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Hetaryl Bromides Bearing SO_2F Group – Versatile Substrates for Palladium-Catalyzed C–C Coupling Reactions

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Abstract: Synthesis of novel five- and six-membered heteroaromatic sulfonyl fluorides bearing bromine atom at various positions of the heterocyclic ring is described. Synthetic utility of these compounds is demonstrated by the Suzuki, Stille and Negishi cross-coupling reactions, which proceeded chemoselectively at the aryl bromide moiety with 69–98% yields. Tolerance of the SO_2F group towards the coupling reaction conditions was confirmed in most of experiments. The proposed method was efficient for either sp^2–sp^2 or sp^2–sp^3 C–C couplings. The developed procedure provides rapid access to various substituted heterocyclic sulfonyl fluorides.

Introduction

Sulfonyl fluorides have received significant attention in recent years due to their unique chemical and biological properties.[1] They are typically considered as close analogs of sulfonyl chlorides – commonly used sulfur(VI) electrophiles. Due to the high energy of the S–F bond, sulfonyl fluorides are stable toward hydrolysis, metal catalysis, or reductive reaction conditions as compared to other sulfonyl halides.[2] On the other hand, they undergo selective nucleophilic substitution at the sulfur(VI) electrophilic center under controllable reaction conditions. It is not surprising therefore that sulfur(VI) fluoride exchange (SuFEx) was considered as a new click reaction, with potential extensive applications in organic synthesis and medicinal chemistry.[1,3]

Heteroaromatic sulfonyl fluorides are known as deoxyfluorination agents;[4,5] in particular, commercially available 2-pyridinesulfonyl fluoride (PyFluor™, **1**) (Figure 1) is more stable and less prone to the elimination side reaction as compared to other popular deoxyfluorination agents (Deoxo-Fluor[6], XtalFluor[7], Fluolead[8] or DAST[9]). Moreover, an analog of **1** bearing a ^{18}F nuclei at the sulfonyl fluoride moiety can be used for the preparation of ^{18}F-labeled compounds.[5,10]

In the field of medicinal chemistry, sulfonyl fluorides have found significant utility as reactive probes in chemical biology and molecular pharmacology since they demonstrate appropriate balance of biocompatibility (including aqueous stability) and protein reactivity as the warheads.[11] Sulfonyl fluorides are primarily used as covalent inhibitors; in particular, (2-aminoethyl)benzenesulfonyl fluoride (AEBSF, **2**) is a non-toxic, specific and irreversible inhibitor of serine proteases.[11–13] Compound **3** (DAS1) was developed as a specific reagent for labeling tyrosine residues in peptides.[14] Sulfonyl fluorides are also used for the protein fluorescent labeling: for example, 5-dimethylamino-naphthalene-1-sulfofluoride (Dansyl fluoride, **4**) was found to be more selective analogue of the corresponding sulfonyl chloride due to its lower reactivity and hence specificity towards serine residues.[15] SF-p1-yne (**5**) was designed as a clickable covalent probe targeting a tyrosine residue in the binding site of the decapping scavenger enzyme DcpS.[16] 5'-Fluorosulfonylbenzoyl 5'-adenosine (FSBA, **6**), an ATP-binding protein inhibitor, have been used as a covalent probe targeting lysine residues.[11,17–21] Sulfonyl fluorides **7** were found to be potent covalent kinetic stabilizers of transthyretin (TTR), a transport protein involved into pathologies related to amyloid diseases.[22]

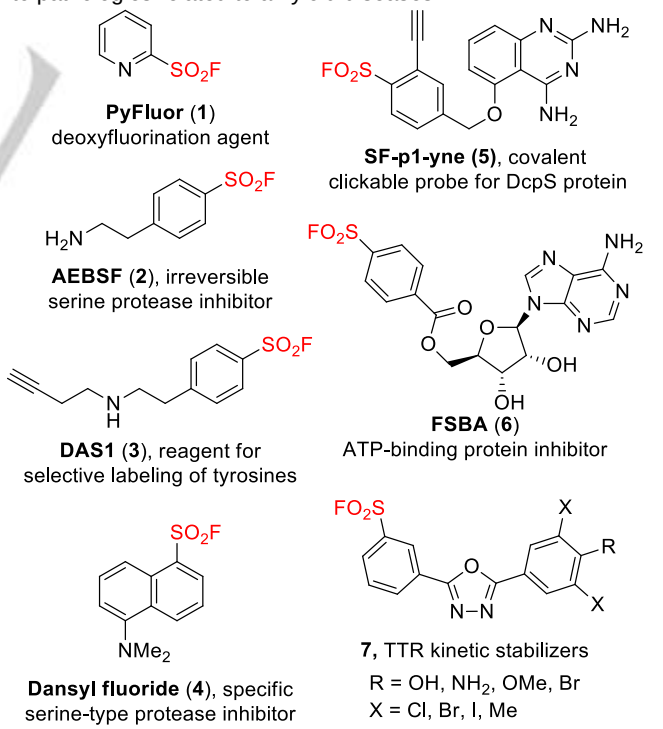

Figure 1. Examples of practically significant sulfonyl fluorides

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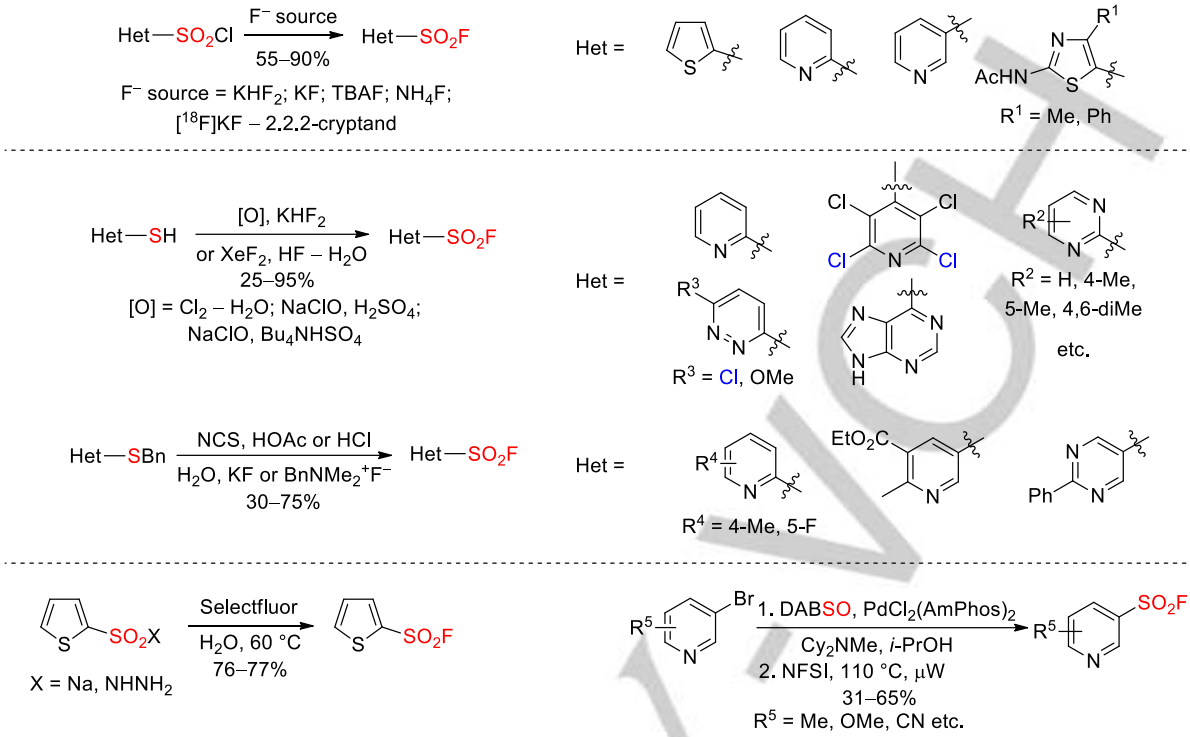
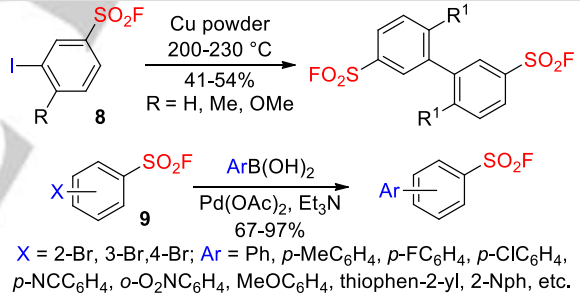


Scheme 1. General methods for the synthesis of heteroaromatic sulfonyl fluorides (DABSO – DABCO-bis(sulfur dioxide); AmPhos – (di-*tert*-butyl(4-dimethyl-aminophenyl)phosphine; NFSI – *N*-fluorobenzenesulfonimide)

Known methods for the synthesis of (hetero)aromatic sulfonyl fluorides fall into one of the following categories (Scheme 1):

