

Cross-Coupling

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Cross-Coupling of Sodium Sulfinates with Aryl, Heteroaryl, and Vinyl Halides by Nickel/Photoredox Dual Catalysis

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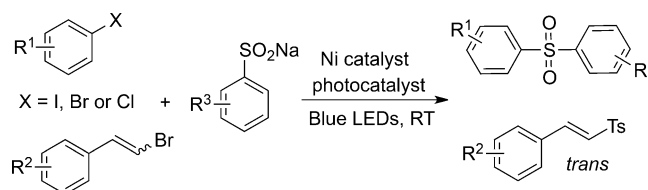
Abstract: An efficient photoredox/nickel catalyzed sulfonylation reaction of aryl, heteroaryl, and vinyl halides has been achieved for the first time. This newly developed sulfonylation protocol provides a versatile method for the synthesis of diverse aromatic sulfones at room temperature and shows excellent functional group tolerance. The electrophilic coupling partners are not limited to aryl, heteroaryl, and vinyl bromides and iodides, but also includes less reactive aryl chlorides as suitable substrates for this transformation.

Sulfones are highly important organic molecules because of their versatile synthetic utility in organic synthesis as well as the widespread presence of sulfonyl groups in pharmaceuticals, agrochemicals, biologically active compounds, and polymer materials.^[1,2] Conventionally, these valuable compounds are synthesized by oxidation of sulfides,^[3] sulfonylation of arenes,^[4] or palladium or copper-catalyzed arylation of sulfinate salts.^[5] These methods suffer from significant drawbacks, including the use of foul-smelling thiols and strong oxidizing reagents, harsh acidic treatments, and high reaction temperatures, which can limit the functional group tolerance and substrate scope. Alternatively, SO₂ surrogates such as DABCO·(SO₂)₂ and K₂S₂O₅ have been applied to the synthesis of sulfones by fixation of sulfur dioxide to generate sulfinate anion intermediates which can then undergo (SO₂)-arylation/alkylation.^[6]

In recent years, increasing attention has been devoted to the field of dual photoredox and transition-metal catalysis, and useful transformations have been achieved by this strategy.^[7–10] In particular, photoredox/nickel catalysis proved attractive because of the unique catalytic properties of nickel catalysts.^[8–10] Pioneering works in this field focused

on C(sp³)–C(sp²) bond formations by coupling aryl halides with benzylic trifluoroborates and α-carboxy sp³-carbon atoms.^[8] Since then, progress has been made in the field of C–C bond formation.^[9] Moreover, this elegant strategy has also been applied to the synthesis of aryl ethers, aryl esters, aryl amines, indolines, triarylphosphine oxides, and thioethers by different C–heteroatom bond formations,^[10] thus confirming the enormous potential of dual photoredox/metal catalysis not only in the improvement of known reactions but also in the discovery of novel catalytic protocols.

As part of our continuing studies in the area of photoredox and transition-metal catalysis, we herein report the first photoredox/metal catalyzed cross-coupling of sulfinate salts with aryl, heteroaryl, and vinyl halides at room temperature (Scheme 1). This protocol provides a versatile approach to aromatic sulfones with a broad substrate scope and excellent functional group tolerance. Notably, less-reactive aryl chlorides could also be converted into the corresponding sulfones.



Scheme 1. Photoredox/nickel catalyzed synthesis of aromatic sulfones at room temperature.

Our study commenced with 4-bromobenzonitrile (**1a**) and sodium 4-methylbenzenesulfinate (**2a**) as model substrates. Initially, the ratio of **1a** and **2a** was set as 1:1 with **PC1** as the photocatalyst, NiCl₂·glyme as the nickel source, dtbbpy as the ligand, and DMF as the solvent, which afforded the corresponding sulfone **3a** in 43% yield only (Table 1, entry 1). The use of K₂CO₃ as a base decreased the yield dramatically (entry 2). The yield of **3a** increased to 70% when two equivalents of **2a** were employed (entry 3). After screening several commonly used photocatalysts, including an organic dye (entries 4–8), the Ir complex **PC4** was found to give the best result (entry 6). A series of nickel catalysts such as NiBr₂·O(CH₂CH₂OCH₃)₂, Ni(OAc)₂·4H₂O, Ni(acac)₂, NiCl₂, and Ni(cod)₂ were subsequently examined, however no further improvement was observed (entries 9–13). The use of DMF as a solvent was found to be crucial for this transformation. When other solvents were utilized, the sulfonylation reaction either did not take place or occurred in low yield (entries 14–16). Performing the reaction under undegassed conditions provided the product in 18% yield,

