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Generation of benzyne from aryl benziodoxaborole triflate under aqueous conditions and its reactions with alkyl aryl sulfides

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Dedicated to Alan R. Katritzky and Charles W. Rees

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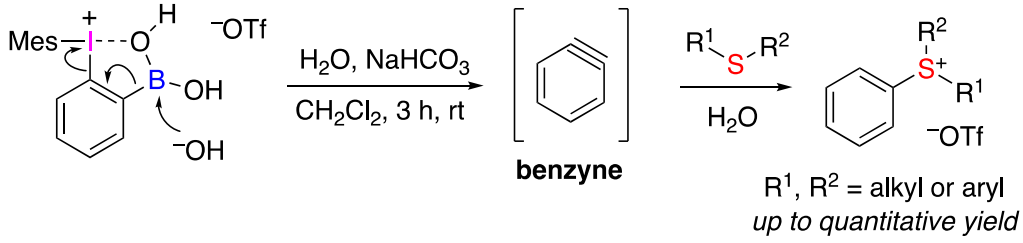
Abstract

Mesityl benziodoxaborole triflate is a unique benzyne precursor under aqueous conditions in the presence of $NaHCO_3$ at room temperature. Reactions of alkyl aryl sulfides with benzyne generated under these conditions selectively afford the corresponding sulfonium salts. In contrast, the previously reported reactions of alkyl aryl sulfides with common benzyne precursors under strongly basic anhydrous conditions lead to various products of cyclization, rearrangement, or elimination but not to sulfonium salts. This very mild procedure can be further extended to the preparation of sulfonium salts from diaryl sulfides, dialkyl sulfides, cyclic alkyl and arylsulfides, as well as a selenonium salt from diphenyl selenide.

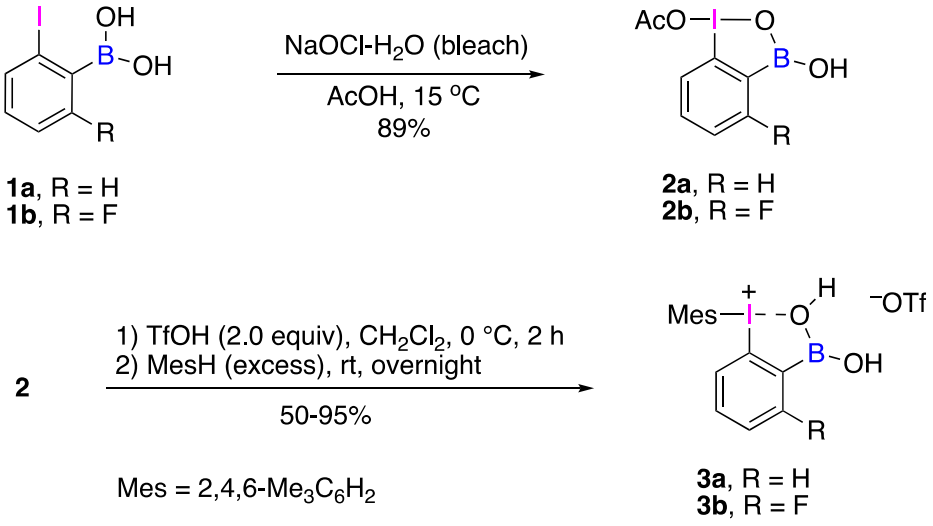


Keywords: Hypervalent iodine, benziodoxaborole, benzyne, iodonium salts, sulfonium salts

