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Nickel-Catalyzed and Benzoic Acid-Promoted Direct **Sulfenylation of Unactivated Arenes**

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A nickel-catalyzed and benzoic acid-promoted direct sulfenylation of unactivated arenes using removable 2-(pyridine-2-yl)-isopropylamine as a directing group is described. This strategy provides an efficient access to valuable aryl sulfides with ample substrate scope and high degree of functional group tolerance.

Transition metal-catalyzed C-H bond functionalization reaction is one of most efficient methods for selective C-C, C-O, C-N and C-halogen bonds forming reactions and continues to be of great appeal in the synthetic chemistry in recent years.¹ In contrast, transition metal-catalyzed C-H activation/C-S bond forming reactions are rare and most examples being relied on the preparation of benzothiazole skeletons,² arylsulfone skeletons,³ sulfenylation of electron-rich arenes⁴ or highly reactive heteroarenes.⁵ Direct sulfenylation of unactivated arenes to aryl sulfides remains, however a poorly developed area, in spite of, the presence of the aryl sulfide structure unit in many biologically active natural products, medicinal compounds and advanced polymer materials.6 Current practical methods for synthesis of these compounds rely mainly on the transition metal-catalyzed/mediated sulfenylation of arylhalides.7 Although these methods can provide various kinds of aryl sulfides, but they essentially require pre-functionalization of arenes and thereby limits the scope of the reaction.

Recently, transition metal-mediated direct sulfenylation of unactivated arenes bearing directing groups has been developed by various groups⁸⁻¹⁰. In this regard, Yu et al. reported the first example of the direct sulfenylation of arylpyridines through a Cu-mediated sp² C-H functionalization process in 2006.8 Followed this, Qing et al. developed Cu-mediated methylthiolation of aryl pyridines using DMSO as a sulfenylation agent.9 Subsequently, Dagulis and co-workers reported an elegant Cu-promoted directed sulfenylation of sp² C-H bonds assisted by 8-aminoquinoline-derived bidentatechelation.¹⁰ However, the catalytic versions of direct C-H sulfenylations have been reported very recently using Pd¹¹ and Rh¹² catalysts with ketoxime, pyridine or their analogues as directing groups, providing desired aryl sulfides in the range of 50-70% yields in general. The absence of the metal catalytic reactions is presumably due to the sulfur atom easily binding to metals, which leads to the deactivation of the metal catalyst.¹³ Therefore, the development of a highly efficient sulfenylation of nonactive arene C-H bonds using low-cost metal catalysts rendering removable directing groups would be of prime synthetic value.

Although the use of earth-abundant first-row transition metals catalysts in the functionalization of C-H bonds, in particular nickel has attracted significant attention due to its cost and availability,^{14,15} there is no report on nickel-catalyzed C-H activation/C-S bond forming reactions. Herein, we report the first example of nickel-catalyzed and benzoic acidpromoted direct sulfenylation of unactivated arenes with the assistance of removable bidentate auxiliary¹⁶ providing functionalized aryl sulfides in good to excellent yield.

Inspired by the considerable importance and prevalence of the nickel catalysis,¹⁴ we began our investigation with the model substrate benzamide (1a) and diphenyl disulfide (2a) using nickel salt as a catalyst (Table 1). To our delight, we found that treatment of 1a with 2.0 equiv of 2a, with 5 mol% of NiCl₂, 10 mol% of PhCOOH and 2.0 equiv Ag₂CO₃ in DCE (1,2-Dichloro ethane) at 140 °C for 10 h, the desired product, 2,6-bis(phenyl-thio)-N-(2-(pyridin-2-yl)propan-2-yl)benzamide (3a) was formed in 90% yield (entry 1). Next, we intended to investigate the effect of catalyst and benzoic acid in due regard, it was observed that the reaction yield was significantly decreased to less than 5% in absence of benzoic acid (entry 2). Similarly, NiCl₂ was indispensible for the catalytic cycle (entry 3). On the basis of this observation, an extensive additive screening was then carried out, results indicated that PhCOOH

