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ABSTRACT

The *ortho*-lithiation of substituted arenes is a powerful methodology to synthesize *ortho*-substituted arenes. While a wide variety of directed metalation groups (DMGs) have been reported, trifluoromethyl sulfone has never been used. We disclose the first example of *ortho*-lithiation of aryl triflones. We found that the trifluoromethyl sulfonyl group is not only an important structural motif in biologically active molecules and specialty materials, but also an excellent DMG moiety for *ortho*-metalation reactions. The use of a base that causes steric hindrance, LTMP, is the key for successful transformation to furnish a variety of *ortho*-substituted aryl triflones in good yields. Further functionalization of resulting *ortho*-substituted aryl triflones was demonstrated by metal-catalyzed coupling reactions.

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1. Introduction

Fluorinated and fluoro-functionalized aromatic compounds are increasingly valuable motifs in applications for specialty materials, pharmaceuticals, herbicides, and fungicides.[1a] Two of the most popular fluorinated aromatic compounds that have succeeded on the market thus far are aryl fluorides (Ar–F) and benzotrifluorides (Ar–CF_3), thus considerable attention has been devoted to the synthesis of Ar–F and Ar–CF_3 in both academia and industry in the past few decades.[1b] In this context, the attention of medicinal chemists has shifted spontaneously to a wide variety of arenes with heteroatom-linked trifluoromethyl modifications, such as trifluoromethoxy arenes (Ar–OCF_3),[2] trifluoromethylthio arenes (Ar–SCF_3)[3] and trifluoromethanesulfonyl arenes (aryl triflones, Ar–SO_2CF_3).[3d,4-10]

Aryl triflones have a functional group, trifluoromethanesulfonyl (-SO_2CF_3), which is strong electron-withdrawing group in organic chemistry while the lipophilicity of the SO_2CF_3 group is moderate (σm = 0.79, σp = 0.93, π = 0.55).[3d,11] Thus, the replacement of a CF_3 moiety in bioactive CF_3-compounds by a SO_2CF_3 group is a potential strategy for the design of new drug candidates. Indeed, aryl triflones are becoming popular as central structural motifs not only in biologically active molecules,[8] but also in functional materials[9] and chiral catalysts (Fig. 1).[10] Although there are many methods for the synthesis of aryl triflones, only a few reports are available for functionalization at the *ortho*-position of aryl triflones, such as nitration,[12] bromination,[13] chlorination,[14] and trifluoroethoxylation.[15]

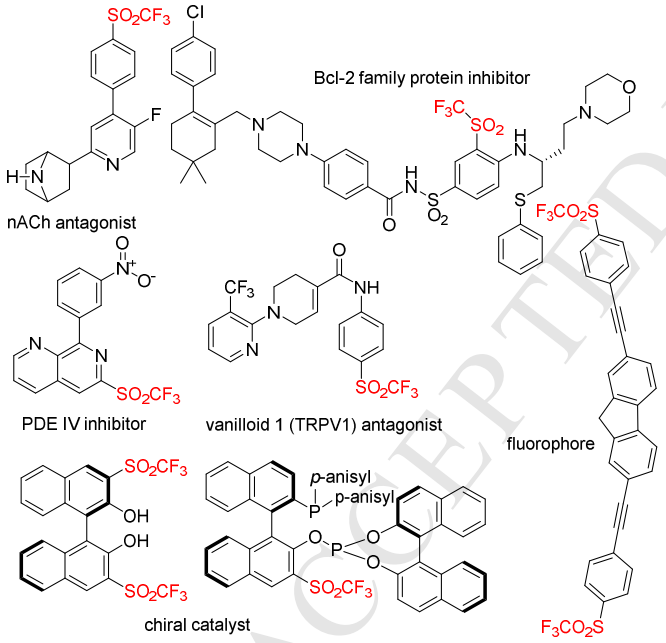
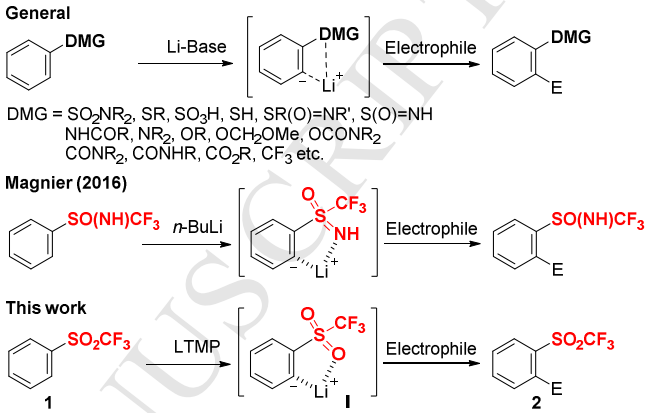


Fig. 1. Examples of aryl triflone-containing biologically attractive molecules and catalysts.

