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Copper-Mediated Di- and Monofluoromethanesulfonylation of Arenediazonium Tetrafluoroborates: Probing the Fluorine Effect

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ABSTRACT A copper-mediated di- and monofluoromethanesulfonylation of arenediazonium tetrafluoroborates using di- and monofluoromethanesulfinate reagents provides aryl difluoromethyl (or monofluoromethyl) sulfones in good yields. It was found that the relative reactivity of these sodium fluoroalkanesulfinates in the present reactions decreases in the following order: CH_2FSO_2Na > CF_2HSO_2Na > CF_3SO_2Na.

KEYWORDS difluoromethanesulfonylation, fluoromethanesulfonylation, arenediazonium, sodium sulfinate, fluorine effect

Introduction

Nowadays, fluorinated organic compounds play increasingly important roles in pharmaceutical and agrochemical industries, owing to the fact that fluorine or fluorine-containing groups could effectively improve the metabolic stability, lipophilicity, and biological potency of a target drug molecule.[1,2] Among various fluorine-containing groups, the *gem*-difluoromethylene (CF_2) is known to be isosteric to the ethereal oxygen atom, and has attracted much attention.[3] Difluoromethyl phenyl sulfone, $PhSO_2CF_2H$, as an effective nucleophilic reagent to introduce CF_2 motif, has been widely used in organic synthesis.[4] The "chemical chameleon"[5] character of the phenylsulfonyl group enables it a highly useful synthon to difluorinated functionalities such as difluoromethylene ($–CF_2–$), difluoromethyl ($–CF_2H$) and difluoromethylidene ($=CF_2$).[6] In addition to their widespread use in organic synthesis, difluoromethyl aryl sulfones (such as PT2399) have recently been reported to show biological activity as HIF-2α antagonist in preclinical kidney cancer models (Figure 1).[7] Despite the wide applications of difluoromethyl aryl sulfones ($ArSO_2CF_2H$) in organic synthesis and life sciences, synthetic methods for their preparation have remained largely unexplored since the first synthesis by Hine and Porter in 1960.[8] Difluoromethyl aryl sulfones are often prepared by oxidation of corresponding difluoromethyl aryl sulfides.[4a,4d]

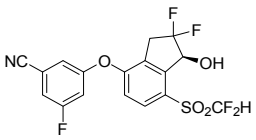
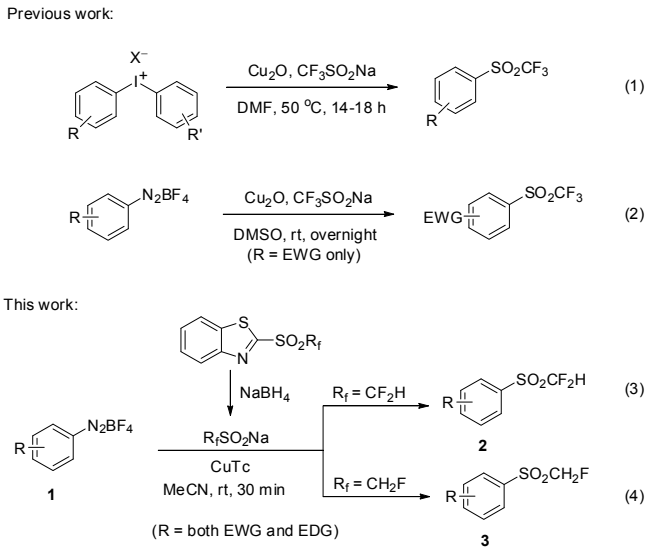


Figure 1 PT2399 as HIF-2α antagonist.

Recently, we were interested in two reports on the preparation of trifluoromethyl aryl sulfones from sodium trifluoromethanesulfinate (CF_3SO_2Na).[9,10] In 2013, Shekhar and co-workers reported a copper-catalyzed coupling of aryl iodonium salts with CF_3SO_2Na (Scheme 1, eq 1).[9] In 2015, Qing and co-workers reported a copper-promoted coupling of arenediazonium tetrafluoroborates with sodium trifluoromethanesulfinate (Scheme 1, eq 2).[10] In these reactions, both iodonium salts and arenediazonium tetrafluoroborates are not able to oxidize CF_3SO_2Na to generate trifluoromethyl radical. Indeed, when an external oxidant (such as *t*-BuOOH) is used, CF_3SO_2Na can be oxidized to give trifluoromethyl radical and a trifluoromethylation (rather than trifluoromethanesulfonylation) reaction takes place.[10] Previously, we reported a practical preparation of sodium fluoroalkanesulfinates (R_fSO_2Na) via $NaBH_4$-mediated reduction of corresponding benzo[*d*]thiazol-2-yl sulfones (Scheme 1, eq 3), and we also found that the reactivity of these sulfinates in radical *fluoroalkylations* decreases in the following order: $PhCF_2SO_2Na$ > CF_2HSO_2Na > CH_2FSO_2Na.[11] As our continuing effort in probing the unique fluorine effects in organic reactions,[12] we were interested in finding out the reactivity order of R_fSO_2Na (R_f=CF_3, CF_2H, and CH_2F) in the *fluoroalkanesulfonylations*. Herein, we report our results on the synthesis of di- and monofluoromethyl aryl sulfones via copper-mediated fluoroalkanesulfonylation reactions between arenediazonium tetrafluoroborates[13] and HCF_2SO_2Na or FCH_2SO_2Na (Scheme 1, eqs 3 and 4), and the relative reactivity of R_fSO_2Na (R_f=CF_3, CF_2H, and CH_2F) in these fluoroalkanesulfonylations.

Scheme 1 Fluoromethanesulfonylations of arenediazonium tetrafluoroborates.



