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Pd-Catalyzed Synthesis of Aryl and Heteroaryl Triflones from Reactions of Sodium Triflinate ($NaSO_2CF_3$) with Aryl(Heteroaryl) Triflates

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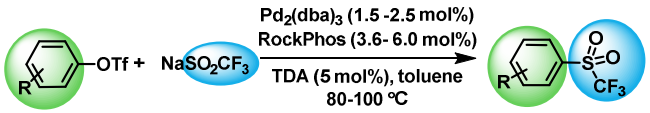
Abstract



A novel method for Pd-catalyzed triflination of aryl and heteroaryl triflates using $NaSO_2CF_3$ as the nucleophile is described. The combination of $Pd_2(dba)_3$ and RockPhos formed the most effective catalyst. A broad range of functional groups and heteroaromatic compounds were tolerated under the neutral reaction conditions. The order of reactivity ArOTf ≥ ArCl ≥ ArBr is consistent with transmetallation being a slow step of the reaction.

Compounds containing the triflone (SO_2CF_3) group exhibit unique chemical and biological properties due to the strong electron-withdrawing ability and high lipophilicity of SO_2CF_3. Aryl and heteroaryl triflones ($ArSO_2CF_3$) are oftentimes present in new molecular entities being explored for the potential treatment of cancer and immunological diseases, among many others.[1-5] This functionality forms building blocks of advanced functional materials such as nonlinear optical chromophores,[6,7] and catalysts and ligands.[8,9]

The widespread application of traditional methods to prepare aryl(heteroaryl) triflones such as Friedel-Crafts triflylations,[10] aryl Grignard additions to $(CF_3SO_2)_2O$,[11] anionic thia-Fries rerrangements,[12-18] oxidation of aryltrifluoromethyl sulfides,[19-23] nucleophilic trifluoromethylation reactions[24,25,26] cycloaddition reactions,[27-29] thermal decomposition,[30] etc. have been limited due to low yields, poor substrate scope, use of expensive reagents, harsh reaction conditions, formation of isomeric products and incompatibility of reaction conditions with common organic functional groups.[31] New synthetic approaches have been reported to complement the existing methods.[32,33] We reported a general method for Cu_2O catalyzed reactions of $NaSO_2CF_3$ with diaryliodonium salts to form aryltriflones under mild reaction conditions.[34] More readily accesible electrophiles, such as aryl halides and pseudohalides, did not react with $NaSO_2CF_3$ under the reported conditions. In addition, one example of formation of a heteroaryl triflone was reported.

Pd- and Cu-catalyzed reactions of aryl halides, pseudohalides, and boronic acids with aryl and alkylsulfinate salts have been well documented;[35,36,37,38,391,40-49] however, the use of $NaSO_2CF_3$ as a nucleophilic coupling partner has never been reported. The strong electron-withdrawing character of the trifluoromethylsulfonyl group (σ_p = 0.96)[50,51] substantially reduces the nucleophilicity of $NaSO_2CF_3$, rendering it a poor coupling partner. Due to the poor nucleophilicity, the transmetalation of $NaSO_2CF_3$ with Pd- or Cu-complexes is likely to be challenging.[52,53] Moreover, C–S reductive elimination from putative Pd(II) and Cu(III) intermediates is expected to be difficult with such an electron-poor nucleophile.[54] Development of sterically-hindered phosphine ligands by Buchwald and co-workers have allowed other electron-poor nucleophiles to couple successfully

with aryl halides and pseudohalides in the presence of Pd catalysts.[52,55,56,57,58,59,60-62] Given our interest in molecules containing aryl triflones,[1] our success in synthesizing aryl triflones from reactions of diaryl iodonium salts with $NaSO_2CF_3$,[34] and recent examples of Pd-catalyzed couplings of electron-poor nucleophiles, we were motivated to investigate the Pd-catalyzed formation of $C(sp^2)$-SO_2CF_3 bonds from reactions of $NaSO_2CF_3$ and aryl (pseudo)halides. Herein, we describe a general method for the synthesis of aryl and heteroaryl triflones from Pd-catalyzed reactions of aryl and heteroaryl triflates with $NaSO_2CF_3$ under neutral reaction conditions. A few examples of Pd-catalyzed reactions of aryl chlorides with $NaSO_2CF_3$ are also reported.

The coupling of $NaSO_2CF_3$ with phenyl triflate (**1a**) was choosen for initial optimization of the reaction conditions because we rationalized that transmetalation of $NaSO_2CF_3$ with a Pd(II) aryl triflate complex obtained from oxidative addition of aryl triflate to Pd(0) is expected to be more facile than transmetalation with the analogous Pd(II) aryl halide intermediate.[63] Since $NaSO_2CF_3$ is only sparingly soluble in common organic solvents used in Pd-catalyzed cross-coupling reactions such as toluene, 1,4-dioxane, *tert*-amyl alcohol, THF, DME, a phase transfer catalyst, tris(3,6-dioxaheptyl)amine (TDA),[52] that was reported to be the optimal phase transfer catalyst for Pd-catalyzed reaction of another poorly soluble nucleophile, $NaNO_2$, was used to further facilitate the reaction. Sterically bulky phosphine ligands that are known to be effective for Pd-catalyzed reactions of other electron-poor nucleophiles were surveyed.

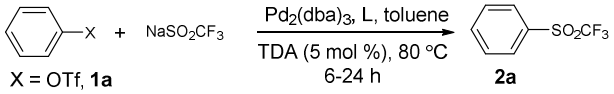
While formation of trace amounts of phenyl triflone (**2a)** was observed in the presence of BrettPhos (**I**) (Table 1, entry 1), the use of the bulkier *tert*-butylBrettPhos (**II**) gave **2a** in 23% yield (entry 2). Surprisingly, with RockPhos (**III**), which is similar in

structure to **II** except for the substituents at the 6-position of the phosphine containing aryl rings, **2a** was formed in quantitative yield (entry 3). A similarly significant difference in the reactivities of Pd catalysts based on ligands **II** and **III** was observed by Buchwald and co-workers in Pd-catalyzed C-O bond forming reactions.[64] The catalyst based on adamantyl-RockPhos (**IV)** formed **2a** in 75% yield after 5 h (entry 4), whereas only trace product formation was observed in the presence of cyclohexyl-RockPhos (**V**) (entry 5), demonstrating that substitutents bulkier than cyclohexyl groups on phosphorous are essential for the catalytic activity. No product formation was observed in the presence of other sterically bulky phosphine and carbene ligands that were evaluated in the reaction (entries 6-8). Biarylphosphines containing electron-withdrawing substitutents on phosphorous are known to accelerate the reductive elimination step;[65] however, no product formation was observed in the presence of **IX** (entry 9). Although faster reaction rate was observed in the presence of TDA than in its absence, the phase transfer catalyst is not essential for the reaction (compare entries 3 and 12). Toluene was found to be the optimal solvent (Table S1). While $Pd_2(dba)_3$ and $[Pd(cinnamyl)Cl]_2$ were effective as Pd-precursors, negligible amount of product was formed when $Pd(OAc)_2$ or $Pd(MeCN)_2Cl_2$ were used as the source of Pd (Table S1).

The substitution of $NaSO_2CF_3$ with KSO_2CF_3 as the coupling partner for **1a** afforded **2a** in a similar yield, however, the use of Baran's reagent, $Zn(SO_2CF_3)_2$, failed to form **2a** in any isolable yield. The coupled product **2a** was observed in less than 5% yield when either chlorobenzene (**1a'**) or bromobenzene (**1a")** was used as the electrophile instead of phenyl triflate (**1a**) under the reaction conditions shown in entry 3. Increasing the reaction temperature to 100 °C formed **2a** in 50% and 7% yield after 25 h

when **1a'** and **1a"** were respectively used as electrophiles (entries 10 and 11).[66] The order of reactivity, PhOTf >> PhCl >> PhBr, is consistent with transmetalation being a slow step of the reaction.[63,67]

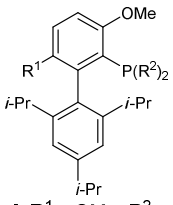
Table 1. Evaluation of reaction parameters for Pd-catalyzed formation of aryltriflone



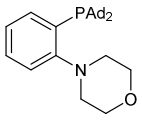
X = OTf, **1a**
X= Cl, **1a'**
X = Br, **1a"**

Entry	X	L (mol%)	Time (h)	**2a** (%)[a]
1	OTf	**I** (10)	6	7
2	OTf	**II** (6)	6	23
3	OTf	**III** (6)	2	>95
4	OTf	**IV** (6)	5	75
5	OTf	**V** (10)	24	5
6	OTf	**VI** (6)	6	0
7[b]	OTf	**VII** (5)	6	0
8[b]	OTf	**VIII** (5)	6	0
9	OTf	**IX** (10)	6	0
10[c]	Cl	**III** (6)	25	50
11[c]	Br	**III** (6)	25	7
12[d]	OTf	**III** (6)	6	74

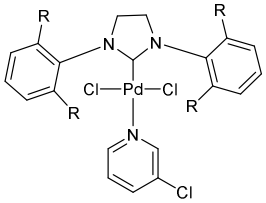
All experiments were conducted with phenyl triflate/chlorobenzene/ bromobenzene (1 equiv), and $NaSO_2CF_3$ (2 equiv) for the indicated time. (a) Assay yield based on HPLC analysis at 210 nm. (b) No $Pd_2(dba)_3$ was added. (c) Reaction at 100 °C. (d) No TDA was added.



