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Iridium-catalyzed regioselective C–H sulfonamidation of 1,2,4-thiadiazoles with sulfonyl azides in water†

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We have developed a regioselective C–N cross-coupling of 1,2,4-thiadiazoles with sulfonyl azides through iridium catalysis in water. This method tactically linked the 1,2,4-thiadiazoles and sulfonamides together, and the novel molecules increased the diversity of 1,2,4-thiadiazoles which may have potential applications.

Introduction

1,2,4-Thiadiazole scaffolds exist as significant structural motifs in a myriad of biologically active compounds,[1] natural products,[2] and materials[3] (Fig. 1). In particular, the 1,2,4-thiadiazole derivatives have been found to have a broad range of biological activities. However, due to the limitations of synthetic methods, these 1,2,4-thiadiazole derivatives are relatively simple, which limit the further optimization and screening of their activities. For the purpose of building drug like libraries, the development of efficient and practical approaches to construct diverse 1,2,4-thiadiazoles is of great significance.

Carbon–hydrogen (C–H) bond functionalizations are attractive tools for the construction of valuable molecules.[4–6] The heterocyclic core of 1,2,4-thiadiazole contains nitrogen-atom, which is generally used as directing group in C–H activation reactions.[7] These considerations made us develop a straightforward C–H functionalization route for generating diverse 1,2,4-thiadiazole derivatives. Under the guidance of this strategy, our laboratory had successfully synthesized 1,2,4-thiadiazole compounds containing succinimide,[8] and those compounds were found to have antitumor activity. Inspired by the fruitful previous work, in this context, we were interested in investigating the amidation of 1,2,4-thiadiazole substrates.

On the other hand, aryl amines are key components in a range of organic molecules as well.[9] As a result, extensive studies have been devoted to transition-metal-catalyzed (such as Ru,[10] Rh,[11] Ir,[12] Co,[13] Mn[14] and Cu[15]) direct C(sp^2)–H amidation reactions (Scheme 1a). Despite the utilities represent, we want to get those valuable compounds in a relatively green way. Traditional chemical process rely heavily on organic solvents for a multitude of tasks, water, termed as a "green" solvent used as a substitute for organic solvents in organic synthesis because of its economical and safe, the development of reactions using water as a reaction medium has flourished recently.[16] Fortunately, our group developed a regioselective C–N cross-coupling of 1,2,4-thiadiazoles with sulfonyl azides using water as the only solvent (Scheme 1b).

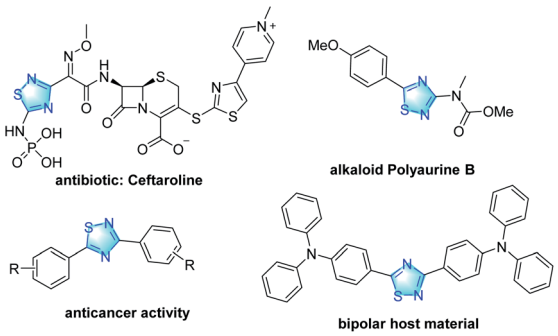
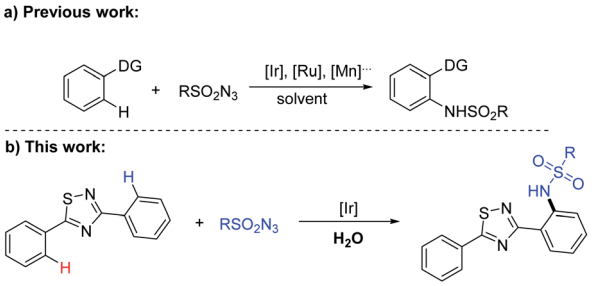


Fig. 1 The application 1,2,4-thiadiazoles derivatives.



Scheme 1 Transition-metal-catalyzed C–H sulfonamidation.

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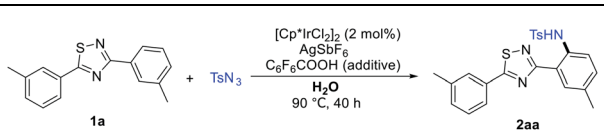
Results and discussion

Model investigations focused on the amidation of **1a** (Table 1). Firstly, the catalyst and solvent were screened (Table 1, entries 1–13), the result showed that $[Cp^*IrCl_2]_2$ was essential for the reaction and the solvent had an important effect on the reaction as well, no product **2aa** were formed in most solvents, only 1,2-DCE and H_2O offered moderate conversion. Although the conversion efficiency of **1a** was very low in water, this positive result greatly encouraged us to continue to evaluate various additives for improving the C–H bond amidation yield (Table 1, entries 14–31). To our delight, a further significant improvement of the reaction was achieved by adding C_6F_5COOH (86%, Table 1, entry 28). Then, a number solvents were screened in the presence of $[Cp^*IrCl_2]_2$ and C_6F_5COOH, and no better results were obtained than water (Table 1, entries 32–37). Similarly, $AgSbF_6$ has an important effect on promoting the yield of **2aa**. After an extensive survey of reaction parameters, we arrived at the optimized conditions in H_2O at 90 °C, affording the desired product **2aa** in 86% isolated yield.