Introduction

In 1990, A. R. Katritzky and co-workers published a ground-breaking structural study on the cyclic structure of 2-iodosyl and 2-iodylbenzoic acids and their derivatives.[1] Since then, various new hypervalent iodine-oxygen five-membered heterocycles (benziodoxoles) have been synthesized and their utility for organic synthesis has been demonstrated.[2-5] In modern organic synthesis, cyclic and pseudocyclic hypervalent iodine compounds are widely used as oxidants and the group-transfer reagents especially useful for arylation, alkynylation, and azidation of organic substrates.[5-7] Benziodoxoles in general have greater stability, higher solubility in non-polar solvents, and modified chemical reactivity in comparison with their non-cyclic analogs.[2-5] Structures of these compounds are characterized by the presence of a planar iodoxol ring with the I-O distance varying in a broad range: 2.18-2.55 Å for cyclic and 2.55-3.00 Å for pseudocyclic benziodoxoles.[5]

In the course of our search for new five-membered hypervalent iodine heterocycles, in 2017 we reported the preparation of pseudocyclic arylbenziodoxaboroles **3** in two steps from commercial 2-iodoboronic acids **1** via acetoxybenziodoxaboroles **2** (Scheme 1). The pseudocyclic structure of arylbenziodoxaboroles with 2.69-2.71 Å I-O bond distance was confirmed by single crystal X-ray analysis.[8] Furthermore, we have reported unique reactivity of arylbenziodoxaborole **3b** as a benzyne precursor that can be triggered under neutral or slightly acidic conditions in aqueous solutions at room temperature.[8] It should be noted that the previously known, common benzyne precursors,[9,10] such as: aryl halides,[11-13] arene-diazonium-2-carboxylates,[14-16] 1,2,3-benzothiadiazole 1,1-dioxides,[17] 1-aminobenzotriazole,[18,19] *ortho*-silylaryl triflates (Kobayashi's reagent),[20] diaryliodonium salts,[21] and *ortho*-silyl phenyl iodonium triflate (Kitamura's reagent),[21,22] require activation by applying heat, irradiation, strong base ($NaNH_2$, BuLi, RMgBr, LiHMDS, etc.), or the anhydrous fluoride anion, which is also a strong base and requires special handling to avoid moisture. In contrast, compound **3b** can generate the corresponding aryne species by stirring its solution in a dichloromethane/water (9:1) mixture at room temperature.[8,23] The generated in aqueous solution arynes can be effectively trapped in the presence of dienes,[8] azides,[8] or organic sulfides.[23] We have also confirmed the formation of aryne from precursor **3b** in these reactions by labelling and kinetics experiments.[23] The non-fluorinated precursor **3a** has demonstrated lower reactivity compared to **3b** and required the presence of $NaHCO_3$ to activate the reaction.[23]



1a, R = H
1b, R = F

2a, R = H
2b, R = F

2

3a, R = H
3b, R = F

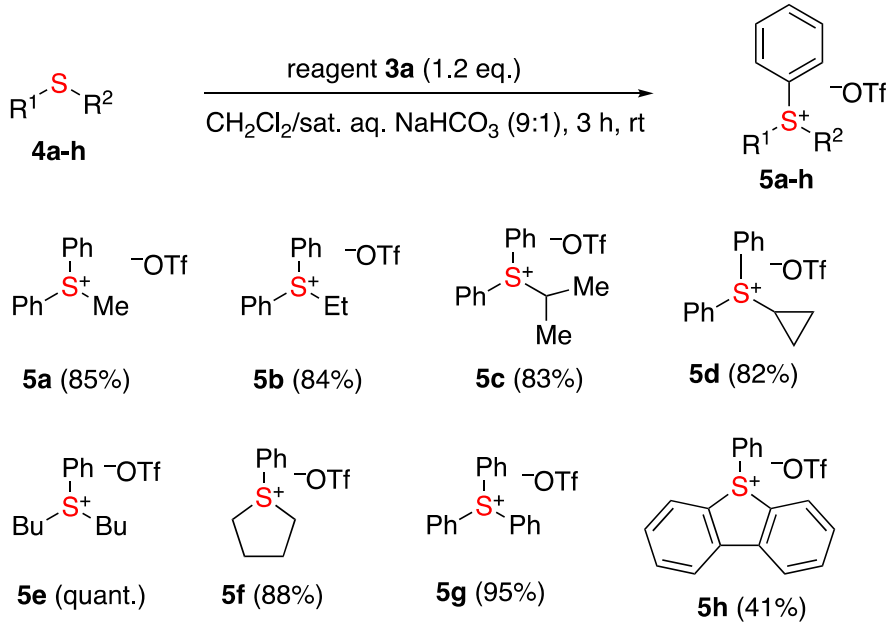
Scheme 1. Preparation of pseudocyclic arylbenziodoxaboroles **3**.