I: R^1 = OMe, R^2 = Cy
II: R^1 = OMe, R^2 = *t*-Bu
III: R^1 = Me, R^2 = *t*-Bu
IV: R^1 = Me, R^2 = Ad
V: R^1 = Me, R^2 = Cy
IX: R^1 = OMe, R^2 = 3,5-CF_3-Ph



VI

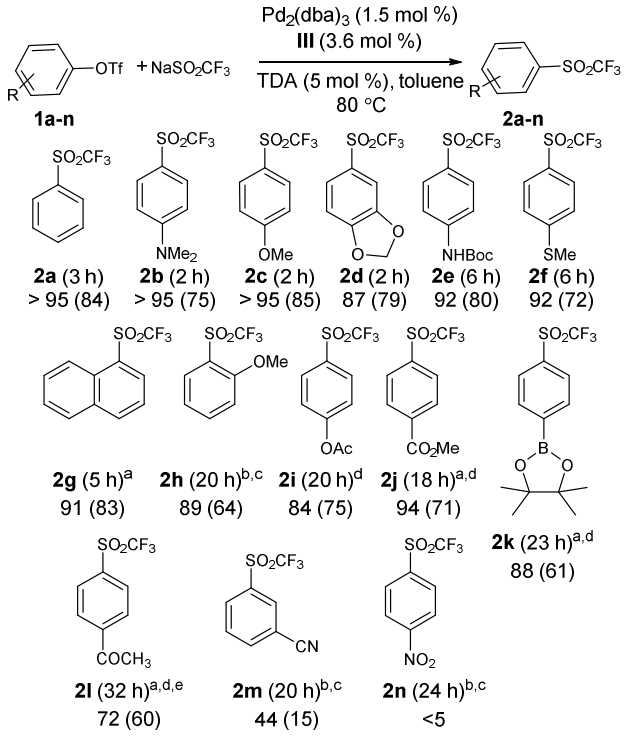


VII: R = $CH(CH_3)_2$
VIII: R = $CH(C_2H_5)_2$

After optimizing the reaction conditions for coupling of **1a** with $Na_2SO_2CF_3$, the reactivities of sterically and electronically diverse aryl triflates were explored (Scheme 1). Aryl triflones (**2a-1**) were isolated in synthetically useful yields from reactions of aryl

triflates containing prevalent functional groups: dimethylamino, ether, acetal, carbamate, thioether, acetate, ester, boronate ester, and acetyl. Aryl triflates containing substitutents with a wide range of electron-donating abilities (NMe_2(σ_p = -0.83) to $COCH_3$ (σ_p = 0.50)) formed the corresponding aryl triflones in high yields. Aryl triflates functionalized with substitutents more electron-deficient than acetyl were poor substrates for the reaction (**1m** and **1n**). Sterically-hindered aryl triflates such as **1g** and **1h** were found to be suitable substrates.

Scheme 1. Scope of Pd-catalyzed reaction of $NaSO_2CF_3$ with aryl triflates

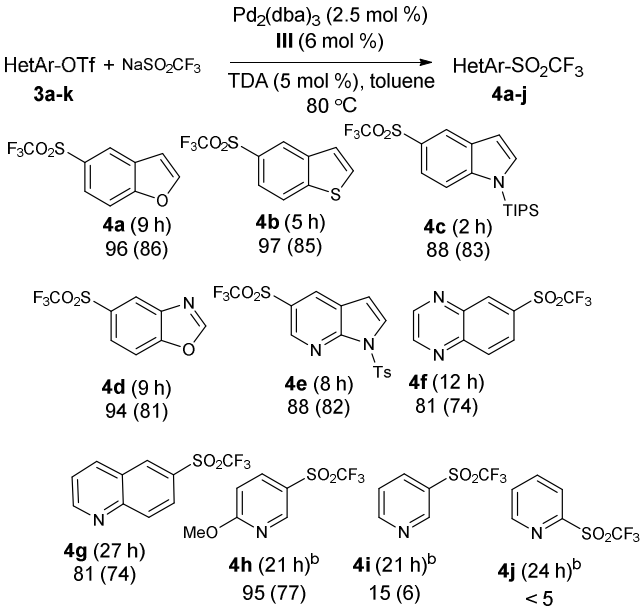


Unless noted otherwise experiments were conducted with aryl triflate (1 equiv),$NaSO_2CF_3$ (1.5 equiv), for the indicated time. Assay yield based on HPLC analysis at 210 nm. The isolated yield is reported within parentheses. (a) $Pd_2(dba)_3$ (2.5 mol %), **III** (6 mol %) (b) $Pd_2(dba)_3$ (4 mol %), **III** (9.6 mol %) (c) Reaction at 100 °C. (d) Reaction at 90 °C. (e) >25% of unreacted **1l** was observed.

Heteroaryl triflates such as benzofuran (**3a**), benzothiophene (**3b**), indole (**3c**), benzoxazole (**3d**), pyrrolopyridine (**3e**), quinoxaline (**3f**), quinoline (**3g**), and pyridine

(**3h**) reacted with $NaSO_2CF_3$ under the standard reaction conditions to afford the corresponding heteroaryl triflones in high yields (Scheme 2). While 6-methoxypyridin-3-yl triflate (**3h**) formed the coupled product **4h** in quantitative yield, the unsubstituted, less electron-rich pyridine, pyridin-3-yl triflate (**3i**), afforded the corresponding triflones **4i** in only 15% yield. Furthermore, pyridin-2-yl triflate (**3j**) failed to react.[68]

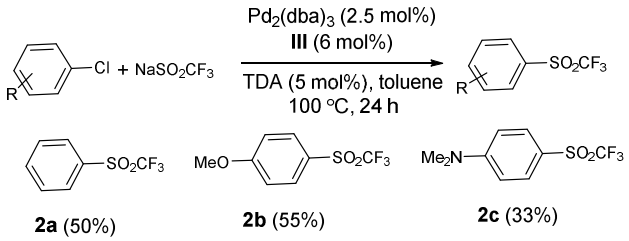
Scheme 2. Scope of Pd-catalyzed reaction of $NaSO_2CF_3$ with heteroaryl triflates



Unless noted otherwise experiments were conducted with heteroaryl triflate (1 equiv),$NaSO_2CF_3$ (1.5 equiv) for the indicated time (a) Assay yield based on HPLC analysis at 210 nm. The isolated yield is reported within parentheses. (b) Reaction at 100 °C.

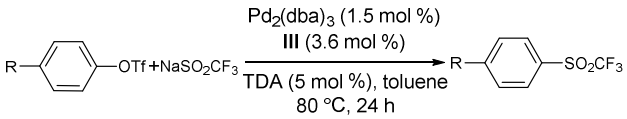
Aryl triflones could also be synthesized in moderate yields from reactions of electron-rich aryl chlorides with $Na_2SO_2CF_3$ (Scheme 3). Electron-deficient aryl chloride 4-acetylphenyl chloride gave <20% yield of product before catalyst decomposition was observed.

Scheme 3. Pd-catalyzed reaction of aryl chlorides with $NaSO_2CF_3$



In general, lower catalyst loading, lower reaction temperature, and shorter reaction times were required for the coupling of electron-rich aryl triflates with $Na_2SO_2CF_3$ than for coupling electron-poor aryl triflates (Scheme 1). Comparison of the initial rates of reaction of **1c**, **1a**, and **1l** revealed that the electron-rich electrophile **1c** reacts approximately 50 times faster with $NaSO_2CF_3$ than the electron-poor electrophile **1l** **(**Table 2). Although a similar dependence of the efficiency of Pd-catalyzed reactions on the electron-donating ability of electrophiles was noted in $C(sp^2)$-NO_2,[52] and $C(sp^2)$-SCF_3[53] bond-forming reactions, the dependence appears to be more pronounced for the formation of $C(sp^2)$-SO_2CF_3 bonds.

