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Intramolecular Aminotrifluoromethanesulfinyloxylation of ω-Aminoalkenes by CF_3SO_2Na/$Pd(OAc)_2$/$PhI(OAc)_2$/^{t}BuOCl/PivOH System

Satoru Suzuki[a]
Tomohiro Kamo[a]
Kazunobu Fukushi[a]
Etsuko Tokunaga[b]
Yuji Sumii[a]
Norio Shibata*[a,b]

[a] Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
nozshiba@nitech.ac.jp
[b] Department of Nanopharmaceutical Sciences, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

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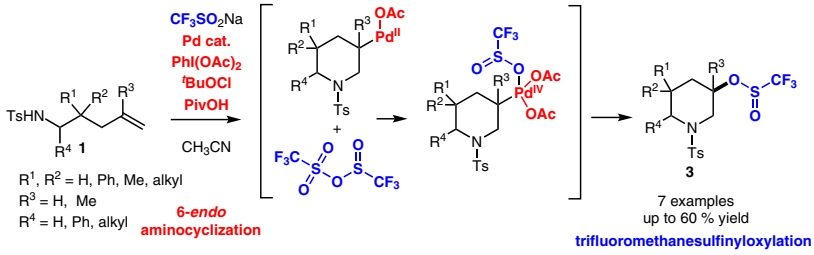

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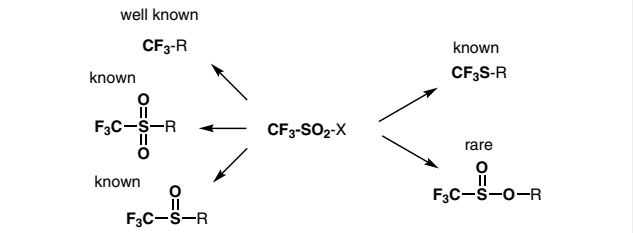
Abstract The first example of palladium-catalyzed intramolecular aminotrifluoromethanesulfinyloxylation of unactivated ω-aminoalkenes has been achieved. Reaction conditions are rather unique with a complex consisting of CF_3SO_2Na/$Pd(OAc)_2$/$PhI(OAc)_2$/^{t}BuOCl/PivOH to provide 6-*endo*-cyclized type products with a piperidine skeleton. Yields are moderate, and SO_2 is not extruded. This method also provides the first synthesis of 3-trifluoromethanesulfinyloxy piperidine derivatives.

Key words amination, alkenes, cyclization, fluorine, halogenation, sulfur, palladium

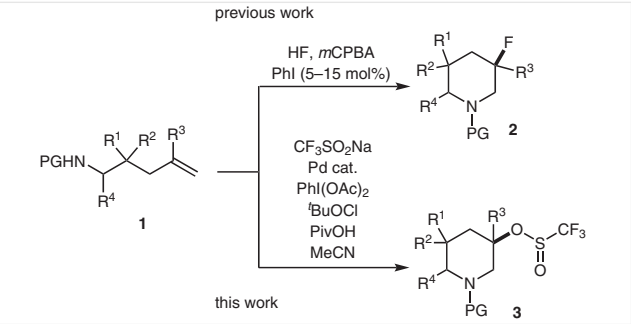
The fluoro functionalization of organic molecules often creates unique properties of parent molecules due to the high lipophilicity, strong electron negativity, and small size of the fluorine atom.[1] Hence, the development of effective methods for the introduction of fluorinated functional groups into target molecules has gained the attention of synthetic chemists in the fields of pharmaceuticals, agrochemicals, and specialty materials.[2,3] Considerable efforts have been expended to install fluorinated functional units such as trifluoromethyl (CF_3)[4] and trifluoromethylthio (SCF_3)[5] groups. We are interested in the use of reagents, trifluoromethanesulfinate derivatives, CF_3SO_2X (X = Na, K, and Cl), and in particular, CF_3SO_2Na, also known as the Langlois reagent.[6] These reagents are commercially available and are going to be a popular source for the installation of the CF_3 unit, especially under radical conditions.[6c,7] In this context, we envisaged that the use of CF_3SO_2X as a source of trifluoromethanesulfonyl (SO_2CF_3) or trifluoromethanesulfinyloxy ($OS(O)CF_3$) instead of the CF_3 reagent for direct introduction into target compounds without extrusion of SO_2 is of great importance to expand the utility of these reagents. Indeed, there is the potential for the introducing five kinds of fluorinated functional groups, CF_3, SO_2CF_3, $OS(O)CF_3$, $S(O)CF_3$, and SCF_3 using CF_3SO_2X reagents (Scheme 1).



