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Direct sulfonamidation of (hetero)aromatic C–H bonds with sulfonyl azides: a novel and efficient route to *N*-(hetero)aryl sulfonamides

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N-Aryl sulfonamides belong to a highly important class of organosulfur compounds which are found in a number of FDA-approved drugs such as dofetilide, dronedarone, ibutilide, sotalol, sulfadiazine, sulfamethizole, vemurafenib, and many more. There is therefore continuing interest in the development of novel and convenient protocols for the preparation of these pharmaceutically important compounds. Recently, direct sulfonamidation of (hetero)aromatic C–H bonds with easily available sulfonyl azides has emerged as an attractive and powerful strategy to access *N*-(hetero)aryl sulfonamides where non-toxic nitrogen gas forms as the sole by-product. This review highlights recent advances and developments (2012–2020) in this fast growing research area with emphasis on the mechanistic features of the reactions.

1. Introduction

Sulfonamides constitute a very important class of drugs which are called sulfa drugs, and display a broad range of pharmacological activities such as antimicrobial, antiretroviral, anticonvulsant, anti-diabetic, antitumor, and anti-depressant.[1] Seventy-two currently marketed drugs contain this privileged structural motif in their structure and one-fourth of them are *N*-(hetero)aryl sulfonamide derivatives.[2] For example (Fig. 1), tipranavir **1** with the brand name of Aptivus is a nonpeptidic protease inhibitor marketed worldwide for the treatment of HIV/AIDS infection.[3] Sulfamethoxazole **2** is an antibiotic that is

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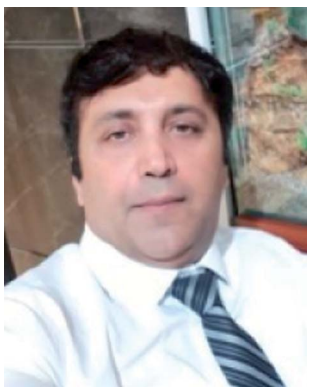

Dr Abdol Ghaffar Ebadi finished his doctoral degree in Environmental Biotechnology (Algology) from Tajik Academy of Sciences. Now he is a researcher in TAS in Tajikistan and faculty member at the Islamic Azad University of Jouybar in Mazandaran. Dr Ebadi published more than 400 scientific papers in qualified international journals and attended more than 50 international conferences. He has cooperation with many research project teams around world such as China, Malaysia, and Thailand. His interests are Environmental Biotechnology, Biochemistry, Gene pathways in the phytoremediation processes.

used for various bacterial infections and is effective against both Gram negative and positive bacteria.[4] Delavirdine **3** with the trade name Rescriptor is an antiretroviral medicine available in many countries worldwide and used as part of highly active antiretroviral therapy for the treatment of HIV type 1 (HIV-1).[5] The newer drug dabrafenib **4** (Tafinlar) is a promising anticancer drug that is used to treat certain types of melanoma (a type of skin cancer) that cannot be removed with surgery or that have spread to other parts of the body.[6] The drug prevents the formation of dihydrofolic acid, a compound that bacteria must be able to make in order to survive. Consequently, there is continuing interest in the development of expedient and efficient protocols for the preparation of this important class of sulfonamide containing scaffolds.[7]

Traditional synthesis of *N*-(hetero)aryl sulfonamides involves the reaction of sulfonyl chloride derivatives with aromatic amines, which suffers from the necessity for a strong base and generation of halide salts as the by-products.[8] Lately, new procedures towards the greener synthesis of the titled compounds have been developed, such as cross-coupling of primary sulfonamides and aryl electrophiles,[9] oxidative coupling of anilines with sodium sulfonates,[10] reduction coupling of nitroarenes with sodium sulfonates,[11] and direct sulfonamidation of aromatic C–H bonds with sulfonyl azides. Among others, transition-metal catalyzed denitrogenative coupling of arenes with sulfonyl azides offers prominent advantages of easily accessible starting materials, high efficiency, and no formation of toxic by-products (Fig. 2).

Despite the significant progress which has been achieved since 2012 in this research area, a comprehensive review has not appeared on this domain in the literature thus far. In connection with our recent works on the synthesis of organosulfur compounds[12] and modern cross-coupling reactions,[13] we summarize here a variety of methods for the synthesis of *N*-(hetero)aryl sulfonamides from the corresponding (hetero)arenes and sulfonyl azides with emphasis on the mechanistic aspects of the reactions. The metal catalysts play main role in the synthesis of organic compounds.[14–18] In this regard, the reactions were classified according to the metal center of catalysts.

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2. Rhodium-catalyzed reactions

In 2012, Cheng's research team reported one the earliest Rh-catalyzed direct sulfonamidation of aromatic C–H bonds with sulfonyl azides utilizing pyridyl as the *ortho*-selective coordinating directing group.[19] Careful screening of various commercially available rhodium catalysts such as $Rh_2(O_2CCF_3)_4$, $[Rh(cod)Cl]_2$, $[RhCp^*Cl_2]_2$, $[Ru(p\text{-cymene})Cl_2]_2$; and additives like $AgBF_4$, $AgSbF_6$, KPF_6 led to $[RhCp^*Cl_2]_2/AgSbF_6$ combination as the most suitable catalytic system for this C–N bond forming reaction and among the various organic solvents (*e.g.*, toluene, 1,2-DCE, *t*-amylOH); DCE proved to be the most efficient solvent. Under optimized conditions, the C2 position of a wide range of 2-phenylpyridine derivatives **5** was selectively activated and underwent coupling with various types of aryl and alkyl sulfonyl azides **6** in the absence of any external oxidant

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Esmail Vessally was born in Sharabiyan, Sarab, Iran, in 1973. He received his B.S. degree in Pure Chemistry from University of Tabriz, Tabriz, Iran, and his M.S. degree in Organic Chemistry from Tehran University, Tehran, Iran, in 1999 under the supervision of Prof. H. Pirelahi. He completed his PhD degree in 2005 under the supervision of Prof. M. Z. Kassaee. Now he is working at Payame Noor University as full Professor of Organic Chemistry. His research interests include Theoretical Organic Chemistry, new methodologies in organic synthesis and spectral studies of organic compounds.

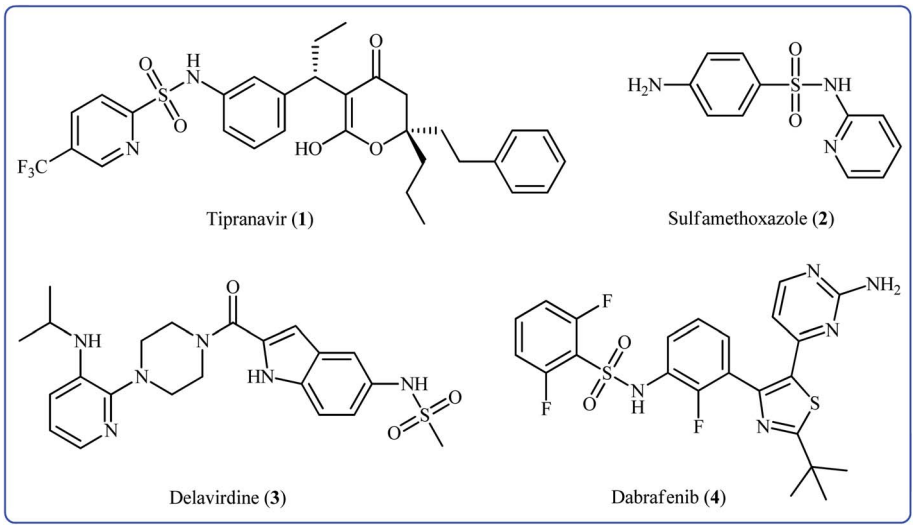


Fig. 1 Selected drugs with *N*-aryl sulfonamide structure motif.