Table 2. Comparison of initial rates of reactions of electronically diverse aryl triflates



Entry	R	σ_p	initial rate (10^{-3} M/min)
1	OCH_3	-0.27	21
2	H	0	4
3	$COCH_3$	0.50	0.4

The superior reactivity of $NaSO_2CF_3$ with aryl triflates compared to aryl chlorides in the presence of a Pd catalyst can indeed be attributed to the more facile transmetalation of $NaSO_2CF_3$ with a cationic L.Pd(Ar)(OTf) intermediate than with a neutral L.Pd(Ar)(Cl)

intermediate.[63] However, it is not apparent if transmetalation is the rate-determing step for the Pd-catalyzed reactions of aryl triflates with $NaSO_2CF_3$. Insight into the most challenging step of this novel transformation will help in further expanding the scope of the methodology to include reactions of electron-poor aryl and heteroaryl triflates.

The formation of aryl triflones from Pd-catalyzed reactions of aryl triflates with $NaSO_2CF_3$ is expected to proceed via the well established sequence of oxidative addition, transmetalation, and reductive elimination steps. Oxidative addition as the rate-limiting step of the reaction can be ruled out because Pd-RockPhos complex is known to react with aryl triflates at room temperature,[69] whereas, much higher temperatures (80-100 °C) are needed for this catalytic reaction. This would suggest that either transmetalation or reductive elimination could be the rate-limiting step. In most Pd-catalyzed $C(sp^2)$-X (X = $C(sp^2)$, N, O, S) bond-forming reactions, both transmetalation[70] and reductive elimination[54] steps are accelerated by electron-poor electrophiles. One notable exception is the more facile reductive elimination of aryl nitriles from arylpalladium(II) cyanide complexes containing more electron-donating electrophiles.[71] Thus, the faster rates of formation of aryl triflones from reactions of $NaSO_2CF_3$ with aryl triflates containing electron-donating substitutents is in contrast to the general reactivity trend observed in most Pd-catalyzed cross-coupling reactions.

The limited solubility of $NaSO_2CF_3$ in toluene made it difficult to determine the dependence of rate of aryl(heteroaryl) triflone formation on the concentration of $NaSO_2CF_3$. Nevertheless, we noticed that the reaction proceeds more effectively with finely ground $NaSO_2CF_3$ than with coarse $NaSO_2CF_3$, which is also consistent with the effect of the phase transfer catalyst. As expected for a heterogeneous reaction of this

nature, efficient agitation of the reaction mixture was also found to be crucial. These physical observations suggest that transmetalation is a challenging step, if not the rate-limiting step, in the Pd-catalyzed reactions of aryl(heteroaryl) triflates with $NaSO_2CF_3$. Stereoelectronic differences in substrate reactivities also offers some insight into the reaction mechanism. The higher catalyst loading and reaction temperature required for 2-methoxyphenyl triflate **1h** (Table 2) compared to the coupling of the electronically similar but *less* bulky 4-methoxyphenyl triflate **1c** suggests that transmetalation is the slowest step of the reaction. Since the Pd-RockPhos complex is readily expected to oxidatively insert into the more sterically-hindered aryl triflate **1h**,[64] transmetalation of $NaSO_2CF_3$ with Pd(II) is likely retarded due to the increased steric bulk introduced by the *ortho*-methoxy group. Furthermore, if reductive elimination was the rate-determining step then it would be anticipated that **1h** would react faster than **1c** because the rate of reductive elimination typically increases with greater steric bulk in the electrophile.[54] We tentatively suggest that transmetalation of $NaSO_2CF_3$ to (RockPhos).Pd(aryl)(triflate) complex is the rate-limiting step of the reaction. We also propose that the rate of transmetalation increases with greater electron-donating ability of the electrophile. Thus, our future efforts will focus on identifying a soluble source of trifluoromethylsulfinate that can more readily participate in the reaction than $NaSO_2CF_3$.

In summary, a novel palladium-catalyzed method for the formation of aryl(heteroaryl)-SO_2CF_3 bonds from the reactions of the corresponding triflates with $NaSO_2CF_3$ is described. Given the ease of synthesis of aryl and heteroaryl triflates from phenols, low cost and availability of $NaSO_2CF_3$, use of a commercially available catalyst, neutral

reaction conditions which affords broad functional group tolerance, this transformation is highly useful for rapidly accessing a wide variety of aryl and heteroaryl triflones.

Experimental Section

General methods. All palladium-catalyzed reactions were performed in a nitrogen glove box. Aryl and hetroaryl triflates and nonaflates that were commercially unavailable were synthesized using literature procedures. Anhydrous grade toluene, 1,4-dioxane, *tert*-AmOH, and, DMF, were purchased is sure-seal bottles from commercial sources and were sparged with nitrogen before use. $Pd_2(dba)_3$, phosphine ligands (**I** to **VI** and **IX**), Pd-carbene complexes (**VII** and **VIII**), phenyl triflate, 4-methoxylphenyl triflate, 4-acetylphenyl triflate, 4-nitrophenyl triflate, naphthalene-1-triflate, quinolin-6-triflate, chlorobenzene, bromobenzene, 4-methoxyphenyl chloride, 4-dimethylaminophenyl chloride, 4-acetylphenyl chloride, various aryl and heteroaryl alcohols, triflic anhydride, N-(5-chloropyridin-2-yl)-1,1,1-trifluoro-N-((trifluoromethyl)sulfonyl)methanesulfonamide, $NaSO_2CF_3$, KSO_2CF_3, and $Zn(SO_2CF_3)_2$ were purchased from commercial sources. $NaSO_2CF_3$ and KSO_2CF_3 were ground with a mortar and pestle and dried overnight in a vacuum oven at 55-60 °C before use. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a 400 or 600 or 700 MHz spectrometer, with shifts reported in parts per million downfield from tetramethylsilane and referenced to residual proton (^1H) or deuterated solvent (^{13}C). HPLC analyses were performed using spectroscopic grades of acetonitrile and water with either 0.1 % H_3PO_4 or 0.1% $HClO_4$ as eluents. HRMS analyses were performed on a time-of-flight mass spectrometer equipped with an ESI source. Elemental analysis was performed using optimum combustion analysis on an elemental analyzer.

General procedure for synthesis of aryl and heteroaryl triflates.

The aryl and heteroaryl triflates were synthesized either using procedure A or procedure B.

Procedure A: A stirred solution of the phenol (1.0 equiv) in CH_2Cl_2 (0.2 M) was cooled to -78 ˚C. DIPEA (1.25 equiv) was added followed by slow addition of 1 M triflic anhydride in CH_2Cl_2 (1.3 equiv). The mixture was allowed to warm to 0 ˚C and the reaction progress was monitored by TLC. When completed, CH_2Cl_2 was added, the organic solution was washed with water followed by aqueous $NaHCO_3$ and dried with Na_2SO_4. Purification was carried out by flash column chromatography over silica gel using an ethyl acetate/heptane gradient.

Procedure B: To a vial with magnetic stirring bar was charged phenol (1 equiv) and N-(5-chloropyridin-2-yl)-1,1,1-trifluoro-N-((trifluoromethyl)sulfonyl)methanesulfonamide (1.1 equiv). The solids were then suspended in CH_2Cl_2 (10 mL/g of phenol). To the reaction was added $^iPr_2EtN$ (4 equiv). The reaction was mixed at room temperature and the

progress was monitored by HPLC. Upon completion of the reaction, the mixture was concentrated and the resulting residue was purified by flash column chromatography on silica gel using ethyl acetate/heptane gradient.

4-(Dimethylamino)phenyl triflate (1b): Following the general procedure A, but without allowing the reaction mixture to warm up to 0 °C (the reaction was complete within 30 min at -78 ˚C), 1.47 g of 4-(dimethylamino)phenol was converted to 1.78 g of 4-(dimethylamino)phenyl trifluoromethanesulfonate (62% yield, 96% purity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 2H), 6.74 – 6.53 (m, 2H), 2.97 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0 (C), 140.3 (C), 121.8 (CH), 118.8 (CF_3, q, J = 320.3 Hz), 112.5 (CH), 40.5 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.8. The proton and carbon data for this compound were consistent with literature report except for the C-F coupling.[72]

Benzo[d][1,3]dioxol-5-yl trifate (1d). Following the general procedure A, 1.00 g of benzo[d][1,3]dioxol-5-ol was converted to 1.82 g of benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (d, J = 8.3 Hz, 1H), 6.78 – 6.73 (m, 2H), 6.05 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5 (C), 147.5 (C), 143.5 (C), 118.7 (CF_3, q, J = 321.0 Hz), 114.4 (CH), 108.2 (CH), 103.4 (CH), 102.5 (CH_2). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.7. The proton data for this compound was consistent with literature data.[72]

4-((*tert*-Butoxycarbonyl)amino)phenyl triflate (1e). Following the general procedure A, 1.50 g of *tert*-butyl (4-hydroxyphenyl)carbamate was converted to 1.49 g of 4-((*tert*-butoxycarbonyl)amino)phenyl trifluoromethanesulfonate (61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.36 (m, 2H), 7.23 – 7.13 (m, 2H), 6.64 (br s, 1H), 1.52 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 152.4 (C), 144.5 (C), 138.5 (C), 121.9 (CH), 119.5 (CH), 118.8 (CF_3, q, J = 320.3 Hz), 81.3 (C), 28.3 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.8. The proton and carbon data for this compound were consistent with literature data.[73]