Scheme 1 Potential use of CF_3SO_2X reagents for fluoro-functionalization

As briefly mentioned above, numerous reports of trifluoromethylation by CF_3SO_2X have been disclosed in recent years,[7] as well as methods to introduce SO_2CF_3,[8] $S(O)CF_3$,[9] and SCF_3[5e,10] using CF_3SO_2X. On the other hand, the direct introduction of the $OS(O)CF_3$ unit using CF_3SO_2X has been studied much less than other types of reactions.[11,12] In 2014, we reported the iodoarene-catalyzed intramolecular aminofluorination of ω-aminoalkenes **1** using an ArI/HF·pyridine/*m*CPBA system to produce six-membered cyclic amines **2** with a fluorinated stereogenic center. The reaction proceeds by in situ generation of a hypervalent iodine compound $ArIF_2$ (Scheme 2).[13] The asymmetric version of this reaction was also achieved by using chiral ArI. As an extension of this catalytic aminofluorocyclization reaction and our continuous research program focusing on the synthesis of trifluoromethanesulfonyl compounds (trifone),[10a,14] we were interested in the reaction of **1** with CF_3SO_2Na. We disclose herein the first example of the intramolecular aminotrifluoromethanesulfinyloxylation of linear ω-aminoalkenes **1** under palladium (Pd) catalysis. Namely, the treatment of ω-aminoalkenes **1** with CF_3SO_2Na

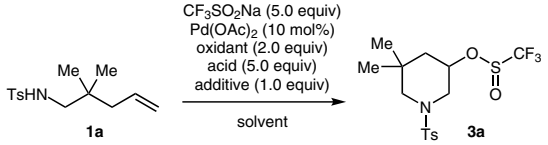
under a rather complex catalysis system consisting of the Pd(II) catalyst, iodobenzene diacetate ($PhI(OAc)_2$, PIDA), *tert*-butyl hypochlorite (^tBuOCl), and pivalic acid (PivOH) to furnish previously unknown piperidine derivatives **3** with a 3-trifluoromethanesulfinyloxy (3-$OS(O)CF_3$) substituent in good yields, instead of expected 3-trifluoromethanesulfonyl (3-SO_2CF_3) compounds.



Scheme 2 Fluoro aminocyclization (previous work) and trifluoromethanesulfinyloxy aminocyclization (this work) of ω-aminoalkenes **1**

First, we attempted the reaction using 10 mol% of Pd(II) acetate ($Pd(OAc)_2$), 2.0 equiv of PIDA, and 5.0 equiv of CF_3SO_2Na in acetonitrile (MeCN, Table 1, entry 1). A complicated mixture containing fluorinated compounds was observed based on ^{19}F NMR analysis, presumably due to the distributions of several trifluoromethylated compounds, including CF_3, SO_2CF_3, and $OS(O)CF_3$. We thus examined additives aimed at preparing a sole product (Table 1, entries 2–4). Interestingly, when ^tBuOCl was used as the additive, 6-*endo*-cyclized trifluoromethanesulfinate **3a** was obtained in 34% yield (Table 1, entry 4). Since the direct synthesis of trifluoromethanesulfinate using CF_3SO_2Na is rare,[11] we decided to advance the examination of this condition. The use of mixed solvent with MeCN and water did not improve yield (Table 1, entries 5 and 6) due to the formation of byproducts such as 3-hydroxy and 3-acetoxy piperidines.[15] In order to stabilize CF_3SO_2Na by suppressing the extrusion of SO_2, we next added pivalic acid (PivOH) to form CF_3SO_2H in situ. Gratifyingly, **3a** was obtained with a moderate yield of 53% (Table 1, entry 7). A potassium salt, CF_3SO_2K, was useless (Table 1, entry 8). Other oxidants such as di-(pivaloyloxy)iodobenzene ($PhI(OPiv)_2$), [bis(trifluoroacetoxy)iodo]benzene (PIFA), and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were also attempted instead of PIDA, but yields did not improve (Table 1, entries 9–12). Finally, the reaction was carried out at 10 °C, and at best, the trifluoromethanesulfinyloxy compound **3a** was obtained in 60% yield (Table 1, entry 13). Although there are several reports for the reaction of aminoalkenes and CF_3SO_2X and related reagents,[7p,16,17] there is no report on the aminotrifluoromethanesulfinyloxylation reaction.