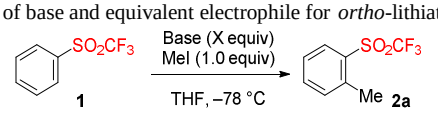
One of the most powerful strategies for the synthesis of *ortho*-substituted arenes is the direct *ortho*-metalation of arenes[16] bearing a "directed metalation group" (DMG) such as thiol (SH),[17] sulfonic acid (-SO_3H),[18] alkyl thiol ether (-SR),[19] alkyl sulfone (-SO_2R),[20] sulfone amide (-$S(O)NR_2$),[21] sulfoximine (-S(O)=NH-R),[22] or *S*-trifluoromethyl sulfoximine (-S(O)=NH-CF_3).[23] Despite the prestigious position of *ortho*-metalation of arenes with DMG in synthetic organic chemistry since the discovery of the *ortho*-metalation by Wittig[24] and Gilman,[25] it is rather surprising that the *ortho*-metalation of aryl triflones has rarely been reported. In recent years, Magnier and co-workers reported the first use of *S*-trifluoromethyl sulfoximine (-S(O)=NH-CF_3) as an *ortho*-directing group for the *ortho*-functionalization of arenes bonded to a trifluoromethyl conjugated sulfur atom.[23] We disclose herein the *ortho*-lithiation of aryl triflones. The SO_2CF_3 group was useful as a DMG when combined with lithium tetramethylpiperidide (LTMP). A wide variety of electrophiles were smoothly reacted with *ortho*-lithiated aryl triflones to provide corresponding *ortho*-substituted triflones in good yields. Since simple aryl triflones are commercially or readily available, our method is simple and straightforward for the preparation of *ortho*-substituted aryl triflones. Besides, to our knowledge, this is the first example of *ortho*-lithiation of aryl triflones.



Scheme 1. Directed *ortho*-lithiation of substituted aromatics.

Starting with the optimization of reaction conditions, bases were screened in the *ortho*-methylation of phenyl triflone **1**. The use of 1.0 equivalent of *n*-BuLi, a general reaction condition of *ortho*-lithiation, gave no desired product with incomplete conversion (Table 1, entry 1). NMR analysis of the obtained byproduct suggests that the CF_3 group was eliminated by the nucleophilic attack of *n*-BuLi to provide *n*-butyl phenyl sulfone. Thus, sterically demanding lithium amides were selected as the base. Even, the use of lithium bis(trimethylsilyl)amide (LHMDS) resulted in no reaction (entry 2), while the use of lithium diisopropylamide (LDA) gave the *ortho*-methylated phenyl triflone (**2a**) in 15% yield (entry 3). The more sterically hindered base LTMP improved yield to 55% (entry 4). The equivalent of LTMP and methyl iodide (MeI) affected yield, and the combination of 1.5 equivalents of LTMP and 2.0 equivalents of MeI successfully provided **2a** in 73% yield (entries 5–8).

Table 1
Optimization of base and equivalent electrophile for *ortho*-lithiation of **1**.[a]



Entry	Base	X (equiv)	Yield (%)
1	*n*-BuLi	1.0	0
2	LiHMDS	1.0	NR
3	LDA	1.0	15
4	LTMP	1.0	55
5	LTMP	1.5	65
6[b]	LTMP	1.5	73
7	LTMP	2.0	44
8[b]	LTMP	2.0	62

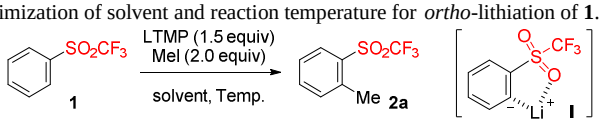
[a] Reactions were performed with **1** (1.0 mmol), Base (X equiv) and MeI (1.0 equiv) in THF (5.0 mL) at –78 °C.