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was found to be optimal (entries 4-7). Encouraged by these results, we then examined different nickel catalysts (entries 8-12) and found that the reaction could be catalyzed by various nickel salts, including NiBr₂, Ni(ClO₄)₂, Ni(OAc)₂ and Ni(acac)₂. This investigation solely conclude that NiCl₂ is the catalyst of choice. Additionally, we found that replacing Ag₂CO₃ with other silver salts could not give desired product (entries 13-14). It is noteworthy to mention that the reaction could furnish higher yield even at a shorter reaction time of 4 hour (entry 15). Furthermore, the reaction yield was decreased with either lower levels of catalyst (entry 16), or reduced amounts of additive (entry 17) as well as at lower reaction temperature (entry 18).

Table 1 Optimization of Reaction Conditions ^a					
N N	N H 1a	+ _{Ph} ^{_S} _{`S} ^{_Ph} - 2 a	Cat. Ni (5 mol%) Acid (10 mol%) Additive (2.0 eq) DCE, 140 °C	, () - () N	O SPh N H PhS 3a
Entry	Ni source	Acid	Additive	Time (h)	Yield (%) ^b
1	NiCl ₂	PhCOOH	Ag ₂ CO ₃	10	90
2	NiCl ₂	-	Ag ₂ CO ₃	10	< 5
3	-	PhCOOH	Ag ₂ CO ₃	4	0
4	NiCl ₂	MesCOOH	Ag ₂ CO ₃	10	79
5	NiCl ₂	4-CIC ₆ H ₄ COOH	Ag ₂ CO ₃	10	85
6	NiCl ₂	4-MeC ₆ H ₄ COOH	Ag ₂ CO ₃	10	81
7	NiCl ₂	1-AdCOOH	Ag ₂ CO ₃	10	87
8	NiF ₂	PhCOOH	Ag ₂ CO ₃	10	< 5
9	NiBr ₂	PhCOOH	Ag ₂ CO ₃	10	88
10	Ni(ClO ₄) ₂	PhCOOH	Ag ₂ CO ₃	10	75
11	Ni(acac) ₂	PhCOOH	Ag ₂ CO ₃	10	50
12	Ni(OAc) ₂	PhCOOH	Ag ₂ CO ₃	10	84
13	NiCl ₂	PhCOOH	Ag ₂ O	10	0
14	NiCl ₂	PhCOOH	AgOTf	10	0
15	NiCl ₂	PhCOOH	Ag ₂ CO ₃	4	96(92 ^c)
16 ^d	NiCl ₂	PhCOOH	Ag ₂ CO ₃	4	68
17 ^e	NiCl ₂	PhCOOH	Ag ₂ CO ₃	4	60
18 ^f	NiCl ₂	PhCOOH	Ag ₂ CO ₃	4	56

^{*a*} Conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Ni source (5 mol%), Acid (10 mol%), Additive (2.0 eq), Solvent (2 mL), 140 °C. ^{*b*} Yields are based on **1a**, determined by crude ¹H NMR using dibromomethane as an internal standard. ^{*c*} Isolated yield. ^{*d*} 2.5 mol% NiCl₂ and 5 mol% PhCOOH. ^{*e*} 1.0 eq Ag₂CO₃. ^{*f*} at 120 °C.

To evaluate the substrate scope of this reaction with the established optimized conditions, wide range of benzamides with the different substituents in phenyl moiety were primarily examined (Table 2). The benzamides bearing both electrondonating as well as electron-withdrawing groups in the paraposition of phenyl group proceeded smoothly to provide the corresponding disulfenylation products in good to excellent yields (**3b-d**). In addition, aromatic ring substituted with various halogens were also tolerated (**3e-g**). It is worthy to mention that the products containing halogens could be useful for the subsequent valuable transformations. Evidently, *o*-substituted benzamides produced the desired monosulfenylation products (**3h-3k**) under the standard conditions. In case of *m*- substituted substrate, wherein the C–H bond at the lesshindered position can be activated selectively. For example, sulfenylation of *m*-methylbenzamide derivative (11) gave monosubstituted product (31) in 86% yield. In addition, the C–H bond having a small functional group nearby could also be activated. For example, *m*-chlorobenzamide (1m) could result in both mono- and di-sulfenylation products (3ma and 3mb) resepctively. Moreover, the scope of this reaction is not limited to benzamide substrates. Thiophene-2-carboxamide (1n) was mono-sulfenylated to provide the desired product (3n) in 52% yield.