Results and Discussion

At the outset of our study, we conducted the experiment in DMSO using benzenediazonium tetrafluoroborate **1a** as substrate and adding CF_2HSO_2Na and Cu_2O as reagents. (Table 1, entry 1). However, no desired product **2a** was detected. Most of the sub-

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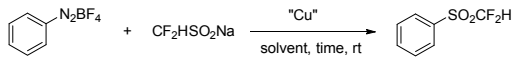
strate **1a** was transformed to the reduced product (benzene) and biphenyl (detected by GC-MS), while CF_2HSO_2Na was dominantly recovered (detected by ^{19}F NMR). Utilizing other copper species such as CuTc and CuOAc, we were delighted to find that the addition of CuTc successfully gave 8% yield of the sulfonylation product **2a** (entry 2). Changing the solvent to MeCN, the yield was increased to 64%, while other copper species displayed low efficiency (entries 4—12). Instead of mixing the substrate **1a** with all the reagents together at the beginning, slow dropwise addition of **1a** to the acetonitrile solution of CuTc and CF_2HSO_2Na could improve the yield to 79% (entry 13). Furthermore, the amount of CuTc could be reduced to 0.5 equivalent (entry 14). Further reducing the amount of CuTc led to the loss of yield (Table 1, entries 15— 17).

Table 1 Optimization of the reaction conditions



1a **2a**

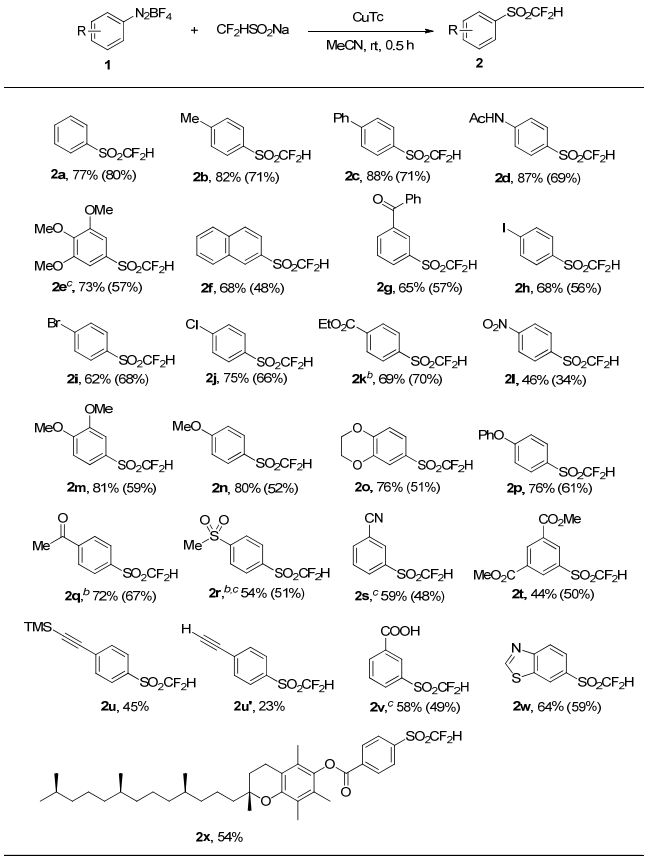
Entry[a]	"Cu"	Solvent	Time	Yield
1	Cu_2O	DMSO	12 h	none
2	CuTc	DMSO	12 h	8%
3	CuOAc	DMSO	12 h	none
4	CuTc	MeCN	12 h	64%
5	Cu_2O	MeCN	12 h	none
6	CuOAc	MeCN	12 h	none
7	$Cu(OAc)_2$	MeCN	12 h	48%
8	$CuSO_4$	MeCN	12 h	none
9	$Cu(acac)_2$	MeCN	12 h	16%
10	CuCN	MeCN	12 h	19%
11	CuF_2	MeCN	12 h	none
12	$Cu(MeCN)_4(PF_6)_2$	MeCN	12 h	35%
13[b]	CuTc	MeCN	12 h	79%
14[b,c]	CuTc	MeCN	12 h	80%
15[b,d]	CuTc	MeCN	12 h	58%
16[b,e]	CuTc	MeCN	12 h	47%
17[b,f]	CuTc	MeCN	12 h	34%
18[b]	CuTc	MeCN	0.5 h	80%
19[b,c]	CuTc	MeCN	0.5 h	80%

[a] The reaction was conducted on 0.2 mmol scale: **1a** (1.0 equiv), "Cu" (1.0 equiv), and CF_2HSO_2Na (1.5 equiv) were mixed together and 2.0 mL solvent was added. The reaction was stirred for the time indicated in the Table. The yield was determined by ^{19}F NMR with trifluoromethylbenzene as internal standard. [b] 1.0 mL of solution of **1a** (1.0 equiv) was added via syringe to 1.0 mL of solution of CuTc (1.0 equiv) and CF_2HSO_2Na (1.5 equiv). [c] 0.5 equiv of CuTc was used. [d] 0.4 equiv of CuTc was used. [e] 0.3 equiv of CuTc was used. [f] 0.2 equiv of CuTc was used.

With the optimized conditions in hand (Table 1, entry 18), we examined the scope of this reaction, which is shown in Scheme 2. Although the reaction gave the same results for **1a** using either 0.5 or 1.0 equivalent of CuTc (Table 1, entries 18 and 19), for most substrates, reaction with 0.5 equivalent of CuTc delivered 5%—10% lower yields than those utilizing 1.0 equivalent of CuTc, therefore, the latter conditions were applied in Scheme 2 (For the results using 0.5 equivalent of CuTc, see the yields in parentheses in Scheme 2).

As shown in Table 2, our method has a good compatibility with various functional groups, giving the corresponding products **2** in moderate to good yields. The substrates bearing electron-donating groups give better yields than the electron-deficient ones, which might attribute to the latter's higher reactivity with CuTc, thus resulting in undesired coupling reaction with thiophene carboxylate (Tc). The reaction conditions are compatible with halogens (**2h**—**2j**), ketones (**2g, 2q**), carboxylate esters (**2k, 2t**), nitrile (**2s**) and trimethylsilylacetylene (**2u**), which makes these compounds ready for further transformations to more complicated structures. To be noted, sulfones containing acidic protons, such as carboxylic acid (**2v**) and amide (**2d**), which are difficult to prepare using conventional methods, were accessible with high yields. For substrate **1u**, the trimethylsilyl group was partially transformed to hydrogen, which delivered the unmasked acetylene compound directly (**2u'**). Finally, to show the synthetic utility of this method in organic synthesis, the α-Tocopherol derivative was synthesized using this new method in 54% yield (**2x**).

