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Journal Name

ARTICLE

Mild Synthesis of Triarylsulfonium Salts with Arynes

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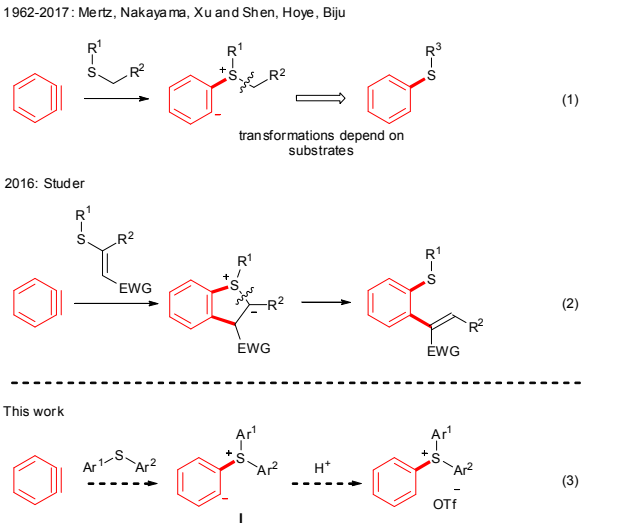
Reactions between arynes and alkyl sulfides have been extensively studied over the past few decades. These reactions commonly end with a dealkylation process and thus deliver thioethers as final products. In contrast, the transformation described furnishes valuable triarylsulfonium salts, in lieu of thioethers, from arynes and diarylsulfides. The reaction features mild conditions and a broad substrate scope. A suite of functional groups such as ketones, esters, nitriles, aryl ethers and aryl halides are tolerated, which can be issues faced by traditional synthetic methods. The practicality of the reaction and its extension to the synthesis of triphenyl selenonium salt are also exhibited herein.

Introduction

Arynes are widely used as highly electrophilic aryl synthons in the synthesis of natural products and bioactive compounds.[1,2] Owing to the bent triple bond, distorted aromatic ring and low-lying LUMO,[3] arynes can directly arylate amines,[4] phosphines,[5] sulfides,[6] carbonyls[7] and various O-nucleophiles[8]. Among them, sulfur compounds recognized as soft nucleophile properly cooperate with the soft nature of arynes.[9] As a result, significant efforts from synthetic community have been made on incorporation of thioethers into aryne chemistry.[6a-i] The reported reactions essentially consist of two common steps including the formation of arylsulfonium salts and subsequent dealkylation process (Scheme 1, eq 1 and 2). The sulfonium intermediates can be formed by either nucleophilic addition of alkyl sulfides to benzyne[6a-g] or [3+2] cycloaddtion of vinyl sulfides to benzyne[6i]. Eventually these transformations were terminated by S-dealkylation of sulfoniums to deliver thioethers as final products.

Triarylsulfonium salts are well known for their capability of releasing proton under UV conditions and thus they have been widely used as superior photo initiators in polymerization reactions[10] and lithographic process[11]. They also serve as useful aryl sources in various organic transformations.[12] Therefore, efficient and practical methods to access these compounds are highly desired.[13] Inspired by the reported nucleophilicity[6] of sulfides toward arynes, alongside our continuing interests in the synthesis of triarylsulfonium salts,[14] we envisioned that a simple treatment of benzyne with diarylsulfides might directly produce a betaine intermediate **I** (Scheme 1, eq 3). Subsequent protonation of phenyl anion of intermediate **I** would accomplish the desired triarylsulfonium salt.[15] Since the stability of triarylsulfoniums under similar conditions has been well established,[14a] it can be expected that dearylation of triarylsulfoniums would not occur even though its analogy, the dealkylation of alkyl sulfoniums has been encountered rather frequently in this area (Scheme 1, eq 1 and 2).[6]



Scheme 1 Reactions of benzyne with thioethers

Results and discussion

To test the hypothesis, we selected Kobayashi aryne precursor **1a**[16] and diphenyl sulfide **2a** as model substrates to optimize reaction conditions (Table 1). Pleasingly, the desired triphenylsulfonium salt **3aa** was obtained in the first trial albeit

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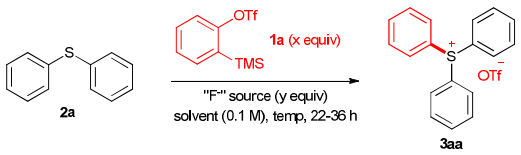
with a relatively low yield (entry 1). "F⁻" sources (KF and TBAT) other than CsF proved to be ineffective for the reaction (entries 2 and 3). In view of the weak nucleophility of diphenyl sulfide, we raised the reaction temperature to 50 ℃, but no improvement was observed (entry 4). Further attempts by lowering the reaction temperature (entry 5) or switching to other solvents (entry 6, for solvent screen, see supporting information) did not enhance the selectivity of the reaction. Notably the deterioration of benzyne precursor was observed during the optimization study (entries 1-6). To compensate for its consumption, excess of **1a** was used in further optimizations. Indeed, the chemical yield of **3aa** was significantly improved when 2.0 or 3.0 equiv of **1a** was employed (entries 7 and 8). Eventually we found that delivering CsF to the reaction mixture in three portions over time afforded **3aa** in the best yield (entry 9).

