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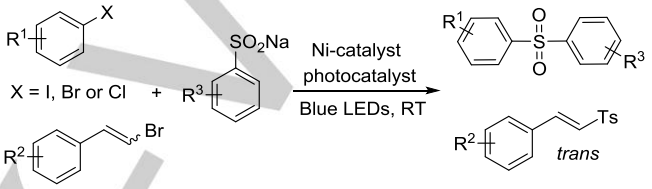
Cross-coupling of sodium sulfinates with aryl, heteroaryl and vinyl Halides by Nickel/photoredox dual catalysis

Huifeng Yue[a]+, Chen Zhu[a]+, and Magnus Rueping[a,b]*

Abstract: An efficient photoredox/nickel dual 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 less reactive aryl chlorides are suitable substrates for this transformation.

Sulfones are highly important organic molecules due to 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 via oxidation of sulfides,[3] sulfonylation of arenes,[4] or palladium or copper-catalyzed arylation of sulfinate salts.[5] These methods may suffer from significant drawbacks including the use of foul-smelling thiols and strong oxidizing reagents, harsh acidic treatment, or high temperature, which can limit the functional group tolerance and substrate scope. Alternatively, SO_2 surrogates such as DABCO·$(SO_2)_2$ and $K_2S_2O_5$ have been applied to the synthesis of sulfones via fixation of sulfur dioxide to generate sulfinate anion intermediates which can then undergo (SO_2)-arylation/alkylation.[6]

In recent years, increasing attention has been devoted to the field of photoredox and transition-metal dual catalysis and useful transformations have been achieved via this strategy.[7-10] In particular, photoredox/nickel dual catalysis proved attractive due to the unique catalytic properties of nickel catalysts.[8-10] Pioneering works in this field focused on C(sp^3)-C(sp^2) bond formations via coupling of aryl halides with benzylic trifluoroborates and Ŭ-carboxyl sp^3-carbons, respectively.[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 via different C-heteroatom bond formations,[10] confirming the enormous potential of photoredox/metal dual catalysis not only in the improvement of known reactions but also in the discovery of novel catalytic protocols.



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

As part of our continuing studies in the area of photoredox and transition-metal dual catalysis, we herein report the first dual 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.

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 to 1 with **PC1** as photocatalyst, $NiCl_2$ glyme as nickel source, dtbbpy as ligand, and DMF as solvent, which afforded the corresponding sulfone **3a** in 43% yield only (Table 1, entry 1). The use of K_2CO_3 as base decreased the yield dramatically (entry 2). The yield of sulfone **3a** increased to 70% when two equivalents of 4-methylbenzenesulfinate (**2a**) were employed (entry 3). After screening several commonly used photocatalysts including an organic dye (entries 4-8), Ir complex **PC4** was found to give the best result (89%, entry 6). A series of nickel catalysts such as $NiBr_2·O(CH_2CH_2OCH_3)_2$, $Ni(OAc)_2·4H_2O$, $Ni(acac)_2$, $NiCl_2$ and $Ni(cod)_2$ were subsequently examined, however no further improvement was observed (entries 9-13). The use of DMF as solvent was found to be crucial for this transformation. When other solvents were utilized, the sulfonylation reaction did not take place or occurred in low yield (entries 14-16). Performing the reaction under undegassed conditions, provided the product in 18% yield, indicating the importance of avoiding the presence of molecular oxygen in the reaction (entry 17). Control experiments confirmed the role of photocatalyst, light, and nickel catalyst for the reaction (entries 18 and 19). In addition, a CF-Lamp was tested and proved suitable for this transformation, providing the corresponding product in 57%

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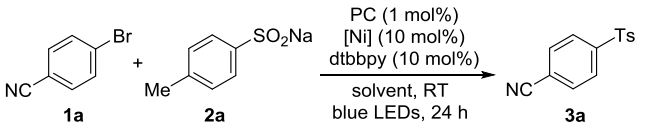
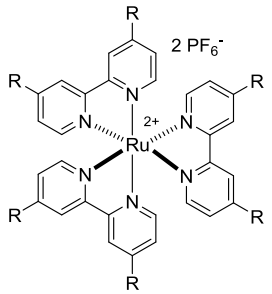
yield (entry 20).