Scheme 2 Copper-mediated difluoromethanesulfonylation of arenediazonium tetrafluoroborates[a]

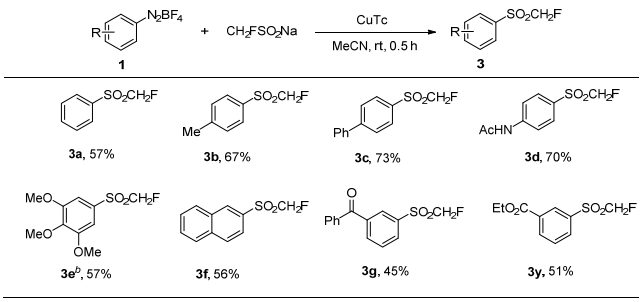


[a] The reaction was conducted on 0.5-mmol scale: a solution of substrate **1** (1.0 equiv) was added dropwise to the solution of CuTc (1.0 equiv) and CF_2HSO_2Na (1.5 equiv). Isolated yields are given. [b] 0.5 equiv of CuTc was used instead. [c] More solvent was used to dissolve the substrate.

This reaction could be expanded to synthesize aromatic sulfones containing other fluoroalkyls, such as mono- and trifluoromethyl groups (Schemes 3 and 4). It was found that the monofluoromethanesulfonylation of arenediazonium tetrafluoroborates gave the products **3** in moderate to good yields (Scheme 3). Electron-neutral and electron-rich substrates (**1a**—**1f**) displayed better reactivity than those bearing electron-withdrawing groups (**1g** and **1y**), which is consistent with the electronic effect. For trifluoromethanesulfonylation of arenediazonium salts, we chose **1c** as the model compound owing to its high reactivity towards sulfonylation as exhibited in Schemes 1 and 2. Although the desired trifluoromethanesulfonylation product **4** was obtained only

in moderate yield (Table 2, entry 11), it is encouraging for us to develop a complementary procedure to synthesize sulfones with electron-rich groups (Scheme 4), which were not easily accessible using known methods.[10]

Scheme 3 Copper-mediated monofluoromethanesulfonylation of arenediazonium tetrafluoroborates[a]

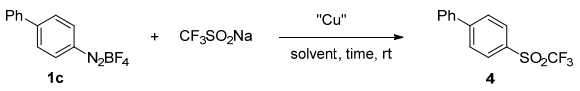


[a] The reaction was conducted on 0.5 mmol scale: a solution of substrate **1** (1.0 equiv) was added dropwise to the solution of CuTc (1.0 equiv) and CH_2FSO_2Na (1.5 equiv). Isolated yields are given. [b] More amount of solvent was used to dissolve the substrate.

In 2015, we compared the reactivity of different sodium sulfinates in radical fluoroalkylation reactions.[11] In the oxidative radical fluoroalkylations, the reactivity of sodium sulfinates decreases in the following order: $PhCF_2SO_2Na$ > CF_2HSO_2Na > CH_2FSO_2Na. Since arenediazonium tetrafluoroborates were not able to oxidize the sulfinates to the fluoroalkyl radicals,[10] it is reasonable to presume that the sodium fluoromethanesulfinates in our reactions react as nucleophiles rather than radical precursors. As our continuing effort in probing the unique fluorine effects in organic reactions,[12] we were interested in probing the reactivity order of R_fSO_2Na (R_f = CF_3, CF_2H, and CH_2F) in the current fluoroalkanesulfonylations (Scheme 5). To rule out the influence of solubility of different sulfinates, a mixture of MeCN/H_2O was utilized as a co-solvent system (in MeCN, the solubility of these sodium sulfinates decreases as follows: CF_3SO_2Na > HCF_2SO_2Na >> FCH_2SO_2Na). When **1c** was subjected to a mixture of CF_2HSO_2Na and CH_2FSO_2Na, **3c** was formed as the major product with a ratio of **3c**/**2c**=100/13 (Scheme 5, eq A). When **1c** was exposed to a mixture of CH_2FSO_2Na and CF_3SO_2Na, the ratio of **3c** to **4c** was about 100/0.6 (Scheme 5, eq B). As for the reaction between **1c** and CF_2HSO_2Na/CF_3SO_2Na, the ratio of compound **2c** to **4c** was 100/6 (Scheme 5, eq C). Based on the results of these competition experiments, it can be concluded that the relative reactivity of sodium fluoroalkanesulfinates decreases in the following order: CH_2FSO_2Na > CF_2HSO_2Na > CF_3SO_2Na, which can be explained by their relative nucleophilicity (more electron-rich sulfinates possess higher nucleophilicity). However, this trend is remarkably different from their reactivity in oxidative radical fluoroalkylations.[11] In the radical process, CF_3SO_2Na usually displays high tendency to extrude SO_2 to generate CF_3 radical once oxidized. However, in our present reaction as shown in Table 2 and Scheme 4, trifluoromethylation was not observed when no external oxidant was added. Indeed, most of the CF_3SO_2Na remained unreacted under our reaction conditions. Furthermore, considering the relatively higher reactivity of CH_2FSO_2Na and CF_2HSO_2Na (compared to CF_3SO_2Na) in our reactions, it is reasonable to hypothesize that the sodium sulfinates R_fSO_2Na (R_f = CF_3, CF_2H, and CH_2F) do not undergo oxidation to generate radicals but probably react as nucleophiles.

Based on the aforementioned information, we propose a plausible reaction mechanism as shown in Scheme 6. In the first step (Scheme 6, eq a), a copper species CuX, either X=Tc or R_fSO_2, serves as an initiator to generate aromatic radical through single electron reansfer (SET), and the latter species reacts with fluoroalkylsulfinate to a radical anion (Scheme 6, eq b). Then the radical anion can be quenched by either another molecule of substrate (nucleophilic radical chain reaction) or the cuprous compound (redox process).

