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Functionalization of C−H Bonds via Metal-Catalyzed Desulfitative Coupling: An Alternative Tool for Access to Aryl- or Alkyl-Substituted (Hetero)arenes

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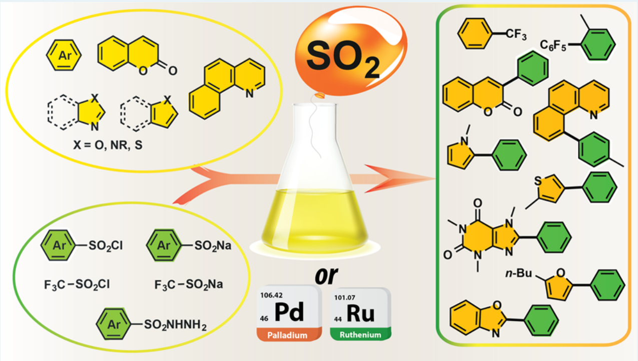

ABSTRACT: In recent years, palladium-catalyzed direct arylation of (hetero)aromatics with aryl halides via a C−H bond activation has become a popular method for generating carbon−carbon bonds; however, such couplings still suffer from several limitations due to the limited functional group tolerance, the lack of regioselectivity of some of these couplings, or the poor reactivity of some substrates. For example, the presence of several halide functional groups on arenes is often not tolerated. In recent years, several new alternative coupling partners have been successfully employed for such couplings, such as RSO_2R' derivatives using Pd or Ru catalysts to afford, after a desulfitative coupling, a variety of biaryls or alkylated arenes which in several cases cannot be obtained using aryl or alkyl halides as the coupling partners. This methodology allows the synthesis of complex molecules in only a few steps and will certainly give simpler access to a very wide variety of new biaryls or alkylated arenes useful to material chemistry and also to biochemists in coming years.

KEYWORDS: *C−H bond activation, arylation, catalysis, desulfitative, palladium, heteroarenes*

1. INTRODUCTION

The arylation or alkylation of (hetero)aromatics via metal-catalyzed C−H bond activation provides, in several cases, a simpler access to the corresponding aryl- or alkyl-(hetero)aryl derivatives than the more classical Suzuki, Stille, or Negishi couplings.[1] Palladium catalysis is the most widely used method for such direct cross-coupling reactions,[2−8] but several contributions have been reported using ruthenium catalysis[9,10] and other transitions metals.[11−21] Transition-metal-free conditions for such cross-couplings have been also described.[22] Initially, alkyl- and especially aryl-halides were the most commonly employed coupling partners for such reactions.[23−26]

In recent years, several alternative coupling partners, such as benzoic acids,[27−29] arylboronic acids,[30,31] or aryl tosylates,[32] have also been successfully employed to prepare bi(hetero)aryls via C−H bond activation/functionalization. Among them, one of the most promising type is certainly RSO_2R' derivatives, such as RSO_2Na or RSO_2Cl. Advantages of these substrates are that many of them are commercially available and easy to handle. RSO_2Cl derivatives can also be easily prepared from sulfonic acids or sulfur substrates by chlorination,[33−37] and RSO_2Na can be prepared by the reduction of the corresponding RSO_2Cl.[38] A chief advantage of such coupling partners is that, in some cases, they give access to alternative regioisomers. Moreover, the use of halo-substituted $ArSO_2R$ derivatives affords biaryls without cleavage of the Ar−Br or Ar−I bonds, allowing further transformations. For these reasons, such couplings should give new viable accesses to important bi(hetero)aryls derivatives.

Transition-metal-catalyzed direct arylation of (hetero)-aromatics has been covered in recent years by several relevant reviews or accounts. Some of them have focused on direct arylation of heteroarenes,[39−41] benzene derivatives,[42−44] or sp^3 C−H bond arylation.[45−47] Other reviews have been dedicated to the applications of C−H bond activation in the synthesis of complex molecules,[48−50] or polymers.[51] Direct C−H functionalizations under mild conditions,[52] or in green solvents have also been reviewed.[53]

However, to the best of our knowledge, there has been no review focusing on metal-catalyzed C−H bond activation/functionalization using RSO_2R' as coupling partners for access to bi(hetero)aryls or alkylated arenes. Since the early report of Kamigata in 1990, the use of new catalysts, other $ArSO_2R$ derivatives, a wider variety of (hetero)aryl coupling partners and also improved reaction conditions have been reported. In this review, we will outline the developments and advances in metal-catalyzed desulfitative direct functionalization. In the first section, the metal-catalyzed direct functionalization of six-membered ring derivatives shall be reviewed. The second part deals with the metal-catalyzed direct functionalization of five-

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membered rings containing one heteroelement (thiophenes, furans, and pyrroles). The reactivity of five membered rings containing more than one heteroelement (benzoxaoles, benzothiazoles, ...) for desulfitative functionalization will be presented in the third part. The remaining challenges in the field are discussed in the General Conclusion and Perspectives. This review focuses on the direct arylation or alkylation using $AlkSO_2R$ or $ArSO_2R$ derivatives as the coupling partners; however, it should be mentioned that $ArSO_2R$ derivatives have also been used in several other coupling processes, such as Mizoroki−Heck,[54−56] Suzuki−Miyaura,[57,58] Corriu−Kumada,[59] Sonogashira,[60] and also several other metal-catalyzed desulfitative cross-coupling reactions.[61−81]

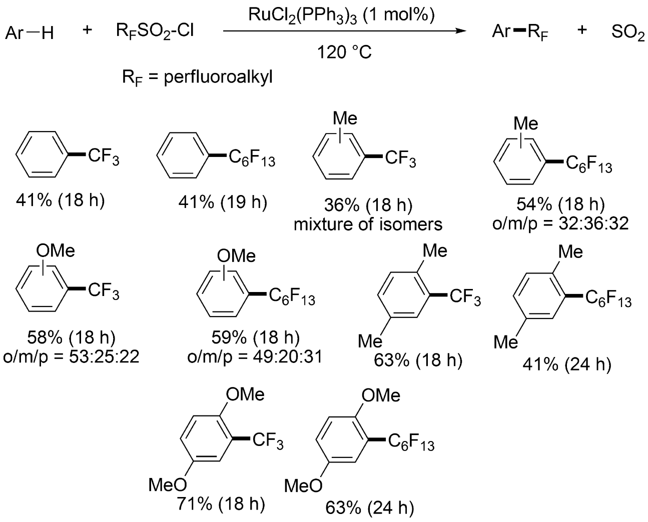
2. DIRECT DESULFITATIVE FUNCTIONALIZATION OF SIX-MEMBERED RING (HETERO)ARENES

This part will focus on transition-metal-catalyzed direct desulfitative arylation or alkylation of six-membered ring (hetero)arenes. Simple arenes containing several reactive C−H bonds under desulfitative conditions will be first described. Then, desulfitative C−H bond functionalizations of arenes bearing a directing group will be presented, including electron-deficient arenes and heteroatom-containing molecules.

2.1. Direct Desulfitative Functionalization of Arenes.

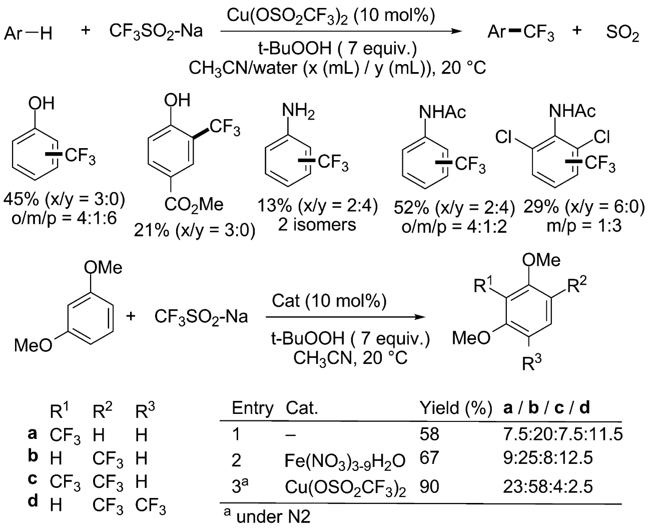
With respect to ruthenium(II) catalysis, Kamigata and co-workers pioneered the use of readily available perfluoroalkylsulfonyl chlorides in a direct desulfitative cross-coupling reaction through a C−H bond activation of simples arenes for fluorinated molecule synthesis (Scheme 1).[82] $RuCl_2(PPh_3)_3$ catalyst promotes the perfluoroalkylation of simples arenes with trifluoromethanesulfonyl chloride or tridecafluorohexane-1-sulfonyl chloride. It is important to note that the reaction proceeds smoothly for such aromatic compounds possessing electron-donating groups, such as toluene, anisole, *p*-xylene, 1,4-dimethoxybenzene, whereas chlorobenzene, bromobenzene, and ethyl terephthalate proved to be unsuitable substrates for this reaction.

