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

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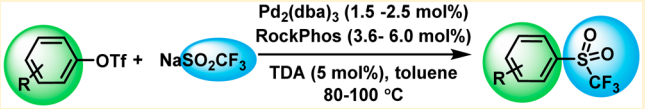
Supporting Information

**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 transmetalation 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 is present 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[24−26] cycloaddition reactions,[27−29] thermal decomposition,[30] etc. has 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 accessible electrophiles, such as aryl halides and pseudohalides, did not react with $NaSO_2CF_3$ under the reported conditions. In addition, only 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;[35−39,1,40−49] 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 ($\sigma_p$ = 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.[52,55−62] 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 chosen 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, and 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

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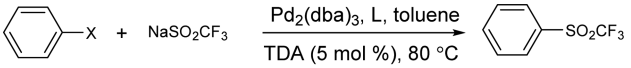
bulky phosphine ligands that are known to be effective for Pd-catalyzed reactions of other electron-poor nucleophiles were surveyed.

While formation of trace amounts of phenyl triflone (**2a**) was observed in the presence of BrettPhos (**I**) (Table 1, entry 1), however, no product formation was observed in the presence of **IX** (entry 9). Although a 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, a negligible amount of product was formed when $Pd(OAc)_2$ or $Pd(MeCN)_2Cl_2$ was 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 used, respectively, 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]

After the reaction conditions for coupling of **1a** with $Na_2SO_2CF_3$ were optimized, the reactivities of sterically and electronically diverse aryl triflates were explored (Scheme 1). Aryl triflones (**2a**–**l**) were isolated in synthetically useful yields from reactions of aryl triflates containing prevalent functional groups: dimethylamino, ether, acetal, carbamate, thioether, acetate, ester,

**Table 1. Evaluation of Reaction Parameters for Pd-Catalyzed Formation of Aryltriflone**[a]

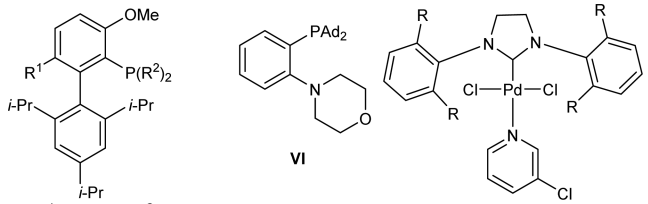



X = OTf, **1a**
X= Cl, **1a'**
X = Br, **1a"**

**2a**

| entry | X | L (mol %) | time (h) | **2a**[b] (%) |
|---|---|---|---|---|
| 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[c] | OTf | **VII** (5) | 6 | 0 |
| 8[c] | OTf | **VIII** (5) | 6 | 0 |
| 9 | OTf | **IX** (10) | 6 | 0 |
| 10[d] | Cl | **III** (6) | 25 | 50 |
| 11[d] | Br | **III** (6) | 25 | 7 |
| 12[e] | OTf | **III** (6) | 6 | 74 |

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

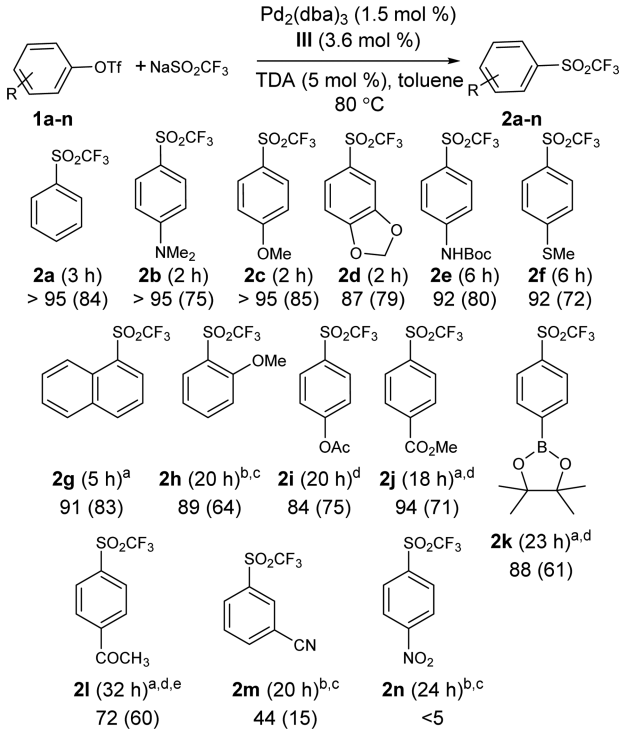



**I**: $R^1$ = OMe, $R^2$ = Cy
**II**: $R^1$ = OMe, $R^2$ = *t*-Bu
**III**: $R^1$ = Me, $R^2$ = *t*-Bu
**IV**: $R^1$ = Me, $R^2$ = Ad
**V**: $R^1$ = Me, $R^2$ = Cy
**IX**: $R^1$ = OMe, $R^2$ = 3,5-$CF_3$-Ph

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

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 phosphorus 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 phosphorus are known to accelerate the reductive elimination step;[65]

**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) and $NaSO_2CF_3$ (1.5 equiv) for the indicated time. Assay yield based on HPLC analysis at 210 nm. The isolated yield is reported in 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.