[b] MeI (2.0 equiv) was used.

We next tested the affection between reaction temperature and solvent. When the reaction was performed at 0 °C, no desired product was obtained (Table 2, entry 1). After testing lower temperatures, an *ortho*-methylated product **2a** was obtained only when the reaction was performed at –78 °C (entries 2–5). After solvent screening, we found that the use of THF as a solvent is essential for this *ortho*-lithiation reaction while the use of other solvents (hexane, toluene, Et_2O) produced almost no desired product (entries 6–8). Addition of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) deceased the yield which suggested the importance of chelation between *ortho*-lithium and oxygen of triflone for this transformation (entry 9). These results suggest that the *ortho*-lithiated intermediate **I** is unstable but is stabilized by valance coordination of the triflyl group and THF.

Table 2

Optimization of solvent and reaction temperature for *ortho*-lithiation of **1**. [a]



Entry	Solvent	Temp. (°C)	Yield (%)[b]
1	THF	0	0
2	THF	–20	0
3	THF	–40	0
4	THF	–60	0
5	THF	–78	73
6	Hexane	–78	0
7	Toluene	–78	0
8	Et_2O	–78	2
9[c]	THF	–78	59

[a] Reactions were performed with **1** (1.0 mmol), LTMP (1.5 equiv) and MeI (2.0 equiv) in solvent (5.0 mL) at the given temperature.

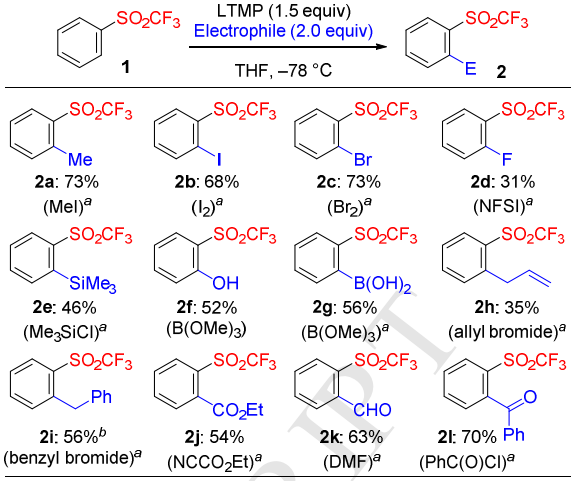
[b] Yields were determined by ^{19}F NMR with trifluoromethylbenzene as the internal standard.

[c] TMEDA (1.5 equiv) was added to the reaction mixture.

With the optimized reaction conditions in hand, we investigated the use of several electrophiles in the *ortho*-substitution reaction of phenyl triflone **1** (Table 3). Methyl-, I-, and Br-substituted phenyl triflones **2a**–**c** were obtained in good yields. Fluorination by using *N*-fluoro-bis(phenylsulfonyl)imide (NFSI) produced *ortho*-fluoro phenyl triflone **2d** in low yield. Silylation and hydroxylation provided the corresponding *ortho*-trimethylsilyl phenyl triflone **2e** and *ortho*-hydroxy phenyl triflone **2f**, respectively in moderate yields. Phenyl triflone with boronic acid at the *ortho*-position **2g** was obtained in 56% yield by using $B(OMe)_3$ as an electrophile with an acidic work up. The use of allyl bromide or benzyl bromide provided the corresponding *ortho*-alkylated phenyl triflone **2h** and **2i** with acceptable yields. It should be interesting to note that the addition of a carbonyl group provided phenyl triflones having an ester (**2j**), aldehyde (**2k**) or ketone group (**2l**) at the *ortho*-position in good yields, in spite of the products containing a reactive carbonyl group.

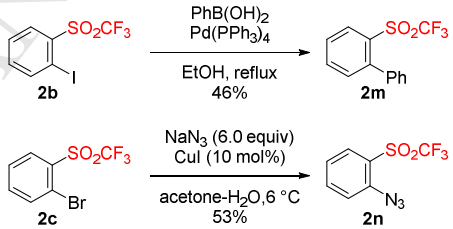
Table 3

Substrate scopes of *ortho*-lithiation of **1**.



[a] Electrophile. [b] LTMP (1.0 equiv) was used.