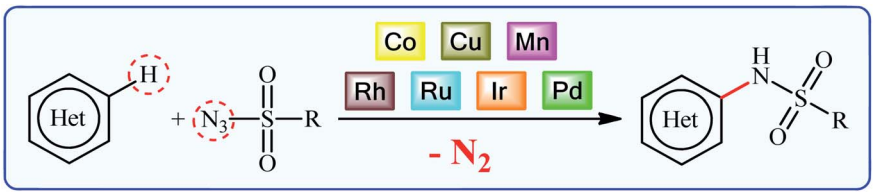
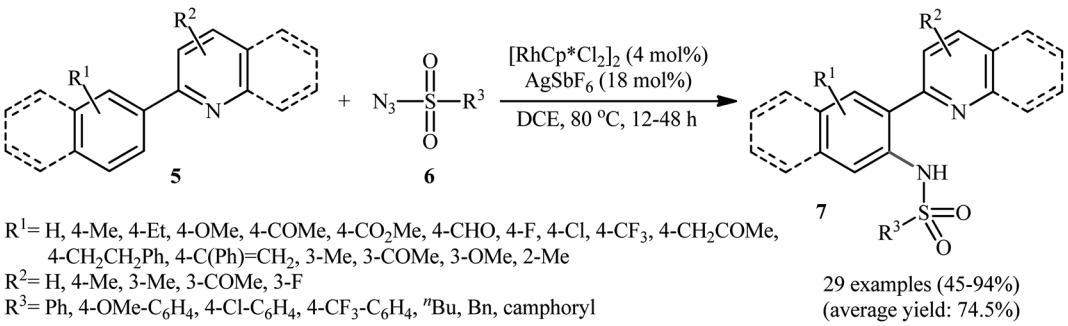


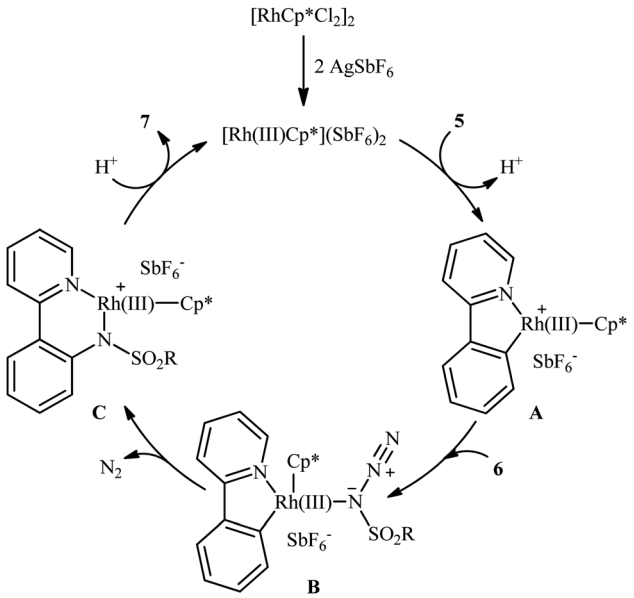
Fig. 2 Transition-metal catalyzed direct sulfonamidation of (hetero)aromatic C–H bonds with sulfonyl azides.



Scheme 1 Cheng's synthesis of *N*-aryl sulfonamides **7**.

under atmospheric environment and afforded the target *N*-aryl sulfonamides **7** in moderate to excellent yields (Scheme 1). It should be noticed that other directing groups, such as pyrazole, pyrimidine, and oxime were also found to effectively mediate this transformation. Based on kinetic isotope effect studies and X-ray crystallographic analysis, the following mechanism is proposed by the authors for this transformation (Scheme 2). Firstly, a cationic Rh(III) species $[Rh(III)Cp^*][SbF_6]_2$ generated upon treatment of the $[RhCp^*Cl_2]_2$ precursor with $AgSbF_6$. Next, coordination of nitrogen atom of the phenylpyridine **5** to this species followed by *ortho*-metalation affords a five-membered rhodacyclic intermediate **A**. Subsequently, coordination of azide **6** to **A** leads to the intermediate **B** that, after insertion of a sulfonamido moiety into the rhodacycle forms a Rh(III) amido complex **C**. Finally, protonolysis of **C** produces the desired product **7** and regenerates the cationic Rh(III) species. Later, based on density functional theory (DFT) calculations, the same authors suggested that the liberation of N_2 from intermediate **B** forms a key Rh(V)-nitrenoid species and then a collapse of this intermediate affords the insertion intermediate **C**.[20]

In the same year, Zhou and Li along with their co-workers described an interesting regioselective Rh-catalyzed direct C2-sulfonamidation of indoles **8** bearing a 2-pyrimidyl unit as a directing group through C–H activation by using sulfonyl azides **9** as the sulfonamide source.[21] The reactions were carried out in the presence of a catalytic amount of $[Cp^*Rh(MeCN)_3]$

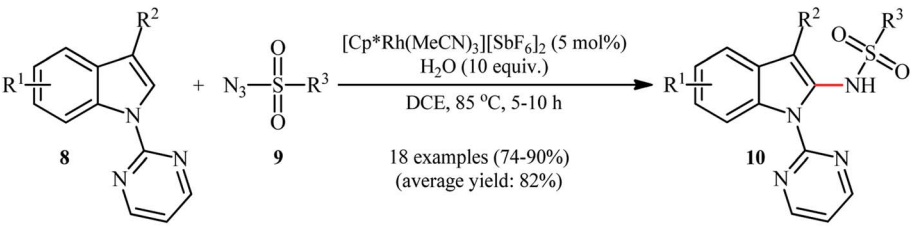


Scheme 2 Proposed mechanism for Rh-catalyzed sulfonamidation of phenylpyridines **5** with sulfonyl azides **6**.

$[SbF_6]_2$ and ten equivalents of water as an additive under an open air, tolerated various election-rich and electron-poor functional groups on both coupling partners and provided the expected C2-sulfonamidated indoles **10** in good to excellent yields (Scheme 3). Noteworthy, no product was observed by replacing of pyrimidyl directing group with other groups (*e.g.*, Me, Boc, Ac, Me_2NCO). NH-free indoles were also failed to participate in this reaction. It should be mentioned that the 2-pyrimidyl directing group can be easily removed through hydrolysis to yield the corresponding NH-free sulfonamidated indoles under alkaline conditions.

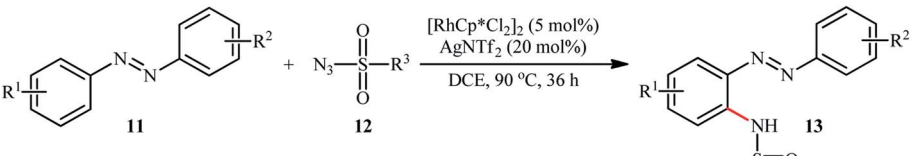
In 2014, Jia and Han disclosed that the treatment of azobenzenes **11** with sulfonyl azides **12** in the presence of 5 mol% of $[RhCp^*Cl_2]_2$ and 20 mol% of $AgNTf_2$ in DCE under an air atmosphere afforded the corresponding *ortho*-sulfonamidated azobenzene derivatives **13** in moderate to almost quantitative yields, ranging from 35% to 98% (Scheme 4).[22] Some of the most important results obtained in this investigation are listed below: (i) the reaction was almost equally efficient for aromatic, heteroaromatic, and aliphatic sulfonyl azides; (ii) electron-rich azobenzenes compare to the electron-poor ones gave higher yield of the expected products; and (iii) unsymmetrical azobenzenes mainly gave the sulfonamidation products on the electron-rich aromatic rings. Concurrently, Xu and colleagues reported a similar strategy to construct *ortho*-sulfonamidated azobenzenes by using Cheng's standard reaction condition.[23] Although this methodology turned out to be highly efficient for the sulfonamidation of *ortho*- and *meta*-substituted azobenzenes, its application for the sulfonamidation of unsubstituted and *para*-substituted azobenzenes is restricted, since the selectivity of mono- and di-sulfonamidation products was generally poor.