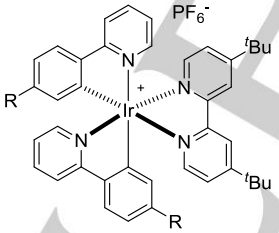
Table 1. Optimization of the reaction conditions.[a]



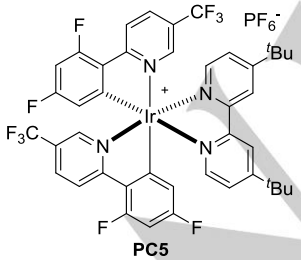
Entry	PC	[Ni]	Solvent	Yield (%)[b]
1[c]	**PC1**	$NiCl_2$·glyme	DMF	43
2[c,d]	**PC1**	$NiCl_2$·glyme	DMF	trace
3	**PC1**	$NiCl_2$·glyme	DMF	70
4	**PC2**	$NiCl_2$·glyme	DMF	74
5	**PC3**	$NiCl_2$·glyme	DMF	75
6	**PC4**	**$NiCl_2$·glyme**	**DMF**	**89(86[e])**
7	**PC5**	$NiCl_2$·glyme	DMF	60
8	**PC6**	$NiCl_2$·glyme	DMF	63
9	**PC4**	$NiBr_2{\cdot}O(CH_2CH_2OCH_3)_2$	DMF	86
10	**PC4**	$Ni(OAc)_2{\cdot}4H_2O$	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_3CN	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