Table 1 Optimization of Reaction Conditions from **1a** to **3a**[a]



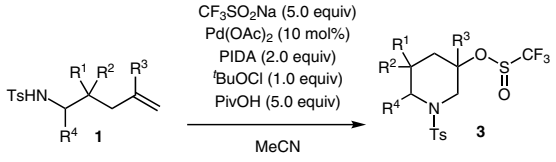
Entry	Oxidant	Additive	Acid	Solvent	Yield (%)
1	PIDA	none	–	MeCN	0
2	PIDA	TBHP	–	MeCN	0
3	PIDA	$(NH_4)_2S_2O_8$	–	MeCN	0
4	PIDA	^tBuOCl	–	MeCN	34
5	PIDA	^tBuOCl	–	MeCN/H_2O (9:1)	16
6	PIDA	^tBuOCl	–	MeCN/H_2O (1:1)	28
7	PIDA	^tBuOCl	PivOH	MeCN	53
8[b]	PIDA	^tBuOCl	–	MeCN	trace
9	$PhI(OPiv)_2$	^tBuOCl	PivOH	MeCN	trace
10[c]	$PhI(OPiv)_2$	^tBuOCl	PivOH	MeCN	33
11	PIFA	^tBuOCl	PivOH	MeCN	38
12	DDQ	^tBuOCl	PivOH	MeCN	trace
13[d]	$PhI(OAc)_2$	^tBuOCl	PivOH	MeCN	60

[a] Reaction was conducted with **1** (0.1 mmol), CF_3SO_2Na (5.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $Pd(OAc)_2$ (10 mol%), PivOH (5.0 equiv), and ^tBuOCl (1.0 equiv) in MeCN (0.5 mL) at rt for 15 h under N_2.
[b] CF_3SO_2K was used instead of CF_3SO_2Na.
[c] Reaction was performed at 30 °C.
[d] Reaction was performed at 10 °C.

With optimized reaction conditions in hand,[18] we examined the generality of ω-aminoalkenes **1** (Table 2). In the intramolecular aminotrifluoromethanesulfinyloxylation, the protecting group of amine strongly influenced reactivity. 4-Nitrobenzenesulfonyl- (Ns) and Boc-protected ω-aminoalkenes **1b**,**c** provided the corresponding cyclized product **3b**,**c** in low yields under the same reaction conditions (Table 2, entries 2 and 3). 2-Monosubstituted ω-aminoketones **1d**,**e** and spiro-ω-aminoalkene **1f** were nicely converted into the corresponding six-membered cyclized products **3d–f** in 42–53% yields (Table 2, entries 4–6). On the other hand, highly methyl-substituted vinyl sulfonyl amide **1g** decreased reactivity and product **3g** was observed in a trace amount (Table 2, entry 7). The *cis*-cyclohexyl amine substrate **1h** afforded the trifluoromethanesulfinyloxylated octahydro quinoline **3h** in moderated yield (48%) having a *cis*-configuration selectively. On the other hand, the *trans*-cyclohexyl amine substrate **1i** afforded the trifluorometh-

anesulfinyloxylated octahydro quinoline **3i** in moderated yield (48%) as a mixture of two isomers. The *N*-Ts aniline derivative **1j** did not afford the desired product **3j**. In all cases, the sulfinates **3**, which have a stereocenter on the sulfur atom, were obtained as inseparable diastereomixtures. It should be noted that while the synthesis of 3-trifluoromethanesulfonyloxypiperidines (3-OSO_2CF_3-piperidines) has been reported,[19] 3-trifluoromethanesulfinyloxy piperidines such as **3** have never appeared in the literature. This is the first example of their synthesis.