In the present paper, we describe the reactions of benzyne precursor **3a** with organic sulfides triggered by water in the presence of $NaHCO_3$ at room temperature and leading to selective formation of various sulfonium salts. This result is sharply different from the previously reported reactions of common benzyne precursors with organic sulfides under anhydrous basic conditions generally leading to various products of cyclization, rearrangement, or elimination but not to sulfonium salts.[24,25]

Results and Discussion

Reagent **3a** was prepared in gram-scale by a modified, combined procedure based on our previous works.[8,26] Acetoxybenziodoxaborole **2a** was prepared by the hypochlorite oxidation in acetic acid (Scheme 1) and used without purification for conversion to mesityl benziodoxaborole triflate **3a** by treatment with mesitylene in the presence of triflic acid (Scheme 1). Compound **3a** was isolated in 80% overall yield after 2 steps as a stable colourless solid that can be stored for long time in a refrigerator in the absence of moisture.

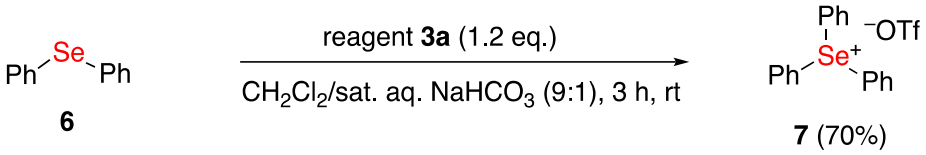
We have investigated reactions of various alkyl aryl sulfides **4a-f** with reagent **3a** in a dichloromethane/water (9:1) mixture in the presence of $NaHCO_3$ at room temperature. All reactions were complete in 3 hours and after simple work-up afforded analytically pure alkyl aryl sulfonium salts **5a-f** in excellent yields (Scheme 2). The procedure worked well for the preparation of alkyl sulfonium salts from alkyl phenyl sulfides **4a-d** with methyl, ethyl, isopropyl, and cyclopropyl groups, as well as from dibutyl sulfide **4e** and tetrahydrothiophene **4f**. Noteworthy, the reaction of ethyl phenyl sulfide **4b** with aryne generated from reagent **3a** in aqueous solution produced sulfonium salt **5b** in 84% yield. For comparison, the previously reported similar reaction of ethyl phenyl sulfide with benzyne generated from benzenediazonium-2-carboxylate under anhydrous conditions proceeded with elimination of ethylene leading to the corresponding diphenyl sulfide (Ph_2S) in 92% yield.[27]



Scheme 2. Reactions of reagent **3a** with organic sulfides.

