

BCSJ Award Article

Facile Synthesis of Aryl- and Alkyl-bis(trifluoromethylsulfonyl)methanes

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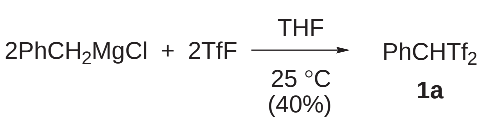
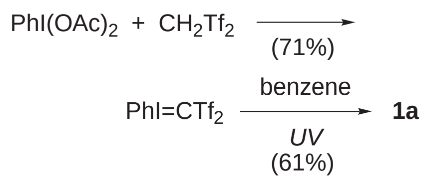
Various arylbis(trifluoromethylsulfonyl)methanes (**1**) have been synthesized by reacting the corresponding benzylic halides with sodium trifluoromethanesulfinate and then with triflic anhydride. In addition, when the aryl group of **1** is a pentafluorophenyl group, the nucleophilic *para*-substitution of the aryl group with alkyllithiums and sodium alkoxides occurs. This reaction is useful for the design of new Brønsted acids.

The trifluoromethylsulfonyl (triflyl, Tf) group is one of the strongest neutral electron-withdrawing groups.[1] Triflic acid (TfOH),[2] bis(triflyl)imide (Tf_2NH),[3,4a] and tris(triflyl)methane (Tf_3CH)[4b,5] are known to be strong acids and effective catalysts for various organic reactions. Their conjugate bases are useful as counterions for strong Lewis acid catalysts such as Me_3SiOTf,[6] Me_3SiNTf_2,[4c,7] and $Sc(CTf_3)_3$.[4b,8] However, it is difficult to modify these acids, which is a disadvantage in the design of a Brønsted acid or Lewis acid. Thus, we focused on phenylbis(triflyl)methane (**1a**, $pK_a = 7.83$ in MeCN,[9] 12.5 in CD_3CO_2D[10]) because the steric and electronic effects of the aromatic ring in arylbis(triflyl)methanes were expected to greatly influence their Brønsted acidity and their catalytic activity and selectivity for organic reactions. To the best our knowledge, only two methods have been reported for the synthesis of **1a**: the reaction of benzylmagnesium chloride with triflyl fluoride[11a] and the photochemical reaction of phenyliodonium bis(triflyl)methanide with benzene[11b] give **1a** in yields of 40 and 61%, respectively (Eqs. 1 and 2).

The former method requires gaseous triflyl fluoride (bp −21 °C), which is not commercially available, as an electrophilic triflyl source, while the latter requires a large amount of benzene as a solvent; upon photochemical reaction with arenes bearing electron-withdrawing groups such as fluorobenzene, no corresponding arylbis(triflyl)methanes are formed. Zhu et al. have reported a new synthetic route to **1a**.[11c] According to that report, **1a** can be prepared in 73% yield by the pyrolysis of benzenediazonium bis(triflyl)methanide. This synthetic route was very attractive to us as a general method for the preparation of various arylbis(triflyl)methanes. Unfortunately, however, we obtained *O*-phenylation product in 71% yield instead of **1a** (Eq. 3).[12]



(1)



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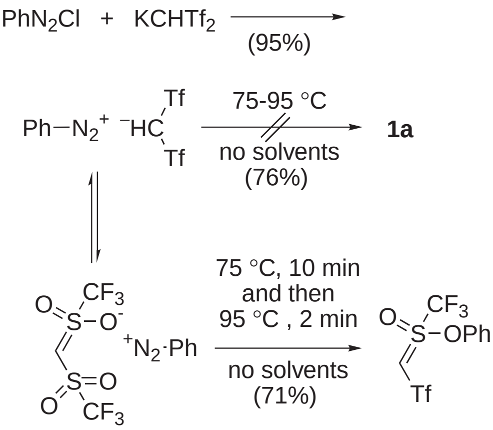


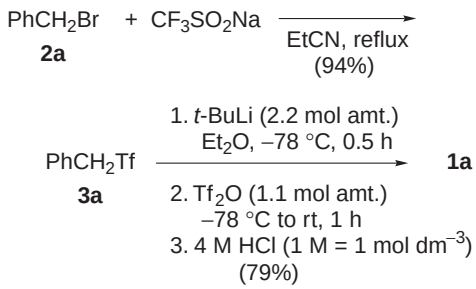
(3)

We report here a practical and convenient two-step synthesis of arylbis(triflyl)methanes and the design of Brønsted acids using nucleophilic *para*-substitution for pentafluorophenylbis(triflyl)methane.

Results and Discussion

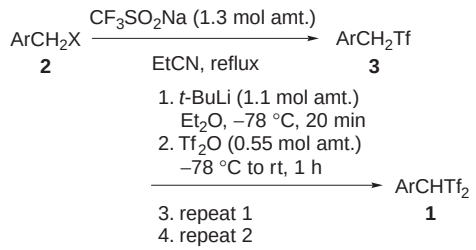
This new process involves the preparation of benzyl trifluoromethyl sulfone (**3a**) by the nucleophilic substitution of benzyl bromide (**2a**) with sodium trifluoromethanesulfinate (CF_3SO_2Na) and the subsequent reaction of the lithium salt of **3a** with triflic anhydride to give the desired compound **1a** (Scheme 1). The first step was accomplished by a slight modification of the method described by Hendrickson et al.[1] although the original procedure is not efficient when the aromat-

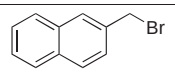
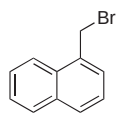
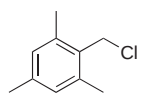
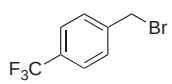
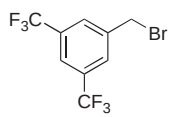
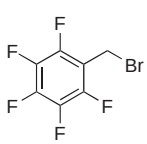
Published on the web August 4, 2005; DOI 10.1246/bcsj.78.1401



Scheme 1. Preparation of **1a**.

Table 1. Preparation of Arylbis(triflyl)methanes **1**



Run	**2**	**3**, %[a]	**1**, %[b]
1	 **2b**	**3b**, >99	**1b**, 84
2	 **2c**	**3c**, 99	**1c**, 98
3	 **2d**	**3d**, 90	**1d**, 89
4	 **2e**	**3e**, >99	**1e**, 87
5	 **2f**	**3f**, 76	**1f**, 75
6	 **2g**	**3g**, 89	**1g**, 45[c] (95)[d]

a) Isolated yield from **2**. b) Isolated yield from **3**. c) Desired compounds **1g** and **6a** were produced as a 1:1 mixture in 90% yield. d) Yield based on triflic anhydride, when *t*-BuLi (1.1 mol amt.) and Tf_2O (0.55 mol amt.) per **3g** were added with one portion, is indicated in parentheses.

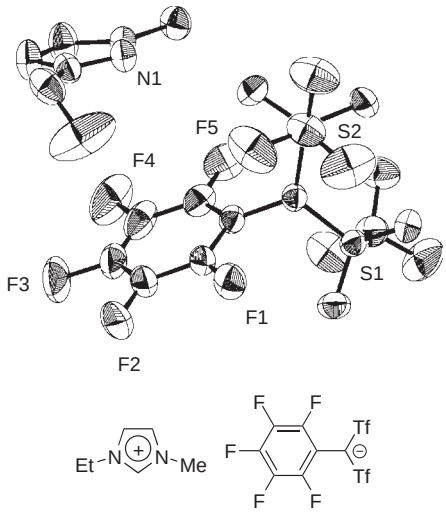


Fig. 1. The X-ray crystal structure of **5**.

ic ring is deactivated by electron-withdrawing groups,[1b] the reactivity was strongly enhanced by refluxing in propiononitrile instead of acetonitrile. The second step was accomplished by the successive addition of *t*-BuLi (2.2 molar amounts) and triflic anhydride (1.1 molar amounts) to a solution of **3a**.

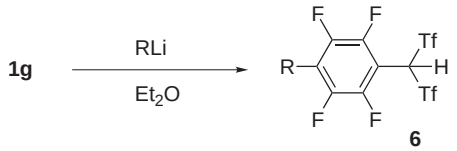
Various arylbis(triflyl)methanes **1** were prepared from arylmethyl halides **2** in high yield by applying this new methodology (Table 1).[13] Two portional additions of *t*-BuLi (1.1 molar amount × 2) and of triflic anhydride (0.55 molar amount × 2) were more effective to increase chemical yield of **1**. Notably, several novel compounds **1**, which had been difficult to synthesize, could be easily prepared from deactivated **2**; for example, a sterically-hindered halide **2d** and electron-deficient benzylic halides **2e–g**. Especially, **1g** derived from **2g** was a remarkably strong acid ($pK_a = 1.5$ in CD_3CO_2D; superacid) and exhibited extremely high catalytic activity for the acetylation of (−)-menthol with acetic anhydride.[14a] In addition, a silicon Lewis acid, which had a conjugate base of **1g** as a ligand, was a highly effective catalyst in comparison with Me_3SiOTf and Me_3SiNTf_2 for the condensation of trimethylhydroquinone with isophytol to give (±)-α-tocopherol.[14d]

The structure of the imidazolium salt of **1g** (**5**) was confirmed by single-crystal X-ray analysis (Fig. 1).