Scheme 1



During recent decades, trifluoromethylation reactions have attracted much attention because of the presence of trifluoromethyl groups in blockbuster pharmaceuticals, agrochemicals, liquid crystals, dyes, and polymers.[83−86] In 1992, Langlois and co-workers established that trifluoromethyl radicals can be generated from monoelectronic oxidation of sodium trifluoromethanesulfinate and trapped by different nucleophiles, such as disulfides or aromatic compounds, to deliver thioethers or trifluoroalkylated arenes (Scheme 2).[87]

Scheme 2



	R^1	R^2	R^3
a	CF_3	H	H
b	H	CF_3	H
c	CF_3	CF_3	H
d	H	CF_3	CF_3

Entry	Cat.	Yield (%)	a / b / c / d
1	–	58	7.5:20:7.5:11.5
2	$Fe(NO_3)_3$-$9H_2O$	67	9:25:8:12.5
3[a]	$Cu(OSO_2CF_3)_2$	90	23:58:4:2.5

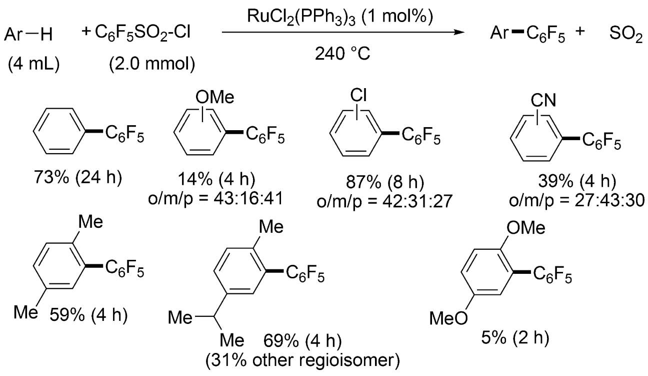
[a] under N2

This radical cation was generated using *t*-butylperoxide as oxidant in the presence of $Cu(OSO_2CF_3)_2$ as catalyst. Easily oxidizable substrates (e.g., aniline) did not offer the simple trifluoromethylated compounds in good yields, but less nucleophilic aniline and acetanilide were trifluoromethylated in moderate to good yields. Phenylacetate was unreactive under these conditions, probably because of its low nucleophilic character; however, phenol derivatives were successfully trifluoromethylated in good yields, but mixtures of regioisomers were obtained. The reaction with 1,3-dimethoxybenzene highlighted the huge effect of copper(II) catalyst on the selectivity compared with iron(III) or metal-free conditions (Scheme 2, bottom). Finally, the authors demonstrated that these reactions conditions could also be applied to *N*-actetylpyrrole to allow the regioselective trifluoromethylation at the C-2 position, albeit in a low 35% yield. Langlois reagent and zinc analogues have been used later in the direct trifluoromethylation or difluoromethylation of heteroarenes under metal-free conditions.[88−95]

In 1998, Kamigata and co-workers extended the scope of RSO_2Cl reagents to pentafluorobenzenesulfonyl chloride as the aryl source in Ru-catalyzed direct desulfitative arylation of aromatics compounds (Scheme 3).[96] In contrast to the perfluoroalkylsulfonyl chlorides, which react preferentially with electron-rich arenes (Scheme 1), pentafluorobenzenesulfonyl chloride allows the formation of desired biaryls in good yields with electron-deficient arenes. The reaction proceeds in solvent-free conditions, but at a very high temperature (i.e., 240 °C).

The proposed mechanism involves a redox-transfer reaction between pentafluorobenzenesulfonyl chloride and the Ru(II) catalyst to afford the radical anion **A**, which could be cleaved homolytically to give the pentafluorobenzenesulfonyl radical **B** and Ru^{III}−Cl (Figure 1). The pentafluorophenyl radical **C**, formed from the radical **B** by extrusion of sulfur dioxide, adds to the aromatic nucleus to give the cyclohexadienyl radical **D**.

Scheme 3



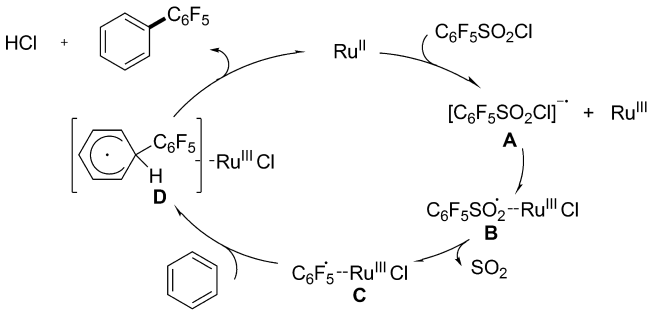
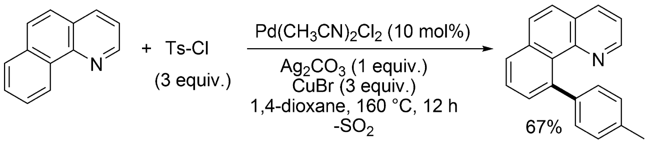


Figure 1.

The subsequent hydrogen atom abstraction by a Ru^{III}−Cl species from the radical **D** affords the desired arylated product and hydrogen chloride, and the ruthenium(II) catalyst is regenerated. The radicals **B**, **C**, and **D** are considered to be confined in the coordination sphere of the ruthenium complex.

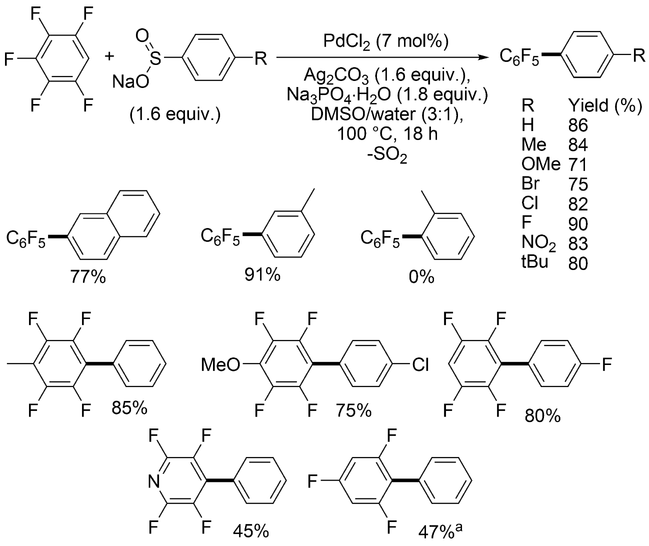
2.2. Direct Desulfitative Functionalization of Arenes Bearing a Directing Group. After quite a long break in this research area and the impressive development of transition metal-catalyzed C−H bond activation/functionalization, Dong and co-workers disclosed Pd-catalyzed direct arylation of benzoquinoline using tolylsulfonyl chloride as the coupling partner, through a desulfitative cross-coupling reaction (Scheme 4).[97] Indeed, during the course of their studies on Pd-catalyzed C−H bond sulfonylation of phenylpyridine with benzenesulfonyl chlorides, the authors found that using benzoquinoline as the substrate and in the presence of additional copper bromide, a desulfitative cross-coupling reaction took place to afford an unexpected arylated product in 67% yield. Only one example had been reported, but this result represents a major breakthrough in this emerging field.

Scheme 4



Wang and co-workers reported in 2014 the direct desulfitative arylation of electron-deficient polyfluoroarenes using sodium arenesulfinates as the coupling partners (Scheme 5).[98] Biaryls containing polyfluoroarene core structures represent an important class of compounds in medicinal chemistry as well as in electronic devices. Recently, their synthesis via direct C−H bond arylation has emerged as one of the most reliable accesses with many described protocols; among them, the use of aryl bromides as coupling partners is the most popular.[44] Pd-catalyzed direct desulfitative C−H bond arylation provides a suitable alternative in which aromatic sulfinic acids (or salts) are used as the arylating reagents. The best reaction conditions were 7 mol % $PdCl_2$ as catalyst in the presence of silver carbonate (Ag_2CO_3) as oxidant and hydrated sodium triphosphate ($Na_3PO_4·H_2O$) as base in wet DMSO. Most examples employed pentafluorobenzene as the model substrate. The reaction was found to be insensitive to the electronic properties of the aromatic sulfinic acids, whereas a huge effect of the steric hindrance was observed. For example, sodium 2-methylbenzenesulfinate did not allow the formation of the desired arylated product. Less-electron-deficient arenes, such as tetrafluorobenzene derivatives or 1,3,5-trifluorobenzene, were also arylated in moderate yields. In addition, 1,2,4,5-tetrafluoropyridine also displays a lower reactivity with sodium benzenesulfinate because 2,3,5,6-tetrafluoro-4-phenylpyridine was isolated in only 45% yield. The authors explained this lack of reactivity by a nitrogen atom coordination to the palladium catalyst, which reduces its catalytic activity.

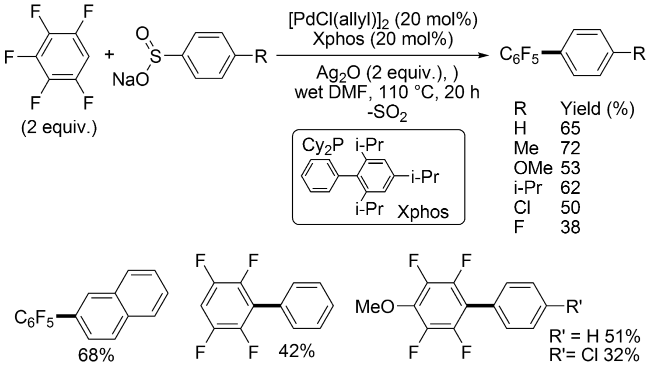
Scheme 5[a]



[a]1,3,5-Trifluorobenzene (3 equiv) was used.

The same reaction was reported by Weng and co-workers (Scheme 6):[99] 20 mol % $[PdCl(allyl)]_2$ associated with 20 mol % 2-dicyclohexylphosphino-2,4,6-triisopropylbiphenyl (Xphos)

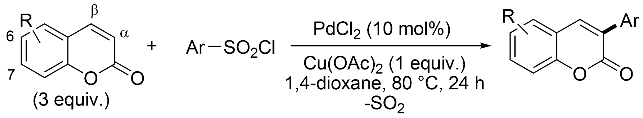
Scheme 6



in the presence of 2 equiv of silver oxide (Ag_2O) as additive in wet dimethylformamide (DMF) at 110 °C was selected as the best catalytic system. It is important to note that traces of water have an accelerating effect on the reaction; as in anhydrous DMF, the desired product was obtained in only 4% yield, albeit 72% in wet DMF. However, in all cases, the arylated polyfluorobenzenes were isolated in lower yields than under the previously described conditions (Scheme 5), and 1,3,5-trifluorobenzene was completely unreactive under these new reaction conditions.