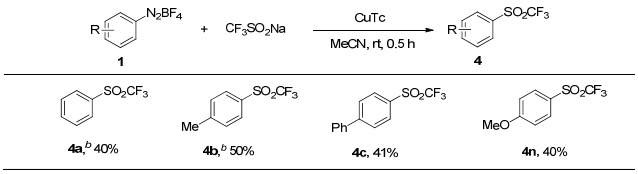
Table 2 Optimization of conditions for trifluoromethanesulfonylation of substrate **1c**



Entry[a]	"Cu"	Solvent	Time	Yield
1	Cu_2O	DMSO	12 h	23%
2	CuTc	DMSO	12 h	15%
3	$Cu(OAc)_2·H_2O$	DMSO	12 h	19%
4	CuOTf	DMSO	12 h	21%
5	Cu_2O	MeCN	12 h	7%
6	CuTc	MeCN	12 h	37%
7	$Cu(OAc)_2·H_2O$	MeCN	12 h	16%
8	CuOTf	MeCN	12 h	9%
9	CuTc	MeCN	0.5 h	34%
10[b]	CuTc	MeCN	0.5 h	33%
11[c]	CuTc	MeCN	0.5 h	40%

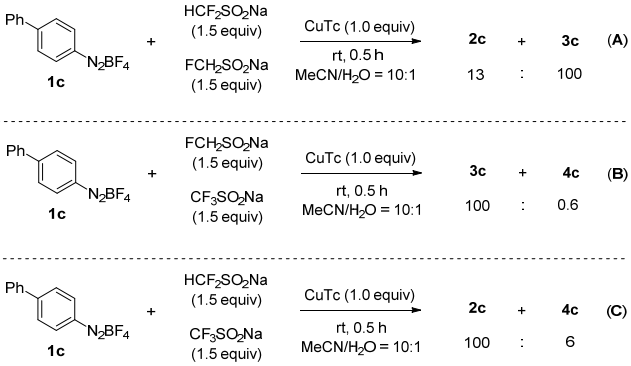
[a] The reaction was conducted on 0.2 mmol scale: **1c** (1.0 equiv), CuTc (1.0 equiv), CF_3SO_2Na (1.5 equiv), solvent (2.0 mL). Yield was detected by ^{19}F NMR. [b] The reaction was heated at 50 °C. [c] The reaction was conducted on 0.5 mmol scale. Isolated yield was given.

Scheme 4 Copper-mediated trifluoromethanesulfonylation of arenediazonium tetrafluoroborates[a]



[a] The reaction was conducted on 0.5 mmol scale: a solution of substrate **1** (1.0 equiv) was added dropwisely to the solution of CuTc (1.0 equiv) and R_fSO_2Na (1.5 equiv). Isolated yields are given. [b] Not isolatable from the by-product. Yield was detected by ^{19}F NMR.

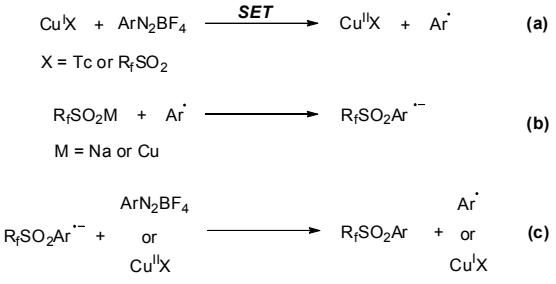
Scheme 5 Competition experiments of sodium fluoromethanesulfinates reacting with compound **1c**



Conclusions

In summary, we have developed copper-mediated di- and monofluoromethanesulfonylation of arenediazonium salts using CF_2HSO_2Na and CH_2FSO_2Na reagents, which can be readily

Scheme 6 Proposed mechanism



prepared from the corresponding benzo[*d*]thiazol-2-yl sulfones.[11] Various structurally diverse di- and monofluoromethyl aryl sulfones can be readily synthesized in good yields. This method also offers an alternative protocol for the synthesis of electron-rich trifluoromethyl sulfones. Furthermore, it was found that the relative reactivity of these fluoroalkanesulfinates in the current fluoroalkanesulfonylations decreases in the following order: CH_2FSO_2Na > CF_2HSO_2Na > CF_3SO_2Na. This reactivity order is consistent with their innate nucleophilicity, but different from their relative reactivity in oxidative radical fluoroalkylations.[11]

Experimental

General Information. Unless otherwise mentioned, reagents were purchased from commercial sources and used as received. CF_2HSO_2Na and CH_2FSO_2Na were prepared as per the reported literature,[11] while CF_3SO_2Na was purchased from TCI. The aromatic diazonium tetrafluoroborates were synthesized according to reported procedure.[13c] All the reactions were carried out under N_2 atmosphere. MeCN and DMSO were distilled over CaH_2 and kept over activated 4 Å MS. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 or 500 MHz NMR spectrometer. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of the residual solvent peak: $CHCl_3$ in $CDCl_3$: δ 7.26, DMSO in d_6-DMSO: δ 2.54. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Data for ^{1}H, ^{13}C and ^{19}F NMR were recorded as follows: chemical shift (δ), multiplicity (s＝singlet, d＝doublet, t＝triplet, q＝quartet, m＝multiplet). Coupling constants are reported in hertz (Hz). High-resolution mass data were recorded on a HR-MS in the EI mode or ESI mode.

General procedure for the preparation of diazonium salts 1. Method A. In a 50 mL round-bottom flask, the aniline (10.0 mmol) was dissolved in a mixture of absolute ethanol (3.0 mL) and an aqueous solution of HBF_4 (48%, 2.5 mL), followed by dropwise addition of ^{t}BuONO (2.7 mL) at 0 °C. After stirring at room temperature for 1 h, diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. After filtration and washing with diethyl ether (3×10 mL), the product was dried in vacuo (10^{-3} mbar) for 10 min and stored in refrigerator under N_2 atmosphere.

Method B. In a 50 mL round-bottom flask, aniline (5.0 mmol) was dissolved in a mixture of H_2O (1.0 mL) and an aqueous solution of HBF_4 (48%, 1.9 mL), followed by dropwise addition of an aqueous solution of $NaNO_2$ (680 mg in 1.0 mL H_2O). After being stirred at 0 °C for 30 min, the reaction mixture was worked up by filtration, washing successively with a small amount of ice water, alcohol and diethyl ether, and the arenediazonium tetrafluoroborate was dried in vacuo (10^{-3} mbar) for 10 min and stored in refrigerator under N_2 atmosphere.