- electrophilic substitution using fluorosulfonic acid;[23,24]
- reaction of sulfonyl chlorides with fluorine anion source (KHF_2,[5] KF,[25] TBAF,[26] NH_4F,[27,28] or [^{18}F]KF – 2.2.2-cryptand,[5,26]);
- oxidative chlorination of thiols,[29–34] sulfides[35,36] (Cl_2, NaClO, NCS), followed by *in situ* nucleophilic substitution by fluorine anion (KHF_2 or $BnNMe_3^+F^-$);
- electrophilic fluorination of sulfinates or sulfonyl hydrazides.[37] A recently developed modification of this approach relies on *in situ* generation of sulfinate *via* palladium-catalyzed reaction of the corresponding aryl halides with DABSO, followed by oxidation with Selectfluor or NFSI;[38,39]
- cycloaddition and heterocyclization reactions.[40–42]

It should be noted that to the best of our knowledge, heteroaromatic sulfonyl fluorides bearing a bromine or iodine atom suitable for metal-catalyzed C–C coupling reactions were not described in the literature to date (although some representatives of SO_2F-substituted hetaryl chlorides were known, see Scheme 1). A few examples of metal-catalyzed C–C couplings involving the substrates with SO_2F group were reported. In particular, aryl halides **8** were introduced into the Ullmann reaction as early as in 1930 (Scheme 2).[43] Nevertheless, first examples of the palladium-catalyzed cross-coupling (*i.e.* the Suzuki reaction) of bromo/iodo derivatives of benzenesulfonyl fluorides **9** were reported only in 2016.[23]



Scheme 2. Literature examples of metal-catalyzed C–C coupling reactions with aryl halides having SO_2F group

In this work, we report synthesis of six novel hetaryl bromides **10**–**15** – derivatives of pyridine, furan and thiophene – bearing sulfonyl fluoride group (Figure 2). In addition to that, utility of these building blocks for the Suzuki, Stille and Negishi C–C coupling reactions is also demonstrated, which provides rapid access to various substituted heterocyclic sulfonyl fluorides.

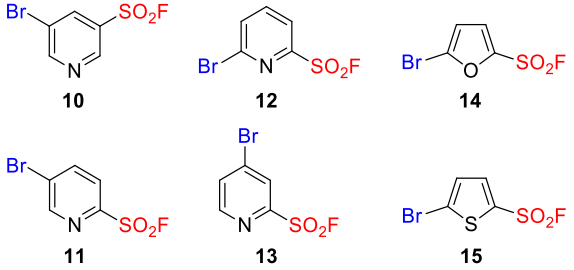


Figure 2. Target molecules of this work

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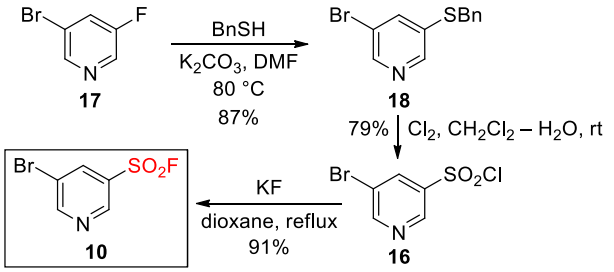
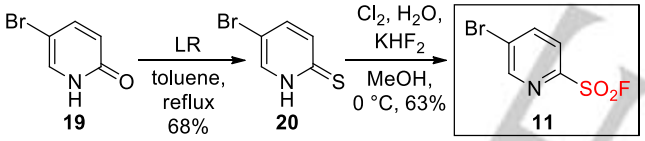
Results and Discussion

In the first part of this work, we have aimed at the preparation of 5-bromopyridine-3-sulfonyl fluoride (**10**). Since pyridine derivatives with SO_2Cl group at the β position are stable compounds, we anticipated reaction of the known sulfonyl chloride **16**[44] with KF as a possible approach to the synthesis of **10**. To obtain **16**, we have developed an original method including reaction of 3-bromo-5-fluoropyridine (**17**) and benzyl thiol in the presence of K_2CO_3 (87% yield), followed by oxidative chlorination of the corresponding sulfide **18** (79% yield). Reaction of **18** with KF proceeded smoothly in refluxing dioxane and gave the target sulfonyl fluoride in 91% yield (Scheme 3).



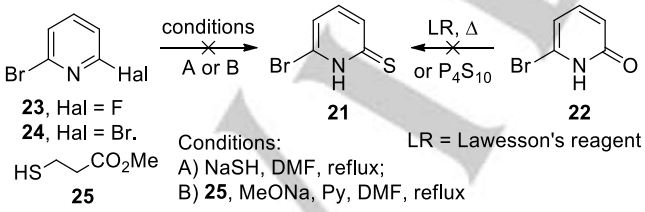
Scheme 3. Synthesis of 5-bromopyridine-3-sulfonyl fluoride (**10**)

Synthesis of 5-bromopyridine-2-sulfonyl fluoride (**11**) commenced from the readily available 5-bromopyridin-2(1*H*)-one (**19**). Reaction of **19** with Lawesson's reagent gave thione **20** (68% yield). Subsequent oxidative chlorination of **20** in the presence of KHF_2 gave the target compound **11** in 63% yield (Scheme 4).



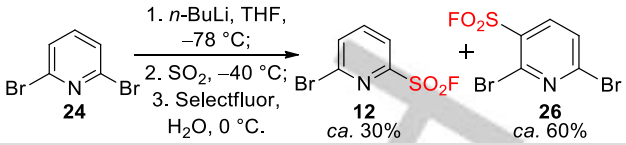
Scheme 4. Preparation of 5-bromopyridine-2-sulfonyl fluoride (**11**)

For the synthesis of isomeric 6-bromopyridine-2-sulfonyl fluoride (**12**), we have envisaged analogous strategy. Unfortunately, all attempts to prepare thione **21**, namely, thionation of pyridone **22** with Lawesson's reagent or P_4S_{10}, as well as reaction of 2,6-dihalopyridines **23** or **24** with NaSH in DMF, or with methyl 3-mercaptopropanoate **25**, followed by retro-Michael fragmentation, were not fruitful (Scheme 5).



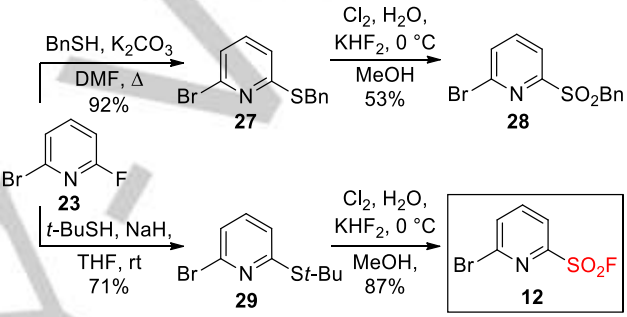
Scheme 5. Attempted synthesis of 6-bromopyridine-2(1*H*)-thione (**21**)

Furthermore, lithiation of 2,6-dibromopyridine (**24**) with *n*-BuLi, followed by subsequent treatment of the corresponding organolithium intermediates with sulfur (IV) oxide and Selectfluor, was not regioselective and gave *ca.* 1:2 mixture sulfonyl fluorides **12** and **26** (Scheme 6). Several attempts to optimize the metallation step of this reaction sequence by using *i*-PrMgBr, *i*-PrMgBr – *n*-BuLi, or *t*-BuLi were also unsuccessful.



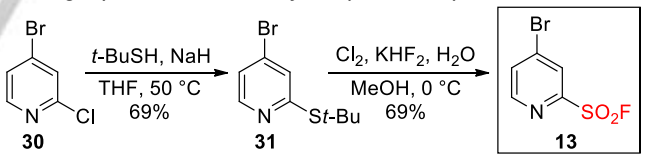
Scheme 6. Products of sulfination of 2,6-dibromopyridine (**24**)

Next, benzyl sulfide **27** was synthesized from 2-bromo-6-fluoropyridine (**23**) in 92% yield. To our surprise, oxidative chlorination of **27** was not accompanied by cleavage of benzyl group, so that sulfone **28** was obtained as white precipitate formed upon reaction conditions (83% yield, 53% after recrystallization). Therefore, we prepared *tert*-butyl sulfide **29** (71% yield from **23**). In this case, oxidative chlorination in the presence of KHF_2 was successful and gave the target sulfonyl fluoride **12** in 87% yield (Scheme 7).