The last example of direct desulfitative arylation for the 6-membered ring molecules concerns Pd-catalyzed regioselective arylation of coumarins using benzenesulfonyl chlorides as coupling partners (Scheme 7).[100] Interestingly, unlike to the standard Heck reaction, in which the arylation takes place at the β-position using aryl bromide as the aryl source, the reaction with benzenesulfonyl chlorides provides the more challenging α-arylated products. The reaction proceeds using an excess of coumarins (3 equiv) in the presence of 10 mol % $PdCl_2$ and 1 equiv of $Cu(OAc)_2$ as oxidant under both base and ligand-free conditions. The reaction tolerates a wide range of substituents on both coupling partners. For example, the reaction proceeds in the presence of hydroxy or tertiary amine functions on coumarins without the use of protecting groups; however, electron-deficient coumarins were unreactive. Moreover, the authors advised that benzyl- or methylsulfonyl chloride remained unreacted under these reaction conditions.

Scheme 7

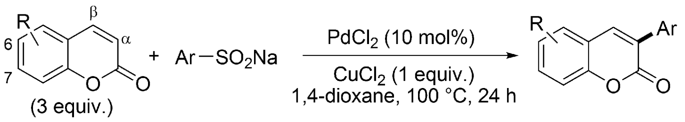


R =	Ar =	Yield (%)	R=	Ar =	Yield (%)
H	4-tolyl	78	6-Me	phenyl	66
H	4-anisole	66	7-NEt_2	phenyl	57
H	4-pentylbenzene	72	7-OEt	4-anisole	64
H	phenyl	68	6-OMe	phenyl	72
H	2-naphtyl	47	7-OMe	2-naphtyl	65
6-Me	4-isopropylbenzene	75	7-OMe	4-tolyl	87
6-Me	2-naphtyl	63	7-OH	phenyl	60
6-Me	4-tolyl	80	6-NO_2	4-tolyl	traces

In addition to their work with benzenesulfonyl chlorides, Jafarpour and co-workers investigated the desulfitative arylation of coumarins using sodium arenesulfinates as the aryl source (Scheme 8).[100] Slightly altered reaction conditions (i.e., $CuCl_2$ instead of $Cu(OAc)_2$ at 100 °C) afforded the desired 3-arylcoumarins, albeit in lower yields than the reaction performed using the corresponding benzenesulfonyl chlorides (Scheme 7).

As described in this section, only a few catalytic systems have been reported for the direct desulfitative alkylations or arylations of 6-membered ring arenes. The ruthenium(II) catalytic system was first developed by Kamigata, but the reaction was limited to perfluorinated alkylsulfonyl or pentafluorobenzenesulfonyl chlorides. The major drawback of these reactions is the regioselectivity issue because, in almost all cases, complex mixtures of 2 or 3 regioisomers were obtained. To overcome this issue, Dong and co-workers reported a strategy similar to several other transition-metal-catalyzed direct arylations of arenes[101] with the use of a directing group, albeit only one example was reported. The use of electron-deficient arenes such as pentafluorobenzene proved to be a good strategy to provide the desired arylated products in high regioselectivities.

Scheme 8



R =	Ar =	Yield (%)
H	phenyl	49
6-Me	4-tolyl	67
6-Me	phenyl	58
7-OEt	4-anisole	61
6-OMe	phenyl	63

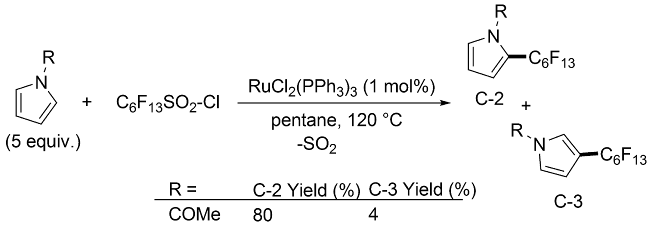
3. DIRECT DESULFITATIVE FUNCTIONALIZATION OF FIVE-MEMBERED RING HETEROARENES CONTAINING ONE HETEROELEMENT

The arylated heteroaryl motifs are present in many high-value manufactured chemicals, including pharmaceuticals, natural products, and materials. Over the most recent decades, several protocols have been developed for their synthesis in connection with the respect of environment. Among them, transition-metal-catalyzed direct arylations of the corresponding heteroarenes through a C−H bond activation are certainly one of the most eco-friendly pathway to date.[63] Therefore, the use of desulfitative couplings for such reactions with heteroarenes represents an emerging field delivering a method as an alternative to the one employing aryl halides. One advantage of the use of heteroarenes instead of arenes is the strong directing effect of the presence of the heteroatom on the ring. Moreover, several furan, thiophene, and pyrrole substrates are readily available from natural sources, and many of them are commercially available. This chapter is divided into three parts, depending on the nature of the heteroatom on the ring: N with pyrroles and indoles, S with (benzo)thiophenes, or O with (benzo)furans.

3.1. Pyrrole and Indole Derivatives.

In 1994, after having successfully perfluoroalkylated arenes using perfluorosulfonyl chlorides via ruthenium(II) catalysis, Kamigata and co-workers extended this methodology to pyrroles (Scheme 9).[102] N-

Scheme 9[a]



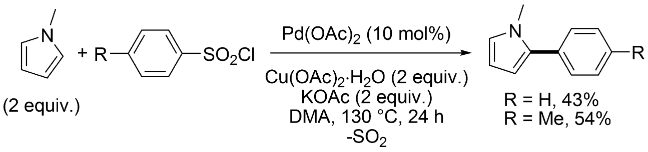
R =	C-2 Yield (%)	C-3 Yield (%)
COMe	80	4
SO_2Ph	65	7
COPh	92	6
CO_2Me	55	1
$SiMe_3$	53[a]	8
Si(i-$Pr)_3$	25	59

[a] 2-Tridecafluorohexylpyrrole (R = H) was also obtainted in 25% yield.

Protected pyrroles were alkylated using 1 mol % of $RuCl_2(PPh_3)_3$ at 120 °C in pentane. Usually, the alkylation took place preferentially at the C-2 position, except with tri(isopropyl)silylpyrrole, which afforded a mixture of C2- and C3-alkylated products in a 25:59 ratio.

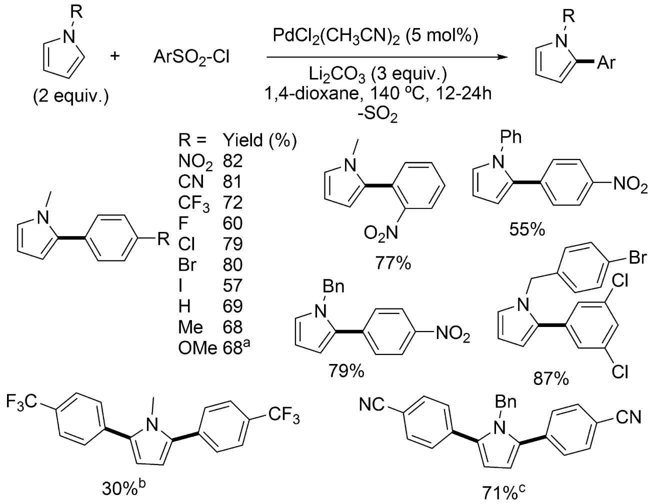
Twenty years latter, Jafarpour and co-workers rediscovered the direct desulfitative arylation of pyrroles when studying the regioselective arylation of coumarins (Scheme 10).[100] In the course of their investigations on Pd-catalyzed direct α-arylation of coumarins using benzenesulfonyl chlorides (Scheme 7), they also employed N-methylpyrrole as the substrate. Slightly modified conditions (i.e., $Pd(OAc)_2$ as catalyst associated with 2 equiv of $Cu(OAc)_2$ in dimethylacetamide in the presence of KOAc as base) afforded the α-arylated pyrroles in moderate yields. Only two examples of this reaction have been described.

Scheme 10



In 2014, Doucet and co-workers generalized the scope of the α-arylation of pyrrole derivatives using benzenesulfonyl chlorides as coupling partners but under copper-free conditions (Scheme 11).[103] The optimized conditions (i.e., 5 mol % of $PdCl_2(CH_3CN)_2$ in the presence of lithium carbonate (Li_2CO_3) in 1,4-dioxane at 140 °C) allowed the formation of the 2-arylated pyrroles in high yields and high regioselectivities. N-Methylpyrrole was used as the model substrate, and the reaction tolerated a wide range of substituents on the benzenesulfonyl chloride part, including halides such as bromo and iodo, which are normally very reactive in the presence of palladium catalysts. The authors highlighted that the C−Br or C−I bonds are not cleaved during the reaction and showed their potentials for a second direct arylation, allowing the formation of triaryl compounds. Other protected pyrroles, such as N-phenylpyrrole or N-benzylpyrroles, were arylated at the C-2 position in moderate to high yields. Interestingly, an N-benzylpyrrole bearing a C−Br bond on the benzyl moiety also reacted without the cleavage of the C−Br bond. Using larger amounts of benzenesulfonyl chlorides, diarylations at both the C-2 and C-5 positions of pyrroles were also successful.

Scheme 11[a,b,c]



[a] 4 equiv of 1-methylpyrrole was used. [b] 3 equiv of $ArSO_2Cl$ was used. [c] 2.5 equiv of $ArSO_2Cl$ was used.