4-(Methylthio)phenyl triflate (1f): Following the general procedure A, 1.50 g of 4-(methylthio)phenol was converted to 1.68 g of 4-(methylthio)phenyl trifluoromethanesulfonate (92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9 (C), 139.8 (C), 127.6 (CH), 121.7 (CH), 118.8 (CF_3, q, J = 321.0 Hz), 15.8 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.8. The proton, carbon and fluorine data for this compound were consistent with literature data.[59]

2-Methoxyphenyl triflate (1h). Following the general procedure A, 1.00 g of 2-methoxyphenol was converted to 1.73 g of 2-methoxyphenyl trifluoromethanesulfonate (84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 1H), 7.22 (dd, J = 8.2, 1.6 Hz, 1H), 7.04 (dd, J = 8.3, 1.5 Hz, 1H), 6.98 (td, J = 7.8, 1.5 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151. 5 (C), 138.8 (C), 129.2 (CH), 122.5 (CH), 120.9 (CH), 118.8 (CF_3, q, J = 320.4 Hz), 113.2 (CH), 56.1 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.9. The proton and carbon data for this compound were consistent with literature data.[74]

4-(((Trifluoromethyl)sulfonyl)oxy)phenyl acetate (1i): Following the general procedure A, 1.50 g of 4-hydroxyphenyl acetate was converted to 2.32 g of 4-(((trifluoromethyl)sulfonyl)oxy)phenyl acetate. (83% yield). The compound was isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.15 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9 (C), 150.1 (C), 146.7 (C), 123.4(CH), 122.4 (CH), 118.8 (CF_3, q, J = 320.6 Hz), 21.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.8. Anal. Calcd for $C_9H_7F_3O_5S$: C, 38.04; H, 2.48. Found: C, 38.36; H, 2.32.

Methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (1j): Following the general procedure A, 1.50 g of methyl 4-hydroxybenzoate was converted to 2.69 g of methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (96% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.08 (m, 2H), 7.43 – 7.29 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5 (C), 152.5 (C), 131.9 (CH), 130.4 (C), 121.4 (CH), 118.8 (CF_3, q, J = 321.0 Hz), 52.6 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.8. The proton and carbon data for this compound were consistent with literature data.[75]

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl triflate (1k): Following the general procedure B, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (767 mg, 3.5 mmol) was converted to 600 mg of benzo[d]oxazol-5-yl triflate (49% yield). The compound was isolated as crystalline white solid. ^{1}H NMR (600 MHz, $CDCl_3$) 7.89 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 1.35 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8 (C), 136.9 (CH), 120.6 (CH), 118.7 (CF_3, q, J = 320.8 Hz), 84.3 (C), 24.9 (CH_3); ^{19}F NMR (564 MHz, $CDCl_3$) δ -72.9. Anal. Calcd for $C_{13}H_{16}BF_3O_5S$: C, 44.34; H, 4.58. Found: C, 43.75; H, 4.30. mp 104–106 °C.

3-Cyanophenyl triflate (1m): Following the general procedure A, 1.50 g of 3-hydroxybenzonitrile was converted to 1.48 g of 3-cyanophenyl trifluoromethanesulfonate (47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dt, J = 7.7, 1.3 Hz, 1H), 7.63 (t, J = 8.1 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.56 (ddd, J = 8.3, 2.5, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3 (C), 132.2 (CH), 131.4 (CH), 126.2 (CH), 125.1 (CH), 118.7 (CF_3, q, J = 321.1 Hz), 116.7(C), 114.7 (C). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.5. The proton, carbon and fluorine data for this compound were consistent with literature data.[76]

Benzofuran-5-yl triflate (3a): Following the general procedure B, benzofuran-5-ol (500 mg, 3.7 mmol) was converted to benzofuran-5-yl trifluoromethanesulfonate (672 mg, 68% yield). The compound was isolated as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 2.2 Hz, 1H), 7.55 (dd, J = 9.0, 0.9 Hz, 1H), 7.53 (d, J = 2.5 Hz, 1H), 7.21 (dd, J = 8.9, 2.6 Hz, 1H), 6.83 (dd, J = 2.3, 0.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5 (C), 147.5 (CH), 145.3 (C), 128.5 (C), 118.8 (CF_3, q, J = 320.8 Hz), 117.5 (CH), 114.0 (CH), 112.6 (CH), 107.0 (CH); ^{19}F NMR (564 MHz, $CDCl_3$) δ -73.7; HRMS (m/z): $[M-H]^-$ calcd for $C_9H_5F_3O_4S$ 264.9788; found 264.9790.

Benzo[b]thiophen-5-yl triflate (3b): Following the general procedure B, benzo[b]thiophen-5-ol (800 mg, 5.3 mmol) was converted to **3b** (1.1 g, 73% yield) following flash column chromatography over silica gel using an ethyl acetate/heptanes gradient. The compound was isolated as colorless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ

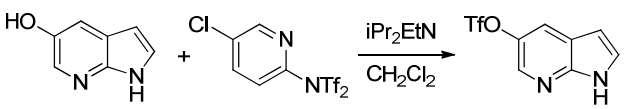
7.92 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 5.4 Hz, 1H), 7.38 (d, *J* = 5.4 Hz, 1H), 7.26 (dd, *J* = 8.8, 2.1 Hz, 1H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 147.0 (C), 140.3 (C), 139.3(CO), 129.8 (CH), 124.0 (CH), 123.8 (CH), 118.8 (CF_3, q, *J* = 320.8 Hz), 117.4 (CH), 115.9 (CH); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.8; Anal. Calcd for $C_9H_5F_3O_3S_2$: C, 38.30; H, 1.79. Found: C, 38.30; H, 1.52.

1-(Triisopropylsilyl)-1H-indol-5-yl triflate (3c): To a solution of 5-(benzyloxy)-1H-indole (2.50 g, 11.2 mmol) in DME (37 mL) at 0 ˚C was added NaH (50 wt% in mineral oil, 1.08 g, 22.4 mmol, 2 equiv). After stirring at 0 ˚C for 20 min TIPS-Cl (3.56 mL, 16.8 mmol, 1.5 equiv) was added and the mixture allowed to warm to room temperature and stirred for a further 2 h. Brine was added,the product was extracted into EtOAc (x3) and the combined organics dried (brine, Na_2SO_4). Purification was carried out by flash column chromatography over silica gel using an ethyl acetate/heptane gradient to give 4.25 g of 5-(benzyloxy)-1-(triisopropylsilyl)-1H-indole (100% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.41 – 7.37 (m, 3H), 7.34 – 7.29 (m, 1H), 7.23 (d, *J* = 3.2 Hz, 1H), 7.17 (d, *J* = 2.6 Hz, 1H), 6.88 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.54 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.10 (s, 2H), 1.67 (h, *J* = 7.6 Hz, 3H), 1.14 (d, *J* = 7.5 Hz, 18H).
To a solution of 5-(benzyloxy)-1-(triisopropylsilyl)-1H-indole (4.25 g, 11.2 mmol) in IPA:EtOAc:heptane (1:1:1, 93 mL) was added 10% Pd/C (298 mg,0.28 mmol, 0.025 equiv). This mixture was stirred at room temperature in an atmosphere of H_2 for 4 h, filtered through celite and the solvent removed to give a quantitative yield of 1-(triisopropylsilyl)-1H-indol-5-ol, which was used directly in the next step.

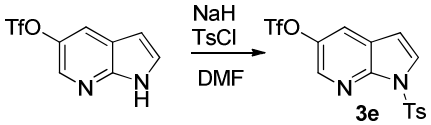
Triflation was carried out using the general procedure A. From 2.00 g of 1-(triisopropylsilyl)-1H-indol-5-ol, 1.64 g of 1-(triisopropylsilyl)-1H-indol-5-yl trifluoromethanesulfonate was obtained (56% yield). The compound was isolated as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.35 (d, *J* = 3.2 Hz, 1H), 7.03 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.66 (dd, *J* = 3.1, 0.8 Hz, 1H), 1.68 (h, *J* = 7.6 Hz, 3H), 1.14 (d, *J* = 7.6 Hz, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7 (C), 139.7 (C), 133.8 (CH), 131.8 (C), 118.9 (CF_3, q, *J* = 320.9 Hz), 114.5 (CH), 114.3 (CH), 112.7 (CH), 105.4 (CH), 18.0 (CH_3), 12.8 (CH). ^{19}F NMR (471 MHz, $CDCl_3$) δ -72.87. Anal. Calcd for $C_{18}H_{26}F_3NO_3SSi$: C, 51.29; H, 6.22. Found: C, 51.13; H, 6.35.