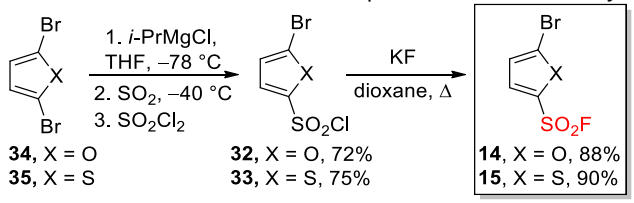
Scheme 7. Synthesis of the target 6-bromopyridine-2-sulfonyl fluoride (**12**)

4-Bromopyridine-2-sulfonyl fluoride (**13**) was prepared from 4-bromo-2-chloropyridine (**30**) using the similar reaction sequence. In this case, the nucleophilic substitution step required heating to 50 °C since the substrate **30** appeared to be less reactive as compared to **23**. The sulfide **31** (69% yield) was subjected to oxidative fluorination conditions described above, which gave the target product **13** in 69% yield (Scheme 8).



Scheme 8. Synthesis of 4-bromopyridine-2-sulfonyl fluoride (**13**)

5-Bromofuran- and -thiophene-2-sulfonyl fluorides (**14** and **15**) were obtained from the corresponding suflonyl chlorides **32** and **33** by reaction with with KF in refluxing dioxane (88% and 90% yield, respectively) (Scheme 9). In turn, the compounds **32** and **33** were obtained from 2,5-dibromofuran (**34**) and 2,5-dibromothiophene (**35**), respectively, using the method described in the literature for the thiophene derivative, namely,



Scheme 9. Synthesis of 5-bromofuran-2-sulfonyl fluoride (**14**) and 5-bromothiophene-2-sulfonyl fluoride (**15**)

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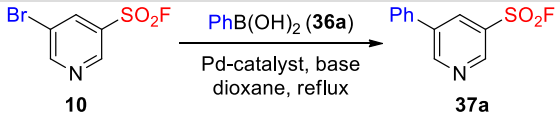
metallation and subsequent reaction with sulfur (IV) oxide and then – sulfuryl chloride (72% and 75% yield, respectively).[45]

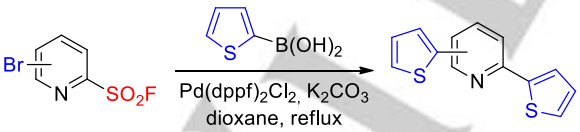
Table 1. Optimization of the Suzuki reaction conditions



Entry	Pd-catalyst	Base	Yield,%
1	$Pd(PPh_3)_2Cl_2$	K_2CO_3	98
2	$Pd(PPh_3)_2Cl_2$	Et_3N	87
3	$Pd(PPh_3)_2Cl_2$	DIPEA	91
4	$Pd(PPh_3)_2Cl_2$	DBU	0
5	$Pd(dppf)_2Cl_2$	DIPEA	92
6	$Pd(PPh_3)_4$	DIPEA	70
7	$Pd(OAc)_2$	Et_3N	30

All the bromo derivatives of hetaryl sulfonyl fluorides **10–15** were introduced in the Suzuki-Miyaura cross-coupling reaction. First of all, optimization of the Suzuki reaction conditions was performed using 5-bromopyridine-3-sulfonyl fluoride (**10**) and phenylboronic acid (**36a**) as the model compounds (Table 1). It was found that the best results were obtained when the reaction was performed in the presence of $Pd(PPh_3)_2Cl_2$ and K_2CO_3 in refluxing dioxane. Under these optimized conditions, phenyl (**37a–42a**), furan-2-yl (**37b–42b**) and thiophene-2-yl (**37c–42c**) derivatives of hetaryl sulfonyl fluorides **10–15** were obtained using corresponding aryl boronic acids **36a–c** (Table 2, Entries 1–3, 5–7, 9–11, 13–15, 17–19, 21–23).

It should be noted that all our attempts to prepare thienyl derivatives **38c** and **40c** from the corresponding aryl bromides **11** and **13** were unfruitful. In this case, the products of double substitution **43** (39% yield) and **44** (46% yield) were formed under the standard conditions (Scheme 10). Formation of these products might be rationalized *via* oxidative addition of a Pd(0) complex at the C–S bond of the starting sulfonyl fluoride – a transformation which has been described for sulfonyl chlorides.[46–48]



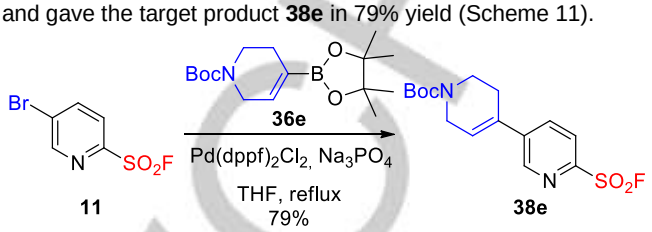
11, 2,5-isomer
13, 2,4-isomer

43, 2,5-isomer, 39%
44, 2,4-isomer, 46%

Scheme 10. Reaction of hetaryl bromides **11** and **13** with boronic acid **36c**

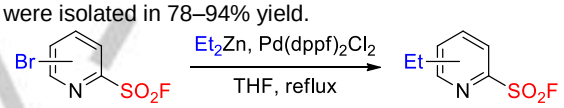
Unfortunately, reaction of hetaryl bromides **10–15** with cyclopropylboronic acid (**36d**) under the conditions described above was not successful; only starting compounds were recovered. Further optimization of the reaction conditions showed that switching to less-coordinating THF, as well as using $Pd(dppf)_2Cl_2$ as a catalyst and Na_3PO_4 as a base allows for the preparation of the target cyclopropyl derivatives **37d–42d** (Table 2, Entries 4, 8, 12, 16, 20, 24).

Furthermore, reaction of the bromo derivative **11** and vinyl pinacolate **36e** under the conditions described above for the cyclopropylboronic acid (**36d**) proceeded smoothly for 2 weeks and gave the target product **38e** in 79% yield (Scheme 11).



Scheme 11. Reaction of hetaryl bromide **11** and pinacolate **36e**

In the next part of this work, 4-, 5- and 6-bromopyridine-2-sulfonyl fluorides (**11–13**) were introduced into the Negishi cross-coupling reaction with diethylzinc. The best results of this sp^2–sp^3 coupling were obtained using $Pd(dppf)_2Cl_2$ as a catalyst in refluxing THF (Scheme 12). The corresponding products **45–47** were isolated in 78–94% yield.

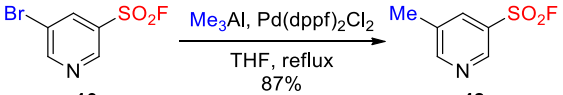


11, 2,5-isomer
12, 2,6-isomer
13, 2,4-isomer

45, 2,5-isomer, 85%
46, 2,6-isomer, 94%
47, 2,4-isomer, 78%

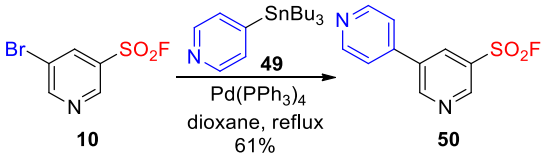
Scheme 12. The Negishi reaction of 4-, 5- and 6-bromopyridine-2-sulfonyl fluorides (**11–13**)

In addition to that, 5-bromopyridine-3-sulfonyl fluoride (**10**) was subjected to the reaction with trimethylaluminium (Me_3Al) under analogous conditions. This transformation resulted in the formation of known compound **48**[39] in 87% yield (Scheme 13).



Scheme 13. Preparation of 5-methylpyridine-3-sulfonyl fluoride (**44**)

Finally, the Stille reaction of hetaryl bromide **10** and 4-(tributylstannyl)pyridine (**49**) was studied (Scheme 14); this transformation gave bipyridyl sulfonyl fluoride **50** upon $Pd(PPh_3)_4$ catalysis in refluxing dioxane media (61% yield).



Scheme 14. The Stille reaction of 4-bromopyridine-2-sulfonyl fluoride (**10**)

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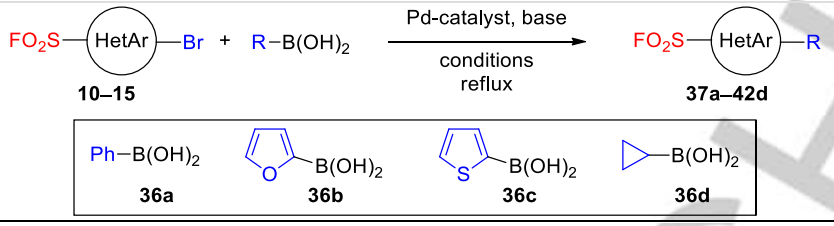
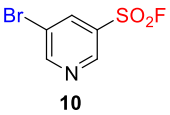
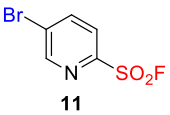
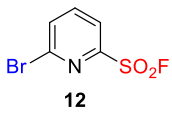
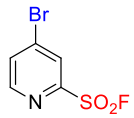
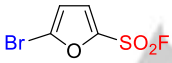
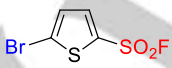
Table 2. Synthesis of bi(het)aryl sulfonyl fluorides using the Suzuki reaction