Surprisingly, 4-*tert*-butyl-2,3,5,6-tetrafluorophenylbis(triflyl)methane (**6a**) was obtained with **1g** in the reaction of **3g** with triflic anhydride. The use of *t*-BuLi (1.1 mol amt.) and triflic anhydride (0.55 mol amt.) completely suppressed the formation of **6a** and **1g** was obtained in 95% yield based on triflic anhydride. To explore the generality and scope of the nucleophilic *para*-substitution of **1g**, we examined the reaction with several alkyllithium reagents (Table 2). Surprisingly, even less-nucleophilic 3,4,5-trifluorophenyllithium and 3,5-bis(trifluoromethyl)phenyllithium also reacted with **1g** to give **6** in good yield. Compound **6** regiospecifically produced as a single isomer without exceptions.[14a]

Furthermore, the nucleophilic *para*-substitution reaction of **1g** could also be adapted to prepare 4-alkoxy-2,3,5,6-tetrafluorophenylbis(triflyl)methane **7** (Table 3). Several alcohols were examined by reacting a lithium salt of **1g** with the corresponding sodium alkoxides in pyridine at room temperature.

Table 2. Regiospecific Nucleophilic *para*-Substitution of **1g**

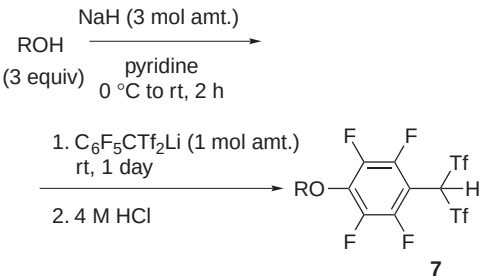


6

RLi (mol amt.)	Conditions	**6**, %
t-BuLi (3)[a)]	−78 °C, 1 h	**6a**, 87
n-BuLi (3)[a)]	−78 °C, 1 h	**6b**, >95
BnLi (5)	−78 °C, 6 h	**6c**, 83[b)]
PhLi (3)[a)]	−78 °C to rt, 1 day	**6d**, 83
3,4,5-$F_3C_6H_2Li$ (5)	−20 °C to rt, 3 h	**6e**, 75[b)]
3,5-$(CF_3)_2C_6H_3Li$ (5)	−20 °C to rt, 3 h	**6f**, 70[c)]

a) Ref. 8a. b) Starting material **1g** was remained. c) Isolated yield after sublimation.

Table 3. Regiospecific Nucleophilic *para*-Substitution of **1g** with Alcohols



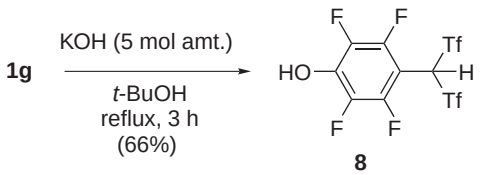
7

ROH	7, %
$C_6H_{13}OH$[a)]	**7a**, 83
$MeOCH_2CH_2OCH_2CH_2OH$	**7b**, 74
PhOH[b)]	**7c**, >69
CF_3CH_2OH[b)]	**7d**, 78

a) Ref. 8c. b) After addition of $C_6F_5CTf_2Li$, the reaction mixture was heated at 70 °C.

Pyridine was more effective as a solvent. In contrast, this reaction did not occur smoothly in diethyl ether, which was effective in the *para*-substitution reactions with alkyllithiums. Since sodium phenoxide was less reactive than aliphatic alkoxide, the reaction required a slightly higher temperature. As a result, compounds **7** were obtained in good yields. Surprisingly, even when an electron-deficient alcohol such as CF_3CH_2OH was used, the reaction proceeded smoothly to give **7d** in good yield.

Furthermore, it was also possible to introduce a hydroxy group as well as alkyl and alkoxy groups. Compound **1g** was reacted with potassium hydroxide to give 4-hydroxy-2,3,5,6-tetrafluorophenylbis(triflyl)methane (**8**) (Eq. 4).



(4)

8

We previously reported that the nucleophilic *para*-substitution reaction of **1g** could be adapted to prepare an organic-solvent-swellable resin-bound super Brønsted acid, Polystyrene-bound 2,3,5,6-tetrafluorophenylbis(triflyl)methane (**9**), and a fluorous super Brønsted acid, 4-(1*H*,1*H*-perfluorotetradecyloxy)-2,3,5,6-tetrafluorophenylbis(triflyl)methane (**10**) (Fig. 2).[14]

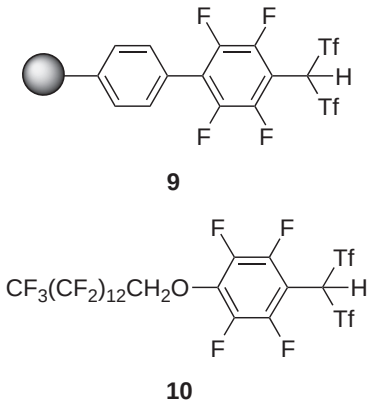
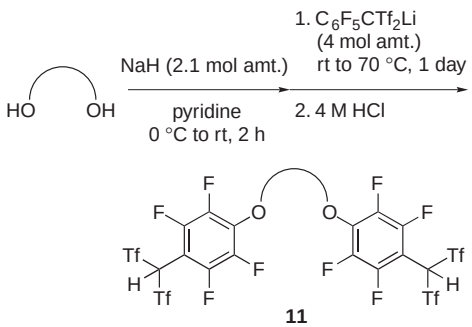
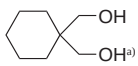


Fig. 2. Polystyrene-bound and fluorous Brønsted acids.

Table 4. Regiospecific Nucleophilic *para*-Substitution of **1g** with Diols



11

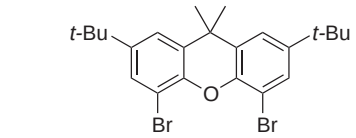
Diol	**11**, %
$HO(CH_2)_3OH$	**11a**, 85
$HO(CH_2)_4OH$	**11b**, 86
	**11c**, 70
	**11d**, 78

a) The alcohol was prepared by hydrogenation of 3-cyclohexene-1,1-dimethanol.

In addition, various diols were examined as nucleophiles instead of monoalcohols under similar conditions, and gave dibasic acids **11** (Table 4). Dibasic acid is expected to have higher catalytic activity than monobasic acid due to the synergistic effect of two acidic protons.

Diol-bound dibasic acids may be flexible bidentate acid catalysts because diols show high flexibility. The intramolecular interaction between two protons in a dibasic acid is expected to be increased when its linker is changed from a flexible diol to a rigid skeletal compound. Initially, 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**12**), which is commercially available, was used as a precursor for a nucleophile. The lithium salt of **1g** was added to **12** lithiated with *t*-BuLi, and the reaction mixture was heated at 50 °C to give the desired dibasic

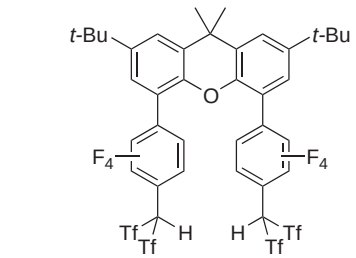
acid **13a** in 28% yield (Eq. 5). The pK_a value of **13a** in CD_3CO_2D was measured by the ^1H NMR method of Schantl and co-workers.[10] Compound **13a** was a superacid like **1g**, although the *para*-substitution of **1g** by a phenyl group lowered its Brønsted acidity.



12

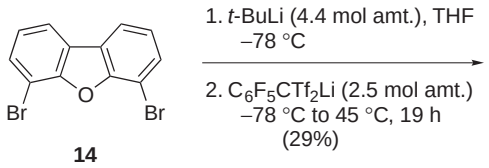
1. *t*-BuLi (4.4 mol amt.), THF, –78 °C, 1 h
2. $C_6F_5CTf_2Li$ (2.5 mol amt.), –78 °C to 50 °C, 42 h (28%)

(5)



13a (pK_a = 6.3)

The distance between the two acidic protons of a dibasic acid may affect its Brønsted acidity and catalytic activity. Therefore, we decided to synthesize new linkers, 1,8-dibromodibenzofuran (**14**)[15] and 1,8-dibromobiphenylene (**16**).[16] Lithiation of **14** was followed by reaction of the lithium salt of **1g** under similar conditions to afford **13b** in 29% yield (Eq. 6).