Table 1 Optimization of reaction conditions[a]

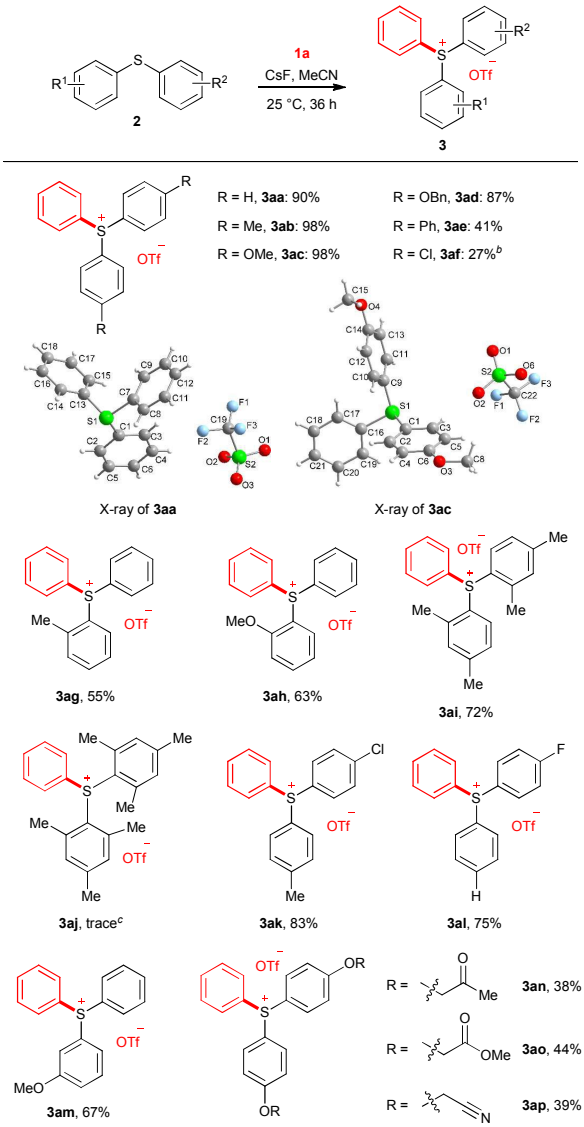


entry	"F⁻" source /solvent	temp (℃)	x/y	yield (%)[b]
1	CsF/MeCN	25	1.0/2.0	33[c]
2	KF/18-crown-6/THF	25	1.0/2.0	trace[c]
3	TBAT/THF	25	1.0/2.0	trace[c]
4	CsF/MeCN	50	1.0/2.0	21[c]
5	CsF/MeCN	0	1.0/2.0	34[c,d]
6	CsF/MeCN/toluene[e]	25	1.0/2.0	28[c]
7	CsF/MeCN	25	2.0/2.0	54
8	CsF/MeCN	25	3.0/3.0	67
9	CsF/MeCN	25	3.0/3.0	92(90)[d,f,g]

[a]Unless otherwise noted, reactions were performed with **1a** (x equiv), diphenyl sulfide **2a** (0.2 mmol), and "F" source (y equiv) for 22 h. [b]NMR yield (mesitylene as the internal standard); [c]**1a** decomposed after reaction; [d]Reaction time is 36 h. [e]MeCN/toluene=3/1. [f]Isolated yield in parenthesis. [g]CsF was added in three portions. For details, see supporting information.

With suitable reaction conditions in hand, we first evaluated the scope of diarylsulfides as shown in Table 2. A wide range of diarylsulfides were successfully phenylated by benzyne to produce the desired triarylsulfonium salts **3** in typically good to excellent yield. Electron-donating *para*-substituents (-Me, -OMe, -OBn) are beneficial for the reaction yielding **3ab**, **3ac**, **3ad** in excellent yields. In contrast, electron withdrawing groups (-Ph, -Cl) have detrimental influence resulting in relative low yields of triarylsulfoniums (**3ea** and **3ef**). The dramatically decreased reactivity might be ascribed to the weaker nucleophilicity of electron poor diarylsulfides toward benzyne. Sterically hindered substrates with *ortho*-substituents (**2g**-**2i**) also proved to be suitable to the reaction and produced synthetic useful yields. However more hindered substrate, the fully *ortho*-substituted diarylsulfide **2j** is inert to the reaction conditions. Mono-halogenated diarylsulfides (**2k** and **2l**) exhibited much better reactivity than the bi-halogenated sulfide **2f**.

Table 2 Scope of diaryl sulfide[a]



[a]All the reactions were performed in 0.3 mmol scale under optimum conditions. [b]70% of sulfide **2f** was recovered. [c]85% of sulfide **2j** was recovered.

Notably, an array of functional groups including a ketone (**2n**), an ester (**2o**), a nitrile (**2p**), aryl ethers (**2c**, **2d**, **2h** and **2m**) and aryl halides (**2k** and **2l**) are tolerated in the reaction. In view of limitations of conventional methods[13] to prepare triarylsulfonium salts, the reaction proceeding with such functional group compatibility is particularly noteworthy.

Interestingly, a cyclic ketone sulfide **2q** dually capatured one benzene with its nucleophilic "S" atom and electronphilic carbonyl group.[17] As a consequence, a novel axial symmetry triarylsulfonium **3aq** was achieved in good yield (78%). According to our hypothesis (eq 3, Scheme 1), the formation of **3aq** may involve S-phenylation of diarylsulfide **2q**, subsequent