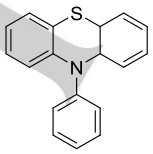
PC1: R = H
PC2: R = ^{t}Bu



PC3: R = H
PC4: R = ^{t}Bu



PC5

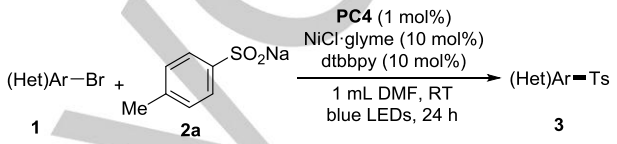


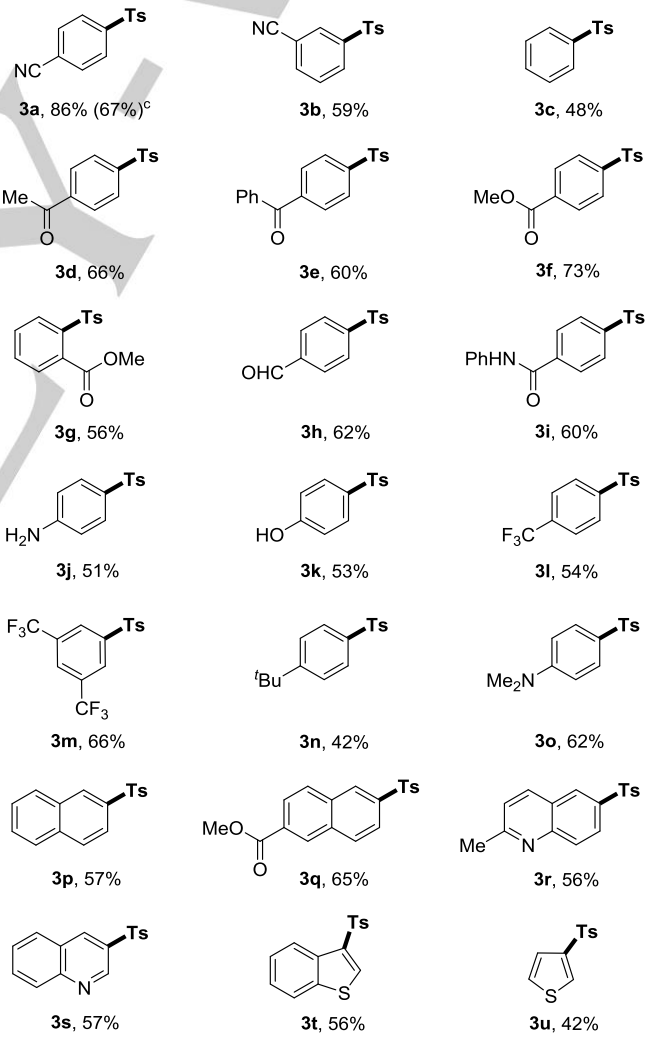
PC6

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), photocatalyst (0.001 mmol), [Ni] (0.01 mmol), ligand (0.01 mmol), degassed solvent (1.0 ml), room temperature, irradiation with 2.6W blue LED strips for 24 h. [b] GC yield. [c] **2a** (1 equiv.). [d] K_2CO_3 (2 equiv.) was added. [e] Isolated yield. [f] undegassed. [g] no light. [h] CF-Lamp was used instead of blue LED strips.

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 aryl bromides **1a** and **1f** possessing para substituents but also substrates **1b** and **1g**, bearing substituents in meta and ortho position, 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**), tertiary amine (**3o**). Notably, 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, giving the corresponding products in good yields.

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





[a] Reaction conditions: Aryl bromide **1** (0.1 mmol), **2a** (0.2 mmol), **PC4** (0.001 mmol), $NiCl_2$·glyme (0.01 mmol), dtbbpy (0.01 mmol), degassed DMF (1 mL), room temperature, irradiation with 2.6W blue LED strips for 24 h. [b] Yield after purification. [c] Reaction performed on a 2.0 mmol scale.

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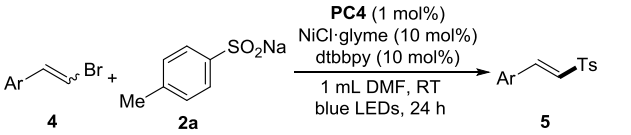
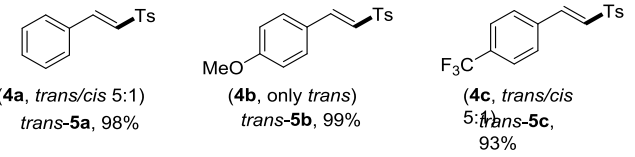
Significantly, the scope of this protocol could be extended to pharmaceutically relevant heteroaromatic bromides such as quinoline (**1r** and **1s**), benzothiophene (**1t**), and thiophene (**1u**) derivatives. Noteworthy, product **3a** was obtained in a good yield of 67% when the reaction was performed on a 2.0 mmol scale in the presence of 0.5 mol% photocatalyst, indicating the scalability and practicability of this mild sulfonylation 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 Ŭ,ƀ-unsaturated sulfones **5a-c** in excellent yields (93-99%). It is important to note that only the trans products were generated, even when vinyl bromides **4a** and **4c** containing a trans/cis mixture were employed.

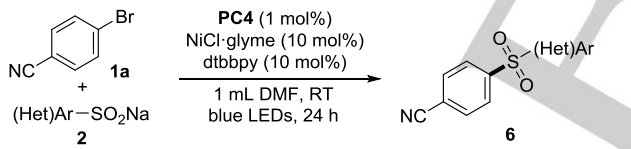
Table 3. Scope of vinyl bromides.[a, b]

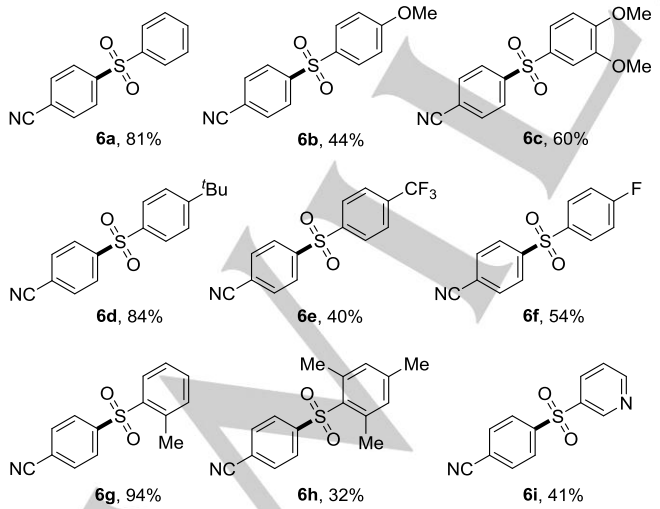




[a] Reaction conditions: vinyl bromide **4** (0.1 mmol), **2a** (0.2 mmol), **PC4** (0.001 mmol), $NiCl_2$·glyme (0.01 mmol), dtbbpy (0.01 mmol), degassed DMF (1 mL), room temperature, irradiation with 2.6W blue LED strips for 24 h. [b] Yield after purification.

