature of metalation, we performed the reaction in the presence of D_2O. The absence of H−D exchange at the aromatic ring in the amide **1a** and product inferred an irreversible C−H metalation process (Scheme 5a).

Scheme 4. Application in Olefination Reaction with Benzyl Alcohols[a]



[a]Reaction conditions: **6** (0.2 mmol, 1 equiv), **7** (0.3 mmol, 1.5 equiv), $NiBr_2$ (0.025 mmol), ligand **3a** (0.025 mmol), ^{t}BuOK (1 equiv), toluene (0.7 mL) under an Ar atmosphere.

Scheme 5. Mechanistic Studies



Kinetic isotope effect studies with k_H/k_D = 7.78 (parallel experiment) and p_H/p_D = 5.67 (competitive experiment) indicated the C−H bond activation as the possible rate-determining step (Scheme 5b). Furthermore, the presence of over-stoichiometric amounts of radical scavengers did not significantly inhibit the catalytic outcome, refuting the possibility of a single-electron transfer (SET) process or the involvement of radical intermediates (Scheme 5c).

On the basis of the aforementioned mechanistic investigations and previous literature precedents, a plausible reaction mechanism is shown in Scheme 6. At first, complex **A** is formed through the complexation of 8-aminoquinoline-derived benzamide **1** with copper(II) catalyst. After that, basic ligand-promoted proximity-induced *ortho*-C−H bond activation of benzamide **1** leads to the formation of cyclometalated Cu(II) intermediate **B**. Subsequent ligand exchange provides the intermediate **C**, which further undergoes oxidation or disproportionation to deliver Cu(III) species **D**. Finally, reductive elimination delivers the desired *N*-arylation product **3** with the generation of Cu(I) species, where molecular oxygen plays the role of a terminal oxidant to regenerate the active Cu(II) catalyst.

In conclusion, we have demonstrated a general copper-catalyzed cross-dehydrogenative C−H/N−H coupling reaction, which provides expedite access to a diverse range of *N*-arylated sulfoximines. The reaction is scalable and has a broad

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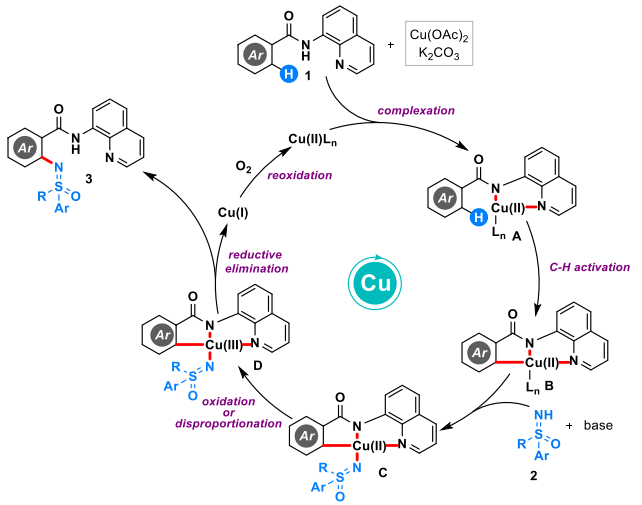
Scheme 6. Plausible Reaction Mechanism



scope, accommodating an electronically wide range of substituted benzamides and tolerating various sensitive functional groups such as bromo, iodo, alkynyl, styryl, and so on. We have also showcased the potential of this process through the unprecedented synthesis of *N*-heteroaryl and *N*-alkenyl sulfoximines through cross-dehydrogenative coupling. Our findings suggest that these *N*-arylated sulfoximine derivatives can act as potential *N,N,N*-type tridentate ligands for a Ni-catalyzed ADC reaction. Mechanistic insights revealed that the reaction proceeds through an organometallic pathway, where the C−H bond cleavage is irreversible and possibly involved in the rate-determining step. We anticipate that these findings will be of increasing importance in terms of the step- and atom-economical *N*-arylation of sulfoximines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00545.

Complete experimental details and characterization data for the prepared compounds (PDF)

Accession Codes

CCDC 1982765 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Mahiuddin Baidya − *Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India;* orcid.org/0000-0001-9415-7137; Email: mbaidya@iitm.ac.in

Authors

Gowri Sankar Grandhi − *Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India*

Suman Dana − *Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India*

Anup Mandal − *Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c00545

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge DST-SERB (CRG/2019/001003), India for financial support. G.S.G. and A.M. acknowledge UGC for the SRF, and S.D. acknowledges IIT Madras for providing the HTRA Fellowship. M.B. thanks IIT Madras for the support through the Institute Research Development Award (IRDA).

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