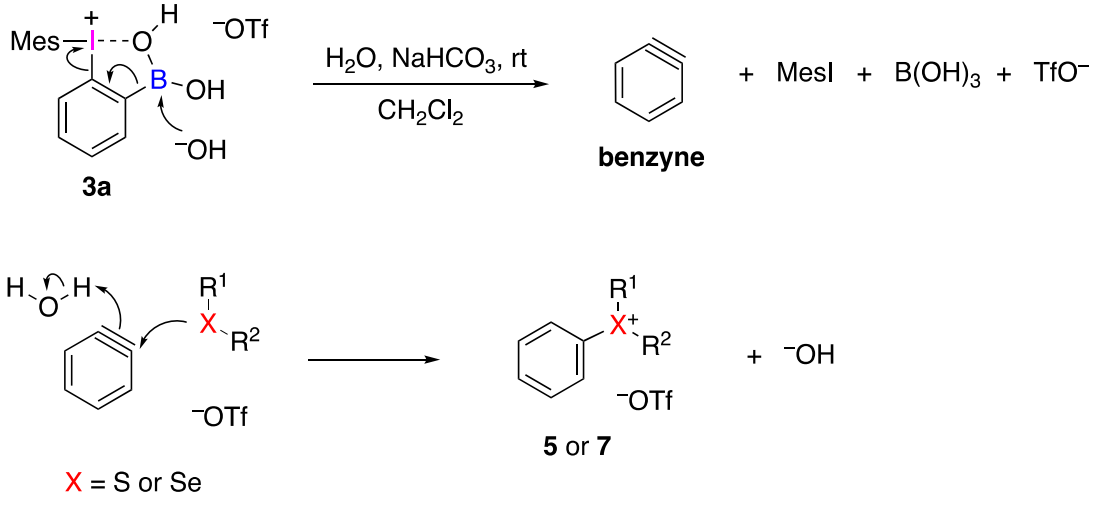
It is important to note that the reactions of diphenyl sulfide **4g** and dibenzothiophene **4h** with reagent **3a** at room temperature in aqueous solution afforded the corresponding triaryl sulfonium salts **5g** and **5h**. For comparison, the most common existing approach to triaryl sulfonium salts is based on aryl transfer from diaryliodonium salts to diaryl sulfides at 120-230 °C and usually in the presence of copper catalysts.[28-31] Preparation of triaryl sulfonium salts in moderate yields using the Kobayashi aryne precursor in acetonitrile (25 °C, 36 h) in the presence of CsF under dry conditions has recently been reported.[32] Based on the labeling experiments, the authors assumed that the molecule of acetonitrile acted as the source of protons in this reaction.[32]

The reactions of reagent **3a** can be further extended to organic selenides. Reagent **3a** reacts with diphenyl selenide **6** in CH_2Cl_2-H_2O (9:1) in the presence of $NaHCO_3$ to give the corresponding triphenyl selenonium salt **7** in good yield (Scheme 3). Previously reported synthesis of selenonium salt **7** required heating of diphenyl selenide with diphenyliodonium triflate in a chloroform solution in a thick-walled glass tube sealed with a Teflon screwcap maintained at 120 °C for 24 h.[30]



Scheme 3. Reaction of reagent **3a** with diphenyl selenide.

Based on our previously published studies,[8,23] we propose a two-step mechanism for the reactions of reagent **3a** with organic sulfides and selenide (Scheme 4). At the first step, benzyne is generated by nucleophilic addition of a hydroxide anion (present in the aqueous solution of $NaHCO_3$) to the boron atom of reagent **3a**, followed by immediate elimination of boronic acid and mesityl iodide. Mesityl iodide (MesI), formed as a by-product in this step, was detected by NMR in the reaction mixture. This step is facilitated by the oxophilic character of the -$B(OH)_2$ group and by the hypernucleofugic properties of the $MesI^+$ moiety in the iodonium salt **3a**. At the second step, the addition of sulfide to the benzyne followed by protonation by water molecule gives the final product **5** or **7**.



Scheme 4. Mechanism of reactions of reagent **3a** with organic sulfides and selenide.

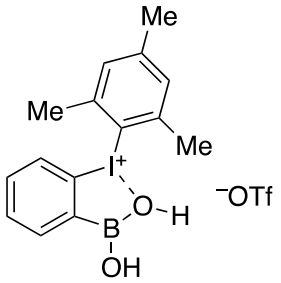
Conclusions

In summary, we have demonstrated that mesityl benziodoxaborole triflate **3a** is a unique benzyne precursor under aqueous conditions in the presence of $NaHCO_3$ at room temperature. Reactions of alkyl aryl sulfides with benzyne generated under these conditions selectively afford the corresponding sulfonium salts, which is in contrast with the previously reported non-selective reactions of sulfides with common benzyne precursors under strongly basic anhydrous conditions. This very mild procedure works well for the preparation of sulfonium salts from alkyl aryl sulfides, diaryl sulfides, cyclopropyl phenyl sulfide, dialkyl sulfides, cyclic alkyl and arylsulfides, as well as selenonium salt from diphenyl selenide.