A competitive reaction using an equimolar mixture of 4-nitrobenzenesulfonyl chloride and 4-chlorobenzenesulfonyl chloride confirmed that the arylation occurred preferentially with the most electron-deficient benzenesulfonyl chloride (Scheme 12).[103]

Moreover, a pyrrole derivative bearing an electron-withdrawing group, such as methyl 1-methylpyrrole-2-carboxylate, was completely unreactive in the desulfitative direct arylation with benzenesulfonyl chloride. A competitive reaction between 1-methylpyrrole and 1-methylpyrrole-2-carboxylate showed a complete selectivity for the C-2 arylation of 1-methyl pyrrole, whereas reactions using bromobenzene instead of benzenesulfonyl chloride afforded a mixture of both arylated pyrroles (Scheme 13).[103]

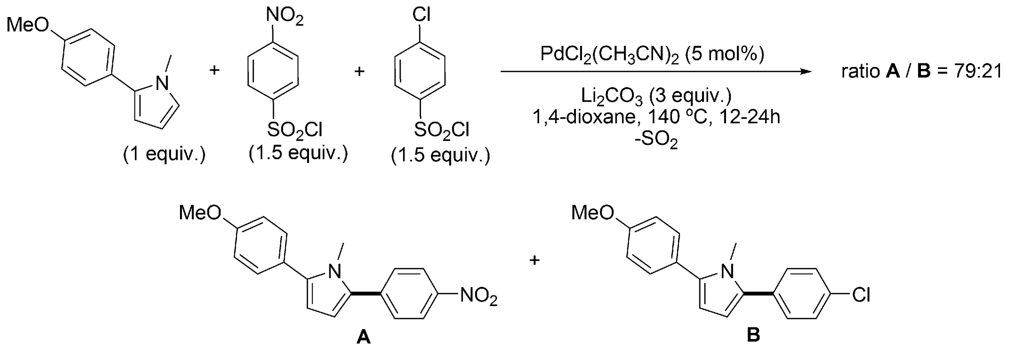
The reactivity of N-methylindole was also investigated under these reaction conditions. Using bulky mesitylene-2-sulfonyl chloride, the arylation occurred mainly at the C-3 position, whereas using less-hindered 4-bromobenzenesulfonyl chloride, an equimolar mixture of C-2- and C-3-arylated products was formed (Scheme 14).

The Pd-catalyzed direct desulfitative arylation of indoles had been earlier reported by Deng, Luo, and co-workers in 2012 using sodium sulfinates instead of benzenesulfonyl chlorides as the coupling partners (Scheme 15).[104] With these coupling partners, the indole derivatives were exclusively arylated at the C-2 position using a palladium(II) catalyst in the presence of 2 equiv of copper(II) salts as oxidant in toluene/dioxane as a mixed solvent at 100 °C. A wide variety of functional groups, such as methyl, methoxy, bromo, fluoro, nitro, and even ester moieties, on the N-methylindole part was tolerated. Moreover, N-ethylindole or N-acetylindole reacted also in good yields, whereas no reaction occurred using free NH-indole. Various arylsulfinic acid sodium salts have been employed under these conditions, but only nitro as the functional group was found to be unreactive. It is important to note that the optimized conditions tolerate the presence of C−Br bonds during the reaction, allowing further metal-catalyzed transformations.

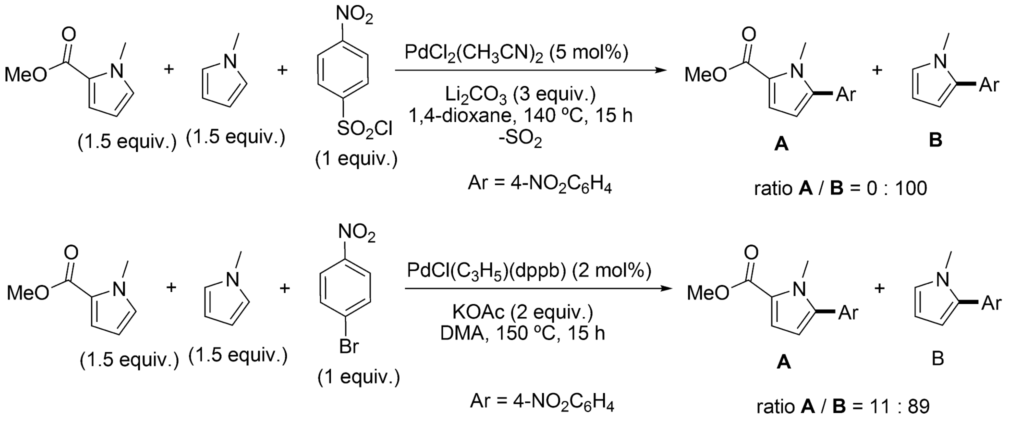
Although the exact mechanism of this desulfitative coupling reaction is still not clear, the authors proposed a plausible mechanism (Figure 2).[104] First, the Pd(II) catalyst reacts with the indole **1** at the C-2 position to form the HetAr−Pd(II)−X intermediate **A** with X = OAc, which is subsequently displaced by sulfinic acid **2** to form intermediate **B**. This intermediate species undergoes desulfination to generate the aryl−palladium complex **C**. A reductive elimination of **C** affords the desired product **3**, and the Pd(0) catalyst is reoxidized to Pd(II) by $CuCl_2$, thus closing the catalytic cycle.

Free NH-indoles were arylated by Wang and co-workers using microwave heating via a Pd-catalyzed desulfitative coupling reaction with arenesulfinic acids (Scheme 16).[105] The reaction proceeded in the presence of silver acetate (AgOAc, 2 equiv) as oxidant and sulfuric acid (2 equiv) as additive. The authors explained that the use of H_2SO_4 might minimize the decomposition of indoles and facilitate the regioselective functionalization at the C-2 position of the indoles. The substrate scope included both electron-donating

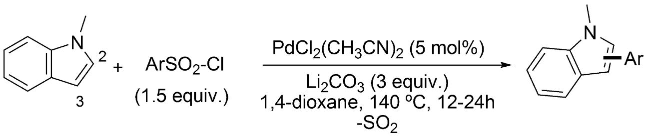
Scheme 12



Scheme 13



Scheme 14



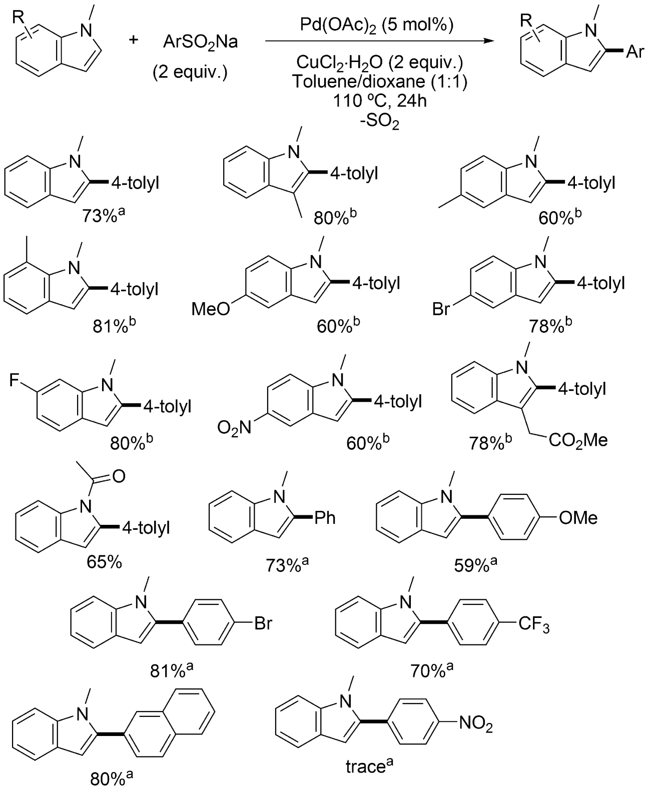
Ar =	**C-2** Yield (%)	**C-3** Yield (%)	**C-2/C-3**
4-Br-C_6H_4	30	41	47:53
Mesityl	4	48	10:90

and electron-withdrawing functional groups on both coupling partners and also ortho substituents. The proposed mechanism is similar to the one in Figure 2.[104]

3.2. Thiophenes and Benzothiophenes. Again, the first example of direct desulfitative arylation of thiophene derivatives was reported by Kamigata in 1998 using a ruthenium(II) catalyst (Scheme 17).[96] The major drawbacks of this reaction are the high temperature (240 °C) and the lack of regioselectivity because mixtures of two or three regioisomers were obtained. Only 2,5-disubstituted thiophenes allowed the selective formation of the 3-arylated thiophenes in moderate yields. Notably, sensitive C−Br and C−Si bonds were tolerated by these harsh reaction conditions. Moreover, perfluoroalkanesulfonyl chlorides could also be used as coupling partners under milder conditions (i.e., 120 °C in pentane) to provide the 2-(perfluorohexyl)thiophene derivatives in moderate yields.[106]

In 2014, Doucet and co-workers reported the Pd-catalyzed direct desulfitative arylation of thiophenes with benzenesulfonyl chlorides as the coupling partners (Scheme 18).[107] The reaction conditions are milder compared with those described with ruthenium catalysts (i.e., 140 °C in dioxane), and interestingly, the arylation took place exclusively at the C-3

Scheme 15[a,b]



[a] Pd(COD)Cl_2 was used instead of Pd$(OAc)_2$. [b] Reaction performed at 120 °C.