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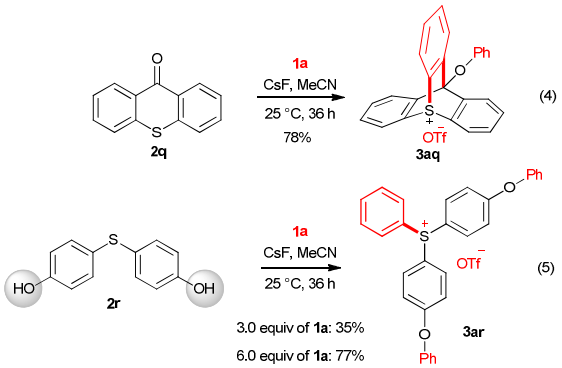
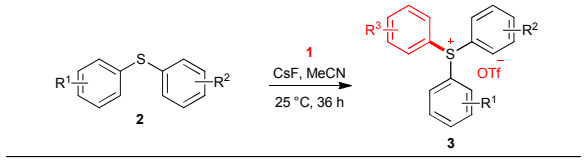
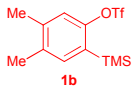
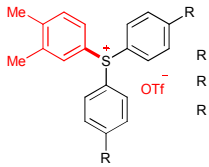
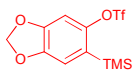
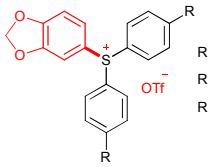
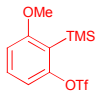
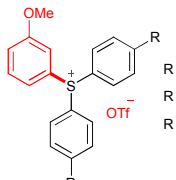
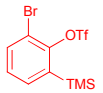
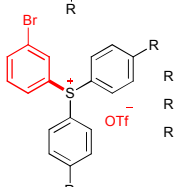
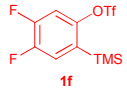
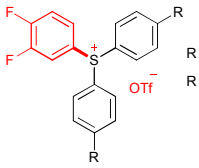


Table 3 Reactions of diarylsulfides with benzynes[a]



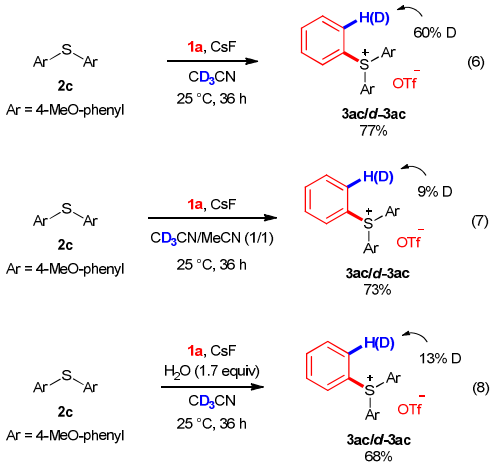
aryne precursor 1	product 3
	 R = H, **3ba**: 63%; R = Me, **3bb**: 71%; R = OMe, **3bc**: 81%
	 R = H, **3ca**: 61%; R = Me, **3cb**: 74%; R = OMe, **3cc**: 78%
	 R = H, **3da**: 59%; R = Me, **3db**: 96%; R = OMe, **3dc**: 94%
	 R = H, **3ea**: 67%; R = Me, **3eb**: 86%; R = OMe, **3ec**: 94%
	 R = H, **3fa**: trace[b]; R = Me, **3fb**: 43%

[a]All the reactions were performed in 0.3 mmol scale under optimum conditions. [b]84% of sulfide **2a** was recovered.

nucleophilic addition of phenyl anion to carbonyl of ketone and O-phenylation of tertiary alcohol (eq 4). While sulfide **2r** bearing two phenol groups was submitted to the reaction, the S- and O-arylation of **2r** occurred in one batch. Three aryl moieties were all anchored on **2r** to assemble a phenyloxy sulfonium salt **3ar** (eq 5).[4c,8a] Although the chemical yield was relative low (35%) from the optimum conditions, it could be significantly enhanced to 77% by increasing the use of aryne precusor **1a**.

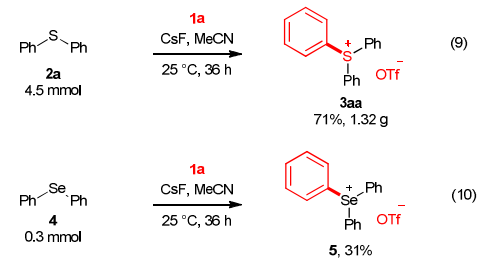
Next we evaluated the reaction using various aryne precursors and diarylsulfides (Table 3). To our delight, regardless of the substituents, aryne precursors **1b**-**1e** afforded triarylsulfonium salts **3** in synthetic useful yields although slightly lower than the prototype **1a**. In contrast, difluorinated benzyne from **1f** exhibited less reactivity with sulfide **2a** in which no desired **3fa** was attained. However, electron rich sulfide **2b** could still capture the electron poor benzyne to furnish **3fb** in a respectable yield (43%).

Scheme 2 Deuterium-labeling experiments



To gain insight into the reaction process, labeling experiments were conducted as shown in Scheme 2. The reaction using CD_3CN as solvent afforded a mixture of **3ac**/***d*-3ac** in a ratio of 40/60 (eq 6). The formation of *ortho*-deuterated sulfonium salt ***d*-3ac** is consistent with our original hypothesis (Scheme 1, eq 3).

Meanwhile we found the formation of ***d*-3ac** can be dramatically inhibited by introducing other proton sources like MeCN and H_2O (eq 7 and 8). This result indicates that the unlabeled-**3ac** shown in eq 5 might be attributed to the protonation by small amount of MeCN (CD_3CN, Isotopic Enrichment, 99.8%) or trace amount of water.



The practicability of the reaction was then examined by a gram-scale reaction as shown in eq 9. Under optimum

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conditions, 4.5 mmol of diphenylsulfide **2a** was efficiently converted to triphenylsulfonium salt **3aa** in a good yield (71%). Triggered by the obtained results, we became curious whether the reaction could be extended to the synthesis of triarylselenonium salts (eq 10). Delightfully, diphenylselane **4** indeed incorporated with benzyne to furnish the expected triphenylselenonium **5**, albeit in a relative low yield (31%).