Experimental Section

General. All reactions were performed under dry argon atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane and acetonitrile were distilled from CaH_2 immediately prior to use. Diethyl ether was distilled from Na/benzophenone. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker 400 MHz or JEOL JNM-AL300 NMR spectrometers. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to tetramethylsilane.

Preparation of mesityl-1-phenyboronic acid-2-iodonium triflate (3a) from 2-iodophenylboronic acid[8,33]

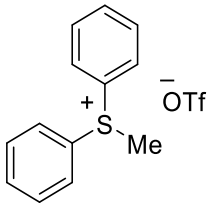


A solution of commercial 2-iodophenylboronic acid **1a** (620 mg, 2.5 mmol) in acetic acid (6 mL) was cooled to 15 °C, and the commercial bleach solution (6.5 mL of ~5% aqueous NaOCl) was added by small portions (about 0.1 mL each) under stirring. The stirring was continued at rt for overnight. After reaction, the colourless precipitate was filtered, washed with water, hexane, and ether, then dried in vacuum to afford 677.2 mg (89%) of 1-acetoxy-benziodoxaborole **2a**, which was used in the next step without purification. The colourless solid was dissolved in dichloromethane (2.2 mL), cooled to 0 °C and TfOH (300.2 mg, 4.43 mmol) was added under stirring. The reaction mixture was stirred at 0 °C for 2 hours, then mesitylene (3.32 mL) was added to the reaction mixture, and stirring was continued overnight at room temperature. After reaction, the solvent was removed under reduced pressure to give an oily product, which was washed with diethyl ether several times then dried in vacuum to give mesityl-1-phenyboronic acid-2-iodonium triflate **3a**, 1.037 g (80% yield; 2 steps), as a colourless solid (mp 160.8-164.3 °C).[8] ^{1}H NMR (CD_3CN): δ 8.09 (d, *J* 7.6 Hz, 1H), 7.66-7.59 (m, 1H), 7.53-7.42 (m, 2H), 7.36 (s, 2H), 6.83 (d, *J* 8.4 Hz, 1H), 2.53 (s, 6H), 2.46 (s, 3H).

Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate with sulfides or selenide

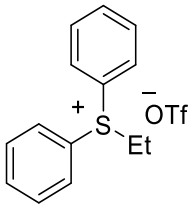
Sulfide **4** or diphenylselenide **6** (0.1 mmol) was added to a solution of mesityl-1-phenyboronic acid-2-iodonium triflate **3a** (0.12 mmol) in a mixture of dichloromethane (0.9 mL) and sat. $NaHCO_3$ (0.1 mL). The reaction was stirred at room temperature for 3 hours. After reaction, water (5 mL) was added and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was washed with diethyl ether several times and then dried in vacuum to give the analytically pure sulfonium triflates **5** or selenonium triflate **7**.

Methyl-diphenylsulfonium triflate (5a)[34]



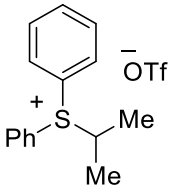
Reaction of thioanisole **4a** (12.4 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 29.7 mg (85%) of product **5a**, isolated as a colourless solid: mp 95.1-96.8 °C (lit. mp 95-96.5 °C);[34] IR (KBr) cm^{-1} 3098, 3077, 3024, 2938, 1587, 1484, 1255, 1222, 1158, 1029, 635; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* 7.2 Hz, 4H), 7.77-7.60 (m, 6H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 134.9, 131.8, 130.5, 126.8, 121.7 (q, $^1J_{CF}$ = 318.8 Hz), 28.1; ^{19}F NMR (376 MHz, CD_3CN): δ -79.3; HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{13}S$ ([M-OTf])$^+$: 201.0732, found: 207.0731.