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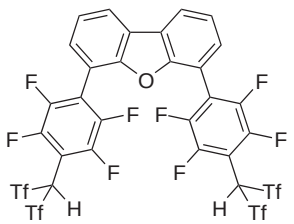
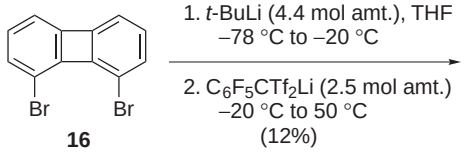


(6)

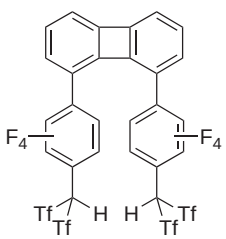
13b

The structure of the bipyridinium salt of **13b** (**15**) was confirmed by single-crystal X-ray analysis (Fig. 3).

Lithiation of **16**[17] was followed by the reaction of lithium salt of **1g** under similar conditions to afford **13c** in 12% yield (Eq. 7).



16



(7)

13c

1,1-Bis(triflyl)alkanes could also be prepared (Scheme 2). Trifluoromethyl sulfones can be prepared by the nucleophilic substitution of alkyl halides with sodium trifluoromethanesul-

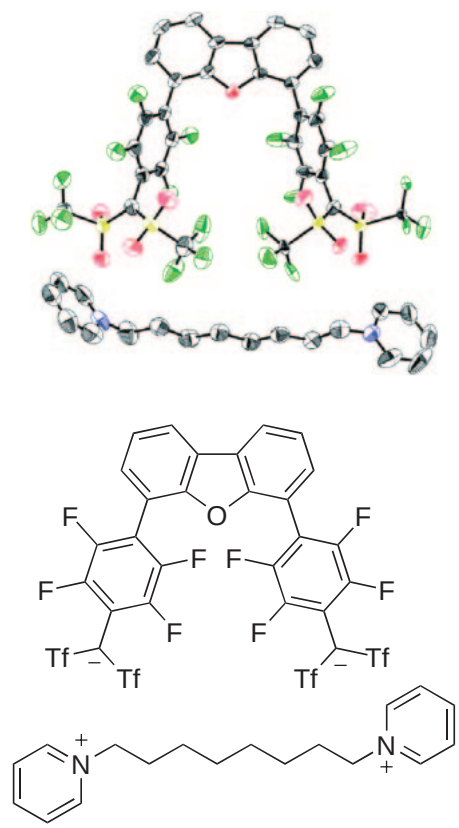
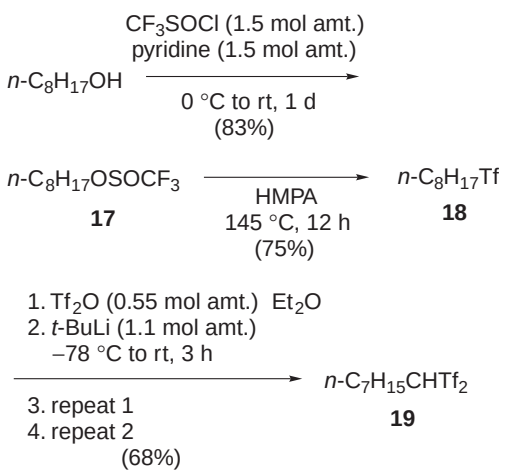


Fig. 3. The X-ray crystal structure of **15**.



Scheme 2. Preparation of 1,1-bis(triflyl)octane (**19**).

finate. However, this reaction proceeds very slowly with primary halides due to the low nucleophilicity of the rather stable anion. An alternative synthesis of trifluoromethyl sulfones from alcohols was examined by following the literature.[17] The reaction of the alcohol and CF_3SOCl in the presence of pyridine provided the triflinate **17**. The triflinate cleanly rearranged to the corresponding trifluoromethyl sulfone **18** on heating at 145 °C in HMPA, and subsequent reaction of the lithium salt of **18** with triflic anhydride as in the preparation of arylbis(triflyl)methanes gave 1,1-bis(triflyl)octane (**19**).

Conclusion

We have discovered a practical method for synthesizing arylbis(triflyl)methanes **1** starting from commercially available benzylic halides and 1,1-bis(triflyl)alkanes starting from commercially available 1-alkanols. Furthermore, we also found that the nucleophilic *para*-substitution reaction for **1g** occurred with some kinds of nucleophiles. The present methods made it possible to design new Brønsted acids such as **6**, **7**, **11**, and **13**. Their Brønsted acidity and catalytic activity depended on the substituent at C-4 of **1g**. In addition, conjugate bases of these acids are expected to be effective ligands for Lewis acid catalysts.

Experimental

General. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Gemini-300 instrument. Unless otherwise noted, ^{1}H, ^{13}C, and ^{19}F NMR spectra are referenced against internal tetramethylsilane ($\delta = 0$), $CDCl_3$ ($\delta = 77.0$), and $CF_3C_6H_5$ ($\delta = -64.0$), respectively. High-resolution mass (HRMS) analyses were carried out by Daikin Industries, Ltd., or at the Chemical Instrument Center, Nagoya University. Microanalyses were performed at the Chemical Instrument Center, Nagoya University. Unless otherwise indicated, all compounds were purchased. Commercial reagents were used as received with the following exceptions: pyridine and HMPA were distilled from calcium hydride (CaH_2). Et_2O and THF were distilled from sodium diphenylketyl. Flash chromatography was performed using silica gel 60 (230–400 mesh), purchased from Merck. All reactions were carried out under an atmosphere of nitrogen.

General Procedure for the Preparation of Benzylic Trifluoromethyl Sulfone (3) (Table 1). A solution of a benzylic halide **2** (10 mmol) and CF_3SO_2Na (2.0 g, 13 mmol) in propiononitrile (30 mL) was heated at reflux temperature. While disappearance of the starting halide was monitored by TLC, the mixture was cooled, the salts were removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using a linear AcOEt gradient in hexane to give **3** as a solid.

2-Benzyl Trifluoromethyl Sulfone (3a):[1c] IR (KBr) 1362, 1347, 1223, 1198, 1188, 1125, 776, 698, 640, 525, 507 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.48 (s, 2H), 7.42–7.47 (m, 5H). ^{19}F NMR (282 MHz, $CDCl_3$) δ −77.6 (s, 3F, CF_3).

2-Naphthylmethyl Trifluoromethyl Sulfone (3b): IR (KBr) 1358, 1345, 1221, 1194, 1125, 831, 756, 658, 608, 486 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.65 (s, 2H), 7.50 (dd, $J = 1.8$, 8.4 Hz, 1H), 7.54–7.58 (m, 2H), 7.86–7.94 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.3, 119.8 (q, $J_{CF} = 326$ Hz, 1C, CF_3), 120.3, 126.9, 127.4, 127.5, 127.8, 128.1, 129.2, 131.5, 133.1, 133.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ −77.6 (s, 3F, CF_3). Anal. Calcd for $C_{12}H_9F_3O_2S$: C, 52.55; H, 3.31%. Found: C, 52.52; H, 3.18%.

1-Naphthylmethyl Trifluoromethyl Sulfone (3c): IR (KBr) 1510, 1358, 1223, 1200, 804, 776, 658, 486 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99 (s, 2H), 7.53 (dd, $J = 7.8$, 8.4 Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.58 (ddd, $J = 0.9$, 6.9, 8.3 Hz, 1H), 7.65 (ddd, $J = 1.5$, 6.9, 8.4 Hz, 1H), 7.93 (dd, $J = 1.5$, 8.3 Hz, 1H), 7.98 (dd, $J = 8.4$ Hz, 1H), 8.04 (dd, $J = 0.9$, 8.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.0, 119.2, 120.0 (q, $J_{CF} = 326$ Hz, 1C, CF_3), 123.3, 125.3, 126.5, 127.5, 129.0, 131.1, 131.5, 132.3, 134.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −78.1 (s, 3F, CF_3). Anal. Calcd for $C_{12}H_9F_3O_2S$: C, 52.55; H, 3.31%. Found: C, 52.28; H, 3.31%.

2,4,6-Trimethylphenyl Trifluoromethyl Sulfone (3d): IR (KBr) 1358, 1206, 1117, 864, 619, 550, 500, 469 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.43 (s, 6H), 4.62 (s, 2H), 6.96 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.3, 21.0 (2C), 49.8, 117.0, 120.0 (q, $J_{CF} = 326$ Hz, 1C, CF_3), 129.9 (2C), 139.7 (2C), 139.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −79.7 (s, 3F, CF_3).

4-Trifluromethylphenylmethyl Trifloromethyl Sulfone (3e):[1b] IR (KBr) 1356, 1341, 1227, 1210, 1144, 1121, 855, 658, 513 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (s, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.5, 119.7 (q, $J_{CF} = 327$ Hz, 1C, CF_3), 123.7 (q, $J_{CF} = 271$ Hz, 1C, CF_3), 126.3 (q, $J_{CF} = 3.8$ Hz, 2C), 127.3 (s, 1C), 131.8 (s, 2C), 132.3 (q, $J_{CF} = 33$ Hz, 1C). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 119.6 (q, $J_{CF} = 326$ Hz, 1C, CF_3), 123.6 (q, $J_{CF} = 271$ Hz, 1C, CF_3), 126.2 (q, $J_{CF} = 41$ Hz, 2C), 127.3, 131.7 (2C), 132.2 (q, $J_{CF} = 33$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −77.5 (s, 3F, CF_3), −64.3 (s, 3F, CF_3). HRMS (EI) calcd for $C_9H_6F_6O_2S$: $[M]^+$ 291.9993. Found: 292.0012.

