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Reactions of Arylsulfonate Electrophiles with NMe_4F: Mechanistic Insight, Reactivity, and Scope

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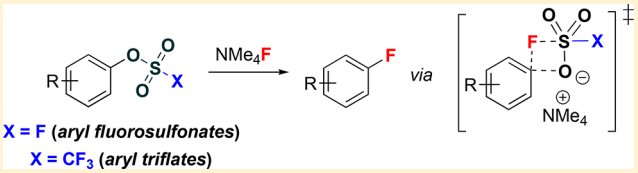
Supporting Information

ABSTRACT: This paper describes a detailed study of the deoxyfluorination of aryl fluorosulfonates with tetramethylammonium fluoride (NMe_4F) and ultimately identifies other sulfonate electrophiles that participate in this transformation. ^{19}F NMR spectroscopic monitoring of the deoxyfluorination of aryl fluorosulfonates revealed the rapid formation of diaryl sulfates under the reaction conditions. These intermediates can proceed to fluorinated products; however, diaryl sulfate derivatives bearing electron-donating substituents react very slowly with NMe_4F. Based on these findings, aryl triflate and aryl nonaflate derivatives were explored, since these cannot react to form diaryl sulfates. Aryl triflates were found to be particularly effective electrophiles for deoxyfluorination with NMe_4F, and certain derivatives (i.e., those bearing electron-neutral/donating substituents) afforded higher yields than their aryl fluorosulfonate counterparts. Computational studies implicate a similar mechanism for deoxyfluorination of all the sulfonate electrophiles.



INTRODUCTION

Fluorinated (hetero)arenes appear in a wide variety of pharmaceuticals and agrochemicals.[1,2] Nucleophilic aromatic substitution (S_NAr) is the most common industrial method for the formation of aromatic C−F bonds.[3] S_NAr fluorination reactions typically involve the conversion of an aryl chloride or nitroarene to the corresponding aryl fluoride via treatment with an alkali metal fluoride salt (Figure 1A).[3,4] However, these transformations remain limited by the requirement for high temperatures (generally >100 °C) and long reaction times. These forcing conditions often lead to poor functional group tolerance as well as the formation of side products.[5,6] In addition, the scope of S_NAr fluorination reactions is typically restricted to substrates bearing strongly electron-withdrawing substituents, which are needed to stabilize the high energy Meisenheimer intermediates/transition states (Figure 1A).[3b] Recent work has demonstrated the use of soluble anhydrous tetraalkylammonium fluoride salts to achieve the S_NAr fluorination of aryl chloride and nitroarene substrates under milder conditions.[7−9] However, these transformations still remain limited to highly electron-deficient ArX electrophiles.

In 2011, the Ritter group showed that the combination of PhenoFluor and CsF is effective for the conversion of phenols to aryl fluorides (Figure 1B).[10−12] This reaction represents a major advance for the field because it proceeds under relatively mild conditions (80−110 °C) and enables the deoxyfluorination of electronically diverse phenol derivatives. The authors propose that these attributes derive from a novel mechanism, involving the formation of a 2-phenoxyimidazolium bifluoride intermediate **A** that undergoes concerted intramolecular delivery of fluoride to the *ipso* carbon via **TSA** (Figure 1B).[12]

We recently developed a related method for the deoxyfluorination of phenols involving aryl fluorosulfonate intermediates of general structure **B** (Figure 1C).[13−15] *Ab initio* calculations show the feasibility of a mechanism involving F^- attack at the electrophilic sulfur of **B**[16,17] and subsequent intramolecular delivery of fluoride to the *ipso* carbon via **TSB** (Figure 1C). This transformation proved applicable to electronically diverse aryl fluorosulfonate derivatives. Furthermore, in contrast to the PhenoFluor system, both the fluoride source (NMe_4F)[18] and the leaving group (SO_3F)[19] are formed from inexpensive commodity chemicals. Finally, the aryl fluorosulfonates are stable, isolable intermediates, enabling mechanistic investigations of the fluorination process.

In this Article, we probe the mechanism and side products of reactions between aryl fluorosulfonates and NMe_4F. These investigations reveal markedly different electronic effects relative to the PhenoFluor system. In addition, they show that diaryl sulfates form rapidly under the reaction conditions, and that these intermediates can have a detrimental impact on both the reaction rate and yield. Ultimately, these insights led to the discovery that readily available aryl triflates are also effective electrophiles for deoxyfluorination with NMe_4F under mild conditions.

RESULTS AND DISCUSSION

Substituent Effects on Reaction Rates. We first examined the impact of arene substitution on the rate of the deoxyfluorination of aryl fluorosulfonates with NMe_4F. Rate studies were conducted at 80 °C in DMF, using 1 equiv of the

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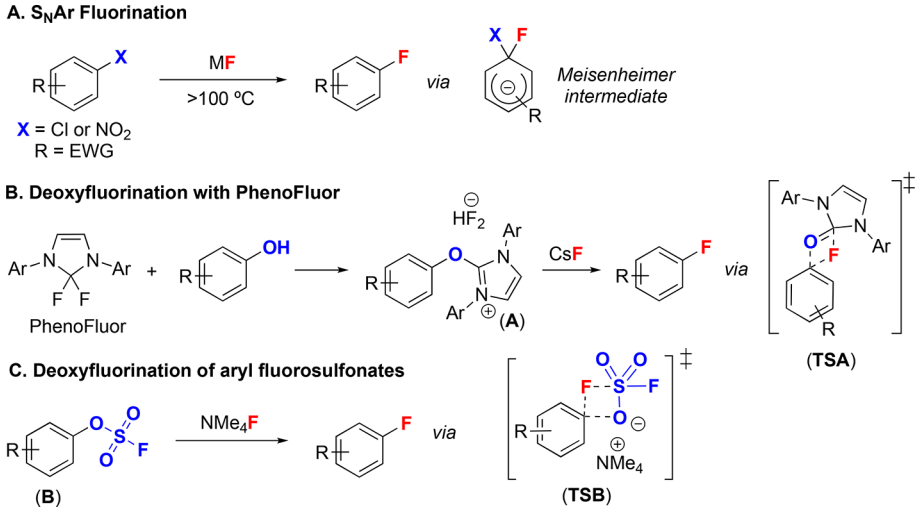

Figure 1. Examples of nucleophilic aromatic fluorination reactions.

aryl fluorosulfonate substrate and 2 equiv of NMe_4F. The initial rate of each reaction was determined by monitoring the first ~10% conversion under these conditions via NMR spectroscopy. As shown in Figure 2, a Hammett plot of these

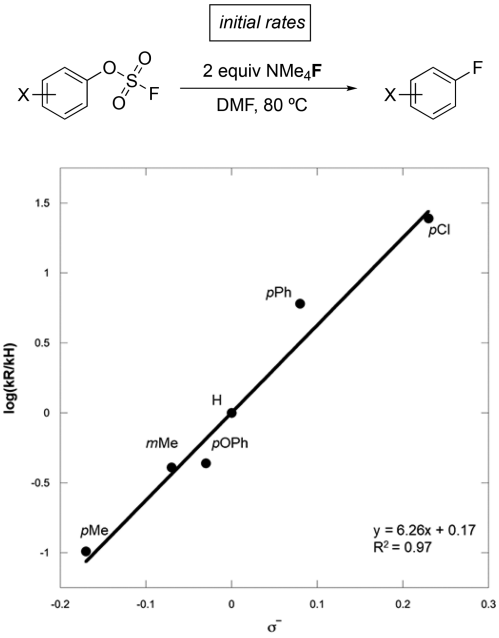

Figure 2. Hammett plot for the reaction of aryl fluorosulfonates with NMe_4F at 80 °C.

data shows a ρ value of +6.26, with the best fit obtained using σ^- values for each of the substituents.[20] This value is in striking contrast to the much smaller ρ value observed for the PhenoFluor reaction (ρ = +1.79, with σ values giving the best fit).[12] This ρ of +6.26 is similar to that observed for conventional S_NAr reactions (where ρ values between 3 to 8 have been reported).[21] Overall, these results suggest that the fluorosulfonate leaving groups serve to reduce the overall barrier for nucleophilic fluorination relative to that with, for example, chloride leaving groups. However, in contrast to PhenoFluor, the electronic requirements of this transformation versus S_NAr fluorination of more conventional aryl chloride substrates do not appear to fundamentally change. This likely explains why the deoxyfluorination of arylfluorosulfonates remains slow and relatively low yielding with substrates bearing strong electron donor substituents (e.g., *para*-OMe) on the aromatic ring.

NMR Studies of Reaction Intermediates. We next probed intermediates and side products formed during the reaction of aryl fluorosulfonates with NMe_4F. 3-Fluorophenyl sulfofluoridate (**1-OFs**) was selected as the substrate for these investigations, as it contains two fluorine substituents that can be tracked using ^{19}F NMR spectroscopy. In an initial experiment, **1-OFs** was combined with 1 equiv of NMe_4F in anhydrous DMF (Figure 3). After 30 min at room temperature, the C_{aryl}–F ^{19}F NMR signal of **1-OFs** (−109.9 ppm) broadened significantly, suggesting possible equilibration with pentacoordinate intermediate **1-Int** (compare Figure 3A and 3B). Notably, an analogous pentacoordinate sulfur species has been detected upon the treatment of SO_2F_2 with NMe_4F.[16b] After 30 min at 25 °C, a new C_{aryl}–F ^{19}F NMR signal was observed at −110.6 ppm, which corresponds to the bis(3-fluorophenyl)sulfate (**1-sulfate**; Figure 3B). After 24 h at room temperature, product **1-F** was observed in ~11% yield (C_{aryl}–F signal at −111.4 ppm), and both **1-sulfate** and the broad resonance that is tentatively assigned to **1-OFs**/**1-Int** remained (Figure 3C).