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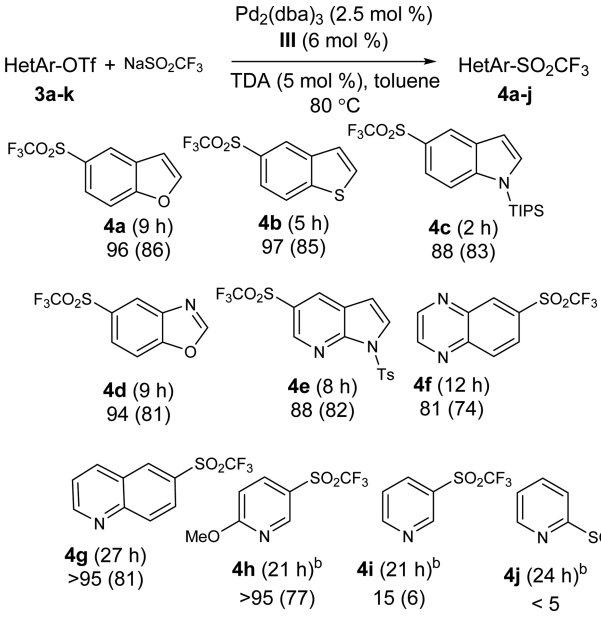
boronate ester, and acetyl. Aryl triflates containing substitutents with a wide range of electron-donating abilities ($NMe_2$ ($\sigma_p$ = −0.83) to $COCH_3$ ($\sigma_p$ = 0.50)) formed the corresponding aryl triflones in high yields. Aryl triflates functionalized with substitutents more electron-deficient than acetyl were poor substrates for the reaction (**1m** and **1n**). Ortho substituted aryl triflates such as **1g** and **1h** were found to be suitable substrates.

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

**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. [c]Reaction at 100 °C.

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]

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.

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]

**Scheme 3. Pd-Catalyzed Reaction of Aryl Chlorides with $NaSO_2CF_3$**

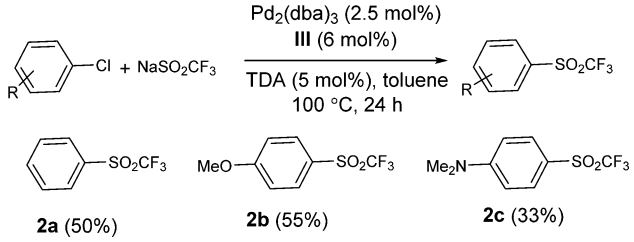
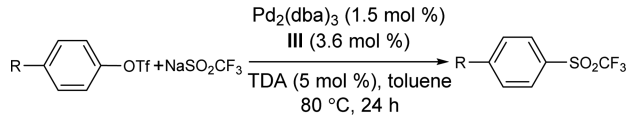



**Table 2. Comparison of Initial Rates of Reactions of Electronically Diverse Aryl Triflates**




| entry | R | $\sigma_p$ | initial rate ($10^{-3}$ M/min) |
|---|---|---|---|
| 1 | $OCH_3$ | −0.27 | 21 |
| 2 | H | 0 | 4 |
| 3 | $COCH_3$ | 0.50 | 0.4 |

bond-forming reactions, the dependence appears to be more pronounced for the formation of $C(sp^2)$−$SO_2CF_3$ bonds.

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



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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 offer 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** suggest 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 *o*-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, and neutral reaction conditions which afford 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 glovebox. 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 in sure-seal bottles from commercial sources and were sparged with nitrogen before use. $Pd_2(dba)_3$, phosphine ligands (**I**−**VI** and **IX**), Pd−carbene complexes (**VII** and **VIII**), phenyl triflate, 4-methoxylphenyl triflate, 4-acetylphenyl triflate, 4-nitrophenyl triflate, naphthalenyl 1-triflate, quinolinyl 6-triflate, chlorobenzene, bromobenzene, 4-methoxyphenyl chloride, 4-(dimethylamino)-phenyl 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 eluent. 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 HPLC. When completed, $CH_2Cl_2$ was added, and 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 on silica gel using an ethyl acetate/heptane gradient.