Ethyl-diphenylsulfonium triflate (5b)[35]



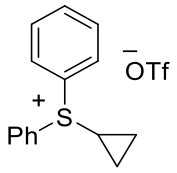
Reaction of ethyl phenyl sulfide **4b** (13.8 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 30.7 mg (84%) of product **5b**, isolated as a colourless oil; IR (neat) cm^{-1} 3092, 3065, 2984, 2944, 1582, 1481, 1261, 1225, 1157, 1030, 638; ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* 8.4 Hz, 4H), 7.77-7.62 (m, 6H), 4.28 (q, *J* 7.2 Hz, 2H), 1.47 (t, *J* 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 131.6, 130.7, 124.1, 120.9 (q, $^1J_{CF}$ = 318.5 Hz), 40.3, 9.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -78.2.; HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{15}S$ ([M-OTf])$^+$: 215.0889, found: 215.0891.

Isopropyl-diphenylsulfonium triflate (5c)[36]



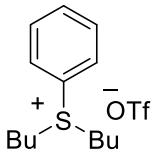
Reaction of isopropyl phenyl sulfide **4c** (15.2 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 31.4 mg (83%) of product **5c**, isolated as a colourless oil; IR (neat) cm^{-1} 3100, 3066, 2988, 1582, 1479, 1260, 1225, 1158, 1030, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* 8.0 Hz, 1.6 Hz, 4H), 7.79-7.68 (m, 6H), 5.42 (sept, *J* 6.4 Hz, 1H), 1.52 (d, *J* 6.4 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 135.5, 132.1, 131.9, 124.1, 121.8 (q, $^1J_{CF}$ = 318.9 Hz), 51.5, 18..; ^{19}F NMR (376 MHz, CD_3CN): δ -79.2.; HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{17}S$ ([M-OTf])$^+$: 229.1045, found: 229.1055.

Cyclopropyl-diphenylsulfonium triflate (5d)[36]



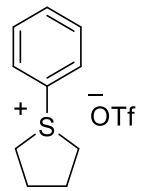
Reaction of cyclopropyl phenyl sulfide **4d** (15 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 30.7 mg (82%) of product **5d**, isolated as a light yellow oil; IR (neat) cm^{-1} 3145, 3050, 1581, 1480, 1261, 1224, 1157, 1030, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* 6.8 Hz, 4H), 7.76-7.62 (m, 6H), 4.03-3.94 (m, 1H), 1.72-1.63 (m, 2H), 1.49-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 131.4, 130.2, 126.5, 120.9 (q, $^1J_{CF}$ = 318.7 Hz), 22.5, 8.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -78.2; HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{15}S$ ([M-OTf])$^+$: 227.0889, found: 227.0882.

Dibutyl-phenylsulfonium triflate (5e)[37]



Reaction of dibutyl sulfide **4e** (14.6 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 37.1 mg (100%) of product **5e**, isolated as a light yellow oil; IR (neat) cm^{-1} 3065, 2964, 2938, 2878, 1468, 1260, 1225, 1157, 1030, 638; ^{1}H NMR (400 MHz, CD_3CN): δ 7.94-7.85 (m, 3H), 7.77 (t, *J* 7.6 Hz, 2H), 3.65-3.49 (m, 4H), 1.67-1.56 (m, 4H), 1.51-1.41 (m, 4H), 0.92 (t, *J* 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 135.6, 131.8, 121.8 (q, $^1J_{CF}$ = 318.9 Hz), 121.7, 44.2, 26.6, 21.5, 13.1. ^{19}F NMR (376 MHz, CD_3CN): δ -79.3; HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{23}S$ ([M-OTf])$^+$: 223.1515, found: 223.1519.