As a continuation of these studies, Peng and co-workers reported the steric hindrance controlled regioselective Rh-catalyzed direct C–H sulfonamidation of 2,4-diarylquinazolines **14** with sulfonyl azides **15** using Cheng's standard reaction condition (Scheme 5).[24] They showed that when the *meta* position of the phenyl ring at the 2-position of quinazolines was blocked by a substituent group, the mono-sulfonamidated products **16** were exclusively obtained without any of di-sulfonamidated product. Likewise, *ortho*-substituted



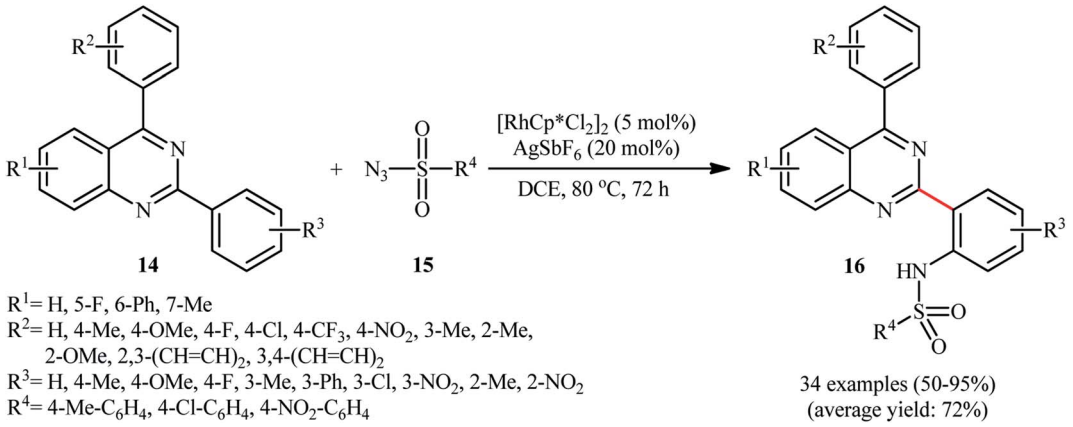
R^1= H, 4-Cl, 5-Me, 5-OMe, 5-F, 5-Cl, 5-Br, 5-CO_2Me, 5-NO_2, 6-Me, 6-OMe, 6-CF_3, 6-Br, 6-NO_2
R^2= H, Me, -$CH_2CH_2CO_2Me$
R^3= 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-NO_2-C_6H_4

Scheme 3 Rh-catalyzed site-selective sulfonamidation of indoles **8** with sulfonyl azides **9**.

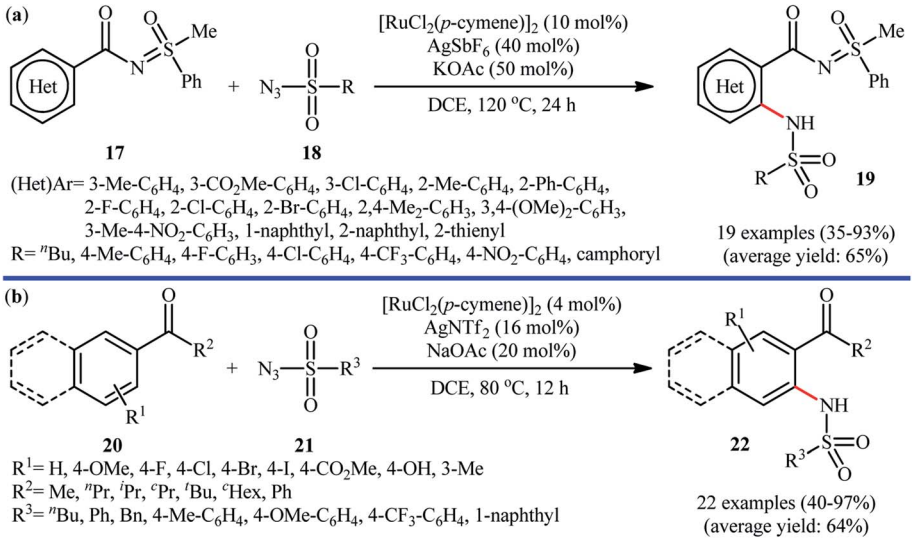


R^1= H, 4-Me, 4-OMe, 4-F, 4-Cl, 4-OCF_3, 3-Me, 3-NO_2
R^2= H, 4-Me, 4-OMe, 4-F, 4-Cl, 4-Br, 4-OCF_3, 3-Me, 3-NO_2
R^3= ^{n}Bu, Ph, 4-Me-C_6H_4, 4-^{t}Bu-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-CF_3-C_6H_4, 3-NO_2-C_6H_4, 2-naphthyl, 2-thienyl

Scheme 4 Direct sulfonamidation of azobenzenes **11** with sulfonyl azides **12** catalyzed by $[RhCp^*Cl_2]_2$.

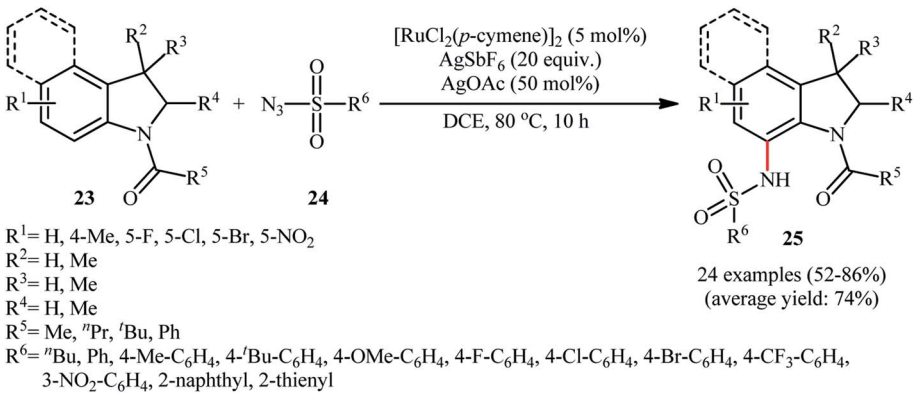


Scheme 5 Rh-catalyzed direct C–H sulfonamidation of 2,4-diarylquinazolines **14** with sulfonyl azides **15** developed by Peng.



Scheme 6 (a) Sulfoximine directed Ru-catalyzed C–H sulfonamidation of arenes **17** with sulfonyl azides **18**; (b) Ru-catalyzed synthesis of 2-sulfonamidated aromatic ketones **22** from ketones **20** and sulfonyl azides **21**.

substrates selectively afforded the corresponding mono-sulfonamidated products. By contrast, the substrates with a substituent at the *para* position resulted in a mixture of mono- and di-sulfonamidated products. Of note, different substituents on the quinazoline ring failed to enhance the selectivity, albeit total yields were affected by the introduction of various substituents on this ring. Unfortunately, the exact mechanism of this transformation has not been elucidated yet.

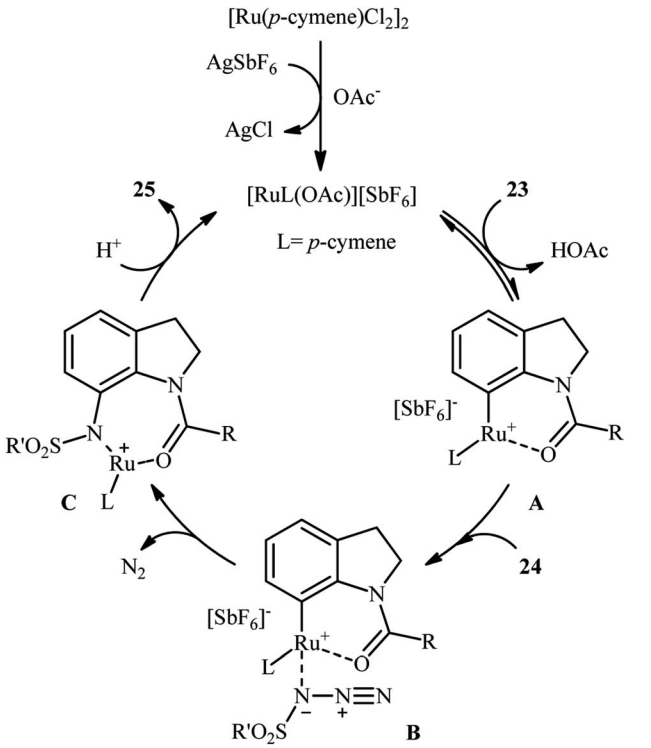


Scheme 7 Ru-catalyzed site-selective C–H sulfonamidation of *N*-carbonylated indolines **23** with sulfonyl azides **24**.

