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Aryl fluorosulfates: powerful and versatile partners in cross-coupling reactions

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Aryl fluorosulfates are versatile building blocks in organic synthesis and have gained increasing attention in SuFEx (Sulfur Fluoride Exchange) click chemistry. They are easily and conveniently prepared from phenols using sulfuryl fluoride SO_2F_2 as a low-cost sulfonyl fluoride provider. Recently, they served as less toxic and more atom economical alternatives to triflates in an impressive number of carbon–carbon and carbon-heteroatom cross-coupling reactions. In this review, we summarize the current advances and developments in applying aryl fluorosulfates as electrophilic partners in cross-coupling reactions.

1 Introduction

Organic halides are extensively used as electrophilic partners for transition-metal-catalyzed cross-coupling reactions.[1] However, their environmental toxicity (due to the generation of stoichiometric quantities of halide waste) and high costs limited their utility in large-scale syntheses in industrial applications.[2] Therefore, considerable attention has been paid to phenol derivatives as easily accessible and naturally abundant alternative electrophiles.[3]

Due to their superior performance as electrophilic coupling partners, triflates have long been used as alternatives and/or replacements for halogens in cross-coupling reactions.[4] However, despite their excellent reactivity, they suffer from several disadvantages, such as instability, environmental toxicity, high cost of preparation, and poor atom economy.[2] These problems ultimately limit their application profile on larger scales. Consequently, many efforts have been spotted in seeking alternatives to triflates and several complementary O-based pseudohalides such as tosylates, mesylates, nonaflates, and fluorosulfates has been developed as viable electrophilic partners.[5] Although tosylates and mesylates are less expensive and more stable than triflates; however, they are considerably less reactive electrophiles than triflates.[6] Nonaflates are not only more cost effective and stable than triflates but also have comparable if not greater levels of reactivity.[7] However, they are less atom economic and creating more toxic long-chain fluorocarbon waste. On the other hand aryl fluorosulfates have become increasingly popular as coupling partners in organic synthesis due to several advantages over traditional aryl halides, such as bromides and chlorides. One of the main benefits of using aryl fluorosulfates is their higher reactivity and selectivity towards transition metal-catalyzed coupling reactions.[8] This makes them attractive for efficient and selective transformations. Additionally, the reaction conditions for aryl fluorosulfates are often milder compared to aryl halides, which reduces the occurrence of unwanted side reactions and allows for the use of more sensitive functional groups. Furthermore, aryl fluorosulfates are less toxic and more environmentally friendly than aryl halides, making them a more appealing choice for large-scale industrial applications.[8,9] Overall, the use of aryl fluorosulfates as coupling partners offers significant advantages over traditional aryl halides and has become a valuable tool in modern organic synthesis. Moreover, they can be easily prepared from the reactions of phenol or alcohol derivatives with various sulfonyl fluoride (SO_2F) sources such as sulfuryl fluoride, fluorosulfonic acid, sulfuryl chloride fluoride, and fluorosulfonic anhydride.[8]

As early as 1991, the first report on the usefulness of aryl fluorosulfates as electrophilic partners in cross-coupling reactions was published by Roth *et al.*[9] However, since then, this page of cross-coupling reactions did not attract the attention of chemists for nearly 25 years. Since 2015, several research groups investigated the scope and limitation of these new classes of

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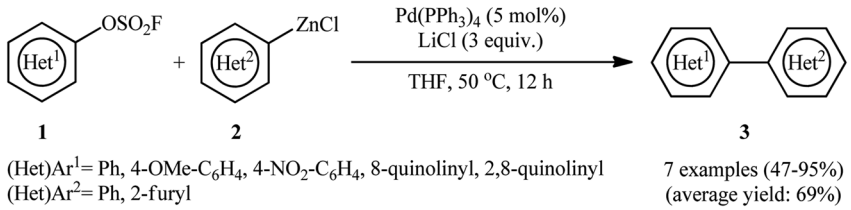


Scheme 1 Roth's synthesis of bi(hetero)aryls **3**.

electrophilic components in various carbon–carbon and carbon-heteroatom cross-coupling reactions. In 2018, Qin and co-workers published an interesting review paper entitled "Synthesis and Chemical Transformations of Fluorosulfates" that highlights some of the advances in this interesting research topics; albeit with only 7 examples.[8] Since a number of remarkable advances and developments in this domain have occurred during the past few decades, seems it is an appropriate time to summarize those discoveries in a comprehensive review. In continuation of our preceding works on cross-coupling reactions[10] and modern organic synthesis,[11] in this review, we intend to highlight the most important explorations and developments in the cross-coupling reactions using fluorosulfates from 1991 till today. For clarity, the topic is divided into two major parts. The first section covers the available literature on carbon–carbon cross-coupling reactions using fluorosulfates, while the second focuses exclusively on the carbon-heteroatom (nitrogen, oxygen, phosphorus) cross-coupling reactions. We hope that this review will inspire researchers to make further progress in this attractive research arena.

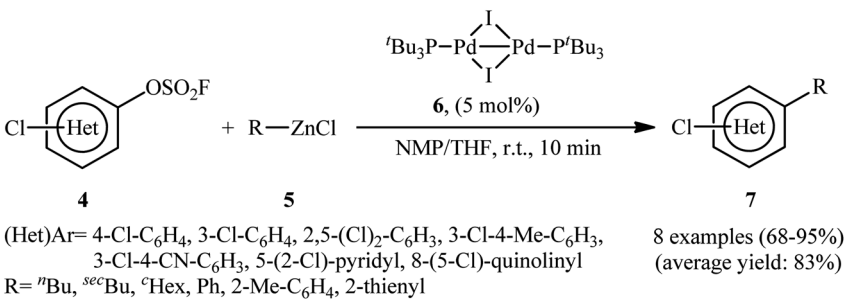
2 Carbon–carbon cross-coupling reactions

In this section, we describe the current literature on C–C cross-coupling reactions utilizing aryl fluorosulfonates as electrophilic partners. Cross-coupling reactions with organometallic nucleophiles are discussed first. This is followed by Suzuki–Miyaura and Sonogashira cross-coupling reactions. Finally, reported examples on carbonylative cross-coupling reactions will be covered at the end of the section.

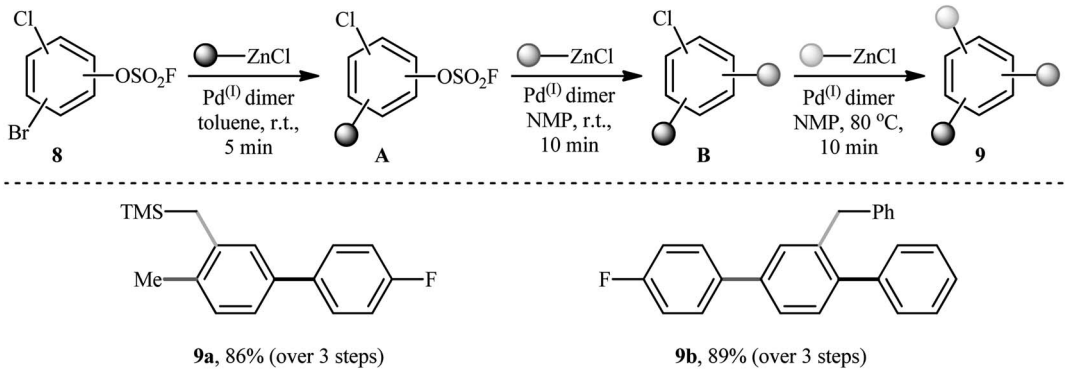
2.1. Negishi cross-coupling

The Negishi cross-coupling can be best described as the reaction between organic (pseudo)halides with organozinc compounds to construct new carbon–carbon bonds with the aid of a transition metal catalyst, mainly palladium complexes.[12] This synthetic method has gained increasing popularity among synthetic chemists especially in the field of natural products total synthesis.[13] In 1991, Roth and Fuller reported the first examples of the Negishi coupling utilizing fluorosulfonates in the place of the halide component.[9] They showed that the reaction of (hetero)aryl fluorosulfonates **1** with a small library of organozinc chlorides **2** in the presence of a catalytic amount of $Pd(Ph_3)_4$ in THF afforded corresponding bi(hetero)aryls **3** in moderate to excellent yields (Scheme 1). Notably, the reaction was not limited to using organozincs as the nucleophilic coupling partner. Organostannanes were also competent coupling partners, providing biaryl and styrene derivatives in good yields.