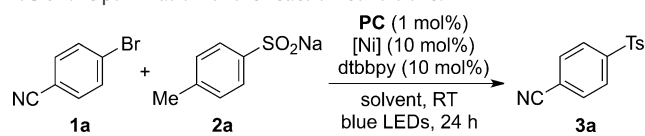
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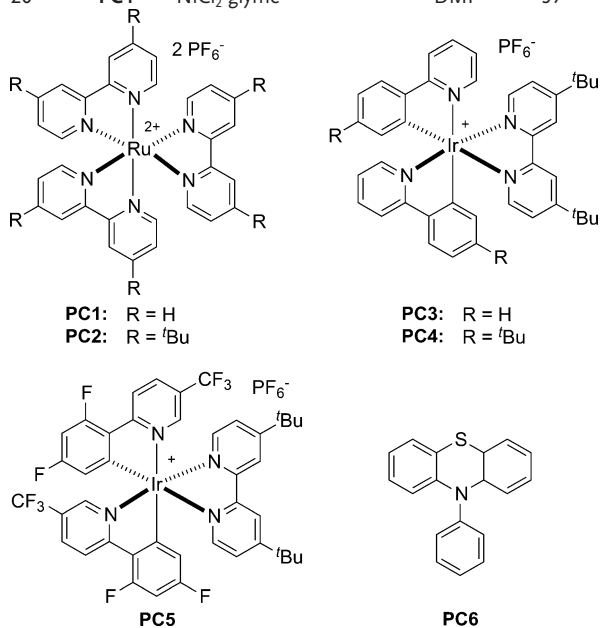
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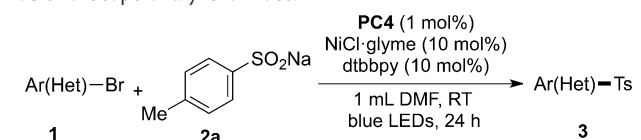
Table 1: Optimization of the reaction conditions.^[a]

Entry	PC	[Ni]	Solvent	Yield [%] ^[b]
1 ^[c]	PC1	NiCl ₂ -glyme	DMF	43
2 ^[c,d]	PC1	NiCl ₂ -glyme	DMF	trace
3	PC1	NiCl ₂ -glyme	DMF	70
4	PC2	NiCl ₂ -glyme	DMF	74
5	PC3	NiCl ₂ -glyme	DMF	75
6	PC4	NiCl ₂ -glyme	DMF	89 (86 ^[e])
7	PC5	NiCl ₂ -glyme	DMF	60
8	PC6	NiCl ₂ -glyme	DMF	63
9	PC4	NiBr ₂ O(CH ₂ CH ₂ OCH ₃) ₂	DMF	86
10	PC4	Ni(OAc) ₂ ·4 H ₂ O	DMF	44
11	PC4	Ni(acac) ₂	DMF	57
12	PC4	NiCl ₂	DMF	30
13	PC4	Ni(cod) ₂	DMF	69
14	PC4	NiCl ₂ -glyme	CH ₃ CN	0
15	PC4	NiCl ₂ -glyme	PhCF ₃	0
16	PC4	NiCl ₂ -glyme	THF	trace
17 ^[f]	PC4	NiCl ₂ -glyme	DMF	18
18 ^[g]	–	NiCl ₂ -glyme	DMF	0
19	PC4	–	DMF	0
20 ^[h]	PC4	NiCl ₂ -glyme	DMF	57



[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), photocatalyst (0.001 mmol), [Ni] (0.01 mmol), ligand (0.01 mmol), and degassed solvent (1.0 mL) at room temperature under irradiation with 2.6 W blue LED strips for 24 h. [b] Yield determined by GC. [c] **2a** (1 equiv). [d] K₂CO₃ (2 equiv) was added. [e] Yield of isolated product. [f] Undegassed. [g] No light. [h] CF-Lamp was used instead of blue LED strips. cod = 1,5-cyclooctadiene, dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, Ts = 4-toluenesulfonyl.

thus indicating the importance of avoiding the presence of molecular oxygen in the reaction (entry 17). Control experiments confirmed the role of the photocatalyst, light, and nickel catalyst for the reaction (entries 18 and 19). In addition, a CFLamp was tested and proved suitable for this

Table 2: Scope of aryl bromides.^[a,b]