Conclusions

In summary, we have developed an efficient and practical synthesis of triarylsulfonium salts using diarylsulfides and arynes. The reaction proceeds under mild conditions providing a wide range of triarylsulfonium salts in good yields. Remarkably, an array of functional groups including ketones, esters, nitriles, aryl ethers and aryl halides were tolerated in the reaction which can be challenges faced by conventional approaches. In addition, the reaction proceeding in a gram-scale with high efficiency demonstrated its practicality. However, excess amount of aryne precursors is required to maintain the chemical yield in a satisfactory level. Further studies aiming to reduce the use of aryne precursors and application of the method to prepare new photo initiators are currently under way.

Experimental section

General Information

Unless otherwise indicated, all glassware was oven dried by a heat gun before use and all reactions were performed under an atmosphere of Nitrogen. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers. Melting points reported here were measured using a melting point instrument and are uncorrected. Neat infrared spectra were recorded using a NEXUS670 FT-IR spectrometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a 400 or 600 MHz NMR. High-resolution mass spectroscopy (HRMS) analysis was performed by a TOF MS instrument using an ESI source. The products were purified by column chromatography using silica gel (160-200 mesh).

General procedure for the reaction between aryne precursor 1 and diarylsulfide 2.

To a flame-dried reaction tube (25 mL) was added CsF (45.5 mg, 0.3 mmol, 1.0 equiv) under nitrogen atmosphere. Then MeCN (3 mL), diarylsulfide **2** (0.3 mmol,) and aryne precursor **1** (0.9 mmol) were sequentially added to the reaction tube. After stirring under 25 ℃ for the first 12 h, another portion of CsF (1.0 equiv) was added to the mixture. It was then stirred for the second 12 h and the last portion of CsF (1.0 equiv) was added to the mixture. After stirring for the last 12 h, the mixture was filtrated through a short plug of silica gel, concentrated and purified by flash column chromatography on silica gel to afford the desired product.

triphenylsulfonium trifluoromethanesulfonate (3aa). White solid, mp: 135-136 ℃, 111.2 mg, 90% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$: δ 7.70 – 7.66 (m, 3H), 7.65 – 7.55 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 134.4, 131.3, 130.7, 123.8, 120.5 (q, *J* = 323.1 Hz, TfO^-). ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.0. IR (neat): 3089, 3062, 1474, 1447, 1258, 1223, 1148, 1066, 1030, 996, 840, 752, 681, 636. HRMS: calculated for $C_{18}H_{15}S^+([M\text{-}TfO^-]^+)$: 263.0895; found: 263.0883. The **3aa** is a known compound[13e,18,19].

phenyldi-*p*-tolylsulfonium trifluoromethanesulfonate (3ab). Yellow solid, mp: 98-100 ℃, 129.5 mg, 98% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 – 7.68 (m, 1H), 7.67 – 7.59 (m, 4H), 7.55-7.52 (m, 4H), 7.46-7.44 (m, 4H), 2.41 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.1, 134.3, 132.2, 131.4, 130. 8, 130.5, 124.8, 120.8 (q, *J* = 323.1 Hz, TfO^-), 120.6, 21.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3060, 2925, 1591, 1448, 1259, 1145, 1072, 1029, 807, 748, 684, 634. HRMS: calculated for $C_{20}H_{19}S^+([M\text{-}TfO^-]^+)$: 291.1208; found: 291.1200.

bis(4-methoxyphenyl)(phenyl)sulfonium trifluoromethane sulfonate (3ac). Yellow solid, mp: 114-116 ℃, 138.9 mg, 98% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 –7.66 (m, 1H), 7.65 –7.62 (m, 6H), 7.58 – 7.55 (m, 2H), 7.17-7.14 (m, 4H), 3.86 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.5, 133.9, 133.1, 131.3, 129.9, 126.2, 120.9 (q, *J* = 324.7 Hz, TfO^-), 117.2, 113.9, 56.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3056, 2976, 2941, 1588, 1574, 1493, 1259, 1223, 1176, 1147, 1073, 1029, 827, 761, 688, 635. HRMS: calculated for $C_{20}H_{19}O_2S^+([M\text{-}TfO^-]^+)$: 323.1106; found: 323.1103. The 3ac is a known compound[20].

bis(4-(benzyloxy)phenyl)(phenyl)sulfonium trifluoro methanesulfonate (3ad). Yellow oil, 163.0 mg, 87% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.57 (m, 9H), 7.42 – 7.37 (m, 8H), 7.36 – 7.33 (m, 2H), 7.25-7.22 (m, 4H), 5.13 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.6, 135.2, 134.0, 133.2, 131.4, 130.1, 128.7, 128.5, 127.7, 126.3, 120.9 (q, *J* = 314.8 Hz, TfO^-), 118.0, 114.3, 70.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3098, 3064, 1587, 1492, 1252, 1175, 1149, 1028, 830, 743, 698, 635. HRMS: calculated for $C_{32}H_{27}O_2S^+([M\text{-}TfO^-]^+)$:475.1732; found: 475.1726.

di([1,1'-biphenyl]-4-yl)(phenyl)sulfonium trifluoromethane sulfonate (3ae). Yellow solid, mp: 117-118 ℃, 76.8 mg, 41% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 – 7.88 (m, 4H), 7.86 – 7.84 (m, 4H), 7.81 – 7.74 (m, 3H), 7.73– 7.70 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 4H), 7.50 – 7.42 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.7, 138.0, 134.5, 131.7, 131.6, 131.0, 130.0, 129.3, 127.4, 124.8, 122.5. Carbon of triflate anion cannot be found. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3065, 2952, 2916, 1593, 1478, 1446, 1253, 1150, 1028, 750, 682, 636. HRMS: calculated for $C_{30}H_{23}S^+([M\text{-}TfO^-]^+)$:415.1521; found: 415.1511.