Benzo[d]oxazol-5-yl triflate (3d): Following the general procedure B, 1-benzo[d]oxazol-5-ol (400 mg, 3.0 mmol) was converted to benzo[d]oxazol-5-yl triflate (600 mg, 76% yield). The compound was isolated as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.75 (d, *J* = 2.5 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.35 (dd, *J* = 8.9, 2.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7 (CH), 149.0 (C), 146.3 (C), 141.1 (C), 119.3 (CH), 118.8 (CF_3, q, *J* = 20.9 Hz), 114.1 (CH), 112.1 (CH); ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.0; HRMS (m/z): $[M-H]^-$ calcd for $C_8H_4F_3NO_4S$ 265.97397; found 265.97404.

1H-Pyrrolo[2,3-b]pyridin-5-yl trifluoromethanesulfonate (3e):



Following the general procedure B, 1H-pyrrolo[2,3-b]pyridin-5-ol (1 g, 7.5 mmol) was converted to 1H-pyrrolo[2,3-b]pyridin-5-triflate (1.6 g, 81% yield) following flash column chromatography on SiO_2 using an ethyl acetate/heptanes gradient. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (bs, 1H), 8.29 (d, J = 2.6 Hz, 1H), 7.89 (dd, J = 2.6, 0.7 Hz, 1H), 7.48 (dd, J = 3.3, 2.6 Hz, 1H), 6.60 (dd, J = 3.6, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2 (C), 141.7 (C), 135.7 (CH), 128.1(CH), 121.6 (CH), 120.5 (C), 118.8 (CF_3, q, J = 320.6 Hz), 101.9 (CH); HRMS (m/z): $[M+H]^+$ calcd for $C_8H_5F_3N_2O_3S$ 267.0046; found 267.0049. mp 122.5-123.5 °C.



A round-bottom flask with magnetic stirring bar was charged with DMF (10 mL) under N_2 atmosphere. NaH (60 wt% in mineral oil, 180 mg, 1.2 equiv) was added and the solution was cooled to 0 °C. 1H-Pyrrolo[2,3-b]pyridin-5-triflate (1.0 g, 3.8 mmol) was added. The reaction was warmed to room temperature and was mixed for 15 minutes. TsCl (0.788 g, 1.1 equiv) was added in one portion and the reaction mixture was stirred overnight. The reaction was slowly quenched with addition of water (5 mL). The mixture was transferred to a separatory funnel and extracted with MTBE (20 mL). The aqueous layer was back extracted with MTBE (10 mL). The combined organic layers were washed with aqueous saturated NaCl (10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in $CHCl_3$ (2 mL) and purified by flash column chromatography on a 120 g silica gel column with an EtOAc/heptanes gradient. Compound **3e** was isolated as crystalline white solid (1.2 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.6 Hz, 1 H), 8.10-8.05 (m, 2H), 7.87 (dd, J = 4.1, 0.4 Hz, 1H), 7.79 (d, J = 2.64 Hz, 1H), 7.32-7.30 (m, 2H), 6.64 (d, J = 4.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 145.8 (C), 145.4 (C), 143.4 (C), 137.5 (CH), 134.8 (C), 129.9 (CH), 129.4 (CH), 128.3 (CH), 123.4 (C), 122.3 (CH), 118.7 (CF_3, q, J = 320.8 Hz), 104.9 (CH), 21.7 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.5; HRMS (m/z): $[M+H]^+$ calcd for $C_{15}H_{11}F_3N_2O_5S_2$ 421.0134; found 421.0132. mp 128-129 °C.

Quinoxalin-6-yl triflate (3f): Following the general procedure B, quinoxalin-6-ol (937 mg, 6.4 mmol) was converted to quinoxalin-6-yl triflate (1.31 g, 73% yield). The compound was isolated as crystalline white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 2H), 8.24 (dd, J = 9.2, 0.5 Hz, 1H), 8.07 (d, J = 2.7 Hz, 1H), 7.71 (dd, J = 9.2, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (C), 145.4 (CH), 145.1 (CH), 143.0 (C), 142.0 (C), 132.1 (CH), 124.0 (CH), 121.3 (CH), 118.8 (CF_3, q, J = 320.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.6; HRMS (m/z): $[M+H]^+$ calcd for $C_9H_5F_3N_2O_3S$ 279.0046; found 279.0043. mp 76-77 °C.

6-Methoxypyridin-3-yl triflate (3h): Following general procedure A, using pyridine (4.0 mL. 50.0 mmol) as the base, 6-methoxy-3-hydroxypyridine (2.5 g, 20.0 mmol) was converted to 6-methoxypyridin-3-yl triflate (5.1 g, 92% yield). The compound was isolated as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 3.2 Hz, 1H), 7.50 (dd, J = 9.2, 2.8 Hz, 1H), 6.81 (dd, J = 9.2, 0.8 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 163.2 (C), 141.6 (C), 139.5 (CH), 132.0 (CH), 118.7 (CF_3, q, J = 318 Hz) 112.2 (CH), 54.2 (CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.5. HRMS (m/z): $[M-H]^-$ calcd for $C_7H_6F_3NO_4S$ 255.98969; found 255.99021.

General procedure for Pd-catalyzed reactions of phenyl triflate with $NaSO_2CF_3$ (Table 1). Inside an inert atmosphere glove box, $Pd_2(dba)_3$ (0.02 g, 0.02 mmol) and phosphine ligand (0.05 mmol) were charged to a 1-dram vial equipped with a magnetic stir bar and Teflon screw cap. Solvent (0.8 mL) was added, the vial was placed on a metal heating block, temperature was raised to 80 °C and mixed for approximately 30 min. Phenyl triflate (0.20 g, 0.88 mmol), and tris(3,6-dioxaheptyl)amine (TDA) (0.014 g, 0.05 mmol) were charged to a separate 1-dram vial. Toluene (0.8 mL) was added to obtain a clear solution. The first 1-dram vial was removed from the metal heating plate. The solution of phenyl triflate and TDA was transferred to the 1-dram vial containing the catalyst with a syringe. $NaSO_2CF_3$ (0.28 g, 1.8 mmol) was charged, the 1-dram vial was returned to the heating block and the reaction mixture was vigorously stirred for the time indicated in Table 1. The reaction mixture was removed from the heating block, cooled to room temperature, brought outside the glove box, filtered through a Whatman 0.2 μm PTFE filter, rinsed with dichloromethane (~15-20 mL) and was collected in a tared 25-mL Erlenmeyer flask. The weight of filtered solution (Wt_{prod}) was recorded. A portion (~ 1.0-1.5 g) of the solution was weighed into a tared 25-mL volumetric flask (Wt_{sample}), diluted to 25 mL with acetonitrile and was injected into an HPLC instrument. The area corresponding to the product **2a** was recorded (A_{prod}).

Assay yield calculation: A known weight of the commercial sample of **2a** was was weighed into a 50-mL volumetric flask (Wt_{std}), dissolved in 50 mL acetonitrile and injected into a HPLC instrument. The area corresponding to the product was recorded (A_{std}). The assay yield of **2a** in entries 1-19, table 1 was determined by using the following formula.

$$\text{Assay yield (\%)} = \frac{A_{prod} \times Wt_{prod} \times Wt_{std} \times 100}{A_{std} \times Wt_{sample} \times \text{theroretical yield (g)}}$$

General procedure for Pd-catalyzed reactions of aryl and heteroaryl triflates with $NaSO_2CF_3$ (Table 2 and Table 3). Inside an inert atmosphere glove box, $Pd_2(dba)_3$ (1.5 mol %) and **III** (3.6 mol %) were charged to a 20-mL vial equipped with a magnetic stir bar, Teflon screw cap, and glass balls of 4 mm diameter (5-10).[77] Toluene (1-1.5 mL) was added, the vial was placed on a metal heating block, temperature was raised to 80 °C and mixed for approximately 30 min. Aryl (heteroaryl) triflate (1 equiv), and TDA (5 mol %) were charged to a separate 1-dram vial. Additional toluene was added to obtain the final concentration of 0.30 to 0.40 M. The 20-mL vial was removed from the metal heating plate. The solution of aryl (heteroaryl) triflate and TDA was transferred to the 20-mL vial containing the catalyst with a syringe. $NaSO_2CF_3$ (1.5 equiv) was charged, the 20-mL vial was returned to the heating block and the reaction mixture was heated for the indicated time. The reaction mixture was removed from the heating block, cooled to room temperature, brought outside the glove box, filtered through a Whatman 0.2 μm

PTFE filter, rinsed with dichloromethane (~15-20 mL) and was collected in a tared 50-mL Erlenmeyer flask. The weight of filtered solution (Wt_{prod}) was recorded. A portion (~ 0.2-0.5 g) of the solution was weighed into a tared 50-mL volumetric flask (Wt_{sample}), diluted to 50 mL with acetonitrile and was injected into an HPLC instrument. The area corresponding to the corresponding aryl (heteroaryl) triflones product was recorded (A_{prod}). The filtrate was concentrated *in vacuo*. The crude product was isolated via flash column chromatography. After the pure product was isolated, approximately 10-15 mg of the pure product was weighed into a 50-mL volumetric flask, dissolved in 50-mL acetonitrile and injected onto a HPLC instrument. The area corresponding to the product was recorded (A_{std}). The yield of the product in the crude reaction mixture was calculated using the formula shown above.