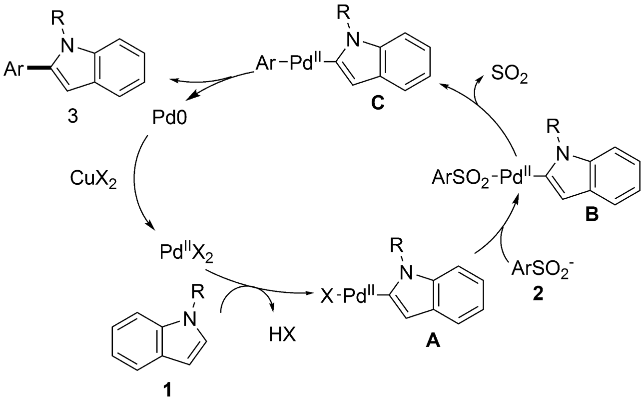
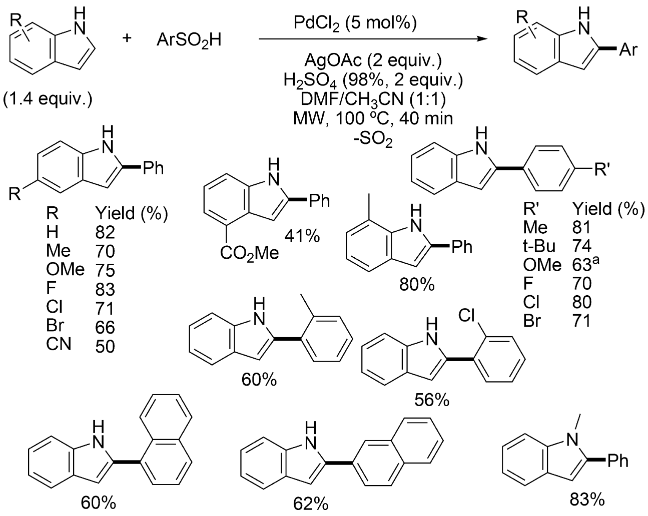


Figure 2.

Scheme 16[a]

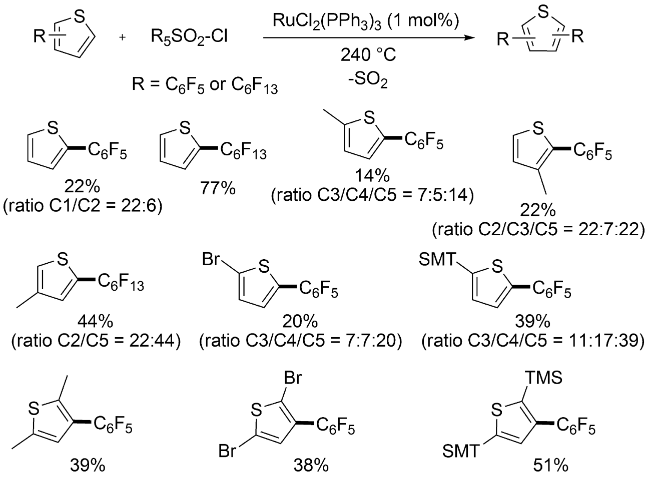


R	Yield (%)
H	82
Me	70
OMe	75
F	83
Cl	71
Br	66
CN	50

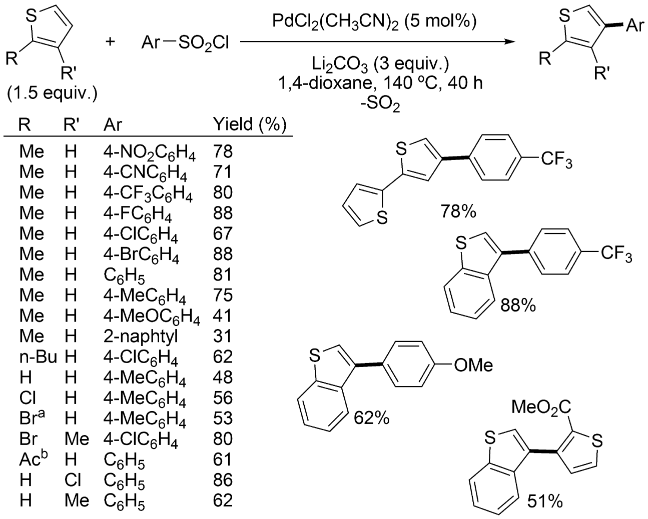
R'	Yield (%)
Me	81
t-Bu	74
OMe	63[a]
F	70
Cl	80
Br	71

[a] 10 mol % $PdCl_2$ was used.

Scheme 17



Scheme 18[a,b]



R	R'	Ar	Yield (%)
Me	H	4-NO$_2$C$_6$H$_4$	78
Me	H	4-CNC$_6$H$_4$	71
Me	H	4-CF$_3$C$_6$H$_4$	80
Me	H	4-FC$_6$H$_4$	88
Me	H	4-ClC$_6$H$_4$	67
Me	H	4-BrC$_6$H$_4$	88
Me	H	C$_6$H$_5$	81
Me	H	4-MeC$_6$H$_4$	75
Me	H	4-MeOC$_6$H$_4$	41
Me	H	2-naphtyl	31
n-Bu	H	4-ClC$_6$H$_4$	62
H	H	4-MeC$_6$H$_4$	48
Cl	H	4-MeC$_6$H$_4$	56
Br[a]	H	4-MeC$_6$H$_4$	53
Br	Me	4-ClC$_6$H$_4$	80
Ac[b]	H	C$_6$H$_5$	61
H	Cl	C$_6$H$_5$	86
H	Me	C$_6$H$_5$	62

[a] The reaction was performed using 1 equiv of 2-bromothiopene and 2 equiv of ArS0$_2$Cl. [b] The reactionwas performed from 1 equiv of 2-methyl-2-thiopene-2-yl-[1,3]-dioxolane and 2 equiv of ArS0$_2$Cl.

position, which is not the most common coupling position in Pd-catalyzed direct arylations of thiophene derivatives.[108−116] Electrophilic palladium(II) in the presence of 3 equiv of lithium carbonate (Li_2CO_3) as base provides a general method to access C-3 arylated thiophenes in high yields with a wide substrate scope, which includes sensitive functional groups, such as cyano, bromo, nitro, ester, etc. Following the same procedure, benzothiophene was also arylated at the β-position in high yields.

Albeit no mechanistic investigation has been performed, the authors proposed a mechanism pathway (Figure 3),[107] based on a Pd^{II}/Pd^{IV} catalytic system.[117−119] Indeed, it is known that benzenesulfonyl chlorides can oxidize Pd(II) into Pd(IV) by oxidative addition.[98] The reaction of benzenesulfonyl chloride with $PdCl_2(CH_3CN)_2$ might afford the intermediate **A**,[97,120] then **A** undergoes desulfonylation, followed by the coordination of thiophene to give the complex intermediate **B**. The migration of the aryl group to the β-carbon atom of thiophene gives **C**. Finally, base-assisted proton abstraction affords the β-arylated thiophene and regenerates the Pd(II) species.

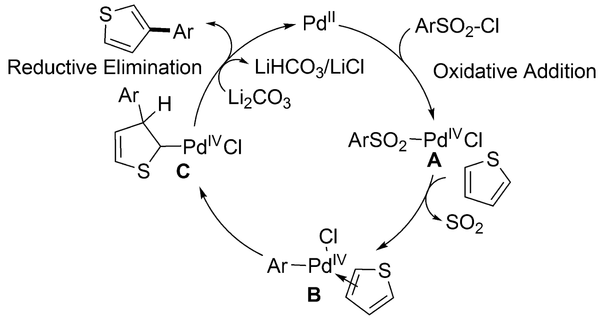
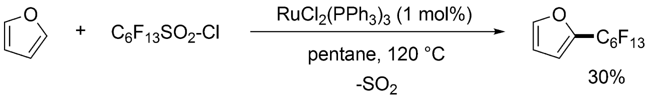


Figure 3.

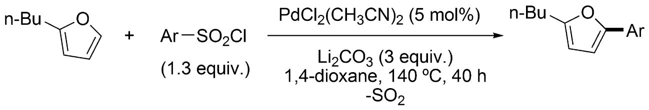
3.3. Furans and Benzofurans. In the course of their intensive work on Ru-catalyzed desulfitative perfluoroalkylation, and among other substrates such as arenes, pyrroles, or thiophenes, Kamigata and co-workers reported the reaction between furan and tridecafluorohexane-1-sulfonyl chloride (Scheme 19).[121] Only unsubstituted furan was tested, and the C2-arylated furan was isolated in a low 30% yield using the previously reported conditions: namely, 1 mol % $RuCl_2(PPh_3)_3$ in pentane at 120 °C.

Recently, Doucet and co-workers applied their reaction conditions to furan derivatives (Scheme 20).[122] *n*-Butylfuran or

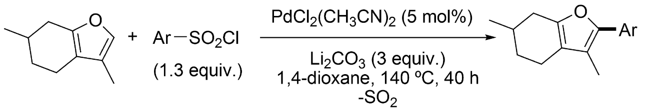
Scheme 19



Scheme 20



Ar	Yield (%)	Ar	Yield (%)
4-$NO_2C_6H_4$	88	4-BrC_6H_4	64
4-CNC_6H_4	89	C_6H_5	40
4-$CF_3C_6H_4$	79	2-CNC_6H_4	83
4-FC_6H_4	32	2-FC_6H_4	89
4-ClC_6H_4	50	1-naphtyl	44

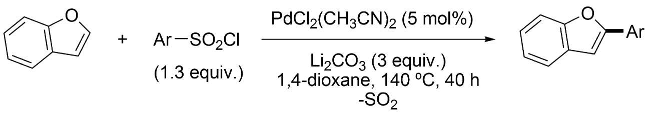


Ar	Yield (%)	Ar	Yield (%)
4-$NO_2C_6H_4$	80	4-ClC_6H_4	63
4-CNC_6H_4	82	4-BrC_6H_4	76
4-$CF_3C_6H_4$	78	C_6H_5	61
4-FC_6H_4	70	2-CNC_6H_4	83

menthofuran was reacted with a wide range of benzenesulfonyl chlorides in the presence of 5 mol % $PdCl_2(CH_3CN)_2$ catalyst to afford the desired C2-arylated products in moderate to high yields. However, furans bearing electron-withdrawing or electron-donating substituents as an additional functional group (e.g., furan-2-carbonitrile or 2-methoxyfuran) were found to be unreactive under these reaction conditions. A competitive reaction between 2-butylfuran and furan-2-carbonitrile showed a complete selectivity for the C-5 arylation of 2-butylfuran, whereas reactions using bromobenzene instead of benzenesulfonyl chloride afforded a mixture of both C-5 arylated furans (Scheme 21).[122]