With the optimized reaction conditions in hand, we began to explore the generality and selectivity of the Ir-catalyzed C–N

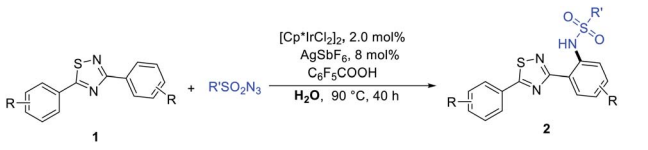
Table 1 Optimization of the reaction conditions[a,b]

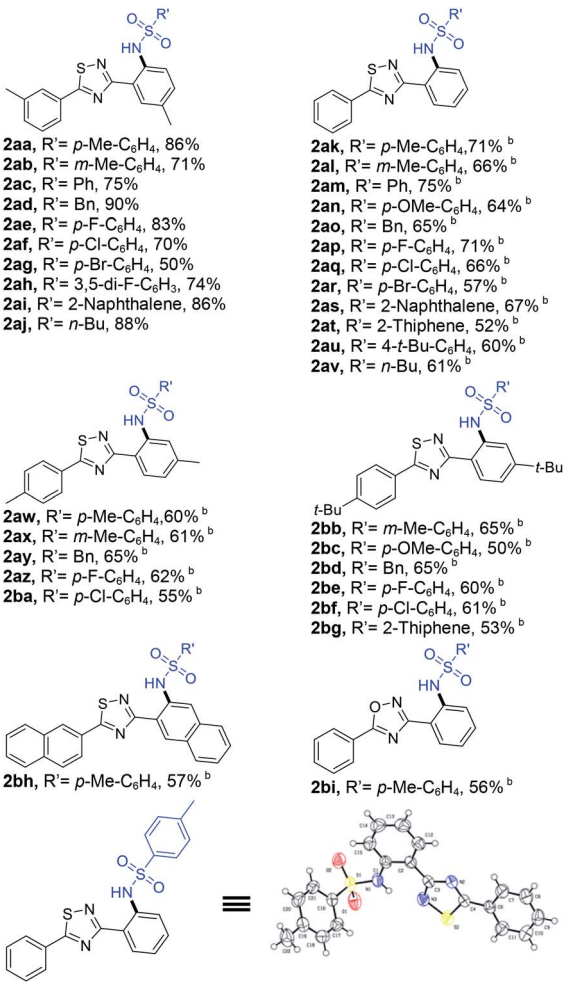


Entry	Catalyst	Solvent	Additive	Yield[c] (%)
1	$[Cp^*RhCl_2]_2$	1,2-DCE	None	15
2	$[Cp^*IrCl_2]_2$	1,2-DCE	None	76
3	$[CodIrCl]_2$	1,2-DCE	None	0
4	$[CodIrOMe]_2$	1,2-DCE	None	0
5	$Cp^*Co(CO)I_2$	1,2-DCE	None	0
6	$(Cp^*)_2CoPF_6$	1,2-DCE	None	0
7[b]	$[Cp^*IrCl_2]_2$	1,2-DCE	None	20
8	None	1,2-DCE	None	0
9	$[Cp^*IrCl_2]_2$	DMF	None	0
10	$[Cp^*IrCl_2]_2$	DMSO	None	0
11	$[Cp^*IrCl_2]_2$	H_2O	None	35
12	$[Cp^*IrCl_2]_2$	CH_3CN	None	0
13	$[Cp^*IrCl_2]_2$	CH_3CH_2OH	None	0
14	$[Cp^*IrCl_2]_2$	H_2O	$NaHCO_3$	0
15	$[Cp^*IrCl_2]_2$	H_2O	KPF_6	0
16	$[Cp^*IrCl_2]_2$	H_2O	Na_2CO_3	0
17	$[Cp^*IrCl_2]_2$	H_2O	K_2CO_3	0
18	$[Cp^*IrCl_2]_2$	H_2O	NaOH	0
19	$[Cp^*IrCl_2]_2$	H_2O	KOH	0
20	$[Cp^*IrCl_2]_2$	H_2O	AcOH	Trace
21	$[Cp^*IrCl_2]_2$	H_2O	PivOH	Trace
22	$[Cp^*IrCl_2]_2$	H_2O	HBF_4	Trace
23	$[Cp^*IrCl_2]_2$	H_2O	Benzoic acid	37
24	$[[Cp^*IrCl_2]_2$	H_2O	TsOH	Trace
25	$[Cp^*IrCl_2]_2$	H_2O	MesCOOH	46