bis(4-chlorophenyl)(phenyl)sulfonium trifluoromethane sulfonate (3af). Yellow oil, 39.0 mg, 27% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.77 (m, 7H), 7.72 – 7.68 (m, 2H), 7.67 – 7.63 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.0, 134.9, 132.6, 131.9 131.8, 131.0, 123.8, 122.4, 120.7 (q, *J* = 320.1 Hz, TfO^-). ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.2. IR (neat): 3088, 3009, 1568, 1475, 1397,

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1254, 1153, 1091, 1029, 824, 743, 683, 637. HRMS: calculated for $C_{18}H_{13}Cl_2S^+$([M-TfO$^-$]$^+$): 331.0115; found: 331.0105.

diphenyl(*o*-tolyl)sulfonium trifluoromethanesulfonate (3ag). Yellow solid, mp: 122-123 ℃, 70.4 mg, 55% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 – 7.74 (m, 2H), 7.72 – 7.67 (m, 4H), 7.67 – 7.63 (m, 4H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.05 (d, *J* = 9.0 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.6, 134.7, 134.5, 133.1, 131.7, 131.2, 129.8, 129.1, 123.1, 122.6, 120.7 (q, *J* = 322.4 Hz, TfO$^-$), 19.7. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3067, 2916, 1474, 1446, 1258, 1149, 1029, 754, 683, 635. HRMS: calculated for $C_{19}H_{17}S^+$([M-TfO$^-$]$^+$): 277.1051; found: 277.1043.

(2-methoxyphenyl)diphenylsulfonium trifluoromethane sulfonate (3ah). Yellow solid, mp: 120-122 ℃, 83.6 mg, 63% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 – 7.72 (m, 3H), 7.70 – 7.67 (m, 4H), 7.60 – 7.56 (m, 4H), 7.24 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.18 – 7.15 (m, 1H), 6.94 (dd, *J* = 8.1, 1.5 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 157.9, 137.0, 134.6, 131.6, 130.7, 130.5, 123.1, 122.8, 113.5, 110.7, 57.1. Carbon of triflate anion cannot be found. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3063, 2950, 2854, 1587, 1477, 1447, 1254, 1221, 1148, 1072, 1029, 753, 685, 635. HRMS: calculated for $C_{19}H_{17}OS^+$([M-TfO$^-$]$^+$): 293.1000; found: 293.0999.

bis(2,4-dimethylphenyl)(phenyl)sulfonium trifluoro methanesulfonate (3ai). Yellow solid, mp: 103-105 ℃, 101.2 mg, 72% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.70 (m, 3H), 7.62 – 7.60 (m, 2H), 7.32 (s, 2H), 7.27 – 7.25 (m, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 2.48 (s, 6H), 2.41 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.1, 140.4, 134.7, 133.9, 131.8, 131.2, 130.1, 129.9, 121.9, 120.8 (q, *J* = 322.4 Hz, TfO$^-$), 118.5, 21.4, 19.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3065, 2922, 1600, 1476, 1446, 1256, 1142, 1028, 809, 757, 688, 634. HRMS: calculated for $C_{22}H_{23}S^+$([M-TfO$^-$]$^+$): 319.1521; found: 319.1519.

(4-chlorophenyl)(phenyl)(*p*-tolyl)sulfonium trifluoro methanesulfonate (3ak). Yellow oil, 114.8 mg, 83% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 – 7.66 (m, 7H), 7.65 – 7.60 (m, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.6, 141.6, 134.6, 132.5, 132.4, 131.8, 131.7, 131.1, 130.9, 124.4, 123.1, 120.8 (q, *J* = 320.9 Hz, TfO$^-$), 120.2, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3088, 3067, 2926, 1590, 1477, 1447, 1258, 1155, 1029, 745, 638. HRMS: calculated for $C_{19}H_{16}ClS^+$([M-TfO$^-$]$^+$): 311.0661; found: 311.0660.

(4-fluorophenyl)diphenylsulfonium trifluoromethane sulfonate (3al). Yellow solid, mp: 111-113 ℃, mg, 75% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 – 7.82 (m, 2H), 7.77 – 7.73 (m, 2H), 7.72 – 7.67 (m, 8H), 7.41 – 7.35 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.2 (d, *J*= 259.7 Hz), 134.7, 134.3, 134.2, 131.7, 130.9, 124.3, 120.8 (q, *J*= 320.9 Hz, TfO$^-$), 119.3 (d, *J*= 24.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1, -100.3. IR (neat): 3097, 3066, 1588, 1492, 1473, 1261, 1223, 1147, 1030, 746, 680, 636. HRMS: calculated for $C_{18}H_{14}FS^+$([M-TfO$^-$]$^+$): 281.0800; found: 281.0790. The 3al is a known compound[20].