3,5-Bis(trifluoromethyl)phenylmethyl Trifluoromethyl Sulfone (3f): IR (KBr) 1376, 1362, 1277, 1175, 1117, 918, 910, 669 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (s, 2H), 7.91 (s, 2H), 8.01 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.0, 119.6 (q, $J_{CF} = 326$ Hz, 1C, CF_3), 122.6 (q, $J_{CF} = 272$ Hz, 2C, $2CF_3$), 124.2 (septet, $J_{CF} = 4$ Hz, 1C), 126.1, 131.3 (2C), 132.9 (q, $J_{CF} = 34$ Hz, 2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −77.4 (s, 3F, CF_3), −64.3 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{10}H_5F_9O_2S$: $[M]^+$ 359.9867. Found: 359.9863.

Pentafluorophenylmethyl Trifluoromethyl Sulfone (3g): IR (KBr) 1509, 1374, 1210, 1121, 995 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 44.3, 100.0 (dt, $J_{CF} = 4$, 17 Hz, 1C, *ipso*-C), 119.5 (q, $J_{CF} = 326$ Hz, 1C, CF_3), 137.9 (d, $J_{CF} = 251$ Hz, 2C, 2*m*-C), 142.8 (d, $J_{CF} = 258$ Hz, 1C, *p*-C), 145.9 (d, $J_{CF} = 258$ Hz, 2C, 2*o*-C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −160.0 (d, $J = 15.2$ Hz, 2F, 2*m*-F), −149.0 (s, 1F, *p*-F), −139.4 (d, $J = 15.2$ Hz, 2F, 2*o*-F), −78.3 (s, 3F, CF_3).

General Procedure for the Preparation of Arylbis(triflyl)-methanes 1a–f (Fig. 1). To a solution of **3** (0.5 mmol) in dry Et_2O (3 mL) was added *t*-BuLi (0.34 mL, 0.55 mmol, 1.6 M solution in hexane) dropwise at −78 °C, and the resulting mixture was stirred for 20 min. Triflic anhydride (92 μL, 0.28 mmol) was then added, and the resulting mixture was allowed to warm to room temperature over a period of 1 h. After the reaction mixture was cooled to −78 °C, *t*-BuLi (0.34 mL, 0.55 mmol, 1.6 M in hexane) was added dropwise, and the resulting mixture was stirred for 20 min. Triflic anhydride (0.28 mmol) was then added, and the resulting mixture was allowed to reach room temperature over a period of 1 h before the reaction was quenched with water. The resultant mixture was neutralized and washed with hexane. The aqueous

phase was acidified with 4 M aqueous HCl and extracted with ether twice. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was subjected to bulb-to-bulb distillation to give **1** as a solid.

Phenylbis(triflyl)methane (1a):[11] IR (KBr) 2950, 1381, 1242, 1219, 1184, 1102, 806, 695, 660, 608, 585, 507 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 5.97 (s, 1H), 7.54–7.68 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 80.7, 119.3 (q, $J_{CF} = 329$ Hz, 2C, $2CF_3$), 130.0 (2C), 131.8 (br), 132.9 (2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.8 (s, 6F, $2CF_3$).

2-Naphthylbis(triflyl)methane (1b): IR (KBr) 1393, 1381, 1244, 1213, 1103, 646, 586 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.10 (s, 1H), 7.61–7.71 (m, 3H), 7.92–7.99 (m, 2H), 8.03 (d, $J =$ 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 80.9, 116.3, 119.3 (q, $J_{CF} = 329$ Hz, 2C, $2CF_3$), 127.7, 128.0, 129.1, 130.1, 132.8, 133.4, 134.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.6 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{13}H_8O_4F_6S_2$: $[M]^+$ 405.9768. Found: 405.9761.

1-Naphthylbis(triflyl)methane (1c): IR (KBr) 1389, 1383, 1215, 1111, 770, 650, 504 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.87 (s, 1H), 7.62–7.80 (m, 4H), 8.02 (d, $J = 8.4$ Hz, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 8.37 (d, $J = 7.5$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 74.6, 114.1, 119.4 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 119.9, 125.4, 127.0, 128.9, 130.1, 131.5, 131.7, 133.8, 134.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.2 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{13}H_8O_4F_6S_2$: $[M]^+$ 405.9768. Found: 405.9761.

2,4,6-Trimethylphenylbis(triflyl)methane (1d): IR (KBr) 1397, 1383, 1217, 1119, 1107, 642, 590 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.35 (s, 3H), 2.61 (s, 3H), 6.48 (s, 1H), 7.00 (s, 1H), 7.08 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 21.1, 22.2, 77.7, 115.9, 119.4 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 130.4, 132.2, 140.0, 142.2, 142.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{13}H_{12}O_4F_6S_2$: $[M]^+$ 398.0081. Found: 398.0089.

4-Trifluoromethylphenylbis(triflyl)methane (1e): IR (KBr) 1393, 1383, 1327, 1231, 1171, 1136, 1111, 860, 671, 610 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 5.98 (s, 3H), 7.84 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 80.4, 120.0 (q, $J_{CF} = 329$ Hz, 2C, $2CF_3$), 123.8 (q, $J_{CF} = 271$ Hz, 1C, CF_3), 124.2, 127.6 (q, $J =$ 4 Hz, 2C), 130.0 (2C), 135.6 (q, $J_{CF} = 33$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.5 (s, 6F, $2CF_3$), −64.7 (s, 3F, CF_3). HRMS (EI) calcd for $C_{10}H_5O_4F_9S_2$: $[M]^+$ 423.9486. Found: 423.9471.

3,5-Bis(trifluoromethyl)phenylbis(triflyl)methane (1f): IR (KBr) 1395, 1374, 1285, 1223, 1194, 1179, 1144, 1105, 936, 909, 629, 519 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.05 (s, 1H), 8.13 (s, 2H), 8.18 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.9, 119.2 (q, $J_{CF} = 329$ Hz, 2C, $2CF_3$), 122.2 (q, $J_{CF} = 329$ Hz, 2C, $2CF_3$), 122.9, 126.7 (septet, $J_{CF} = 4$ Hz, 1C), 131.6 (s, 2C), 133.8 (q, $J_{CF} = 35$ Hz, 2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.2 (s, 6F, $2CF_3$), −64.3 (s, 3F, CF_3). HRMS (EI) calcd for $C_{11}H_4O_4F_{12}S_2$: $[M]^+$ 472.9375. Found: 472.9372.

Procedure for the Preparation of Pentafluorophenylbis(triflyl)methane (1g): To a solution of **3g** (0.5 mmol) in dry Et_2O (3 mL) was added *t*-BuLi (0.34 mL, 0.55 mmol, 1.6 M solution in hexane) dropwise at −78 °C, and the resulting mixture was stirred for 20 min. Triflic anhydride (92 μL, 0.28 mmol) was then added, and the resulting mixture was allowed to warm to room temperature over a period of 1 h before the reaction was quenched with water. The resultant mixture was neutralized and washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with ether twice. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was subjected to bulb-to-bulb distillation (85 °C, 0.05 Torr) to give **1g** as a solid. mp 86–87 °C. IR (KBr) 1522, 1501, 1347, 1321, 1198, 1127, 1024, 988, 613 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.21 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.4, 98.0 (s, 1C, *ipso*-C), 119.2 (q, $J_{CF} = 330$ Hz, 2C, $2CF_3$), 137.8 (d, $J_{CF} = 258$ Hz, 1C, *m*-C), 138.6 (d, $J_{CF} =$ 257 Hz, 1C, *m*-C), 144.7 (d, $J_{CF} = 264$ Hz, 1C, *p*-C), 145.4 (d, $J_{CF} = 262$ Hz, 1C, *o*-C), 147.2 (d, $J_{CF} = 262$ Hz, 1C, *o*-C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −157.9 (dt, $J = 6.2$, 21.5 Hz, 1F, *m*-F), −156.8 (dt, $J = 6.2$, 21.5 Hz, 1F, *m*-F), −142.6 (tt, $J = 5.9$, 21.5 Hz, 1F, *p*-F), −140.3 (br, 1F, *o*-F), −127.7 (ddd, $J = 5.9$, 15.2, 21.5 Hz, 1F, *o*-F), −75.2 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_9HO_4F_{11}S_2$: $[M]^+$ 445.9141. Found: 445.9137.