26	$[Cp^*IrCl_2]_2$	H_2O	*o*-Nitrobenzoic acid	41
27	$[Cp^*IrCl_2]_2$	H_2O	1-AdCOOH	40
28	$[Cp^*IrCl_2]_2$	H_2O	C_6F_5COOH	86
29	$[Cp^*IrCl_2]_2$	H_2O	*N*-Acetylglycine	0
30	$[Cp^*IrCl_2]_2$	H_2O	Dipicolinic acid	0
31	$[Cp^*IrCl_2]_2$	H_2O	Quinaldic acid	0
32	$[Cp^*IrCl_2]_2$	1,2-DCE	C_6F_5COOH	80
33	$[Cp^*IrCl_2]_2$	DMF	C_6F_5COOH	0
34	$[Cp^*IrCl_2]_2$	DMSO	C_6F_5COOH	0
36	$[Cp^*IrCl_2]_2$	CH_3CH_2OH	C_6F_5COOH	0
37	$[Cp^*IrCl_2]_2$	CH_3CN	C_6F_5COOH	0
38[b]	$[Cp^*IrCl_2]_2$	H_2O	C_6F_5COOH	56

[a] Reaction conditions: **2a** 0.2 mmol, TsN_3 0.3 mmol, catalyst 2.0 mol%, $AgSbF_6$ 8 mol%, additive 40 mol%, solvent 1.0 mL, 90 °C, 24 h. [b] No $AgSbF_6$. [c] Isolated yield.

Table 2 Reaction between 1,2,4-thiadiazoles and sulfonyl azides[a,b,c]



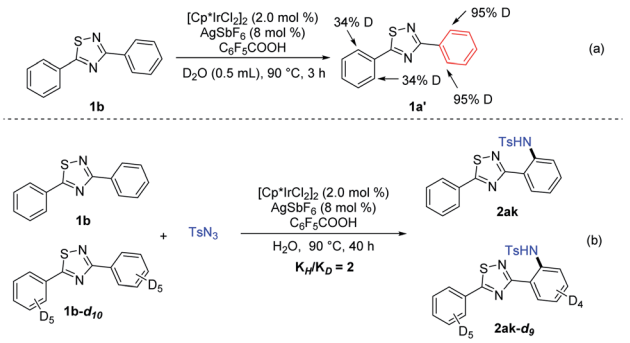


[a] Reaction conditions: **1** 0.2 mmol, $R'SO_2N_3$ 0.3 mmol, $[Cp^*IrCl_2]_2$ 2.0 mol%, $AgSbF_6$ 8.0 mol%, C_6F_5COOH 40 mol%, H_2O 1.0 mL, 90 °C, 40 h. [b] Reaction conditions: **1** 0.2 mmol, $R'SO_2N_3$ 0.3 mmol, $[Cp^*IrCl_2]_2$ 2.0 mol%, $AgSbF_6$ 8.0 mol%, C_6F_5COONa 40 mol%, H_2O 1.0 mL, 90 °C, 40 h. [c] Isolated yield.