Entry No.	Sulfonyl fluoride	Boronic acid (R)	Pd-catalyst / base / solvent	Product	Yield,%
1	 **10**	phenyl- (**36a**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**37a**	98
2		furan-2-yl- (**36b**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**37b**	92
3		thiophen-2-yl- (**36c**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**37c**	79
4		cyclopropyl- (**36d**)	$Pd(dppf)_2Cl_2$ / Na_3PO_4 / THF	**37d**	83
5	 **11**	phenyl- (**36a**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**38a**	93
6		furan-2-yl- (**36b**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**38b**	94
7		thiophen-2-yl- (**36c**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**38c**	0[a]
8		cyclopropyl- (**36d**)	$Pd(dppf)_2Cl_2$ / Na_3PO_4 / THF	**38d**	79
9	 **12**	phenyl- (**36a**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**39a**	91
10		furan-2-yl- (**36b**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**39b**	90
11		thiophen-2-yl- (**36c**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**39c**	81
12		cyclopropyl- (**36d**)	$Pd(dppf)_2Cl_2$ / Na_3PO_4 / THF	**39d**	71
13	 **13**	phenyl- (**36a**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**40a**	81
14		furan-2-yl- (**36b**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**40b**	84
15		thiophen-2-yl- (**36c**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**40c**	0[a]
16		cyclopropyl- (**36d**)	$Pd(dppf)_2Cl_2$ / Na_3PO_4 / THF	**40d**	69
17	 **14**	furan-2-yl- (**36b**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**41b**	97
18		thiophen-2-yl- (**36c**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**41c**	83
19		phenyl- (**36a**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**41a**	91
20		cyclopropyl- (**36d**)	$Pd(dppf)_2Cl_2$ / Na_3PO_4 / THF	**41d**	85
21	 **15**	phenyl- (**36a**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**42a**	90
22		furan-2-yl- (**36b**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**42b**	89
23		thiophen-2-yl- (**36c**)	$Pd(PPh_3)_2Cl_2$ / K_2CO_3 / dioxane	**42c**	85
24		cyclopropyl- (**36d**)	$Pd(dppf)_2Cl_2$ / Na_3PO_4 / THF	**42d**	81

[a]The product **43** or **44** was isolated instead the expected sulfonyl fluoride, see Scheme 11

Conclusions

Isomeric bromopyridinesulfonyl fluorides, as well as the corresponding furan and thiophene derivatives are stable compounds which can be prepared on at least *ca.* 30 g scale using the procedures developed in this work. They are efficient substrates for the palladium-catalyzed sp^2–sp^2 and sp^2–sp^3 C–C coupling, *i.e.* the Suzuki–Miyaura, Stille and Negishi reactions. In 28 of the 30 cases studied, the reaction proceeded in a regioselective manner at the hetaryl bromide moiety, so that the sulfonyl fluoride function remained intact under basic reaction conditions and/or upon heating. Since nearly all the Pd-

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catalyzed couplings mentioned above were successful, we believe that the methods developed in this work might be of a general application. Therefore, the title bifunctional building blocks, as well the products of their C–C coupling are promising reagents for the SuFEx click chemistry; they also have great potential as the starting points and synthetic intermediates for early drug discovery.

Experimental Section

Compound **33** was prepared according to the literature method.[45] All other reagents were available from Enamine Ltd. The solvents were purified according to standard procedures.[49] When organic solutions were concentrated under reduced pressure, a 35–40 °C bath was used. Column chromatography was performed on silica gel 60 (230–400 mesh) as the stationary phase. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded at 400 and 500 MHz (for ^{1}H NMR), 100 and 125 MHz (for ^{13}C NMR), 376 and 470 MHz (for ^{19}F NMR). NMR chemical shifts are reported in ppm (δ scale) and are referenced using residual NMR solvent peaks at 7.26 and 77.16 ppm for ^{1}H and ^{13}C in $CDCl_3$, 2.50 and 39.52 ppm for ^{1}H and ^{13}C in DMSO-*d*$_6$. Coupling constants (*J*) are shown in Hz. Spectra are reported as follows: chemical shift (δ, ppm), multiplicity, integration, coupling constants (Hz). LC-MS data were acquired on Agilent 1200 HPLC system equipped with DAD/ELSD/LCMS-6120 diode matrix and mass-selective detector, Poroshell 120 SBC_{18}, 4.6×30 mm column. Eluent: gradient MeCN–H_2O (99 : 1) with 0.1% TFA to H_2O with 0.1% TFA.

5-Bromopyridine-3-sulfonyl chloride (16).[44] Sulfide **18** (35.1 g, 0.125 mol) was dissolved in CH_2Cl_2 – H_2O (1:1 v/v, 700 mL); then, gaseous Cl_2 was bubbled through the stirred reaction mixture for 75 min at rt. The organic phase was separated and washed with H_2O (3×75 mL) and brine H_2O (2×75 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo* to dryness. Yield 25.3 g (79%); white solid; mp 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 2.1 Hz, 1H), 8.99 (d, *J* = 2.1 Hz, 1H), 8.42 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 145.4, 141.5, 136.8, 121.2. MS (CI): *m/z* = 156/158 $[M+H-SO_2F]^+$. Anal. calcd. for $C_5H_3BrClNO_2S$: C, 23.41; H, 1.18; N, 5.46; S, 12.50; Cl, 13.82; Br, 31.15. Found: C, 23.06; H, 0.97; N, 5.24; S, 12.14; Cl, 13.73; Br, 31.15.

3-(Benzylthio)-5-bromopyridine (18). 3-Bromo-5-fluoropyridine (**17**) (45.0 g, 0.256 mol), K_2CO_3 (42.4 g, 0.307 mol) and BnSH (31.8 g, 0.256 mol) were dissolved in DMF (400 mL); the reaction mixture was stirred at 80 °C overnight. Then, the solution was poured into H_2O (900 mL) and extracted with EtOAc (3×500 mL). The organic phase was separated and additionally washed with H_2O (3×150 mL) and brine (100 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo* to dryness to give compound **18**. Yield 62.4 g (87%); white powder; mp 40–42 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.39 (s, 1H), 7.67 (s, 1H), 7.32 – 7.30 (m, 1H), 7.29 – 7.25 (m, 4H), 4.11 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 148.4, 139.5, 136.1, 134.9, 128.9, 128.7, 127.7, 120.5, 38.9. MS (CI): *m/z* = 280/282 $[M+H]^+$. Anal. calcd. for $C_{12}H_{10}BrNS$: C, 51.44; H, 3.60; N, 5.00; S, 11.44; Br, 28.52. Found: C, 51.59; H, 3.65; N, 4.63; S, 11.29; Br, 28.90.

2-(Benzylthio)-6-bromopyridine (27). The compound **27** was prepared from **23** using the procedure described above for **18**. Yield 66.0 g (92%). For spectral and physical data, see ref.[50,51]

5-Bromopyridine-2(1*H*)-thione (20). 5-Bromopyridin-2(1*H*)-one (**19**) (40.4 g, 0.232 mol) was dissolved in toluene (400 mL), and Lawesson's reagent (46.9 g, 0.116 mol) was added in portions to the stirred solution at rt. The reaction mixture was refluxed for 2 h, then cooled to rt. The formed precipitate was filtered and washed with cold toluene (3×30 mL). Yield 30.0 g (68%); yellowish solid; mp 197–199 °C. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 13.76 (br s, 1H), 7.86 (s, 1H), 7.50 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.18 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 177.6, 140.0, 138.7, 135.0, 105.8. MS (CI): *m/z* = 190/192 $[M+H]^+$. Anal. calcd. for C_5H_4BrNS: C, 31.60; H, 2.12; N, 7.37; S, 16.87; Br, 42.04. Found: C, 31.58; H, 1.82; N, 7.54; S, 16.80; Br, 41.72.

2-(Benzylsulfonyl)-6-bromopyridine (28). KHF_2 (27.9 g, 0.357 mol) was added to a stirred suspension of benzyl sulfide **27** (20.0 g, 71.4 mmol) in MeOH – H_2O (1:1 v/v, 400 mL) and the reaction mixture was cooled to 0 °C. Then, gaseous Cl_2 was bubbled through stirred reaction mixture at 0 °C for 1 h (NOTE: the temperature shouldn't exceed 5 °C). The corresponding sulfone **28** was formed as white precipitate upon reaction conditions. The crude sulfone was filtered and recrystallized from MeOH (*ca*. 250 mL). Yield 11.8 g (53%); white solid; mp 121–123 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 6.2, 2.3 Hz, 1H), 7.68 (d, *J* = 6.5 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.25 (s, 1H), 4.67 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 142.3, 139.9, 132.2, 131.1, 128.9, 128.7, 127.0, 121.7, 58.1. MS (CI): *m/z* = 312/314 $[M+H]^+$. Anal. calcd. for $C_{12}H_{10}BrNO_2S$: C, 46.17; H, 3.23; N, 4.49; S, 10.27; Br, 25.60. Found: C, 46.17; H, 3.04; N, 4.61; S, 10.44; Br, 25.69.