(3-methoxyphenyl)diphenylsulfonium trifluoromethane sulfonate (3am). Yellow oil, 88.9 mg, 67% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 – 7.71 (m, 2H), 7.70 – 7.65 (m, 8H), 7.59 – 7.54 (m, 1H), 7.26 – 7.25 (m, 1H), 7.23 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.9 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 161.4, 134.7, 132.4, 131.6, 131.0, 125.0, 124.1, 122.4, 120.8, 120.8 (q, *J* = 321.6 Hz, TfO$^-$), 116.0, 56.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3070, 2941, 2834, 1597, 1488, 1446, 1328, 1251, 1160, 1137, 1026, 795, 750, 690, 635. HRMS: calculated for $C_{19}H_{17}OS^+$([M-TfO$^-$]$^+$): 293.1000; found: 293.0989.

bis(4-(2-oxopropoxy)phenyl)(phenyl)sulfonium trifluoro methanesulfonate (3an). Yellow oil, 63.5 mg, 38% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71– 7.69 (m, 1H), 7.66 – 7.62 (m, 2H), 7.60 – 7.57(m, 4H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.20 – 7.15 (m, 4H), 4.80 (s, 4H), 2.24 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 202.6, 162.8, 134.2, 133.1, 131.5, 130.0, 125.8, 120.8 (q, *J* = 320.6 Hz, TfO$^-$), 117.9, 114.6, 72.8, 26.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3096, 3017, 2918, 1731, 1587, 1493, 1446, 1257, 1171, 1073, 1029, 832, 749, 684, 637. HRMS: calculated for $C_{24}H_{23}O_4S^+$([M-TfO$^-$]$^+$): 407.1317; found: 407.1310.

bis(4-(2-methoxy-2-oxoethoxy)phenyl)(phenyl)sulfonium tri-fluoromethanesulfonate (3ao). Yellow oil, 77.7 mg, 44% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 – 7.61 (m, 7H), 7.62 – 7.56 (m, 2H), 7.20 – 7.14 (m, 4H), 4.73 (s, 4H), 3.78 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 168.1, 162.6, 134.2, 133.2, 131.4, 130.1, 125.7, 120.8 (q, *J* = 321.6 Hz, TfO$^-$), 117.8, 115.2, 65.1, 52.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3096, 3017, 2956, 1749, 1587, 1492, 1445, 1256, 1212, 1171, 1073, 1029, 832, 751, 699, 636. HRMS: calculated for $C_{24}H_{23}O_6S^+$([M-TfO$^-$]$^+$): 439.1215; found: 439.1199.

bis(4-(cyanomethoxy)phenyl)(phenyl)sulfonium trifluoro methanesulfonate (3ap). Yellow oil, 61.1 mg, 39% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.79 – 7.75 (m, 1H), 7.72 – 7.68 (m, 6H), 7.64 – 7.61 (m, 2H), 7.35-7.31 (m, 4H), 4.96 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 161.3, 134.6, 133.4, 131.7, 130.4, 125.1, 118.2, 116.4, 114.2, 53.77. Carbon of triflate anion cannot be found. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.2. IR (neat): 3026, 2919, 2849, 2232, 1602, 1493, 1452, 1261, 1156, 1029, 966, 911, 759, 699, 636. HRMS: calculated for $C_{22}H_{17}N_2O_2S^+$([M-TfO$^-$]$^+$): 373.1011; found: 373.1010.

9-phenoxy-9H-9,10-[1,2]benzenothioxanthen-10-ium trifluoromethanesulfonate (3aq). Yellow solid, mp: 235-236 ℃, 121.0 mg, 78% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (dd, *J* = 7.7, 0.6 Hz, 3H), 7.82 (dd, *J* = 7.7, 0.9 Hz, 3H), 7.49 – 7.45 (m, 3H), 7.43 – 7.40 (m, 3H), 7.35 – 7.30 (m, 2H), 7.16 – 7.13 (m, 1H), 6.99– 6.96 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.5, 142.2, 132.2, 130.4, 129.3, 129.2, 128.2, 126.8, 122.8, 120.7 (q, *J* = 320.9 Hz, TfO$^-$), 117.9, 84.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.0. IR (neat): 3072, 2966, 2358, 1598, 1488, 1447, 1250, 1222, 1160, 1140, 1026, 750, 635. HRMS: calculated for $C_{25}H_{17}OS^+$([M-TfO$^-$]$^+$): 365.1000; found: 365.0983.

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bis(4-phenoxyphenyl)(phenyl)sulfonium trifluoromethane sulfonate (3ar). Yellow oil, 62.6 mg, 35% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 – 7.66 (m, 9H), 7.43 – 7.38 (m, 4H), 7.25 – 7.22 (m, 2H), 7.18 – 7.14 (m, 4H), 7.08 – 7.04 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.4, 154.0, 134.2, 133.3, 131.5, 130.4, 125.8, 125.7, 120.8 (q, *J* = 320.1 Hz, TfO^-), 120.7, 119.6, 116.0. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3093, 3063, 1575, 1483, 1245, 1167, 1071, 1029, 869, 755, 694, 637. HRMS: calculated for $C_{30}H_{23}O_2S^+$([M-TfO^-]$^+$): 447.1418; found: 4447.1405.

(3,4-dimethylphenyl)diphenylsulfonium trifluoromethane sulfonate (3ba). Yellow oil, 83.3 mg, 63% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 – 7.71 (m, 2H), 7.70 – 7.64 (m, 8H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.35 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.2, 141.1, 134.4, 132.6, 131.6, 131.5, 130.8, 128.4, 124.6, 120.8 (q, *J* = 320.1 Hz, TfO^-), 120.2, 20.0, 19.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3064, 2924, 1605, 1447, 1255, 1153, 1029, 750, 684, 636. HRMS: calculated for $C_{20}H_{19}S^+$([M-TfO^-]$^+$): 291.1207; found: 291.1204.