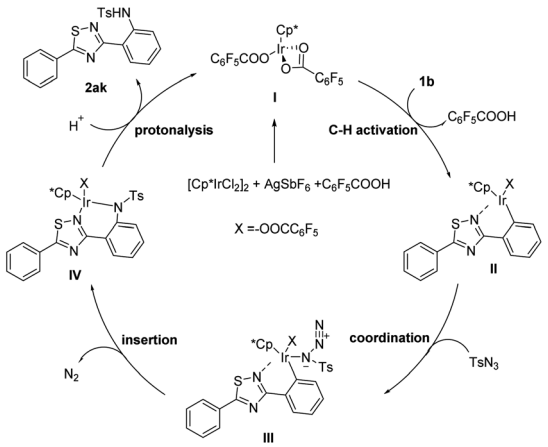
bond coupling by using sulfonyl azide as coupling partner (Table 2). The substrates with various sulfonyl azides derivatives bearing desirable functionality, such as phenyl, benzyl, naphthyl, alkyl, and heterocyclyl, proceeded efficiently, providing access to functionalized 1,2,4-thiadiazole derivatives (**2aa–2bh**) with yields ranging from 50 to 90%. The substituent was at the *m*-position of benzene ring proved to be amenable to this reaction better, most substrates delivering the corresponding products in good yields (**2aa–2aj**). In contrast, for the substrates with *para*-substituents or no substituent exhibited diminished reactivity (**2ak–2bg**). We speculated that the reason for this result is that substituent in the *m*-position of the benzene ring, almost no diaminylation products are formed due to steric hindrance, however, when there is no substituent group on the benzene ring or the substituent group is in *para* position, there will be diaminylation products were formed, resulting in a corresponding decrease in the yield of monoaminylation product. When 3,5-di(naphthalen-2-yl)-1,2,4-thiadiazole or 3,5-diphenyl-1,2,4-oxadiazole as material, they can also react with 4-methylbenzenesulfonyl azide to obtain corresponding product (**2bh**, **2bi**). In addition, the molecular structure of product **2ak** was further confirmed by X-ray crystallography.

To demonstrate the applicability of the reaction system, we next investigated its efficacy on *N*,3-diphenyl-1,2,4-thiadiazol-5-amine derivatives. To our delight, the corresponding products can also be isolated in moderate yields (Table 3).

A series of control experiments were further carried out to study the reaction mechanism. A significant level of deuterium



Scheme 2 Mechanism studies.



Scheme 3 Proposed mechanism.

Table 3 Reaction between *N*,3-diphenyl-1,2,4-thiadiazol-5-amines and sulfonyl azides[a,b,c]

4a, R'= *p*-Me-C_6H_4, 76%
4b, R'= 4-*t*-Bu-C_6H_4, 79%
4c, R'= *p*-OMe-C_6H_4, 73%
4d, R'= *p*-Cl-C_6H_4, 57%
4e, R'= *n*-Bu, 76%
4f, R'= 2-Thiphene, 60%
4g, R'= *p*-Me-C_6H_4, 71%
4h, R'= *p*-OMe-C_6H_4, 61%
4i, R'= *p*-Cl-C_6H_4, 51%
4j, R'= *p*-Br-C_6H_4, 50%
4k, R'= *n*-Bu, 72%
4l, R'= *p*-Me-C_6H_4,60% [b]
4m, R'= *m*-Me-C_6H_4, 57% [b]

[a] Reaction conditions: **3** 0.2 mmol, R'SO_2N_3 0.3 mmol, $[Cp^*IrCl_2]_2$ 2.0 mol%, $AgSbF_6$ 8.0 mol%, C_6F_5COOH 40 mol%, H_2O 1.0 mL, 90 °C, 40 h. [b] Reaction conditions: **3** 0.2 mmol, R'SO_2N_3 0.3 mmol, $[Cp^*IrCl_2]_2$ 2.0 mol%, $AgSbF_6$ 8.0 mol%, C_6F_5COONa 40 mol%, H_2O 1.0 mL, 90 °C, 40 h. [c] Isolated yield.

incorporation (95%) was observed at the *ortho* position of the red benzene ring when it was subjected to the Ir-catalytic system in D_2O in the absence of sulfonyl azides to suggest that the C–H bond cleavage is reversible (Scheme 2a). Furthermore, the experimental KIE value indicated that the cleavage of the C–H bond might play a significant role in the reaction (Scheme 2b).

Based on the experimental date and previous literature reports,[12] a possible reaction mechanism was discussed (Scheme 3). First, treatment of the $[Cp^*IrCl_2]_2$ precursor in the presence of $AgSbF_6$ and C_6F_5COOH generates catalytic species (**I**) then, the catalytic species (**I**) coordinates with the nitrogen atom of 1,2,4-thiadiazoles (**1b**) and then undergoes the C–H metalation process to form intermediate **II**. After that, the catalyst in intermediate **II** coordinates with TsN_3 to form complex **III**, which subsequently goes through migratory insertion directly by releasing a nitrogen molecule to deliver a six-membered cyclometalated intermediate **IV**. Finally, desired product (**2ak**) is obtained through protonation and the catalytic species (**I**) is released to continue the catalytic cycle.

Conclusions

In summary, we have developed an iridium-catalyzed direct C–N cross-coupling of 1,2,4-thiadiazoles with sulfonyl azides in water. The amidation releases N_2 as the single byproduct and

the reaction showed excellent regioselectivity. Further efforts on the application of 1,2,4-thiadiazoles derivatives are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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