Doucet and co-workers also investigated the direct desulfitative arylation of benzofuran with benzenesulfonyl chlorides (Scheme 22).[123] Using the same reaction conditions, they successfully arylated benzofuran at the C-2 position. It should be noted that the reaction was completely regioselective, whereas reaction using aryl bromides as coupling partners generally afforded a mixture of C2- and C3-arylated products or poor yields.[123−126]

Scheme 22



Ar	Yield (%)	Ar	Yield (%)
4-$NO_2C_6H_4$	69	4-MeC_6H_4	89
4-CNC_6H_4	80	4-$MeOC_6H_4$	39
4-$CF_3C_6H_4$	71	3-$CF_3C_6H_4$	64
4-FC_6H_4	90	3,5-$(CF_3)_2C_6H_3$	77
4-ClC_6H_4	77	3,5-$(Cl)_2C_6H_3$	85
4-BrC_6H_4	88	2-CNC_6H_4	50
C_6H_5	81	2-naphtyl	73

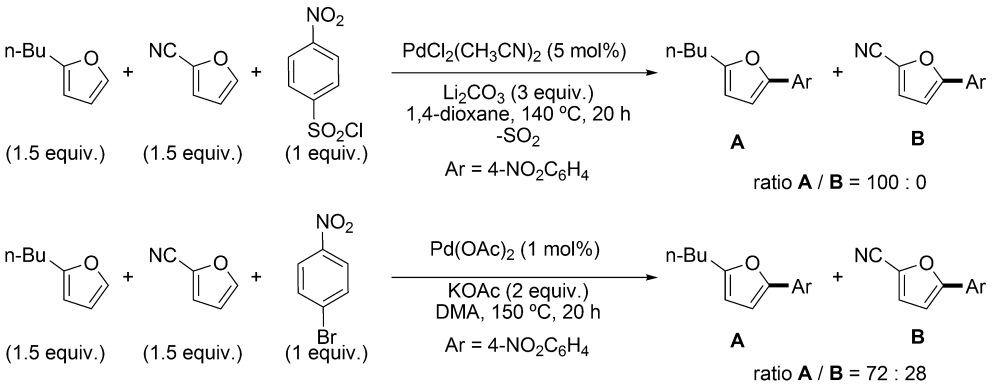
In summary, both ruthenium and palladium catalysis have been reported for the direct arylation of pyrroles, furans, or thiophenes using benzenesulfonyl chlorides as reactant. Although ruthenium catalysis showed poor regioselectivities and low yields and required harsh conditions, because the new ruthenium system showed high reactivity in modern C−H bond activation/functionalization,[10] they represent an important research area in the near future. In contrast to the ruthenium catalysis, palladium catalysis demonstrated a very good reactivity with sometimes unexpected regioselectivities (c.f., Scheme 18) for the direct desulfitative arylations of heteroarenes, albeit no example of direct alkylations has been reported. Using arenesulfinic acids instead of benzenesulfonyl chlorides, the direct desulfitative arylations of indoles has been performed even in the presence of NH-free indoles.

4. DIRECT DESULFITATIVE FUNCTIONALIZATION OF FIVE-MEMBERED RING HETEROARENES CONTAINING MORE THAN ONE HETEROELEMENT

Heteroarenes containing more than one heteroelement, such as benzoxazoles, thiazoles, imidazoles, or purine derivatives, are also important building blocks in organic chemistry, especially in pharmacology.[40] Recently, their modifications through direct C−H bond activation has emerged as one of the most suitable and reliable pathway to modify such structures. Most of them react at the most acidic position, which is the C−H bond flanked by the two heteroelements. This part will deal with the direct desulfitative arylation of such heteroarenes and is classified by the nature of the $ArSO_2R$ coupling partner (i.e, benzenesulfonyl chlorides, arenesulfinate salts, and arylsulfonyl hydrazides).

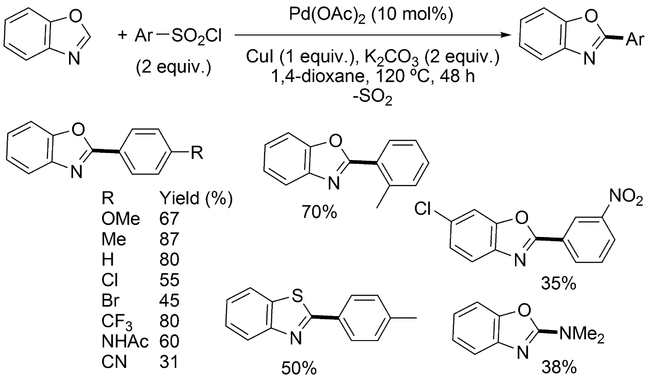
4.1. Benzenesulfonyl Chlorides As Coupling Partners. In 2011, Cheng and co-workers reported the first Pd-catalyzed

Scheme 21



direct desulfitative arylation of benzoxazole derivatives using benzenesulfonyl chlorides as coupling partners (Scheme 23).[127]

Scheme 23



The reaction displays a broad scope, including substrates bearing C−Br bonds. Under the same reaction conditions, benzothiazole was arylated in moderate yield. The authors extended this reaction to direct amination using dimethylsulfamoyl chloride as coupling partner, albeit in low yield.

The authors explained that the addition of copper salt is critical for the reactivity and rationalized its use by the formation of cuprate derivatives through an electrophilic attack of CuI on the benzoxazole C−H bond (Figure 4).

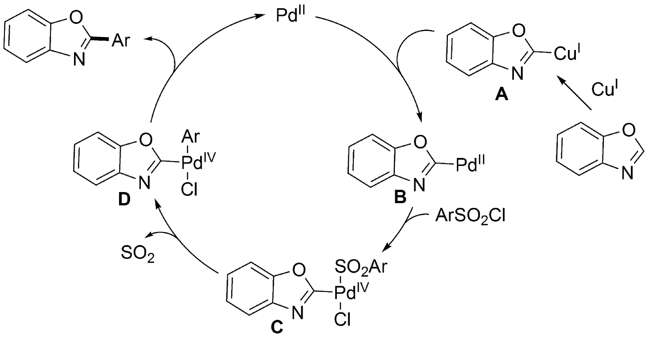


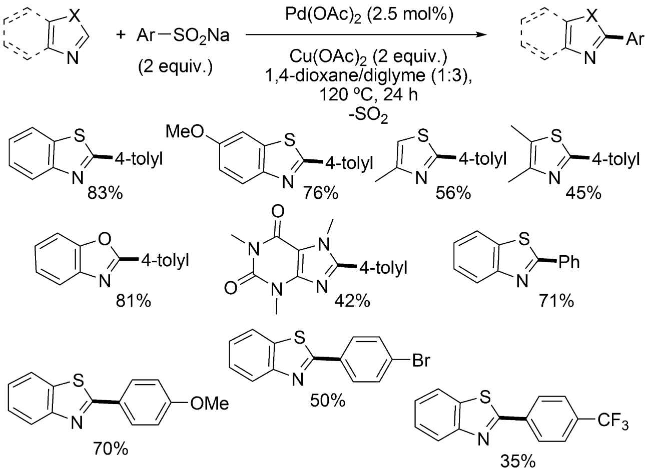
Figure 4.

4.2. Arenesulfinate Salts As Coupling Partners.

The same year, Deng reported a similar approach for the Pd-catalyzed direct desulfitative arylation of azoles but using sodium sulfinates as the aryl source (Scheme 24).[128] Several azoles, such as benzothiazoles, benzoxazoles, thiazoles, or caffeine, were arylated in moderate to high yields. Diverse substituents on the sulfinate benzene ring were tolerated, albeit the presence of electron-withdrawing groups decreased the reaction yields. Again, copper salts, which are used to oxidize Pd(0) into Pd(II), were used as an additive.

A similar mechanism involving a Pd^{II}/Pd^{0} catalytic cycle has been proposed (Figure 5).

Scheme 24



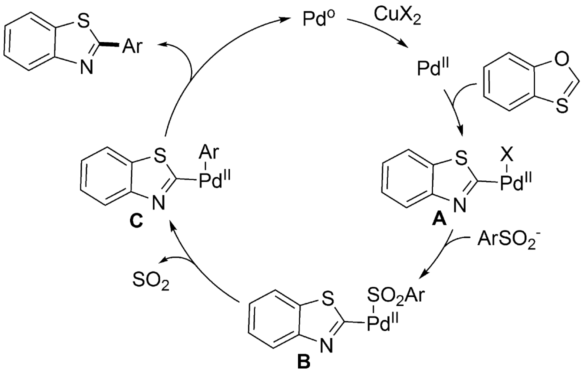
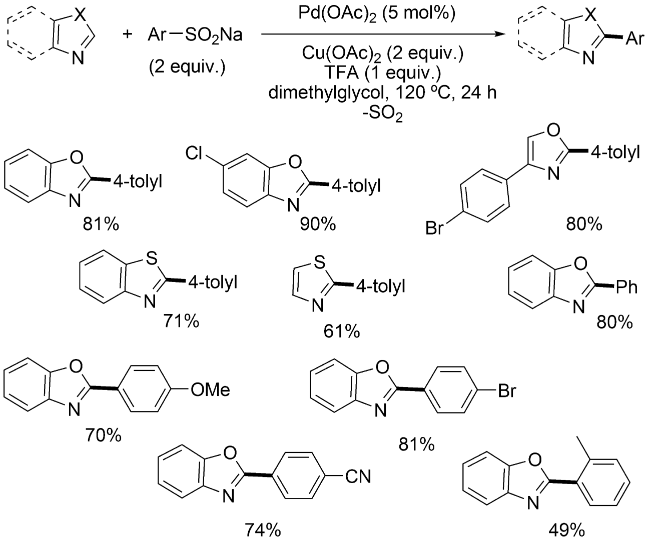


Figure 5.