3. Ruthenium-catalyzed reactions

Ruthenium is a rare transition metal placed in period V of the periodic table, adjacent to rhodium and is much cheaper than it. Therefore, it is reasonable to investigate the catalytic ability of this noble metal in direct C–H sulfonamidation of aromatic compounds with sulfonyl azides. In 2013, Sahoo and co-workers first reported the usefulness of ruthenium catalysts for such transformations.[25] They showed that the treatment of *ortho*- and *meta*-substituted *N*-benzoylated sulfoximines **17** with various aromatic and aliphatic sulfonyl azides **18** in the presence of $[RuCl_2(p\text{-cymene})]_2/AgSbF_6/KOAc$ combination as a catalytic system in DCE afforded the corresponding mono-sulfonamidated products **19** in modest to excellent yields and outstanding *ortho*-selectivity (Scheme 6a). However, *para*-substituted *N*-benzoylated sulfoximines provided a mixture of mono- and di-functionalized products with poor selectivity. The authors also successfully applied this strategy to the high yielding synthesis of ataciguat, a drug candidate for the treatment of aortic valve stenosis. They demonstrated that the methylphenyl sulfoximine directing group can be efficiently removed by hydrolysis of the final products under basic conditions (NaOH in $MeOH/H_2O$ at 60 °C in 6 h), providing the corresponding anthranilic acid derivatives in excellent yields. Subsequently, the same authors broadened the substrate scope of their methodology to aromatic ketones.[26] In this report, thirty-three *N*-aryl sulfonamides were synthesized in relatively poor to excellent yields by means of 5 mol% of $[RuCl_2(p\text{-cymene})]_2$ and 20 mol% of $AgSbF_6$ in DCE at 100 °C in the presence of 50 mol% of $Cu(OAc)_2\cdot H_2O$ as a base. In contrast to their previous work, *para*-substituted substrates were also furnished *ortho*-sulfonamidated products with high mono-selectivity. At the same time, Chang and colleagues reported independently a similar strategy for the preparation of 2-sulfonamidated aromatic ketones **22** from ketones **20** and sulfonyl azides **21** by using a catalytic amount of $[RuCl_2(p\text{-cymene})]_2$ in combination with $AgNTf_2$ and NaOAc (Scheme 6b).[27] Noteworthy, the authors proposed mechanism for this transformation is analogous to the one depicted for Rh-catalyzed reaction in Scheme 2. Shortly afterwards, by using a slightly modified catalytic system ($[RuCl_2(p\text{-cymene})]_2/AgSbF_6/NaOAc$/DCE, 60 °C), Ackermann and co-workers described the formation of *N*-aryl sulfonamides from the corresponding hetero-aromatic (pyrimidine, pyridines, and pyrazole) directing-group-containing arenes and sulfonyl azides.[28] Following these works, other coordinating directing groups, such as benzo[*d*]thiazole,[29] 1,2,3-triazole,[30] and azo[31] were also successfully utilized in this reaction.

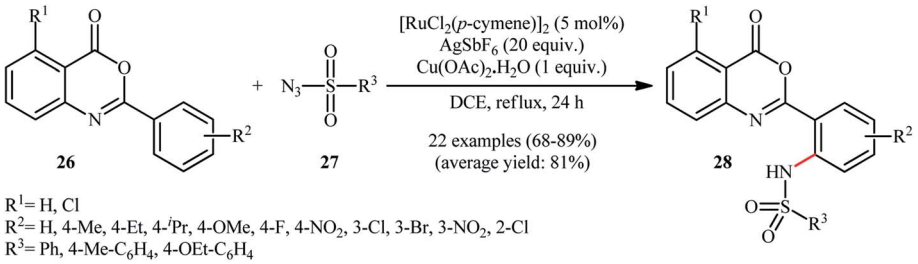
Along this line, Zhu and co-workers elaborated a synthetic route to prepare sulfonamidated indolines **25** *via* a Ru-catalyzed site-selective C–H sulfonamidation of *N*-carbonylated indolines **23** with sulfonyl azides **24** (Scheme 7).[32] The couplings took place in the presence of $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), $AgSbF_6$ (20 mol%), AgOAc (50 mol%), at 80 °C in DCE and selectively provided C7-functionalized products in moderate to high yields. Based on preliminary mechanistic investigations involving



Scheme 8 Mechanistic proposal for the reaction in Scheme 7.

kinetic isotope effect studies and radical trapping experiments, the authors suggested that this reaction proceeds through the following key steps (Scheme 8): (i) initial formation of active Ru(II) catalyst **A** *via* removing of the Cl^- ligand from the $[\{RuCl_2(p\text{-cymene})\}_2]$ complex by silver salt; (ii) coordination of the carbonyl oxygen of the indoline **23** to the Ru(II) catalyst **A** to give the metallacycle intermediate **B**; (iii) coordination of the azide group of the sulfonyl azide **24** to intermediate **B** to afford the Ru-species **C**; (iv) insertion of the sulfonamido moiety with evolution of N_2 gas into the intermediate **C** leads to the intermediate **D**; and (v) protonolysis of **D** to form the final product **25** and regenerates ruthenium complex **A**. The above-mentioned catalytic system was then utilized by Reddy's research group in the C8-selective sulfonamidation of 1-tetralones with sulfonyl azides.[33] Kim and co-workers also reported a similar strategy to construct 1-sulfonamido-xanthones, 5-sulfonamido-chromones, and 5-sulfonamido-flavonoid derivatives by switching the additive to $Cu(OAc)_2$ and solvent to DCM.[34]

Very recently, Bakthadoss and co-workers illustrated a similar site-selective C–H sulfonamidation of oxobenzoxazine derivatives **26** with a range of aromatic sulfonyl azides **27** for the synthesis of *ortho*-sulfonamido oxobenzoxazine frameworks **28** using $[RuCl_2(p\text{-cymene})]_2$ as the catalyst, $AgSbF_6$ an additive and $Cu(OAc)_2\cdot H_2O$ as an oxidant (Scheme 9).[35] The results demonstrated that oxobenzoxazines possessing electron-withdrawing groups afforded higher yields compared to the electron-rich oxobenzoxazines and the reaction was equally efficient for both electron-neutral and electron-rich aryl sulfonyl azides. However, no examples were given with aliphatic and electron-



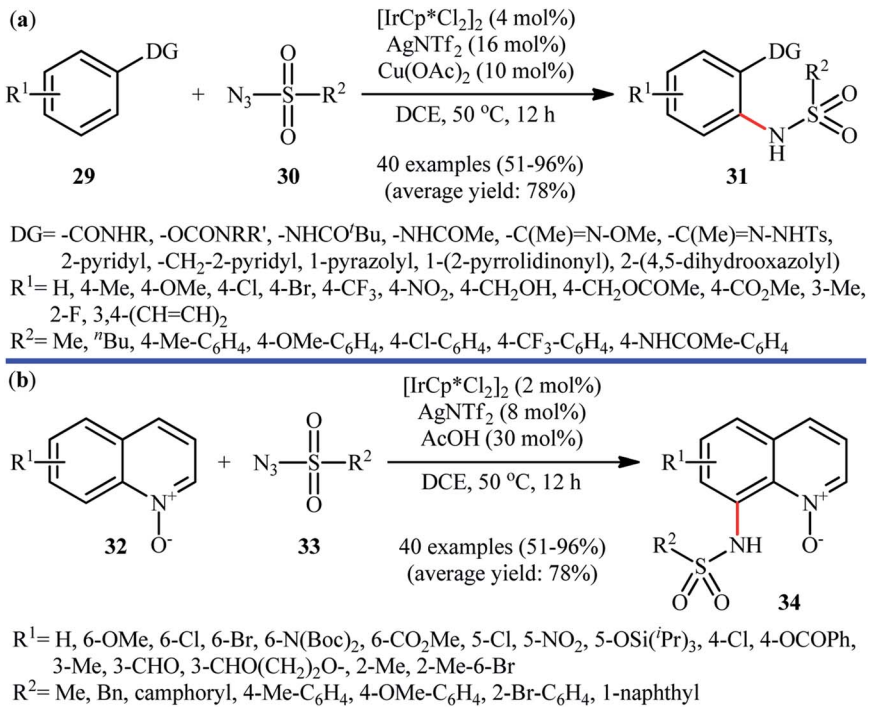
Scheme 9 Synthesis of *ortho*-sulfonamido oxobenzoxazine frameworks **28** reported by Bakthadoss.[35]

poor aromatic sulfonyl azides as the amide partners. To demonstrate the synthetic application of their methodology, the authors performed further late-stage functional group transformation reactions. They showed that hydrolysis of the synthesized compounds under basic conditions (*e.g.*, NaOH/acetone, KO^{t}Bu/^{t}BuOH) or in the presence of HBr in AcOH provided the corresponding 2-(2-sulfonaminobenzamido)benzoic acids in excellent yields, while hydrolysis in the presence of NaOMe in refluxing MeOH gave 2-sulfonaminobenzoic acid derivatives in near quantitative yields.