We next monitored the reaction of **1-OFs** with 2 equiv of NMe_4F at 80 °C (Figure 4). At this temperature, the C_{aryl}–F ^{19}F NMR signal corresponding to **1-OFs** broadened within minutes and subsequently disappeared. **1-Sulfate** also appeared within minutes and was then consumed over the course of 2 h. Product **1-F** was formed in 75% yield after 2 h.

A proposed pathway for the conversion of **1-OFs** to **1-sulfate** is shown in Scheme 1. In the first step, aryl fluorosulfonate **1-OFs** reacts with NMe_4F to form the pentacoordinate sulfur intermediate **1-Int** (step *i*). As detailed below, *ab initio* calculations suggest that this step is enthalpically favorable at room temperature. **1-Int** can then undergo two competing reactions: formation of the fluorinated product **1-F** (step *ii*) or release of SO_2F_2 and phenoxide **1-O[NMe$_4$]** (step *iii*). The phenoxide can then attack 1 equiv of starting material, **1-OFs**, to form a new pentacoordinate sulfur intermediate (step *iv*) that collapses into **1-sulfate** and NMe_4F (step *v*).[22] Thus, the equilibria proposed in Scheme 1 provide

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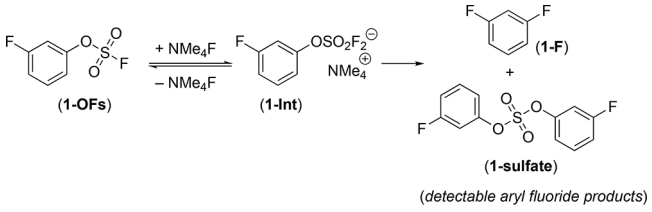


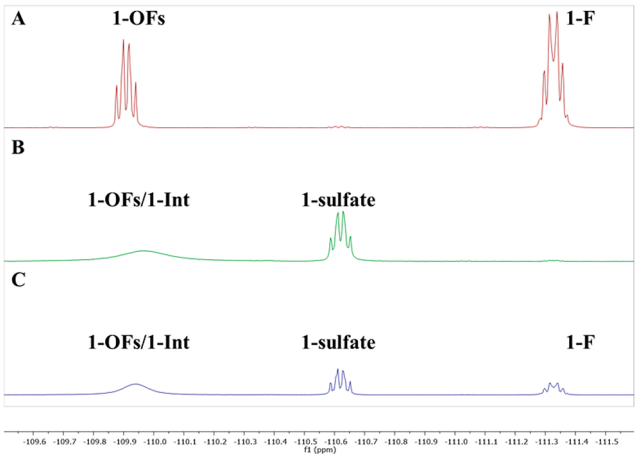


Figure 3. ^{19}F NMR study of the reaction between **1-OFs** and 1 equiv of NMe_4F at 25 °C. (A) Aromatic region of the ^{19}F NMR spectrum of a mixture of starting material **1-OFs** and product **1-F**. (B) Aromatic region of the ^{19}F NMR spectrum of the reaction between **1-OFs** (0.1 mmol, 1.0 equiv) and NMe_4F (0.1 mmol, 1.0 equiv) in DMF (0.2 M) at 25 °C after 30 min. (C) Aromatic region of the ^{19}F NMR spectrum of the reaction between **1-OFs** (0.1 mmol, 1.0 equiv) and NMe_4F (0.1 mmol, 1.0 equiv) in DMF (0.2 M) at 25 °C after 24 h.

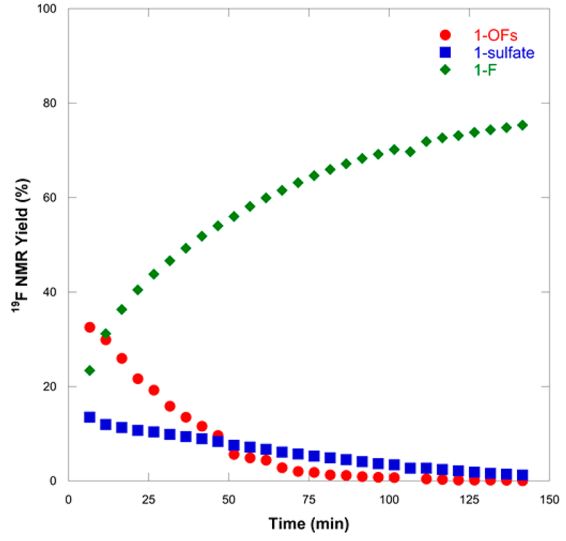
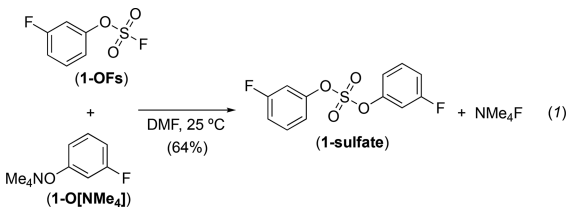


Figure 4. Reaction of **1-OFs** with 2 equiv of NMe_4F at 80 °C. Conditions: **1-OFs** (0.1 mmol, 1.0 equiv) and NMe_4F (0.2 mmol, 2.0 equiv) in DMF (0.2 M) at 80 °C. ^{19}F NMR spectra collected every 5 min for a total of 2 h. Yields determined by ^{19}F NMR spectroscopy with 4-fluoroanisole as standard. **1-O[NMe$_4$]** is also produced during the course of the reaction but is not shown in the plot.

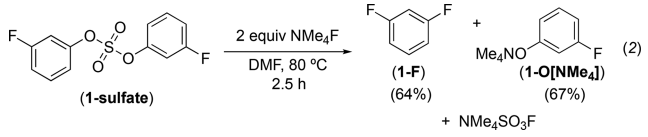
an explanation for both the formation of **1-sulfate** as well as its ability to proceed to the fluorinated product **1-F**.

Additional studies were conducted to investigate the pathways proposed in Scheme 1. First, we examined the feasibility of step *iv*. As shown in eq 1, the reaction of

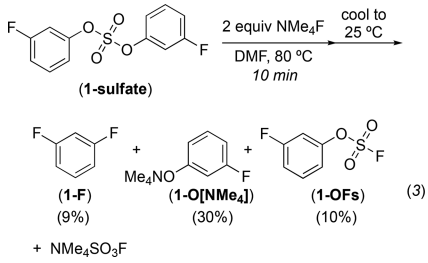


independently synthesized tetramethylammonium 3-fluorophenoxide (**1-O[NMe$_4$]**) with 3-fluorophenyl sulfofluoridate (**1-OFs**) afforded **1-sulfate** in 64% yield within 24 h at 25 °C (eq 1).[22]

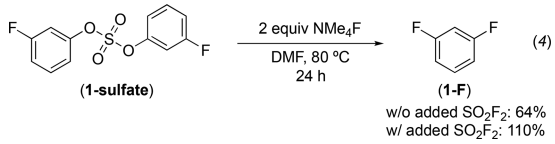
We next studied the conversion of **1-sulfate** to **1-F** by independently synthesizing bis(3-fluorophenyl)sulfate (**1-sulfate**) and then treating it with 2 equiv of NMe_4F at 80 °C. As shown in eq 2, this reaction afforded **1-F** in 64% yield within 2.5 h. As expected, an equimolar quantity of **1-O[NMe$_4$]** was also generated under these conditions.



The pathway in Scheme 1 suggests that **1-OFs** might be detectable during the fluorination of **1-sulfate**. At 80 °C, the ^{19}F NMR signal for **1-OFs** is too broad to observe. However, when the reaction was heated to 80 °C for 10 min and then immediately cooled to 25 °C, we observed a ^{19}F NMR signal consistent with the aromatic fluorine of **1-OFs** (−109.9 ppm) in 10% yield, along with **1-F** (9%), **1-O[NMe$_4$]** (30%), and unreacted **1-sulfate** (80%) (eq 3).