Scheme 25



Wang and co-workers also reported a protocol for the direct desulfitative arylation of azoles with sodium sulfinates as the aryl source.[129] However, in contrast to classical C−H bond functionalization of azoles, which employs basic conditions, trifluoroacetic acid was used as the additive. The authors did not explain the role of this acid (Scheme 25). The scope of the reaction is similar to the one proposed by Deng, but additional heteroarenes such as simple oxazoles and 1,3,4-oxadiazoles also displayed high reactivities in these direct desulfitative arylations.

The proposed mechanism involves a carbopalladation of arylpalladium complex, generated via a desulfitation of intermediate **A**, on benzoxazole to form the intermediate **B**, followed by a *β*-hydride elimination (Figure 6). Again, no experiments were conducted to probe this mechanism.

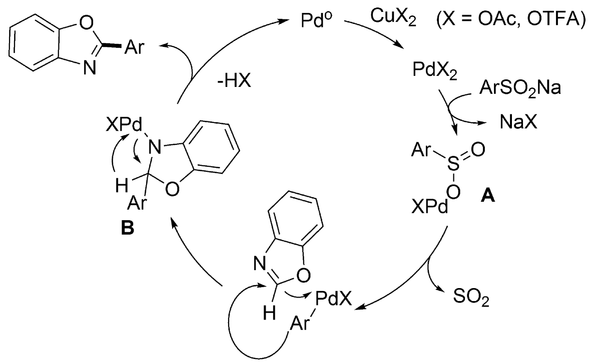
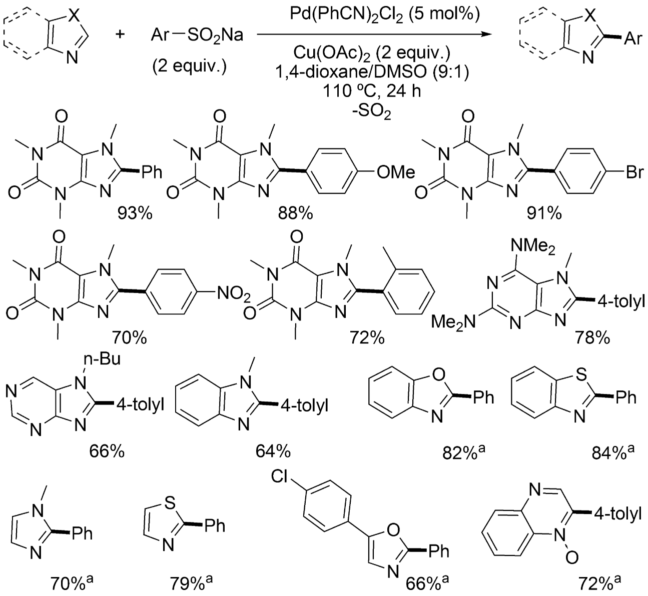


Figure 6.

You and co-workers also employed sodium sulfinates for the direct desulfitative arylation of heteroarenes (Scheme 26).[130]

Scheme 26[a]

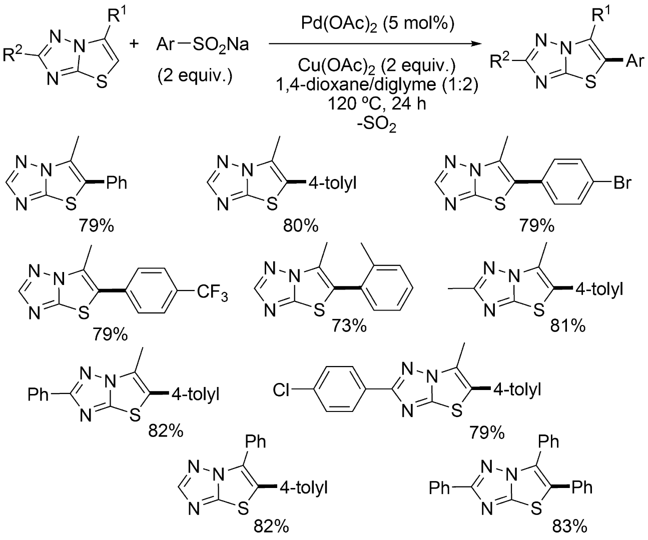


[a]Pd(OAc)2 (5 mol %) in combination of TBAB (20 mol %).

The reaction conditions were similar to those reported by Deng in Scheme 24 except for the source of palladium and the use of DMSO instead of diglyme as the cosolvent. The scope of the reaction focused mainly on caffeine derivatives, but some new heteroarenes, such as purine derivatives, imidazoles, and quinoxaline *N*-oxide, were also introduced for such desulfitative cross couplings.

In 2014, Liu and co-workers reported the Pd-catalyzed direct arylation of thiazolo[3,2-*b*]-1,2,4-triazoles with sodium sulfinates (Scheme 27).[131] The desired desulfitative arylation products were isolated in moderate to high yields using 5 mol % $Pd(OAc)_2$ as catalyst, and 2 equiv of $Cu(OAc)_2$ as oxidant in dioxane/diglyme at 120 °C. The solvent exhibited a significant effect on the reaction yields, and the best ratio between dioxane and diglyme was 1:2. The yield slightly decreased with an increasing proportion of diglyme. It is noteworthy that only C-5-arylated product was formed. As in the previous reports, no major effect of the sodium arylsulfinate substituents was observed. Moreover, a wide scope of substituted thiazolo[3,2-*b*]-1,2,4-triazoles could be arylated under these reaction conditions.

Scheme 27



A Pd(0)/Pd(II) mechanism was proposed, in which Pd(II)-catalyzes the C−H bond activation process, followed by a desulfitation and reductive elimination to afford the desired arylated product and Pd(0), which was reoxidized into Pd(II) by the copper salts (Figure 7).

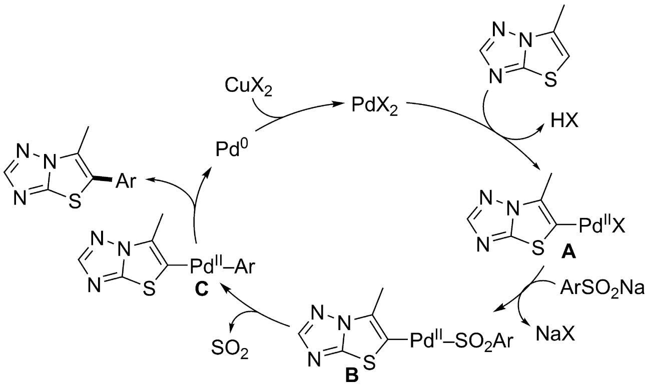
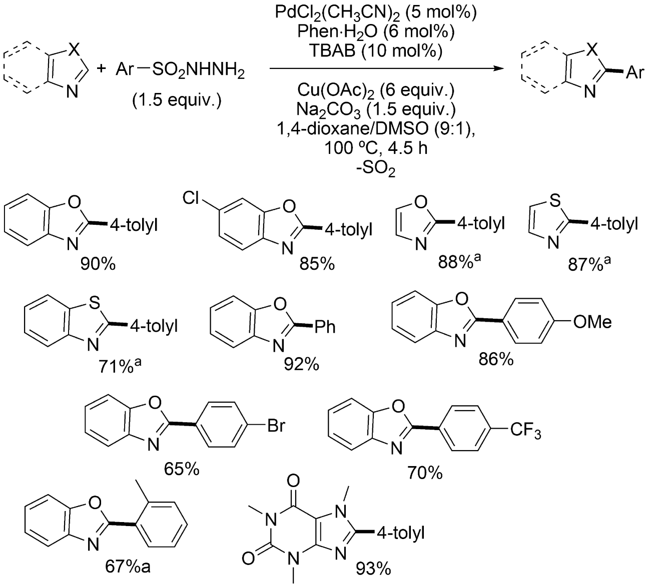


Figure 7.

4.3. Arylsulfonyl Hydrazides As Coupling Partners. In 2012, Wan and co-workers demonstrated that arylsulfonyl hydrazides could also be used as aryl sources in Pd-catalyzed desulfitative arylation of azoles (Scheme 28).[132] $PdCl_2(CH_3CN)_2$ associated with 1,10-phenantroline and tetra-*n*-butylammonium bromide, which favors the stabilization of active palladium specie, in the presence of copper and Na_2CO_3 as base in a mixture of dioxane/DMSO in 9:1 ratio was selected as the best catalytic system. The scope of this reaction includes benzoxazoles, oxazoles, benzothiazoles, thiazoles, and caffeine. Almost no effect of the substitution on the arylsulfonyl hydrazide partners was observed.

On the basis of control experiments, the authors proposed the mechanism shown in Figure 8. Copper-mediated denitrogenative and desulfitative oxidation of $TsNHNH_2$ affords the copper(II) aryl sulfonyl species **A**, which undergoes transmetalation to afford palladium *p*-tolyl intermediate **B**, which can subsequently lead to the 4,4′-dimethylbiphenyl byproduct **F**. This palladium *p*-toyl intermediate, **B**, is proposed to interact with benzoxazole, leading to C−H bond activation

Scheme 28[a]



[a]Without TBAB.