Procedure for the Preparation of 1-Ethyl-3-methylimidazolium Pentafluorophenylbis(triflyl)methanide (5). A solution of 1-ethyl-3-methylimidazolium bromide (955 mg, 5.0 mmol) and lithium pentafluorophenylbis(triflyl)methanide (2.26 g, 5.0 mmol) in H_2O (8 mL) were stirred at 70 °C for 1 d. The resulting mixture was extracted with AcOEt. The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral aluminum oxide (eluent: AcOEt) to give **5**. Finally, the product was dried under reduced pressure (80 °C, 0.67 hPa, overnight). mp 52 °C. IR (KBr) 1517, 1493, 1347, 1328, 1177, 1129, 1020, 608 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ 1.40 (t, $J =$ 7.2 Hz, 3H), 3.84 (s, 3H), 4.18 (q, $J = 7.2$ Hz, 2H), 7.69 (s, 1H), 7.78 (s, 1H), 9.10 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1, 35.7, 44.2, 55.0, 107.6, 120.8 (q, $J_{CF} = 330$ Hz, 2C, $2CF_3$), 122.0, 123.7, 136.3, 136.6 (d, $J_{CF} = 230$ Hz, 2C), 147.5 (d, $J_{CF} = 247$ Hz, 3C). ^{19}F NMR (282 MHz, CD_3CN) δ −166.0 (m, 2F), −155.3 (m, 1F), −136.4 (m, 2F), −81.2 (s, 6F, $2CF_3$). Anal. Calcd for $C_{15}H_{11}F_{11}N_2O_4S_2$: C, 32.32; H, 2.17; N, 5.03%. Found: C, 32.57; H, 2.08; N, 5.12%.

X-ray Crystallographic Analysis of 5: Crystal data: $C_{15}H_{11}F_{11}N_2O_4S_2$, Mw = 556.38, crystal dimensions 0.20 × 0.20 × 0.15 mm^3, monoclinic, space group $P2_1/n$ (#14), $a =$ 10.4467(19), $b = 14.491(3)$, $c = 14.507(3)$ Å, $V = 2139.5(7)$ $Å^3$, $Z = 4$, $D_c = 1.727$ g/cm^3, $\mu = 0.370$ mm^{-1}, $T = 223$ K. X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, Mo Kα radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded using Fourier techniques. 5674 reflections were independent and unique, and 4535 with $I > 2\sigma(I)$ ($2\theta_{max} =$ 29.12°) were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. $R = 0.0461$ and $Rw = 0.1376$.

General Procedure for the Preparation of 4-Alkyl- or 4-Aryl-2,3,5,6-tetrafluorophenylbis(triflyl)methane (6). To a solution of **1g** (0.22 g, 0.5 mmol) in Et_2O (3 mL) was added a solution of alkyl- or aryllithium [*t*-BuLi (1.5 mmol), *n*-BuLi (1.5 mmol), BnLi (2.5 mmol),[18] PhLi (1.5 mmol), and 3,4,5-$F_3C_6H_2Li$ (2.5 mmol)[19]] at −78 °C, and the resulting mixture was stirred under the following conditions: *t*-BuLi (−78 °C, 1 h), *n*-BuLi (−78 °C, 1 h), BnLi (−78 °C, 6 h), PhLi (−78 °C to rt, 1 d), and 3,4,5-$F_3C_6H_2Li$ (−20 °C to rt, 3 h) before the reaction was quenched with water. The resultant mixture was neutralized with 1 M aqueous HCl and washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with Et_2O twice. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to give **6** as a light brown solid.

4-*tert*-Butyl-2,3,5,6-tetrafluorophenylbis(triflyl)methane (6a):

IR ($CHCl_3$) 3021, 1480, 1456, 1117, 967, 669 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 9H), 6.24 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.4 (3C), 37.9, 70.8, 99.3 (t, $J_{CF} = 16$ Hz, 1C), 119.2 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 134.2 (t, $J_{CF} = 13$ Hz, 1C), 145.2 (d, $J_{CF} = 251$ Hz, 1C, *m*-C), 145.6 (d, $J_{CF} = 250$ Hz, 1C, *o*-C), 146.4 (d, $J_{CF} = 251$ Hz, 1C, *o*-C), 147.0 (d, $J_{CF} = 258$ Hz, 1C, *m*-C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −142.8 (m, 1F), −135.1 (dd, $J = 10.6$, 18.3 Hz, 1F, *m*-F), −133.9 (dd, $J = 10.6$, 18.3 Hz, 1F, *m*-F), −130.3 (m, $J = 9.0$, 21.4 Hz, 1F, *o*-F), −75.4 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{13}H_{10}O_4F_{10}S_2$: $[M]^+$ 483.9861. Found: 483.9852.

4-Butyl-2,3,5,6-tetrafluorophenylbis(triflyl)methane (6b): IR ($CHCl_3$) 3021, 1497, 1483, 1410, 1117, 669 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, $J = 7.6$ Hz, 3H), 1.40 (septet, $J = 7.6$ Hz, 2H), 1.64 (quintet, $J = 7.6$ Hz, 2H), 2.83 (t, $J = 7.6$ Hz, 2H), 6.25 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 22.4, 23.3, 30.9, 70.9, 99.2 (t, $J = 16$ Hz, 1C), 128.2 (t, $J = 18$ Hz, 1C), 144.4 (d, $J_{CF} = 251$ Hz, 1C), 144.8 (d, $J_{CF} = 250$ Hz, 1C), 145.6 (d, $J_{CF} = 250$ Hz, 1C), 146.3 (d, $J_{CF} = 258$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −142.8 (br, 1F, *o*-F), −141.6 (dd, $J = 12.3$, 21.4 Hz, 1F, *m*-F), −140.4 (dd, $J = 12.3$, 21.4 Hz, 1F, *m*-F), −130.6––130.4 (m, 1F, *o*-F), −75.4 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{13}H_{10}O_4F_{10}S_2$: $[M]^+$ 483.9861. Found: 483.9873.

4-Benzyl-2,3,5,6-tetrafluorophenylbis(triflyl)methane (6c): IR ($CHCl_3$) 3021, 1497, 1410, 1347, 1117, 1022, 992, 669 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 4.15 (s, 2H), 6.24 (s, 1H), 7.24–7.34 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.3, 70.8, 100.1 (t, $J_{CF} = 16$ Hz, 1C), 119.2 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 126.5 (t, $J_{CF} = 18$ Hz, 1C), 127.5, 128.5 (s, 2C), 135.9, 144.6 (d, $J_{CF} = 251$ Hz, 1C), 144.7 (d, $J_{CF} = 249$ Hz, 1C), 145.5 (d, $J_{CF} = 249$ Hz, 1C), 146.3 (d, $J_{CF} = 259$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −142.0 (br, 1F, *o*-F), −140.4 (dd, $J = 13.0$, 22.0 Hz, 1F, *m*-F), −139.3 (dd, $J = 13.0$, 22.0 Hz, 1F, *m*-F), −129.7––129.6 (m, 1F, *o*-F), −75.3 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{16}H_8O_4F_{10}S_2$: $[M]^+$ 517.9704. Found: 517.9694.

4-Phenyl-2,3,5,6-tetrafluorophenylbis(triflyl)methane (6d): IR (KBr) 1487, 1441, 1410, 1395, 1225, 1186, 1117, 1107, 974 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (s, 1H), 7.46–7.60 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.9, 100.6 (q, $J_{CF} = 16$ Hz, 1C), 119.3 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 125.7, 126.8 (t, $J = 16$ Hz, 1C), 128.9 (2C), 130.0 (2C), 130.3, 139.3 (d, $J_{CF} = 255$ Hz, 1C), 144.5 (d, $J_{CF} = 245$ Hz, 1C), 145.0 (d, $J_{CF} = 252$ Hz, 1C), 146.7 (d, $J_{CF} = 256$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −145.0 (m, 1F, *o*-F), −140.7 (dd, $J = 12.1$, 21.4 Hz, 1F, *m*-F), −139.5 (dd, $J = 12.1$, 21.4 Hz, 1F, *m*-F), −129.6–−129.4 (m, 1F, *o*-F), −75.3 (s, 6F, $2CF_3$). HRMS (EI) calcd for $C_{15}H_6O_4F_{10}S_2$: $[M]^+$ 503.9548. Found: 503.9560.

4-(3,4,5-Trifluoromethyl)-2,3,5,6-tetrafluorophenylbis(triflyl)methane (6e): ^1H NMR (300 MHz, $CDCl_3$) δ 6.30 (s, 1H), 7.20–7.24 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ −156.4 (dt, $J = 6.1$, 21.4 Hz, 1F), −140.8––140.7 (m, 2F), −140.3 (dd, $J = 12.3$, 24.4 Hz, 1F), −139.0 (dd, $J = 12.3$, 24.4 Hz, 1F), −132.9–−132.8 (m, 2F), −128.2––128.1 (m, 1F), −75.2 (s, 6F, $2CF_3$).