Table 4. Scope of sodium sulfinates.[a, b]



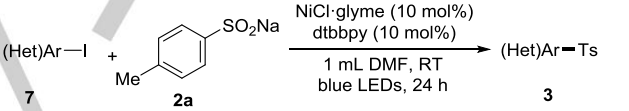


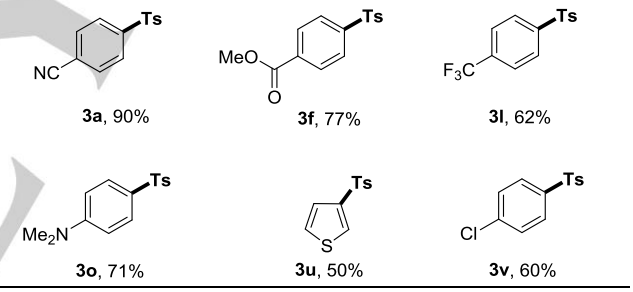
[a] Reaction conditions: **1a** (0.1 mmol), sodium sulfinate **2** (0.2 mmol), **PC4** (0.001 mmol), $NiCl_2$·glyme (0.01 mmol), dtbbpy (0.01 mmol), degassed DMF (1 mL), room temperature, irradiation with 2.6W blue LED strips for 24 h. [b] Yield after purification.

Next, the scope of sodium sulfinates was explored (Table 4). A wide range of structurally diverse sodium sulfinates were suitable substrates for this transformation. For example, benzenesulfinate and sodium sulfinates bearing methoxy groups could generate the corresponding diarylsulfones **6a-c** in moderate to excellent yields. Also, functional groups such *t*-butyl (**6d**), trifluoromethyl (**6e**), 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, 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 heterocyclic sodium sulfinate **2i**, giving the heterocyclic containing sulfone **6i** which is important in medicinal chemistry.

Moreover, aryl iodides were also suitable substrates for this transformation (Table 5). Likewise, substrates bearing electron-donating and electron-withdrawing functional groups both afforded the corresponding products in good to high yields. Interestingly, chloro group was well tolerated under the present conditions.

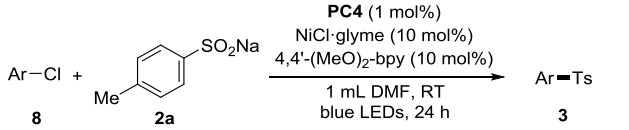
Table 5. Scope of aryl iodides.[a, b]

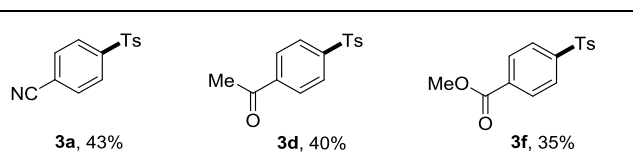




[a] Reaction conditions: aryl iodide **7** (0.1 mmol), **2a** (0.2 mmol), **PC4** (0.001 mmol), $NiCl_2$·glyme (0.01 mmol), dtbbpy (0.01 mmol), degassed DMF (1 mL), room temperature, irradiation with 2.6W blue LED strips for 24 h. [b] Yield after purification.

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), $NiCl_2$·glyme (0.01 mmol), 4,4ĉ(MeO)$_2$-bpy (0.01 mmol), degassed DMF (1 mL), room temperature, irradiation with 2.6W blue LED strips for 24 h. [b] Yield after purification.