Three decades later, in 2020, Schoenebeck's research group described an effective site-selective coupling of Cl-substituted (hetero)aryl fluorosulfonates **4** with various aliphatic, aromatic, and heteroaromatic organozinc reagents **5** using a dinuclear Pd(I)-iodo-dimer catalyst **6**.[14] This synthetic transformation exhibited an efficient and attractive method for the high yielding synthesis of Cl-substituted bi(hetero)aryl and (hetero)aryl-alkyl derivatives **7** at room temperature under additive-free conditions within minutes (Scheme 2). Of note, the reaction exhibited extremely high degree of site-selectivity, in which functionalization is exclusively took place on the carbon atom attached to the fluorosulfonate group in arenes (C–OSO_2F *vs.* C–Cl). Interestingly, when Cl was replaced with Br, exclusive coupling at C–Br was seen under the identical conditions (C–Br



Scheme 2 Dinuclear Pd-catalyzed coupling of (hetero)aryl fluorosulfonates **4** with organozinc reagents **5**.



Scheme 3 Triply selective sequential functionalization of (hetero)arenes **8** developed by Schoenebeck *et al.*

vs. C–OSO_2F). The authors, nicely applied these principles for the diversification of (hetero)arenes **8** with multiple competing coupling sites (–OSO_2F, –Cl, –Br) with organozinc chlorides by doubly and triply selective sequential functionalization in the sequence C–Br, then C–OSO_2F, then C–Cl (Scheme 3). In this report, the authors also undertook computational studies regarding the reactivity scale for oxidative addition of Ar–OSO_2R derivatives (R = OMs, OTs, OFs, OTf, and ONf). Therefore, M06 density functional theory studies on the oxidative addition of $PhOSO_2R$ derivatives with $Pd(0)P(^tBu)_3$ as a model catalyst, suggested a 5-membered neutral transition states arrangement to be favored for C–OSO_2F activation and predicted virtually identical activation barriers as for triflates and nonaflates.

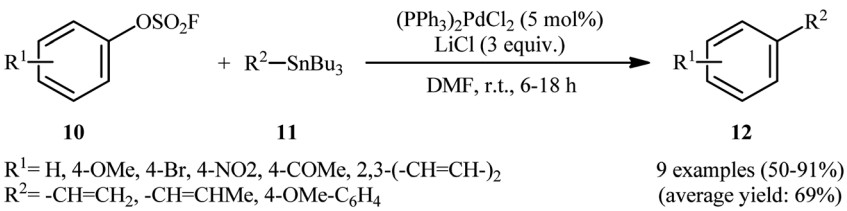
2.2. Stille cross-coupling

In 1991, in the same paper describing the first example of Negishi cross-coupling utilizing aryl fluorosulfonates as coupling partner in the presence of catalytic amounts of palladium, Roth and Fuller also reported the usefulness of these electrophilic components in the Stille cross-coupling.[9] Thus, in the presence of a combination of $(PPh_3)_2PdCl$ and LiCl in DMF at ambient temperature, the reaction of various aryl fluorosulfonates **10** bearing both electron-withdrawing and electron-donating groups with a range of aryl- and vinyl-stannanes **11** furnished the corresponding coupling products **12** in moderate to excellent isolated yields, ranging from 50% to 91% (Scheme 4). Notably, in the case of internal vinyl-stannanes substrates, the preferential formation of the (*Z*)-isomers was observed as evidenced by ^1H NMR. To the best of our knowledge this is the only example on the Stille coupling employing aryl fluorosulfonates reported till date.

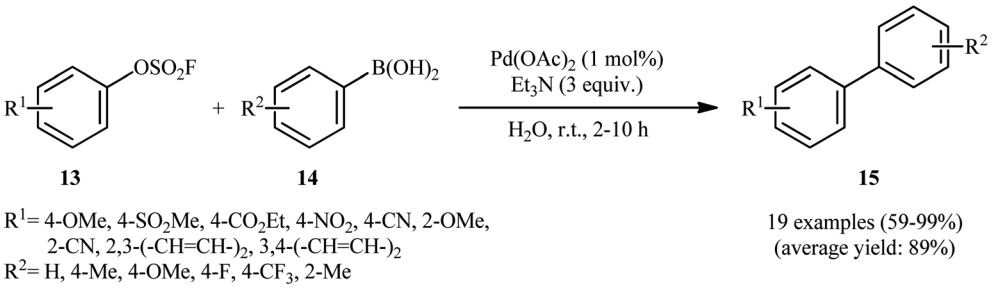
2.3. Suzuki–Miyaura cross-coupling

The Suzuki–Miyaura cross-coupling involves the coupling of an organoboron reagent with a (pseudo)halide for the construction of C–C bonds.[15] This coupling is one of the widely used reactions in the manufacture of pharmaceuticals and is the most common biaryl bond forming reaction.[16]

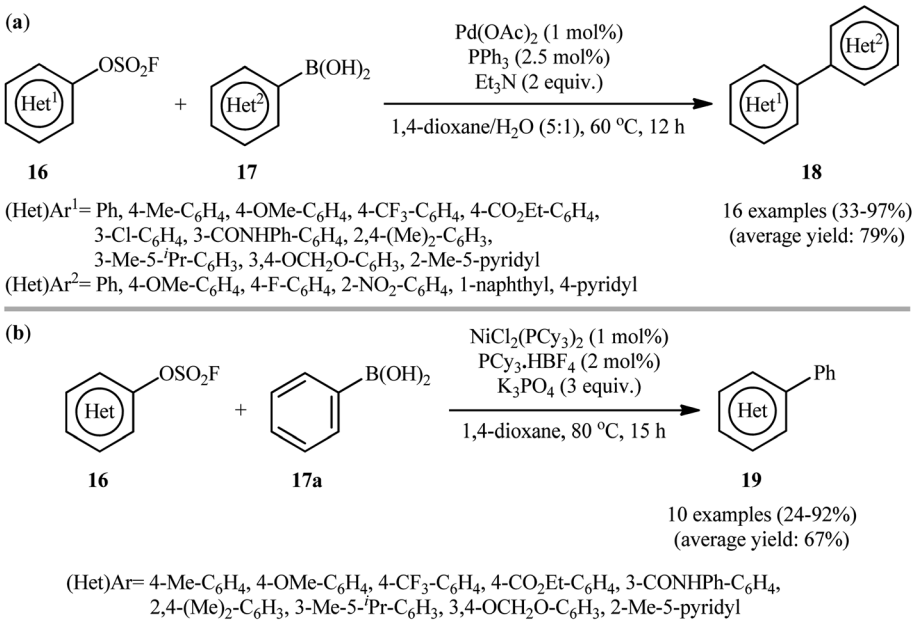
In 2015, Sharpless and Jiang along with their co-workers published one of the earliest reports on the Suzuki–Miyaura coupling reaction using aryl fluorosulfates as electrophilic coupling partners.[17] They showed that the treatment of various aryl fluorosulfates **13** with aryl boronic acids **14** in the presence of a combination of $Pd(OAc)_2$ and Et_3N in the most environmentally benign solvent, water, resulted in the formation of the corresponding biaryls **15** in good to quantitative yields (Scheme 5). The reaction is noteworthy in that both electron-rich and electron-poor aryl boronic acids were well tolerated. However, due to lower reactivity of electron-rich aryl fluorosulfates in compared to electron-deficient substrates, a higher catalyst and base loading as well as longer reaction time were required to obtain satisfactory results. It should be mentioned that compared with other traditional electrophilic coupling partners, including aryl halides, triflates, tosylates and mesylates, aryl fluorosulfates gave much better yields in Suzuki–Miyaura reaction with boronic acids under the identical conditions. Intriguingly, the catalytic system also showed good reactivity in double Suzuki couplings of diaryl-OSO_2F to afford the corresponding products in excellent yields. The authors also disclosed that aryl fluorosulfates are amenable coupling partners in other types of coupling reactions, including Heck, Sonogashira, and homocoupling reactions. However, only single examples have been reported for each of those reactions.