2-Bromo-6-(*tert*-butylthio)pyridine (29). *t*-BuSH (37.8 g, 0.419 mol) was added dropwise to a stirred suspension of NaH (60%, 11.2 g, 0.281 mol) in THF (350 mL) at 0 °C; the reaction mixture was stirred additionally at 0 °C for 1 h. Then, the solution of corresponding halopyridine **23** or **30** (0.281 mol) in THF (225 mL) was added dropwise to stirred reaction mixture at 0 °C; the solution was warmed up to rt (for **23**) or to 50 °C (for **30**). The completion of the reaction was controlled by TLC. The reaction mixture was washed with brine (3×100 mL), the organic phase was separated, dried over Na_2SO_4 and evaporated in *vacuo*. The product was purified by distillation in *vacuo* (bp 83–85 °C / 0.2 mmHg). Yield 49.1 g (71%); yellowish liquid; bp 83–85 °C / 0.2 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 8.2 Hz, 2H), 1.52 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 140.9, 137.8, 123.9, 123.9, 48.3, 30.7. MS (EI): *m/z* = 245/247 $[M]^+$. Anal. calcd. for $C_9H_{12}BrNS$: C, 43.91; H, 4.91; N, 5.69; S, 13.02; Br, 32.46. Found: C, 43.57; H, 4.98; N, 5.32; S, 13.20; Br, 32.54.

4-Bromo-2-(*tert*-butylthio)pyridine (31). The compound **31** was prepared from **30** using the procedure described above for **29**. The product was purified by column chromatography on silica gel using hexanes – EtOAc (9:1) as eluent. Yield 47.7 g (71%); white crystals; bp 91–93 °C / 0.2 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.5 Hz, 1H), 7.44 (s, 1H), 7.18 (d, *J* = 4.5 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 149.8, 132.1, 128.7, 123.6, 48.3, 30.9. MS (EI): *m/z* = 246 $[M]^+$. Anal. calcd. for $C_9H_{12}BrNS$: C, 43.91; H, 4.91; N, 5.69; S, 13.02; Br, 32.46. Found: C, 44.18; H, 4.84; N, 6.01; S, 12.97; Br, 32.37.

5-Bromofuran-2-sulfonyl chloride (32). 2,5-Dibromofuran (**34**) (23.8 g, 0.105 mol) was dissolved in THF (250 mL), and *i*-PrMgCl (2 M in THF, 52.5 mL, 0.105 mol) was added dropwise to the stirred solution at –78 °C under argon atmosphere. The resulting mixture was stirred at –78 °C for 1 h; then, an ice-cold solution of SO_2 (13.5 g, 0.210 mol) in THF (200 mL) was added, and the reaction mixture was stirred for additional 15 min. SO_2Cl_2 (10.2 mL, 17.0 g, 0.126 mol) was added dropwise, and the solution was stirred for 15 min; then H_2O (250 mL) was added, and the resulting mixture was extracted with EtOAc (3×250 mL). The combined organic phases were dried over Na_2SO_4 and evaporated in *vacuo*. Yield 18.6 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.7 Hz, 1H), 6.60 (d, *J* = 3.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 130.9, 121.1,

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114.3. MS (EI): *m/z* = 244/246 $[M]^+$. Anal. calcd. for $C_4H_2BrClO_3S$: C, 19.57; H, 0.82; S, 13.06; Cl, 14.44; Br, 32.55. Found: C, 19.89; H, 1.07; S, 13.40; Cl, 14.28; Br, 32.16.

General procedure for the preparation of 10, 14, and 15

The corresponding sulfonyl chloride **16**, **32** or **33** (58.5 mmol) and KF (17.0 g, 0.292 mol) were dissolved in dioxane (150 mL), and the reaction mixture was refluxed until the reaction was complete (monitored by ^{1}H NMR). Then, most of dioxane was evaporated in *vacuo* and the residue was dissolved in EtOAc (250 mL) and washed with H_2O (3×75 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo*.

5-Bromopyridine-3-sulfonyl fluoride (10). The product was purified by trituration with cold MeOH (3×30 mL). Yield 12.8 g (91%); white crystals; mp 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 9.03 (s, 1H), 8.40 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 146.8, 138.2, 131.0 (d, *J* = 26.5 Hz), 121.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ 68.0. MS (EI): *m/z* = 239/241 $[M]^+$. Anal. calcd. for $C_5H_3BrFNO_2S$: C, 25.02; H, 1.26; N, 5.84; S, 13.36; Br, 33.29. Found: C, 25.01; H, 1.15; N, 5.84; S, 13.38; Br, 33.30.

5-Bromofuran-2-sulfonyl fluoride (14). The product was purified by distillation in *vacuo* (bp 87–89 °C / 0.2 mmHg). Yield 11.8 g (88%); colorless liquid; bp 87–89 °C / 0.2 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 3.3, 1.3 Hz, 1H), 6.64 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0 (d, *J* = 38.4 Hz), 131.7 (d, *J* = 3.0 Hz), 124.1 (d, *J* = 3.2 Hz), 114.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ 63.8. MS (EI): *m/z* = 228/230 $[M]^+$. Anal. calcd. for $C_4H_2BrFO_3S$: C, 20.98; H, 0.88; S, 14.00; Br, 34.89. Found: C, 20.58; H, 0.89; S, 13.70; Br, 34.66.

5-Bromothiophene-2-sulfonyl fluoride (15). The product was purified by distillation in *vacuo* (bp 89–91 °C / 0.2 mmHg). Yield 12.9 g (90%); colorless liquid; bp 89–91 °C / 0.2 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 4.2, 1.2 Hz, 1H), 7.20 (dd, *J* = 4.2, 0.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2 (d, *J* = 1.3 Hz), 131.9 (d, *J* = 31.6 Hz), 131.2, 125.3 (d, *J* = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 70.9. MS (EI): *m/z* = 244/246 $[M]^+$. Anal. calcd. for $C_4H_2BrFO_2S_2$: C, 19.60; H, 0.82; S, 26.16; Br, 32.60. Found: C, 19.52; H, 0.74; S, 26.24; Br, 32.77.

General procedure for the preparation of 11–13

KHF_2 (85.9 g, 1.10 mol) was added to a stirred suspension of the corresponding compound **20**, **29** or **31** (0.158 mol) in MeOH – H_2O (8:3 v/v, 550 mL), and the reaction mixture was cooled to 0 °C. Then, gaseous Cl_2 was bubbled through the stirred reaction mixture for 3 h at 0 °C (NOTE: the temperature shouldn't exceed 5 °C). Subsequently, the reaction mixture was extracted with CH_2Cl_2 (3×300 mL). The combined organic phases were dried over Na_2SO_4 and evaporated in *vacuo*.

5-Bromopyridine-2-sulfonyl fluoride (11). The compound was purified by washing with cold MeOH (3×75 mL). Yield 23.9 g (63%); white crystals; mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, *J* = 1.2 Hz), 149.5 (d, *J* = 31.9 Hz), 141.2, 127.6, 125.2 (d, *J* = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 56.2. . MS (EI): *m/z* = 239/241 $[M]^+$. Anal. calcd. for $C_5H_3BrFNO_2S$: C, 25.02; H, 1.26; N, 5.84; S, 13.36; Br, 33.29. Found: C, 24.66; H, 1.39; N, 6.11; S, 13.40; Br, 33.65.

6-Bromopyridine-2-sulfonyl fluoride (12). The compound was purified by trituration with cold MeOH (3×75 mL). Yield 33.0 g (87%); white crystals; mp 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.7 Hz, 1H), 7.93 – 7.86 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1 (d, *J* = 31.9 Hz), 143.3, 140.4, 134.3, 123.0 (d, *J* = 2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 55.3. MS (EI): *m/z* = 239/241 $[M]^+$. Anal. calcd. for $C_5H_3BrFNO_2S$: C, 25.02; H, 1.26; N, 5.84; S, 13.36; Br, 33.29. Found: C, 24.94; H, 1.41; N, 5.80; S, 13.69; Br, 33.13.

4-Bromopyridine-2-sulfonyl fluoride (13). The compound was purified by trituration with cold MeOH (3×75 mL). Yield 26.2 g (69%); white crystals; mp 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.2 Hz, 1H), 8.25 (d, *J* = 1.8 Hz, 1H), 7.85 (dd, *J* = 5.2, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0 (d, *J* = 31.6 Hz), 151.5, 135.2, 132.5, 127.5 (d, *J* = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 55.7. MS (EI): *m/z* = 239/241 $[M]^+$. Anal. calcd. for $C_5H_3BrFNO_2S$: C, 25.02; H, 1.26; N, 5.84; S, 13.36; Br, 33.29. Found: C, 24.73; H, 1.00; N, 6.20; S, 13.74; Br, 33.15.