Finally, we attempted the transformation of halogen groups at the *ortho*-position of phenyl triflones. Suzuki-Miyaura cross coupling with *ortho*-iodo phenyl triflone **2b** and phenyl boronic acid proceeded to afford biphenyl triflone **2m** in 46% yield. Introduction of an azide group by sodium azide under copper catalysis from *ortho*-bromo phenyl triflone **2b** provided *ortho*-azide phenyl triflone **2n** in 53% yield.



Scheme 2. Coupling reaction of *ortho*-iodo and *ortho*-bromo phenyl triflones.

In summary, we disclosed the *ortho*-lithiation of aryl triflones. The trifluoromethyl sulfonyl group is not only an important structural motif in biologically active molecules and specialty materials, but also an excellent moiety of DMG for *ortho*-metalation reactions. Various types of electrophiles have shown to be compatible with this transformation resulting in a wide variety of *ortho*-substituted aryl triflones in good yields in a regioselective manner. The use of a base such as LTMP that causes steric hindrance is key for the success of this transformation as it suppresses the nucleophilic attack of lithiated bases on the sulfur atom at the sulfonyl center. Extension of this methodology to obtain structurally more complex *ortho*-substituted aryl triflones by combining our previous method for the synthesis of aryl triflones via benzynes is currently under investigation.

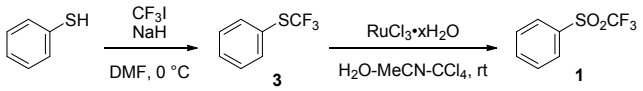
2. Experimental section

2.1. General methods

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210. The ^1H NMR (300 and 500 MHz), ^{19}F NMR (282 MHz), ^{13}C NMR (150.9 MHz) spectra for solution in $CDCl_3$ were recorded on a Bruker Avance 500 spectrometers. Chemical shifts (δ) are

expressed in ppm downfield from internal TMS (δ = 0.00), $CHCl_3$ (δ = 77.0), C_6F_6 (δ = –162.2). High resolution mass spectrometries were recorded on a SHIMADZU GCMS-QP5050A (EI-MS). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer.

*2.2. Phenyl(trifluoromethyl)sulfide (**3**)*[26]



To a stirring mixture of NaH (60% w/w in oil, 1.04 g, 26.0 mmol) in dry DMF (20.0 mL) was added thiophenol (2.04 mL, 20.0 mmol) at 0 °C, and the mixture was stirred at 0 °C for 20 min. CF_3I (3.10 g, 26.0 mmol) was added to the mixture via balloon, and the mixture was stirred at 0 °C for 12 h. H_2O was added to the mixture and the mixture was extracted with Et_2O. 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 to give Ph-SCF_3 **3** (2.33 g, 65%) as yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 7.5 Hz, 2H), 7.52–7.40 (m, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −43.2 (s, 3H) ppm.

*2.3. ((Trifluoromethyl)sulfonyl)benzene (**1**)*[27]

To a stirring mixture of Ph-SCF_3 **3** (2.32 g, 13.0 mmol) in H_2O-MeCN-CCl_4 (16.0 mL, 2:1:1) was added $RuCl_3$•xH_2O (135 mg, 0.65 mmol) at rt, and the mixture was stirred for 5 min. $NaIO_4$ (8.34 g, 39.0 mmol) was added to the mixture, and the mixture was stirred at rt for 1 h. The reaction mixture was diluted with Et_2O and filtered through the Celite®. The organic layer was separated and the aqueous layer was extracted with Et_2O. 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 to give phenyl triflone **1** (1.80 g, 65%) as yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.1 Hz, 2H), 7.86 (t, *J* = 8.3 Hz, 1H), 7.72–7.67 (m, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −78.9 (s, 3H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 119.7 (q, *J* = 325.8 Hz), 129.9, 130.7, 131.3, 136.6 ppm; IR (KBr): 1369, 1219, 1142, 1074, 771, 721, 685, 603 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_7H_5O_2F_3S$ $[M]^+$ 209.9962, Found: 209.9991.

2.4. General procedure of ortho-lithiation and addition

To a stirring mixture of 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL) was added *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol) at –78 °C, and the mixture was stirred at 0 °C for 30 min. The mixture was cooled to –78 °C, phenyltriflone **1** (210 mg, 1.00 mmol) was slowly added to the mixture, and the mixture was stirred at –78 °C for 2 h. Electrophile (2.00 mmol) was added to the mixture and the mixture was stirred at –78 °C for overnight. H_2O was added at rt and the mixture was diluted with Et_2O. The organic layer was separated and the aqueous layer was extracted with Et_2O. 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 to give *ortho*-substituted phenyl triflone **2**.