(Trifluoromethylsulfonyl)benzene (**2a**): Following the general procedure, a mixture of **1a** (0.25 g, 1.1 mmol), $NaSO_2CF_3$ (0.21 g, 1.3 mmol), $Pd_2(dba)_3$ (0.025 g, 0.028 mmol), **III** (0.031 g, 0.066 mmol), and TDA (0.018 g, 0.055 mmol) were heated in toluene for 3 h. The desired product **2b** (0.22 g, 96%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-20% EtOAc/heptanes as eluent to provide the title compound (0.20 g, 0.93 mmol, 84%) as colorless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.05 (d, J = 7 Hz, 2H), 7.86 (tt, J = 7, 1.4 Hz, 1H), 7.69 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 136.6 (CH), 131.3 (q, J = 1.8. C), 130.8 (CH), 129.9 (CH), 119.8 (CF_3, q, J = 334 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ -79.5. The proton, carbon and fluorine data for this compound were consistent with literature data.[34]

1-Dimethylamino-4-(trifluoromethyl)sulfonyl)benzene (**2b**): Following the general procedure, a mixture of **1b** (0.50 g, 1.9 mmol), $NaSO_2CF_3$ (0.44 g, 2.8 mmol), $Pd_2(dba)_3$ (0.026 g, 0.028 mmol), **III** (0.031 g, 0.067 mmol), and TDA (0.030 g, 0.093 mmol) were heated in toluene (5 mL) for 2 h. The desired product **2b** (0.45 g, 98%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-10% EtOAc/heptanes as eluent to provide the title compound (0.35 g, 1.4 mmol, 75%) as crystalline off-white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 6 Hz, 2H), 6.76 (d, J = 6 Hz, 2H), 3.15 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1 (C), 132.6 (CH), 123.04 (CF_3, q, J = 326 Hz), 113.4 (C), 111.3 (CH), 40.1 (CH_3). ^{19}F NMR (564 MHz, $CDCl_3$) δ -79.3; HRMS (m/z): $[M+H]^+$ calcd for $C_9H_{10}F_3NO_2S$ 253.03843; found 253.03874. mp 139-140 °C.

1-Methoxy-4-(trifluoromethyl)sulfonyl)benzene (**2c**): Following the general procedure, a mixture of 1c (0.50 g, 2.0 mmol), $NaSO_2CF_3$ (0.46 g, 2.9 mmol), $Pd_2(dba)_3$ (0.027 g, 0.029 mmol), **III** (0.033 g, 0.070 mmol), and TDA (0.032 g, 0.098 mmol) were heated in toluene (5 mL) for 2 h. The desired product **2c** (0.46 g, 98%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-10% EtOAc/heptanes as eluent to provide the title compound (0.40 g, 1. mmol, 85%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.96, 7.96, (d *app*t, J = 8.4, 3.5 Hz, 2H), 7.11 (d *app*t, J = 9.1, 2.8 Hz, 2H), 3.94 (S, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.2 (C), 133.3 (CH), 122.0 (C), 119.0 (CF_3, q, J = 326 Hz),

115.3 (CH), 56.0 (CH_3).[19]F NMR (376 MHz, $CDCl_3$) δ -82.8. The proton, carbon and fluorine data for this compound were consistent with literature data.[34]

5-((Trifluoromethyl)sulfonyl)benzo[d][1,3]dioxole (**2d**): Following the general procedure, a mixture of **1d** (0.50 g, 1.9 mmol), $NaSO_2CF_3$ (0.43 g, 2.8 mmol), $Pd_2(dba)_3$ (0.026 g, 0.028 mmol), **III** (0.031 g, 0.067 mmol), and TDA (0.030 g, 0.093 mmol) were heated in toluene (5 mL) for 2 h. The desired product **2d** (0.41 g, 87%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-10% EtOAc/heptanes as eluent to provide benzo[d][1,3]dioxol-5-yl triflone (0.37 g, 1.5 mmol, 79%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.63 (dd, J = 8.4, 2.1 Hz, 1H), 7.38 (d, J = 2.1 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.18 (s, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 154.9 (C), 148.9 (C), 128.0 (CH), 123.7 (C), 119.5 (CF_3, q, J = 324 Hz), 109.9 (CH), 109.2 (CH), 103.1 (CH_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.6 Anal. Calcd for $C_8H_5F_3O_4S$: C, 37.80; H, 1.98. Found: C, 38.10; H, 1.83. mp 98-100 °C.

***tert*-Butyl(4-((trifluoromethyl)sulfonyl)phenyl)carbamate** (**2e**): Following the general procedure, a mixture of **1e** (0.50 g, 1.5 mmol), $NaSO_2CF_3$ (0.34 g, 2.2 mmol), $Pd_2(dba)_3$ (0.020 g, 0.022 mmol), **III** (0.025 g, 0.053 mmol), and TDA (0.024 g, 0.073 mmol) were heated in toluene (4.5 mL) for 5.5 h. The desired product **2e** (0.44 g, 92%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-10% EtOAc/heptanes as eluent to provide the title compound (0.38 g, 1.2 mmol, 80%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.94 (d *app*t, J = 7.0, 2.1 Hz, 2H), 7.66 (d *app*t, J = 9.1, 2.1 Hz, 2H), 6.90 (s, 1H), 1.15 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 151.7 (C), 146.3 (C), 132.5 (CH), 123.6 (C), 119.9 (CF_3, q, J = 326 Hz), 118.2 (CH), 82.4 (C), 28.2 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.7. HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{14}F_3NO_4S$ 325.05956; found 325.05979. mp 105-107 °C.

Methyl(4-((trifluoromethyl)sulfonyl)phenyl)sulfane (**2f**): Following the general procedure, a mixture of **1f** (0.50 g, 1.8 mmol), $NaSO_2CF_3$ (0.43 g, 2.8 mmol), $Pd_2(dba)_3$ (0.025 g, 0.028 mmol), **III** (0.031 g, 0.066 mmol), and TDA (0.030 g, 0.092 mmol) were heated in toluene (5 mL) for 12 h. The desired product **2f** (0.44 g, 92%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-5% EtOAc/heptanes as eluent to provide the title compound (0.34 g, 1.3 mmol, 72%) as amorphous white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.89 (d *app*t, J = 8.4, 2.8 Hz, 2H), 7.43 (d *app*t, J = 7.7, 2.1 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9 (C), 130.8 (CH), 125.9 (C), 125.5 (CH), 119.8 (CF_3, q, J = 329 Hz), 14.5 (CH_3). ^{19}F NMR (564 MHz, $CDCl_3$) δ -78.6. Anal. Calcd for $C_8H_5F_3O_2S_2$: C, 37.49; H, 2.75. Found: C, 37.52; H, 2.78.

1-((Trifluoromethyl)sulfonyl)naphthalene (**2g**): Following the general procedure, a mixture of **1g** (0.50 g, 1.8 mmol), $NaSO_2CF_3$ (0.42 g, 2.7 mmol), $Pd_2(dba)_3$ (0.041 g, 0.045 mmol), **III** (0.051 g, 0.11 mmol), and TDA (0.029 g, 0.091 mmol) were heated in toluene (5 mL) for 4.5 h. The desired product **2g** (0.43 g, 92%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column

chromatography using 0-8% EtOAc/heptanes as eluent to provide the title compound (0.39 g, 1.5 mmol, 83%) as crystalline white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.8 Hz, 1H), 8.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.78 (m, 1H), 7.68 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 138.5 (CH), 135.2 (CH), 134.3 (C), 130.2 (C), 129.7 (CH), 129.3 (CH), 127.8 (CH), 126.9 (C), 124.5 (CH), 124.4 (CH), 120.3 (CF_3, q, *J* = 326 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -77.8. Anal. Calcd for $C_{11}H_7F_3O_2S$: C, 50.77; H, 2.71. Found: C, 50.92; H, 2.29. mp 56-58 °C.

1-Methoxy-2-((trifluoromethyl)sulfonyl)benzene (**2h**): Following the general procedure, a mixture of **1h** (0.50 g, 1.9 mmol), $NaSO_2CF_3$ (0.61 g, 3.9 mmol), $Pd_2(dba)_3$ (0.071 g, 0.078 mmol), **III** (0.088 g, 0.19 mmol), and TDA (0.032 g, 0.10 mmol) were heated in toluene (5.5 mL) for 20 h. The desired product **2h** (0.42 g, 89%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-8% EtOAc/heptanes as eluent to provide the title compound (0.30 g, 1.2 mmol, 64%) as white solid in approximately 90% purity by HPLC. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.75 (m, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 159.9 (C), 138.5 (CH), 133.5 (CH), 121.0 (CH), 119.9 (CF_3, *J* = 354 Hz), 119.8 (C), 113.0 (CH), 56.5 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.9.