Table 2 Substrate Scope of ω-Aminoalkenes **1**[a]



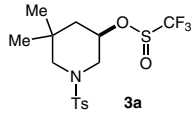
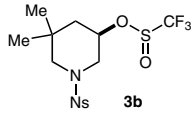
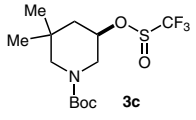
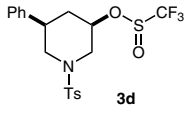
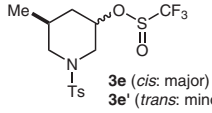
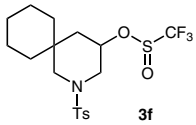
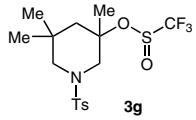
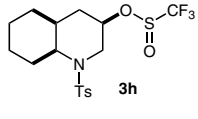
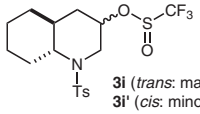
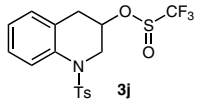
Entry	Product **3**	Yield (%)	dr
1	 **3a**	60	54:46
2	 **3b**	7	56:44
3	 **3c**	trace	ND
4	 **3d**	42	54:46
5	 **3e** (*cis*: major) **3e'** (*trans*: minor)	53[b]	**3e** 55:45 **3e'** 58:42
6	 **3f**	49	52:48
7	 **3g**	trace	ND
8	 **3h**	48	65:35

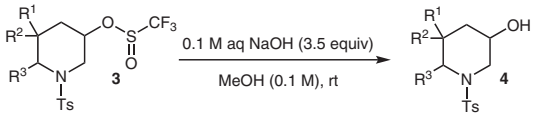
Table 2 (continued)

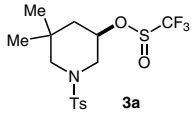
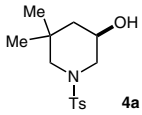
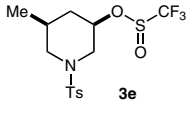
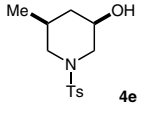
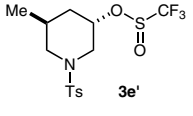
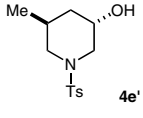
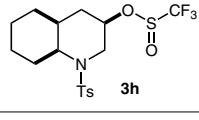
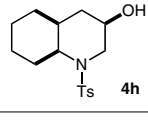
Entry	Product **3**	Yield (%)	dr
9	 **3i** (*trans*: major) **3i'** (*cis*: minor)	48[c]	**3i** 55:45 **3i'** 55:45
10	 **3j**	trace	ND

[a] Reaction was conducted with **1** (0.1 mmol), CF_3SO_2Na (5.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $Pd(OAc)_2$ (10 mol%), PivOH (5.0 equiv), ^{t}BuOCl (1.0 equiv) in MeCN (0.5 mL) at rt for 15 h under N_2.
[b] *cis*/*trans* = 4:1.
[c] *cis*/*trans* = 1:2.7.

All of the structures obtained for **3** were assigned by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR spectroscopy and HRMS. They were also rigorously characterized by comparison to spectral data of reported hydroxylated product **4a**[15] after hydrolysis of **3a** using 0.1 M NaOH in MeOH at room temperature for 18 h. The hydrolysis of **3** was also carried out for three more compounds **3e**, **3e′**, and **3h** to show the generality to furnish **4e**, **4e′**, and **4h**[15] in good yields.