*2.5. 1-Methyl-2-((trifluoromethyl)sulfonyl)benzene (**2a**)* [27]

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and methyl iodide (124 µL, 2.00 mmol) gave the title compound (165 mg, 73%) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.49–7.42 (m, 2H), 2.72 (s, 3F) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −78.8 (s, 3H) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 20.6, 120.1 (q, *J* = 326.7 Hz), 127.2, 129.7, 133.3, 133.6, 136.4, 142.2 ppm; IR (KBr): 1363, 1203, 1145, 1122, 1057, 1043, 758, 690, 607 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_8H_7O_2F_3S$ $[M]^+$ 224.0119, Found: 224.0143.

*2.6. 1-Iodo-2-((trifluoromethyl)sulfonyl)benzene (**2b**)* [4v]

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and I_2 (508 mg, 2.00 mmol) in dry THF (2.0 mL) gave the title compound (227 mg, 68%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.28–8.24 (m, 2H), 7.70–7.64 (m, 1H), 7.45–7.39 (m, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −75.9 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 119.5 (q, *J* = 327.7 Hz), 129.2, 134.1, 134.8, 136.8, 144.3, 145.8 ppm; IR (KBr): 1714, 1369, 1213, 1139, 760, 725 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_7H_4O_2F_3SI$ $[M]^+$ 335.8929, Found: 335.8911.

*2.7. 1-Bromo-2-((trifluoromethyl)sulfonyl)benzene (**2c**)* [4v]

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and Br_2 (102 µL, 2.00 mmol) gave the title compound (210 mg, 73%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.23 (d, *J* = 4.8 Hz, 1H), 7.89 (d, *J* = 4.8 Hz, 1H), 7.64–7.61 (m, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −76.2 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 119.7 (q, *J* = 327.4 Hz), 123.5, 128.5, 131.4, 135.1, 137.1, 137.2 ppm; IR (KBr): 1373, 1215, 1142, 1090, 7026, 756, 604 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_7H_4O_2F_3SBr$ $[M]^+$ 287.9067, Found: 287.9088, calcd for C_6H_4Br $[M–SO_2CF_3]^+$ 154.9496, Found: 154.9510.

*2.8. 1-Fluoro-2-((trifluoromethyl)sulfonyl)benzene (**2d**)* [27,28]

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and *N*-fluorobenzenesulfoimide (631 mg, 2.00 mmol) in THF (2.0 mL) gave the title compound (71.7 mg, 31%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.05–8.00 (m, 1H), 7.85–7.81 (m, 1H), 7.48–7.43 (m, 1H), 7.39–7.33 (m, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −78.8 (d, *J* = 9.0 Hz, 3F), –104.2 (s, 1F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 118.2 (d, *J* = 19.6 Hz), 125.3, 133.4, 139.4 (d, *J* = 9.0 Hz), 161.2 (d, *J* = 265.0 Hz) ppm.

*2.9. Trimethyl(2-((trifluoromethyl)sulfonyl)phenyl)silane (**2e**)*

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and TMSCl (253 µL, 2.00 mmol) in THF (2.0 mL) gave the title compound (71.7 mg, 31%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.78–7.73 (m, 1H), 7.68–7.62 (m, 1H), 0.43 (s, 9H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −77.8 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 0.93, 119.9 (q, *J* = 327.5 Hz), 130.1, 132.9, 135.1, 136.3, 137.4, 145.0 ppm; IR (KBr): 1365, 1255, 1211, 1140, 849, 756, 663, 607 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_9H_{10}O_2F_3SiS$ $[M–Me]^+$ 267.0123, Found: 267.0120.