Scheme 4 Pd-catalyzed coupling of aryl fluorosulfonates **10** with aryl- and vinyl-stannanes **11**.



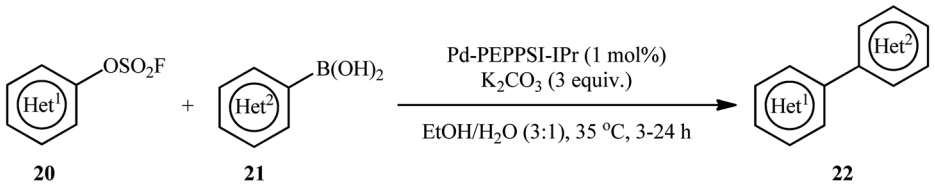
Scheme 5 Suzuki–Miyaura coupling of aryl fluorosulfates **13** with aryl boronic acids **14** in water.



Scheme 6 (a) Hanley's synthesis of biaryls **18**; (b) Ni-catalyzed Suzuki reaction using aryl fluorosulfates **16**.

Concurrently, Hanley and co-workers reported a closely related coupling between aryl fluorosulfonates **16** and (hetero) aryl boronic acids **17** employing the combination of $Pd(OAc)_2$, PPh_3, and Et_3N as catalytic system.[18] The reaction was conducted in the binary solvent 1,4-dioxane/H_2O (5 : 1), tolerated various important functional groups (*e.g.*, OMe, F, Cl, NO_2, CONHPh), and provided the desired biaryls **18** in moderate to excellent yields (Scheme 6a). However, amino group was incompatible in this system. Interestingly, one-pot version of this transformation using *in situ* generated aryl fluorosulfonates from the corresponding phenols was also examined under the optimized conditions and the desired products were obtained in satisfactory yields. It is noteworthy that a series of competition experiments between phenyl boronic acid, tolyl fluorosulfonate and traditional electrophilic coupling partners (1 : 1 : 1 mixture) under the standard conditions revealed that the relative reactivity of examined electrophiles follows the trend I > Br > OTf ≈ OFs ≫ Cl, OTs, OMs. In this study, the authors also disclosed the usefulness of nickel catalysts as cheaper alternatives to palladium-based catalysts for this transformation. Thus, with the $NiCl_2(PCy_3)_2/PCy_3 \cdot HBF_4/K_3PO_4$ catalytic system, the same set of aryl fluorosulfonates **16** efficiently reacted with phenyl boronic acid **17a** to give the corresponding biaryl products **19** in good yields (Scheme 6b). Of note, in contrast to reactions performed with palladium catalysts, higher yields of products were obtained for electron-rich aryl fluorosulfonates than for electron-poor ones in reactions catalyzed by nickel. However, the nickel system was less tolerant to hierarchy sterically hindered fluorosulfonates than the palladium system. More importantly, in comparison to the complete lack of activity of the Pd-catalyst system with the primary amine containing fluorosulfonate, the Ni-catalyst system showed good compatibility with amino-group.

Drawing inspiration from these elegant works, Zhang, Sharpless and colleagues discovered that treatment of various nitrogen- and sulfur-containing heteroaromatic fluorosulfonates **20** with (hetero)aryl boronic acids **21** in the presence of Pd-PEPPSI-IPr/K_2CO_3 combination as the catalytic system in EtOH/H_2O (3 : 1) afforded the corresponding bi(hetero)aryls **22** in good to quantitative yields, ranging from 67% to 99% (Scheme 7); in addition, a tolerance for vinyl boronic acid was also demonstrated.[19] A series of important competition studies



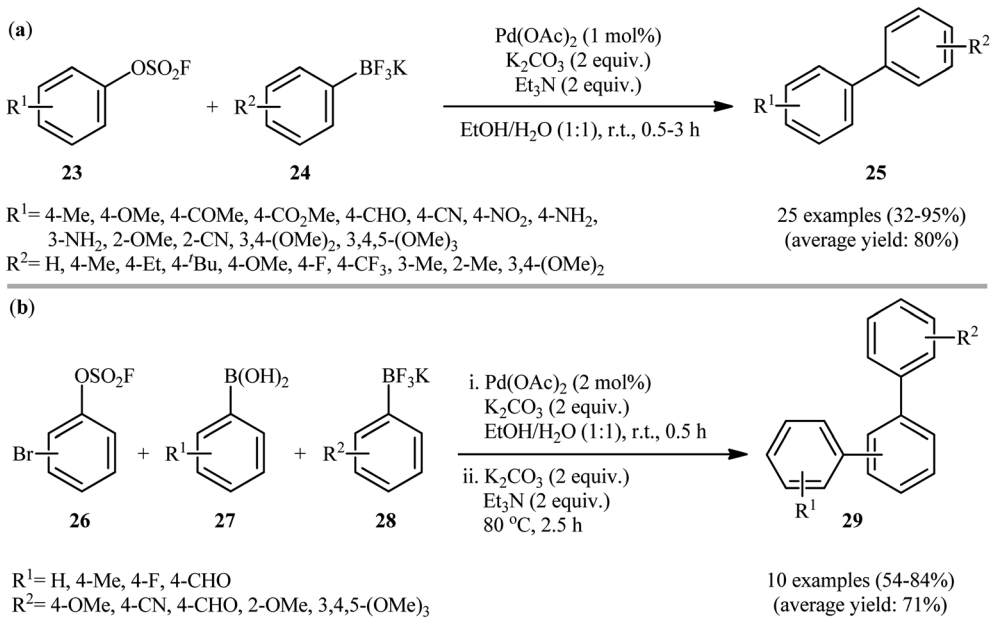
(Het)Ar^1= 2-pyridyl, 3-Me-2-pyridyl, 4-Me-2-pyridyl, 5-Me-2-pyridyl, 6-Me-2-pyridyl, 4-CO_2Me-2-pyridyl, 3-pyridyl, 6-F-3-pyridyl, 2-CO_2Me-3-thienyl, 4-benzothienyl, 8-quinolinyl, 1-SO_2F-5-indolyl
(Het)Ar^2= Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-CF_3-C_6H_4, 4-CN-C_6H_4, 4-CHO-C_6H_4, 4-CO_2Et-C_6H_4, 4-SO_2Me-C_6H_4, 3-CH_2OH-C_6H_4, 3-OH-C_6H_4, 3-NHCOMe-C_6H_4, 3-NO_2-C_6H_4, 1-naphthyl, 4-pyridyl, 2-Me-5-pyridyl, 2-CHO-5-furyl

Scheme 7 Suzuki reaction of heteroaromatic fluorosulfonates **20** with (hetero)aryl boronic acids **21** catalyzed by Pd-PEPPSI-IPr.

demonstrated the relative reactivity of examined leaving groups on substituted pyridines to be Br ≥ OTf > OSO_2F > Cl, which was in agreement with the finding of Hanley *et al.*[18] In order to further value the applicability of their methodology, the authors successfully synthesized Etoricoxib, an anti-inflammatory drug, from 5-bromo-6-chloropyridin-3-yl fluorosulfate through chemoselective sequential Suzuki cross-coupling reactions in an overall yield of 40.3%.