4-((Trifluoromethyl)sulfonyl)phenyl acetate (**2i**): Following the general procedure, a mixture of **1i** (0.50 g, 1.8 mmol), $NaSO_2CF_3$ (0.41 g, 2.6 mmol), $Pd_2(dba)_3$ (0.024 g, 0.026 mmol), **III** (0.030 g, 0.063 mmol), and TDA (0.028 g, 0.088 mmol) were heated in toluene (5 mL) for 20 h. The desired product **2i** (0.40 g, 84%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-8% EtOAc/heptanes as eluent to provide the title compound (0.36 g, 1.3 mmol, 75%) as clear oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d *aap*t, *J* = 6.6, 3.0 Hz, 2H), 7.46 (d *app*t, *J* = 7.2, 3.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1 (C), 157.1 (C), 132.6 (CH), 128.1 (C), 123.2 (CH), 119.7 (CF_3, *J* = 326 Hz), 21.1 (CH_3). ^{19}F NMR (564 MHz, $CDCl_3$) δ -78.4. Anal. Calcd for $C_9H_7F_3O_4S$: C, 40.30; H, 2.63. Found: C, 40.37; H, 2.49.

Methyl 4-((trifluoromethyl)sulfonyl)benzoate (**2j**): Following the general procedure, a mixture of **1j** (0.50 g, 1.8 mmol), $NaSO_2CF_3$ (0.41 g, 2.6 mmol), $Pd_2(dba)_3$ (0.040 g, 0.044 mmol), **III** (0.049 g, 0.11 mmol), and TDA (0.028 g, 0.088 mmol) were heated in toluene (5 mL) at 90 °C for 18 h. The crude product was purified by flash column chromatography using 0-8% EtOAc/heptanes as eluent to provide the title compound (0.36 g, 1.3 mmol, 75%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.32 (d *aap*t, *J* = 8.4, 2.1 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H), 4.0 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 164.9 (C), 137.4 (C), 135.2 (C), 130.9 (CH), 130.8 (CH), 119.7 (CF_3, *J* = 327 Hz), 53.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.0. Anal. Calcd for $C_9H_7F_3O_4S$: C, 40.30; H, 2.63. Found: C, 40.25; H, 2.38. mp 56-58 °C.

4,4,5,5-Tetramethyl-2-(4-((trifluoromethyl)sulfonyl)phenyl)-1,3,2-dioxaborolane (**2k**): Following the general procedure, a mixture of **1k** (0.25 g, 0.71 mmol), $NaSO_2CF_3$ (0.17 g, 1.1 mmol), $Pd_2(dba)_3$ (0.016 g, 0.018 mmol), **III** (0.020 g, 0.043 mmol), and

TDA (0.029 g, 0.089 mmol) were heated in toluene (2.2 mL) at 90 °C for 23 h. The desired product **2k** (0.21 g, 88%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-8% EtOAc/heptanes as eluent to provide the title compound (0.15 g, 0.43 mmol, 61%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 2H), 8.02 (d, *J* = 7.7 Hz, 2H), 1.37 (s, 12H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 135.8 (CH), 133.3 (C), 129.6 (CH), 119.8 (CF_3, *J* = 326 Hz), 84.9 (C), 24.9 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4. Anal. Calcd for $C_{13}H_{16}BF_3O_4S$: C, 46.45; H, 4.80. Found: C, 47.08; H, 4.89. mp 87-88 °C.

1-(4-(Trifluoromethyl)sulfonyl)phenyl)ethanone (**2l**): Following the general procedure, a mixture of **1l** (0.50 g, 1.9 mmol), $NaSO_2CF_3$ (0.44 g, 2.8 mmol), $Pd_2(dba)_3$ (0.051 g, 0.056 mmol), **III** (0.063 g, 0.13 mmol), and TDA (0.030, 0.093 mmol) were heated in toluene (5 mL) at 90 °C for 32 h. The desired product **2l** (0.34 g, 72%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-8% EtOAc/heptanes as eluent to provide the title compound (0.28 g, 1.1 mmol, 60%) as crystalline white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d *aap*t, *J* = 8.8, 1.6 Hz, 2H), 8.16 (m, 2H), 2.74 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 196.9 (C), 142.9 (C), 135.1 (C), 131.3 (CH), 129.4 (CH), 119.7 (CF_3, *J* = 326 Hz), 27.0 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.0. Anal. Calcd for $C_9H_7F_3O_3S$: C, 42.86; H, 2.80. Found: C, 43.15; H, 2.58. mp 58-60 °C.

3-((Trifluoromethyl)sulfonyl)benzonitrile (**2m**): Following the general procedure, a mixture of **1m** (0.50 g, 2.0 mmol), $NaSO_2CF_3$ (0.47 g, 3.0 mmol), $Pd_2(dba)_3$ (0.046 g, 0.050 mmol), **III** (0.056 g, 0.12 mmol), and TDA (0.032 g, 0.10 mmol) were heated in toluene (5.5 mL) at 100 °C for 20 h. The desired product **2m** (0.19 g, 41%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using 0-8% EtOAc/heptanes as eluent to provide the title compound (0.05 g, 0.21 mmol, 11%) as amorphous white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.30 (d, *J* = 7.0 Hz, 1H), 8.14 (d *aap*t, *J* = 6.6, 1.2 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.4 (CH), 134.5 (CH), 134.2 (CH), 133.4 (C), 133.1 (CH), 119.5 (CF_3, *J* = 326 Hz), 116.1 (C), 115.0 (C). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.0. Anal. Calcd for $C_9H_7F_3O_3S$: C, 42.86; H, 2.80. Found: C, 43.15; H, 2.58.

5-((Trifluoromethyl)sulfonyl)benzofuran (**4a**): Following the general procedure, a mixture of **3a** (0.20 g, 0.75 mmol), $NaSO_2CF_3$ (0.18 g, 3.0 mmol), $Pd_2(dba)_3$ (0.017 g, 0.019 mmol), **III** (0.021 g, 0.045 mmol), and TDA (0.012 g, 0.038 mmol) were heated in toluene (2.1 mL) at 80 °C for 9 h. The desired product **4a** (0.18 g, 96%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using dichloromethane as eluent to provide the title compound (0.16 g, 0.65 mmol, 86%) as crystalline white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.8 Hz, 1H), 7.98 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8 (C), 148.1 (CH), 128.7 (C), 126.6 (CH), 125.8 (CH), 125.6 (C), 119.9 (CF_3, *J* = 326 Hz), 113.1 (CH),

107.2 (CH). ^{19}F NMR (564 MHz, $CDCl_3$) δ -78.5. Anal. Calcd for $C_9H_5F_3O_3S$: C, 43.29; H, 2.01. Found: C, 43.27; H, 1.86. mp 80-81 °C.

5-((Trifluoromethyl)sulfonyl)benzo[b]thiophene (**4b**): Following the general procedure, a mixture of **3b** (0.50 g, 1.8 mmol), $NaSO_2CF_3$ (0.42 g, 2.7 mmol), $Pd_2(dba)_3$ (0.041 g, 0.04 mmol), **III** (0.050 g, 0.11 mmol), and TDA (0.029 g, 0.089 mmol) were heated in toluene (5.5 mL) at 80 °C for 5 h. The desired product **4b** (0.46 g, 97%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using dichloromethane as eluent to provide the title compound (0.40 g, 1.5 mmol, 85%) as crystalline white solid.
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.4 Hz, 1H), 8.15 (d *app*t, *J* = 8.4, 0.7 Hz, 1H), 7.92 (dd, *J* = 7.4, 2.1 Hz 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 5.6, 0.7 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 147.86 (C), 139.6 (C), 130.27 (CH), 127.3 (CH), 127.0 (C), 124.4 (CH), 124.0 (CH), 119.7 (CF_3, *J* = 326 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4. Anal. Calcd for $C_9H_5F_3O_2S_2$: C, 40.60; H, 1.89. Found: C, 40.52; H, 1.59. mp 100-102 °C.