Finally, the pathway in Scheme 1 suggests that the addition of SO_2F_2 should push the equilibrium between **1-sulfate** and **1-Int** toward **1-Int**, thereby ultimately driving the reaction to **1-F**. Indeed, the addition of 1 equiv of SO_2F_2 to the reaction of **1-sulfate** with NMe_4F resulted in an increase in yield of **1-F** from 64% to 110% (eq 4). This supports the proposed



pathway, as SO_2F_2 is expected to capture **1-O[NMe$_4$]**, thus producing more of the aryl fluorosulfonate **1-OFs** that can undergo the productive fluorination reaction.[23]

Comparison of Ar_2SO_4 to ArOFs Electrophiles. When the diaryl sulfates were synthesized independently and used as substrates for deoxyfluorination with NMe_4F, they afforded lower yields of aryl fluoride products relative to their aryl

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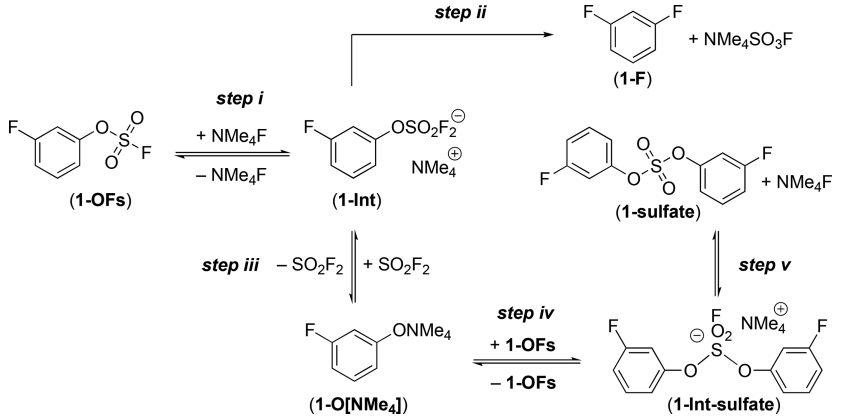
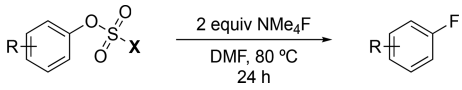
Scheme 1. Proposed Pathway for the Formation of 1-Sulfate



fluorosulfonate analogues (Table 1). Furthermore, with electron-deficient diaryl sulfates, the yield of aryl fluoride

Table 1. Fluorination of Aryl Fluorosulfonates Compared to Diaryl Sulfates[a]



entry	R =	(OFs)	(sulfate)
1	*m*-F (**1**)	80	64
2	*p*-CN (**2**)	92	54
3	*p*-Cl (**3**)	75	70
4	*p*-Ph (**4**)	77	29
5	*p*-OPh (**5**)	29	3

[a]Conditions: Substrate (0.1 mmol, 1.0 equiv) and NMe_4F (0.2 mmol, 2.0 equiv) stirred in DMF (0.2 M) at 80 °C for 24 h. Yields determined by ^{19}F NMR spectroscopy with 1,3,5-trifluorobenzene as standard.

decreased with increasing reaction times, due to competing consumption of the fluorinated product. For example, **2-sulfate** afforded **2-F** in 78% yield after 15 min at 80 °C but in just 54% yield after 24 h at 80 °C (entry 2). The corresponding diaryl ether was observed as a byproduct in the latter reaction. The diaryl ether likely forms via the reaction of **2-F** with tetramethylammonium 4-cyanophenoxide, which is generated during the course of the fluorination reaction.[3b,4] This competing reaction can be suppressed by reducing the temperature to 25 °C (resulting in 75% yield of **2-F** after 24 h) or lowering the reaction time.

Electron-neutral and -rich diaryl sulfates showed particularly low reactivity with NMe_4F (entries 4 and 5). For instance, the reaction of **5-sulfate** with NMe_4F afforded only 3% of **5-F** (entry 5), with >90% unreacted starting material remaining after 24 h at 80 °C. This is likely due to the low electrophilicity of sulfur, which slows the reaction of the sulfate with NMe_4F (step *v* in Scheme 1). Rate studies confirm that the diaryl sulfates react significantly slower than the corresponding aryl fluorosulfonates. For example, as shown in Figure 5, the initial rate of product formation in the reaction between NMe_4F and **4-sulfate** is approximately an order of magnitude slower than that for **4-OFs**.

Use of Aryl Triflate and Aryl Nonaflate Electrophiles. The results above show that the formation of diaryl sulfate

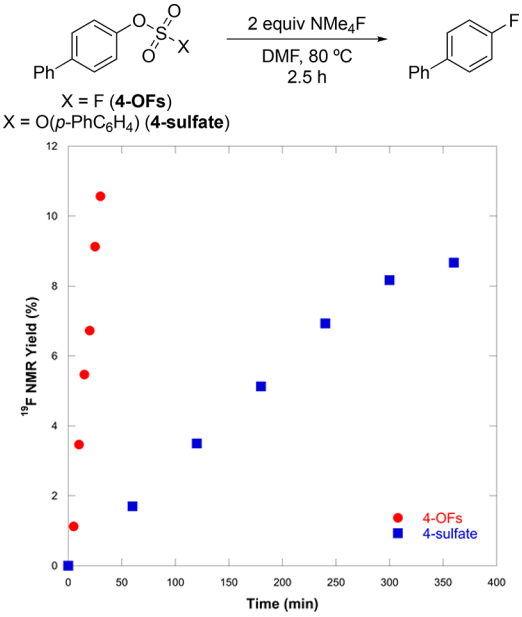


Figure 5. Initial rates of deoxyfluorination of **4-OFs** and **4-sulfate** at 80 °C. Conditions: Substrate (**4-OFs** or **4-sulfate**, 0.1 mmol, 1.0 equiv) and NMe_4F (0.2 mmol, 2.0 equiv) stirred in DMF (0.2 M) at 80 °C for the given time. Yields determined by ^{19}F NMR spectroscopy with 1,3,5-trifluorobenzene as standard. For **4-OFs**, $y = 0.36x - 0.25$, $R^2 = 0.9946$. For **4-sulfate**, $y = 0.025x + 0.332$, $R^2 = 0.98$.

intermediates has a negative impact on the desired deoxyfluorination reaction. We noted that aryl triflates and nonaflates are widely used sulfonate derivatives that have comparable electronic properties to their fluorosulfonate analogues.[24−27] However, in contrast to aryl fluorosulfonates, these electrophiles do not contain a second leaving group on the sulfur. As such, aryl triflates and nonaflates should not be capable of forming Ar_2SO_4 intermediates.[28] Triflates and nonaflates offer the additional advantage that they can be conveniently synthesized on laboratory scale without the need for sulfuryl fluoride, a gas that is not readily available in some research settings.[29,30]

A series of ArOFs, ArOTf,[31] and ArONf[32,33] analogues were next compared as substrates for deoxyfluorination with NMe_4F (Table 2). For derivatives bearing the strongly electron-withdrawing cyano group (entry 2), **2-OFs** afforded the highest yield of the fluorinated product **2-F** (92%). Aryl triflate

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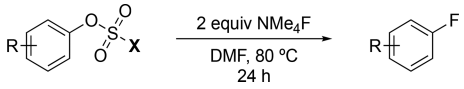
Table 2. Deoxyfluorination of Different Sulfonate Electrophiles with NMe_4F[a]



entry	R =	(OFs)	(OTf)	(ONf)
1	*m*-F (**1**)	80	76	53
2	*p*-CN (**2**)	92	66	73
3	*p*-Cl (**3**)	75	85	64
4	*p*-Ph (**4**)	77	87	53
5	*p*-OPh (**5**)	29	34	13

[a]Conditions: Substrate (0.1 mmol, 1.0 equiv) and NMe_4F (0.2 mmol, 2.0 equiv) stirred in DMF (0.2 M) at 80 °C for 24 h. Yields determined by ^{19}F NMR spectroscopy with 1,3,5-trifluorobenzene as standard.

2-OTf afforded only a modest yield (66%), and byproducts including 4-cyanophenol were observed by GCMS. The presence of this byproduct suggests that competing hydrolysis of **2-OTf** is occurring under the reaction conditions. The analogous nonaflate **2-ONf** afforded 73% yield of **2-F**, and <5% of hydrolysis-derived byproducts were detected in this case. Time studies of the reactions of **2-OFs**, **2-OTf**, and **2-ONf** (Figure 6) show that the relative rates track with the final yields (i.e., **2-OFs** reacts to form **2-F** faster than **2-ONf**, which reacts faster than **2-OTf**).[24,34]

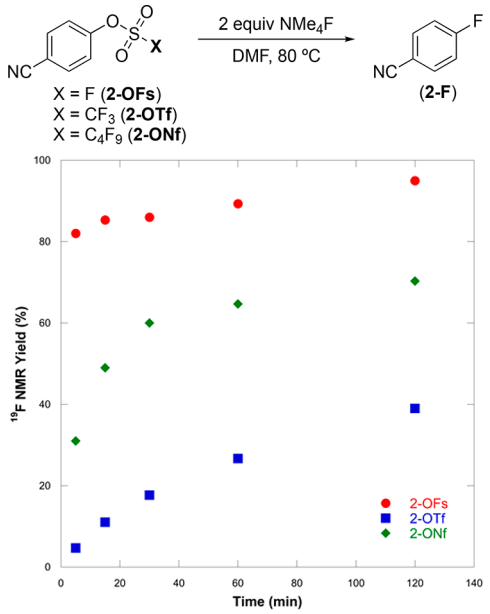


Figure 6. Time study of reactions of **2-OFs**, **2-OTf**, and **2-ONf** with NMe_4F to form **2-F**. Conditions: Substrate (0.1 mmol, 1.0 equiv) and NMe_4F (0.2 mmol, 2.0 equiv) stirred in DMF (0.2 M) at 80 °C for the given time. Yields determined by ^{19}F NMR spectroscopy with 1,3,5-trifluorobenzene as standard.