Subsequently, Li-Yuan's research group extended the substrates scope of organoboron compounds in the above procedure to potassium aryl trifluoroborates employing $Pd(OAc)_2$ as the catalyst and a combination of Et_3N and K_2CO_3 as the mix base.[20] The binary solvent EtOH/H_2O (1 : 1) was found to be the best medium for the reaction and, among several solvents tested, MeCN was found to be less effective. Apparently, the outcome of reaction was also dependent on the selected atmosphere. Also the same product yields were obtained under air and O_2 atmosphere. The reaction rate was quite slower under N_2 atmosphere. Therefore, it can be concluded that oxygen has a promoting effect on this transformation. Under optimized conditions, a wide range of aryl fluorosulfonates **23** bearing both electron withdrawing and donating groups including primary amine coupled with a variety of aryl trifluoroborates **24** to give the desired biaryls **25** in moderate to excellent yields (Scheme 8a). Additionally, this synthetic strategy was extended to one-pot double Suzuki–Miyaura reactions of bromophenyl fluorosulfates **26**, aryl boronic acids **27** and potassium aryltrifluoroborates **28**, allowing the synthesis of various biologically important unsymmetrical terphenyl derivatives **29** (Scheme 8b).

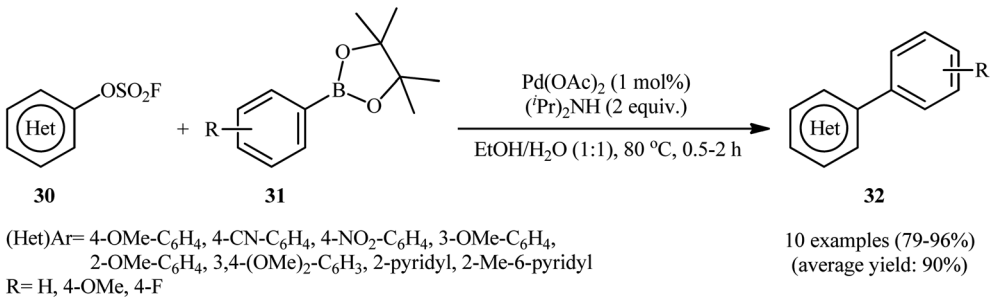
Shortly afterwards, the same research group reported the usefulness of arylboronic acid esters as coupling partners in the titled reaction.[21] Thus, by using a closely similar system [$Pd(OAc)_2$, (^{i}Pr)$_2$NH, EtOH/H_2O], the reaction of a series of



R^1= 4-Me, 4-OMe, 4-COMe, 4-CO_2Me, 4-CHO, 4-CN, 4-NO_2, 4-NH_2, 3-NH_2, 2-OMe, 2-CN, 3,4-$(OMe)_2$, 3,4,5-$(OMe)_3$
R^2= H, 4-Me, 4-Et, 4-^{t}Bu, 4-OMe, 4-F, 4-CF_3, 3-Me, 2-Me, 3,4-$(OMe)_2$

R^1= H, 4-Me, 4-F, 4-CHO
R^2= 4-OMe, 4-CN, 4-CHO, 2-OMe, 3,4,5-$(OMe)_3$

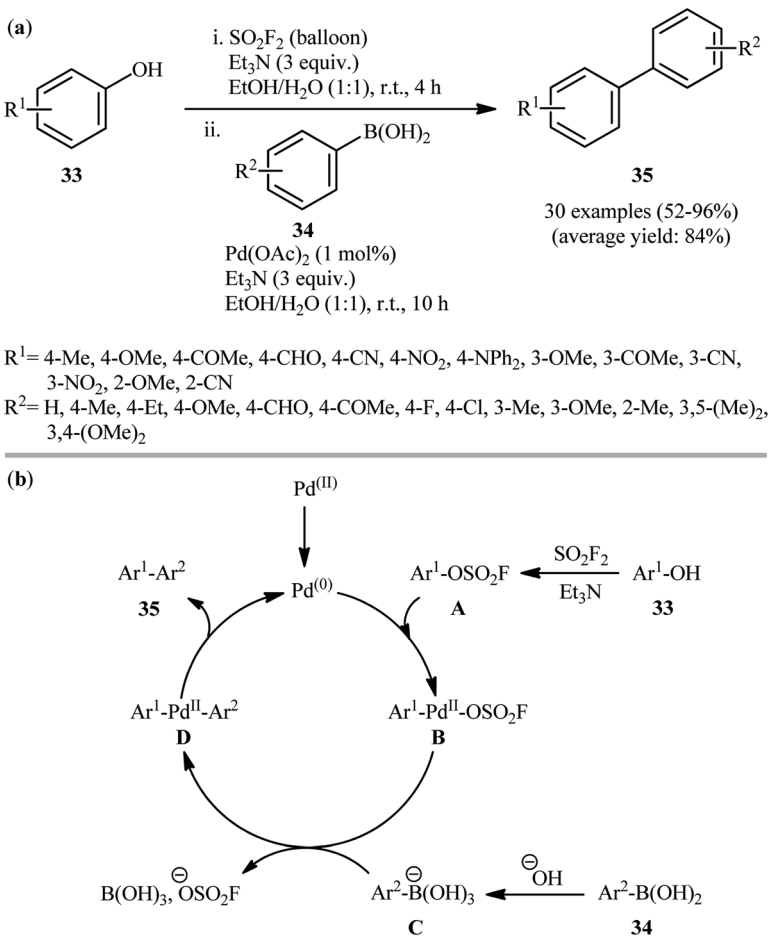
Scheme 8 (a) Suzuki reaction of aryl fluorosulfates **23** and potassium aryltrifluoroborates **24**; (b) Li-Yuan's synthesis of terphenyls **29**.



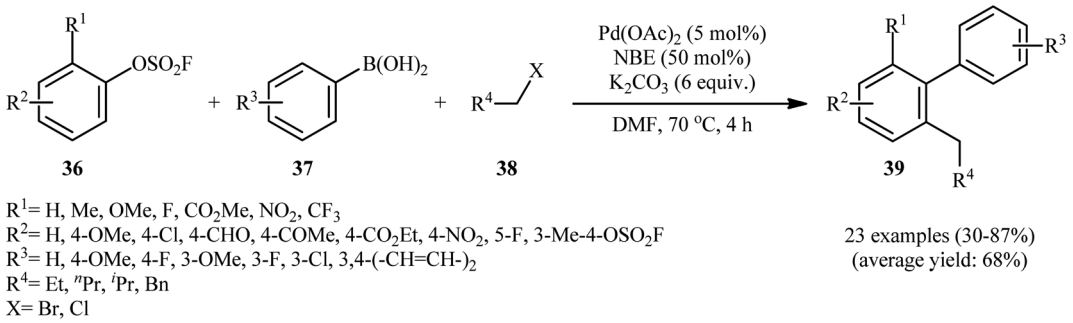
Scheme 9 Suzuki reaction of (hetero)aryl fluorosulfates **30** and arylboronic acid pinacol esters **31**.