5-((Trifluoromethyl)sulfonyl)-1-(triisopropylsilyl)-1H-indole (**4c**): Following the general procedure, a mixture of **3c** (0.50 g, 1.2 mmol), $NaSO_2CF_3$ (0.28 g, 1.8 mmol), $Pd_2(dba)_3$ (0.027 g, 0.030 mmol), **III** (0.33 g, 0.071 mmol), and TDA (0.019 g, 0.050 mmol) were heated in toluene (3.8 mL) at 80 °C for 2 h. The desired product **4c** (0.42 g, 88%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using dichloromethane as eluent to provide the title compound (0.40 g, 0.99 mmol, 83%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.1 Hz, 1H), 7.74 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.68 (d, *J* = 9.1 Hz 1H), 7.45 (d, *J* = 3.5 Hz, 1H), 6.83 (d, *J* = 9.1 Hz, 1H), 1.72 (sept, *J* = 6.3 Hz, 3H), 1.15 (d, J = 7.7 Hz, 18 H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 145.1 (C), 134.5 (CH), 131.5 (C), 125.4 (CH), 122.6 (CH), 121.2 (C), 120.1 (CF_3, *J* = 326 Hz), 114.7 (CH), 106.5 (CH), 17.9 (CH_3), 12.7 (CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.5. Anal. Calcd for $C_{18}H_{26}F_3NO_2SSi$: C, 53.31; H, 6.46; N, 3.45. Found: C, 53.26; H, 6.53; N, 3.34. mp 124-126 °C.

5-((Trifluoromethyl)sulfonyl)benzo[d]oxazole (**4d**): Following the general procedure, a mixture of **3d** (0.20 g, 0.75 mmol), $NaSO_2CF_3$ (0.18 g, 1.1 mmol), $Pd_2(dba)_3$ (0.017 g, 0.019 mmol), **III** (0.021 g, 0.045 mmol), and TDA (0.012 g, 0.037 mmol) were heated in toluene (2.1 mL) at 80 °C for 9.5 h. The desired product **4d** (0.18 g, 94%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using EtOAc/heptanes (0-12%) as eluent to provide the title compound (0.15 g, 0.61 mmol, 81%) as crystalline white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.8 Hz, 1H), 7.33 (s, 1H), 8.12 (dd, *J* = 9.0, 1.8 Hz 1H), 7.89 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1 (CH), 154.8 (C), 141.1 (C), 128.3 (CH), 128.0 (C), 124.9 (CH), 119.8 (CF_3, *J* = 326 Hz), 112.8 (CH).^{19}F NMR (564 MHz, $CDCl_3$) δ -78.2. HRMS (m/z): $[M+H]^+$ calcd for $C_8H_4F_3NO_3S$ 250.98668; found 250.98640. mp 88-89 °C.

1-Tosyl-5-((trifluoromethyl)sulfonyl)-1H-pyrrolo[2,3-b]pyridine (**4e**): Following the general procedure, a mixture of **3e** (0.20 g, 0.48 mmol), $NaSO_2CF_3$ (0.11 g, 0.71 mmol), $Pd_2(dba)_3$ (0.011 g, 0.012 mmol), **III** (0.013 g, 0.029 mmol), and TDA (0.008 g, 0.024 mmol) were heated in toluene (2.1 mL) at 80 °C for 8 h. The desired product **4e** (0.17 g, 88%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using dichloromethane as eluent to provide the title compound (0.16 g, 0.39 mmol, 82%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.1 Hz, 1H), 8.55 (d, *J* = 2.8 Hz, 1H), 8.18 (d *app*t, *J* = 8.4, 2.1 Hz 2H), 8.05 (d, *J* = 3.5 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2 H), 6.85 (d, *J* = 3.5 Hz, 1 H), 2.47 (S = 3 H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 149.6 (C), 146.5 (C), 146.1 (CH), 134.3 (C), 132.8 (CH), 130.0 (CH), 129.9 (CH), 128.6 (CH), 122.8 (C), 122.6 (C), 119.7 (CF_3, *J* = 324 Hz), 105.3 (CH), 21.8 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4 HRMS (m/z): $[M+H]^+$ calcd for $C_{15}H_{11}F_3N_2O_4S_2$ 405.01851; found 405.01856. mp 151-152 °C.

6-((Trifluoromethyl)sulfonyl)quinoxaline (**4f**): Following the general procedure, a mixture of **3f** (0.40 g, 1.4 mmol), $NaSO_2CF_3$ (0.34 g, 2.2 mmol), $Pd_2(dba)_3$ (0.033 g, 0.036 mmol), **III** (0.040 g, 0.086 mmol), and TDA (0.023 g, 0.072 mmol) were heated in toluene (4 mL) at 80 °C for 12 h. The desired product **4f** (0.31 g, 81%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using ethyl acetate/heptanes (0-15%) as eluent to provide the title compound (0.28 g, 1.1 mmol, 74%) as crystalline white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.4 Hz, 2H), 8.97 (s, 1H), 8.43 (d, *J* = 9.0 Hz, 1H), 8.31 (dd, *J* = 8.4, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7 (CH), 147.4 (C), 146.1 (C), 141.9 (C), 135.5 (CH), 132.9 (C), 132.5 (CH), 128.2 (CH), 119.8 (CF_3, *J* = 328 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ -77.7 HRMS (m/z): $[M+H]^+$ calcd for $C_9H_5F_3N_2O_2S$ 263.00966; found 263.01071. mp 89-90 °C.

6-((Trifluoromethyl)sulfonyl)quinoline (**4g**): Following the general procedure, a mixture of **3g** (0.30 g, 1.1 mmol), $NaSO_2CF_3$ (0.37 g, 2.2 mmol), $Pd_2(dba)_3$ (0.025 g, 0.027 mmol), **III** (0.030 g, 0.065 mmol), and TDA (0.018 g, 0.054 mmol) were heated in toluene (4 mL) at 80 °C for 27.5 h. The crude product was purified by flash column chromatography using ethyl acetate/heptanes (0-15%) as eluent to provide the title compound (0.23 g, 0.89 mmol, 82%) as crystalline white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.23 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.73 (d, *J* = 2.1 Hz, 1H), 8.45 (dd, *J* = 9.1, 1.4 Hz, 1H), 8.43 (d, *J* =9.1 Hz, 1H), 8.26 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.70 (dd, *J* = 8.4, 4.2 Hz, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.0 (CH), 150.9 (C), 137.7 (CH), 134.2 (CH), 132.1 (CH), 129.1 (C), 127.6 (CH), 127.4 (C), 123.3 (CH), 119.9 (CF_3, *J* = 326 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.1. HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_6F_3NO_2S$ 262.01450; found 262.01456. mp 70-71 °C.

2-Methoxy-5-((trifluoromethyl)sulfonyl)pyridine (**4h**): Following the general procedure, a mixture of **3h** (0.50 g, 1.9 mmol), $NaSO_2CF_3$ (0.46 g, 2.9 mmol), $Pd_2(dba)_3$ (0.045 g, 0.049 mmol), **III** (0.055 g, 0.12 mmol), and TDA (0.031 g, 0.097 mmol) were heated in toluene (5 mL) at 100 °C for 21 h. The desired product **4h** (0.47 g, >99%) was calculated to be present in the crude reaction mixture. The crude product was purified by flash column chromatography using ethyl acetate/heptanes (0-15%) as eluent to provide

the title compound (0.36 g, 1.5 mmol, 77%) as crystallinewhite solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 2.4 Hz, 1H), 8.08 (ddq, J = 8.8, 2.4, 0.8 Hz, 1H), 6.96 (dd, J = 8.8, 0.8 Hz, 1H), 4.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (C), 152.1 (CH), 139.8 (CH), 120.3 (C), 119.7 (CF_3, J = 323 Hz), 112.4 (CH), 55.0 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.9. Anal. Calcd for $C_7H_6F_3NO_3S$: C, 34.86; H, 2.51; N, 5.81. Found: C, 35.27; H, 2.39; N, 5.67. mp 41-3 °C.

3-((Trifluoromethyl)sulfonyl)pyridine (**4i**): Following the general procedure, a mixture of **3i** (0.50 g, 2.2 mmol), $NaSO_2CF_3$ (0.52 g, 3.3 mmol), $Pd_2(dba)_3$ (0.050 g, 0.055 mmol), **III** (0.062 g, 0.13 mmol), and TDA (0.036 g, 0.11 mmol) were heated in toluene (5 mL) at 100 °C for 21 h. The desired product **4i** (0.071 g, 15%) was calculated to be present in the crude reaction mixture. By normal phase SiO_2 chromatography, triflate **3i** and product **4i** were found to co-elute. To purify **4i**, the unreacted triflate was hydrolyzed using Cs_2CO_3,[78] then the crude product was purified by flash column chromatography using dichloromethane as eluent to provide the title compound (0.026 g, 0.12 mmol, 6%) as amorphous white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, J = 2.4 Hz, 1H), 9.06 (dd, J = 4.8, 1.6 Hz, 1H), 8.34 (m, 1H), 7.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (CH), 151.3 (CH), 138.3 (CH), 128.5 (C), 124.3 (CH), 119.5 (CF_3, J = 324 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.3. LRMS (m/z): $[M+H]^+$ calcd for $C_6H_5F_3NO_2S$ 212.0; found 212.0.

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Supporting Information Available: ^{1}H, ^{19}F and ^{13}C NMR spectra of aryl(heteroaryl)triflones.

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