Table 3 Base Hydrolysis of Sulfinates

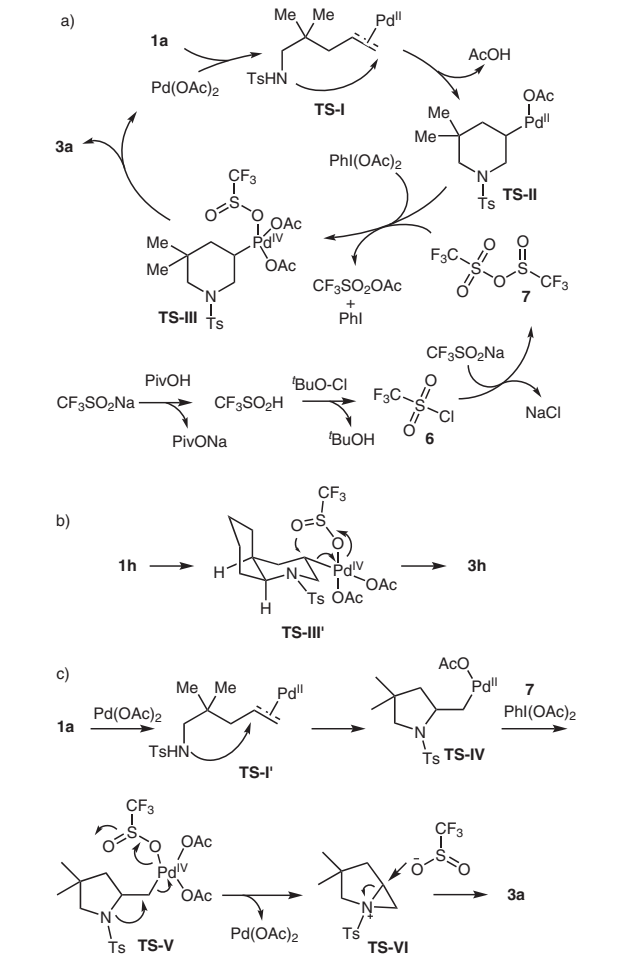


Entry	Sulfinate	Product	Yield (%)
1	 **3a**	 **4a**	60
2	 **3e**	 **4e**	43
3	 **3e'**	 **4e'**	61
4	 **3h**	 **4h**	64

[a] Reaction was conducted with trifluoromethanesulfinate **3** (0.1 mmol), 1 N NaOH (0.35 mL, 0.35 mmol, 3.5 equiv) in MeOH (1 mL, 0.1 M) at rt.

A plausible mechanism for this trifluoromethanesulfinyloxy aminocyclization could be explained by a Pd(II)-mediated oxidative addition/reductive elimination process from **1a** to **3a**, as outlined in Scheme 3 (a). Initially, the alkene moiety in **1a** is activated by Pd(II) inducing an intramolecular attack of the nitrogen in a 6-*endo* fashion via **TS-I** to provide **TS-II** upon deprotonation by acetate. PIDA ($PhI(OAc)_2$) oxidizes Pd(II) in **TS-II** in the presence of trifluoromethanesulfinyl triflate ($CF_3SO_2OS(O)CF_3$, **7**)[9d] to form intermediate **TS-III**, with the release of trifluoromethanesulfonyl acetate (CF_3SO_2OAc) and iodobenzene (PhI). The trifluoromethanesulfinyl triflate (**7**) is generated in situ by the reaction of CF_3SO_2Na with trifluoromethanesulfonyl chloride ($CF_3S(O)_2Cl$, **6**)[20] resulting from the oxidation of CF_3SO_2H with ^{t}BuOCl. The in situ generated species, CF_3SO_2H, **6**, and **7**, were detected by ^{19}F NMR analysis.[21] Finally, direct reductive elimination in **TS-III** would afford an observed amino-cyclized trifluoromethanesulfinyloxy product **3a** with the regeneration of $Pd(OAc)_2$, which enters the catalytic cycle. Stereoselective formation of *cis*-product **3h** from **1h** could be explained by the transition-state model **TS-III′** (Scheme 3, b). Another reaction pathway containing 5-*exo*-cyclization (**TS-I′** to **TS-IV**), oxidative addition (**TS-IV** to **TS-V**) followed by aziridine formation (**TS-V** to **TS-VI**) and ring opening by the $OS(O)CF_3$ anion (**TS-VI** to **3a**) is also possible (Scheme 3, c). Details of the reaction mechanism are not clear and a more mechanistic study is required.