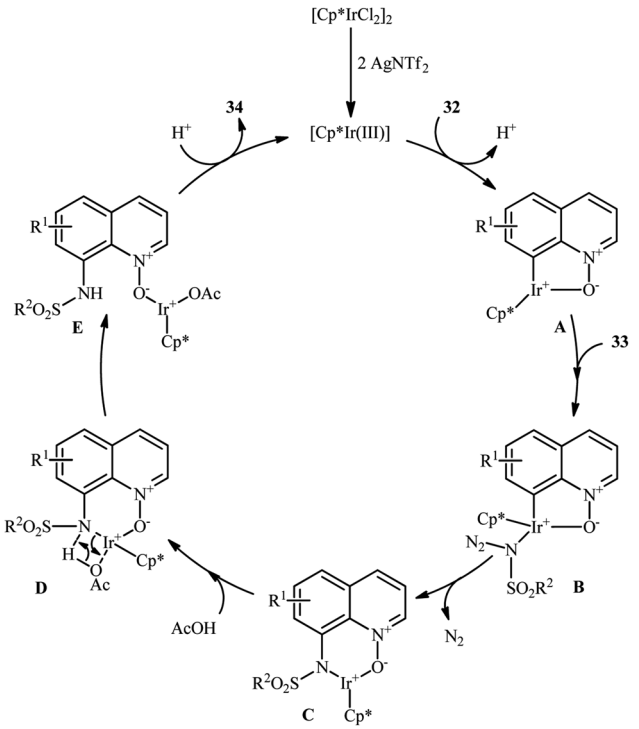
4. Iridium-catalyzed reactions

Of the large amount of published literature, without question, iridium was the most widely used catalyst for the synthesis of *N*-aryl sulfonamides *via* denitrogenative coupling of the corresponding aromatic compounds and sulfonyl azides.

In 2013, Chang and co-workers communicated the first example of iridium-catalyzed direct sulfonamidation of aromatic C–H bonds with sulfonyl azides.[36] They showed that a coordinating directing group (*e.g.*, amide, anilide, ketoxime, hydrazone, carbamate, 2-pyridine, 2-pyrazol, and 2-azoline derivatives) attached to the arene rings leads to sulfonamidated products at the *ortho* position, adjacent to these groups. Thus, by employing the combination of $[IrCp^*Cl_2]_2$ with $AgNTf_2$ as an effective catalytic system, mono-selective amidation of aromatic compounds **29** with various aryl and alkyl sulfonyl azides **30** afforded the corresponding *ortho*-sulfonamidated arenes **31** in moderate to excellent yields (Scheme 10a). The protocol was compatible with various important functional groups such as fluoro, chloro, bromo, nitro, ether, ester, amide and aldehyde functionalities that are useful for further manipulation of products. Noteworthy, the protocol was also applicable for the site-selective amination of arenes with aryl azides. The same authors have next elegantly extended their methodology to



Scheme 10 (a) Ir-catalyzed *ortho*-selective sulfonamidation of aromatic compounds **29** with sulfonyl azides **30**; (b) Chang's synthesis of C8-sulfonamidated quinoline *N*-oxides **34**.



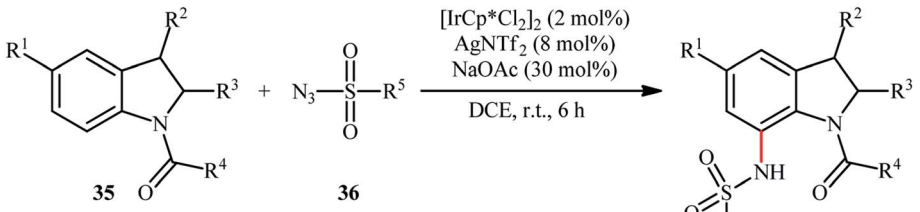
Scheme 11 Mechanism for Ir-catalyzed sulfonamidation of quinoline *N*-oxides **32** and sulfonyl azides **33**.

access C8-sulfonamidated quinoline *N*-oxides **34** from the corresponding quinoline *N*-oxides **32** and sulfonyl azides **33** under a slightly modified condition (Scheme 10b).[37] The present synthetic strategy was also successfully applied by the authors for the high yielding synthesis of Zinquin ethyl ester, a derivative of important fluorescent sensors for Zn(II). According to the authors proposed mechanism (Scheme 11), the unique regioselectivity of this synthesis was based on the formation of *N*-oxide-chelated iridacycle intermediate **A**, which was isolated and characterized by X-ray crystallographic analysis. Noteworthy, the proposed role of acid additive (AcOH) was to promote the rate-determining protodemetalation step. In a subsequent extension of the substrate scope of the protocol, it was shown that weakly coordinating directing group (ketone and ester) containing arenes could be also selectively amidated with sulfonyl azides at the *ortho*-position by using the combination of $[IrCp^*Cl_2]_2$, $AgNTf_2$, AcOH, and Li_2CO_3.[38]

Later, this innovative research group reported further examples of Ir-catalyzed sulfonamidation of aromatic C–H bonds using indolines as the arene reagent.[39] Upon treatment with 4 mol% of $[IrCp^*Cl_2]_2$, 8 mol% of $AgNTf_2$, and 30 mol% of NaOAc in DCE at room temperature, various *N*-protected indolines **35** underwent regioselective C7-amidation with sulfonyl azides **36** to give C7-sulfonamidated indolines **37** in good to excellent yields, ranging from 66% to 98% (Scheme 12). Shortly thereafter, Zhou and Li along with their co-workers disclosed that this reaction could also successfully performed in the absence of NaOAc additive.[40]

In 2016, Kim, Park, and Chang employed $IrCp^*(OAc)_2$ catalyst, in combination with $AgNTf_2$ for site-selective amidation of *N*-protected indole derivatives **38** with various aryl, alkyl, and vinyl sulfonyl azides **39**.[41] These reactions were performed in DCE under air atmosphere, completed within 12 h at room temperature, and provided the expected C7-amidated products **40** in relatively modest to excellent yields (Scheme 13a). The results proved that the efficiency of this C–N bond forming reaction strongly depended on the electronic character of the substituents on the indole ring, clearly in favor of electron-donating groups. Unfortunately, C2-substituted indoles totally failed to enter into this amidation reaction. Notably, the reaction was not operative with Rh or Ru catalyst systems. Drawing inspiration from these works, J. You and colleagues showed that indoles **41** bearing a carbonyl directing group (*e.g.*, aldehyde, ketone, ester, amide) at the C3-position can be selectively sulfonamidated on the C4-position by sulfonyl azides **42** using $IrCp^*(OAc)_2$ as a catalyst and $AgNTf_2$ as an additive in DCE under ambient conditions (Scheme 13b).[42] The reaction is noteworthy in that both NH-free and *N*-protected indoles were well tolerated. In addition, the reaction could be scaled up to produce the target secondary sulfonamide in good yield without difficulty. In a closely related investigation, Lanke and Prabhur also described the synthesis of C4-sulfonamidated indoles form the corresponding indole-3-carbaldehydes and sulfonyl azides using Chang's standard condition.[43]