(hetero)aryl fluorosulfonates **30** with arylboronic acid pinacol (BPin) esters **31** furnished the expected bi(hetero)aryls **32** within 30–120 min (Scheme 9). Notably, compare to the corresponding aryl trifluoroborates, pinacol arylboronates afforded higher yield of the target products under the identical conditions. The coupling of aryl *N*-methyliminodiacetic acid (MIDA) boronates was also feasible in this system, albeit in diminished efficiency.

Recently, in another important development, the same research group demonstrated that phenols **33** can be converted to biaryls **35** in a one-pot process *via* Suzuki coupling of *in situ* formed fluorosulfonates with aryl boronic acids **34**.[22] The authors identified a combination of $Pd(OAc)_2$ and Et_3N as the optimal system for this transformation. As shown in Scheme 10a, the reactions proceed well with both electron-rich and electron-poor partners; however, pyridin-ol derivatives and highly hindered aryl boronic acids (*e.g.*, 2,6-dimethylbenzeneboronic acid) are not suitable substrates for this cross-coupling. This tandem reaction could also be easily scaled up to the gram-scale as exemplified by the formation of 4′-methyl-[1,1′-biphenyl]-2-carbonitrile on a 1.26 g scale (81.5%). Noteworthy,



Scheme 10 (a) Synthesis of biaryls **35** through a one-pot sequential fluorosulfonation-Suzuki coupling approach developed by Li-Yuan's group; (b) mechanistic explanation for the formation of biaryls **35**.



Scheme 11 Synthesis of multisubstituted arenes **39** *via* three-component reaction between aryl fluorosulfonates **36**, boronic acids **37**, and alkyl halides **38**.

the authors demonstrated the applicability of their methodology in the preparation of terphenyls from biaryl fluorosulfates. The authors proposed mechanistic pathway for this sequential reaction is depicted in Scheme 10b. Initially, an aryl fluorosulfate intermediate **A** was formed *via* a base-promoted reaction of phenols **33** with SO_2F_2 gas, which subsequently underwent an oxidative addition with Pd^0 to furnish Ar–Pd–OSO_2F **B**. The transmetallation of trihydroxyboronate **C** (generated from boronic acid **34**) with complex **B** then gave Ar^1–Pd(II)–Ar^2 complex **D**. Finally, the reductive elimination of this complex **D** resulted in the formation of the target biaryl **35** while regenerating the Pd^0. It should be mentioned that this catalytic platform was also elegantly applied by Yang, Lerner, and coworkers in on-DNA Suzuki–Miyaura cross-coupling reaction of a series of DNA-conjugated aryl fluorosulfonates with various boronic acids.[23] Noteworthy, the presence of Et_3N is crucial for the success of this reaction. Replacing Et_3N with some other bases (*e.g.*, DIPEA, Na_2CO_3, K_2CO_3, NaOH) led to much lower yields or even no product at all. Following these works, Zhao *et al.* investigated the coupling of genetically encoded fluorosulfate-L-tyrosine with various boronic acid substrates for protein modification.[24] The reaction was run at pH 8.0 in phosphate buffer using $Pd(OAc)_2$ and aminopyrimidine-4,6-diol (L1) as effective and water-soluble catalyst and ligand, respectively. The authors showed that this protein modification strategy can be used for protein fluorogenic labeling that enables *in vitro* and *in vivo* imaging of proteins with minimal background noises. It is worthwhile to note that beside $Pd(OAc)_2$ and Pd-PEPPSI-IPr, other palladium catalysts were also successfully applied in the coupling of fluorosulfonates with boronic acids, such as $Pd_2(dba)_3$ (ref. 25) and [Pd(NHC)(μ-Cl)Cl]$_2$ precatalysts.[26]

In a significant contribution in this field, Bieliūnas and De Borggraeve found that treatment of 2-substituted aryl fluorosulfonates **36** with aryl boronic acids **37** and primary alkyl halides **38** in the presence of $Pd(OAc)_2$/norbornene (NBE)/K_2CO_3 combination as catalytic system in DMF resulted in corresponding multisubstituted arenes **39** in modest to high yields (Scheme 11).[27] The results indicated that the presence of at least one relatively strong electron-withdrawing substituents in the phenyl ring periphery of aryl fluorosulfonates was crucial for this Catellani-type reaction, while the use of compounds bearing weakly electron-withdrawing substituents led to poor yields. Incompatibility of the reaction with substrates possessing aldehyde or nitrile moieties at the 2-position, was another limitation which was reported by the authors for their methodology. Notably, under the standard conditions, a symmetrical bis(fluorosulfate) reacted once, while the second fluorosulfate moiety served as an activating group and remained intact. Interestingly, this cascade chemistry was successfully extended to S-heterocyclic fluorosulfonates; however, N-heterocyclic systems let to low yields or none at all.

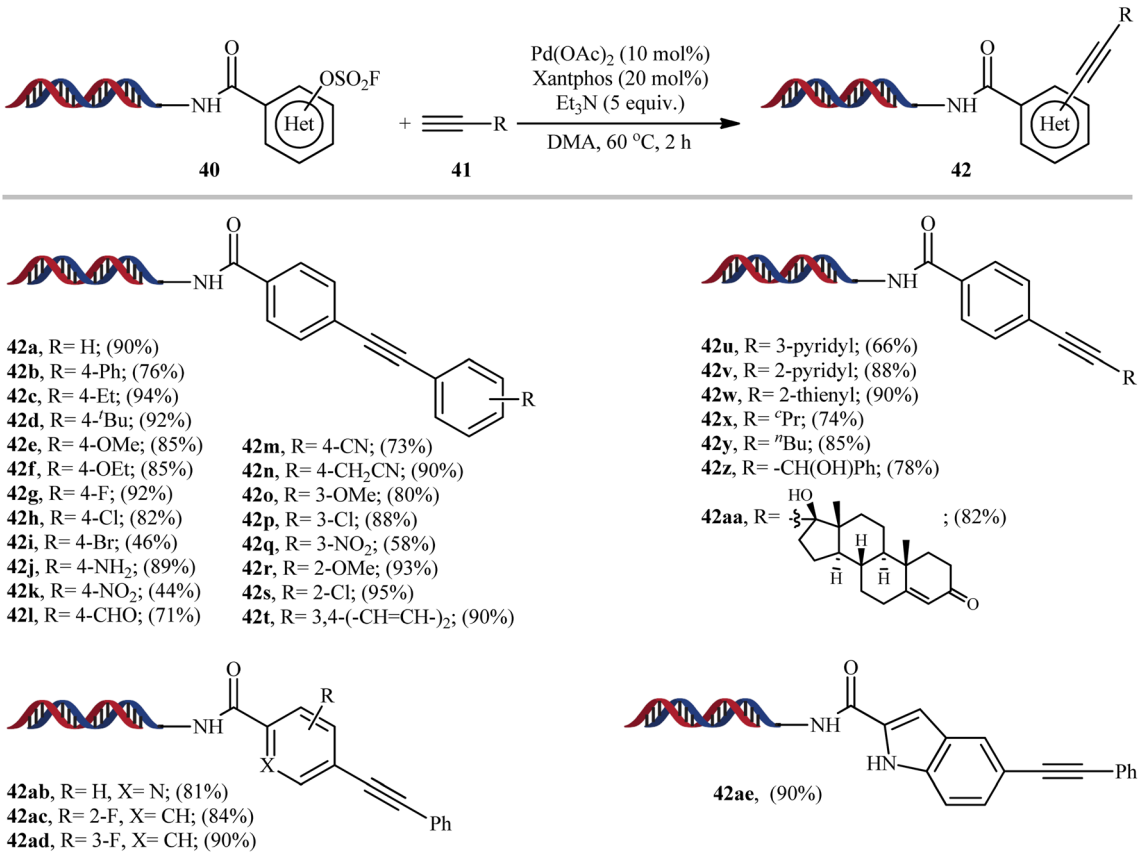
2.4. Sonogashira cross-coupling

About half a century ago, Sonogashira *et al.* developed coupling reaction of terminal alkynes with aryl halides in the presence of a Pd(II)/Cu(I) system.[28] Today this reaction is one of the most versatile and powerful processes to generate aryl alkynes[29] and is an essential tool within the pharmaceutical industries.[30]