In summary, the first palladium-catalyzed intramolecular aminotrifluoromethanesulfinyloxylation of unactivated ω-aminoalkenes **1** has been achieved. Reaction conditions are rather unique with a complex consisting of $CF_3SO_2Na/Pd(OAc)_2/PhI(OAc)_2/^t$BuOCl/PivOH to provide 6-*endo*-cyclized type products **3** with a piperidine skeleton in moderate yields. Trifluoromethanesulfinyloxy products **3** were obtained without the extrusion of SO_2. This method is not only the first example of an aminotrifluoromethanesulfinyloxylation reaction, but is also the first synthesis of 3-trifluoromethanesulfinyloxy piperidine derivatives. Although plausible reaction pathways have been suggested, detailed studies to elucidate the reaction mechanism are currently underway.



Scheme 3 Proposed reaction mechanisms of intramolecular aminotrifluoromethanesulfinyloxylation reaction: a) 6-*endo*-mode pathway; b) stereoselective formation of *cis*-product; c) 5-*exo*-mode pathway.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591720.

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(18) **General Procedure**

To a stirring mixture of ω-aminoalkenes **1** (0.1 mmol), PIDA (64.2 mg, 0.2 mmol, 2.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol%), CF_3SO_2Na (78.0 mg, 0.5 mmol, 5.0 equiv), and PivOH (51.0 mg, 0.5 mmol, 5.0 equiv) in MeCN (0.5 mL, 0.2 M) at 10 °C, ^{t}BuOCl (10.9 mg, 11 µL, 0.1 mmol, 1.0 equiv) was added under nitrogen atmosphere. The mixture was stirred at room temperature for 15 h. The resulting mixture was cooled to 0 °C, quenched with sat. $NaHCO_3$ aqueous solution, and extracted with EtOAc three times. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (benzene/EtOAc = 98:2) to give product **3**.

5,5-Dimethyl-1-tosylpiperidin-3-yl Trifluoromethanesulfinate (3a)

60% yield (dr = 54:46, mixture of diastereoisomer at sulfur atom); white solid.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (q, *J* = 3.2 Hz, 2 H), 7.36–7.33 (m, 2 H), 4.82–4.68 (m, 1 H), 4.00 (q, *J* = 5.4 Hz, 0.5 H), 3.85 (q, *J* = 5.4 Hz, 0.5 H), 3.28 (d, *J* = 11.5 Hz, 0.5 H), 3.20 (d, *J* = 11.5 Hz, 0.5 H), 2.44 (s, 3 H), 2.37–2.30 (m, 1 H), 2.18 (d, *J* = 11.5 Hz, 0.5 H), 2.10 (d, *J* = 11.5 Hz, 0.5 H), 1.87 (td, *J* = 12.1, 4.6 Hz, 1 H), 1.43–1.26 (m, 1 H), 1.11 (s, 1.5 H), 1.10 (s, 1.5 H), 1.01 (s, 1.5 H), 0.99 (s, 1.5 H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.0 (major, s), –80.2 (minor, s). ^{13}C NMR (176 MHz, $CDCl_3$): δ = 143.9, 133.2, 129.8, 127.4, 127.3, 122.5 (q, *J* = 336.9 Hz), 122.4 (q, *J* = 336.0 Hz), 56.4, 56.3, 50.1, 50.0, 43.8, 43.5, 32.4, 32.3, 28.0, 27.9, 26.9, 24.9, 24.7, 21.4. IR (KBr) 2962, 2928, 1470, 1346, 1196, 1159, 1129, 950, 907, 857, 677 cm^{-1}. ESI-MS: *m/z* = 422 $[M + Na]^+$. ESI-HRMS: *m/z* calcd for $C_{15}H_{20}NO_4F_3NaS_2$: 422.0684; found: 422.0679.

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(20) The ^{19}F NMR (282 MHz) spectra of the mixture of CF_3SO_2Na (1.0 equiv), PivOH (1.0 equiv), and ^{t}BuOCl (1.0 equiv) in CD_3CN indicated two singlet signals at δ = –74.01 ppm (CF_3SO_2Cl) and –77.14 ppm (**7**).

(21) The^{19}F NMR (282 MHz) spectra of the mixture of **6** (1.0 equiv) and CF_3SO_2Na (1.0 equiv) in CD_3CN indicated three singlet signals at δ = –73.98 ppm (CF_3SO_2Cl), –77.14 ppm (**7**), and –83.00 ppm (CF_3SO_2Na).