3a , 86% (67% ^c)	3b , 59%	3c , 48%
3d , 66%	3e , 60%	3f , 73%
3g , 56%	3h , 62%	3i , 60%
3j , 51%	3k , 53%	3l , 54%
3m , 66%	3n , 42%	3o , 62%
3p , 57%	3q , 65%	3r , 56%
3s , 57%	3t , 56%	3u , 42%

[a] Reaction conditions: Aryl bromide **1** (0.1 mmol), **2a** (0.2 mmol), **PC4** (0.001 mmol), NiCl₂-glyme (0.01 mmol), dtbbpy (0.01 mmol), and degassed DMF (1 mL) at room temperature under irradiation with 2.6 W blue LED strips for 24 h. [b] Yield after purification. [c] Reaction performed on a 2.0 mmol scale.

transformation, thus providing the corresponding product in 57% yield (entry 20).

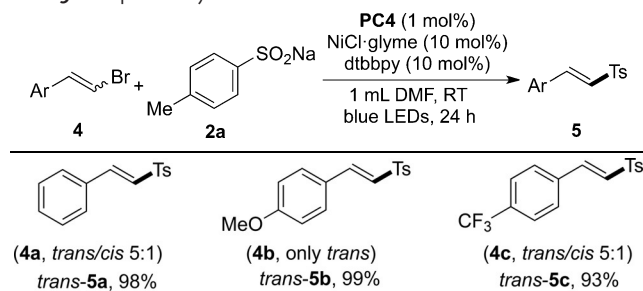
With the optimized reaction conditions in hand, the scope with respect to the aryl bromides was firstly evaluated (Table 2). A wide variety of aryl bromides bearing electron-donating and electron-withdrawing functional groups gave the corresponding products in moderate to excellent yields. The position of the substituents on the aryl ring had a minor effect on the efficiency of this transformation. For example, not only the aryl bromides **1a** and **1f** possessing *para* substituents but also the substrates **1b** and **1g**, bearing substituents in *meta* and *ortho* positions, afforded the corresponding products in good yields. In addition, our

newly developed protocol tolerated a variety of functionalities, including ketone (**3d** and **3e**), methylester (**3f**, **3g**, and **3q**), aldehyde (**3h**), amide (**3i**), trifluoromethyl (**3l** and **3m**), *t*-butyl (**3n**), and tertiary amine (**3o**). Notably, a reactive primary amine and hydroxy group on the aromatic ring were also tolerated (**3j** and **3k**). Moreover, naphthyl bromides (**1p** and **1q**) also underwent this reaction efficiently, thus giving the corresponding products in good yields.

Significantly, the scope of this protocol could be extended to pharmaceutically relevant heteroaromatic bromides such as quinoline (**1r** and **1s**), benzothiofene (**1t**), and thiophene (**1u**) derivatives (Table 2). Noteworthy, **3a** was obtained in a good yield of 67% when the reaction was performed on a 2.0 mmol scale in the presence of 0.5 mol% photocatalyst, thus indicating the scalability and practicability of this mild sulfonation protocol.

In addition, our newly developed protocol could also be readily extended to vinyl bromides (Table 3). Accordingly, substrates possessing electron-donating and electron-withdrawing functional groups gave the α,β -unsaturated sulfones **5a–c** in excellent yields (93–99%). It is important to note that only the *trans* products were generated, even when the vinyl bromides **4a** and **4c**, containing a *trans/cis* mixture, were employed.

Table 3: Scope of vinyl bromides.^[a,b]

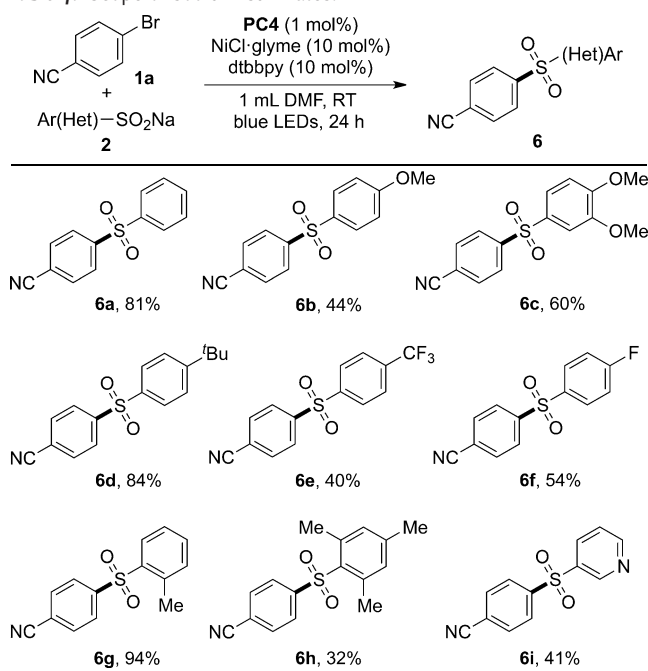


[a] Reaction conditions: vinyl bromide **4** (0.1 mmol), **2a** (0.2 mmol), PC4 (0.001 mmol), NiCl₂-glyme (0.01 mmol), dtbbpy (0.01 mmol), and degassed DMF (1 mL) at room temperature under irradiation with 2.6 W blue LED strips for 24 h. [b] Yield after purification.