4-[3,5-Bis(trifluoromethyl)phenyl]-2,3,5,6-tetrafluorophenylbis(triflyl)methane (6f). To a solution of 3,5-bis(trifluoromethyl)bromobenzene (96 μL, 0.55 mmol) in Et_2O (1 mL) was added BuLi (0.32 mL, 0.51 mmol, 1.6 M solution in hexane) as −78 °C, and the resulting mixture was allowed to warm to −20 °C over a period of 1 h. To a solution of 3,5-bis(trifluoromethyl)-phenyllithium[19] generated in situ was added a solution of **1g** (46 mg, 0.1 mmol) in Et_2O (1 mL) at the same temperature, and the resulting mixture was allowed to warm to room temperature over a period of 3 h before the reaction was quenched with water. The resultant mixture was neutralized with 1 M aqueous HCl and washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with ether twice. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to give a brown solid that was subjected to vacuum sublimation (150 °C, 6.7 Pa) to give **6f** as a colorless solid. IR (KBr) 1489, 1375, 1285, 1210, 1173, 1136, 1119 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.31 (s, 1H), 8.01 (s, 2H), 8.07 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.6, 103.0 (t, $J_{CF} = 15$ Hz, 1C), 119.3 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 122.7 (q, $J_{CF} = 272$ Hz, 2C, $2CF_3$), 123.3 (t, $J_{CF} = 15$ Hz, 1C), 124.2–124.4 (m, 1C), 127.8, 130.3 (2C), 132.8 (q, $J_{CF} = 34$ Hz, 2C), 143.7 (d, $J_{CF} = 254$ Hz, 1C), 144.5 (d, $J_{CF} = 253$ Hz, 1C), 145.1 (d, $J_{CF} = 255$ Hz, 1C), 146.8 (d, $J_{CF} = 261$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −140.3–−140.2 (m, 2F), −139.1 (dd, $J = 9.3$, 22.8 Hz, 1F), −127.9–−127.6 (m, 1F), −75.2 (s, 6F), −64.2 (s, 6F). HRMS (EI) calcd for $C_{17}H_{14}O_4F_{16}S_2$: $[M]^+$ 639.9296. Found: 639.9307.

General Procedure for the Preparation of 4-Alkoxy-2,3,5,6-tetrafluorophenylbis(triflyl)methane (7). To a solution of NaH (0.48 g, 12 mmol, 60% oil suspension) in pyridine (15 mL) was added alcohol (12 mmol) at 0 °C. The resulting mixture was allowed to reach room temperature over a period of 1 h. After cooling to 0 °C, lithium pentafluorophenylbis(triflyl)methanide (1.8 g, 4 mmol) was added to the mixture. The resulting mixture was allowed to reach room temperature and stirred at the same temperature (PhOH, 70 °C) for 1 d before the reaction was quenched with water at 0 °C. The resultant mixture was neutralized with 1 M aqueous HCl and washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with ether twice. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Furthermore, excess alcohol in the residue was removed by vacuum sublimation to give **7**. If the product was solid, it was recrystallized from $CHCl_3$–toluene.

4-Hexyloxy-2,3,5,6-tetrafluorophenylbis(triflyl)methane (7a): See Ref. 14c.

4-[2-(2-Methoxyethoxy)ethoxy]-2,3,5,6-tetrafluorophenylbis(triflyl)methane (7b): IR (neat) 3501, 2944, 1501, 1348, 1195, 1119, 1063, 1020, 982, 759, 611 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.29 (s, 3H), 3.43 (t, $J = 4.5$ Hz, 2H), 3.59 (t, $J = 4.5$ Hz, 2H), 3.80 (t, $J = 4.2$ Hz, 2H), 4.52 (brs, 2H), 6.13 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 58.9, 70.2, 70.8, 70.9, 71.8, 74.4, 94.2 (t, $J_{CF} = 15$ Hz, 1C), 119.2 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 140.6 (d, $J_{CF} = 248$ Hz, 1C), 141.3 (d, $J_{CF} = 250$ Hz, 1C), 142.6–142.8 (m, 1C), 145.5 (d, $J_{CF} = 248$ Hz, 1C), 147.0 (d, $J_{CF} = 257$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.1 (dd, $J = 6.0$, 21.3 Hz, 1F), −153.2 (dd, $J = 6.0$, 21.3 Hz, 1F), −142.6–−124.7 (m, 1F), −130.5 (dt, $J = 9.0$, 21.3 Hz, 1F), −75.0 (s, 6F, $2CF_3$). HRMS (FAB) calcd for $C_{14}H_{12}F_{10}O_7S_2$: $[M + H]^+$ 546.9943. Found: 546.9941.

4-Phenoxy-2,3,5,6-tetrafluorophenylbis(triflyl)methane (7c): IR (KBr) 3046, 2942, 1650, 1592, 1499, 1347, 1214, 1200, 1118, 1023, 1001, 978, 754, 641, 614, 579 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.25 (s, 1H), 7.03 (d, $J = 8.1$ Hz, 2H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.8, 97.4 (t, $J_{CF} = 18$ Hz, 1C), 116.2 (2C), 119.3 (q, $J_{CF} = 329$ Hz, 2C, $2CF_3$), 124.9, 130.1 (2C), 139.0 (t, $J_{CF} = 11$ Hz, 1C), 141.4 (d, $J_{CF} = 256$ Hz, 1C), 142.2 (d, $J_{CF} = 255$ Hz, 1C), 145.6 (d, $J_{CF} = 260$ Hz, 1C), 147.3 (d, $J_{CF} = 260$ Hz, 1C),

156.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ −150.6 (dd, J = 9.0, 21.4 Hz, 1F), −149.3 (dd, J = 9.2, 21.4 Hz, 1F), −141.1–−141.0 (m, 1F), −128.5 (dt, J = 9.2, 21.4 Hz, 1F), −74.8 (s, 6F, $2CF_3$). HRMS (FAB) calcd for $C_{15}H_6F_{10}O_5S_2$: $[M + 2Na - H]^+$ 564.9214. Found: 564.9219.

4-Trifluoroethoxy-2,3,5,6-tetrafluorophenylbis(triflyl)methane (7d): See Ref. 14c.

Procedure for the Preparation of 4-Hydroxy-2,3,5,6-tetrafluorophenylbis(triflyl)methane (8). Pentafluorophenylbis(triflyl)methane (0.22 g, 0.5 mmol) and potassium hydroxide (0.14 g, 2.5 mmol) were dissolved in *t*-BuOH (1.0 mL). The reaction mixture was stirred for 3 h at reflux condition. After the mixture was cooled to room temperature, it was diluted with H_2O and acidified with 4 M HCl. The resultant mixture was extracted with Et_2O. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Impurities were removed by vacuum sublimation (10 Pa, 50 °C) to give **8** in 66% yield. IR (KBr) 3464, 2912, 1530, 1510, 1216, 1109, 999, 957, 647, 624, 511 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (s, 1H). ^{13}C NMR (125 MHz, CD_3OD) δ 53.7–53.9 (m, 1C), 99.1 (t, J_{CF} = 19.1 Hz, 1C), 119.7 (q, J_{CF} = 325 Hz, 2C, $2CF_3$), 135.8–136.2 (m, 1C), 136.3 (d, J_{CF} = 227 Hz, 2C), 146.8 (d, J_{CF} = 239 Hz, 2C). ^{19}F NMR (282 MHz, CD_3OD) δ −167.1 (dd, J = 6.1, 21.3 Hz, 2F), −139.6–−139.5 (m, 2F), −81.8 (s, 6F). HRMS (FAB) calcd for $C_9H_2F_{10}O_5S_2$: $[M + 2Na - H]^+$ 488.8901. Found: 488.8885.

General Procedure for the Preparation of Dibasic Acid 11. To a solution of NaH (42 mg, 1.05 mmol, 60% oil suspension) in pyridine (1.5 mL) was added diol (0.5 mmol) at 0 °C. The resulting mixture was allowed to reach room temperature over a period of 2 h. Lithium pentafluorophenylbis(triflyl)methanide (0.9 g, 2 mmol) was added to the mixture. The resulting mixture was heated at 70 °C and stirred at the same temperature for 1 day before the reaction was quenched with water at 0 °C. The resultant mixture was neutralized with 1 M aqueous HCl and washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with ether twice. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Furthermore, any excess pentafluorophenylbis(triflyl)methane that was contained in the residue was removed by vacuum sublimation (10 Pa, 100 °C) to give **11**. If the product was solid, it was recrystallized from $CHCl_3$–toluene.

1,3-Bis[1-bis(triflyl)methyl-2,3,5,6-tetrafluorophenoxy]propane (11a): IR ($CHCl_3$) 1651, 1505, 1401, 1217, 1116, 1039, 1013, 980, 761 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (quintet, J = 5.9 Hz, 2H), 4.67 (t, J = 5.9 Hz, 4H), 6.19 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.4, 70.8 (2C), 70.9 (t, J_{CF} = 4.1 Hz, 2C), 94.8 (t, J_{CF} = 16.1 Hz, 2C), 119.2 (q, J_{CF} = 328 Hz, 4C, $4CF_3$), 140.4 (d, J_{CF} = 250 Hz, 2C), 141.2 (d, J_{CF} = 250 Hz, 2C), 142.0–142.2 (m, 2C), 145.5 (d, J_{CF} = 252 Hz, 2C), 147.2 (d, J_{CF} = 245 Hz, 2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.7 (dd, J = 6.2, 21.4 Hz, 2F), −153.5 (dd, J = 6.2, 21.4 Hz, 2F), −142.0–−141.9 (m, 2F), −129.5 (dt, J = 9.0, 21.4 Hz, 2F), −74.9 (s, 12F, $4CF_3$). HRMS(FAB) calcd for $C_{21}H_8F_{20}O_{10}S_4$: $[M + 3Na - 2H]^+$ 994.8218. Found: 994.8214.