General procedure for the preparation of 37a–42c

The corresponding aryl bromide **10**–**15** (4.20 mmol) was dissolved in dioxane (15 mL). Arylboronic acid **36a**–**36c** (8.40 mmol), $Pd(PPh_3)_2Cl_2$ (295 mg, 0.42 mmol), and DIPEA (1.63 g, 2.20 mL, 12.6 mmol) were added under argon atmosphere; the resulting mixture was refluxed until the reaction was complete (monitored by TLC). Then, EtOAc (40 mL) was added and the resulting solution was washed with H_2O (3×15 mL) and brine H_2O (3×10 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo*.

5-Phenylpyridine-3-sulfonyl fluoride (37a). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.75. Yield 977 mg (98%); white solid; mp = 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 8.9 Hz, 2H), 8.42 (s, 1H), 7.61 (d, *J* = 6.8 Hz, 2H), 7.58 – 7.46 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 147.1, 137.8, 134.9, 133.8, 130.3 (d, *J* = 25.3 Hz), 129.7, 129.6, 127.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ 67.7. MS (EI): *m/z* = 237 $[M]^+$. Anal. calcd. for $C_{11}H_8FNO_2S$: C, 55.69; H, 3.40; N, 5.90; S, 13.51. Found: C, 55.92; H, 3.24; N, 6.13; S, 13.57.

5-Phenylpyridine-2-sulfonyl fluoride (38a). The product was purified by column chromatography on silica gel using hexanes – EtOAc (4:1) as eluent. R_f = 0.75. Yield 927 mg (93%); white solid; mp = 118–120 °C. ^{1}H NMR (500 MHz, DMSO) δ 9.04 (s, 1H), 8.20 (s, 2H), 7.71 – 7.62 (m, 2H), 7.62 – 7.49 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5 (d, *J* = 30.4 Hz), 149.4, 142.4, 136.3, 135.2, 129.9, 129.6, 127.6, 124.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ 56.2. MS (EI): *m/z* = 237 $[M]^+$. Anal. calcd. for $C_{11}H_8FNO_2S$: C, 55.69; H, 3.40; N, 5.90; S, 13.51. Found: C, 55.84; H, 3.15; N, 6.16; S, 13.24.

6-Phenylpyridine-2-sulfonyl fluoride (39a). The product was purified by column chromatography on silica gel using hexanes – EtOAc (4:1) as eluent. R_f = 0.70. Yield 907 mg (91%); white solid; mp = 73–75 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.04 (m, 4H), 8.01 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.61 – 7.44 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 151.2 (d, *J* = 29.8 Hz), 139.3, 136.3, 130.7, 129.1, 127.3, 125.4, 121.9 (d, *J* = 1.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 54.1. MS (EI): *m/z* = 237 $[M]^+$. Anal. calcd. for $C_{11}H_8FNO_2S$: C, 55.69; H, 3.40; N, 5.90; S, 13.51. Found: C, 55.41; H, 3.74; N, 6.00; S, 13.78.

4-Phenylpyridine-2-sulfonyl fluoride (40a). The product was purified by column chromatography on silica gel using hexanes – EtOAc (7:3) as eluent. R_f = 0.80. Yield 807 mg (81%); white solid; mp = 72–74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.9 Hz, 1H), 8.34 (s, 1H), 7.92 – 7.87 (m, 1H), 7.75 – 7.67 (m, 2H), 7.61 – 7.55 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0 (d, *J* = 30.1 Hz), 151.7, 151.4, 135.6, 130.6, 129.7, 127.2, 126.6, 121.9 (d, *J* = 2.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 55.4. MS (EI): *m/z* = 237 $[M]^+$. Anal. calcd. for $C_{11}H_8FNO_2S$: C, 55.69; H, 3.40; N, 5.90; S, 13.51. Found: C, 56.03; H, 3.12; N, 6.27; S, 13.68.

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5-Phenylfuran-2-sulfonyl fluoride (41a). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.75. Yield 845 mg (91%); white solid; mp = 41–43 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.51 – 7.43 (m, 4H), 6.85 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 130.3, 129.1, 128.0, 125.3, 124.0, 123.9, 106.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ 64.6. MS (EI): *m/z* = 226 $[M]^+$. Anal. calcd. for $C_{10}H_7FO_3S$: C, 53.09; H, 3.12; S, 14.17. Found: C, 52.97; H, 3.07; S, 14.25.

5-Phenylthiophene-2-sulfonyl fluoride (42a). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.75. Yield 916 mg (90%); white solid; mp = 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 4.0 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.45 (d, *J* = 4.4 Hz, 3H), 7.33 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 137.8, 131.7, 130.2, 129.5, 128.9 (d, *J* = 30.5 Hz), 126.6, 123.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ 71.3. MS (EI): *m/z* = 242 $[M]^+$. Anal. calcd. for $C_{10}H_7FO_2S_2$: C, 49.57; H, 2.91; S, 26.47. Found: C, 49.40; H, 3.02; S, 26.36.

5-(Furan-2-yl)pyridine-3-sulfonyl fluoride (37b). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.55. Yield 878 mg (92%); white solid; mp = 73–75 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 9.05 (s, 1H), 8.48 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 2.3 Hz, 1H), 6.96 (t, *J* = 2.9 Hz, 1H), 6.60 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 148.2, 146.2, 144.7, 130.4 (d, *J* = 25.8 Hz), 129.9, 127.7, 112.5, 109.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ 67.3. MS (EI): *m/z* = 227 $[M]^+$. Anal. calcd. for $C_9H_6FNO_3S$: C, 47.58; H, 2.66; N, 6.16; S, 14.11. Found: C, 47.79; H, 3.02; N, 6.33; S, 14.06.

5-(Furan-2-yl)pyridine-2-sulfonyl fluoride (38b). The product was purified by column chromatography on silica gel using hexanes – EtOAc (1:1) as eluent. R_f = 0.65. Yield 897 mg (94%); white solid; mp = 111–113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.66 (s, 1H), 7.03 (d, *J* = 3.3 Hz, 1H), 6.62 (dd, *J* = 3.4, 1.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 148.3 (d, *J* = 31.1 Hz), 146.01 (s), 145.3, 131.8, 131.7, 124.5 (d, *J* = 2.0 Hz), 112.7, 110.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ 56.3. MS (EI): *m/z* = 227 $[M]^+$. Anal. calcd. for $C_9H_6FNO_3S$: C, 47.58; H, 2.66; N, 6.16; S, 14.11. Found: C, 47.70; H, 3.01; N, 6.50; S, 13.82.

6-(Furan-2-yl)pyridine-2-sulfonyl fluoride (39b). The product was purified by column chromatography on silica gel using hexanes – EtOAc (1:1) as eluent. R_f = 0.6. Yield 859 mg (90%); white solid; mp = 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.92 – 7.83 (m, 1H), 7.56 (d, *J* = 0.8 Hz, 1H), 7.25 (d, *J* = 3.9 Hz, 1H), 6.56 (dd, *J* = 3.4, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 151.2, 150.9 (d, *J* = 14.9 Hz), 144.9, 139.1, 123.4, 121.2 (d, *J* = 2.2 Hz), 112.7, 112.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ 54.0. MS (EI): *m/z* = 227 $[M]^+$. Anal. calcd. for $C_9H_6FNO_3S$: C, 47.58; H, 2.66; N, 6.16; S, 14.11. Found: C, 47.81; H, 2.73; N, 6.17; S, 14.10.

4-(Furan-2-yl)pyridine-2-sulfonyl fluoride (40b). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.5. Yield 802 mg (84%); white solid; mp = 71–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.63 (m, 1H), 8.20 (s, 1H), 7.78 (d, *J* = 5.0 Hz, 1H), 7.58 (s, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.63 – 6.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8 (d, *J* = 30.2 Hz), 151.3, 148.9, 145.6, 140.2, 122.2, 117.9 (d, *J* = 2.2 Hz), 112.9, 111.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ 54.9. MS (EI): *m/z* = 227 $[M]^+$. Anal. calcd. for $C_9H_6FNO_3S$: C, 47.58; H, 2.66; N, 6.16; S, 14.11. Found: C, 47.44; H, 2.99; N, 6.43; S, 13.79.

[2,2'-Bifuran]-5-sulfonyl fluoride (41b). The product was purified by column chromatography on silica gel using hexanes – EtOAc (2:3) as eluent. R_f = 0.55. Yield 881 mg (97%); white solid; mp = 51–53 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 3.8, 1.8 Hz, 1H), 6.88 (d, *J* = 3.5 Hz, 1H), 6.72 – 6.67 (m, 1H), 6.53 (dd, *J* = 3.6, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 144.4, 143.7, 138.8 (d, *J* = 37.0 Hz), 124.0 (d, *J* = 3.3 Hz), 112.1, 110.3, 106.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ 64.3. MS (EI): *m/z* = 216 $[M]^+$. Anal. calcd. for $C_8H_5FO_4S$: C, 44.45; H, 2.33; S, 14.83. Found: C, 44.53; H, 2.62; S, 14.87.