Next, the scope with respect to the sodium sulfonates **2** was explored (Table 4). A wide range of structurally diverse sodium sulfonates were suitable substrates for this transformation. For example, benzenesulfonate and sodium sulfonates bearing methoxy groups could generate the corresponding diarylsulfones **6a–c** in moderate to excellent yields. Also, functional groups such as *t*-butyl (**6d**), trifluoromethyl (**6e**), and fluoro (**6f**) were well tolerated under our reaction conditions. Strikingly, sodium sulfinate possessing a methyl group in the *ortho* position of the aromatic ring could undergo this reaction smoothly, thus affording the corresponding product **6g** in 94% yield. However, continuously increasing steric hindrance led to diminished yield (**6h**). Likewise, the reaction could also be applied to the heterocyclic sodium sulfinate **2i**, thus giving the heterocycle-containing sulfone **6i**, which is important in medicinal chemistry.

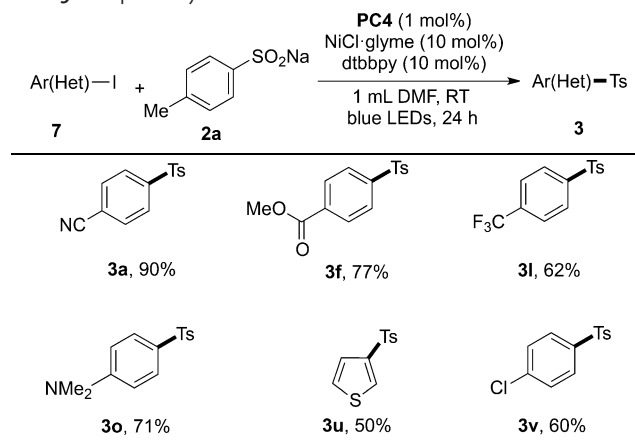
Moreover, aryl iodides were also suitable substrates for this transformation (Table 5). Likewise, substrates bearing

Table 4: Scope of sodium sulfonates.^[a,b]



[a] Reaction conditions: **1a** (0.1 mmol), sodium sulfinate **2** (0.2 mmol), PC4 (0.001 mmol), NiCl₂-glyme (0.01 mmol), dtbbpy (0.01 mmol), and degassed DMF (1 mL) at room temperature under irradiation with 2.6 W blue LED strips for 24 h. [b] Yield after purification.

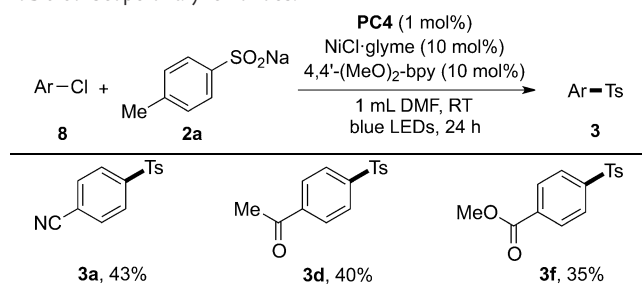
Table 5: Scope of aryl iodides.^[a,b]



[a] Reaction conditions: aryl iodide **7** (0.1 mmol), **2a** (0.2 mmol), PC4 (0.001 mmol), NiCl₂-glyme (0.01 mmol), dtbbpy (0.01 mmol), and degassed DMF (1 mL) at room temperature under irradiation with 2.6 W blue LED strips for 24 h. [b] Yield after purification.

electron-donating and electron-withdrawing functional groups both afforded the corresponding products in good to high yields. Interestingly, a chloro group was well tolerated under the present conditions.