*2.10. 2-((Trifluoromethyl)sulfonyl)phenol (**2f**)* [29]

To a stirring mixture of 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL) was added *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol) at –78 °C, and the mixture was stirred at 0 °C for 30 min. The mixture was cooled to –78 °C, phenyltriflone **1** (210 mg, 1.00 mmol) was slowly added to the mixture, and the mixture was stirred at –78 °C for 2 h. $(MeO)_3B$ (223 µL, 2.00 mmol) was added to the mixture and the mixture was stirred at –78 °C for overnight. 3.0 M NaOH and 30% H_2O_2 were added to the mixture. The reaction mixture was neutralized with 1M HCl and extracted with Et_2O. 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 to give the title compound **3f** (117 mg, 52%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76–7.70 (m, 2H), 7.16–7.11 (m, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −79.8 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 112.9, 119.7, 119.8 (q, *J* = 325.6 Hz), 121.3, 131.5, 139.8, 158.9 ppm.

*2.11. (2-((Trifluoromethyl)sulfonyl)phenyl)boronic acid (**2g**)*

To a stirring mixture of 2,2,6,6-tetramethylpiperidine (1.28 mL, 7.50 mmol) in dry THF (15.0 mL) was added *n*-BuLi (1.30 M solution in hexane, 5.77 mL, 7.50 mmol) at –78 °C, and the mixture was stirred at 0 °C for 30 min. The mixture was cooled to –78 °C, phenyltriflone **1** (1.05 g, 5.00 mmol) was slowly added to the mixture, and the mixture was stirred at –78 °C for 2 h. $(MeO)_3B$ (1.12 mL, 10.0 mmol) was added to the mixture and the mixture was stirred at –78 °C for overnight. The reaction mixture was acidified with 10% HCl and extracted with Et_2O. 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 to give the title compound **3g** (712 mg, 56%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.14 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 6.9 Hz, 1H), 7.87–7.82 (m, 1H), 7.75–7.70 (m, 1H), 5.45 (s, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −77.9 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, acetone-d_6) δ: 120.2 (q, *J* = 326.3 Hz), 129.7, 130.9, 132.5, 133.4, 136.0 ppm, one carbon could not observed; IR (KBr): 3645, 1360, 1215, 1144, 764, 687, 607 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_7H_6BO_4F_3S$ $[M]^+$ 254.0032, Found: 254.0036.

*2.12. 1-Allyl-2-((trifluoromethyl)sulfonyl)benzene (**2h**)*

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and allyl bromide (173 µL, 2.00 mmol) gave the title compound (86.6 mg, 35%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 7.8 Hz, 1H), 7.69–7.64 (m, 1H), 7.46–7.40 (m, 2H), 5.94–5.85 (m, 1H), 5.09–5.01 (m, 2H), 3.79 (d, *J* = 6.0 Hz, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −78.8 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 37.0, 117.5, 119.6 (q, *J* = 326.8 Hz), 127.5, 129.5, 132.8, 133.3, 135.7, 136.4, 144.2 ppm; IR (KBr): 1365, 1213, 1144, 920, 762, 698, 606 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{10}H_9O_2F_3S$ $[M]^+$ 250.0275, Found: 250.0277.

*2.13. 1-Benzyl-2-((trifluoromethyl)sulfonyl)benzene (**2i**)*

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and BnBr (237 µL, 2.00 mmol) gave the title compound (168 mg, 56%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 7.2, 6.9 Hz, 1H), 7.49 (dd, *J* = 7.8, 7.5 Hz, 1H), 7.35–7.17 (m, 6H), 4.49 (s, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −78.7 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 38.0, 120.0 (q, *J* = 326.7 Hz), 126.7, 127.5, 128.7, 129.3, 129.7, 133.2, 133.3, 136.4, 138.9, 145.1 ppm; IR (KBr): 1363, 1217, 1140, 1111, 1059, 758, 698, 606 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{14}H_{11}O_2F_3S$ $[M]^+$ 300.0432, Found: 300.0424.

*2.14. Ethyl 2-((trifluoromethyl)sulfonyl)benzoate (**2j**)*

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and ethyl cyanoformate (198 µL, 2.00 mmol) gave the title compound (151 mg, 54%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 7.8 Hz, 1H), 7.88–7.85 (m, 1H), 7.77–7.71 (m, 2H), 4.47–4.40 (m, 2H), 1.40–1.36 (m, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −75.8 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 13.6, 62.8, 119.7 (q, *J* = 327.6 Hz), 129.3, 129.8, 131.0, 132.5, 136.3, 136.6, 165.9 ppm; IR (KBr): 1739, 1371, 1294, 1259, 1211, 1144, 1105, 1055, 773, 725, 606 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{10}H_9O_4F_3S$ $[M]^+$ 282.0174, Found: 282.0192.