5-(Furan-2-yl)thiophene-2-sulfonyl fluoride (42b). The product was purified by column chromatography on silica gel using hexanes – EtOAc (2:3) as eluent. R_f = 0.5. Yield 868 mg (89%); white solid; mp = 37–39 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.16 (m, 2H), 6.79 (d, *J* = 3.2 Hz, 1H), 6.55 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 144.0, 143.6, 137.1, 127.5, 121.5, 112.0, 109.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ 72.1. MS (EI): *m/z* = 232 $[M]^+$. Anal. calcd. for $C_8H_5FO_3S_2$: C, 41.37; H, 2.17; S, 27.61. Found: C, 41.04; H, 1.77; S, 27.44.

5-(Thiophen-2-yl)pyridine-3-sulfonyl fluoride (37c). The product was purified by column chromatography on silica gel using hexanes – EtOAc (2:3) as eluent. R_f = 0.55. Yield 807 mg (79%); white solid; mp = 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 2.2 Hz, 1H), 9.05 (s, 1H), 8.37 (d, *J* = 2.2 Hz, 1H), 7.49 (d, *J* = 3.8 Hz, 2H), 7.20 – 7.16 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6 (d, *J* = 1.0 Hz), 146.6, 137.0, 132.0, 131.6, 130.4 (d, *J* = 25.6 Hz), 128.9, 128.3, 126.4.^{19}F NMR (376 MHz, $CDCl_3$) δ 67.6. MS (EI): *m/z* = 243 $[M]^+$. Anal. calcd. for $C_9H_6FNO_2S_2$: C, 44.44; H, 2.49; N, 5.76; S, 26.36. Found: C, 44.23; H, 2.13; N, 5.94; S, 26.06.

6-(Thiophen-2-yl)pyridine-2-sulfonyl fluoride (39c). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.55. Yield 828 mg (81%); white solid; mp = 104–106 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.82 – 7.73 (m, 1H), 7.53 (d, *J* = 2.8 Hz, 1H), 7.23 – 7.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 151.0 (d, J = 30.0 Hz), 141.5, 139.0, 130.1, 128.5, 127.4, 124.0, 121.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ 53.9. MS (EI): *m/z* = 243 $[M]^+$. Anal. calcd. for $C_9H_6FNO_2S_2$: C, 44.44; H, 2.49; N, 5.76; S, 26.36. Found: C, 44.47; H, 2.29; N, 6.16; S, 26.13.

5-(Thiophen-2-yl)furan-2-sulfonyl fluoride (41c). The product was purified by column chromatography on silica gel using hexanes – EtOAc (1:1) as eluent. R_f = 0.60. Yield 810 mg (83%); white solid; mp = 46–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 3.4 Hz, 1H), 7.42 (t, *J* = 4.5 Hz, 2H), 7.10 (t, *J* = 4.3 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8 (d, *J* = 2.5 Hz), 138.1 (d, *J* = 36.9 Hz), 129.5, 127.7 (d, *J* = 7.6 Hz), 126.5, 123.8, 123.7, 105.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ 72.1. MS (EI): *m/z* = 232 $[M]^+$. Anal. calcd. for $C_8H_5FO_3S_2$: C, 41.37; H, 2.17; S, 27.61. Found: C, 41.29; H, 2.22; S, 27.81.

[2,2'-Bithiophene]-5-sulfonyl fluoride (42c). The product was purified by column chromatography on silica gel using hexanes – EtOAc (1:1) as eluent. R_f = 0.65. Yield 887 mg (85%); white solid; mp = 58–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.33 (s, 1H), 7.21 – 7.17 (m, 1H), 7.10 – 7.06 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 137.2, 133.6, 128.3, 128.1, 127.5, 126.4, 123.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ 71.4. MS (EI): *m/z* = 248 $[M]^+$. Anal. calcd. for $C_8H_5FO_2S_3$: C, 38.70; H, 2.03; S, 38.74. Found: C, 38.89; H, 2.23; S, 38.37.

General procedure for the preparation of 37d–42d, 43 and 44

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The corresponding aryl bromide **10–15** (4.20 mmol) was dissolved in THF (15 mL), and cyclopropylboronic acid (**36d**) (0.72 g, 8.40 mmol), $Pd(dppf)_2Cl_2$ (307 mg, 0.42 mmol), Na_3PO_4 (2.06 g, 12.6 mmol) were added under argon atmosphere; the resulting mixture was refluxed and the completion of reaction was controlled by TLC. Then, EtOAc (40 mL) was added and the resulting solution was washed with H_2O (3×15 mL) and brine H_2O (3×10 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo*.

5-Cyclopropylpyridine-3-sulfonyl fluoride (37d). The product was purified by column chromatography on silica gel using hexanes – EtOAc (1:1) as eluent. R_f = 0.7. Yield 701 mg (83%); white solid; mp = 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.74 (d, *J* = 2.4 Hz, 1H), 7.81 (d, *J* = 2.3 Hz, 1H), 2.02 (tt, *J* = 8.4, 5.0 Hz, 1H), 1.21 – 1.15 (m, 2H), 0.87 – 0.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 145.6, 141.4, 132.0, 127.7, 13.1, 10.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ 67.4. MS (EI): *m/z* = 201 $[M]^+$. Anal. calcd. for $C_8H_8FNO_2S$: C, 47.75; H, 4.01; N, 6.96; S, 15.93. Found: C, 47.45; H, 3.92; N, 6.93; S, 15.55.

5-Cyclopropylpyridine-2-sulfonyl fluoride (38d). The product was purified by column chromatography on silica gel using hexanes – EtOAc (4:1) as eluent. R_f = 0.4. Yield 668 mg (79%); white solid; mp = 78–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 – 8.53 (m, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 2.04 (s, 1H), 1.25 (d, *J* = 5.2 Hz, 2H), 0.89 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 146.8, 133.4, 128.7, 123.4, 13.1, 10.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ 56.2. MS (EI): *m/z* = 201 $[M]^+$. Anal. calcd. for $C_8H_8FNO_2S$: C, 47.75; H, 4.01; N, 6.96; S, 15.93. Found: C, 47.40; H, 4.37; N, 6.89; S, 16.01.

6-Cyclopropylpyridine-2-sulfonyl fluoride (39d). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.55. Yield 600 mg (71%); white solid; mp = 81–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.74 (m, 2H), 7.59 – 7.43 (m, 1H), 2.25 – 2.09 (m, 1H), 1.16 (d, *J* = 13.8 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 150.9 (d, *J* = 29.1 Hz), 137.8, 126.9, 120.3 (d, *J* = 2.2 Hz), 17.2, 11.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ 53.3. MS (EI): *m/z* = 201 $[M]^+$. Anal. calcd. for $C_8H_8FNO_2S$: C, 47.75; H, 4.01; N, 6.96; S, 15.93. Found: C, 47.79; H, 4.30; N, 7.34; S, 15.70.

4-Cyclopropylpyridine-2-sulfonyl fluoride (40d). The product was purified by column chromatography on silica gel using hexanes – EtOAc (2:3) as eluent. R_f = 0.5. Yield 583 mg (69%); white solid; mp = 50–52 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.0 Hz, 1H), 7.73 (s, 1H), 7.31 (d, *J* = 4.9 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.31 – 1.25 (m, 2H), 0.97 – 0.89 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 150.8 (d, *J* = 29.6 Hz), 149.9, 125.4, 120.4 (d, *J* = 1.9 Hz), 15.1, 11.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ 55.2. MS (EI): *m/z* = 201 $[M]^+$. Anal. calcd. for $C_8H_8FNO_2S$: C, 47.75; H, 4.01; N, 6.96; S, 15.93. Found: C, 47.55; H, 3.77; N, 7.00; S, 15.61.

5-Cyclopropylfuran-2-sulfonyl fluoride (41d). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.55. Yield 727 mg (91%); yellowish liquid; bp = 69–71 °C / 1 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.20 (d, *J* = 3.6 Hz, 1H), 2.01 (tt, *J* = 8.4, 5.1 Hz, 1H), 1.11 – 1.06 (m, 2H), 1.01 – 0.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8 (d, *J* = 2.4 Hz), 137.0 (d, *J* = 36.2 Hz), 123.3 (d, *J* = 3.2 Hz), 105.6, 9.0, 8.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ 64.2. MS (EI): *m/z* = 290 $[M]^+$. Anal. calcd. for $C_7H_7FO_3S$: C, 44.21; H, 3.71; S, 16.86. Found: C, 43.89; H, 3.44; S, 16.47.