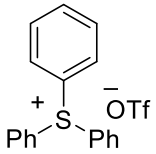
1-Phenyltetrahydro-1*H*-1-thiophenium triflate (5f)[38]



Reaction of tetrahydrothiophene **4f** (8.8 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 27.5 mg (88%) of product **5f**, isolated as a colourless oil; IR (neat) cm^{-1} 3061, 2919, 2863, 1448, 1266, 1159, 1026, 637; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84-7.76 (m, 2H), 7.76-7.63 (m, 3H), 4.34-4.19 (m, 2H), 3.76-3.61 (m, 2H), 2.64-2.52 (s, 4H); ^{13}C NMR (75 MHz, CD_3CN): δ 134.5, 131.6, 129.9, 126.4, 120.9 (q, $^1J_{CF}$

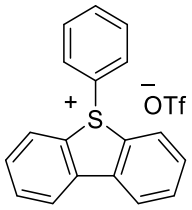
= 318.5 Hz), 48.8, 29.3; ^{19}F NMR (376 MHz, CD_3CN): δ -79.3; HRMS (ESI-TOF-positive mode): calcd for $C_{10}H_{13}S$ ([M-OTf])$^+$: 165.0732, found: 165.0725.

Triphenylsulfonium triflate (5g)[30]



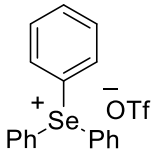
Reaction of diphenyl sulfide **4g** (18.6 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 39.1 mg (95%) of product **5g**, isolated as a colourless solid: mp 132.1-133.6 °C (lit. mp 133-136 °C);[30] IR (KBr) cm^{-1} 3090, 3063, 1581, 1477, 1275, 1225, 1155, 1030, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.65 (m, 15H); ^{13}C NMR (100 MHz, CD_3CN): δ 135.3, 132.1, 131.7, 125.1, 121.8 (q, $^1J_{CF}$ = 319.1 Hz); ^{19}F NMR (376 MHz, CD_3CN): δ -79.2; HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{15}S$ ([M-OTf])$^+$: 263.0889, found: 263.0882.

5-Phenyl-5*H*-dibenzo[*b,d*]thiophen-5-ium triflate (5h)[39]



Reaction of dibenzothiophene **4h** (18.4 mg, 0.1 mmol) and **3a** (61.9 mg, 0.2 mmol) according to the general procedure afforded 16.7 mg (41%) of product **5h**, isolated as a colourless solid: mp 187.0-188.1 °C (lit. mp 187-188 °C);[39] IR (KBr) cm^{-1} 3027, 2921, 2851, 1636, 1574, 1463, 1269, 1154, 1030, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* 8.0 Hz, 2H), 8.15 (d, *J* 7.6 Hz, 2H), 7.91-7.83 (m, 2H), 7.76-7.62 (m, 5H), 7.59-7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 134.9, 134.3, 132.1, 131.8, 131.6, 130.8, 128.9, 126.6, 123.9, 120.8 ($^1J_{CF}$ = 318.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -78.2; HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{13}S$ ([M-OTf])$^+$: 261.0732, found: 261.0728.

Triphenylselenonium triflate (7)[30]



Reaction of diphenyl selenide **6** (23.3 mg, 0.1 mmol) and **3a** (61.9 mg, 0.12 mmol) according to the general procedure afforded 32.3 mg (70%) of product **7**, isolated as a light yellow oil; IR (neat) cm^{-1} 3088, 3062, 2950, 2875, 1573, 1479, 1261, 1224, 1029, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.69 (m, 3H), 7.67-7.59 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8, 131.7, 131.2, 126.3, 120.8 (q, $^1J_{CF}$ = 318.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -78.2; HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{15}Se$ ([M-OTf])$^+$: 311.0333, found: 311.0327.

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Supplementary Material

NMR spectra of compounds are provided in the supplementary material file associated with this manuscript.

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