In contrast, for the 4-chloro-substituted sulfonate electrophiles, aryl triflate **3-OTf** afforded a higher yield of **3-F** than aryl fluorosulfonate **3-OFs** (85% versus 75%, entry 3), while the lowest yield (64%) was obtained with the aryl nonaflate **3-ONf**. A similar trend was observed with the 4-phenyl and 4-phenoxy derivatives (entries 4 and 5). Rate studies with these substrates (**3**–**5**, Figure 7) show that the initial rate of product formation with ArOTf increases relative to that for ArOFs upon moving to substrates bearing more electron-donating substituents (i.e., moving from **3** to **4** to **5**). Additionally, the ArOTf affords a slightly higher yield than the ArOFs in all three of these systems (Table 3, entries 3–5). Notably, diaryl sulfate intermediates are observed at initial time points in the reactions of **3-OFs**, **4-OFs**, and **5-OFs**, and these intermediates likely play a role in the slower initial rates with these substrates.

Computational Studies of ArOFs and ArOTf. We next compared the mechanisms of the deoxyfluorination of **1**–**5-OFs** and **1**–**5-OTf** using *ab initio* calculations.[35,36] As summarized in Scheme 2, the calculations show that the fluorosulfonate and triflate substrates react by analogous pathways. Binding of fluoride to sulfur to form the pentacoordinate species, **1-Int**, is enthalpically favorable in all cases, with ΔH_{bind} ranging from −0.3 to −4.1 kcal/mol.[37] Notably, there are five possible isomers of the trigonal bipyramidal structure **1-Int**. The isomer shown in Scheme 2 [with fluorine *trans* to X (X = F or CF_3)] is the lowest energy in all cases. Details about the other isomers are provided in the Supporting Information. Carbon–fluorine bond formation then proceeds without the formation of a discrete Meisenheimer intermediate. Instead, the fluoride is transferred to the *ipso* carbon via the transition state **TS**. In all cases, the calculated value of $\Delta H^{\ddagger}$ is similar between the fluorosulfonate and triflate analogues, with the triflate derivatives being slightly lower (by 1–3 kcal/mol) in all cases. As expected, the calculated values of $\Delta H^{\ddagger}$ vary significantly depending on substitution patterns on the aromatic ring. The lowest barrier is predicted (and observed experimentally) for the electron-deficient *p*-CN substrates **2-OFs** and **2-OTf**, while the highest is predicted (and observed experimentally) for the electron-rich *p*-OPh systems **5-OFs** and **5-OTf**.

Substrate Scope with Aryl Triflates. With a better understanding of the reactivity of aryl triflates, the substrate scope for this deoxyfluorination reaction was evaluated and compared to that of the corresponding aryl fluorosulfonates (Figure 8). ArOTf substrates bearing strongly electron-withdrawing substituents generally afforded lower yields than the analogous ArOFs. This appears to be due, at least in part, to competing hydrolysis of the aryl triflate starting materials.[38] With substrates bearing electron-neutral substituents, the difference in the yield of the fluorinated product with ArOFs versus ArOTf becomes less pronounced. However, in general, slightly higher yields were obtained with the ArOTf (for example, **3**–**5** and **8** in Figure 8). For substrates bearing stronger electron-donating substituents, both ArOFs and ArOTf show modest reactivity, but higher yields were generally obtained with the aryl fluorosulfonates (for example, **9** and **10** in Figure 8). Overall, these studies show that readily accessible aryl triflate electrophiles exhibit comparable reactivity to their ArOFs counterparts in deoxyfluorination with NMe_4F.

CONCLUSIONS

In conclusion, this report describes studies of the mechanism and side products involved in deoxyfluorination reactions of aryl fluorosulfonates with NMe_4F. These studies reveal markedly different electronic effects relative to Ritter's PhenoFluor system. In addition, they show that aryl fluorosulfonates are in equilibrium with diaryl sulfates under the reaction conditions and that the formation of diaryl sulfates can impede the productive deoxyfluorination reaction, particularly with electron-neutral and electron-rich substrates.

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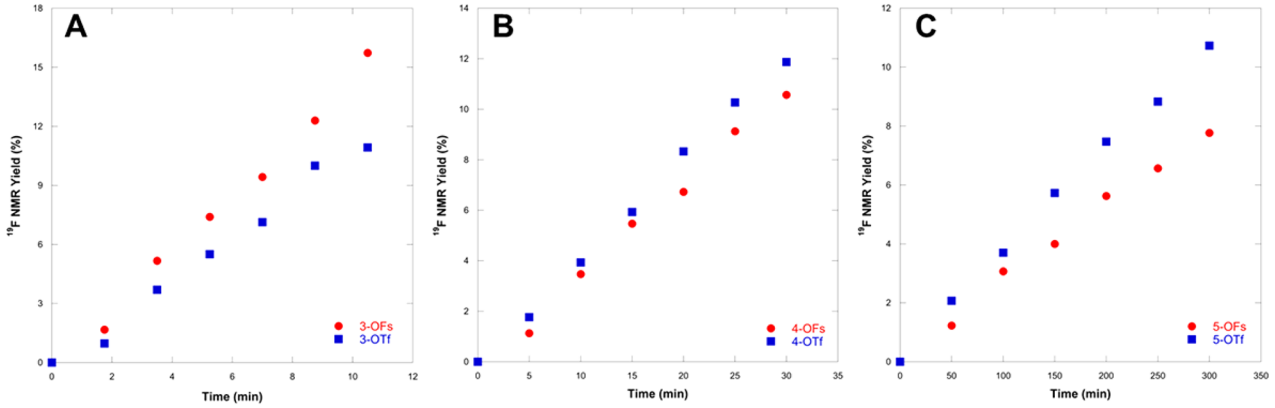
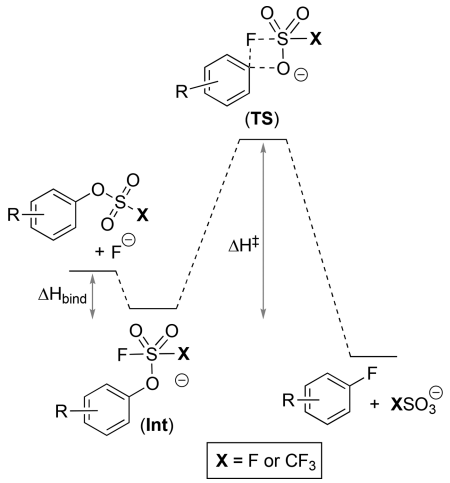


Figure 7. Initial rates for reaction of aryl fluorosulfonates versus the corresponding aryl triflates with NMe_4F for substrates **3**–**5**. (A) Initial rate of product formation for reactions of **3-OFs** and **3-OTf** with NMe_4F. (B) Initial rate of product formation for the reactions of **4-OFs** and **4-OTf** with NMe_4F. (C) Initial rate of product formation for the reactions of **5-OFs** and **5-OTf** with NMe_4F.

Table 3. Computed Enthalpies of Reaction (ΔH_{bind}) for Pentacoordinate Intermediate Formation and Enthalpies of Activation ($\Delta H^{‡}$) of Different Substrates

entry	R =	(OFs)		(OTf)	
		ΔH_{bind}	$\Delta H^{‡}$	ΔH_{bind}	$\Delta H^{‡}$
1	*m*-F (**1**)	–2.3	15.6	–2.5	14.4
2	*p*-CN (**2**)	–4.1	9.1	–3.8	8.3
3	*p*-Cl (**3**)	–2.7	16.9	–2.3	15.7
4	*p*-Ph (**4**)	–1.4	17.8	–1.4	16.7
5	*p*-OPh (**5**)	–0.3	20.2	–1.7	17.8

Scheme 2. Energy Diagram for the Reaction of Sulfonate Derivatives with Fluoride



These insights led to the examination of other aryl sulfonate electrophiles that cannot form diaryl sulfate intermediates. These aryl triflates and aryl nonaflates are demonstrated to be effective electrophiles for deoxyfluorination with NMe_4F, thus expanding the scope of substrates for these mild arene fluorination reactions.

EXPERIMENTAL SECTION

Materials and Methods. NMR spectra were obtained on a 400 MHz (400.52 MHz for ^{1}H; 376.87 MHz for ^{19}F; 100.71 MHz for ^{13}C), a 500 MHz (500.01 MHz for ^{1}H; 125.75 MHz for ^{13}C; 470.56 MHz for ^{19}F), a 700 MHz (699.76 MHz for ^{1}H; 175.95 MHz for ^{13}C), or a 500 MHz (499.90 MHz for ^{1}H; 125.70 for ^{13}C) NMR spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm), with the residual solvent peak used as an internal reference ($CDCl_3$; ^{1}H δ 7.26 ppm; ^{13}C δ 77.16 ppm). ^{19}F NMR spectra are referenced based on the internal standard 1,3,5-trifluorobenzene, which appears at −108.33 ppm, or 4-fluoroanisole, which appears at −125.55 ppm. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), doublet of triplets (dt). Coupling constants (J) are reported in Hz. For GCMS analysis, the products were separated on a crossbond 5% diphenyl-95% dimethyl polysiloxane column (30 m length by 0.25 mm ID, 0.25 μm df). Helium was employed as the carrier gas, with a constant column flow of 1.5 mL/min. The injector temperature was held constant at 250 °C. The GC oven temperature program for low molecular weight compounds was as follows: 32 °C hold 5 min, ramp 15 °C/min to 250 °C, and hold for 1.5 min. Melting points are uncorrected. High-resolution mass spectra were recorded on a Magnetic Sector mass spectrometer.