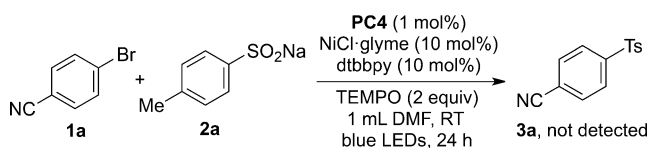
It is noteworthy that minor modification of the standard conditions, by just switching the dtbbpy ligand to the more electron rich 4,4'-dimethoxy-2,2'-bipyridine (4,4'-(MeO)₂-bpy) ligand, made this protocol applicable to more challenging aryl chloride substrates (**8**), thus indicating the potential of

Table 6: Scope of aryl chlorides.^[a,b]

[a] Reaction conditions: Aryl chloride **8** (0.1 mmol), **2a** (0.2 mmol), PC4 (0.001 mmol), NiCl₂·glyme (0.01 mmol), 4,4'-(MeO)₂-bpy (0.01 mmol), and degassed DMF (1 mL) at room temperature under irradiation with 2.6 W blue LED strips for 24 h. [b] Yield after purification.

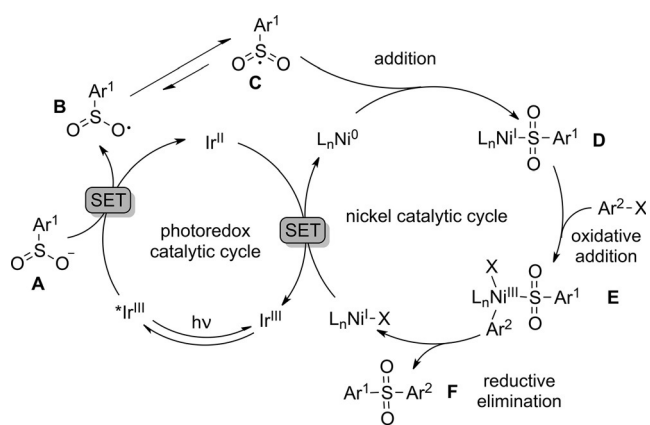
our newly developed sulfonylation protocol in applying less reactive electrophiles (Table 6).

To shed light on the mechanism of this protocol, a radical-trapping experiment was conducted with two equivalents of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy; Scheme 2). The reaction was completely suppressed and no desired product was detected, thus suggesting the involvement of a sulfonyl radical in the transformation.



Scheme 2. Radical-trapping experiment.

Based on our results and previous studies^[9a,11] a mechanism for this new photoredox/nickel catalyzed sulfonylation protocol is proposed in Scheme 3. Firstly, the Ir^{III} complex absorbs visible light and gives a long-lived triplet excited state (PC4, $E_{1/2}^{\text{red}}[*\text{Ir}^{\text{III}}/\text{Ir}^{\text{II}}] = +0.99$ V versus SCE in CH₃CN),^[12] which then reacts with the sodium sulfinate **A** (TsNa, $E^{\text{red}} = +0.45$ V versus SCE in CH₃CN)^[12] to afford the intermediate **B** along with the formation of the Ir^{II} reductant (PC4, $E_{1/2}^{\text{red}}$



Scheme 3. Proposed mechanism for the new photoredox/nickel catalyzed sulfonylation reaction.

[Ir^{III}/Ir^{II}] = -1.48 V versus SCE in CH₃CN).^[12] **B** then resonates to the radical **C**, which subsequently adds to Ni⁰ to form the Ni^I intermediate **D**. The oxidative addition of aryl halide to **D** delivers the Ni^{III} intermediate **E**, which is prone to undergoing reductive elimination to produce the coupling product **F** and a Ni^I complex. Finally, the Ni^I complex undergoes one-electron reduction with the Ir^{II} reductant to regenerate Ni⁰ ($E_{1/2}^{\text{red}}[\text{Ni}^{\text{I}}/\text{Ni}^{\text{0}}] > E_{1/2}^{\text{red}}[\text{Ni}^{\text{II}}/\text{Ni}^{\text{0}}] = -1.2$ V versus SCE in DMF)^[8b] along with the ground-state Ir^{III} complex.

In summary, we have developed a novel and efficient method for the synthesis of sulfones by photoredox/nickel catalysis for the first time. This protocol allows the cross-coupling of a series of sodium sulfonates with a wide range of aryl, heteroaryl, and vinyl bromides and iodides, as well as more challenging aryl chlorides. Importantly neither sacrificial reagents nor organic electron mediators are necessary in this reaction. Moreover, the utility of sodium sulfonates as precursors of sulfonyl radicals and the generation of reactive Ni^{III} intermediates promote this transformation at room temperature. Therefore, the reaction possesses a broad tolerance of functional groups, showing its advantages in comparison to the traditional methods.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aryl halides · cross-coupling · nickel · photochemistry · sulfone

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