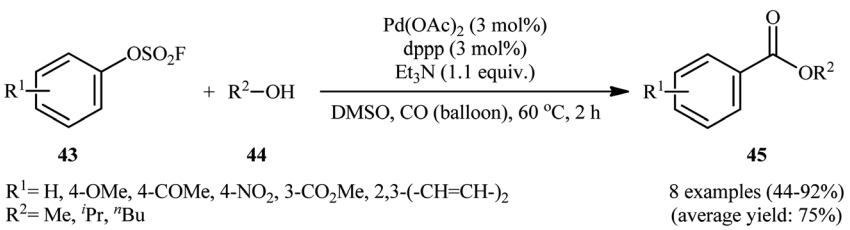
In 2019, Yang-Lerner's research group reported an interesting Pd-catalyzed Sonogashira cross-coupling of DNA-encoded (hetero)aryl fluorosulfates **40** with various terminal alkynes **41** (Scheme 12).[23] This represents the first Sonogashira reaction using aryl fluorosulfates. Various aliphatic, aromatic and heteroaromatic alkynes were employed successfully in this system and good yields of the expected C(sp^2)–C(sp) coupling products are obtained (44–95%). The results indicated that both electron-neutral and electron-rich terminal aryl alkynes afforded better yields compared to electron-deficient ones. Unfortunately, the reaction failed in the case of a CF_3-substituted aryl alkynes. Interestingly, the outcome of reaction almost was not dependent on the electronic nature of the aryl fluorosulfates.

2.5. Carbonylative cross-coupling reactions

In 1992, aryl fhorosulfonates **43** as activated phenol derivatives were employed in palladium-catalyzed carbonylative reactions with simple alcohols **44** by Roth and Thomas.[31] This represents the first Pd-catalyzed alkoxycarbonylation of aryl fhorosulfonates. The reactions were carried out under carbon monoxide (CO) atmosphere, tolerated the presence of various functional groups, and provided the desired esters **45** in moderate to high isolated yields (Scheme 13). The results demonstrated that the nature of ligand had a major impact on the success of this



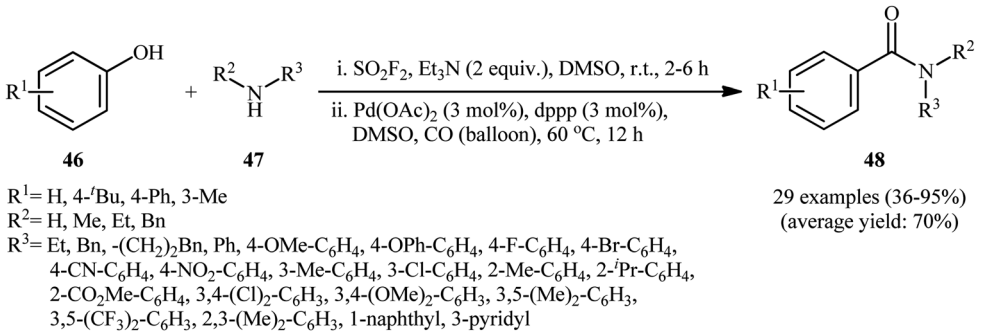
Scheme 12 Selected examples of Pd-catalyzed Sonogashira cross-coupling of DNA-encoded (hetero)aryl fluorosulfates **40** with alkynes **41** reported by Yang-Lerner's research group.



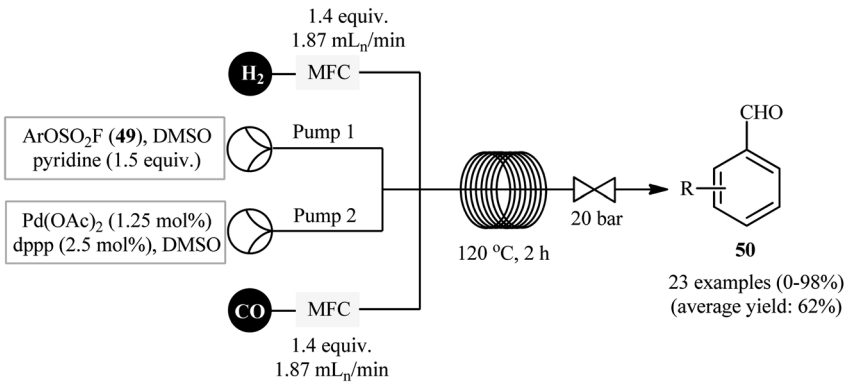
Scheme 13 Pd-catalyzed alkoxycarbonylation of aryl fhorosulfonates **43** developed by Roth.

alkoxycarbonylation. When 1,3-bis(diphenylphosphino) propane (dppp) ligand was replaced with 1,1′-bis(diphenylphosphino)ferrocene (dppf), the desired products were obtained in much lower yields.

Drawing inspiration from this preliminary study, Qin's research team developed a general and efficient methodology for the synthesis of arylcarboxylic amide derivatives through *in situ* conversion of the phenols into their aryl fluorosulfonates and the subsequent carbonylative cross-coupling reaction with amines in a single pot.[32] In this study, twenty-nine amides **48** were synthesized *via* C–O bond activation of phenols **46** using sulfuryl fluoride (SO_2F_2) follow by treatment of *in situ* generated aryl fhorosulfonates with various amines **47** under CO atmosphere, in the presence of $Pd(OAc)_2$/dppp combination as the catalytic system in DMSO at 60 °C (Scheme 14). These authors demonstrated significant scope of the amines, but limited scope of the phenols substrate. The scope of amines that underwent coupling was broad enough to include acyclic aliphatic, benzylic, aromatic, and heteroaromatic derivatives, and all of which were found to be highly suitable amino sources. However, the same reaction provided sulfonamides if cyclic amines were used. Guided by the same principle, recently Hone, Kappe, and co-workers synthesized a library of aryl aldehydes **50** by Pd-catalyzed formylation of the corresponding aryl fluorosulfonates **49** under continuous-flow conditions (Scheme 15).[33]



Scheme 14 Qin's synthesis of amides **48**.



Scheme 15 Continuous flow synthesis of aryl aldehydes **50** from aryl fluorosulfonates **49**.