Commercial reagents were used as received unless otherwise noted. Anhydrous tetramethylammonium fluoride (NMe_4F) was obtained from Sigma-Aldrich. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Alfa Aesar. Phenyl trifluoromethanesulfonate (**6-OTf**) was purchased from Oakwood Products and stored at −33 °C in the freezer of a N_2-filled glovebox. Sulfuryl fluoride (SO_2F_2) was purchased from SynQuest Laboratories. Triflic anhydride and perfluoro-1-butanesulfonyl fluoride were purchased from Oakwood Products.

3-Fluorophenyl sulfofluoridate (**1-OFs**), 4-cyanophenyl sulfofluoridate (**2-OFs**), 4-chlorophenyl sulfofluoridate (**3-OFs**), [1,1′-biphenyl]-4-yl sulfofluoridate (**4-OFs**), 4-phenoxyphenyl sulfofluoridate (**5-OFs**), phenyl sulfofluoridate (**6-OFs**), 3-methoxyphenyl sulfofluoridate (**7-OFs**), *m*-tolylfluorosulfonate (**8-OFs**), *p*-tolylfluor-

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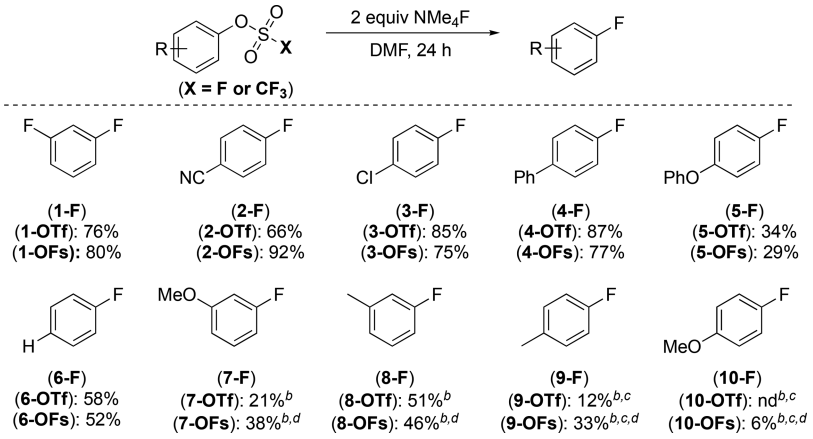

Figure 8. Substrate scope for the fluorination of aryl triflates compared to aryl fluorosulfonates. Conditions: Substrate (0.1 mmol, 1.0 equiv) and NMe_4F (0.02 mmol, 2.0 equiv) in DMF (0.2 M) at 80 °C for 24 h. Yields were determined by ^{19}F NMR spectroscopy with 1,3,5-trifluorobenzene as internal standard. [a]100 °C. [b]5 equiv NMe_4F. [c]Yield from ref 13.

osulfonate (**9-OFs**), and 4-methoxyphenyl sulfofluoridate (**10-OFs**) were synthesized according to the literature procedures.[13,39] A 1.5 wt % solution of sulfuryl fluoride in anhydrous DMF was prepared as described previously in the literature.[13] ***Caution: sulfuryl fluoride is a highly toxic gas.*** As such, all preparations of sulfuryl fluoride solutions were carried out in a well-ventilated fume hood and in the presence of a sulfuryl fluoride detector.

Synthesis of Diaryl Sulfates. Diaryl sulfates were synthesized according to literature procedures as described below.[40,41] All products were dried under vacuum in the presence of P_2O_5 prior to use in deoxyfluorination reactions.

*Bis(3-fluorophenyl) Sulfate (**1-sulfate**).* In a N_2-filled drybox, a 20 mL vial equipped with a magnetic stir bar was charged with 3-fluorophenyl sulfofluoridate (**1-OFs**) (194.0 mg, 1.0 mmol, 1.0 equiv), tetramethylammonium 3-fluorophenoxide (**1-O[NMe$_4$]**)[42] (185.0 mg, 1.0 mmol, 1.0 equiv), and anhydrous DMF (5.0 mL). The vial was sealed with a Teflon-lined cap, and the reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was extracted with diethyl ether (10 mL) and water (20 mL). The organic layer was washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated. The product was purified by column chromatography on silica gel (eluent = 5% diethyl ether in pentane). Product **1-sulfate** was obtained as a colorless oil (182.8 mg, 64% yield, R_f = 0.39 in 5% diethyl ether in pentane). ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 (m, 2H), 7.15−7.06 (multiple peaks, 6H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 160.0 (d, J = 250 Hz), 148.0 (d, J = 86 Hz), 128.4 (d, J = 9.2 Hz), 114.2 (d, J = 3.6 Hz), 112.5 (d, J = 21 Hz), 106.8 (d, J = 22 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −108.6 (m, 2F). HRMS EI (m/z): $[M]^+$ calcd $C_{12}H_8F_2O_4S$, 286.0111; found, 286.0111.

*Bis(4-cyanophenyl) Sulfate (**2-sulfate**).* A 20 mL vial equipped with a magnetic stir bar was charged with 4-cyanophenyl sulfofluoridate **2-OFs** (300.0 mg, 1.5 mmol, 1.0 equiv), 4-((*tert*-butyldimethylsilyl)oxy)benzonitrile[43] (349.5 mg, 1.5 mmol, 1.0 equiv), and 8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.04 mL, 0.3 mmol, 20 mol %) in CH_3CN (4.0 mL). The vial was sealed with a Teflon-lined cap, and the reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was concentrated under vacuum. The crude product was dissolved in CH_2Cl_2 (20 mL), and the organic layer was extracted with water (1 × 20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The product was recrystallized from ethyl acetate and hexanes. Product **2-sulfate** was obtained as a crystalline white solid (257.9 mg, 57% yield, mp = 152.0−154.0 °C). ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 9.0 Hz, 4H), 7.45 (d, J = 9.0 Hz, 4H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 152.8, 134.6, 122.1, 117.3, 112.5. HRMS EI (m/z): $[M]^+$ calcd $C_{14}H_8N_2O_4S$, 300.0205; found, 300.0203.

*Bis(4-chlorophenyl) Sulfate (**3-sulfate**).* In a N_2-filled drybox, a 20 mL vial equipped with a magnetic stir bar was charged with 4-chlorophenol (1.93 g, 15.0 mmol, 3.0 equiv), Cs_2CO_3 (1.63 g, 5.0 mmol, 1.0 equiv), *N,N′*-sulfuryldiimidazole (992.0 mg, 5.0 mmol, 1.0 equiv), and THF (5.0 mL). The vial was sealed with a Teflon-lined cap, and the reaction mixture was heated at 66 °C overnight. The reaction solution was cooled to room temperature, filtered through Celite, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = 10% EtOAc in hexanes). Product **3-sulfate** was obtained as a white solid (1.04 g, 66% yield, mp = 70.0−72.0 °C, R_f = 0.66 in 10% EtOAc in hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 9.9 Hz, 4H), 7.25 (d, J = 9.9 Hz, 4H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 148.7, 133.6, 130.3, 122.6. HRMS EI (m/z): $[M]^+$ calcd $C_{12}H_8Cl_2O_4S$, 317.9520; found, 317.9520.

*Di([1,1′-biphenyl]4-yl) Sulfate (**4-sulfate**).* In a N_2-filled drybox, a 4 mL vial equipped with a magnetic stir bar was charged with 4-phenylphenol (510.8 mg, 3.0 mmol, 3.0 equiv), Cs_2CO_3 (325.8 mg, 1.0 mmol, 1.0 equiv), *N,N′*-sulfuryldiimidazole (198.2 mg, 1.0 mmol, 1.0 equiv), and THF (1.0 mL). The vial was sealed with a Teflon-lined cap, and the reaction mixture was heated at 66 °C overnight. The reaction solution was cooled to room temperature, filtered through Celite, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = 5% EtOAc in hexanes). Product **4-sulfate** was obtained as a white solid (258.2 mg, 64% yield, mp = 132.6−133.8 °C, R_f = 0.41 in 5% EtOAc in hexanes). The ^1H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[40] HRMS EI (m/z): $[M]^+$ calcd $C_{24}H_{18}O_4S$, 402.0926; found, 402.0924.

*Bis(4-phenoxyphenyl) Sulfate (**5-sulfate**).* In a N_2-filled drybox, a 20 mL vial equipped with a magnetic stir bar was charged with 4-phenoxyphenol (2.79 g, 15.0 mmol, 3.0 equiv), Cs_2CO_3 (1.63 g, 5.0 mmol, 1.0 equiv), *N,N′*-sulfuryldiimidazole (992.0 mg, 5.0 mmol, 1.0 equiv), and THF (5.0 mL). The vial was sealed with a Teflon-lined cap, and the reaction mixture was heated at 66 °C overnight. The reaction solution was cooled to room temperature, filtered through Celite, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = 5% EtOAc in hexanes). Product **5-sulfate** was obtained as a white solid (1.82 g, 84% yield, mp = 49.7−50.8 °C, R_f = 0.33 in 5% EtOAc in hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 (t, J = 7.5 Hz, 4H), 7.27 (d, J = 9.2 Hz, 4H), 7.15 (t, J = 7.5 Hz, 2H), 7.02−7.00 (multiple peaks, 8H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 156.7, 156.5, 146.5, 130.1, 124.2, 122.6, 119.6, 119.5. HRMS ESI$^+$ (m/z): $[M + Na]^+$ calcd $C_{24}H_{18}O_6SNa$, 457.0716; found, 457.0716.