General procedure for the preparation of compound 2. To an oven-dried Schlenk tube equipped with a stirring bar and rubber septum stopper was added CuTc (95.0 mg, 0.5 mmol), CF_2HSO_2Na (103.5 mg, 0.75 mmol) and MeCN (2.5 mL). After stirring for 5 min, a solution of arenediazonium tetrafluoroborates **1** (0.5 mmol) in MeCN (2.5 mL) was added dropwise in 15 min. Then the mixture was sealed and stirred for 30 min, followed by filtration on celite and washing with ethyl acetate. The filtrate was treated with saturated aqueous $NaHCO_3$, and the mixture was extracted by ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography. *To be noted: (a) Aqueous NH_4Cl was used instead of $NaHCO_3$ for compounds **2u** and **2v**; (b) 5.0 mL of MeCN was used to dissolve substrates **1e, 1r, 1s** and **1v**.*

((Difluoromethyl)sulfonyl)benzene (2a). Yellow liquid (72.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (dd, J＝8.1, 0.8 Hz, 2H), 7.86—7.78 (m, 1H), 7.67 (t, J＝7.8 Hz, 2H), 6.20 (t, J＝53.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.1, 132.0, 130.9, 129.9, 114.9 (t, J＝285.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.59 (d, J＝53.4 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_7H_6F_2O_2S$: 192.0057; found: 192.0061.

1-((Difluoromethyl)sulfonyl)-4-methylbenzene (2b). Yellow solid (84.6 mg, 82%), mp: 68—70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J＝8.3 Hz, 2H), 7.45 (d, J＝8.0 Hz, 2H), 6.17 (t, J＝53.5 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.7, 130.9, 130.6, 128.9, 114.9 (t, J＝285.6 Hz), 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.75 (d, J＝53.5 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_8H_8F_2O_2S$: 206.0213; found: 206.0220.

4-((Difluoromethyl)sulfonyl)-1,1'-biphenyl (2c). Yellow solid (117.8 mg, 88%), mp: 71—73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, J＝8.5 Hz, 2H), 7.89—7.83 (m, 2H), 7.67—7.63 (m, 2H), 7.56—7.45 (m, 3H), 6.23 (t, J＝53.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.9, 138.7, 131.2, 130.1, 129.3, 129.2, 128.2, 127.6, 114.8 (t, J＝285.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.50 (d, J＝53.5 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{13}H_{10}F_2O_2S$: 268.0370; found: 268.0368.

***N*-(4-((Difluoromethyl)sulfonyl)phenyl)acetamide (2d).** Yellow solid (108.6 mg, 87%), mp: 136—137 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ: 10.59 (s, 1H), 7.98—7.86 (m, 4H), 7.23 (t, J＝52.3 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ: 170.0, 146.7, 132.2, 124.6, 119.5, 115.1 (t, J＝281.9 Hz), 24.7. ^{19}F NMR (376 MHz, d_6-DMSO) δ: –124.39 (d, J＝52.3 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_9H_9NF_2O_3S$: 249.0271; found: 249.0277.

5-((Difluoromethyl)sulfonyl)-1,2,3-trimethoxybenzene (2e). White solid (102.7 mg, 73%), mp: 77—79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (s, 2H), 6.20 (t, J＝53.5 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.7, 144.5, 125.7, 114.7 (t, J＝285.9 Hz), 107.8, 61.2, 56.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.53 (d, J ＝ 53.6 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{10}H_{12}F_2O_5S$: 282.0374; found: 282.0378.

2-((Difluoromethyl)sulfonyl)naphthalene (2f). Red solid (82.1 mg, 68%), mp: 54—55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (s, 1H), 8.07 (t, J＝7.1 Hz, 2H), 7.99 (d, J＝8.3 Hz, 1H), 7.93 (dd, J＝8.7, 1.7 Hz, 1H), 7.76 (ddd, J＝8.2, 7.0, 1.3 Hz, 1H), 7.70 (ddd, J＝8.1, 7.0, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.4, 133.7, 132.2, 130.5, 129.9, 129.8, 128.7, 128.2 (d, J＝2.8 Hz), 124.1, 114.9 (t, J＝285.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.39 (d, J＝53.4 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{11}H_8F_2O_2S$: 242.0213; found: 242.0216.

(3-((Difluoromethyl)sulfonyl)phenyl)(phenyl)methanone (2g). Yellow solid (96.6 mg, 65%), mp: 72—73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (s, 1H), 8.24 (ddd, J＝13.5, 7.3, 4.6 Hz, 2H), 7.88—7.78 (m, 3H), 7.72—7.63 (m, 1H), 7.54 (dd, J＝10.7, 4.7 Hz, 2H), 6.26 (t, J＝53.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.1, 139.2, 136.8, 136.2, 133.8, 133.5, 132.3, 131.9, 130.1, 130.0, 128.8, 114.7 (t, J＝286.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.07 (d, J＝53.3 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{14}H_{10}F_2O_3S$: 296.0319; found: 296.0316.

1-((Difluoromethyl)sulfonyl)-4-iodobenzene (2h). Yellow sol-

id (108.6 mg, 68%), mp: 92—93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, J=8.6 Hz, 2H), 7.68 (d, J=8.5 Hz, 2H), 6.19 (t, J=53.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.1, 131.7, 131.3, 114.6 (t, J=286.1 Hz), 104.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.27 (d, J=53.4 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_7H_5F_2O_2SI$: 317.9023; found: 317.9033.

1-Bromo-4-((difluoromethyl)sulfonyl)benzene (2i). Yellow solid (83.5 mg, 62%), mp: 67—69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (q, J=8.8 Hz, 4H), 6.20 (t, J=53.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 133.1, 132.1, 132.0, 130.7, 114.6 (t, J=286.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.22 (d, J=53.4 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_7H_5F_2O_2SBr$: 269.9162; found: 269.9157.

1-Chloro-4-((difluoromethyl)sulfonyl)benzene (2j). Yellow solid (84.6 mg, 75%), mp: 66—67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97—7.91 (m, 2H), 7.70—7.60 (m, 2H), 6.20 (t, J=53.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.2, 132.1, 130.1, 114.7 (t, J=285.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.25 (d, J=53.4 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_7H_5F_2O_2SCl$: 225.9667; found: 225.9668.

Ethyl 4-((difluoromethyl)sulfonyl)benzoate (2k). Yellow liquid (91.4 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J=8.7 Hz, 2H), 8.09 (d, J=8.5 Hz, 2H), 6.24 (t, J=53.3 Hz, 1H), 4.47 (q, J=7.1 Hz, 2H), 1.45 (t, J=7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.9, 137.4, 135.7, 131.0, 130.8, 114.9 (t, J=286.4 Hz), 62.3, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.20 (d, J=53.2 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{10}H_{10}F_2O_4S$: 264.0268; found: 264.0264.