*Procedure B.* To a vial with magnetic stirring bar were 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 procedure A, but without allowing the reaction mixture to warm 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): $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.16−7.07 (m, 2H), 6.74−6.53 (m, 2H), 2.97 (s, 6H); $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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 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): $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.80 (d, $J$ = 8.3 Hz, 1H), 6.78−6.73 (m, 2H), 6.05 (s, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −72.7. The proton data for this compound were consistent with literature data.[72]

*4-((tert-Butoxycarbonyl)amino)phenyl Triflate (**1e**).* Following 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): $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 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) $\delta$ 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, $CDCl_3$) $\delta$ −72.8. The proton and carbon data for this compound were consistent with literature data.[73]

*4-(Methylthio)phenyl Triflate (**1f**).* Following procedure A, 1.50 g of 4-(methylthio)phenol was converted to 2.68 g of 4-(methylthio)-phenyl trifluoromethanesulfonate (92% yield): $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.31−7.26 (m, 2H), 7.22−7.15 (m, 2H), 2.49 (s, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −72.8. The proton, carbon, and fluorine data for this compound were consistent with literature data.[59]

*2-Methoxyphenyl Triflate (**1h**).* Following procedure A, 1.00 g of 2-methoxyphenol was converted to 1.73 g of 2-methoxyphenyl trifluoromethanesulfonate (84% yield): $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −73.9. The proton and carbon data for this compound were consistent with literature data.[74]

*4-(((Trifluoromethyl)sulfonyl)oxy)phenyl Acetate (**1i**).* Following 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 a colorless oil: $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.32−7.26 (m, 2H), 7.23−7.15 (m, 2H), 2.31 (s, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −72.8. Anal. Calcd for $C_9H_7F_3O_5S$: C, 38.04; H, 2.48. Found: C, 38.36; H, 2.32.



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*Methyl 4-(((Trifluoromethyl)sulfonyl)oxy)benzoate (**1j**).* Following 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, $CDCl_3$) $\delta$ 8.23−8.08 (m, 2H), 7.43−7.29 (m, 2H), 3.95 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −72.5. The proton, carbon, and fluorine data for this compound were consistent with literature data.[76]

*Benzofuran-5-yl Triflate (**3a**).* Following 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −73.7; HRMS ($m/z$) [M − H]$^-$ calcd for $C_9H_5F_3O_4S$ 264.9788, found 264.9790.

*Benzo[b]thiophene-5-yl Triflate (**3b**).* Following procedure B, benzo[*b*]thiophene-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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −72.8. Anal. Calcd for $C_9H_5F_3O_3S_2$: C, 38.30; H, 1.79. Found: C, 38.30; H, 1.52.

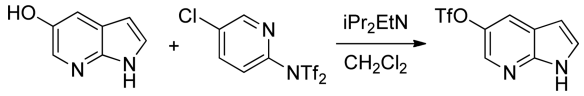
*1-(Triisopropylsilyl)-1H-indol-5-yl Triflate (**3c**).* To a solution of 5-(benzyloxy)-1*H*-indole (2.50 g, 11.2 mmol) in DME (37 mL) at 0 °C was added NaH (50 wt % in mineral oil, 1.08 g, 22.4 mmol, 2 equiv). After the mixture was stirred at 0 °C for 20 min, TIPS-Cl (3.56 mL, 16.8 mmol, 1.5 equiv) 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 were 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)-1*H*-indole (100% yield): $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 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)-1*H*-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 and filtered through Celite and the solvent removed to give a quantitative yield of 1-(triisopropylsilyl)-1*H*-indol-5-ol, which was used directly in the next step.

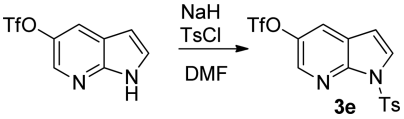
Triflation was carried out using procedure A. From 2.00 g of 1-(triisopropylsilyl)-1*H*-indol-5-ol, 1.64 g of 1-(triisopropylsilyl)-1*H*-indol-5-yl trifluoromethanesulfonate was obtained (56% yield). The compound was isolated as a colorless oil: $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.53−7.47 (m, 2H), 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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 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 a colorless oil: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 157.7 (CH), 149.0 (C), 146.3 (C), 141.1 (C), 119.3 (CH), 118.8 ($CF_3$, q, $J$ = 319.5 Hz), 114.1 (CH), 112.1 (CH); $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −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 procedure B, 1*H*-pyrrolo[2,3-*b*]pyridin-5-ol (1 g, 7.5 mmol) was converted to 1*H*-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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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 267.004; mp 122.5−123.5 °C.