*2.15. 2-((Trifluoromethyl)sulfonyl)benzaldehyde (**2k**)*

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and DMF (155 µL, 2.00 mmol) gave the title compound (150 mg, 63%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.8 (s, 1H), 8.27–8.21 (m, 2H), 8.00 (dd, *J* = 11.1, 0.9 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.5 Hz, 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −78.8 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 119.5 (q, *J* = 326.0 Hz), 130.4, 131.9, 133.3, 134.0, 136.9, 137.0, 188.2 ppm; IR (KBr): 1705, 1367, 1219, 1142, 1107, 775, 606 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_8H_5O_3F_3S$ $[M]^+$ 237.9912, Found: 237.9904.

*2.16. Phenyl(2-((trifluoromethyl)sulfonyl)phenyl)methanone (**2l**)*

According to the general procedure, 2,2,6,6-tetramethylpiperidine (255 µL, 1.50 mmol) in dry THF (5.0 mL), *n*-BuLi (1.30 M solution in hexane, 1.15 mL, 1.50 mmol), phenyltriflone **1** (210 mg, 1.00 mmol) and PhCOCl (232 µL, 2.00 mmol) gave the title compound (220 mg, 70%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 7.8 Hz, 1H), 7.92–7.87 (m, 1H), 7.81–7.73 (m, 3H), 7.63–7.58 (m, 1H), 7.51–7.46 (m, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −77.4 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 119.5 (q, *J* = 326.9 Hz), 128.6, 128.9, 129.7, 130.0, 130.4, 132.8, 134.0, 136.0, 136.2, 143.3, 193.4 ppm; IR (KBr): 1680, 1369, 1273, 1213, 1146, 1113, 930, 773, 708, 606 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{14}H_9O_3F_3S$ $[M]^+$ 314.0225, Found: 314.0211.

*2.17. 2-((Trifluoromethyl)sulfonyl)-1,1'-biphenyl (**2m**)*

The mixture of **2b** (370 mg, 1.10 mmol), phenyl boronic acid (122 mg, 1.00 mmol), $Pd(PPh_3)_4$ (35.0 mg, 0.03 mmol) in EtOH (5.0 mL) was refluxed for 6h. Saturated NH_4Cl aq was added to the mixture and the mixture was extracted with EtOAc. The organic layer was separated and the aqueous layer was extracted with Et_2O. 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 to give the title compound (131 mg, 46%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.1 Hz, 1H), 7.83–7.77 (m, 1H), 7.69–7.63 (m, 1H), 7.47–7.26 (m, 6H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −78.0 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 119.6 (q, *J* = 327.0 Hz), 127.3, 128.3, 128.6, 129.4,

129.7, 133.0, 133.9, 135.7, 137.5, 145.9 ppm; IR (KBr): 1684, 1369, 1215, 1144, 1119, 1074, 764, 604 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{13}H_9O_2F_3S$ $[M]^+$ 286.0275, Found: 286.0290.

*2.18. 1-Azido-2-((trifluoromethyl)sulfonyl)benzene (**2n**)*

The mixture of **2c** (145 mg, 0.5 mmol), NaN_3 (98.0 mg, 3.0 mmol), CuI (10.0 mg, 0.05 mmol) in acetone-H_2O (4.0 mL, 3:1) was stirred at 60 °C for 12h. CuI (10.0 mg, 0.05 mmol) was added to the mixture and the mixture was stirred at 80 °C for 2h. Removal of the solvent in vacue and the residue was dissolved in H_2O and Et_2O. The organic layer was separated and the aqueous layer was extracted with Et_2O. 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 to give the title compound (66.7 mg, 53%) as brown oil. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 7.8 Hz, 1H), 7.86–7.81 (m, 1H), 7.44–7.37 (m, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: −77.1 (s, 3F) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 119.8 (q, *J* = 326.7 Hz), 120.5, 121.8, 125.2, 134.2, 137.8, 142.5 ppm; IR (KBr): 2129, 1587, 1473, 1369, 1290, 1213, 1136, 1109, 1055, 731, 650, 603 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_7H_4N_3O_2F_3S$ $[M]^+$ 250.9976, Found: 250.9988.

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Supplementary data

Supplementary data related to this article can be found at

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