Synthesis of Aryl Triflates. Aryl triflates were synthesized according to the following procedure adapted from the literature.[44] Under a N_2 atmosphere, the corresponding phenol (1.0 equiv),

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pyridine (1.5 equiv), and dichloromethane (0.3 M) were combined in a round-bottom flask equipped with a magnetic stir bar. The flask was cooled to 0 °C in an ice bath, and triflic anhydride (1.2 equiv) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was filtered through a plug of silica gel that was then washed with hexanes. The resulting solution was concentrated under vacuum, and the product was purified by column chromatography on silica gel using gradients of either diethyl ether and pentane or hexanes and ethyl acetate as the eluent. All products were dried under vacuum in the presence of P_2O_5 prior to use in deoxyfluorination reactions.

*3-Fluorophenyl Trifluoromethanesulfonate (**1-OTf**).* The reaction was performed using 3-fluorophenol (500.0 mg, 4.5 mmol, 1.0 equiv), pyridine (0.5 mL, 6.7 mmol, 1.5 equiv), and triflic anhydride (0.9 mL, 5.4 mmol, 1.2 equiv) in dichloromethane (15 mL) in a 50 mL flask. Product **1-OTf** was obtained as a colorless oil (541.8 mg, 50% yield, R_f = 0.37 in pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (m, 1H), 7.15−7.10 (multiple peaks, 2H), 7.04 (dt, J = 8.5, 2.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 163.0 (d, J = 252 Hz), 149.8 (d, J = 10.6 Hz), 131.2 (d, J = 8.8 Hz), 118.0 (q, J = 320 Hz), 117.4 (d, J = 3.5 Hz), 115.9 (d, J = 21 Hz), 110.0 (d, J = 26 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −72.7 (s, 3F), −108.1 (m, 1F). HRMS EI (m/z): $[M]^+$ calcd for $C_7H_4F_4O_3S$, 243.9871; found, 243.9867.

*4-Cyanophenyl Trifluoromethanesulfonate (**2-OTf**).* The reaction was performed using 4-cyanophenol (595.6 mg, 5.0 mmol, 1.0 equiv), pyridine (0.6 mL, 7.5 mmol, 1.5 equiv), and triflic anhydride (1.0 mL, 6.0 mmol, 1.2 equiv) in dichloromethane (15.0 mL) in a 50 mL flask. Product **2-OTf** was obtained as a colorless oil (1.01 g, 88% yield, R_f = 0.42 in 8:1 hexanes/EtOAc). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[45] HRMS EI (m/z): $[M]^+$ calcd for $C_8H_4F_3NO_3S$, 250.9864; found, 250.9862.

*4-Chlorophenyl Trifluoromethanesulftonate (**3-OTf**).* The reaction was performed using 4-chlorophenol (1.0 g, 7.8 mmol, 1.0 equiv), pyridine (0.94 mL, 11.7 mmol, 1.5 equiv), and triflic anhydride (1.57 mL, 9.3 mmol, 1.2 equiv) in dichloromethane (30.0 mL) in a 100 mL flask. Product **3-OTf** was obtained as a colorless oil (1.31 g, 65% yield, R_f = 0.48 in pentane). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[46] HRMS EI (m/z): $[M]^+$ calcd $C_7H_4ClF_3O_3S$ 259.9522; found 259.9518.

*[1,1′-Biphenyl]-4-yl Trifluoromethanesulfonate (**4-OTf**).* The reaction was performed using 4-phenylphenol (1.70 g, 10.0 mmol, 1.0 equiv), pyridine (1.62 mL, 20.0 mmol, 2.0 equiv), and triflic anhydride (2.03 mL, 12.0 mmol, 1.2 equiv) in dichloromethane (20.0 mL) in a 50 mL flask. Product **4-OTf** was obtained as a white solid (2.26 g, 72% yield, mp = 47.2−48.0 °C, R_f = 0.64 in 10:1 hexanes/EtOAc). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[45] HRMS EI (m/z): $[M]^+$ calcd $C_{13}H_9F_3O_3S$, 302.0224; found, 302.0230.

*4-Phenoxyphenyl trifluoromethanesulfonate (**5-OTf**).* The reaction was performed using 4-phenoxyphenol (500.0 mg, 2.7 mmol, 1.0 equiv), pyridine (0.32 mL, 4.0 mmol, 1.5 equiv), and triflic anhydride (0.54 mL, 3.2 mL, 1.2 equiv) in dichloromethane (15.0 mL) in a 50 mL flask. Product **5-OTf** was obtained as a colorless oil (751.5 mg, 88% yield, R_f = 0.25 in pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, J = 8.0 Hz, 2H), 7.21 (d, J = 9.1 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.03 (t, J = 9.1 Hz, 4H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 157.5, 156.2, 144.6, 130.2, 124.5, 122.8, 119.8, 119.5, 117.0 (q, J = 320 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ 72.8 (s, 3F). HRMS EI (m/z): $[M]^+$ calcd $C_{13}H_9F_3O_4S$, 318.0174; found, 318.0180.

*3-Methoxyphenyl Trifluoromethanesulfonate (**7-OTf**).* The reaction was performed using 3-methoxyphenol (500.0 mg, 4.0 mmol, 1.0 equiv), pyridine (0.5 mL, 6.0 mmol, 1.5 equiv), and triflic anhydride (0.8 mL, 4.8 mmol, 1.2 equiv) in dichloromethane (20.0 mL) in a 50 mL flask. Product **7-OTf** was obtained as a pale yellow oil (592.9 mg, 58% yield, R_f = 0.56 in 5% diethyl ether in pentane). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[45] HRMS EI (m/z): $[M]^+$ calcd $C_8H_7F_3O_4S$, 256.0017; found, 256.0027.

*m-Tolyl Trifluoromethanesulfonate (**8-OTf**).* The reaction was performed using *m*-cresol (540.5 mg, 5.0 mmol, 1.0 equiv), pyridine (0.6 mL, 7.5 mmol, 1.5 equiv), and triflic anhydride (1.0 mL, 6.0 mmol, 1.2 equiv) in dichloromethane (15.0 mL) in a 50 mL flask. Product **8-OTf** was obtained as a colorless oil (739.4 mg, 62% yield, R_f = 0.68 in 5% EtOAc in hexanes). The ^{1}H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[47] ^{19}F NMR (376 MHz, $CDCl_3$): δ 73.0 (s, 3F). HRMS EI (m/z): $[M]^+$ calcd $C_8H_7F_3O_3S$, 240.0068; found, 240.0075.

*p-Tolyl Trifluoromethanesulfonate (**9-OTf**).* The reaction was performed using *p*-cresol (1.0 g, 9.3 mmol, 1.0 equiv), pyridine (1.1 mL, 14.0 mmol, 1.5 equiv), and triflic anhydride (1.9 mL, 11.1 mmol, 1.2 equiv) in dichloromethane (30.0 mL) in a 100 mL flask. Product **9-OTf** was obtained as a colorless oil (2.09 g, 94% yield, R_f = 0.38 in pentane). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[48] HRMS EI (m/z): $[M]^+$ calcd $C_8H_7F_3O_3S$, 240.0068; found, 240.0075.

*4-Methoxyphenyl Trifluoromethanesulfonate (**10-OTf**).* The reaction was performed using 4-methoxyphenol (620.0 mg, 5.0 mmol, 1.0 equiv), pyridine (0.6 mL, 7.5 mmol, 1.5 equiv), and triflic anhydride (1.0 mL, 6.0 mL, 1.2 equiv) in dichloromethane (15.0 mL) in a 50 mL flask. Product **10-OTf** was obtained as a colorless oil (1.04 g, 81% yield, R_f = 0.45 in 8:1 hexanes/EtOAc). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[49] HRMS EI (m/z): $[M]^+$ calcd $C_8H_7F_3O_4S$, 256.0017; found, 256.0028.

Synthesis of Aryl Nonaflates. Aryl nonaflates were synthesized according to procedures adapted from the literature.[50] All products were dried under vacuum in the presence of P_2O_5 prior to use in deoxyfluorination reactions.