A round-bottom flask with a 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. 1*H*-Pyrrolo[2,3-*b*]pyridinyl 5-triflate (1.0 g, 3.8 mmol) was added. The reaction was warmed to room temperature and was mixed for 15 min. 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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 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, $CDCl_3$) $\delta$ 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);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$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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 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 (4.7 g, 92% yield). The compound was isolated as a colorless oil: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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 glovebox, $Pd_2(dba)_3$ (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, the temperature was raised to 80 °C, and the contents were 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 glovebox, filtered through a Whatman 0.2 $\mu$m PTFE filter, rinsed with dichloromethane (∼15−20 mL), and collected in a tared 25 mL Erlenmeyer flask. The weight of filtered solution ($W_{prod}$) was recorded. A portion (∼1.0−1.5 g) of the solution was weighed into a tared 25 mL volumetric flask ($W_{sample}$), diluted to 25 mL with acetonitrile, and 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 ($W_{std}$), dissolved in 50 mL of 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:

$$\text{assay yield (\%)} = \frac{A_{prod} \times W_{prod} \times W_{std} \times 100}{A_{std} \times W_{sample} \times \text{theoretical yield (g)}}$$

**General Procedure for Pd-Catalyzed Reactions of Aryl and Heteroaryl Triflates with $NaSO_2CF_3$ (Schemes 1 and 2).** Inside an inert atmosphere glovebox, $Pd_2(dba)_3$ (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, the temperature was raised to 80 °C, and the contents were 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 0.30−0.40 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 glovebox, filtered through a Whatman 0.2 $\mu$m PTFE filter, rinsed with dichloromethane (∼15−20 mL), and collected in a tared 50 mL Erlenmeyer flask. The weight of filtered solution ($W_{prod}$) was recorded. A portion (∼0.2−0.5 g) of the solution was weighed into a tared 50 mL volumetric flask ($W_{sample}$), diluted to 50 mL with acetonitrile, and 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 of 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) was 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 a colorless oil: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline off-white solid: $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.80 (d, $J$ = 6 Hz, 2H), 6.76 (d, $J$ = 6 Hz, 2H), 3.15 (s, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was heated in



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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 a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 an amorphous white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −77.8; mp 56−58 °C. Anal. Calcd for $C_{11}H_7F_3O_2S$: C, 50.77; H, 2.71. Found: C, 50.92; H, 2.29.

*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) was 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 a white solid in approximately 90% purity by HPLC: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a clear oil: $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.09 (d app 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was heated in toluene (5 mL) at 90 °C for 18 h. The desired product **2j** (0.44 g, 94%) was calculated to be present in the crude reaction mixture after 27.5 h. The crude product was purified by flash column chromatography using 0−8% EtOAc/heptanes as eluent to provide the title compound (0.33 g, 1.25 mmol, 71%) as a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 8.32 (d app 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.21 (d app t, $J$ = 8.8, 1.6 Hz, 2H), 8.16 (m, 2H), 2.74 (s, 3H); $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was heated in toluene (5.5 mL) at 100 °C for 20 h. The desired product **2m** (0.19 g, 44%) 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 an amorphous white solid. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.35 (s, 1H), 8.30 (d, $J$ = 7.0 Hz, 1H), 8.14 (d app t, $J$ = 6.6, 1.2 Hz, 1H), 7.88 (t, $J$ = 7.8 Hz, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 158.8 (C), 148.1 (CH), 128.7 (C),



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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, $CDCl_3$) $\delta$ −78.5; mp 80−81 °C. Anal. Calcd for $C_9H_5F_3O_3S$: C, 43.29; H, 2.01. Found: C, 43.27; H, 1.86.

*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) was 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 a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was heated in toluene (4 mL) at 80 °C for 27.5 h. The desired product **4g** (0.27 g, 96%) was calculated to be present in the crude reaction mixture after 18 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 a crystalline white solid: $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −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) was 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 a crystalline white solid: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −78.9; mp 41−43 °C. 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.

*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) was 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 coelute. To purify **4i**, the unreacted triflate was hydrolyzed using $Cs_2CO_3$,[78] and 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 an amorphous white solid: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ 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, $CDCl_3$) $\delta$ −78.3; LRMS ($m/z$) $[M + H]^+$ calcd for $C_6H_5F_3NO_2S$ 212.0, found 212.0.

## ■ ASSOCIATED CONTENT

### Supporting Information

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$^1$H, $^{19}$F, and $^{13}$C NMR spectra of aryl(heteroaryl)triflones (PDF)



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### Notes

The authors declare no competing financial interest.

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