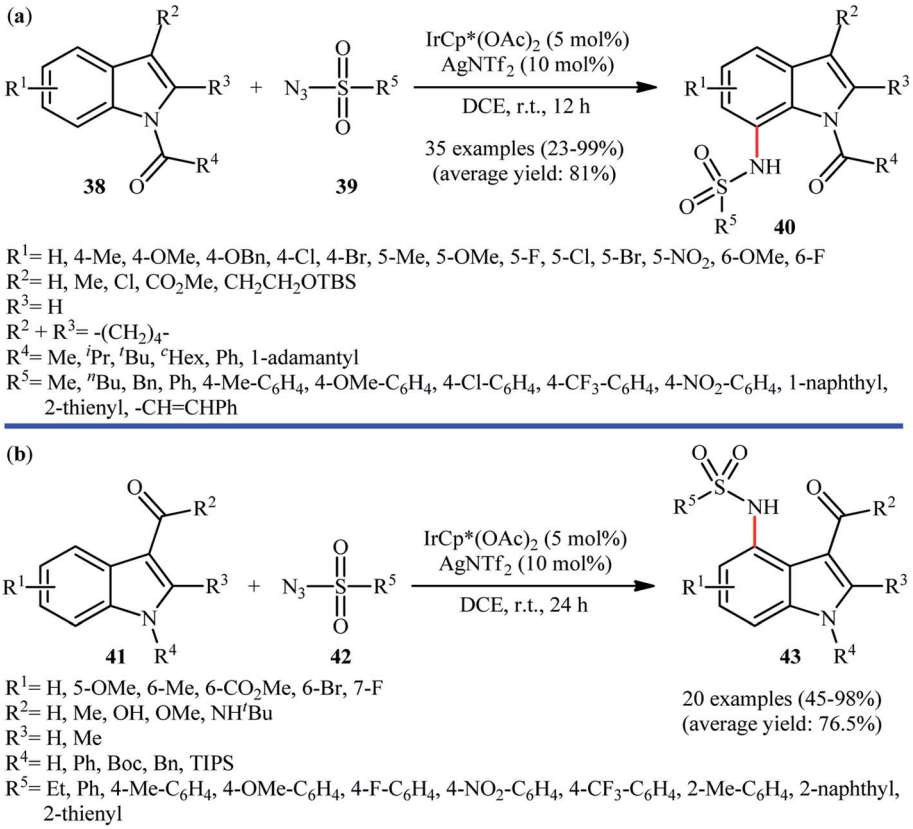
In this context, employing the standard $[IrCp^*Cl_2]_2$ catalyst, different research groups were devised *ortho*-C–H sulfonamidation reactions of arenes bearing many other directing groups



R^1= H, Me, OMe, Cl, Br, NO_2
R^2= H, Me
R^3= H, Me
R^4= Me, OBn, O^{t}Bu, NEt_2
R^5= Me, Bn, Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-Cl-C_6H_4, 4-CF_3-C_6H_4, 1-naphthyl

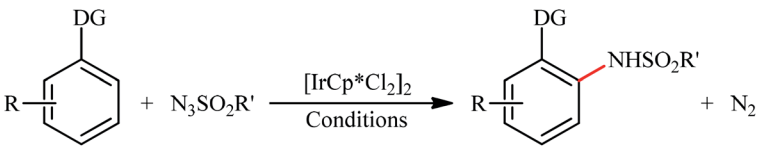
18 examples (66-98%)
(average yield: 89%)

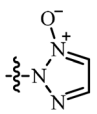
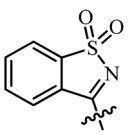
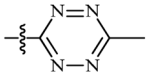
Scheme 12 Direct C-7 sulfonamination of indolines **35** with sulfonyl azids **36** catalyzed by $[IrCp^*Cl_2]_2$.



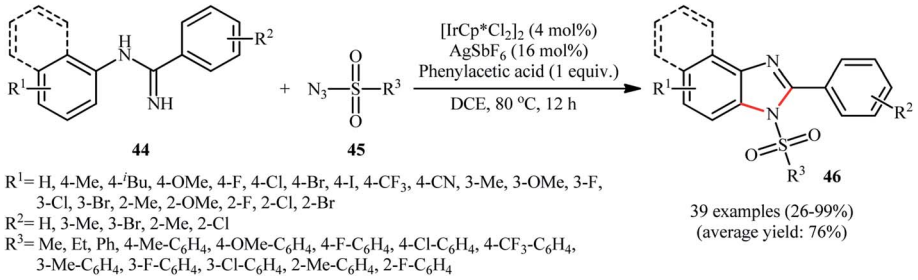
Scheme 13 (a) Synthesis of C7-sulfonamidated indoles **40** reported by Chang; (b) You's synthesis of C4-sulfonamidated indoles **43**.

Table 1 Directing group-assisted $[IrCp^*Cl_2]_2$-catalyzed *ortho*-selective sulfonamidation of aromatic compounds with sulfonyl azides



Entry	Conditions	Directing group	N.E.[a]	Yield (%) Range	Yield (%) Average	Ref.
1	$AgNTf_2$, HOAc, Li_2CO_3, DCE, 80 °C	$-CO_2H$	26	40–99	81	44
2	$AgBF_4$, AgOAc, ball milling, 30 Hz	–CONHR	18	42–97	76	45
3	Ag_2CO_3, HOAc, DCE, 80 °C	$-SO_2NHR$	21	71–95	83.5	46
4	$AgNTf_2$, DCE, r.t.	$-CH{=}N^+(O^-)R$	28	27–99	87	47
5	$AgNTf_2$, DCE, r.t.	–CH=NTs	21	46–95	75	48
6	$AgSbF_6$, DCE, 80 °C	2-Amino-pyrimidine	21	57–99	87.5	49
7	$AgNTf_2$, PivOH, DCE, 60 °C		29	15–97	73	50
8	$AgNTf_2$, CF_3CH_2OH, 80 °C		27	67–99	90	51
9	$AgSbF_6$, AcOH, DCE, 80 °C	2-Quinazolinonyl	13	45–90	78	52
10	$AgNTf_2$, AgTFA, DCE, 100 °C		21	56–98	81	53

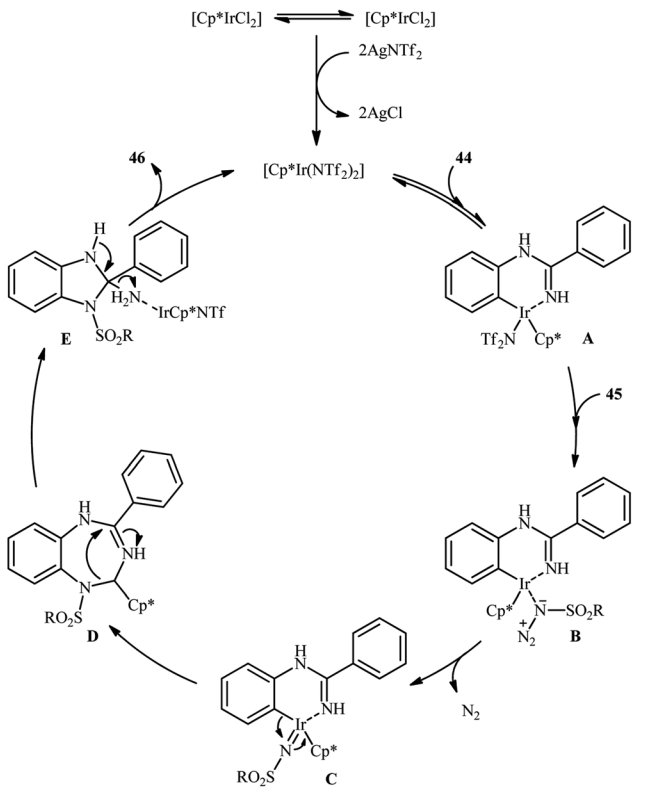
[a] Number of examples.



Scheme 14 Synthesis of 1-(sulfonyl)-2-aryl-1*H*-benzo[*d*]imidazoles **46** from *N*-phenylbenzimidamides **44** and sulfonyl azides **45** through a C–H activation, sulfonamidation and annulation cascade.

(*e.g.*, carboxylate, amide, sulfonamide, imine, nitrone, triazole *N*-oxide, benzo[*d*]isothiazole 1,1-dioxide, pyrimidine, quinazolinone and tetrazine) with sulfonyl azides (Table 1).[44–53]

An important contribution to this field was reported by Cui and co-workers in 2017.[54] They showed that treatment of *N*-phenylbenzimidamide derivatives **44** with sulfonyl azides **45** in the presence of $[IrCp^*Cl_2]_2$/$AgNTf_2$/phenylacetic acid combination in DCE afforded the corresponding 1-(sulfonyl)-2-aryl-1*H*-benzo[*d*]imidazoles **46** through C–H activation, sulfonamidation and annulation cascade (Scheme 14). Moderate to high yields, excellent regioselectivity, and broad substrate scope were the advantages, mentioned for this strategy. The suggested reaction mechanism for this transformation is displayed in Scheme 15. The reaction starts with the formation of active catalyst, $[Cp^*Ir(NTf_2)]_2$, through anion exchange. Next, coordination of *N*-phenylbenzimidamide **44** to this catalyst and subsequent cyclometalation generates iridacyclic intermediate **A**, which after coordination with azide **45** affords the intermediate **B**. Subsequently, elimination of N_2 from this intermediate produces iridium carbene species **C** that, after migratory insertion of the Ir–Ar bond into the carbene unit gives intermediate **D**. The $Ir–N_{(sulfonamide)}$ bond then undergoes migratory insertion into the $C–N_{(imide)}$ bond to form amide species **E**. Finally, elimination of the active Ir(III) catalyst and one molecule of NH_3 from intermediate **E** upon protonolysis affords the expected 1-(sulfonyl)-2-aryl-1*H*-benzo[*d*]imidazole product **46**.