5-Cyclopropylthiophene-2-sulfonyl fluoride (42d). The product was purified by column chromatography on silica gel using hexanes – EtOAc (4:1) as eluent. R_f = 0.4. Yield 702 mg (81%); yellowish liquid; bp = 93–95 °C / 1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 4.1 Hz, 1H), 6.82 (d, *J* = 4.1 Hz, 1H), 2.16 (tt, *J* = 8.7, 5.0 Hz, 1H), 1.24 – 1.15 (m, 2H), 0.90 – 0.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 137.3, 126.0 (d, *J* = 29.8 Hz), 123.5, 12.0, 11.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ 71.0. MS (EI): *m/z* = 206 $[M]^+$. Anal. calcd. for $C_7H_7FO_2S_2$: C, 40.76; H, 3.42; S, 31.09. Found: C, 40.99; H, 3.58; S, 30.74.

2,5-Di(thiophen-2-yl)pyridine (43). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 – 8.83 (m, 1H), 7.88 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 3.5 Hz, 1H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.14 (t, *J* = 4.8, 3.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 146.6, 144.5, 140.4, 133.6, 128.6, 128.3, 128.1, 127.7, 125.8, 124.6, 123.9, 118.7. MS (EI): *m/z* = 243 $[M]^+$. Anal. calcd. for $C_{13}H_9NS_2$: C, 64.17; H, 3.73; N, 5.76; S, 26.35. Found: C, 63.85; H, 3.68; N, 6.12; S, 26.65.

2,4-Di(thiophen-2-yl)pyridine (44). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.3 Hz, 1H), 7.84 (s, 1H), 7.67 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.56 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.36 (dd, *J* = 5.2, 1.8 Hz, 1H), 7.22 – 7.11 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 150.1, 144.6, 142.2, 141.2, 128.4, 128.0, 127.8, 127.2, 125.4, 124.7, 118.3, 115.0. MS (EI): *m/z* = 243 $[M]^+$. Anal. calcd. for $C_{13}H_9NS_2$: C, 64.17; H, 3.73; N, 5.76; S, 26.35. Found: C, 64.36; H, 3.66; N, 5.82; S, 26.32.

***tert*-Butyl 6-(fluorosulfonyl)-5',6'-dihydro-[3,4'-bipyridine]-1'(2'*H*)-carboxylate (38e).** 5-Bromopyridine-2-sulfonyl fluoride (11) (1.01 g, 4.20 mmol) was dissolved in THF (15 mL), and pinacolate **36e** (2.60 g, 8.40 mmol), $Pd(dppf)_2Cl_2$ (307 mg, 0.42 mmol), Na_3PO_4 (2.06 g, 12.6 mmol) were added under argon atmosphere. The resulting mixture was refluxed until the reaction was complete (monitored by TLC, *ca.* 2 weeks). Then, EtOAc (40 mL) was added and the resulting solution was washed with H_2O (3×15 mL) and brine (3×10 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo*. The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.7. Yield 1.13 g (79%); white solid; mp = 96–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 2.2 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 6.32 (s, 1H), 4.14 (d, *J* = 4.1 Hz, 2H), 3.67 (t, *J* = 5.6 Hz, 2H), 2.53 (s, 2H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 149.1 (d, J = 30.4 Hz), 147.7, 141.6, 133.9, 124.0 (d, *J* = 2.2 Hz), 80.5, 80.2, 41.2, 28.4 (d, *J* = 6.8 Hz), 26.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ 56.1. MS (EI): *m/z* = 342 $[M]^+$. Anal. calcd. for $C_{15}H_{19}FN_2O_4S$: C, 52.62; H, 5.59; N, 8.18; S, 9.36. Found: C, 52.29; H, 5.92; N, 8.45; S, 9.28.

General procedure for the preparation of 45–47

The corresponding sulfonyl fluoride **10–13** (101 mg, 4.20 mmol) was dissolved in THF (15 mL), and $Pd(dppf)_2Cl_2$ (307 mg, 0.42 mmol) was added under argon atmosphere. Et_2Zn solution in hexanes (1M, 6.30 mL, 6.30 mmol) was added dropwise and resulting mixture was refluxed and the completion of reaction was controlled by TLC. Then, EtOAc (40 mL) was added to the reaction mixture and the resultion solution was washed with H_2O (3×15 mL) and brine H_2O (3×10 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo*.

5-Ethylpyridine-2-sulfonyl fluoride (45). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.8. Yield 675 mg (85%); yellowish oil; bp = 66–68 °C / 0.2 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 2.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 148.6 (d, *J* = 30.5 Hz), 146.4, 137.5, 124.0 (d, *J* = 2.2 Hz), 26.2, 14.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ 55.9. MS (EI): *m/z* = 189 $[M]^+$. Anal. calcd. for $C_7H_8FNO_2S$: C, 44.44; H, 4.26; N, 7.40; S, 16.95. Found: C, 44.77; H, 4.03; N, 7.05; S, 17.13.

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6-Ethylpyridine-2-sulfonyl fluoride (46). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.75. Yield 747 mg (94%); white solid; mp = 55–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.82 (m, 2H), 7.53 (dd, *J* = 6.0, 2.8 Hz, 1H), 2.95 (q, *J* = 7.7 Hz, 2H), 1.34 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 150.7 (d, *J* = 29.1 Hz), 138.6, 127.9, 121.3 (d, *J* = 2.2 Hz), 31.1, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ 54.3. MS (EI): *m/z* = 189 $[M]^+$. Anal. calcd. for $C_7H_8FNO_2S$: C, 44.44; H, 4.26; N, 7.40; S, 16.95. Found: C, 44.82; H, 4.48; N, 7.26; S, 17.15.

4-Ethylpyridine-2-sulfonyl fluoride (47). The product was purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.75. Yield 620 mg (78%); yellowish oil; bp = 75–77 °C / 0.2 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.8 Hz, 1H), 7.93 (s, 1H), 7.51 (d, *J* = 4.8 Hz, 1H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 151.2 (d, *J* = 29.4 Hz), 150.8, 128.7, 123.7 (d, *J* = 2.1 Hz), 28.3, 13.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ 55.7. MS (EI): *m/z* = 189 $[M]^+$. Anal. calcd. for $C_7H_8FNO_2S$: C, 44.44; H, 4.26; N, 7.40; S, 16.95. Found: C, 44.41; H, 4.48; N, 7.06; S, 17.07.

5-Methylpyridine-3-sulfonyl fluoride (48). 5-Bromopyridine-3-sulfonyl fluoride (**10**) (1.00 g, 4.17 mmol) was dissolved in THF (15 mL), and $Pd(PPh_3)_4$ (482 mg, 0.417 mmol), Me_3Al (2 M in hexanes, 2.09 mL, 4.17 mmol) were added under nitrogen atmosphere; the resulting mixture was stirred overnight. Then, EtOAc (40 mL) was added to the reaction mixture, and the resulting solution was washed with H_2O (3×15 mL) and brine H_2O (3×10 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo*. Yield 636 mg (87%). For spectral and physical data, see ref.[39]

[3,4'-Bipyridine]-5-sulfonyl fluoride (50). 5-Bromopyridine-3-sulfonyl fluoride (**10**) (1.01 g, 4.20 mmol) was dissolved in dioxane (15 mL) and 4-(tributylstannyl)pyridine (**49**) (1.55 g, 4.20 mmol), $Pd(PPh_3)_4$ (485 mg, 0.42 mmol) were added under argon atmosphere; the resulting mixture was refluxed and the completion of reaction was controlled by TLC. Then, EtOAc (40 mL) was added to the reaction mixture and the resulting solution was washed with H_2O (3×15 mL) and brine H_2O (3×10 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated in *vacuo*. Purified by column chromatography on silica gel using hexanes – EtOAc (3:2) as eluent. R_f = 0.5. Yield 610 mg (61%); white solid; mp = 172–174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (s, 1H), 9.25 (s, 1H), 8.83 (d, *J* = 4.6 Hz, 2H), 8.50 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 4.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 151.0, 148.8, 142.4, 135.0, 134.1, 130.7 (d, *J* = 26.2 Hz), 121.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ 68.4. MS (EI): *m/z* = 238 $[M]^+$. Anal. calcd. for $C_{10}H_7FN_2O_2S$: C, 50.42; H, 2.96; N, 11.76; S, 13.46. Found: C, 50.81; H, 2.64; N, 11.85; S, 13.67.

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Keywords: Heterocyclic, sulfonyl fluoride, Suzuki coupling, Negishi coupling. Stille coupling

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Synthesis of novel five- and six-membered heteroaromatic sulfonyl fluorides bearing bromine atom at various positions of the heterocyclic ring is described. Synthetic utility of these compounds is demonstrated by the chemoselective Suzuki, Stille and Negishi sp^2–sp^2 or sp^2–sp^3 C–C cross-coupling reactions, which proceeded at the aryl bromide moiety with 69–98% yields with expected tolerance of the SO_2F group towards the coupling reaction conditions.

Sulfonyl fluorides

*Artem Yu. Cherepakha, Kateryna O. Stepannikova, Bohdan V. Vashchenko, Marian V. Gorichko, Andrey A. Tolmachev, Oleksandr O. Grygorenko**

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