1-((Difluoromethyl)sulfonyl)-4-nitrobenzene (2l). Yellow solid (54.2 mg, 46%), mp: 119—120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55—8.46 (m, 2H), 8.22 (d, J=8.8 Hz, 2H), 6.29 (t, J=53.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.2, 137.4, 132.3, 124.7, 114.7 (t, J=286.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –120.60 (d, J=53.0 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_7H_5NF_2O_4S$: 236.9907; found: 236.9912.

4-((Difluoromethyl)sulfonyl)-1,2-dimethoxybenzene (2m). Yellow solid (101.9 mg, 81%), mp: 100—101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (dd, J=8.5, 2.1 Hz, 1H), 7.37 (d, J=2.0 Hz, 1H), 7.06 (d, J=8.5 Hz, 1H), 6.18 (t, J=53.7 Hz, 1H), 3.99 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.4, 149.6, 125.5, 122.7, 114.7 (t, J=285.2 Hz), 112.1, 111.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.69 (d, J=53.7 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_9H_{10}F_2O_4S$: 252.0268; found: 252.0267.

1-((Difluoromethyl)sulfonyl)-4-methoxybenzene (2n). Yellow liquid (89.1 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95—7.89 (m, 2H), 7.15—7.07 (m, 2H), 6.17 (t, J=53.7 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.7, 133.1, 122.7, 115.0, 114.7 (t, J=285.0 Hz), 55.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.75 (d, J=53.6 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_9H_8F_2O_3S$: 222.0162; found: 222.0167.

6-((Difluoromethyl)sulfonyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (2o). Yellow solid (94.5 mg, 76%), mp: 100—101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dt, J=8.4, 2.1 Hz, 2H), 7.07 (d, J=8.4 Hz, 1H), 6.15 (t, J=53.6 Hz, 1H), 4.41—4.36 (m, 2H), 4.36—4.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.4, 144.1, 124.6, 123.5, 120.2, 118.5, 114.6 (t, J=285.3 Hz), 64.8, 64.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.68 (d, J=53.6 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_9H_8F_2O_4S$: 250.0111; found: 250.0110.

1-((Difluoromethyl)sulfonyl)-4-phenoxybenzene (2p). Yellow solid (107.5 mg, 76%), mp: 65—66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=8.9 Hz, 2H), 7.46 (t, J=7.9 Hz, 2H), 7.34—7.25 (m, 1H), 7.20—7.09 (m, 4H), 6.18 (t, J=53.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.7, 154.3, 133.2, 130. 5, 125.7, 124.3, 120.8, 117.7, 114.7 (t, J=285.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.57 (d, J=53.6 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{13}H_{10}F_2O_3S$: 284.0319; found: 284.0310.

1-(4-((Difluoromethyl)sulfonyl)phenyl)ethan-1-one (2q). Yellow solid (83.8 mg, 72%), mp: 93—94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, J=8.6 Hz, 2H), 8.12 (d, J=8.5 Hz, 2H), 6.23 (t, J=53.2 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.5, 142.5, 135.5, 131.2, 129.2, 114.8 (t, J=286.5 Hz), 27.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.11 (d, J=53.3 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_9H_8F_2O_3S$: 234.0162; found: 234.0159.

1-((Difluoromethyl)sulfonyl)-4-(methylsulfonyl)benzene (2r). White solid (73.2 mg, 54%), mp: 152—154 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.34 (d, J=8.5 Hz, 2H), 8.28 (d, J=8.5 Hz, 2H), 7.45 (t, J=51.8 Hz, 1H), 3.39 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ: 147.8, 136.5, 131.9, 129.2, 115.2 (t, J=283.2 Hz), 43.4. ^{19}F NMR (376 MHz, d_6-DMSO) δ: –124.04 (d, J=51.8 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_8H_8F_2O_4S_2$: 269.9832; found: 269.9835.

3-((Difluoromethyl)sulfonyl)benzonitrile (2s). Yellow solid (63.5 mg, 59%), mp: 85—86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 1H), 8.23 (d, J=8.0 Hz, 1H), 8.09 (d, J=7.8 Hz, 1H), 7.84 (t, J=7.9 Hz, 1H), 6.28 (t, J=53.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.8, 134.5, 134.2, 133.7, 130.8, 116.4, 114.7, 114.7 (t, J=286.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –120.67 (d, J=53.1 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_8H_5NF_2O_2S$: 217.0009; found: 217.0004.

Dimethyl 5-((difluoromethyl)sulfonyl)isophthalate (2t). White solid (67.3 mg, 44%), mp: 108—109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.07 (s, 1H), 8.80 (s, 2H), 6.29 (t, J=53.2 Hz, 1H), 4.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1, 137.3, 135.3, 133.5, 132.7, 114.7 (t, J=286.6 Hz), 53.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –120.73 (d, J=53.2 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{11}H_{10}F_2O_6S$: 308.0166; found: 308.0160.

((4-((Difluoromethyl)sulfonyl)phenyl)ethynyl)trimethylsilane (2u). Yellow solid (64.3 mg, 45%), mp: 56—57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=8.4 Hz, 2H), 7.69 (d, J=8.5 Hz, 2H), 6.19 (t, J=53.4 Hz, 1H), 0.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 133.1, 131.6, 131.15, 130.8, 115.0 (t, J=285.9 Hz), 102.8, 101.5, 0.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.45 (d, J=53.5 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{12}H_{14}SiF_2O_2S$: 288.0452; found: 288.0455.

1-((Difluoromethyl)sulfonyl)-4-ethynylbenzene (2u'). Yellow solid (24.5 mg, 23%), mp: 76—78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, J=8.4 Hz, 2H), 7.74 (d, J=8.5 Hz, 2H), 6.21 (t, J=53.4 Hz, 1H), 3.39 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 133.1, 131.5, 130.6, 130.2, 114.7 (t, J=286.0 Hz), 82.7, 81.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.32 (d, J=53.4 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_9H_6F_2O_2S$: 216.0057; found: 216.0050.