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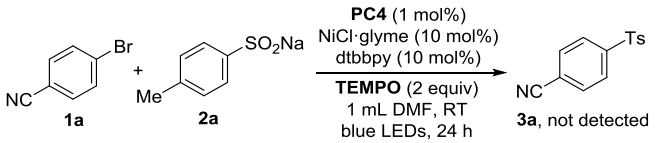
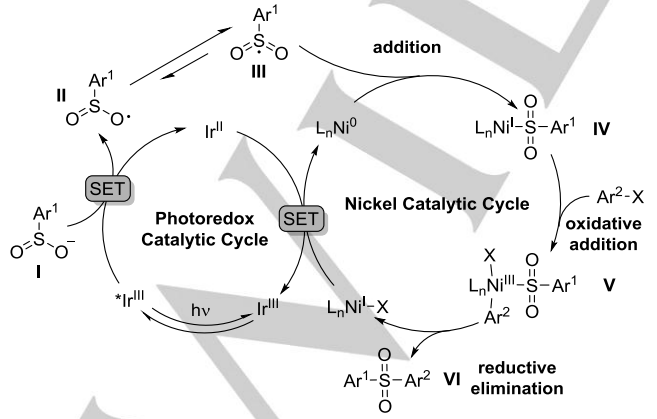
It is noteworthy that minor modification of the standard conditions by just switching the dtbbpy ligand to the more electron rich 4,4ô-dimethoxy-2,2ô-bipyridine (4,4ô-$(MeO)_2$-bpy) ligand made this protocol applicable to more challenging aryl chloride substrates **8**, indicating the vast potential of 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, 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 dual 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**, $E_{1/2}^{red}$ [$*Ir^{III}/Ir^{II}$] = +0.99 V versus SCE in CH_3CN},[12] which then reacts with sodium sulfinate **I** (TsNa, E^{red} = +0.45 V versus SCE in CH_3CN)[12] to afford intermediate **II** along with the formation of Ir^{II} reductant {**PC4**, $E_{1/2}^{red}$ [Ir^{III}/Ir^{II}] = -1.48 V versus SCE in CH_3CN}[12] Intermediate **II** then resonates to radical **III**, which subsequently adds to Ni^0 to form the Ni^I intermediate **IV**. The oxidative addition of aryl halide to **IV** delivers Ni^{III} intermediate **V**, which is prone to undergo reductive elimination to produce the coupling product **VI** and a Ni^I complex. Finally, the Ni^I complex undergoes one-electron reduction with the Ir^{II} reductant to regenerate Ni^0 {$E_{1/2}^{red}$ [Ni^I/Ni^0] > $E_{1/2}^{red}$ [Ni^{II}/Ni^0] = ï 1.2 V versus SCE in DMF}[8b] along with the ground-state Ir^{III} complex.



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

In summary, we have developed a novel and efficient method for the synthesis of sulfones via photoredox/nickel dual catalysis for the first time. This protocol allows the cross-coupling of a series of sodium sulfinates with a wide range of aryl, heteroaryl, and vinyl bromides and iodides as well as more challenging aryl chlorides. Importantly no sacrificial reagents or organic electron mediators are necessary in this reaction. Moreover, the utility of sodium sulfinates 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.

Acknowledgements

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Keywords: sulfone Åphotoredox Ånickel Åcross-coupling Åaryl halide

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[12] See the cyclic voltammetry measurements of photocatalyst **PC4** and TsNa in the supporting information in detail.

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Layout 2:

COMMUNICATION

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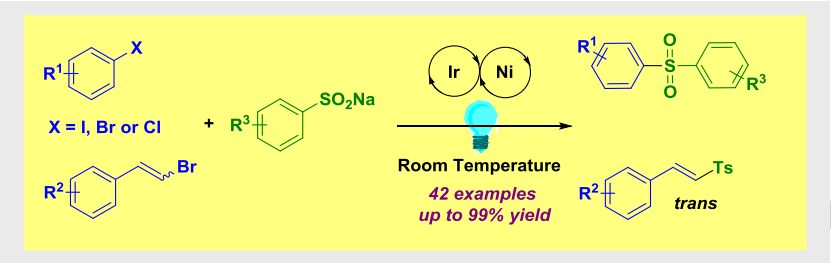
Cross-Coupling of Sodium Sulfinates with Aryl, Heteroaryl and Vinyl Halides by Nickel/photoredox dual catalysis



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