(3,4-dimethylphenyl)di-p-tolylsulfonium trifluoromethane sulfonate (3bb). Yellow solid, mp: 100-102 ℃, 99.8 mg, 71% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.50 (m, 4H), 7.46 – 7.44 (m, 4H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 8.1, 2.2 Hz, 1H), 2.42 (s, 6H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.9, 144.8, 141.0, 132.5, 132.1, 131.1, 130.6, 128.0, 121.1, 120.9, 120.8 (q, *J* = 321.6 Hz, TfO^-), 21.5, 19.9, 19.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3048, 2927, 1591, 1489, 1449, 1259, 1221, 1189, 1149, 1076, 1028, 810, 754, 700, 636. HRMS: calculated for $C_{22}H_{23}S^+$([M-TfO^-]$^+$): 319.1521; found: 319.1518.

(3,4-dimethylphenyl)bis(4-methoxyphenyl)sulfonium trifluoromethanesulfonate (3bc). Yellow oil, 121.6 mg, 81% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 – 7.56 (m, 4H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 1.9 Hz, 1H), 7.23 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.15 – 7.12 (m, 4H), 3.84 (s, 6H), 2.29 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.2, 144.2, 140.8, 132.7, 132.3, 130.4, 127.3, 122.2, 120.8 (q, *J* = 321.6 Hz, TfO^-), 117.0, 114.3, 55.9, 19.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3017, 2928, 2844, 2357, 1590, 1497, 1257, 1231, 1170, 1034, 834, 766, 631. HRMS: calculated for $C_{22}H_{23}O_2S^+$([M-TfO^-]$^+$):351.1419; found: 351.1417.

benzo[d][1,3]dioxol-5-yldiphenylsulfonium trifluoro methanesulfonate (3ca). Yellow oil, 83.5 mg, 61% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 – 7.70 (m, 2H), 7.69 – 7.63 (m, 8H), 7.37 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 2.1 Hz, 1H), 6.12 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.6, 150.4, 134.4, 131.5, 130.5, 128.5, 124.9, 120.8 (q, *J* = 320.1 Hz, TfO^-), 114.4, 110.6, 109.7, 103.4. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3070, 2918, 1600, 1477, 1446, 1250, 1140, 1026, 924, 747, 685, 634. HRMS: calculated for $C_{19}H_{15}O_2S^+$([M-TfO^-]$^+$): 307.0793; found: 307.0787.

benzo[d][1,3]dioxol-5-yldi-*p*-tolylsulfoniumtrifluoro methanesulfonate (3cb). Yellow oil, 107.6 mg, 74% yield. (Rf = 0.28, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 – 7.52 (m, 4H), 7.48 – 7.46 (m, 4H), 7.33 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.13 (s, 2H), 2.45 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.4, 150.3, 146.0, 132.2, 130.5, 128.0, 121.6, 120.8 (q, *J* = 321.6 Hz, $^-$ TfO^-), 115.5, 110.6, 109.6, 103.3, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3084, 3048, 2920, 1591, 1479, 1245, 1151, 1027, 926, 807, 636. HRMS: calculated for $C_{21}H_{19}O_2S^+$([M-TfO^-]$^+$): 335.1106; found: 335.1089.

benzo[d][1,3]dioxol-5-ylbis(4-methoxyphenyl)sulfonium trifluoromethanesulfonate (3cc). Yellow oil, 120.9 mg, 78% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 4H), 7.20 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.16 – 7.13 (m, 4H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.11 (s, 2H), 3.86 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$):δ 164.3, 153.0, 150.2, 132.6, 126.9, 120.8 (q, *J* = 321.6 Hz, TfO^-), 117.1, 116.9, 114.7, 110.4, 109.1, 103.3, 56.0. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3093, 3012, 2916, 1587, 1479, 1246, 1153, 1027, 927, 833, 755, 637. HRMS: calculated for $C_{21}H_{19}O_4S^+$([M-TfO^-]$^+$): 367.1004; found: 367.1001.

(3-methoxyphenyl)diphenylsulfonium trifluoromethane sulfonate (3da). Yellow oil, 78.3 mg, 59% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1).^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 – 7.72 (m, 2H), 7.71 – 7.67 (m, 8H), 7.58 – 7.56 (m, 1H), 7.28 – 7.27 (m, 1H), 7.24 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 161.4, 134.7, 132.4, 131.6, 131.0, 125.0, 124.1, 122.5, 120.8, 120.8 (q, *J* = 320.1 Hz, TfO^-), 116.1, 56.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3070, 2941, 2834, 1597, 1488, 1446, 1328, 1251, 1160, 1137, 1026, 795, 750, 690, 635. HRMS: calculated for $C_{19}H_{17}OS^+$([M-TfO^-]$^+$): 293.1000; found: 293.0989.

(3-methoxyphenyl)di-*p*-tolylsulfonium trifluoromethane sulfonate (3db). Yellow oil, 135.5 mg, 96% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 – 7.51 (m, 5H), 7.46-7.44 (m, 4H), 7.22 – 7.16 (m, 2H), 7.08 – 7.04 (m, 1H), 3.80 (s, 3H), 2.42 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 161.3, 146.1, 132.3, 132.2, 130.8, 125.8, 122.0, 120.8 (q, *J* = 320.1 Hz, TfO^-), 120.6, 120.3, 115.6, 56.0, 21.5. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.2. IR (neat): 3070, 2964, 1592, 1485, 1451, 1251, 1222, 1151, 1027, 754, 695, 636. HRMS: calculated for $C_{21}H_{21}OS^+$([M-TfO^-]$^+$): 321.1313; found: 321.1307.