3-((Difluoromethyl)sulfonyl)benzoic acid (2v). White solid (68.5 mg, 58%), mp: 167—168 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.45 (d, J=7.8 Hz, 1H), 8.42 (s, 1H), 8.24 (d, J=7.9 Hz, 1H), 7.94 (t, J=7.8 Hz, 1H), 7.41 (t, J=52.0 Hz, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ: 165.9, 137.1, 134.5, 133.3, 132.7, 131.5, 130.9, 115.1 (t, J=282.6 Hz). ^{19}F NMR (376 MHz, d_6-DMSO) δ: –124.42 (d, J=52.0 Hz). HR-MS (ESI): *m/z* calcd for $[M\text{-}H]^-$ $C_8H_5F_2O_4S$: 234.9882; found: 234.9880.

6-((Difluoromethyl)sulfonyl)benzo[*d*]thiazole (2w). Yellow solid (80.2 mg, 64%), mp: 106—107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.34 (s, 1H), 8.69 (d, J=1.7 Hz, 1H), 8.38 (d, J=8.6 Hz, 1H), 8.11 (dd, J=8.7, 1.8 Hz, 1H), 6.27 (t, J=53.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.8, 157.6, 134.8, 128.6, 127.6, 126.2, 124.9, 114.7 (t, J=286.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.04 (d, J=53.3 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_8H_5NF_2O_2S_2$: 248.9730; found: 248.9725.

(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-chroman-6-yl ((difluoromethyl)sulfonyl)benzoate (2x). White solid (191.5 mg, 59%), mp: 77—79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, J=8.4 Hz, 2H), 8.17 (d, J=8.3 Hz, 2H), 6.27 (t, J=53.2 Hz, 1H), 2.65 (t, J=6.5 Hz, 2H), 2.15 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.86 (td, J=13.9, 7.0 Hz, 2H), 1.64—1.04 (m, 24H), 0.88 (t, J=6.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.3, 149.9, 140.4, 136.3, 136.1, 131.1, 131.0, 126.5, 124.8, 123.4, 117.7, 114.8 (t, J=286.4 Hz), 75.3, 39.4, 37.5 (ddd, J=12.4, 9.8, 4.9 Hz), 32.8 (dd, J=8.4, 1.9 Hz), 28.0, 24.8 (d, J=1.4 Hz), 24.5, 22.7, 22.6, 21.1, 20.7, 19.8, 19.7 (dd, J=5.9, 2.7 Hz), 13.1, 12.3, 11.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –121.06 (d, J=53.2 Hz). HR-MS (ESI): *m/z* calcd for

$[M+H]^+$ $C_{37}H_{55}F_2O_5S$: 649.3733; found: 649.3727.

General procedure for the preparation of compound 3. To an oven-dried Schlenk tube equipped with a stirring bar and rubber septum stopper was added CuTc (95.0 mg, 0.5 mmol), CH_2FSO_2Na (90.0 mg, 0.75 mmol) and MeCN (2.5 mL). After stirring for 5 min, a solution of arenediazonium tetrafluoroborates **1** (0.5 mmol) in MeCN (2.5 mL) was added dropwise in 15 min. Then the mixture was sealed and stirred for 30 min, followed by filtration on celite and washing with ethyl acetate. The filtrate was treated with saturated aqueous $NaHCO_3$, and the mixture was extracted by ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography. *To be noted: 5.0 mL of MeCN was used to dissolve substrate **1e**.*

((Fluoromethyl)sulfonyl)benzene (3a). Colorless liquid (50.0 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, J=7.4 Hz, 2H), 7.78—7.72 (m, 1H), 7.63 (t, J=7.7 Hz, 2H), 5.15 (d, J=47.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.0, 134.9, 129.5, 129.0, 92.0 (d, J=220.2 Hz). ^{19}F NMR (376 MHz, CDCl3) δ: –210.67 (t, J=47.2 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_7H_7FO_2S$: 174.0151; found: 174.0147.

1-((Fluoromethyl)sulfonyl)-4-methylbenzene (3b). White solid (62.6 mg, 67%), mp: 100—101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=8.3 Hz, 1H), 7.41 (d, J=8.0 Hz, 1H), 5.12 (d, J=47.2 Hz, 1H), 2.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 146.2, 133.0, 130.2, 129.1, 92.1 (d, J=219.8 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –210.64 (t, J=47.3 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_8H_9FO_2S$: 188.0307; found: 188.0304.

4-((Fluoromethyl)sulfonyl)-1,1'-biphenyl (3c). White solid (91.5 mg, 73%), mp: 102—103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, J=8.3 Hz, 2H), 7.82 (d, J=8.6 Hz, 2H), 7.65—7.62 (m, 2H), 7.58—7.40 (m, 3H), 5.18 (d, J=47.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.9, 138.9, 134.3, 129.6, 129.2, 128.9, 128.2, 127.5, 92.1 (d, J=220.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –210.48 (t, J=47.1 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{13}H_{11}FO_2S$: 250.0464; found: 250.0472.

***N*-(4-((Fluoromethyl)sulfonyl)phenyl)acetamide (3d).** Yellow solid (80.4 mg, 70%), mp: 170—171 °C. ^{1}H NMR (400 MHz, d_6-DMSO) δ: 10.48 (s, 1H), 7.87 (s, 4H), 5.63 (d, J=46.0 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ: 169.8, 145.4, 130.5, 129.5, 119.3, 92.4 (d, J=211.1 Hz), 24.7. ^{19}F NMR (376 MHz, d_6-DMSO) δ: –213.09 (d, J=45.9 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_9H_{10}NFO_3S$: 231.0365; found: 231.0369.

5-((Fluoromethyl)sulfonyl)-1,2,3-trimethoxybenzene (3e). Yellow solid (75.6 mg, 57%), mp: 93—94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (s, 2H), 5.13 (d, J=47.1 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.7, 143.5, 130.2, 106.2, 92.1 (d, J=220.3 Hz), 61.1, 56.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –209.81 (t, J=47.1 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{10}H_{13}FO_5S$: 264.0468; found: 264.0469.