1,4-Bis[1-bis(triflyl)methyl-2,3,5,6-tetrafluorophenoxy]butane (11b): IR (KBr) 2939, 1651, 1506, 1407, 1226, 1114, 1022, 981, 618, 579, 499 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.08 (quintet, J = 3.0 Hz, 4H), 4.54 (br, 4H), 6.19 (s, 1H), 6.20 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 25.8, 29.2, 39.8, 70.8 (2C), 94.7 (t, J_{CF} = 15.9 Hz, 2C), 119.2 (q, J_{CF} = 328 Hz, 4C, $4CF_3$), 140.4 (d, J_{CF} = 250 Hz, 2C), 141.2 (d, J_{CF} = 250 Hz, 2C), 142.5–142.7 (m, 2C), 145.5 (d, J_{CF} = 249 Hz, 2C), 147.1 (d, J_{CF} = 259 Hz, 2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.7 (dd, J = 6.1, 21.3 Hz, 2F), −153.5 (dd, J = 6.1, 21.3 Hz, 2F), −142.2–−142.1 (m, 2F), −129.7 (dt, J = 9.3, 21.2 Hz, 2F), −74.8 (s, 12F, $4CF_3$). HRMS(FAB) calcd for $C_{22}H_{10}F_{20}O_{10}S_4$: $[M + 3Na - 2H]^+$ 1008.8374. Found: 1008.8391.

4,4-Bis[4-bis(triflyl)methyl-2,3,5,6-tetrafluorophenoxymethyl]-1-cyclohexene (11c): IR (KBr) 2939, 1649, 1503, 1406, 1109, 1023, 616, 579, 499 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (t, J = 6.3 Hz, 2H), 2.16 (br, 4H), 4.42 (d, J = 9.3 Hz, 2H), 4.47 (d, J = 9.3 Hz, 2H), 5.68 (d, J = 10.0 Hz, 1H), 5.79 (d, J = 10.0 Hz, 1H), 6.187 (s, 1H), 6.193 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 25.1, 29.0, 38.6, 70.8 (2C), 76.8 (t, J_{CF} = 5.0 Hz, 2C), 94.8 (t, J_{CF} = 16.0 Hz, 2C), 119.2 (q, J_{CF} = 328 Hz, 4C, $4CF_3$), 123.4, 126.6, 140.5 (d, J_{CF} = 250 Hz, 2C), 141.3 (d, J_{CF} = 250 Hz, 2C), 142.3–142.6 (m, 2C), 145.5 (d, J_{CF} = 250 Hz, 2C), 147.2 (d, J_{CF} = 258 Hz, 2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.7 (dd, J = 6.2, 21.3 Hz, 2F), −153.9 (dd, J = 6.2, 21.3 Hz, 2F), −142.1–−142.0 (m, 2F), −129.7 (dt, J = 9.3, 21.3 Hz, 2F), −74.9 (s, 12F, $4CF_3$). HRMS (FAB) calcd for $C_{26}H_{14}F_{20}O_{10}S_4$: $[M + 3Na - 2H]^+$ 1060.8687. Found: 1060.8691.

1,1-Bis[4-bis(triflyl)methyl-2,3,5,6-tetrafluorophenoxymethyl]cyclohexane (11d): IR (KBr) 2938, 1650, 1505, 1407, 1347, 1224, 1112, 1022, 983, 615 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55–1.63 (m, 10H), 4.45 (s, 4H), 6.182 (s, 1H), 6.189 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0 (2C), 25.8, 29.2 (2C), 39.8, 70.8 (2C), 76.8 (t, J_{CF} = 5.0 Hz, 2C), 94.8 (t, J_{CF} = 16.0 Hz, 2C), 119.2 (q, J_{CF} = 328 Hz, 4C, $4CF_3$), 140.4 (d, J_{CF} = 250 Hz, 2C), 141.3 (d, J_{CF} = 250 Hz, 2C), 142.4–142.7 (m, 2C), 145.5 (d, J_{CF} = 251 Hz, 2C), 147.5 (d, J_{CF} = 246 Hz, 2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.5 (dd, J = 6.1, 21.3 Hz, 2F), −153.2 (dd, J = 6.1, 21.3 Hz, 2F), −142.1–−142.0 (m, 2F), −129.6 (dt, J = 9.0, 22.5 Hz, 2F), −74.8 (s, 12F, $4CF_3$). HRMS (FAB) calcd for $C_{26}H_{16}F_{20}O_{10}S_4$: $[M + 3Na - 2H]^+$ 1062.8844. Found: 1062.8868.

General Procedure for Preparation of Dibasic Acid 13. To a solution of dibromoarene (3.0 mmol) in THF (12 mL) was added *t*-BuLi (13.2 mmol, 1.48 M pentane solution) at −78 °C. The resulting mixture was stirred under the following conditions: **13a** (−78 °C, 1 h), **13b** (−78 °C, 1 h), and **13c** (−78 °C, 1 h to −20 °C, 0.5 h). Lithium pentafluorophenylbis(triflyl)methanide (3.39 g, 7.5 mmol) was added to the mixture. The resulting mixture was stirred under the following conditions: **13a** (45 °C, 19 h), **13b** (50 °C, 42 h), and **13c** (50 °C, 19 h) before the reaction was quenched with water. The resulting mixture was washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with Et_2O. The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. Furthermore, any excess pentafluorophenylbis(triflyl)methane that was contained in the residue was removed by vacuum sublimation (10 Pa, 120 °C). The crude product was purified by column chromatography on silica gel (AcOEt:hexane = 1:1 to 100:0 and then AcOEt:AcOH = 10:1) to give dibasic acid as a solid. Finally, the solid was reacidified with 4 M aqueous HCl.

4,5-Bis[4-bis(triflyl)methyl-2,3,5,6-tetrafluorophenyl]-2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (13a): IR(KBr) 1480, 1350, 1261, 1195, 1099, 1023, 800, 612 cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD) δ 1.35 (s, 18H), 1.74 (s, 6H), 7.09 (br, 2H), 7.65 (d, J = 2.4 Hz, 2H). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 18H), 1.72 (s, 3H), 1.74 (s, 3H), 6.40 (s, 1H), 6.51 (s, 1H), 7.14 (br, 2H), 7.63 (d, J = 1.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$)

δ 31.3 (6C), 31.5, 31.7, 33.1, 34.6, 34.9, 71.3, 72.1, 100.9 (m, 2C), 112.7, 112.9, 119.2 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$), 119.5 (q, $J_{CF} = 329$ Hz, 2C, $2CF_3$), 124.2 (m, 2C), 125.1, 125.5, 127.7, 128.3, 130.5, 131.2, 144.0 (d, $J_{CF} = 251$ Hz, 2C), 144.7 (d, $J_{CF} = 248$ Hz, 4C), 145.6, 146.1, 146.3, 146.4 (t, $J_{CF} = 263$ Hz, 2C), 146.5. ^{19}F NMR (282 MHz, CD_3OD) δ −143.6 (s, 4F), −135.5 (s, 4F), −80.4 (s, 6F, $2CF_3$), −80.2 (s, 6F, $2CF_3$). ^{19}F NMR (282 MHz, $CDCl_3$) δ −141.5 (br, 2F), −137.0 (m, 1F), −136.4–−136.1 (m, 2F), −135.2 (m, 1F), −129.0 (m, 2F), −75.9 (s, 6F), −72.9 (s, 6F). HRMS (FAB) calcd for $C_{41}H_{30}F_{20}O_9S_4$: $[M + 3Na - 2H]^+$ 1240.9990. Found: 1240.9999.

4,6-Bis[4-bis(triflyl)methyl-2,3,5,6-tetrafluorophenyl]dibenzofuran (13b): IR (KBr) 2951, 1482, 1393, 1322, 1178, 1102, 976, 746, 626 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (s, 1H), 6.33 (s, 1H), 7.60 (m, 4H), 8.22 (dd, $J = 2.1$, 6.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.7 (2C), 101.8 (t, $J_{CF} = 14.6$ Hz, 2C), 110.4 (2C), 119.2 (q, $J_{CF} = 329$ Hz, 4C, $4CF_3$), 121.4 (2C), 123.5 (2C), 123.7 (2C), 124.7 (2C), 129.4 (2C), 144.1 (d, $J_{CF} = 250$ Hz, 2C), 144.9 (d, $J_{CF} = 249$ Hz, 4C), 146.6 (t, $J_{CF} = 244$ Hz, 2C), 153.1 (2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −142.2 (br, 2F), −136.7 (m, 2F), −136.4 (m, 2F), −129.6 (br, 2F), −75.4 (s, 12F, $4CF_3$). HRMS (FAB) calcd for $C_{20}H_8F_{20}O_9S_4$: $[M + 3Na - 2H]^+$ 1086.8268. Found: 1086.8252.