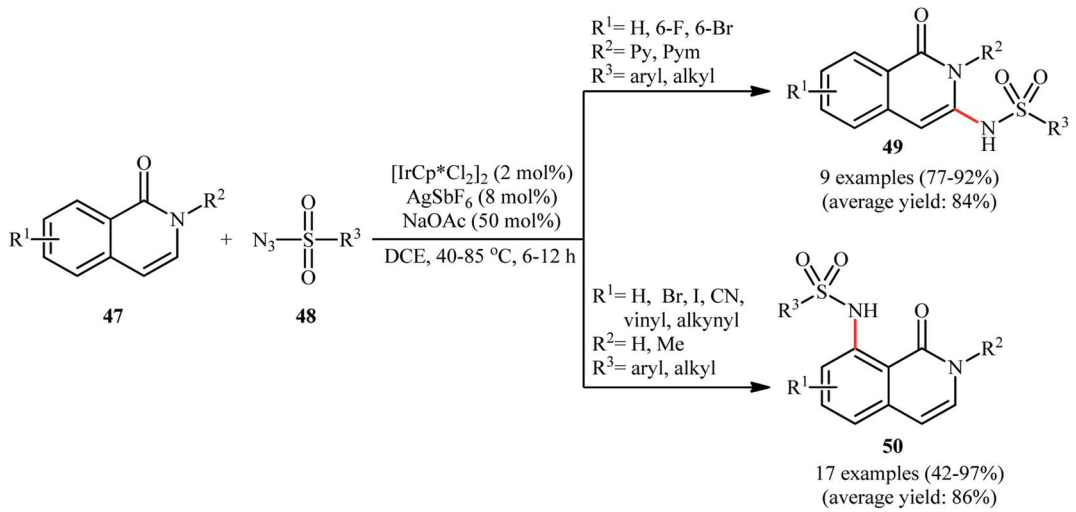


Scheme 15 Proposed mechanistic pathway for construction of 1-(sulfonyl)-2-aryl-1*H*-benzo[*d*]imidazoles **46**.

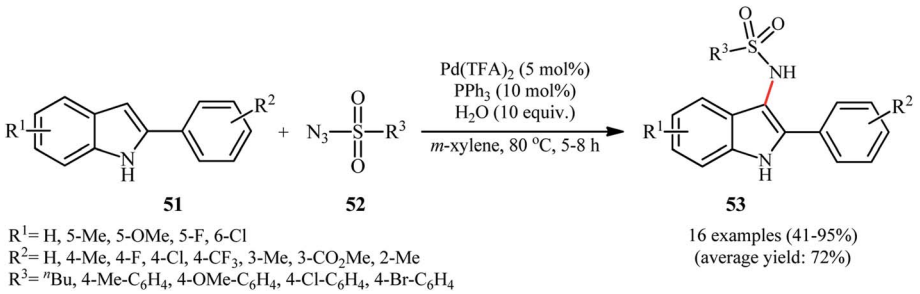
Recently, Das and Samanta disclosed the synthesis of C3-sulfonamidated isoquinolones **49** in modest to excellent yields and complete regioselectivity from the corresponding 2-pyridyl protected isoquinolones **47** through sulfonamidation with sulfonyl azides **48** in the presence of catalytic quantities of $[IrCp^*Cl_2]_2$ and $AgSbF_4$, with 50 mol% of NaOAc as an additive (Scheme 16).[55] Interestingly, when the pyridyl group was switched to H or methyl group, the C8-sulfonamidated isoquinolones **50** were obtained as the sole products. This interesting directing group regiocontrolled reaction was also worked well with different other azides like benzoyl azide, diphenyl phosphoryl azide, and aziodoformate. However, phenyl azide and benzyl azide did not furnish the desired products.

5. Palladium-catalyzed reactions

Despite wide utility of palladium catalysts in numerous C–H bond functionalization reactions,[56] the reported examples of the direct sulfonamidation of C–H bonds with sulfonyl azides using this versatile transition metal are scarce. In fact, only one example of such a reaction was reported in the literature thus far. In this investigation, Hu, Luo, and Zhu described the regioselective introduction of a sulfonamide group at the C-3 position of indoles using $Pd(TFA)_2$ as a catalyst and sulfonyl azides as the nitrogen source.[57] A screening of reaction variables indicated that PPh_3, H_2O, and *m*-xylene were the most effective ligand, additive, and solvent, respectively. With these optimized reaction conditions, a variety of C3-sulfonamidated indoles **53** were obtained in moderate to excellent yields from the corresponding 2-arylindoles **51** and sulfonyl azides **52** (Scheme 17).



Scheme 16 Ir-catalyzed regiocontrolled C3/C8-sulfonamidation of isoquinolones **47** with sulfonyl azides **48**.

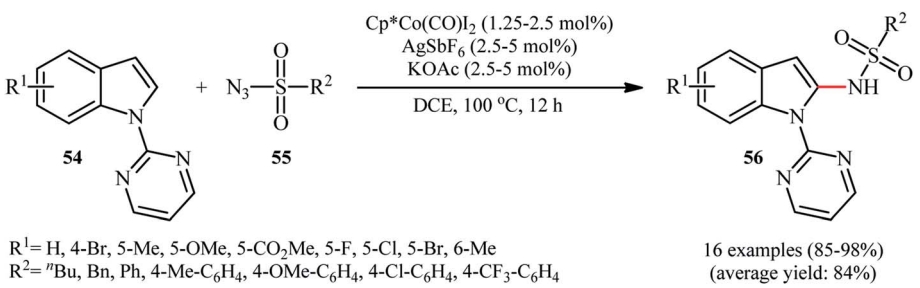


Scheme 17 Pd-catalyzed C–H sulfonamidation of indoles **51** with sulfonyl aides **52**.

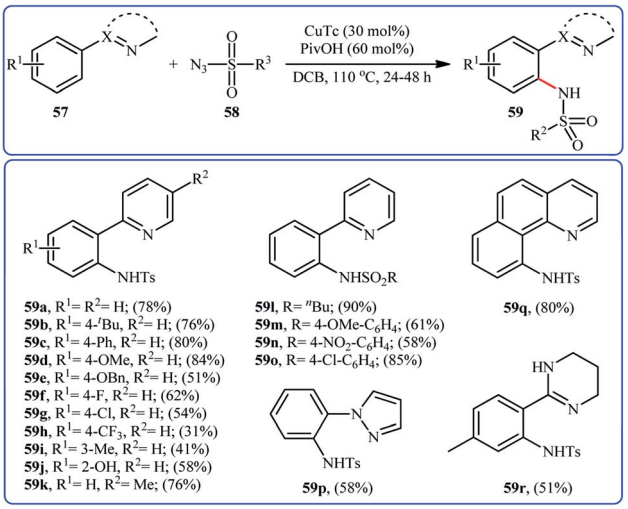
Indole itself did not take part in the reaction and therefore no other C2-unsubstituted indoles were examined in the protocol. In order to evaluate the function of ligand, the authors conducted the reaction under the identical conditions by omitting PPh_3 and found no product was detected. However, the exact role of the ligand has not been elucidated yet.