2.6. Carboxylation reactions

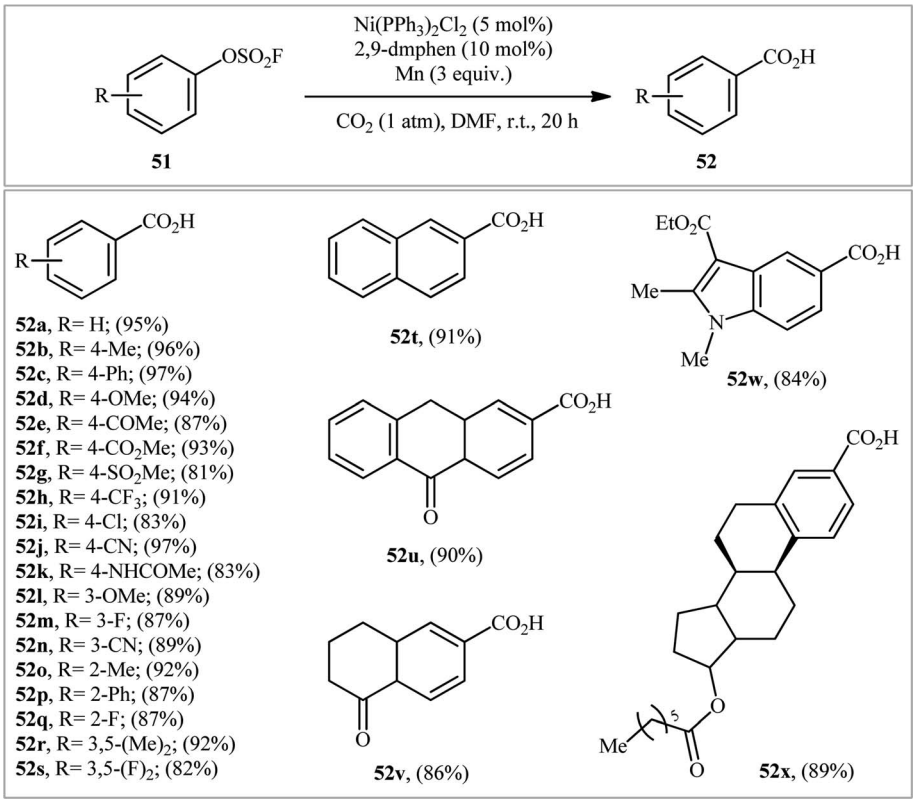
The application of aryl fluorosulfates as aryl sources in carboxylation reactions has been scarcely investigated (Scheme 16). In fact, to the best of our knowledge, only one practical example of such a reaction was reported in literature till date (Scheme 17). In this study, Mei and colleagues disclosed that the treatment of various (hetero)aromatic fluorosulfates **51** containing electron-donating groups (*e.g.*, Me, OMe) and electron-withdrawing groups (*e.g.*, F, Cl, CN, COMe, CO_2Me) with atmospheric CO_2 in the presence of $Ni(PPh_3)_2Cl_2$/2,9-dimethyl-1,10-phenanthroline (2,9-dmphen)/Mn combination as a catalytic system in DMF slowly afforded the corresponding carboxylic acids **52** in good to excellent yields (Scheme 18).[34] It is noteworthy that both Ni catalyst and Mn are essential for this carboxylation. No product was observed in the absence of any of them. In the lack of a ligand, the reaction furnished the carboxylated products, albeit with considerable reduced yields. Besides 2,9-dmphen, other ligands such as PPh_3 and bpy were also found to promote this carboxylation reaction; albeit, in lower yields. Interestingly, under the optimized conditions, twelve aromatic carboxylic acids were also synthesized in good yields (60–79%) through the one-pot version of this carboxylation using *in situ* generated aryl fluorosulfonates from the corresponding phenols. Furthermore, this carboxylation strategy was also successfully applied to a range of biologically and synthetically important pyridyl substrates. In this case, CH_2N_2 was used to methylate the carboxylic acid products to avoid the difficult separation of the pyridine carboxylic acids from water. In the proposed mechanistic pathway (Scheme 19), the authors suggested that this intramolecular C–C bond forming reaction proceeds *via* generation of nickel(0) complex **A** through reduction of the nickel(II) catalyst by Mn. Next, oxidative addition of this complex with an aryl fluorosulfate **51** generates Ni(II) species **B**. Subsequently, single-electron reduction of intermediate **B** by Mn produces intermediate **C**, which after reaction with CO_2 affords complex **D**. The subsequent single-electron reduction of intermediate **D** delivers the desired carboxylated product **E** and regenerates Ni(0) catalyst.

3 Carbon-heteroatom cross-coupling reactions

3.1. C–N cross-coupling

The Pd-catalyzed cross-coupling between aryl halides and amines is known as the Buchwald–Hartwig reaction which represents a powerful tool for the synthesis of arylamines.[35]

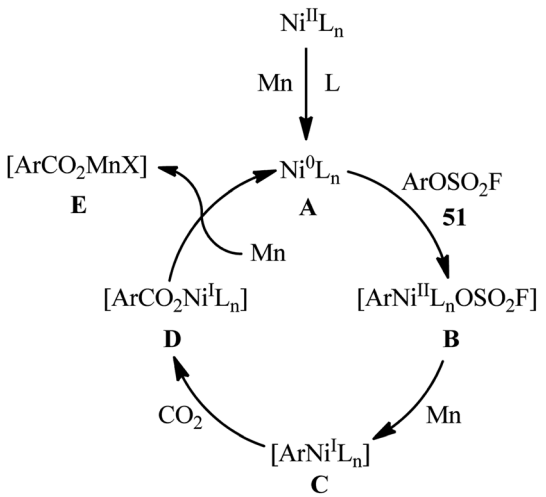
One of the earliest reports on the utilization of aryl fluorosulfonates as electrophilic partners in the Buchwald–Hartwig C–N coupling reaction was published by Hanley and co-workers in 2016,[36] who showed that the treatment of (hetero)aryl



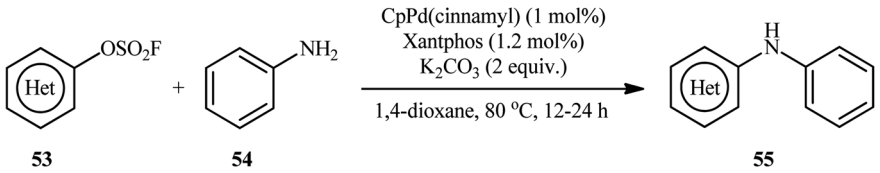
Scheme 16 Ni-catalyzed carboxylation of (hetero)aryl fluorosulfates **51** using CO_2.

fluorosulfonate derivatives **53** with aniline **54** in the presence of catalytic amounts of CpPd(cinnamyl) and Xantphos in 1,4-dioxane, resulted in the formation of the corresponding diarylamines **55** in good to quantitative yields. As shown in Scheme 18, the reaction displayed good reactivity and tolerance to aryl fluorosulfonates with functional groups both electron-rich and electron-deficient, including methoxy, chloro, trifluoromethyl, cyano, ester, and aldehyde functionalities. Apart from aniline, benzyl amine was also compatible with this scenario. However, like aniline, the substrate scope of benzyl amine was not exported in this study. With the aim of development of cheaper and less toxic catalytic system, in this study, the authors developed a Ni-based catalytic system. They showed that merge of 5.0 mol% of $Ni(COD)_2$ with dppf could effectively catalyze this C–N bond forming reaction; albeit in lower efficiency than their Pd-based catalytic system.

Subsequently, in an attempt to further demonstrate the strength of this attractive page of diarylamine synthesis, Lim, Byun, and Kim documented an elegant $Pd(OAc)_2$-catalyzed amination of aryl fluorosulfonates **56** using a range of functionalized primary and secondary aniline derivatives **57**, which allowed high yielding access to the corresponding diarylamine products **58** under ligand-free conditions (Scheme 19).[37] Through exploration and optimization of this C–N coupling reaction, the author identified that the reaction rate is strongly dependent to the nature of base and solvent. Among various bases tested (*e.g.*, Cs_2CO_3, K_2CO_3, Na_2CO_3, K_3PO_4), Cs_2CO_3 dispensed the excellent result, whereas MeCN was found to be the most effective solvent among the solvents tested (*e.g.*, toluene, 1,4-dioxane, DMF, DMA, THF). Notably, the reactivity of aryl fluorosulfonates were compared with other common aryl electrophiles under the standard conditions. Overall the relative reaction rates of tested electrophilic partners followed the order: Ar–OSO_2F > Ar–OTf > Ar–Cl ≥ Ar–Br ≥ Ar–I ≫ Ar–F.