(3-methoxyphenyl)bis(4-methoxyphenyl)sulfonium trifluoromethanesulfonate (3dc). Yellow oil, 141.7 mg, 94% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 – 7.62 (m, 4H), 7.54 – 7.52 (m, 1H), 7.20 – 7.14 (m, 5H), 7.11 – 7.10 (m, 1H), 7.03 (dd, *J* = 7.9, 1.3 Hz, 1H), 3.87 (s, 6H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.5, 161.3, 133.1, 132.2, 127.2, 121.5, 120.8 (q, *J* = 320.9 Hz, TfO^-), 119.9, 117.2, 115.1, 113.9, 56.1, 56.0. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.2. IR (neat): 3093, 2945, 2843, 1588, 1494, 1255, 1152, 1074, 1028, 833, 798, 680, 637. HRMS: calculated for $C_{21}H_{21}O_3S^+$([M-TfO^-]$^+$): 353.1211; found: 353.1200.

(3-bromophenyl)diphenylsulfonium trifluoromethane sulfonate (3ea). Yellow oil, 98.7 mg, 67% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1).^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 – 7.84 (m, 1H), 7.80 – 7.76 (m, 2H), 7.76 – 7.70 (m, 10H), 7.62 – 7.59 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 137.6, 135.0, 133.1,

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132.9, 131.8, 131.2, 129.9, 126.3, 125.0, 123.6, 120.8 (q, *J* = 321.6 Hz, TfO^-). ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3093, 3063, 1476, 1447, 1251, 1223, 1151, 1027,995, 747, 683, 634, 496. HRMS: calculated for $C_{18}H_{14}BrS^+([M\text{-}TfO^-]^+)$: 340.9994; found: 340.9991.

(3-bromophenyl)di-p-tolylsulfonium trifluoromethane sulfonate (3eb). Yellow oil, 134.0 mg, 86% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1).^1H NMR (600 MHz, $CDCl_3$): δ 7.82-7.80 (m, 1H), 7.68 – 7.67 (m, 1H), 7.64 – 7.62 (m, 1H), 7.61 – 7.56 (m, 5H), 7.48 (d, *J* = 8.3 Hz, 4H), 2.44 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.6, 137.4, 132.9, 132.5, 132.4, 131.1, 129.4, 127.1, 124.8, 120.1, 120.8 (q, *J* = 320.1 Hz, TfO^-), 21.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3088, 2921, 2850, 1719, 1589, 1461, 1403, 1255, 1222, 1150, 1026, 806, 753, 672, 636, 501. HRMS: calculated for $C_{20}H_{18}BrS^+([M\text{-}TfO^-]^+)$: 369.0307; found: 369.0306.

(3-bromophenyl)bis(4-methoxyphenyl)sulfonium trifluoromethanesulfonate (3ec). Yellow oil, 155.5 mg, 94% yield. (Rf = 0.30, eluent: DCM/MeOH = 15/1).^1H NMR (600 MHz, $CDCl_3$): δ 7.80 – 7.76 (m, 1H), 7.71 – 7.67 (m, 4H), 7.61 – 7.60 (m, 1H), 7.56 – 7.53 (m, 2H), 7.19 – 7.14 (m, 4H), 3.86 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 164.7, 136.9, 133.3, 132.7, 131.9, 128.6, 128.5, 124.7, 117.3, 113.3, 120.8 (q, *J* = 321.6 Hz, TfO^-), 56.1. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.1. IR (neat): 3081, 2932, 2843, 1586, 1474, 1438, 1342, 1195, 1116, 1072, 1061, 835, 772, 724, 618, 588, 512. HRMS: calculated for $C_{20}H_{18}BrO_2S^+([M\text{-}TfO^-]^+)$: 401.0205; found: 401.0206.

(3,4-difluorophenyl)di-*p*-tolylsulfonium trifluoromethane sulfonate (3fb). Yellow oil, 61.5 mg, 43% yield. (Rf = 0.31, eluent: DCM/MeOH = 15/1). ^1H NMR (600 MHz, $CDCl_3$): δ 7.63 – 7.57 (m, 6H), 7.55 –7.51 (m, 1H), 7.50 – 7.48 (m, 4H), 2.45 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ154.0 (dd, *J* = 262.7 Hz, 12.1 Hz), 151.3 (dd, *J* = 258.2 Hz, 14.3 Hz), 146.6, 132.5, 131.0, 128.69 (dd, *J* = 7.6 Hz, 3.8Hz), 121.3 (m), 120.8 (d, *J* = 19.6 Hz), 120.7 (q, *J* = 320.1 Hz, TfO^-), 120.4 (d, *J* = 21.1 Hz), 120.3, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.2 (s), -125.4 (d, *J* = 21.0 Hz), -129.1 (d, *J* = 21.0 Hz). IR (neat): 3086, 3050, 2926, 1591, 1507, 1489, 1252, 1224, 1155, 1028, 809, 777, 637. HRMS: calculated for $C_{20}H_{17}F_2S^+([M\text{-}TfO^-]^+)$: 327.1019; found: 327.1010.

triphenylselenonium trifluoromethanesulfonate (5). Following the general procedure in which diphenylselane **4** was used instead of diarylsulfide **2**, the title compound was obtained as a yellow oil, 42.7 mg, 31% yield. (Rf = 0.34, eluent: DCM/MeOH = 15/1). ^1H NMR (600 MHz, $CDCl_3$) δ: 7.72 – 7.68 (m, 3H), 7.67 – 7.56 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 133.7, 131.6, 131.1, 126.3. 120.6 (q, *J* = 320.1 Hz, TfO^-). ^{19}F NMR (565 MHz, $CDCl_3$): δ -78.2. IR (neat): 3088, 3062, 1474, 1446, 1258, 1149, 1065, 996, 839, 1029, 754, 635. Compound **5** is a known compound [13e].

Conflict of interest

There are no conflicts to declare.

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