2-((Fluoromethyl)sulfonyl)naphthalene (3f). Red solid (63.2 mg, 56%), mp: 80—81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58 (s, 1H), 8.05 (t, J=7.9 Hz, 2H), 7.97 (d, J=8.1 Hz, 1H), 7.92 (dd, J=8.7, 1.7 Hz, 1H), 7.70 (dtd, J=16.2, 7.0, 1.2 Hz, 2H), 5.22 (d, J=47.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 135. 9, 132.8, 132.2, 131.6, 129.9 (d, J=1.1 Hz), 129.6, 128.1, 128.0, 123.0, 92.1 (d, J=220.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –210.36 (t, J=47.2 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{11}H_9FO_2S$: 224.0307; found: 224.0306.

3-((Fluoromethyl)sulfonyl)phenyl)(phenyl)methanone (3g). Yellow solid (68.5 mg, 45%), mp: 90—91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (s, 1H), 8.19 (t, J=9.0 Hz, 2H), 7.79 (dd, J=13.4, 7.5 Hz, 3H), 7.67 (t, J=7.4 Hz, 1H), 7.54 (t, J=7.8 Hz, 2H), 5.19 (d, J=47.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.4, 139.1, 136.5, 136.3, 135.9, 133.4, 132.4, 130.3, 130.1, 129.9, 128.8, 92.0 (d, J=220.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –210.57 (t, J=47.0 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{14}H_{11}FO_3S$: 278.0413; found: 278.0420.

Ethyl 3-((fluoromethyl)sulfonyl)benzoate (3y). Yellow liquid (62.4 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62 (s, 1H), 8.42 (d, J=7.8 Hz, 1H), 8.16 (d, J=7.9 Hz, 1H), 7.73 (t, J=7.8 Hz, 1H), 5.19 (d, J=47.1 Hz, 2H), 4.45 (q, J=7.1 Hz, 2H), 1.44 (t, J=7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.6, 136.6, 135.7, 133.0, 132.3, 130.1, 129.9, 91.9 (d, J=220.7 Hz), 62.0, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –210.68 (t, J=47.1 Hz). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{10}H_{11}FO_4S$: 246.0362; found: 246.0357.

General procedure for the preparation of compound 4. To an oven-dried Schlenk tube equipped with a stirring bar and rubber septum stopper was added CuTc (95.0 mg, 0.5 mmol), CF_3SO_2Na (117.0 mg, 0.75 mmol) and MeCN (2.5 mL). After stirring for 5 min, a solution of arenediazonium tetrafluoroborates **1** (0.5 mmol) in MeCN (2.5 mL) was added dropwise in 15 min. Then the mixture was sealed and stirred for 30 min, followed by filtration on celite and washing with ethyl acetate. The filtrate was treated with saturated aqueous $NaHCO_3$, and the mixture was extracted by ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the crude product was purified by column chromatography.

4-((Trifluoromethyl)sulfonyl)-1,1'-biphenyl (4c). Yellow solid (58.4 mg, 41%), mp: 72—73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, J=8.2 Hz, 2H), 7.88 (d, J=8.3 Hz, 2H), 7.65 (d, J=7.2 Hz, 2H), 7.57—7.46 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 149.7, 138.5, 131.4, 129.6, 129.4, 129.3, 128.5, 127.6, 119.9 (q, J=325.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: –78.44 (s). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_{13}H_9F_3O_2S$: 286.0275; found: 286.0272.

1-Methoxy-4-((trifluoromethyl)sulfonyl)benzene (4n). Yellow liquid (48.1 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, J=8.9 Hz, 2H), 7.11 (d, J=9.0 Hz, 21H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.2, 133.3, 122.0, 119.9 (q, J=325.5 Hz), 115.3, 56.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ: –78.88 (s). HR-MS (EI): *m/z* calcd for $[M]^+$ $C_8H_7F_3O_3S$: 240.0068; found: 240.0069.

General procedure for the competition experiments. Experiment A. To an oven-dried Schlenk tube equipped with a stirring bar and rubber septum stopper was added CuTc (95.0 mg, 0.5 mmol), CF_2HSO_2Na (103.5 mg, 0.75 mmol), CH_2FSO_2Na (90.0 mg, 0.75 mmol) and MeCN (2.5 mL). After stirring for 5 min, a solution of 4-biphenyldiazonium tetrafluoroborate **1c** (134.0 mg, 0.5 mmol) in MeCN (2.5 mL) was added dropwise in 15 min. Then the mixture was sealed and stirred for 30 min, followed by filtration on celite and washing with ethyl acetate. The filtrate was treated with saturated aqueous $NaHCO_3$, and the mixture was extracted by ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and concentration of the solvent under vacuum, the ratio was detected by ^{19}F NMR spectroscopy.

Experiment B. To an oven-dried Schlenk tube equipped with a stirring bar and rubber septum stopper was added CuTc (95.0 mg, 0.5 mmol), FCH_2SO_2Na (90.0 mg, 0.75 mmol), CF_3SO_2Na (117.0 mg, 0.75 mmol) and MeCN (2.5 mL). After stirring for 5 min, a solution of 4-biphenyldiazonium tetrafluoroborate **1c** (134.0 mg, 0.5 mmol) in MeCN (2.5 mL) was added dropwise in 15 min. Then the mixture was sealed and stirred for 30 min, followed by filtration on celite and washing with ethyl acetate. The filtrate was treated with saturated aqueous $NaHCO_3$, and the mixture was extracted by ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and concentration of the solvent under vacuum, the ratio was detected by ^{19}F NMR spectroscopy.

Experiment C. To an oven-dried Schlenk tube equipped with a stirring bar and rubber septum stopper was added CuTc (95.0 mg, 0.5 mmol), HCF_2SO_2Na (103.5 mg, 0.75 mmol), CF_3SO_2Na (117.0 mg, 0.75 mmol) and MeCN (2.5 mL). After stirring for 5 min, a solution of 4-biphenyldiazonium tetrafluoroborate **1c** (134.0 mg,

0.5 mmol) in MeCN (2.5 mL) was added dropwise in 15 min. Then the mixture was sealed and stirred for 30 min, followed by filtration on celite and washing with ethyl acetate. The filtrate was treated with saturated aqueous $NaHCO_3$, and the mixture was extracted by ethyl acetate (3×15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and concentration of the solvent under vacuum, the ratio was detected by ^{19}F NMR spectroscopy.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.201700748.

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