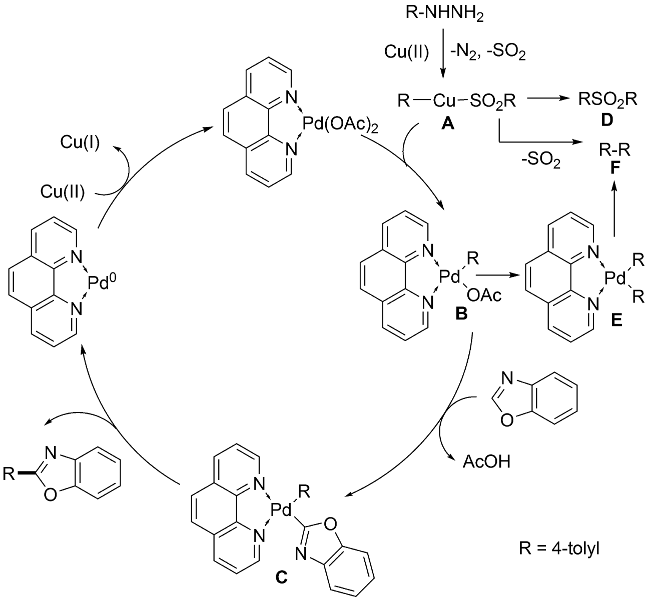


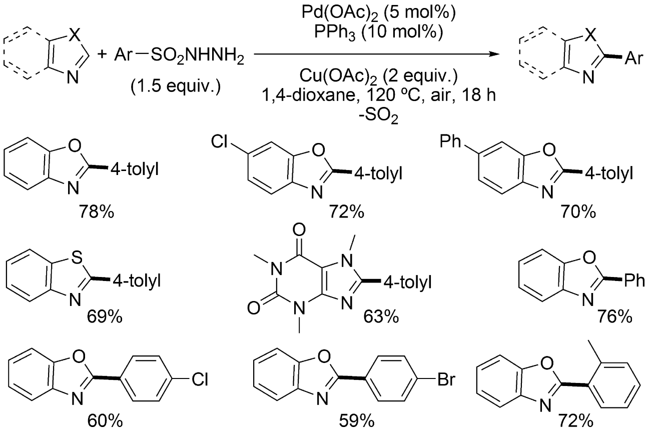
Figure 8.

and formation of the palladium(II) aryl heteroaryl intermediate **C**, then C−C reductive elimination furnishes the desired product. The catalytic cycle is completed by the oxidation of Pd(0) species into Pd(II) mediated by $Cu(OAc)_2$.

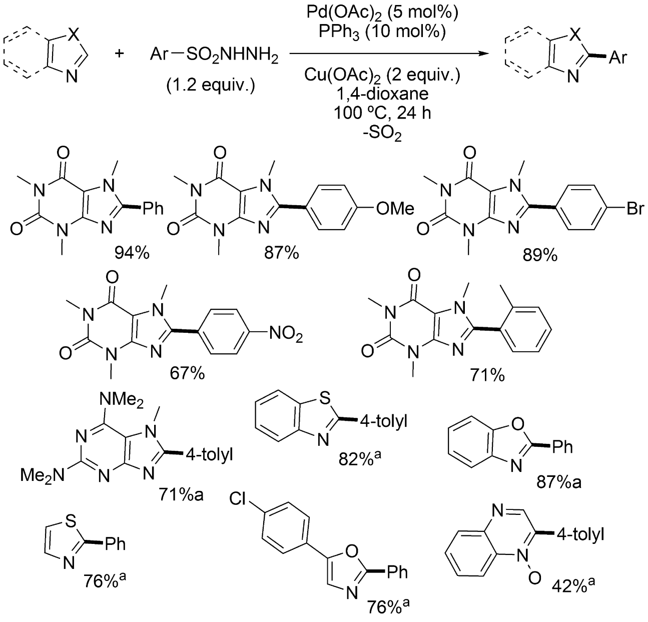
During the same period, Kwong and co-workers also described this transformation but using a simpler catalytic system, namely, $Pd(OAc)_2$ associated with triphenylphosphine, in the presence of only $Cu(OAc)_2$ (2 equiv) as an additive, in dioxane under air atmosphere (Scheme 29).[133]

On the basis of their previous work,[130] You and co-workers also performed the direct desulfitative arylation of heteroarenes using arylsulfonyl hydrazides as aryl source (Scheme 30).[134] The scope of the reaction is similar to the one with sodium sulfinate, and the desired arylated products were isolated in comparable yields.

Scheme 29



Scheme 30[a]



[a]The reactions were carried out using Pd(OAc)2 (0.0125 mmol), Cu(OAc)2 (0.5 mmol), heteroarene (0.25 mmol), and arylsulfonyl hydrazide (0.3 mmol) in dioxane/DMSO at 120 °C for 24 h.

The authors suggested a mechanism different from the copper-mediated desulfitation using arylsulfonyl hydrazides described in Figure 8, where aryl-palladium intermediate **D** was formed though successive deprotonation of the arylsulfonyl hydrazide, *β*-hydride elimination and liberation of N_2 and SO_2 gas. Then, copper promotes the C−H bond activation process of the *N*-heterocycle, followed by a transmetalation to afford the intermediate **E**, which gives the desired product after reductive elimination. Next, the catalytic cycle was closed by the reoxidation of Pd(0) into Pd(II) by the copper salts (Figure 9).

As seen in this section, the direct desulfitative arylations of heteroarenes containing more than one heteroelement has been performed only with palladium catalysts. The benzenesulfonyl chlorides have found applications only for the direct arylation of benzoxazole derivatives because so far, such couplings with other heteroarenes have not been reported. The narrow scope of the reaction with benzenesulfonyl chlorides could be attributed to their specific reactivities because they might

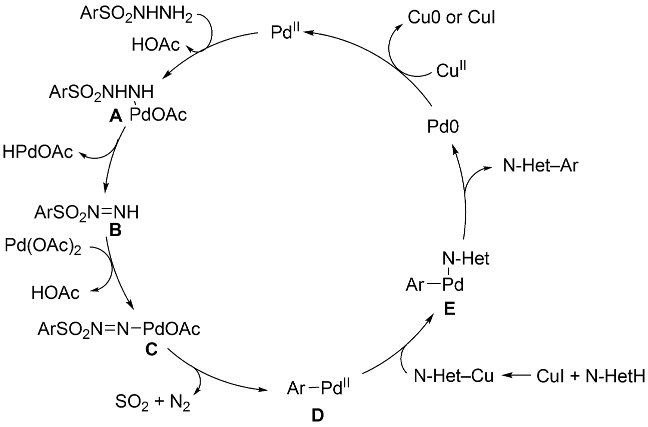


Figure 9.

directly react with heteroarenene derivatives to afford sulfonation products. Arenesulfinate salts as the aryl source display a wider scope: benzoxazoles, benzothiazoles, thiazoles, caffeine, imidazoles, quinoxaline *N*-oxide, or thiazolo[3,2-*b*]-1,2,4-triazoles were arylated in moderate to high yields. However, the direct arylation with such coupling partners requires the use a stoichiometric amount of copper salts as an additive to reoxidize Pd(0) into Pd(II). More recently, arylsulfonyl hydrazides have been introduced for such coupling reactions with similar scope rather than with arenesulfinate salts, again using a stoichiometric amount of copper(II) as an additive.

5. GENERAL CONCLUSION AND PERSPECTIVES

In summary, during the past five years, the scope of the metal-catalyzed direct arylation or alkylation of (hetero)arenes using $AlkSO_2R$ or $ArSO_2R$ derivatives as the coupling partners has been largely extended. The most common catalysts for such couplings remain Pd- and Ru-based systems. On the other hand, the recent modifications of these coupling partners, such as the use of $ArSO_2Na$ or $ArSO_2NHNH_2$, explored for this coupling demonstrate that they are actually regarded as one of the most promising alternatives to aryl halides to arylate or alkylate arenes.

The use of $AlkSO_2R$ or $ArSO_2R$ as coupling partners presents several advantages compared with the reactions with aryl halides. In some cases, such as for the Pd-catalyzed arylation of thiophenes, C3-arylation products were obtained, whereas with aryl halides, regioselective C2-arylated thiophenes were generally produced. A change in the regioselectivity was also observed in the course of the arylation of benzofurans because the use of $ArSO_2Cl$ selectively affords the C2-arylated benzofurans, whereas reactions performed with aryl halides generally afford mixtures of C2- and C3-arylated and also C2,C3-diarylated benzofurans. Moreover, the coupling with most $ArSO_2R$ derivatives tolerates several functional groups, including bromo and iodo substituents, allowing further transformations.

Despite the numerous recent reports, a number of challenges remain. So far, only a few arenes and heteroarenes have been found to be reactive for such direct arylations, and for some couplings, especially with $ArSO_2Cl$ derivatives, the functional group tolerance remains limited. Moreover, some reactions led to mixtures of regioisomers, low yields, or both. Therefore, more efficient catalysts permitting wider substrate scope or lower catalyst loadings need to be discovered to provide more attractive procedures. The influence of the nature of the (hetero)arene on the reactivities and selectivities needs to be explored in more detail. In addition, only a few examples of desulfitative coupling with $AlkSO_2R$ derivatives have been reported because so far, only reactions with perfluorinated reactants using ruthenium catalyst have been employed. Hence, new catalytic systems and other transition metals should be investigated to develop new direct alkylation methods with a wider substrate scope. Concerning catalytic cycles and elementary steps, a large number of interrogations are not addressed. Determining the reasons for the various reactivities and regioselectivities for these reactions could allow further improvement in terms of reaction scope; however, this methodology will undoubtedly help both material and synthetic chemists a great deal, making access to several arene derivatives simpler.

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Notes

The authors declare no competing financial interest.

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