^{*a*} Conditions: **1** (0.2 mmol), **2a** (0.4 mmol), NiCl₂ (5 mol%), PhCOOH (10 mol%), Ag₂CO₃ (2.0 eq), DCE (2 mL), 140 °C, 4 h. ^{*b*} Isolated yields. ^{*c*} 10 h.

Next, we turned our interest to evaluate the substrate scope with respect to various disulfides (Table 3). Diaryl disulfides with either an electron-donating or electron-withdrawing group at the o-, m- or p- positions were found to be well compatible under the standard reaction conditions (**3o-3w**). A wide range of functional groups such as methoxy, methyl, halogen, amide, and nitro groups present in the diaryl disulfides have been tolerated well. In addition to substituted diaryl disulfides, diheteroaromatic disulfide, such as 2-methyl-3-furyl disulfide was also employed and produced aryl sulfide (**3x**) in excellent yield. Dialkyl disulfide failed to yield the desired product (**3y**).

The directing group (2-(pyridine-2-yl)-isopropylamine) can be removed efficiently under the acidic conditions,^{16c-g} which highlight the versatility and generality of this protocol. For example, hydrolysis of **31** could produce benzoic acid **41** (Eq 1), a useful intermediate for medicinal compounds.¹⁷

Table 3 Scope of Disulfides^{a,b}



^{*a*} Conditions: **1a** (0.2 mmol), **2** (0.4 mmol), NiCl₂ (5 mol%), PhCOOH (10 mol%), Ag₂CO₃ (2.0 eq), DCE (2 mL), 140 °C, 4 h. ^{*b*} Isolated yields. ^{*c*} 10 h.

In order to gain an insight into the possible mechanism, a radical trapping experiment was performed. It was found that the addition of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl) inhibited the sulfenylation reaction, and no desired product (**3h**) was produced (see Scheme S1 in ESI). This evidence suggests the probable involvement of single electron transfer (SET) pathway in this reaction. Furthermore, an intermolecular competition experiment between **1h** and **1j** has been performed (see Scheme S2 in ESI), which demonstrated that electron-rich arenes reacted with higher relative rates.



Although the mechanism of the reaction is unclear at this moment, on the basis of the previous reports,¹⁵ the following plausible mechanistic pathway has been proposed (Figure 1). Coordination of amide **1h** to a Ni^{II} species followed by a ligand exchange process generates the Ni^{II} complex **A**, which facilitates the C–H bond activation of substrate **1h** to form the Ar–Ni^{II} intermediate **B**. The Ni^{III} complex **C** could be formed due to the oxidation of the intermediate **B** by phenyl sulfide radical. Reductive elimination of the intermediate **C** followed by protonation generates the desired product **3h** and a Ni^I species. Treatment of the Ni^I species with diphenyl disulfide (**2a**) produces Ni^{II} species and phenyl sulfide radical. However, at current stage, we cannot exclude the Ni^{II}/Ni^{IV} catalytic cycle in which the PhS–SPh bond oxidatively adds to the Ni^{II} species.^{15b-c}



Figure 1 A plausible catalytic cycle.

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In summary, we have developed an efficient nickel-catalyzed and benzoic acid-promoted direct sulfenylation of unactivated arenes through sp² C–H bond functionalization process. This transformation represents the first example of directed sulfenylation of arenes through nickel catalysis assisted by bidentate auxiliary, providing an efficient complementary approach to functionalized aryl sulfide analogs which may find applications in natural products and medicinal chemistry. The present process also benefits from the easy removal of the directed group by hydrolysis. Further studies, including the investigation on mechanistic study and other possible exploration of this strategy are currently under way in our laboratory.

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