1,8-Bis[4-bis(triflyl)-2,3,5,6-tetrafluorophenyl]biphenylene (13c): IR (KBr) 2932, 1492, 1403, 1352, 1318, 1199, 1117, 972, 613 cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD) δ 6.74 (d, $J = 8.1$ Hz, 2H), 6.81 (d, $J = 6.9$ Hz, 2H), 6.94 (dd, $J = 6.9$, 8.1 Hz, 2H). ^{19}F NMR (282 MHz, CD_3OD) δ −145.7 (m, 4F), −134.9 (br, 4F), −80.9 (s, 12F, $4CF_3$). HRMS (FAB) calcd for $C_{30}H_8F_{20}O_8S_4$: $[M + 3Na - 2H]^+$ 1070.8319. Found: 1070.8339.

Procedure for the Preparation of *N*,*N*′-Octamethylenedipyridinium Dibenzofuran-4,6-diylbis(2,3,5,6-tetrafluoro-1,4-phenylene)bis[bis(triflyl)methanide] (15). To a solution of *N*,*N*′-octamethylenedipyridinium dibromide (129 mg, 0.30 mmol) in H_2O–THF 2:1 (2 mL:1 mL), dilithium dibenzofuran-4,6-diylbis(2,3,5,6-tetrafluoro-1,4-phenylene)bis[bis(triflyl)methanide] (129 mg, 0.30 mmol) was added at room temperature and the mixture was stirred under reflux condition for 1 d. After the mixture was cooled to ambient temperature, the solvent was evaporated. The crude product was washed with H_2O and EtOAc several times and dried under reduced precessure (80 °C, 0.7 kPa, overnight) to give **15** in 84% yield. IR (KBr) 3093, 2936, 1636, 1478, 1351, 1172, 1020, 973, 610 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.27 (m, 8H), 1.90 (m, 4H), 4.57 (t, $J = 7.2$ Hz, 4H), 7.62 (t, $J = 7.8$ Hz, 2H), 7.74 (d, $J = 6.9$ Hz, 2H), 8.16 (t, $J = 6.9$ Hz, 4H), 8.44 (d, $J = 6.3$ Hz, 2H), 8.61 (t, $J = 6.3$ Hz, 2H), 9.06 (d, $J = 5.4$ Hz, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 25.5 (2C), 28.4 (2C), 30.8 (2C), 55.5 (2C), 60.9 (2C), 111.2 (2C), 112.4 (2C), 115.9 (2C), 120.9 (q, $J_{CF} = 325$ Hz, 4C, $4CF_3$), 123.8 (2C), 124.1 (2C), 124.4 (2C), 128.2 (4C), 130.6 (2C), 143.2 (d, $J_{CF} = 246$ Hz, 4C), 144.9 (4C), 145.7 (2C), 147.6 (d, $J_{CF} = 244$ Hz, 4C), 152.9 (2C). ^{19}F NMR (282 MHz, DMSO-d_6) δ −145.0 (br, 4F), −137.8 (br, 4F), −82.1 (s, 12F, $4CF_3$).

X-ray Crystallographic Analysis of 15: Crystal data: $C_{50.43}H_{35}F_{20.43}N_3O_{10}S_4$, Mw = 1359.18, crystal dimensions $0.50 \times 0.40 \times 0.20$ mm^3, orthorhombic, space group *Pbca* (#61), $a = 14.6941(17)$, $b = 22.460(2)$, $c = 34.073(4)$ Å, $V = 11245(2)$ Å^3, $Z = 8$, $D_c = 1.606$ g/cm^3, $\mu = 0.296$ mm^{-1}, $T = 173$ K. X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, Mo Kα radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded using Fourier techniques. 15035 reflections were independent and unique, and 9194 with $I > 2\sigma(I)$ ($2\theta_{max} = 29.16°$) were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. $R = 0.0775$ and $Rw = 0.2184$.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC-261827 and 261828 for compound **5** and **15**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Procedure for the Esterification of 1-Octanol with CF_3SOCl.[17] CF_3SO_2Na (2.5 g, 16 mmol) and mesitylenesulfonyl chloride (3.3 g, 15 mmol) were dissolved in MeCN (20 mL) at 25 °C. After being stirred for 1 h, the mixture was cooled to 0 °C and a solution of 1-octanol (1.6 mL, 10 mmol) and pyridine (1.2 mL, 15 mmol) in MeCN (5 mL) was added dropwise. This mixture was allowed to warm to room temperature, stirred for 12 h, diluted with Et_2O (4 vols) and then washed 3 times with H_2O and once with saturated aq NaCl. The ether was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using a linear AcOEt gradient in hexane to give **17** as a colorless oil. IR (neat) 2964, 2929, 2859, 1468, 1381, 1201, 1133, 940, 892, 751 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, $J = 6.8$ Hz, 3H), 1.29–1.33 (m, 10H), 1.76 (quintet, $J = 6.7$ Hz, 2H), 4.11–4.18 (m, 1H), 4.36 (dt, $J = 6.6$, 9.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 25.3, 28.9, 29.0, 29.7, 31.7, 69.2, 122.8 (q, $J_{CF} = 337$ Hz, 1C, CF_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ −79.3 (s, 3F, CF_3).

Procedure for the Preparation Octyl Trifluoromethyl Sulfone (18).[17] Compound **17** (2.1 g, 8.7 mmol) was dissolved in HMPA (8 mL). The reaction mixture was heated under an Ar atmosphere at 145 °C for 12 h. After the mixture was cooled, it was diluted with Et_2O (20 mL) and washed with H_2O and saturated $NaHCO_3$. The organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using a linear EtOAc gradient in hexane to give a brown oil. The oil was then subjected to vacuum sublimation (15 Pa, 80 °C) to give **18** as a colorless oil. IR (neat) 2957, 2930, 2860, 1468, 1366, 1198, 1123, 617 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, $J = 6.9$ Hz, 3H), 1.21–1.27 (m, 8H), 1.41 (quintet, $J = 7.3$ Hz, 2H), 1.87 (quintet, $J = 7.8$ Hz, 2H), 3.14 (dd, $J = 8.1$, 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 20.6, 22.5, 28.3, 28.7 (2C), 31.6, 49.5, 119.4 (q, $J_{CF} = 325$ Hz, 1C, CF_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ −79.0 (s, 3F, CF_3).

Procedure for the Preparation 1-Bis(triflyl)octane (19). To a solution of **18** (0.49 mmol) in dry Et_2O (1 mL) was added *t*-BuLi (0.39 mL, 0.54 mmol, 1.41 M solution in hexane) dropwise at −78 °C, and the resulting mixture was stirred for 20 min. Triflic anhydride (46 µL, 0.27 mmol) was then added, and the resulting mixture was allowed to warm to room temperature over a period of 3 h. After the reaction mixture was cooled to −78 °C, *t*-BuLi (0.39 mL, 0.54 mmol, 1.41 M in hexane) was added dropwise, and the resulting mixture was stirred for 20 min. Triflic anhydride (0.27 mmol) was then added, and the resulting mixture was allowed to room temperature over a period of 1 h before the reaction was quenched with water. The resultant mixture was neutralized and washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with Et_2O twice. The organic lay-

ers were dried over magnesium sulfate, filtered and concentrated under reduced pressure to give **19**. IR (neat) 2964, 2933, 2860, 1468, 1395, 1212, 1117, 693, 591 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, $J = 6.8$ Hz, 3H), 1.20–1.26 (m, 8H), 1.63 (quintet, $J = 7.7$ Hz, 2H), 2.35 (dd, $J = 6.3$, 15.3 Hz, 2H), 4.74 (t, $J = 5.6$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.5, 25.4, 27.2, 28.4, 28.9, 31.5, 77.5, 119.3 (q, $J_{CF} = 328$ Hz, 2C, $2CF_3$). ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.1 (s, 6F, $2CF_3$). HRMS (FAB) calcd for $C_{10}H_5F_9O_2S$: $[M + H]^+$ 379.0472. Found: 379.0489.

We thank Central Glass Co., Ltd., for a generous gift of CF_3SO_2Na. A.H. also acknowledges a JSPS Fellowship for Japanese Junior Scientists. Financial support for this project was provided by SORST, Japan Science and Technology Agency (JST), MEXT.KAKENHI (No. 16033228), the Shorai Foundation for Science and Technology, the Ogasawara Foundation for the Promotion of Science & Engineering, and the Iketani Science and Technology Foundation. We also acknowledge Dr. Manabu Hatano for the single-crystal X-ray analysis.

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