*3-Fluorophenyl 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonate (**1-ONf**).* A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with NaH (260.0 mg (60% dispersion in mineral oil), 6.5 mmol, 1.3 equiv) and diethyl ether (4.0 mL). The flask was cooled to 0 °C in an ice bath, and a solution of 3-fluorophenol (560.2 mg, 5.0 mmol, 1.0 equiv) in diethyl ether (2.5 mL) was added dropwise. After 15 min, perfluoro-1-butanesulfonyl fluoride (1.3 mL, 7.0 mmol, 1.4 equiv) was added dropwise. The solution was allowed to warm to room temperature and then stirred overnight. Water and diethyl ether were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with 5% aqueous NaOH and then brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = pentane). Product **3-ONf** was obtained as a colorless oil (859.3 g, 44% yield, R_f = 0.53 in pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (q, J = 14.5, 8.5 Hz, 1H), 7.15−7.11 (multiple peaks, 2H), 7.06 (dt, J = 8.5, 2.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 163.4 (d, J = 250 Hz), 150.0 (d, J = 10.6 Hz), 131.2 (d, J = 8.8 Hz), 117.4 (d, J = 3.5 Hz), 115.8 (d, J = 21 Hz), 110.0 (d, J = 26 Hz), 108.0−118.2 (multiple peaks, 4C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.6 (t, J = 7.5 Hz, 3F), −108.2 (q, J = 7.5 Hz, 1F), −180.7 (m, 2F), −120.8 (m, 2F), −125.8 (m, 2F). HRMS EI (m/z): $[M]^+$ calcd $C_{10}H_4F_{10}O_3S$, 393.9721; found, 393.9736.

*4-Cyanophenyl 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonate (**2-ONf**).* A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with 4-cyanophenol (595.6 mg, 5.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (DMAP) (30.5 mg, 0.25 mmol, 0.05 equiv), iPr$_2$NEt (1.0 mL, 6.0 mmol, 1.2 equiv), and dichloromethane (8.0 mL). The solution was cooled to 0 °C in an ice bath. Perfluoro-1-butanesulfonyl fluoride (1.0 mL, 5.5 mmol, 1.1 equiv) was added dropwise. The solution was allowed to warm to room temperature and then stirred overnight. The reaction mixture was poured into water. The organic layer was collected, washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = 20% EtOAc in hexanes). Product **2-ONf** was obtained as a white solid (1.80 g, 90% yield, mp =

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32.4−34.0 °C, R_f = 0.62 in 20% EtOAc in hexanes). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[45] HRMS EI (m/z): $[M]^+$ calcd $C_{11}H_4F_9NO_3S$, 400.9768; found, 400.9765.

*4-Chlorophenyl 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonate (**3-ONf**).* A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with NaH (260.0 mg (60% dispersion in mineral oil), 6.5 mmol, 1.3 equiv) and diethyl ether (4.0 mL). The flask was cooled to 0 °C in an ice bath, and a solution of 4-chlorophenol (642.8 mg, 5.0 mmol, 1.0 equiv) in diethyl ether (2.5 mL) was added dropwise. After 15 min, perfluoro-1-butanesulfonyl fluoride (1.3 mL, 7.0 mmol, 1.4 equiv) was added dropwise. The solution was allowed to warm to room temperature and then stirred overnight. Water and diethyl ether were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with 5% aqueous NaOH and then brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = pentane). Product **3-ONf** was obtained as a colorless oil (1.438 g, 70% yield, R_f = 0.54 in pentane). The ^{1}H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[50] ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.6 (t, J = 11.3 Hz, 3F), −108.7 (m, 2F), −120.8 (m, 2F), −125.8 (m, 2F). HRMS EI (m/z): $[M]^+$ calcd $C_{10}H_4ClF_9O_3S$, 409.9426; found, 409.9420.

*[1,1′-Biphenyl]-4-yl 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonate (**4-ONf**).* A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with NaH (260.0 mg (60% dispersion in mineral oil), 6.5 mmol, 1.3 equiv) and diethyl ether (4.0 mL). The flask was cooled to 0 °C in an ice bath, and a solution of 4-phenylphenol (851.0 mg, 5.0 mmol, 1.0 equiv) in diethyl ether (2.5 mL) was added dropwise. After 15 min, perfluoro-1-butanesulfonyl fluoride (1.3 mL, 7.0 mmol, 1.4 equiv) was added dropwise. The solution was allowed to warm to room temperature and then stirred overnight. Water and diethyl ether were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with 5% aqueous NaOH and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = pentane). Product **4-ONf** was obtained as a white solid (1.785 g, 79% yield, mp = 45.5−46.7 °C, R_f = 0.43 in pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66−7.63 (m, 2H), 7.56−7.54 (m, 2H), 7.48−7.45 (m, 2H), 7.43−7.34 (multiple peaks, 3H). $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 149.3, 141.8, 139.4, 129.1, 129.0, 128.2, 127.3, 121.7, 108.0−118.0 (multiple peaks, 4C). ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.6 (t, J = 9.8 Hz, 3F), −108.8 (m, 2F), −120.9 (m, 2F), −125.8 (m, 2F). HRMS EI (m/z): $[M]^+$ calcd $C_{16}H_9F_9O_3S$, 452.0129; found, 452.0133.

*4-Phenyoxyphenyl 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonate (**5-ONf**).* A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with NaH (260.0 mg (60% dispersion in mineral oil), 6.5 mmol, 1.3 equiv) and diethyl ether (4.0 mL). The flask was cooled to 0 °C in an ice bath, and a solution of 4-phenoxyphenol (931.1 mg, 5.0 mmol, 1.0 equiv) in diethyl ether (2.5 mL) was added dropwise. After 15 min, perfluoro-1-butanesulfonyl fluoride (1.3 mL, 7.0 mmol, 1.4 equiv) was added dropwise. The solution was allowed to warm to room temperature and then stirred overnight. Water and diethyl ether were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with 5% aqueous NaOH and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (eluent = 10% EtOAc in hexanes). Product **5-ONf** was obtained as a colorless oil (1.699 g, 73% yield, R_f = 0.64 in 10% ethyl acetate in hexanes). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectra matched those previously reported in the literature.[45] HRMS EI (m/z): $[M]^+$ calcd $C_{16}H_9F_9O_4S$, 468.0078; found, 468.0080.

Computational Details. Calculations were carried out with a modified G3MP2B3 method using the PCM solvation model in DMF. Further details are provided in the Supporting Information.

General Procedures for Fluorination Reactions. *General Procedure A: Experimental Procedure for Initial Rates in Figures 2, 5, and 7.* In a N_2-filled drybox, substrate (0.1 mmol, 1.0 equiv) and NMe_4F (18.6 mg, 0.2 mmol, 2.0 equiv) were weighed into a 4 mL vial equipped with a magnetic stir bar. Anhydrous DMF (0.5 mL) was added, and the vial was sealed with a Teflon-lined cap. The vial was removed from the drybox and heated at 80 °C on a preheated aluminum heat block. After the desired reaction time, the reaction was flash frozen in a liquid N_2 bath. The vial was then warmed to room temperature, and the reaction mixture was diluted with dichloromethane (2.0 mL). 1,3,5-Trifluorobenzene was added as a standard, and the reaction was analyzed by ^{19}F NMR spectroscopy. Yields of product are reported as an average of three independent vial reactions. Yield versus time data were collected from the integration of the ^{19}F NMR signals of product versus internal standard (1,3,5-trifluorobenzene) (see Supporting Information for rate data and plots). The initial rate for each experiment was determined by a linear fit of the appearance of fluorinated product. A plot of Hammett values (Figure 3),[51] σ^-, versus log (k_R/k_H) showed a linear correlation.

General Procedure B: Experimental Procedure for the Room Temperature ^{19}F NMR Spectroscopy Studies in Figure 3. In a N_2-filled drybox, a screw-cap NMR tube was charged with **1-OFs** (19.4 mg, 0.1 mmol, 1.0 equiv), NMe_4F (9.3 mg, 0.1 mmol, 1.0 equiv), and anhydrous DMF (0.5 mL). The NMR tube was sealed with a Teflon-lined cap. After 30 min at room temperature, a ^{19}F NMR spectrum was acquired. The NMR tube was allowed to stand at room temperature for 24 h, and another ^{19}F NMR spectrum was acquired. A truncated ^{19}F NMR spectrum is shown in Figure 3. 4-Fluoroanisole was used as an internal standard. For comparison, an NMR tube was prepared with **1-OFs** and **1-F** and a ^{19}F NMR spectrum was acquired.

General Procedure C: Experimental Procedure for the ^{19}F NMR Spectra Monitoring Shown in Figure 4. In a N_2-filled drybox, a screw-cap NMR tube was charged with **1-OFs** (0.1 mmol, 1.0 equiv), NMe_4F (18.6 mg, 0.2 mmol, 2.0 equiv), and anhydrous DMF (0.5 mL). The NMR tube was sealed with a Teflon-lined cap and removed from the drybox. The NMR tube was then placed into an NMR spectrometer where the probe had been preheated to 80 °C. The fluorination reaction of **1-OFs** to form **1-F** was monitored by ^{19}F NMR spectroscopy at 80 °C. Yield versus time plots were acquired by integration of the ^{19}F NMR signals of **1-OFs**, **1-sulfate**, and **1-F** relative to internal standard (4-fluoroanisole).

*General Procedure D: Experimental Procedure for the ^{19}F NMR Study for the Observation of **1-OFs** in eq 3.* In a N_2-filled drybox, a screw-cap NMR tube was charged with **1-sulfate** (28.6 mg, 0.1 mmol, 1.0 equiv), NMe_4F (18.6 mg, 0.2 mmol, 2.0 equiv), and anhydrous DMF (0.5 mL). The NMR tube was sealed with a Teflon-lined cap and removed from the drybox. The NMR tube was placed into a preheated oil bath at 80 °C such that the solution was completely immersed in the heated oil. After 10 min, the NMR tube was removed from the oil bath, flash frozen in a liquid N_2 bath, and then warmed to room temperature to acquire a ^{19}F NMR spectrum. 4-Fluoroanisole was used as an internal standard.