6. Cobalt-catalyzed reactions

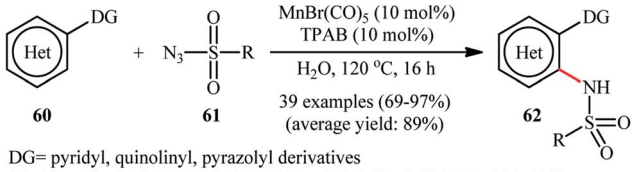
Cobalt-based catalytic systems have played key roles in organic synthesis over decades, due to the high catalytic activity, low-cost and toxicity of this earth-abundant transition metal.[58] The first and only example of Co-catalyzed direct sulfonamidation of aromatic C–H bonds with sulfonyl azides was described by Matsunaga and Kanai in 2014.[59] The authors reported that indoles **54** bearing a pyrimidine ring as the directing group could undergo a smooth site-selective sulfonamidation with various aryl and alkyl sulfonyl azides **55** in the presence of $Cp^*Co(CO)I_2/AgSbF_6/KOAc$ combination as a catalytic system to give the corresponding C2-amidated products **56** in high to excellent yields (Scheme 18). Of note, Cp^*CoI_2-dimer was also found to promote this denitrogenative coupling reaction, albeit at lower efficiency. However, other commercially available cobalt-catalysts such as $Co(acac)_3$, $Co_2(CO)_8$, $Co(NH_3)_6Cl_3$, CoI_2



Scheme 18 Co(III)-catalyzed C2-selective C–H sulfonamidation of indoles **54** with sulfonyl azides **55**.



Scheme 19 Cu-catalyzed directing group-assisted sulfonamidation of arenes **57** with sulfonyl azides **58**.



Scheme 20 Xu's synthesis of *N*-(hetero)aryl sulfonamides **62**.

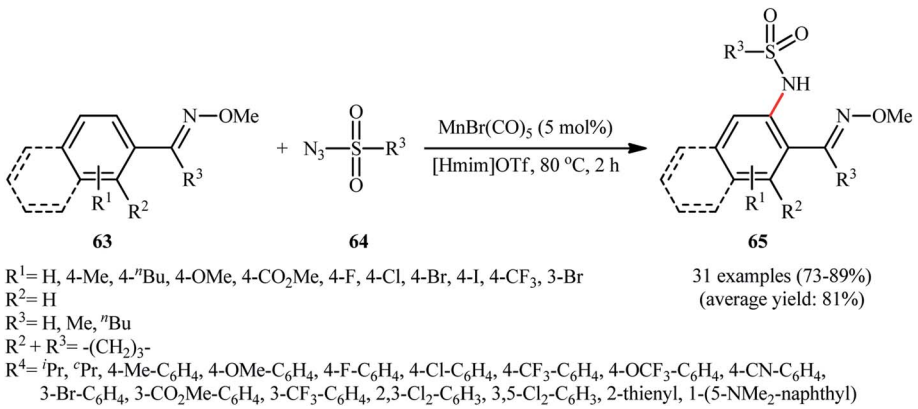
and $[Cp^*Co(C_6H_6)](PF_6)_2$ proved to be completely ineffective. It should be mentioned that the presence of $AgSbF_6$ was crucial for the success of this C–N bond forming reaction. No product was yielded in the absence of $AgSbF_6$. According to the authors proposed mechanism this reaction proceeds through a five-membered cobaltacyclic intermediate formed by the oxidative cyclometalation of the C2–H bond and a nitrogen atom of pyrimidyl group of the substrates to the active cobalt species.

7. Copper-catalyzed reactions

In 2014, Zhu and co-workers informed for the first time the usefulness of copper catalysts for the direct sulfonamidation of aromatic C–H bonds with sulfonyl azides.[60] To evaluate the catalytic activity of different copper salts, 2-phenylpyridine and tosyl azide were chosen as the model substrates. Among the various commercially available Cu-based catalysts [*e.g.*, CuCl, $CuCl_2$, CuTc, $Cu(TFA)_2$, $Cu(OAc)_2$], copper(I) thiophene-2-carboxylate (CuTc) was found to be more effective, which gave a better yield of *ortho*-sulfonamidated product. In a pursuit to further improve the yield, PivOH was added as an additive to the reaction mixture. The solvents such as 1,4-dioxane, MeOH, DMSO, DMF, DCB, and DCE were examined and a good yield of product was obtained when using DCB as the reaction medium. Under the optimized conditions, various arenes **57** bearing a nitrogen-based directing group reacted efficiently with sulfonyl azides **58** to give the corresponding *N*-arylsulfonamides **59** in relatively poor to good yields and excellent *ortho*-selectivity (Scheme 19). The results indicated that arenes possessing electron-donating groups furnished better yields compared to the electron-poor arenes and the relative reaction rates of sulfonyl azides followed the order: aliphatic sulfonyl azides > electron-rich aromatic sulfonyl azides > electron-poor aromatic sulfonyl azides. To the best of our awareness, this is only example dealing with the Cu-catalyzed direct sulfonamidation of aromatic C–H bonds.

8. Manganese-catalyzed reactions

Manganese is one of the latest metals that was joined to the story of direct sulfonamidation of aromatic C–H bonds with sulfonyl azides. In 2018, Kong, Ling, Xu disclosed that arene substrates **60** bearing chelating directing groups, can undergo Mn-catalyzed direct *ortho*-selective sulfonamidation using sulfonyl azides **61** as the nitrogen source (Scheme 20).[61] The optimum reaction conditions relied on the use of $MnBr(CO)_5$ as the catalyst and H_2O as the solvent, at 120 °C. In addition, the presence of 10 mol% of tetrapropylammonium bromide (TPAB) as an additive proved essential for achieving the expected sulfonamidated products **62** in good yields. The methodology was



Scheme 21 Mn-catalyzed amidation of aromatic oximes **63** with sulfonyl azides **64** in ionic liquid.

also useful for C2-selective sulfonamidation of indoles using pyrimidine as the directing group. High to excellent yields, broad substrate scope, and scalability were the main advantages, mentioned of this process. However, the requirement of elevated reaction temperature limited the range of application of this protocol, more or less.

The next year, the same authors applied their manganese catalyst for the sulfonamidation of a diverse range of aromatic oximes **63** with sulfonyl azides **64** by using imidazolium ionic liquid [Hmim]OTf as the solvent (Scheme 21).[62] This time, no additive was used and the couplings were performed under relatively milder conditions. Importantly, $MnBr(CO)_5$/[Hmim]OTf system could be easily separated from the final reaction mixture and reused for at least five times with tangible decrease in its catalytic activity. In addition, the reaction could be easily scaled up and performed on a multi-gram quantity without further optimization.

9. Summary and outlook

Sulfonamides belong to an important class of organosulfur compounds as they display an array of biological activities including antimicrobial, antiretroviral, anticonvulsant, antidiabetic, antitumor, and anti-depressant activities. Interestingly, seventy-two FDA-approved drugs contain this privileged structural motif in their structure and up to 25% of them are *N*-(hetero)arylated derivatives. Therefore, development of facile and efficient procedure for their synthesis from easily available starting materials that meet the objectives of green chemistry is always interesting.

The direct functionalization of C–H bonds represents one of the most atom-economical and environmentally friendly approaches to molecular construction. This methodology enables unprecedented, single-step access to a broad range of carbon–carbon and carbon-heteroatom bonds directly from C–H bonds that are unreactive under traditional methods. In this review, recent advances and developments on the synthesis of biologically important *N*-(hetero)aryl sulfonamides through the transition-metal catalyzed direct sulfonamidation of (hetero)aromatic C–H bonds with easily available sulfonyl azides have been discussed. It is shown that various *N*-aryl and *N*-heteroaryl sulfonamides are readily accessible by using this approach in a straightforward modular way where non-toxic nitrogen gas forms as the sole by-product. Of note, majority of the reactions covered in this review were performed under atmospheric environment and some of them were easily scaled up to the gram levels under relatively mild conditions. These results clearly indicate the potential application of this route of *N*-(hetero)aryl sulfonamide synthesis in industry.

Despite great achievements over the past few years in this fast-growing research area, many challenges remain to be solved. For instance, most of the catalysts used herein are late transition metal catalysts such as Rh, Ru, Ir based-catalysts. Given cost and sustainability concerns, there is a significant need for the development of first-row transition metal-based catalysts. Moreover, despite numerous recent published works on the usefulness of transition metal nanoparticles as highly efficient and reusable catalysts for various C–H functionalization reactions, there have been no reports of the applicability of such catalysts in the titled reactions till date. Thus, the exploration of metallic nanocatalysts for this page of *N*-aryl sulfonamide are highly desirable in terms of cost and environmental benefits. In addition, almost all of the reactions covered in this review employed directing groups for controlling the site-selectivity. However, the requirement of installing and then removing this groups limited the range of application of this synthetic strategy and therefore, of course, catalyst-controlled site-selective processes should be explored.

Conflicts of interest

There are no conflicts to declare.

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