Scheme 17 Proposed mechanistic pathways for the reaction in Scheme 17.

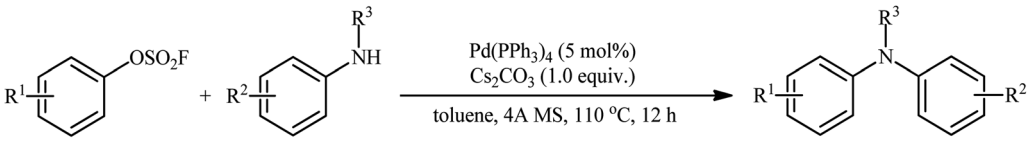


53 **54** **55**

(Het)Ar= 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-CF_3-C_6H_4, 4-CO_2Et-C_6H_4, 4-CN-C_6H_4, 4-CHO-C_6H_4, 3-Cl-C_6H_4, 3-CONHPh-C_6H_4, 3,4-OCH_2O-C_6H_4, 2,4-Me_2-C_6H_3, 2-^{i}Pr-5-Me-C_6H_3, 3-(6-Me)-pyridyl

12 examples (66-99%)
(average yield: 92%)

Scheme 18 Buchwald–Hartwig C–N coupling reaction between (hetero)aryl fluorosulfonates **53** with aniline **54**.

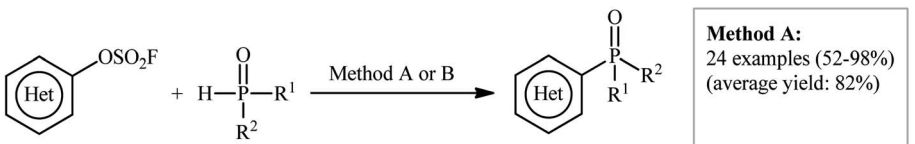


56 **57** **58**

R^1= 4-^{i}Pr, 4-F, 4-Cl, 4-Br, 4-CN, 4-NO_2, 4-COPh, 3,4-(-CH=CH-)$_2$, 3-OMe
R^2= H, 4-Me, 4-OMe, 4-F, 4-NO_2, 4-(4-morpholinyl), 3-OMe, 3-NO_2, 3-CN, 2-OMe, 2-NO_2
R^3= H, Me

20 examples (12-82%)
(average yield: 58%)

Scheme 19 $Pd(PPh_3)_4$-catalyzed amination of aryl fluorosulfonates **56** with aryl amines **57**.



59 **60** **61**

Method A:
24 examples (52-98%)
(average yield: 82%)

Method B:
24 examples (39-98%)
(average yield: 80%)

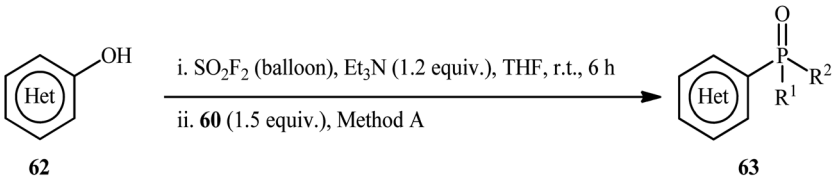
(Het)Ar= Ph, 4-Ph-C_6H_4, 4-OMe-C_6H_4, 4-CO_2Me-C_6H_4, 4-COMe-C_6H_4, 4-CF_3-C_6H_4, 4-SO_2Me-C_6H_4, 4-CN-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 3-Me-C_6H_4, 3-CHO-C_6H_4, 3,4-(-CH=CH-)$_2$, 3,4-OCH_2O-, 3-quinolinyl, 8-quinolinyl, 2-(6-Me)-pyrazinyl, 7-thieno[3,2-*b*]pyridyl, 6-(1-Fs)-indazolyl
R^1= OMe, OEt, O^{n}Bu, Ph
R^2= OMe, OEt, O^{n}Bu, Ph

Method A: $Pd(OAc)_2$ (5 mol%), DPEPhos (6 mol%), K_2CO_3 (2.0 equiv.), THF, 80°C, 12 h
Method B: $NiCl_2$(dme) (5 mol%), Xantphos (6 mol%), Et_3N (2.0 equiv.), Zn (1.5 equiv.), DMF, 100°C, 12 h

Scheme 20 Ni- and Pd-catalyzed cross-coupling of (hetero)aryl fluorosulfonates **59** and hydrogen phosphoryl compounds **60**.

3.2. C–P cross-coupling

Very recently, Ding's research group studied the possibility of synthesis of aryl phosphonates through the transition metal-catalyzed C–P cross-coupling of aryl fluorosulfonates and hydrogen phosphoryl compounds.[38] By employing *p*-biphenyl fluorosulfonate and dibutyl phosphite as the model substrates, the reaction variables such as catalysts, ligands, bases, and solvents were carefully screened. The results indicated that the merge of 5 mol% of $Pd(OAc)_2$ with 6 mol% of DPEPhos and 2.0 equiv. of K_2CO_3 was the most appropriate catalytic system for this conversion and among the various aprotic solvents (*e.g.*, toluene, 1,4-dioxane, THF, DMF, DMSO); THF was found to be the most suitable solvent. Under the optimized conditions, 24 (hetero)aryl phosphonate derivatives **61** were obtained in moderate to excellent yields by reaction of various (hetero)aryl fluorosulfonates **59** with hydrogen phosphoryl compounds **60** (Scheme 20). A wide range of important functional groups including OMe, CF_3, F, Cl, CN, CHO, COMe, CO_2Me and SO_2Me are tolerated by the reaction conditions employed. Thus this procedure offers a versatile synthetic handle for further manipulation of products. Interestingly, all the three kinds of P(O)–H compounds (H-phosphonates, H-phosphinates, and secondary phosphine oxides) were applicable to this reaction. In this study, the authors also developed an alternative Ni-based catalytic system for this transformation. Thus, in the presence of $NiCl_2$(dme)/Xantphos/Et_3N/Zn combination as a catalytic system in DMF, the same set of (hetero)aryl phosphonate derivatives were obtained in comparable yields. They also



Scheme 21 Direct conversion of phenols to the corresponding aryl phosphonates though a sequential fluorosulfonation/C–P coupling approach.

reported one-pot version of the same reaction where the requisite aryl fluorosulfonates were prepared *in situ* from the corresponding phenols and SO_2F_2 (Scheme 21).

4 Conclusion

Aryl fluorosulfates as more stable, more atom economical, and less hazardous alternatives of aryl triflates have drawn great attention over the past few years from organic chemists as powerful and versatile electrophilic partners in cross-coupling reactions. As illustrated, these easy accessible O-based pseudohalides have been successfully employed as electrophilic arylation agents in various carbon–carbon and carbon-heteroatom (N, O, P) cross-coupling reactions. Interestingly, some comparative studies disclosed superior activity of aryl fluorosulfates than the corresponding triflates in various coupling reactions. Challenges that remain to be faced in the future include: (i) identification of catalytic systems based on cheaper and less toxic metals; (ii) exploration of metal-free procedures; (iii) development of the coupling of aliphatic fluorosulfates; (iv) extension of the heteroatom coupling partners beyond simple amines, alcohols, and P(O)–H compounds; and (v) further investigation of the scope and limitation of existed couplings (*e.g.*, Sonogashira coupling).

Ethical approval

This article does not contain any studies with human participants or animals performed by the authors.

Ethics approval and consent to participate

We comply with the ethical standards. We provide our consent to take part.

Consent for publication

All of the authors are giving consent to publish.

Conflicts of interest

There is no conflict of interest by any author.

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