General Procedure E: Experimental Procedure for the Effect of Exogenous SO_2F_2 on Reaction of 1-Sulfate in eq 4. In a N_2-filled drybox, **1-sulfate** (20.1 mg, 0.05 mmol, 1.0 equiv) and NMe_4F (9.3 mg, 0.1 mmol, 2.0 equiv) were weighed into a 4 mL vial equipped with a magnetic stir bar. A solution of SO_2F_2 in anhydrous DMF (0.36 mL of 0.14 M solution, 0.05 mmol, 1.0 equiv) was added, and the vial was quickly sealed with a Teflon-lined cap. The reaction was heated at 80 °C for 24 h. The reaction mixture was cooled to room temperature and then diluted with dichloromethane (2.0 mL). 1,3,5-Trifluorobenzene was added as an internal standard, and the reaction was analyzed by ^{19}F NMR spectroscopy. The yield in eq 2 represents the average of two runs (100% and 120%).

General Procedure F: Experimental Procedure for the Fluorination of Aryl Fluorosulfonates, Diaryl Sulfates, Aryl Triflates, and Aryl Nonaflates in Tables 1−2. In a N_2-filled drybox, substrate (0.1 mmol, 1.0 equiv) and NMe_4F (18.6 mg, 0.2 mmol, 2.0 equiv) were

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weighed into a 4 mL glass vial equipped with a microsized magnetic stir bar. Anhydrous DMF (0.5 mL) was added, and the vial was sealed with a Teflon-lined cap. The reaction mixture was allowed to stir at 80 °C for 24 h. The reaction was then diluted with dichloromethane (2.0 mL). 1,3,5-Trifluorobenzene was added as an internal standard, and the reaction was analyzed by ^{19}F NMR spectroscopy and GCMS. For reactions with diaryl sulfates, the yield was determined based on 0.1 mmol of starting material producing 0.1 mmol fluorinated product. The yields reported in Tables 1 and 2 represent an average of two reactions.

General Procedure G: Experimental Procedure for the Reaction Profiles in Figure 6. In a N_2-filled drybox, substrate **2-X** (0.1 mmol, 1.0 equiv, X = OFs, OTf, ONf) and NMe_4F (18.6 mg, 0.2 mmol, 2.0 equiv) were weighed into a 4 mL glass vial equipped with a magnetic stir bar. Anhydrous DMF (0.5 mL) was added, and the vial was sealed with a Teflon-lined cap. The reaction mixture was allowed to stir at 80 °C for the given time. The reaction was then cooled in an ice bath and diluted with dichloromethane (2.0 mL). 1,3,5-Trifluorobenzene was added as an internal standard, and the reaction was analyzed by ^{19}F NMR spectroscopy.

General Procedure H: Experimental Details for the ^{19}F NMR Yields Reported in Figure 8. Yields for the fluorination reactions of aryl fluorosulfonates **1-OFs**, **2-OFs**, **7-OFs**, **8-OFs**, **9-OFs**, and **10-OFs** are from ref 13.

In a N_2-filled drybox, NMe_4F (18.6 mg, 0.2 mmol, 2 equiv) and the aryl triflate or aryl fluorosulfonate substrate (0.1 mmol, 1 equiv) were weighed into a 4 mL glass vial equipped with a magnetic stir bar. Anhydrous DMF (0.5 mL) was added, and the vial was sealed with a Teflon-lined cap. The reaction mixture was allowed to stir at the given temperature for 24 h. The resulting solution was diluted with dichloromethane (2 mL), and a standard (1,3,4-trifluorobenzene or 4-fluoroanisole, 100 μL of a 0.5 M solution in toluene) was added. An aliquot was removed for analysis by ^{19}F NMR spectroscopy and GCMS.

Product Synthesis and Characterization. *1,3-Difluorobenzene (**1-F**).* General procedure H was followed using 3-fluorophenyl trifluoromethanesulfonate **1-OTf** (24.4 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing product **1-F** in 80% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Matrix, m, −110.9 ppm). The yield reported in Figure 8 is an average of two runs [80% and 71%].

*4-Fluorobenzonitrile (**2-F**).* General procedure H was followed using 4-cyanophenyl trifluoromethanesulfonate **2-OTf** (25.1 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing product **2-F** in 65% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Oakwood Chemicals, m, −103.89 ppm). The identity of the product was further confirmed by GCMS analysis (m/z = 121). The yield reported in Figure 8 is an average of two runs [65% and 66%].

*1-Chloro-4-fluorobenzene (**3-F**).* General procedure H was followed using 4-chlorophenyl trifluoromethanesulfonate **3-OTf** (26.0 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing product **3-F** in 85% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Oakwood Products, m, −116.7 ppm). The identity of the product was further confirmed by GCMS analysis (m/z = 130). The yield reported in Figure 8 is an average of two runs [85% and 85%].

General procedure H was followed using 4-chlorophenyl sulfofluoridate **3-OFs** (21.0 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing product **3-F** in 77% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Oakwood Products, m, −116.7 ppm). The identity of the product was further confirmed by GCMS analysis (m/z = 130). The yield reported in Figure 8 is an average of two runs [77% and 73%].

*4-Fluoro-1,1′-biphenyl (**4-F**).* General procedure H was followed using [1,1′-biphenyl]-4-yl trifluoromethanesulfonate **4-OTf** (30.2 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing **4-F** in 86% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Matrix, m, −116.7 ppm). The identity of the product was further confirmed by GCMS analysis (m/z = 172). The yield reported in Figure 8 is an average of two runs [86% and 87%].

General procedure H was followed using [1,1′-biphenyl]-4-yl sulfofluoridate **4-OFs** (25.3 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing **4-F** in 80% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Matrix, m, −116.7 ppm). The identity of the product was further confirmed by GCMS analysis (m/z = 172). The yield reported in Figure 8 is an average of two runs [80% and 73%].

*1-Fluoro-4-phenoxybenzene (**5-F**).* General procedure H was followed using 4-phenoxyphenyl trifluoromethanesulfonate **5-OTf** (31.8 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing **5-F** in 33% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The product showed a ^{19}F NMR signal at −121.1 ppm in DCM (lit. −120.1 ppm in $CDCl_3$).[13] The identity of the product was further confirmed by GCMS analysis (m/z = 188). The yield reported in Figure 8 is an average of two runs [33% and 34%].

General procedure H was followed using 4-phenoxyphenyl sulfofluoridate **5-OFs** (26.8 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing **5-F** in 30% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The product showed a ^{19}F NMR signal at −121.1 ppm in DCM (lit. −120.1 ppm in $CDCl_3$).[13] The identity of the product was further confirmed by GCMS analysis (m/z = 188). The yield reported in Figure 8 is an average of two runs [30% and 28%].

*Fluorobenzene (**6-F**).* General procedure H was followed using phenyl trifluoromethanesulfonate **6-OTf** (22.6 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing product **6-F** in 56% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Matrix, m, −114.1 ppm). The yield reported in Figure 8 is an average of two runs [56% and 60%].

General procedure H was followed using phenyl sulfofluoridate **6-OFs** (17.6 mg, 0.1 mmol, 1.0 equiv) at 80 °C, providing product **6-F** in 55% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Matrix, m, −114.1 ppm). The yield reported in Figure 8 is an average of two runs [55% and 48%].

*3-Fluoroanisole (**7-F**).* General procedure H was followed using 3-methoxyphenyl trifluoromethanesulfonate **7-OTf** (25.6 mg, 0.1 mmol, 1.0 equiv) at 100 °C, providing **7-F** in 22% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Sigma-Aldrich, m, −112.9 ppm). The identity of the product was further confirmed by GCMS analysis (m/z = 126). The yield reported in Figure 8 is an average of two runs [22% and 19%].

*3-Fluorotoluene (**8-F**).* General procedure H was followed using *m*-tolyl trifluoromethanesulfonate **8-OTf** (24.0 mg, 0.1 mmol, 1.0 equiv) at 100 °C, providing **8-F** in 43% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Matrix, m, −115.2 ppm). The yield reported in Figure 8 is an average of two runs [43% and 46%].

*4-Fluorotoluene (**9-F**).* General procedure H was followed using *p*-tolyl trifluoromethanesulfonate **9-OTf** (24.0 mg, 0.1 mmol, 1.0 equiv) and NMe_4F (46.5 mg, 0.5 mmol, 5.0 equiv) at 100 °C, providing product **9-F** in 23% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched those of an authentic sample (Matrix Scientific, m, −119.5 ppm). The identity of the product was further confirmed by GCMS analysis (m/z = 110). The yield reported in Figure 8 is an average of two runs [12% and 12%].

*4-Fluoroanisole (**10-F**).* General procedure H was followed using 4-methoxyphenyl trifluoromethanesulfonate **10-OTf** (25.6 mg, 0.1 mmol, 1.0 equiv) and NMe_4F (46.5 mg, 0.5 mmol, 5.0 equiv) at 100

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°C, providing none of the desired product **10-F** as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01762.

NMR spectral data of substrates, NMR spectral data for reaction monitoring, summary of kinetic data and plots, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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